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A POSSIBLE GEOMETRICAL INTERPRETATION OF THE ISOSPACE AND OF ITS TRANSFORMATIONS*

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Due to experiments proving the violation of parity conservation the assumption will be advanced that the structure of the space-time world determined by physical interactions may be anisotropic. The natural geometrical model of anisotropic spaces is the line-element geometry being an ensemble of line-elements (x^μ, v^μ) characterized by their position co-ordinates x^μ and homogeneous direction co-ordinates v^μ ($\mu = 0, 1, 2, 3$), respectively. The latter ones can be substituted by inhomogeneous direction co-ordinates x^μ or rather by the quantities $\xi_{(i)} = \cos \theta_i$ ($i = 1, 2, 3$) related to an orthogonal trieder (λ -trieder). The co-ordinates x^μ can be interpreted as the co-ordinates of external and the direction co-ordinates θ_i (or $\xi_{(i)}$) as the co-ordinates of the internal degrees of freedom of the physical field considered. This means that the supposition that the physical field would be excited in anisotropic spaces can be substituted by the more physical term that in the case of field theories also the internal degrees of freedom of the fields have to be considered. Due to this supposition the components of isovectors and isopseudovectors, *etc.*, can easily be defined and the transformations of the isotopic space can be represented by rotation and reflexions of the λ -trieder. Finally, a method will be proposed for the determination of the metrical fundamental tensor of the anisotropic space-time world.

§ 1. Introduction

The development of quantum theory of fields achieved in the last few years several important and interesting results. In the topic of the theory of elementary particles, *e. g.*, the qualitative features — above all the selection rules — of the processes of interactions of elementary particles have been carefully investigated and in spite of the lack of knowledge of the exact form of interaction law the comparison of the results of such investigations with the experiments could be used as a first qualitative test of the systematizations and theories of these particles [1].

In spite of these great successes one can, however, object to two — otherwise mostly accepted — elements of the theory of elementary particles:

(i) Taking the different methods of the theory of elementary particles into account, it can be noticed that these methods have, from certain points of view, two essentially different features. Some of them are closely connected with geometry and obtain such physical laws as conservation of energy and momentum,

* Preliminary reports on this investigation were delivered at the *Conference of Elementary Particles* at Balatonvilágos (Hungary) 17–20, September, 1958 and at the *Congress of Polish Physical Society* at Toruń (Poland) 11–14, September, 1959.

etc.; the others, nevertheless, are rather based on the abstract concept of the isobaric space (in the following: *isospace*) than on current geometrical terms and results in such physical laws as the conservation of charge or of the baryon number, *etc.*, which have not acquired yet any generally accepted geometrical interpretation. In other words, *some of the groups of transformations* — like translations, rotations, and inversions in the four-dimensional space-time world — *posses an immediate geometrical meaning but some of the others* — such as *e. g.* gauge transformations, charge conjugation, charge symmetry and mesoparity transformation — *possess none*. This situation is from the point of view of the unified theory of fields unsatisfactory [2].

(ii) A generally accepted starting point of the theory is the *a priori* supposition that the structure of the space-time continuum — as a geometrical background of physical processes — would be homogeneous and isotropic.

We would like to suggest that this second supposition, in spite of its general acceptability, can be objected from philosophical point of view. Owing to the metaphysical concept of space-time world the structure of space and time, respectively, would be an *a priori* cathegory of human mind. It is, however, well known that this view was refused in the last century by the famous geometrical investigations of BOLYAI and LOBATSHEWSKI. At the beginning of the great development of natural sciences J. BOLYAI was the first scientist who already hundred years ago had suggested that the structure of space is determined by objective physical interactions of the matter. This idea was recalled by RIEMANN and finally as the fundamental idea of EINSTEIN'S theory of gravitation has been scored its revolutional success.

As a matter of fact the gravitational interaction can be neglected in the case of elementary particles. But if we take seriously into account the above point of view then one can say that the homogeneity and isotropy of the space-time world is rather a consequence of symmetry properties of the strong and electromagnetic interactions, respectively, than an *a priori* property of the space-time world. This means, however, that if the violation of parity conservation respectively as a special property of the weak and universal weak interactions can be regarded, due to the view that the structure of the space would be determined by material interactions, it seems that from the anisotropy of the weak interactions, several times proved by careful experiments, the anisotropy of the space can be concluded. The reason that the structure of the space-time world is isotropic in the case of strong and electromagnetic interactions it seems to be that the anisotropic weak interactions are overlapped by these stronger interactions. In other words: the question may arise whether the insistence on the *a priori* pseudo-Euclidian structure of the space-time world is not a rest of the metaphysical concept of space and time?

This is the reason that in this paper the radical idea will be suggested that the second fundamental element of the quantum theory of field mentioned above is responsible for the problems connected with the violation of parity conservation predicted by LEE and YANG [3].

The violation of parity conservation was recently investigated from the point of view of relativistic invariance by WIGNER [4]. As it is well known, the consequence of the cobalt experiment of WU and her collaborators, as well as others of the same type, may be briefly summarized that the symmetry of the real world is smaller than it had been thought. Namely, the whole experimental arrangement,

e. g., in the case of Co^{60} has at the beginning of the experiment a symmetry plane, which would remain valid throughout the further fate of the system. Nevertheless, the intensity of the β -radiation is larger on one side of this plane than on the other one. Should it, however, be true that a symmetry plane always remains a symmetry plane, the initial state of the system in the case of cobalt experiment could not have contained a symmetry plane. Therefore, the radical solution of this paradoxical situation was suggested by WIGNER that the polar and axial transformation character of the electric and magnetic vector of the electromagnetic field has to be changed which has the immediate consequence that the charge density would become a pseudo-scalar rather than a scalar as in the current theory. By this means the problem concerning the cobalt experiment would be solved, as well as the CP invariance predicted by LANDAU [5] would also be explained, however, this proposal should entail further consequences that are at present difficult to foresee and it is inconceivable — at least for us — that such radical change in the case of the theory of the electromagnetic field had not been suggested by any previous experimental effect.

Taking the above considerations into account the conclusion may be drawn again that some physical factors related to the space-time structure have not yet been considered and due to the lack of the expected symmetry plane of the cobalt experiment, *the structure of our physical world seems to be richer than it was previously believed.*

It is remarkable that both objections mentioned above may be eliminated by the radical interpretation of the cobalt experiment that

(1) *as a consequence of weak interactions the structure of the space-time continuum becomes homogeneous but anisotropic.*

(2) *isotropy and homogeneity of the space-time world, which has been previously accepted a priori without any criticism in current field theories, should be only an approximate one and by the decrease of the strength of interactions the anisotropy and inhomogeneity of the space-time world become more and more dominant.*

The natural geometrical model of an anisotropic space is the line-element geometry being the geometry of an ensemble of line-elements rather than that of points in the space as in current geometries. Such a geometry was first proposed by FINSLER [6], then, some years ago, FINSLER's exposition was generalized to fit it more adequate to physical applications [7]. In the course of more recent investigations also the differential structure of classical theory of fields excited in an anisotropic space-time continuum was elaborated; it means that the field equations deduced from a general and also from a special Lagrangian density, respectively, as well as the deduction of the differential conservation laws by means of PAULI's method of infinitesimal transformations were discussed [8]. The latter investigations have been suggested by the recognition that YUKAWA's bilocal theory of fields corresponds to a theory of fields excited in such an anisotropic world.

§ 2. Geometrical Characterization of the Space-time Anisotropy

The fundamental elements of a line-element space — corresponding to an anisotropic space-time continuum — are *line-elements* defined by their four-dimensional space co-ordinates x^μ and by contravariant vectors v^μ ($\mu = 0, 1, 2, 3$) the

direction of which correspond to that of the line-elements. The ensemble of the fundamental elements (x^μ, v^μ) is the so-called *line-element space* \mathcal{L} .

Since only a direction is defined by the vector v^μ , the components v^μ are not independent and their proportion has only meaning. Therefore, *it will be supposed that the metrical fundamental tensor of the space*, i. e. $g_{\mu\nu} = g_{\mu\nu}(x^\mu, v^\mu)$, *the different geometrical and physical quantities, respectively, are homogeneous functions of the so-called direction co-ordinates v^μ of zero degree.*

The geometrical structure of such a space may be determined by the *metrical fundamental tensor* $g_{\mu\nu}$. Owing to the general idea of the suggested theory the explicit form of the metrical fundamental tensor has to be determined by the anisotropy of the physical interaction. Since as a result of the interactions of elementary particles the space-time world becomes homogeneous the metrical fundamental tensor $g_{\mu\nu}$ does not depend on the co-ordinates x^μ , but due to the anisotropy of interactions it can depend on the direction co-ordinates v^μ , this means that $g_{\mu\nu} = g_{\mu\nu}(v^\mu)$. The geometry of such a space is elaborated in details in recent papers [7, 8].

It seems, however, that the geometry of the space has to be slightly changed. Let us, namely, suppose, that the direction of the line-elements is characterized rather by the contravariant vector-density of order (-1) , u^μ :

$$u^{\mu'} = \Delta^{-1} \frac{\partial x^{\mu'}}{\partial x^\mu} u^\mu, \quad \left(\Delta \equiv \det \left| \frac{\partial x^{\mu'}}{\partial x^\mu} \right| \right) \quad (1)$$

than by the contravariant vector v^μ with the transformation law

$$v^{\mu'} = \frac{\partial x^{\mu'}}{\partial x^\mu} v^\mu. \quad (2)$$

The consequences of this new supposition are not interesting from the point of view of the present investigations, therefore it will be dealt with elsewhere.

Let us only mention that a vector-density of unit length in the direction of the line-element (x^μ, u^μ) can be introduced by the definition

$$l^\mu = F^{-1} u^\mu, \quad (F = \{g_{\mu\nu}(u^\mu) u^\mu u^\nu\}^{1/2}) \quad (3)$$

F being the so-called *scalar fundamental function of the space*, and the structure of the space at a point $P(x^\mu)$ is characterized by the *Carathéodoryan indicatrix of the space* which is constructed as follows: Consider all directions crossing over the point P . The end points of the unit vectors l^μ directed towards the different directions starting from P form a hyper-surface in the four-dimensional space \mathcal{L} having the equation

$$F(x^\mu, l^\mu) = 1. \quad (4)$$

Since the space-time world is in our case homogeneous the Carathéodoryan indicatrices at different points of the space are congruent.

In order to take in a covariant way explicitly into account that the geometrical and field quantities, respectively, depend only on three independent direction co-ordinates, let us introduce three linearly independent vectors $\lambda^{\mu(i)}$ ($i = 1, 2, 3$) of unit

length determining three different, otherwise arbitrary, directions. Then the three angles

$$\theta_i = \arccos \{g_{\mu\nu} \lambda^\mu \lambda^\nu\}_{(i)} \quad (g_{\alpha\beta} \lambda^\alpha \lambda^\beta = 1, \text{ no summation over } i) \quad (5)$$

can be obtained regarded as *inhomogeneous directional co-ordinates in all points of the space*. The angles θ_i were introduced in an invariant way. This means that the angles θ_i are pseudo-scalars of the general group of co-ordinate transformations.

The directions of the vectors, λ^μ can be given quite arbitrarily. For sake of simplicity one can, however, suppose that the λ^μ are by pairs orthogonal, *i. e.*

$$g_{\mu\nu} \lambda^\mu \lambda^\nu = \delta_{ij} \quad (6)$$

forming an orthogonal trieder. In the case when the orientation of this trieder coincides with that of the co-ordinate axes it will be denoted as λ^+ -trieder and in the contrary one as λ^- -trieder.

Due to the definition of the inhomogeneous direction co-ordinates θ_i one can see immediately that these angles depend on the orientation of the λ -trieder. Let us suppose that the orientation of the λ^+ -trieder would be *a priori* defined in a suitable way. For sake of simplicity — in this paragraph and also in the following ones — one can briefly denote the λ^+ -trieder as λ -trieder.

For any other orientations of the λ -trieder — which will be noted by λ'_i -trieder — their axes λ'^μ relative to its *a priori* position can be determined by the Eulerian angles ϕ, ψ, ϑ . Then, for the relations between the quantities

$$\xi_{(i)} = \cos \theta_i = g_{\mu\nu} \lambda^\mu \lambda^\nu \quad \text{and} \quad \xi'_{(i)} = \cos \theta'_i = g_{\mu\nu} \lambda'^\mu \lambda'^\nu \quad (7)$$

the well-known equations

$$\begin{aligned} \xi'_{(1)} &= \{\cos \phi \cos \psi - \sin \phi \sin \psi \cos \vartheta\} \xi_{(1)} + \\ &+ \{\cos \phi \sin \psi + \sin \phi \cos \psi \cos \vartheta\} \xi_{(2)} + \sin \phi \sin \vartheta \xi_{(3)} \\ \xi'_{(2)} &= -\{\sin \phi \cos \psi + \cos \phi \sin \psi \cos \vartheta\} \xi_{(1)} + \\ &+ \{-\sin \phi \sin \psi + \cos \phi \cos \psi \cos \vartheta\} \xi_{(2)} + \cos \phi \sin \vartheta \xi_{(3)} \\ \xi'_{(3)} &= \sin \psi \sin \vartheta \xi_{(1)} - \cos \phi \sin \vartheta \xi_{(2)} + \cos \vartheta \xi_{(3)} \end{aligned} \quad (8)$$

can be obtained.

§ 3. General Feature of Theories of Fields Excited in Anisotropic Spaces

In current field theories the physical fields are characterized by one or several space-time functions: $\psi(x^\mu), \psi_{\alpha} = \psi_{\alpha}(x^\mu)$, etc., — fulfilling certain partial differential equations, the so-called field equations — which have to satisfy definite laws of transformations. In the case of physical fields excited in anisotropic spaces, the fields are analogously characterized by such quantities fulfilling the field equations [8] and having also definite laws of transformations, however, these functions

depend on the line-elements (x^μ, u^μ) , *i. e.* $\psi = \psi(x^\mu, u^\mu)$, $\psi_x = \psi_x(x^\mu, u^\mu)$ etc., being — due to the above considerations — homogeneous functions of the direction co-ordinates u^μ of zero degree.

Instead of the homogeneous direction co-ordinates u^μ let us introduce the inhomogeneous direction co-ordinates θ_i or — for the sake of appropriateness — rather the quantities $\xi_{(i)} = \cos \theta_i$, then the field quantity depends on the position co-ordinates x^μ , as well as on the quantities $\xi_{(i)}$, *i. e.*

$$\psi = \psi(x^\mu; \xi_{(1)}, \xi_{(2)}, \xi_{(3)}). \quad (9)$$

To use simple terms one can denote the co-ordinates x^μ as the *co-ordinates of the external degrees of freedom of the fields* and analogously the homogeneous direction co-ordinates u^μ and the quantities $\xi_{(i)}$, respectively, as the *co-ordinates of the internal degrees of freedom of the field*. This means last of all that the supposition introduced above — according to which the structure of the physical field would be anisotropic — in other, perhaps more physical, terms corresponds to the fundamental assumption that *the physical fields have also internal degrees of freedom characterized by the internal co-ordinates*.

Now, let us take into account that the variables x^μ and $\xi_{(i)}$ of the field quantity ψ , *i. e.* the external and internal co-ordinates of the field, respectively, have independent laws of transformation:

(i) The external co-ordinates x^μ are transformed in the case of all co-ordinate transformations in the usual way, however, the internal co-ordinates ξ_i are either invariants or pseudo-scalars of the general group of co-ordinate transformations. Let us denote the general group of co-ordinate transformations in the following by \mathbb{G}_x .

(ii) On the other hand, the internal co-ordinates $\xi_{(i)}$ change in the case of rotations of the λ -trieder, as well as in the case of inversions in respect to the λ -trieder, respectively, but this group of transformations — being isomorph with the three-dimensional rotary reflexion group of transformations — does not involve any changes in the case of external co-ordinates x^μ . The general group of transformations of the internal co-ordinates will be denoted in the following by \mathbb{G}_ξ .

As a matter of fact, in the case of fields excited in anisotropic space-time continuums — or in other words in the case of physical fields with internal degrees of freedom — the general group of transformations is a product of those of external and of internal co-ordinates, *i. e.*

$$\mathbb{G} = \mathbb{G}_x \mathbb{G}_\xi, \quad (10)$$

must be considered. *Both groups \mathbb{G}_x and \mathbb{G}_ξ evidently have representations with immediate geometrical meaning and even this recognition would be the main point of the geometrization of the isospace and its transformations suggested in the next paragraph.*

If these considerations are true at all and would be accepted, one has to conclude that *the integral of action of the field* — being the fundamental quantity of the Lagrangian formalism of the field — *must be the invariant of the general group \mathbb{G} introduced above.* This means that due to the suggested theory more detailed feature of the general law of interaction can be concluded as will be published elsewhere.

§ 4. Geometrical Interpretation of the Isospace and its Transformations

In order to carry out our programme of geometrization of the isospace quite generally, the structure of the anisotropic spacetime world will not yet be fixed, but the following general assumptions would be suggested:

(a) Due to the anisotropy of the space-time continuum some (at least one but at most four) distinguished direction should be determined being also distinguished directions of the Carathéodoryan indicatrix of the space at a point $P(x^\mu)$.

Then, in § 7 an explicit method will be proposed to determine the metrical fundamental tensor if the Carathéodoryan indicatrix is known.

(b) Let us take into account a special orthogonal frame of reference assuming that the directions of its co-ordinate axes coincide with the distinguished directions mentioned in (a). One can easily see that in this frame of reference the Carathéodoryan indicatrix has its most simple explicit form in so far as that only the components $g_{\mu\mu}$ of the metrical fundamental tensor do not vanish (i. e. $g_{\mu\mu} \neq 0$, $g_{\mu\nu} = 0$, if $\mu \neq \nu$).

(c) Let us furthermore suppose too that the vectors λ^μ are parallel with the space-axes of the special frame of reference introduced above. This means on the one hand that in this special frame of reference each vector λ^μ has only space-like components, i. e. $\{\lambda^\mu\} = \{0, \lambda^1, \lambda^2, \lambda^3\} = \{0, \lambda_i\}$, and on the other hand the orientation of the λ^+ -trieder would a priori be fixed in contemporary points relative to the special frame of reference distinguished by the anisotropy of the space-time world.

(d) Finally, let us suppose that the scalar product of the spin vector and the unit vector directed in the direction of the line-elements is an adequate constant. The reason for introducing the characterization of the anisotropy of the space-time world instead of the contravariant direction co-ordinates v^μ , the pseudovector u^μ is that this product is — owing to the transformation character of the spin vector — a scalar.

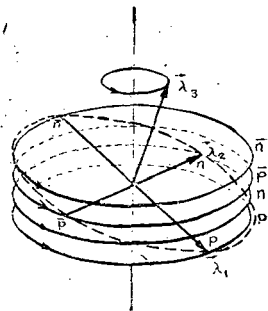


Fig. 1

Sometimes the spin of the field (or in other words: the elementary particles) is defined as an antisymmetrical tensor of second order. In this case it is more convenient to characterize the anisotropy of the space-time world by a surface-element $a^{\mu\nu}$ being an antisymmetric tensor of second order too, the normal vector of which is just a vector-density of order (-1) . Such a space is then an ensemble of $(x^\mu, a^{\mu\nu})$ and usually called as Cartanian space. We will not use this more difficult geometrical method, since the more elementary treatment seems to be adequate for the geometrization of the isospace and its transformations.

The last supposition means, however, that

(i) in the case of fields (or elementary particles being the quanta of the fields regarded) with zero spin the condition introduced in (d) is meaningless, which means that no correlation between the internal and external degrees of freedom of the fields exists and the isospace is three-dimensional.

(ii) in the case of fields with non-zero spin the condition introduced in (d) reduces the internal degrees of freedom by one and therefore the isospace is quasi-

two-dimensional. It is suitable to suppose in this case that the λ^μ axis of the λ^+ -trieder makes a precession around the spin axis with angle $\theta_3 = \text{const.}$ and the two degrees of freedom are characterized by two internal co-ordinates $\xi_{(1)}$ and $\xi_{(2)}$.

§ 5. The Isotriplets of the Pions

To demonstrate the method of geometrization of the isospace and its transformations, let the pions be regarded as being particles with zero spin.

Let $P_x \equiv P$ be the transformation corresponding to the inversion in respect to the origin then follows from (c) that $P\lambda^+ \rightarrow \lambda^-$ and *vice versa*.

Furthermore, the fundamental supposition would be proposed that

$$\psi_I \equiv \psi(x^\mu; 1, 0, 0), \quad \psi_{II} \equiv \psi(x^\mu; 0, 1, 0), \quad \psi_{III} \equiv \psi(x^\mu; 0, 0, 1) \quad (11)$$

— being the values of the field component $\psi(x^\mu; \xi_{(1)}, \xi_{(2)}, \xi_{(3)})$ in the directions of the axes of the λ^+ -trieder — represent the components of the isovector or that of the isopseudovector ψ of the field according to that the field is scalar or pseudoscalar.

One can immediately see that in each direction — determined by the quantities $\xi_{(1)}, \xi_{(2)}, \xi_{(3)}$ — the field quantity $\psi = \psi(x^\mu; \xi_{(1)}, \xi_{(2)}, \xi_{(3)})$ can easily be determined as a linear combination of ψ_{A-s} ($A = I, II, III$).

Namely, due to (8) for the components of the isovector or isopseudovector $\psi'(x^\mu; \xi'_{(1)}, \xi'_{(2)}, \xi'_{(3)}) = \{\psi_I(x^\mu; 1, 0, 0), \psi_{II}(x^\mu; 0, 1, 0), \psi_{III}(x^\mu; 0, 0, 1)\}$ related to the axes of a λ'^+ -trieder having other orientation than the original one — determined by the Eulerian angles ϕ, ψ, ϑ — the formula of transformation

$$\psi' = \psi M \quad (12)$$

can be obtained, where M means the matrix of the transformation which was explicitly given by equation (8). This means, e. g., that

$$\begin{aligned} \psi'_I(x^\mu) &= \{\cos \phi \cos \psi - \sin \phi \sin \psi \cos \vartheta\} \psi_I(x^\mu) + \\ &+ \{\cos \phi \sin \psi + \sin \phi \cos \psi \cos \vartheta\} \psi_{II}(x^\mu) + \sin \phi \sin \vartheta \psi_{III}(x^\mu). \end{aligned} \quad (13)$$

But, by a suitable rotation the λ^+ -trieder its first axis can be put into the direction determined by the internal co-ordinates $\{\xi_{(1)}, \xi_{(2)}, \xi_{(3)}\}$ so far that $\psi(x^\mu; \xi_{(1)}, \xi_{(2)}, \xi_{(3)}) = \psi'(x^\mu; 1, 0, 0)$ and in this way the explicit dependence of $\psi(x^\mu; \xi_{(1)}, \xi_{(2)}, \xi_{(3)})$ on the components ψ_A is obtained by (12).

(i) Let

$$\Psi_{\lambda^+} \equiv \frac{1}{\sqrt{2}} \{\psi_I + i\psi_{II}\}, \quad \Psi_{\lambda^+}^* \equiv \frac{1}{\sqrt{2}} \{\psi_I - i\psi_{II}\}, \quad \Psi_{\lambda^+}^0 \equiv \psi_{III} \quad (14)$$

be the usual components of the combined, charged and neutral field, as well as let us also suppose that the plane determined by the vectors λ and λ of the λ^+ -trieder coincides with a complex plane — being λ and λ , respectively, the unit vectors parallel to the real and imaginary axes — then it can be proposed that in the case of a rotation by an angle α on this plane around the λ -axis the transformation formulae

of the components of the charged and that of the neutral field are

$$\Psi'_{\lambda^+} = \Psi_{\lambda^+} e^{-i\alpha}, \quad \Psi'^*_{\lambda^+} = \Psi^*_{\lambda^+} e^{i\alpha}, \quad \Psi'^0_{\lambda^+} = \Psi^0_{\lambda^+}. \quad (15)$$

This means that the gauge transformation of first kind can be geometrically interpreted as a rotation of the λ -trieder around one of its axes (in our case around the λ -axis).

(3) (ii) Furthermore, if

$$\psi_I = \frac{1}{\sqrt{2}} \{ \Psi_{\lambda^{\pm}}^* + \Psi_{\lambda^{\pm}}^* \}, \quad \psi_{II} = \frac{1}{\sqrt{2}i} \{ \Psi_{\lambda^{\pm}} - \Psi_{\lambda^{\pm}}^* \}, \quad \psi_{III} = \Psi_{\lambda^{\pm}}^0 \quad (16)$$

denote the components of the isovector or that of the isopseudovector of the field related to the λ^+ - and λ^- -trieder, respectively, then one can prove that by the transformation C which changes, e. g. the orientation of the λ -axis of the λ^+ -trieder, without changing the co-ordinates x^μ , in the case of scalar fields the transformation formulae

$$C\psi_A = \psi_A \quad (A = I, II, III) \text{ or } C\Psi_{\lambda^{\pm}} = \Psi_{\lambda^{\pm}}, \quad C\Psi_{\lambda^{\pm}}^* = \Psi_{\lambda^{\pm}}^*, \quad C\Psi_{\lambda^{\pm}}^0 = \Psi_{\lambda^{\pm}}^0 \quad (17)$$

and in the case of pseudoscalar field the transformation formulae

$$C\psi_I = \psi_I, \quad C\psi_{II} = -\psi_{II}, \quad C\psi_{III} = \psi_{III} \text{ or } C\Psi_{\lambda^{\pm}} = \Psi_{\lambda^{\pm}}^*, \quad C\Psi_{\lambda^{\pm}}^* = \Psi_{\lambda^{\pm}}, \quad C\Psi_{\lambda^{\pm}}^0 = \Psi_{\lambda^{\pm}}^0, \quad (18)$$

respectively, can be obtained. This means, however, for pseudoscalar field that the changing of the orientation of the λ -trieder represents the charge conjugation.

Taking the equations (16) into account one can see that the charge conjugation cannot be explained in the case of scalar boson field in this way. Therefore, the suggested theory can only be accepted if pions are pseudo-scalar which seems to be in accordance to other theories [1, 2].

(iii) Taking the definitions of the transformations P and C , respectively, into account we have

$$CP\Psi_{\lambda^{\pm}} = C\Psi_{\lambda^{\mp}} = \Psi_{\lambda^{\pm}} \quad (19)$$

which is just the geometrical interpretation of LANDAU's theory [5].

(iv) Finally, let I_{II} be an inversion with respect to the origo in the plane determined by the axes λ and λ of the λ^+ -trieder then the mesoparity transformation $P_g = P' = CI_{II}$ can be interpreted as the geometrical transformation which is composed of an inversion with respect to the origo in one of the planes determined by the axes of the λ^+ -trieder (in our case in the (λ, λ) plane) and the changing of the orientation of the axes of the λ^+ -trieder being orthogonal to the plane of inversion. It can be namely seen that P'_i in the case of pseudo-scalar fields changes the sign of each component of its isopseudovectors:

$$P'\psi_A = -\psi_A. \quad (20)$$

One can immediately see that due to the definition of the transformations P'_i and P , respectively, analogously to LANDAU's theorem the relation

$$P'P\Psi_{\lambda^{\pm}} = P'\Psi_{\lambda^{\mp}} = \Psi_{\lambda^{\pm}} \quad (21)$$

can be obtained being a *new law of invariance* which has not been observed previously.

In course of the above considerations the λ axis of the λ^+ -trieder has been distinguished by the supposition that the field component⁽³⁾ of the neutral field

$$\Psi_{\lambda^{\pm}}^0 \equiv \Psi_{III} \equiv \psi(x^{\mu}; 0, 0, 1) \quad (22)$$

means the value of the field quantity ψ in its direction. In the case of scalar or pseudo-scalar fields this distinction has not any further consequence.

§ 6. The Isodoublets of Spin One-half Particles

Owing to our supposition (d) in § 4 the isospace is in this case quasi-two-dimensional, *i. e.*, the internal degrees of freedom of the fields are reduced to two. This means, however, that the field components ψ can be written in the form $\psi = \psi(x^{\mu}; \xi_{(1)}, \xi_{(2)})$. For sake of simplicity let only the fields of nucleons $\{p, n\}$ as well as that of the leptons, respectively $\{e, \bar{\nu}\}$ and $\{\mu, \bar{\lambda}\}$, be taken into account supposing that ψ fulfils either the second order equations of FEYNMAN [9] or rather that of MARX [10]. The isospace of photons and xions can be analogously treated without any difficulty.

It is supposed that ψ is a two-component spinor the components of which belong to the two spinstates of the mentioned particles. To distinguish the operators of *charge symmetry* and *mesoparity* let us suppose that $\psi(x^{\mu}; \xi_{(1)}, \xi_{(2)})$ corresponds to the different particle states as follows:

Components of isospinors	Nucleons	Leptons	
$\psi_{11}(x^{\mu}) \equiv \psi(x^{\mu}; 1, 0)$	p -state	e^{-} -state	μ^{-} -state
$\psi_{12}(x^{\mu}) \equiv \psi(x^{\mu}; -1, 0)$	\bar{n} -state	ν -state	λ -state
$\psi_{21}(x^{\mu}) \equiv \psi(x^{\mu}; 0, 1)$	n -state	$\bar{\nu}$ -state	$\bar{\lambda}$ -state
$\psi_{22}(x^{\mu}) \equiv \psi(x^{\mu}; 0, -1)$	\bar{p} -state	e^{+} -state	μ^{+} -state

Due to the two-dimensional character of the isospace the geometrical interpretation of the different isotransformations can be easily illustrated graphically (Fig. 2):

(i) The transformation of *charge symmetry* (Z) means a reflexion with respect to a plain being orthogonal to the two-dimensional isospace (*i. e.*, to the plain containing the λ and λ axes of the λ -trieder) which bisects the angle between the λ and λ axes. This definition of the charge symmetry transformation corresponds its usual definition according to which the proton (antiproton) is transformed into neutron (antineutron).

(ii) Charge conjugation (C) means a reflexion with respect to a plain being also orthogonal to the two-dimensional isospace which bisects the angle between the axes λ and $-\lambda$ of the λ -trieder. This definition of charge conjugation corresponds

(1) (2)
to its usual definition according to which the proton (neutron) is transformed into antiproton (anti-neutron).

(iii) Mesoparity or isoparity transformation (P') exchanges the orientation of the λ^+ -trieder; i. e., the λ^+ -trieder is transformed into the λ^- -trieder. It can be immediately proved that the mesoparity transformation can be composed by the transformations of parity, charge conjugation and charge symmetry operations: $P' = PCZ$ (Fig. 3).

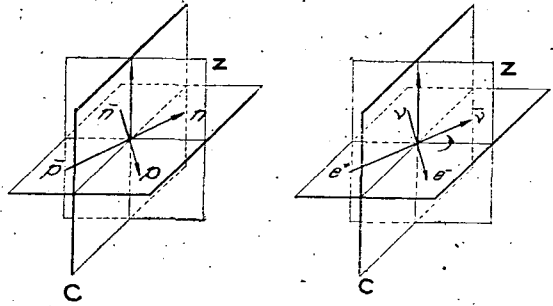


Fig. 2

Remarks. (1) The graphical description of isospace of this paragraph does not differ essentially from that of § 5. Namely, due to FEYNMAN's theory the charge symmetry operator transforms $\pi^{\pm 0}$ into $\pi^{\pm 0}$. This means

$$\begin{aligned} \psi(x^\mu; 1, 0, 0) &= \psi(x^\mu; -1, 0, 0) \equiv \psi_I, \\ \psi(x^\mu; 0, 1, 0) &= \psi(x^\mu; 0, -1, 0) \equiv \psi_{II}, \\ \psi(x^\mu; 0, 0, 1) &= \psi(x^\mu; 0, 0, -1) \equiv \psi_{III}. \end{aligned}$$

But, it can be proved that in this case the charge symmetry operator is equivalent with the operator of charge conjugation (Fig. 4). As a matter of fact this situation caused previously some misunderstandings.

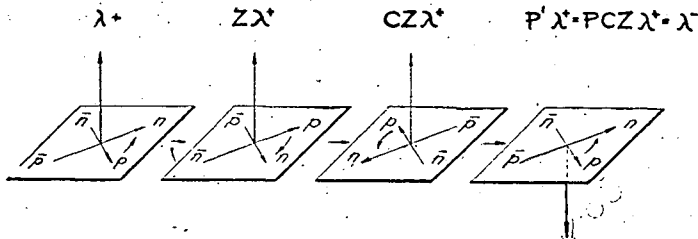


Fig. 3

(2) The electromagnetic interactions are not invariant against the charge symmetry operation. This means that the different members of the isodoublets due to the electromagnetic interaction are different (e. g., the mass difference between proton and neutron, etc.)

(3) It can be seen — as it was previously proved several time — that the number of invariants of weak interactions is not less than that of the electromagnetic inter-

action, but the invariants of the two different interactions are different. E. g., the invariance against the mesoparity transformation P' corresponds in the case of electromagnetic interactions to that of the parity transformation as well as the invariance against the charge symmetry operation Z corresponds to that of charge conjugation C .

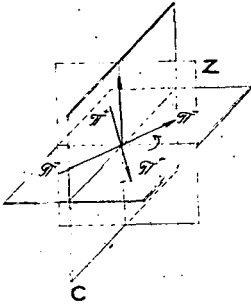


Fig. 4

(4) Fig. 1 shows that because of the rotation of the λ -trieder the ψ_{AB} -s ($A, B = 1, 2$) represent four different levels corresponding to the different particle states. Furthermore, it can be seen that in terms of the suggested theory the isospace is threedimensional in spite of the fact that the internal degree of freedom is only two.

Corrolaria. (1) It can be seen without any difficulty that LANDAU'S PC theorem holds true since the λ^+ -trieder is transformed by the operation PC into the λ^+ -trieder (Fig. 5a). Analogously, the same theorem is valid for $P'Z$ (Fig. 5b).

(2) The invariance against the transformation PP' , i. e. the PP' theorem — as it was shown in § 6 — is naturally valid also in this case (Fig. 6).

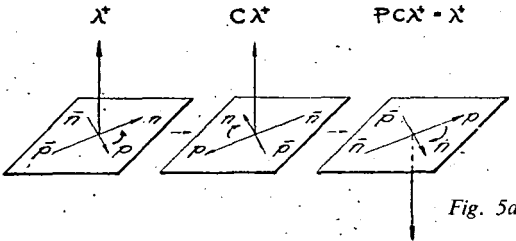


Fig. 5a

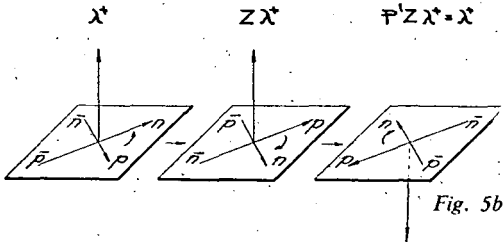


Fig. 5b

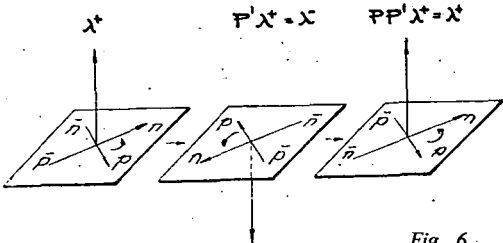


Fig. 6

§ 7. A Method to Determine the Metrical Fundamental Tensor of the Line-element Space

The metrical fundamental tensor $g_{\mu\nu}$ of the space — being for homogeneous and anisotropic spaces a function only of the homogeneous direction co-ordinates u^μ , i. e. $g_{\mu\nu} = g_{\mu\nu}(u^\mu)$ — was considered above as an *a priori* known function. Owing to the fundamental idea of the theory suggested, the anisotropy of the space-time world is induced by the anisotropy of the weak interactions. But, the anisotropy of the weak interactions is characterized, e. g., by the longitudinal polarization of the emitted electrons. If one calculates with the general interaction the probability for an ordinary allowed β -transition in which the electron has a fixed energy W and its spin makes an angle ϑ with its momentum one obtains

$$N(\vartheta) = \text{const.} \{1 + \mathcal{A} \cos \vartheta\} d\Omega_e \quad (23)$$

where $d\Omega_e$ denotes the width of the solid angle of the electron direction, furthermore:

$$\begin{aligned} \mathcal{A} &= d\zeta \frac{v_e}{e} [\zeta(1+bm/W)]^{-1} \\ \zeta &= (|g_S|^2 + |g_V|^2) |M_F|^2 + (|g_T|^2 + |g_A|^2) |M_{GT}|^2 \\ b\zeta &= \left[1 - \left(\frac{e^2}{\hbar c} Z \right)^2 \right]^{\frac{1}{2}} \{ (g_S^* g_V + g_S S g_V^*) |M_F|^2 + (g_T^* g_A + g_T g_A^*) |M_{GT}|^2 \} \\ d\xi &= 2 \operatorname{Re} \{ g_S g_S^* - g_V g_V^* \} |M_F|^2 + 2 \operatorname{Re} \{ g_T g_T^* - g_A g_A^* \} |M_{GT}|^2 - \\ &\quad - i \frac{e^2}{\hbar c} \frac{Zm}{p} [2 \operatorname{Im} \{ g_S g_V^* + g_S^* g_V \} |M_F|^2 + 2 \operatorname{Im} \{ g_T g_A^* + g_T^* g_A \} |M_{GT}|^2] \\ M_F &= \sum_{n=1}^A \int \phi_f^* \tau^{(n)} \phi_i dV, \quad M_{GT} = \sum_{n=1}^{\infty} \int \Phi_f^* \sigma^{(n)} \tau^{(n)} \phi_i dV, \end{aligned}$$

respectively, m and v_e mean the mass and the velocity of the electron; M_F and M_{GT} are the so-called FÉRMÍ and GAMOW—TELLER nuclear matrix elements; at last respectively g_S , g_V , g_T and g_A are the coupling constants of the scalar, vector, tensor and axial vector interactions [11].

Let us suppose that the surface (23) should be identical with the Carathéodoryan indicatrix (4) of the anisotropic space. This means in terms of the theory suggested that the equation of this indicatrix in its parametric form is determined explicitly by

$$\begin{aligned} x^1 &= \{1 + \mathcal{A} \cos \vartheta\} \sin \vartheta \cos \phi, \quad x^2 = \{1 + \mathcal{A} \cos \vartheta\} \sin \vartheta \sin \phi, \\ x^3 &= \{1 + \mathcal{A} \cos \vartheta\} \cos \vartheta. \end{aligned} \quad (24)$$

Then the components of the metrical fundamental tensor of the space is then given by

$$g_{00} = 1, \quad g_{ik}(u^1, u^2, u^3) = \delta_{ik} \{1 + \mathcal{A} v^3 [(v^1)^2 + (v^2)^2 + (v^3)^2]^{-\frac{1}{2}}\}^{-2}. \quad (25)$$

Such a space is the special case of the general line-element spaces¹.

Other method for explicit calculation of the metrical fundamental tensor based on the anisotropy of the Co⁶⁰ experiment was previously proposed [8].

* * *

The author is indebted to Dr. G. MARX and to Dr. A. MOÓR for very valuable discussions.

¹ This space has some interest also from the geometrical point of view. This is, namely, an explicit example for a space, all its three curvature tensors vanish, but is non-Euclidian since its torsion tensor is different from zero.

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ОБ ОДНОЙ ВОЗМОЖНОЙ ИНТЕРПРЕТАЦИИ ИЗОТОПНОГО СПИНОГО ПОЛЯ И ЕГО ПРЕОБРАЗОВАНИЯ

Я. И. Хорват

Автор делал выходы из экспериментов, утверждающих нарушение закон сохранения четности на анизотропность континуума пространства-времени, структура которого определяется физическими взаимодействиями. Геометрическая характеристика анизотропных пространств осуществляется геометрией линейного элемента, которая принимает пространство не как множество точек а множеством линейных элементов (x^μ, v^μ) , где x^μ координата места линейного элемента, v^μ ($\mu = 0, 1, 2, 3$) однородные координаты определяющие направление линейного элемента. Эти последние могут быть замещены Θ_i неоднородными координатами направления, или $\xi_{(i)} = \cos \Theta_i$ ($i = 1, 2, 3$) величинами, относящимися к одному пригодно выбранному трехграннику (λ -трехгранник). x^μ координатами места мы характеризуем внешние степени свободы физического пространства, а неоднородными координатами (x^μ) направления (или с величинами $\xi_{(i)}$) те же внутренние. Значит, наше представление о том что физическое пространство возбуждается в анизотропном континууме времени и пространства равно тем что при установлении теории элементарных частиц мы также должны иметь в виду внутренние степени свободы физических пространств. Это представление делает возможным приписывать простое геометрическое значение компонентам изовекторов, изопсевдовекторов и т. п., а также делать наглядным преобразования изотопного спинного поля, как вращение λ -трехгранника, или как отражение отнесенное к λ -трехграннику. Наконец, мы указываем на метод, при помощи которого метрический основной тензор анизотропного поля может быть явно определен.

BESTIMMUNG DER FLUORESZENZAUSBEUTE UND DES FLUORESZENZSPEKTRUMS MITTELS ERREGUNGSLICHTQUELLEN MIT KONTINUIERLICHEM SPEKTRUM

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Es werden Bestimmungsmethoden für die Quantenausbeute und das Fluoreszenzspektrum von fluoreszierenden Lösungen mittels Erregungslichtquellen mit kontinuierlichem bzw. stark verbreiterte Linien enthaltendem Spektrum beschrieben. Es wird gezeigt, daß auch im Falle nicht streng monochromatischer Erregung verhältnismäßig einfache Auswertungsformeln verwendbar sind. Mit den beschriebenen Methoden wurden Untersuchungen an Lösungen von Fluorescein, Rhodamin B und Trypaflavin durchgeführt. Die erhaltenen Ausbeutewerte und die Fluoreszenzspektren werden tabellarisch mitgeteilt.

§ 1. Bei der Untersuchung einiger Gesetze der molekularen Lumineszenz, wie z. B. bei der Kontrolle des sogenannten WAWIŁOWSchen Gesetzes [1] und der Abhängigkeit des Fluoreszenzspektrums von der Erregungswellenlänge [2], tritt die Notwendigkeit der Verwendung von Erregungslichtquellen mit kontinuierlichem Spektrum auf. Wenn wir bei Untersuchungen mit solchen Lichtquellen die störende Wirkung der Sekundärfluoreszenz durch die Verminderung der Schichtdicke [3] der bestrahlten Lösung beseitigen, oder auf ein leicht in Rechnung zu ziehendes Maß reduzieren wollen, so wird bei Anwendung eines photoelektrischen Spektrophotometers von üblicher Empfindlichkeit [4] die spektrale Bandbreite des Erregungslichtes im allgemeinen 5—10 μ nicht unterschreiten dürfen. (Bei Erregung durch die verbreiterten Linien der oft angewandten Quecksilberhöchstdrucklampen wird ebenfalls mit einer spektralen Bandbreite von 3—6 μ zu rechnen sein [5].) Die größere Bandbreite des Erregungslichtes wird im allgemeinen die Kompliziertheit der zur Auswertung der unmittelbaren Meßergebnisse anzuwendenden Formeln mit sich bringen [6], aber — wie es auch unsere experimentellen Untersuchungen unterstützen — können solche Schichtdicken gewählt werden, bei denen a) die Fluoreszenzintensität noch gut meßbar ist, b) die störende Wirkung der Sekundärfluoreszenz bloß einen Fehler von einigen Prozenten verursacht und gleichzeitig c) die zur Auswertung nötigen mathematischen Zusammenhänge bzw. numerischen Berechnungen selbst bei Reihenuntersuchungen keine besondere Schwierigkeiten bereiten.

§ 2. Zur Bestimmung der absoluten Quantenausbeute η einer fluoreszierenden Lösung oder des Quantenspektrums $f_q(\lambda)$ der Fluoreszenz mittels einer Erregungslichtquelle mit kontinuierlichem Spektrum ist es zweckmäßig, das folgende Verfahren bzw. die folgende Rechnungsmethode anzuwenden.

Zuerst bilden wir auf den Eintrittspalt eines photoelektrischen Spektrophotometers eine Magnesiumoxydfläche ab und bestrahlen wir diese mit einem Erregungslichtbündel von 5—10 m μ Bandbreite des durch ein Interferenzfilter oder einen Monochromator durchgelassenen Lichtes der Lampe, und zwar so, daß das Erregungslichtbündel mit der Kollimatorachse des Spektrophotometers nahezu parallel sei, d. h. mit letzterer einen Winkel $\vartheta < 20^\circ$ einschlieÙe. Bezeichnen wir in diesem Falle mit $I_e(\lambda)$ die Intensität des Photostromes bei Einstellung des Apparates auf eine Wellenlänge λ , und mit $I_f(\lambda)$ bei Belichtung der Magnesiumoxydfläche durch ein aus einer Lichtquelle der Farbtemperatur T gewonnenes Lichtbündel, dessen Quantenverteilung $q(\lambda)$ bekannt ist; sei $q(\lambda)/I_f(\lambda) \equiv Q(\lambda)$. Setzen wir dann an Stelle der Magnesiumoxydfläche eine dünne, planparallele Schicht der zu untersuchenden Lösung, die eine Dicke l besitzt, und bestrahlen wir diese durch das Erregungslichtbündel unter dem erwähnten Winkel ϑ . (Die Vorderfläche der die Lösung enthaltenden Küvette werde senkrecht zur Kollimatorachse des Spektrophotometers eingestellt.) Die Intensität des durch das Fluoreszenzlicht hervorgerufenen Photostromes bei der Einstellung des Spektrophotometers auf die Wellenlänge λ sei mit $I_f(\lambda)$ bezeichnet.

Für den Zusammenhang der Quantenausbeute und der Photoströme $I_e(\lambda)$, bzw. $I_f(\lambda)$ kann eine mit guter Annäherung gültige Formel erhalten werden, bei deren Herleitung die Ausgangsgleichungen der für die Ausbeutemessung ausgearbeiteten WAWILOWschen Methode [7], sowie der wohlbekannte fluoreszenzphotometrische Zusammenhang für breitbandige Erregung [6] benützt wurden. Nach unseren einfachen, aber langwierigen Berechnungen, auf die wir hier nicht eingehen wollen (s. den Anhang), ergab sich, daß für die auf das Erregungsband bezogene mittlere Quantenausbeute η_0 , ohne Korrektion für die Sekundärfluoreszenz, die Gleichung

$$\eta_0 = \frac{I_f(\lambda_0)}{I_{e \max}} \quad (1a)$$

$$= \frac{4n^2rQ(\lambda_0) \cos(\vartheta/n)}{\rho f_q(\lambda_0) \left\{ \frac{1 - e^{-k(\lambda_0)l}}{k(\lambda_0)} \bar{k} - \frac{1}{\cos(\vartheta/n)} \left(\frac{1}{2} - \frac{1}{3} k(\lambda_0)l \right) \bar{k}^2 l^2 + \frac{1}{\cos(\vartheta/n)} \left(\frac{1}{6} - \frac{1}{8} k(\lambda_0)l \right) \bar{k}^3 l^3 \right\}}$$

mit guter Annäherung gültig ist, wenn das Produkt aus dem Maximum des Absorptionskoeffizienten $k(\lambda)$ und der Schichtdicke l nicht größer als $\frac{1}{2}$ ist. In (1a) bedeutet $f_q(\lambda_0)$ den Wert der normierten Quantenverteilungsfunktion der Fluoreszenz bei einer, der Maximumstelle des Emissionsspektrums naheliegenden Wellenlänge λ_0 , n den Brechungsindex der Lösung, r ($\approx 0,98$) den Reflexionskoeffizienten des Magnesiumoxyds; der dem Werte 0,9-nähestehende Faktor ρ bezieht sich auf die Reflexionsverluste; die mit einem Querstriche bezeichneten Größen in (1a)

$$\bar{k}^m = \int_0^\infty \frac{I_e(\lambda)}{I_{e \max}} Q(\lambda) [k(\lambda)]^m d\lambda \quad (m = 1, 2, 3) \quad (2)$$

lassen sich graphisch oder numerisch leicht bestimmen. Die Formel (1a) bzw. die mit ihr verbundene Ausbeutebestimmungsmethode erscheint deshalb als besonders vorteilhaft, weil bei Reihenmessungen, die mit Veränderung der Konzentration

und der Schichtdicke verknüpft sind — z. B. bei der Untersuchung der Konzentrationslöschung — die Integrale \bar{k}^m nur einmal zu bestimmen sind.

Ist die Intensität der Fluoreszenz bzw. die Empfindlichkeit des benützten Spektrophotometers groß genug, so ist es zweckmäßig, den Wert der erwähnten Größe $k_{\max} \cdot l$ durch Wahl von l derart zu verringern, daß die vorige kleiner als etwa 0,1 sei. In diesem Falle vereinfacht sich Gl. (1a) wesentlich, es gilt nämlich, mit einem Fehler nicht größer als 0,5%, die Gleichung

$$\eta_0 = \frac{I_f(\lambda_0)}{I_{e \max}} \cdot \frac{4n^2 r Q(\lambda_0) \cos(\vartheta/n)}{\rho f_q(\lambda_0) \left\{ \bar{k}l - \frac{1}{2 \cos(\vartheta/n)} \bar{k}^2 l^2 \right\}} \quad (1b)$$

Bei der Herleitung dieser Näherungsformel aus (1a) wurde vorausgesetzt, daß der Absorptionskoeffizient bei der Wellenlänge λ_0 nur etwa 1/10 des k_{\max} beträgt. In den meisten Fällen kann man λ_0 tatsächlich so wählen, daß diese Bedingung in der Nähe der Maximumstelle des Fluoreszenzspektrums erfüllt sei.

Ist die Bedingung $k_{\max} \cdot l < 0,1$ erfüllt, so ist die zur Bestimmung des Fluoreszenzspektrums zu verwendende Auswertungsformel ebenfalls sehr einfach. Aus der im Anhang angegebenen Ausgangsgleichung (5) erhalten wir nämlich durch eine leichte Rechnung die Beziehung

$$f_q(\lambda) = \text{const. } I_f(\lambda) Q(\lambda) \frac{\bar{k} - \frac{1}{2} \bar{k}^2 l}{\left(1 - \frac{k(\lambda)l}{2}\right) \bar{k} - \frac{1}{2} \bar{k}^2 l} \quad (3)$$

Wenn weiters noch $\bar{k}^2 l / \bar{k} < 0,2$ ist (s. Anhang), so besteht innerhalb der erwähnten Fehlergrenze die noch einfachere Näherungsformel

$$f_q(\lambda) = \text{const. } I_f(\lambda) Q(\lambda) \frac{1}{1 - \frac{k(\lambda)l}{2}} \quad (4)$$

Die Gültigkeit der auf das Fluoreszenzspektrum bezüglichen beiden letzten Gleichungen wird unter den gegebenen Bedingungen durch die Sekundärfluoreszenz nicht beeinflusst [3]. Wenn dagegen das Intensitätsverhältnis der sekundären und primären Fluoreszenzen nicht mehr zu vernachlässigen ist, so ist die wahre Ausbeute aus den durch (1a) und (1b) gegebenen Näherungswerten nach der in [5] mitgeteilten Methode zu berechnen.

§ 3. Es wurden unter den in § 2 angegebenen Versuchsbedingungen — teilweise auch zur Kontrolle der Verwendbarkeit der beschriebenen Methode — Messungen an wäßrigen Lösungen des Fluoresceins bzw. an Äthylalkohol-Lösungen des Rhodamin B und des Trypflavins durchgeführt. Als Spektrophotometer wurde ein Apparat des Typs „Optica Milano CF4“ verwendet.

Bei der Bestimmung der absoluten Quantenausbeute diente zur Herstellung des Erregungslichtes eine Xenonlampe XBO 501 und ein Doppelmonochromator. Durch das so gewonnene monochromatische Licht wurde ein Flächenstück von 0,7 cm × 1,8 cm an der Vorderfläche der Küvette bestrahlt und etwa 0,2 cm × 1,0 cm die-

ses Flächenstückes auf den Eintrittspalt des Spektrophotometers abgebildet. Für die Bestimmung der Empfindlichkeitsfunktion $Q(\lambda)$ des Spektrophotometers wurde eine von der Firma OSRAM auf bekannte Farbtemperatur eingestellte Lampe verwendet.

Tabelle I

Nr.	Konzentration Mol/l	l cm	$k_{\max} \cdot l$	η_0
1	$2 \cdot 10^{-5}$	$5 \cdot 10^{-2}$	0,111	0,44
2	"	$1,25 \cdot 10^{-1}$	0,278	0,43
3	"	$2,5 \cdot 10^{-1}$	0,555	0,42
4	$5 \cdot 10^{-5}$	$1 \cdot 10^{-2}$	0,055	0,46
5	"	$5 \cdot 10^{-2}$	0,277	0,43
6	"	$1 \cdot 10^{-1}$	0,556	0,42

Nach der Aufnahme der Absorptions- und Emissionsspektren der untersuchten Lösungen wurde der Verlauf der Funktion $I_e(\lambda)$ für die zur Erregung der einzelnen Lösungen benützten Banden bestimmt, und zwar so, daß die Maximumstellen dieser Funktionen mit Hilfe des Doppelmonochromators in die Nähe der Wellenlänge des Absorptionsmaximums der einzelnen Lösungen eingestellt waren. Die Maximumstelle von $I_e(\lambda)$ lag im Falle des Trypflavins, des Fluoresceins und des Rhodamin B der Reihe nach bei 466, 492 und 557 $m\mu$; die für die Messung der Fluoreszenzintensitäten — in der Nähe der Fluoreszenzmaxima — gewählten Wellenlängen waren 490, 512 bzw. 572 $m\mu$.

Tabelle II

Lösung	Konzentration in Mol/l	Erregungswellenlänge in $m\mu$	η
Fluorescein im Wasser mit 3% NaOH..	$5 \cdot 10^{-5}$	≈ 492	0,93
Trypflavin im C_2H_5OH mit $3 \cdot 10^{-3}$ Mol/l HCl	$2 \cdot 10^{-5}$ und $5 \cdot 10^{-5}$	≈ 466	0,43
Rhodamin B im C_2H_5OH mit $3 \cdot 10^{-3}$ Mol/l HCl.....	$4 \cdot 10^{-5}$	≈ 557	0,53

In Tabelle I sind die charakteristischen Versuchsdaten unserer Untersuchungen am Trypflavin sowie die für diesen Stoff erhaltenen Ausbeutewerte als Beispiel dargestellt. Zur Auswertung der Meßdaten wurde in den Fällen 1 und 4 (s. Tabelle I) die sehr einfache Formel (1b), in den übrigen Fällen die Formel (1a) angewendet. Es ist zu bemerken, daß nach den numerischen Berechnungen die Glieder des durch Reihenentwicklung erhaltenen Ausdrucks im Nenner von (1a) im allgemeinen sehr rasch abnehmen, so stehen z. B. im Falle der 5. Zeile der Tabelle I die drei, \bar{k} , \bar{k}^2 , \bar{k}^3 enthaltenden Glieder des Nenners im Verhältnis 100:12,02:0,99 zueinander.

Im Falle des Trypflavins übertraf nach unseren Rechnungen das Intensitätsverhältnis des sekundären und der primären Fluoreszenz in keinem der in Tabelle I angeführten Fälle den Wert 0,03, was besagt, daß bei der angewendeten Methode der von der sekundären Fluoreszenz herrührende Fehler von max. 3% innerhalb der Fehlergrenzen der Messung und Auswertung lag.

Aus den Ergebnissen unserer Messungen zur Bestimmung der absoluten Quantenausbeute ergaben sich als wahrscheinlichste Werte für die Lösungen der drei Stoffe die in Tabelle II mitgeteilten Angaben.

Die Sekundärfluoreszenz verursachte allein bei Rhodamin B eine merkliche, etwa 6% betragende scheinbare Erhöhung der Quantenausbeute, welche rechnerisch in Betracht gezogen wurde. Die Abweichung der Quantenausbeute 0,93 des Fluoresceins von dem bei Erregung einer Lösung derselben Konzentration mit der Wellenlänge 436 μ erhaltenen Werte 0,87 [5] weist auf die Abhängigkeit der absoluten Quantenausbeute von der Erregungswellenlänge *auch in STOKESSchem Gebiete* hin, worauf auch aus den im Gange befindlichen Untersuchungen der Autoren zu schließen ist.

Tabelle III/A

Fluorescein, $5 \cdot 10^{-4}$ Mol/l, im Wasser mit 3% NaOH. Erregungswellenlänge: 436 μ

λ	$100 \frac{f_q(\lambda)}{f_q \max}$	λ	$100 \frac{f_q(\lambda)}{f_q \max}$	λ	$100 \frac{f_q(\lambda)}{f_q \max}$
480	1,5	508	95,0	540	48,2
482	2,1	510	97,2	545	41,7
484	3,3	512	98,9	550	36,9
486	5,6	513	100,0	555	32,0
488	8,4	514	99,1	560	28,1
490	12,5	516	97,8	565	23,5
492	17,6	518	93,7	570	19,7
494	23,1	520	89,0	575	16,8
496	32,3	522	83,7	580	13,5
498	44,2	524	78,8	585	11,4
500	56,3	526	73,6	590	8,3
502	68,4	528	68,2	595	7,6
504	78,7	530	62,2	600	6,5
506	87,8	535	55,0		

Bei der Bestimmung der *Fluoreszenzspektren* auf Grund von (4) ist die Aufnahme der spektralen Verteilung des Erregungslichtes — wie auch aus der Formel ersichtlich — nicht nötig, was übrigens im Falle der zur Erregung sehr geeigneten verbreiterten Spektrallinien der Quecksilberhöchstdrucklampen ziemlich schwierig ist. Diese Schwierigkeit ist zwar auch dadurch auszuschalten, daß durch Verringerung der Spaltbreite des zur Filtrierung des Erregungslichtes dienenden Monochromators das Erregungsbündel in dem Maße monochromatisch gemacht wird, daß zur Bestimmung des Fluoreszenzspektrums die wohlbekanntere Korrektionsformel [6] für monochromatische Erregung benützt werden kann. In solchen Fällen ist aber die Schichtdicke infolge der geringen Erregungsintensität stark zu erhöhen, was das Auftreten der spektralen Störwirkung der Sekundärfluoreszenz nach sich zieht. Die auf (4) beruhende Bestimmungsmethode der Fluoreszenzspektren er-

scheint also bei Verwendung nicht nur von Glüh- und Xenonlampen, sondern auch von Quecksilberhöchstdrucklampen vorteilhaft.

Bei der genauen Bestimmung der Fluoreszenzspektren des Fluoresceins, Trypflavins und des Rhodamin B wurde — mit Rücksicht auf das oben Gesagte —

Tabelle III/B

Trypflavin, $3 \cdot 10^{-4}$ Mol/l, im C_2H_5OH mit $3 \cdot 10^{-3}$ Mol/l HCl.
Erregungswellenlänge: $436 m\mu$

λ	$100 \frac{f_q(\lambda)}{f_q \max}$	λ	$100 \frac{f_q(\lambda)}{f_q \max}$	λ	$100 \frac{f_q(\lambda)}{f_q \max}$
450	0,8	484	90,4	530	48,3
452	1,0	486	94,2	535	44,5
454	1,5	488	98,6	540	39,0
456	2,3	490	100,0	545	34,1
458	2,8	492	99,6	550	29,3
460	5,5	494	99,2	555	25,5
462	8,4	496	96,8	560	21,3
464	12,3	498	94,9	565	19,2
466	17,3	500	91,8	570	15,9
468	24,1	502	88,4	575	13,8
470	31,8	504	84,9	580	11,8
472	41,0	506	82,7	585	9,7
474	50,4	508	79,7	590	8,5
476	60,5	510	76,2	595	7,8
478	70,0	515	68,0	600	6,3
480	77,7	520	62,0	605	5,2
482	85,0	525	55,4	610	4,9

Tabelle III/C

Rhodamin B, $2 \cdot 10^{-5}$ Mol/l, C_2H_5OH mit $3 \cdot 10^{-3}$ Mol/l HCl. Erregungswellenlänge: $546 m\mu$

λ	$100 \frac{f_q(\lambda)}{f_q \max}$	λ	$100 \frac{f_q(\lambda)}{f_q \max}$	λ	$100 \frac{f_q(\lambda)}{f_q \max}$
520	0,6	568	83,6	600	53,7
525	1,7	570	90,4	602	47,6
530	3,3	572	95,6	604	44,9
532	4,9	574	98,6	606	42,0
534	6,0	576	100,0	608	39,7
536	9,1	578	99,9	610	37,7
538	13,7	580	98,4	615	35,6
540	18,3	582	95,4	620	33,0
Erregungsband		584	90,8	625	27,9
554	23,9	586	84,3	630	21,0
556	31,7	588	79,2	635	19,2
558	40,3	590	73,3	640	17,5
560	50,3	592	66,6	645	15,5
562	59,4	594	63,6	650	13,2
564	68,0	596	62,1		
566	76,8	598	56,4		

die Bedingung $k_{\max} \cdot l \leq 0,1$ eingehalten. Zur Aufnahme der Spektren wurde die im Vorhergehenden schon beschriebene Versuchseinrichtung benützt; die Herstellung des Erregungslichtes erfolgte aber mittels des mit einer Quecksilberhöchstdrucklampe HBO 200 kombinierten Doppelmonochromators, den wir schon bei den Ausbeutemessungen verwendet hatten. Außerdem wurden im Falle des Fluoresceins auch Messungen durchgeführt, bei denen zur Herstellung des Erregungslichtes eine von der stabilisierten Stromquelle des Spektrophotometers gespeiste Glühlampe von 50 W und ein Interferenzfilter SIF 460 diente.

Die Werte der Verteilungsfunktion $f_q(\lambda)$ der Fluoreszenz sind in den Tabellen IIIA, IIIB und IIIC zusammengefaßt.

Anhang

a) Bei der Herleitung der in der Arbeit angegebenen Näherungsformeln wurde davon ausgegangen, daß unter den vorausgesetzten Versuchsbedingungen die spektrale Fluoreszenzleuchtdichte $B(\lambda')$, im Quantenstrom ausgedrückt,

$$B(\lambda') = \frac{\eta_0 f_q(\lambda') Q}{4 \pi n^2} \int_0^\infty E(\lambda) \frac{k(\lambda) / \cos(\vartheta/n)}{k(\lambda') + k(\lambda) / \cos(\vartheta/n)} \left[1 - e^{-\left[\frac{k(\lambda)}{\cos(\vartheta/n)} + k(\lambda') \right] l} \right] d\lambda \quad (5)$$

beträgt. Die hier auftretende, bisher nicht definierte Größe $E(\lambda)$ bedeutet die spektrale Quantenstromdichte des Erregungslichtes an der Vorderfläche der bestrahlten Küvette. (Bezüglich dieser Gl. s. S. 38–40 von [6].) In Gl. (5) steht nicht η , sondern η_0 , da hier die Sekundärfluoreszenz nicht berücksichtigt ist. Die Wellenlänge des Fluoreszenzlichtes ist zur Unterscheidung von der Integrationsveränderlichen λ mit λ' bezeichnet. Die im § 2 definierten Photoströme $I_e(\lambda)$ bzw. $I_f(\lambda)$ des Photoelektronenvervielfachers (bzw. Photozelle) des Spektrophotometers hängen mit $B(\lambda)$ bzw. mit $E(\lambda)$ durch die Gleichungen

$$B(\lambda) = C I_f(\lambda) Q(\lambda) \quad (6a)$$

bzw.

$$E(\lambda) = C \frac{\pi}{l} I_e(\lambda) Q(\lambda) \quad (6b)$$

zusammen. C ist eine von der optischen Anordnung und von den Daten des Spektrophotometers abhängige, jedoch von λ unabhängige Konstante. Gl. (6b) beruht auf dem LAMBERTSchen Streuungsgesetz [7]. Die Gleichungen (1a) und (1b) wurden aus (5) derart hergeleitet, daß nach Reihenentwicklung des Exponentialausdruckes — auf Grund entsprechender Abschätzung — Vernachlässigungen vorgenommen wurden, wobei die beschriebene Wahl von λ_0 eine wesentliche Rolle spielte.

b) Gl. (3) läßt sich aus (1a) dadurch ableiten, daß man in dem Nenner der rechten Seite von (1a) das k^3 enthaltende Glied vernachlässigt, λ_0 durch die beliebige Wellenlänge λ ersetzt, im Koeffizienten von k^2 den Ausdruck $k(\lambda)l$ vernachlässigt und den Koeffizienten von k durch $(1 - k(\lambda)l/2)$ annähert. In Gl. (3) sind die von λ unabhängigen Faktoren in einem Faktor der Form $\text{const.} [\bar{k} - k^2 l/2 \cos(\vartheta/n)]$ zusammengezogen; so nähert sich der Bruch in der rechten Seite von (3) für $k(\lambda) \rightarrow 0$ dem Werte Eins.

c) Um (4) statt (3) anwenden zu können, ist es — wie es aus einer einfachen Rechnung hervorgeht — nur notwendig, daß

$$\frac{\bar{k}^2 l}{2 k} < 0,1 \quad (7)$$

sei. Durch Anwendung eines elementaren Mittelwertsatzes der Integralrechnung läßt sich beweisen,

daß die Ungleichung (7) besteht, wenn für das Verhältnis des Minimal- bzw. Maximalwertes k'_{\min} bzw. k'_{\max} des Absorptionskoeffizienten $k(\lambda)$ im Spektralgebiete der Erregungsbande

$$k'_{\min}/k'_{\max} > 5k_{\max} \cdot l \quad (8)$$

gilt. Aus (8) ist es ersichtlich, daß im Falle einer nicht zu breiten Erregungsbande leicht eine Schichtdicke l zu finden ist, bei welcher die äußerst einfache Korrektionsformel (4) anwendbar ist.

* * *

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ОПРЕДЕЛЕНИЕ ВЫХОДА И СПЕКТРА ФЛУОРЕСЦЕНЦИИ ПРИ ПРИМЕНЕНИИ ВОЗБУЖДАЮЩИХ ИСТОЧНИКОВ СВЕТА С РАСШИРЕННЫМИ ЛИНИЯМИ

И. Кечкемети, И. Домби, Р. Хорваи, И. Хевеши и Л. Козма

В работе описываются экспериментальные методы определения абсолютного выхода и спектра флуоресценции растворов при применении возбуждающих источников света, обладающих сплошным спектром или спектром с расширенными линиями. Было показано, что относительно простые формулы могут быть применены для расчета выхода и спектра флуоресценции даже при не строго монохроматическом возбуждении. Авторы сделали измерения описанными методами в случае растворов флуоресценна, родамина Б и триафлавина. Приведены полученные данные для выхода и таблицы спектров флуоресценции.

SPEKTROPHOTOMETRISCHE BESTIMMUNG DER IN LÖSUNGEN VORHANDENEN KOMPLEXE

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Die zum Aufsuchen der Zwischenkomplexe und zur Bestimmung ihrer Zusammensetzung gebräuchlichen Methoden werden mit Rücksicht auf ihre Verwendbarkeit besprochen. Die bestbewährte Methode ist auf Nickel(II)ionenhidrat und Äthylendiamin enthaltende wäßrige Lösungen im Wellenlängenbereich 1500–300 $m\mu$ angewendet. Es wird ein kritischer Vergleich der Methoden gegeben, wonach die Anwendung der hier gebrauchten Methode dadurch begründet erscheint, dass sie — im Gegensatz zum indizierenden Charakter der Methode der stetigen Variationen — mit Nachweischarakter verwendbar ist.

Wird dem Ionenhydrat eines Metalls irgendein Ligand in möglichst verschiedenen Mengenverhältnissen zugegeben, so kann die Anzahl und Zusammensetzung der in der homogenen Lösung vorhandenen Komplexe sehr mannigfaltig sein. Zur Bestimmung der Zusammensetzung findet die JÓBSche Methode der stetigen Variationen [1] ausgedehnte Verwendung. Es wurde aber bereits von JÓB darauf hingewiesen, daß die Methode nur dann anwendbar ist, wenn nur ein Zwischenkomplex entsteht. Bei Halogenkomplexen von Kobalt(II), Kupfer(II) und Nickel(II) werden [2] durch die Methode nicht alle vorhandenen Komplexe nachgewiesen, sondern nur einige indiziert.

Die Methode wurde von VOSBURGH und COOPER [3] für das Vorhandensein mehrerer Zwischenkomplexe weiterentwickelt; GOULD und VOSBURGH [4] rechnen mit dem Vorhandensein eines dritten Stoffes neben den beiden reagierenden Stoffen, das Prinzip der Methode wird aber unangetastet gelassen.

Im allgemeinen ist festzustellen, daß die Bestimmung der nachzuweisenden Komplexe mit der Methode der stetigen Variationen bei einer gewissen ausgewählten Wellenlänge geschieht, was, falls mehr als ein Komplex gebildet wird, zu prinzipiellen Auseinandersetzungen Gelegenheit gibt. WOLDBYE [6] gibt eine Kritik der Methode im Falle der Anwendung zur Bestimmung der Gleichgewichtskonstanten, dann erklärt er als Kritik der Zusammensetzungsbestimmung, daß die Methode bezüglich der Zwischenkomplexe bloß für das Indizieren, nicht für das Ziehen von Folgerungen Bedeutung besitzt. Mit der ausführlichen Kritik und der Anwendung der Methode haben wir uns in einer anderen Arbeit [5] befaßt.

Aus alledem folgt, daß die Methode — den Fall der Bildung eines einzigen Komplexes ausgenommen — zur Bestimmung der Anzahl der vorhandenen Komplexe eindeutig und mit nachweisendem Charakter prinzipiell nicht verwendbar, und nur zum Indizieren einzelner Komplexe geeignet ist. Es ist deshalb gerecht-

fertigt, eine Methode zu suchen, welche die Untersuchungen auf das ganze ausgemessene Wellenlängengebiet erstreckt und so infolge der größeren Exaktheit eindeutige Resultate liefert, welche Nachweischarakter haben, und das Anzeigen von Komplexen abweichender Zusammensetzung ausschließen. Zu diesem Zweck wollen wir die folgenden Methoden betrachten.

Bestimmung der Zusammensetzung eines koordinativ gesättigten Komplexes

Ist die Zusammensetzung eines koordinativ gesättigten Komplexes bekannt, so kann auch über die Anzahl der Zwischenkomplexe eine erste Orientierung erhalten werden. Es werde zu dem Zweck das Massenwirkungsgesetz auf den Fall der Komplexbildung angewendet [7]:

$$\frac{K\varepsilon_x}{E} = \frac{1}{(a - mx)^m - (b - nx)^n}, \quad (1)$$

worin E die Extinktion des Gemisches bezeichnet, wenn das Kation mit der Konzentration a , das Anion mit der Konzentration b in der Reaktion teilnimmt und ein Komplex der Konzentration x entsteht. Aus obiger Gleichung erhält man für $b \gg a$ und $m = 1$:

$$\frac{\varepsilon_x Ka}{E} - K = \frac{1}{b^n}. \quad (2)$$

Da der molare Extinktionskoeffizient ε_x des entstehenden Komplexes einen konstanten Wert hat, wird sich $1/E$ linear mit $1/b^n$ ändern. Zwecks Gebrauch der Gleichung

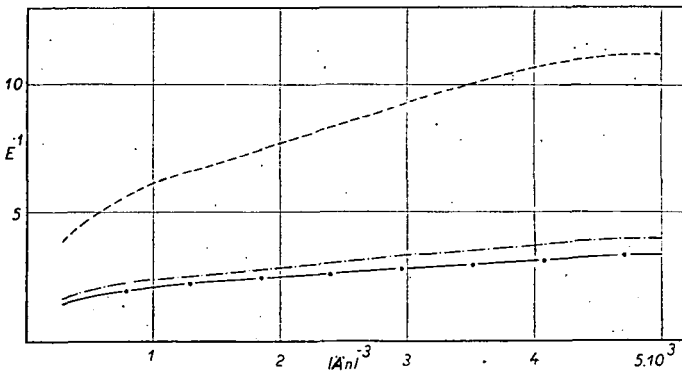


Fig. 1. - - - - - Kurve bei 350 m μ , - - - - - Kurve bei 550 m μ ,
- • - Kurve bei 900 m μ Wellenlänge.

ung wird die Konzentration des Anions — bei konstanter Kationkonzentration — nach Möglichkeit variiert und E gemessen. Die erhaltenen Werte von $1/E$ werden denjenigen von $1/b^n$ für verschiedene n graphisch gegenübergestellt; das Resultat wird durch den n -Wert angezeigt, bei welchem der Verlauf der Kurve am besten

die Gerade annähert. Die lineare Abhängigkeit ist aber infolge der Vernachlässigungen nur näherungsweise gültig [8].

Diese Methode wandten wir auf die Bestimmung der Anzahl der an Nickel(II)ionen gebundenen Äthylendiaminmoleküle ($\bar{A}n$) an. Als Konzentration des Nickel(II)ions wurde 0,2 Mol/l gewählt und die Konzentration des $\bar{A}n$ bis zu Erreichung der Grenzkurve gesteigert [9]. Die erhaltenen Ergebnisse wurden für die Wellenlängen 350, 550 und 900 $m\mu$ den Werten von $1/\bar{A}n^3$ gegenübergestellt (Fig. 1). Es ist deutlich zu sehen, daß die Linearität der Abhängigkeit nur annähernd besteht. Ebenso wurden die Fälle $n = 1$ und $n = 2$ dargestellt; so zeigte sich daß die Kurven sich im Falle $n = 3$ am besten der Geraden näherten.

Aufsuchen der Zwischenkomplexe

Als Bezugssystem der Komplexbildung sei bei konstanter Konzentration des Kations A die variable Konzentration des reagierenden Stoffes B benützt. So verläuft das Intervall der Komplexbildung von 0 bis zu derjenigen Konzentration des Stoffes B , bei der sich der koordinativ gesättigte Komplex ausbildet. Dieses Konzentrationsintervall sei derart additiv aus Teilintervallen zusammengesetzt, daß deren Grenze bei den maximalen Konzentrationswerten des entsprechenden Zwischenkomplexes liege und daß in den einzelnen Teilintervallen jeweils nur die beiden, die Grenzen bestimmenden Zwischenkomplexe vorhanden seien und ineinander übergehen sollen. Diese Annahme ist zwar nur in erster Annäherung richtig, aber sie wird durch die mit ihr erhaltenen Resultate gerechtfertigt. Als erster Beweis der Annahme seien die stabilen Schnittpunkte erwähnt. Diese treten dann auf, wenn in einem Gemisch nur zwei Verbindungen vorhanden sind und sich deren Gleichgewicht verschiebt [10].

Solche Konzentrationsintervalle sind in Nickel(II)ionenhydrat und $\bar{A}n$ enthaltenden wäßrigen Lösungen diejenigen von 0—0,181 Mol/l sowie von 0,460—2,604 Mol/l $\bar{A}n$ -Gehalt [9], in denen wir bei 770, 696 und 386 $m\mu$ bzw. 710, 572, 462 und 348 $m\mu$ stabile Schnittpunkte gefunden haben.

Zum Aufsuchen der Zwischenkomplexe wandten wir die Gleichung

$$E = \sum \varepsilon_i c_i + \sum \varepsilon_x c_x \quad (3)$$

— worin der Index i sich auf die aufeinander wirkenden Stoffe, der Index x auf die entstehenden Komplexe bezieht — innerhalb der einzelnen Teilintervalle an und erhielten so [8]:

$$\varepsilon = c_1 \varepsilon_1 + c_2 \varepsilon_2 \quad (4)$$

worin die Indizes 1, 2 sich auf die beiden vorhandenen Verbindungen, das indexlose Glied auf das Gemisch beziehen. Mittels dieser Gleichung können nach VARSÁNYI [11] diejenigen Stellen des ganzen Konzentrationsintervalls „ertastet“ werden, an denen nur mit dem Gleichgewicht zweier Verbindungen zu rechnen ist [11, 12, 13]. Auf diese Weise können alle Zwischenkomplexe erhalten werden. Die praktische Durchführung dieses Verfahrens geschieht, wie folgt:

Es wird das zu prüfende Konzentrationsteilintervall ausgewählt. Die Indizes 1 und 2 werden auf die Grenzkurven bezogen und als Gemischkurve eine dazwischen liegende Kurve gewählt. Mittels Gleichung (4) werden bei einer gewählten Wellen-

länge die Werte c_1 und c_2 bestimmt. In deren Kenntnis wird die Gemischkurve für das ganze Wellenlängengebiet berechnet. Falls die Grenzen richtig gewählt sind, wird die berechnete Kurve mit der Versuchskurve gut übereinstimmen.

Die praktische Anwendung der Methode führten wir mit einem Nickel(II) ionenhydrat und Äthylendiamin enthaltenden wäßrigen System durch [9]. Bezüglich der Verfahrensweise gingen wir nach der Literatur vor [14].

Zuerst wurden die Kurven des Ionenhydrats und des koordinativ gesättigten Komplexes als Grenzkurven gewählt und in diesem Intervall die Kurve des 0,294 Mol/l $\bar{A}n$ enthaltenden Gemisches berechnet. Wir fanden eine starke Abweichung zwischen der berechneten und der Versuchskurve (Fig. 2), als Zeichen dafür, daß in diesem Intervall außer dem Ionenhydrat und dem koordinativ gesättigten Komplex noch andere Zwischenkomplexe vorkommen.

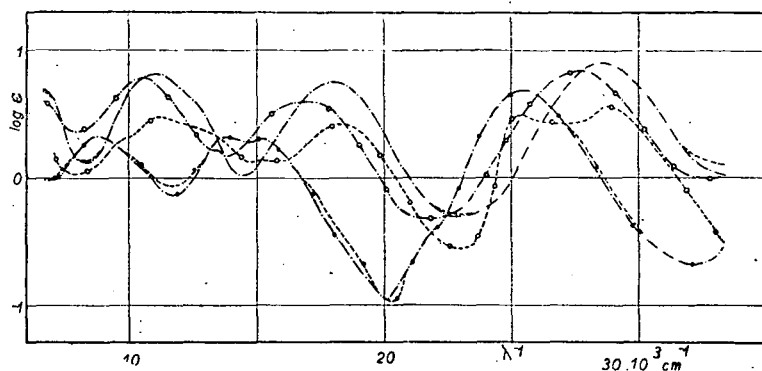


Fig. 2. —●— Versuchskurve, —●— berechnete Kurve für 0,2 Mol/l $Ni(ClO_4)_2 + 0,043$ Mol/l $\bar{A}n$
 —○— Versuchskurve, —○— berechnete Kurve für 0,2 Mol/l $Ni(ClO_4)_2 + 0,294$ Mol/l $\bar{A}n$
 —○— Versuchskurve, —○— berechnete Kurve für 0,2 Mol/l $Ni(ClO_4)_2 + 0,532$ Mol/l $\bar{A}n$

Dann wurde das Konzentrationsintervall, mit Beibehaltung der Ionenhydratkurve als konstanter Grenze, so lange verengert, bis die berechnete und die durch Versuch gefundene Zwischenkurve gut übereinstimmten. Auf diese Weise erhielten wir als Grenzen des ersten Teilintervalls die Kurven des Ionenhydrats und diejenige für 0,181 Mol/l $\bar{A}n$ -Gehalt, da mit diesen bei der Berechnung der Kurve für 0,043 Mol/l $\bar{A}n$ -Gehalt die Übereinstimmung der berechneten und der gefundenen Versuchskurve als gut zu bezeichnen ist (Fig. 2). Die geringe Abweichung an den Minimumstellen der Kurve ist dadurch verursacht, daß wir bei der Definition der Teilintervalle angenommen haben, daß bloß die beiden Grenzkomplexe vorhanden sind. Dies ist aber nur in erster Annäherung richtig, weil im Bildungsbereiche des Monokomplexes auch die Di-, Tri- bzw. die koordinativ gesättigten Komplexe in geringer, mittels der Gleichgewichtskonstanten bestimmbarer Konzentration vorhanden sind. Die aus Fig. 2 ersichtliche geringe Abweichung spricht nicht gegen die Verwendbarkeit der Methode, da, falls die Untersuchung für das ganze Wellenlängengebiet durchgeführt wird, der ähnliche Verlauf und die gute Anschmiegung

der beiden Kurven ohne Unsicherheit feststellbar ist. Die richtige Wahl der Grenzen wird dadurch bewiesen, daß die gefundene geringe Abweichung auch bei der Wahl engerer Grenzen bestehen bleibt. Wir haben auch diese Kontrolle durchgeführt und die Kurve für 0,068 Mol/l $\bar{A}n$ -Gehalt berechnet, indem wir die Ionenhydratkurve und die einem $\bar{A}n$ -Gehalt von 0,154 Mol/l entsprechende als Grenzkurven wählten; die beobachtete geringe Abweichung haben wir auch hier gefunden. Außerdem berechneten wir als Kontrolle noch die Kurve für 0,103 Mol/l $\bar{A}n$ -Gehalt, mit derjenigen der $\bar{A}n$ -Konzentration 0,181 Mol/l als oberer Grenze; die Übereinstimmung war eine ganz ähnliche.

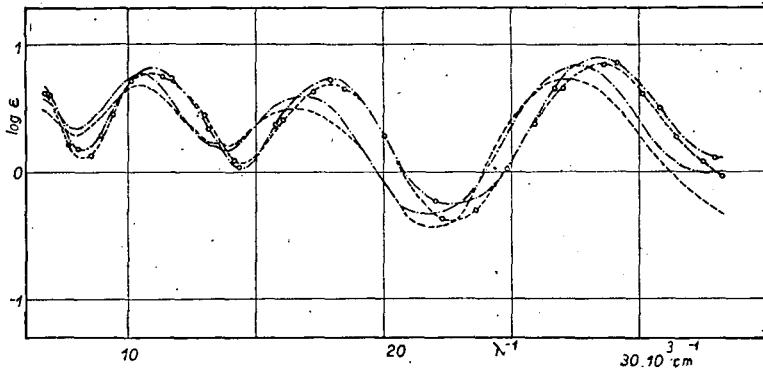


Fig. 3. — · ⊕ · — Versuchskurve, — ⊕ — berechnete Kurve für 0,2 Mol/l $Ni(ClO_4)_2 + 0,294$ Mol/l $\bar{A}n$
 - - - - - Versuchskurve, - - - - - berechnete Kurve für 0,2 Mol/l $Ni(Cl_4)_2 + 0,460$ Mol/l $\bar{A}n$

Danach wurde die Prüfung des unmittelbar vor dem koordinativ gesättigten Komplex liegenden Teilintervalls durchgeführt. Als Grenzkurven wurden die des koordinativ gesättigten Komplexes — 0,711 Mol/l $\bar{A}n$ -Gehalt — und die dem $\bar{A}n$ -Gehalt von 0,181 Mol/l entsprechende gewählt und die Kurve für die Konzentration 0,294 Mol/l berechnet. Die Abweichung der berechneten Kurve von der Versuchskurve war sehr groß, als Zeichen für die zu weite Wahl der Grenzen. Nun wurde das Teilintervall bei konstanter oberer Grenze durch Näherung der unteren Grenzkurve verengert. Mit der Kurve für 0,294 Mol/l $\bar{A}n$ -Gehalt als unterer Grenze berechneten wir die Kurve für die Konzentration 0,460 Mol/l; die Abweichung war kleiner, aber noch immer beträchtlich (Fig. 3). Mit weiterer Verengung des Teilintervalls durch Wahl der Kurve für 0,460 Mol/l als unterer Grenze berechneten wir die Kurve der Konzentration 0,532 Mol/l $\bar{A}n$ (Fig. 2); die Übereinstimmung der berechneten Kurve mit der Versuchskurve zeigte an, daß wir das gesuchte Konzentrationsteilintervall gefunden haben.

Auf Grund unserer Berechnungen ist festzustellen, daß in dem ganzen Konzentrationsgebiete drei Teilintervalle zu finden sind, deren Grenzkurven in den durch die Konzentrationen 0,181—0,294 Mol/l bzw. 0,294—0,460 Mol/l bezeichneten Gebieten liegen. Durch entsprechend dichter angelegte Versuchskurven können die Grenzen der Teilintervalle mit gewünschter Genauigkeit bestimmt werden. Zur

Berechnung der Kurven der Zwischenkomplexe [9] ist das nicht nötig, da diese die Grenzen des Intervalls angeben. Wir haben auch mit den Kurven der Zwischenkomplexe als Grenzkurven Kontrollberechnungen durchgeführt und in dem ersten Konzentrationsteilintervall die Kurven für die $\bar{A}n$ -Konzentrationen 0,043 bzw. 0,103 Mol/l, im zweiten für 0,370 Mol/l und im dritten für 0,532 Mol/l berechnet (Fig. 4, 5). Die gute Übereinstimmung der berechneten und gefundenen Kurven bestätigt die drei Konzentrationsteilintervalle.

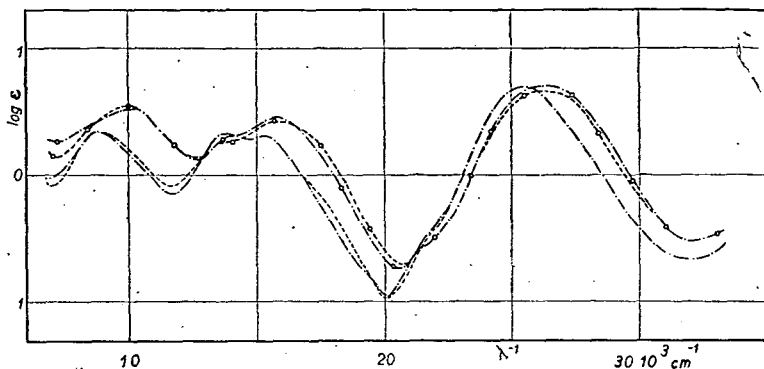


Fig. 4. - - - - - Versuchskurve, — — — berechnete Kurve für 0,2 Mol/l $\text{Ni}(\text{ClO}_4)_2 + 0,043 \text{ Mol/l } \bar{A}n$
 - · ⊖ · - Versuchskurve, - ⊖ - berechnete Kurve für 0,2 Mol/l $\text{Ni}(\text{ClO}_4)_2 + 0,103 \text{ Mol/l } \bar{A}n$

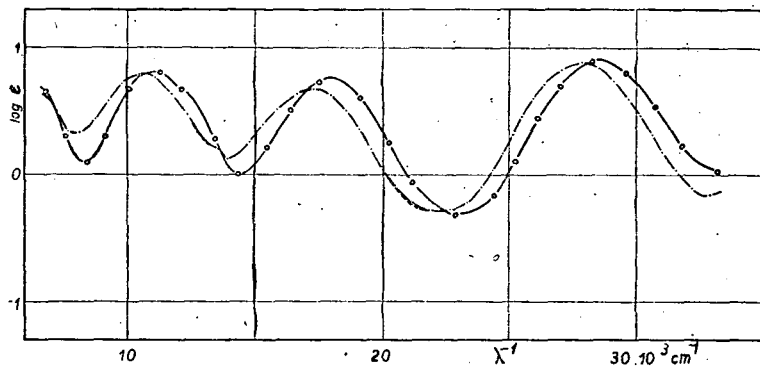


Fig. 5. - - - - - Versuchskurve, — — — berechnete Kurve für 0,2 Mol/l $\text{Ni}(\text{ClO}_4)_2 + 0,370 \text{ Mol/l } \bar{A}n$
 - · ⊖ · - Versuchskurve, - ⊖ - berechnete Kurve für 0,2 Mol/l $\text{Ni}(\text{ClO}_4)_2 + 0,532 \text{ Mol/l } \bar{A}n$

Auf Grund unserer Berechnungen sind in den drei Teilintervallen, also im ganzen Intervall der Komplexbildung die folgenden vier Verbindungen vorhanden:

$\text{Ni}(\text{H}_2\text{O})_6^{2+}$, $\text{Ni}\ddot{\text{A}}\text{n}(\text{H}_2\text{O})_4^{2+}$, $\text{Ni}\ddot{\text{A}}\text{n}_2(\text{H}_2\text{O})_2^{2+}$ und $\text{Ni}\ddot{\text{A}}\text{n}_3^{2+}$. Es waren noch Verbindungen der Zusammensetzung $\text{Ni}_2\ddot{\text{A}}\text{n}_3(\text{H}_2\text{O})_6^{4+}$, $\text{Ni}_2\ddot{\text{A}}\text{n}(\text{H}_2\text{O})_{10}^{4+}$ und $\text{Ni}_2\ddot{\text{A}}\text{n}_5(\text{H}_2\text{O})_2^{4+}$ vor auszusetzen, sie werden aber durch unsere Berechnungen nicht bestatigt und sind deshalb auszuschlieen.

Kritischer Vergleich der Methoden

Fur den Vergleich der hier vorgefuhrten und der Jobschen Methode genugt es, uns auf die Feststellungen von WOLDBYE [6] zu berufen, wonach die Methode der stetigen Variationen keinen nachweisenden, sondern blo indizierenden Charakter besitzt. Auerdem weist schon JOB [1] selbst darauf hin, da seine Methode nicht alle vorhandenen Zwischenkomplexe nachweist, sondern nur einige „anzeigt“ [2]. Auch die Modifizierungen [3, 4] der Methode der stetigen Variationen andern an dem Grundgedanken der Methode nichts, es werden blo weitere Bedingungen bezuglich der Auswahl der Wellenlange aufgestellt.

Dagegen werden durch die von uns angewandte Methode auch bei Vorliegen mehr als eines Komplexes samtliche Zwischenkomplexe berucksichtigt und nachgewiesen. Die durch die Vernachlassigungen hervorgebrachte Abweichung ist gut sichtbar und kann auf Grund der ubereinstimmung der Kurven fallweise beurteilt werden. Wir haben die Berechnungen der Methode auf das Wellenlangengebiet 1500—300 μ ausgedehnt, wodurch auch der aus der Wahl der Wellenlange sich ergebende Fehler beseitigt wird.

Als kritischer Vergleich der beiden Methoden ist schlielich festzustellen, da, falls der Nachweis samtlicher Zwischenkomplexe und die Bestimmung ihrer Zusammensetzung zum Ziele gesetzt wird, die von uns angewandte Methode — entgegen dem indizierenden Charakter der Methode der stetigen Variationen — mit nachweisendem Charakter zu gebrauchen ist, wodurch ihre Anwendung gerechtfertigt erscheint.

* * *

Ich habe Prof. Dr. Arpad KISS meinen Dank dafur auszusprechen, da er die Anfertigung meiner Arbeit in seinem Institut ermoglichte.

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ОПРЕДЕЛЕНИЕ КОМПЛЕКСОВ В РАСТВОРАХ ПУТЕМ СПЕКТРОФОТОМЕТРИИ

Л. Лехотаи

Изложены методы, применяемые для определения комплексов в растворах и применён наиболее испытанный метод для водных растворов, содержащих $Ni(H_2O)_6^{2+}$ и диамин этилена. Дано критическое сопоставление методов.

ON THE ORDER OF INFLUENCED REACTIONS

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The reaction order of catalyzed and inhibited reactions with respect to c_I , the concentration of the influencing substance had been analyzed according to the order definition $\nu = \partial \log w / \partial \log c_I$. For certain cases of the chain influencing this expression had been represented with characteristics of the reaction and its possible variation types had been established. The explanation dealt also with the connection between the reaction order and the influencing factor of the reaction. The considerations had been compared with the experiments, too.

The order of catalyzed and inhibited (summarized: influenced) reactions with respect to the concentration of the influencing substance (catalyst or inhibitor) is not such an exactly defined concept as that of the order of the reactants. As a matter of fact, the concentration dependence

$$w = f(c_a, c_b, \dots; c_I) \quad (1)$$

of the reaction rate on the concentrations c_a, c_b, \dots of the reactants A, B, \dots and c_I of the influencing substance I can be written only in fortunate cases in the form

$$w = kc_a^{n_a}c_b^{n_b} \dots \phi(c_I) \quad (2)$$

expressing the separability of the effect of the influencing substance, where n_a, n_b, \dots denote the reaction orders with respect to concentrations c_a, c_b, \dots , and k is a constant. From these representations of the reaction rate clearly appears that in general case the process cannot be characterized by a reaction order with respect to concentration c_I even in the relatively simple case of representation (2) because the functions f and ϕ do not change according to any power. (In case of general representation (1) even the reaction order with respect to the concentration of the reactants loses its meaning.)

This hardness in characterizing the reaction by a reaction order is expressed most doubtless in the logarithmic plotting of $\log w$ versus $\log c_I$. As it is well-known, this plotting shows linearity only when the reaction has a well-defined order in which case the order agrees with the slop of the plotting. This definiteness of the order is obviously equivalent with the constancy of the derivative $\nu = \frac{\partial \log w}{\partial \log c_I}$. On the contrary, if the previous derivative changes, then it means that no order in the usual sense is defined.

On the other hand there are arguments supporting the introduction of this derivative

$$v = \frac{\partial \log w}{\partial \log c_I} \quad (3)$$

as a generalized reaction order even when in the original meaning the concept seems to be senseless. Such an argument was presented by the endeavours to compare the explanation for the influencing of thermal decomposition of propionic aldehyde by nitrogen monoxide reported by SZABÓ and MÁRTA [1] with HINSHELWOOD and collaborators' interpretation in similar field of influenced thermal decompositions [2—5]. The latter authors characterize the effect of the influencing substance by a reaction order, while SZABÓ and MÁRTA do this by introducing the concept of the influencing factor.

The comparison of the two interpretations becomes possible when the changing of the derivative (3) is not regarded as a criterion of lack of order and v defined by (3) is considered as a reaction order varying during the reaction course. With the aim of realizing this comparison let the scheme of influenced chain reactions developed by SZABÓ, HUHN and BERGH be regarded [6, 7].

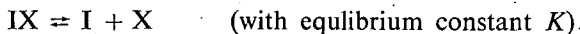
According to this scheme the influencing substance I exerts its effect on the chain



developed by radicals X formed in the initiating reaction



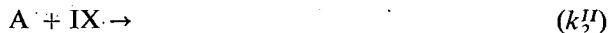
in the way of forming stabilized radicals



also being able to continue the chains or terminate them. Bearing in mind this possibility in the mechanism of the reaction it has been shown that the stationary concentration of the radicals can be given in the form

$$[X]_{st} = x_{st} = f(c_a, c_I) \quad (4)$$

of a simple algebraic function containing only square roots as irrational elements. Considering this structure of x_{st} and the presence of the chain



the reaction rate can be expressed by

$$\begin{aligned} w &= k_2^I c_a f(c_a, c_I) + k_2^{II} \frac{c_a}{K} f(c_a, c_I) = \\ &= k_2^I c_a (1 + \beta c_I) f(c_a, c_I), \end{aligned} \quad (5)$$

where β denotes the ratio $k_2^{II}/k_2^I K$. The expression is therefore of the general type (1) with regard of the feature of function $f(c_a, c_I)$ mentioned before.

In the fortunate case when all the terminating reactions



are bimolecular, the effect of the influencing substance can be separated. For this case in the referred papers the following rate expressions have been given:

$$w_{\text{infl.}} = k_2^I \sqrt{\frac{k_1}{k_4}} c_a^{3/2} \frac{1 + \beta c_I}{\sqrt{1 + 2\delta_1 c_I + \delta_2 c_I^2}} \quad (6)$$

and

$$w_{\text{non infl.}} = k_2^I \sqrt{\frac{k_1}{k_4}} c_a^{3/2}, \quad (6_0)$$

where $\delta_1 = k_4^{II}/k_4^I K$ and $\delta_2 = k_4^{III}/k_4^I K^2$. (The latter equation is included in the previous one with $c_I = 0$.) As it can be seen easily, the effect of the influencing species is expressed with the factor

$$F(c_I) = \frac{1 + \beta c_I}{\sqrt{1 + 2\delta_1 c_I + \delta_2 c_I^2}} \quad (7)$$

defined previously as the influencing factor of the reaction.

This rate expression is obviously of the form (2), accordingly the order defined by it can be represented in a simpler way as given by (3), namely by

$$v = \frac{d \log F(c_I)}{d \log c_I} = \frac{c_I}{F(c_I)} \frac{dF(c_I)}{dc_I}, \quad (8)$$

or in its developing

$$v = c_I \left\{ \frac{\beta}{1 + \beta c_I} - \frac{\delta_1 + \delta_2 c_I}{1 + 2\delta_1 c_I + \delta_2 c_I^2} \right\} = \frac{1 + \delta_1 c_I}{1 + 2\delta_1 c_I + \delta_2 c_I^2} - \frac{1}{1 + \beta c_I} \quad (9)$$

A short judgement of this expression shows at once that its magnitude may correspond to a reaction order with respect to c_I lying between -1 and $+1$, depending on the ratio of the terms 1 , βc_I , $\delta_1 c_I$ and $\delta_2 c_I^2$. (This is sufficiently apparent already from the form (7) of the influencing factor occurring in the expression of $w_{\text{infl.}}$ given by (6).) *E. g.* when in the actual concentration range $\beta c_I \gg 1$ and $2\delta_1 c_I \gg 1 + \delta_2 c_I^2$ then the order becomes nearly $1/2$; or in an other case when $1 \gg \beta c_I$ and $\delta_2 c_I^2 \gg 1 + 2\delta_1 c_I$ then the order will be nearly -1 . At the same time, it is obvious that the ratio of the magnitudes in question, with varying c_I also varies, a fact which implies the possibility of the change of order with varying c_I .

For a more precise evaluation of this change let the order expressions (8) and (9) be regarded. It is almost obvious that $v = 0$ for the two limiting cases $c_I = 0$ and $c_I = \infty$. As v is evidently not a constant, it must have at least an extreme value in the range $0 < c_I < \infty$. When the differential quotient dv/dc_I is evaluated then

it follows in a few steps

$$\begin{aligned} \frac{dv}{dc_I} &= \frac{\beta(1+2\delta_1 c_I + \delta_2 c_I^2)^2 - (1+\beta c_I)^2 (\delta_1 + 2\delta_2 c_I + \delta_1 \delta_2 c_I^2)}{(1+\beta c_I^2)(1+2\delta_1 c_I + \delta_2 c_I^2)^2} \equiv \\ &\equiv \frac{(\beta - \delta_1) + 2(\beta\delta_1 - \delta_2)c_I + \{3\beta\delta_1(\delta_1 - \beta) + (2\beta + \delta_1)(\beta\delta_1 - \delta_2)\}c_I^2}{(1+\beta c_I^2)(1+2\delta_1 c_I + \delta_2 c_I^2)^2} + \\ &+ \frac{2\beta\delta_2(\delta_1 - \beta)c_I^3 + \beta\delta_2(\delta_2 - \beta\delta_1)c_I^4}{(1+\beta c_I^2)(1+2\delta_1 c_I + \delta_2 c_I^2)^2}. \end{aligned} \quad (10)$$

Considering the fact that dv/dc_I has at least one 0-place in the positive concentration range, from this form of the derivative it can be seen easily that equation $dv/dc_I = 0$ has one or two positive roots according to the signs of expressions $(\beta - \delta_1)$ and $(\beta\delta_1 - \delta_2)$ agree or disagree. (In the first case the set of the coefficients contains only one change in the signs, in the second, however, two. Since the number of roots is at least one, the statement follows immediately according to DESCARTES' rule.) Therefore the feature of the variation of v can be given by the following types:

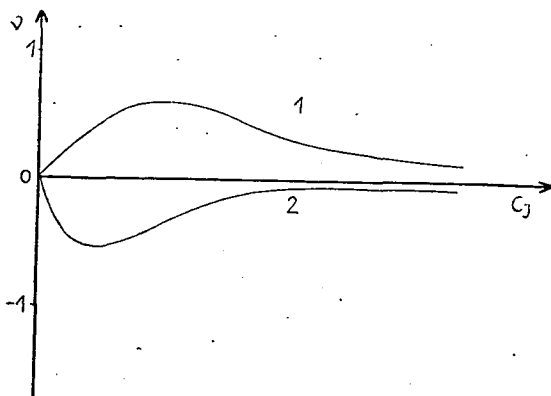


Fig. 1. The change of the order for monotonous influencing. 1 catalysis, 2 inhibition

a) $dv/dc_I = 0$ having only one positive root the order has a single extreme as represented by two type of curves on Fig. 1.

b) $dv/dc_I = 0$ having two positive roots the order has two extremes as illustrated by curves 1 and 2 on Fig. 2.

Regarding the latter curves it has to be mentioned that their 0-place has an evident chemical meaning, it denotes namely that concentration of the influencing substance at which the influencing is extreme. This is apparent from form (8) of v . As explained in the previous papers, this concentration can be given by

$$c_{\text{extr.}} = \frac{\beta - \delta_1}{\delta_2 - \beta\delta_1} \quad (11)$$

whereby also the meaning of the change or consecution in the signs of $(\beta - \delta_1)$

and $(\beta\delta_1 - \delta_2)$ becomes clear. For influencing with extreme the signs in question disagree, while for influencing without extreme they agree. Hence the variation of ν behaves according to types of Fig. 1 or Fig. 2 depending on whether the influencing phenomenon is monotonous or it has an extreme with varying c_I . Between the characteristic difference of types 1 and 2 (in both Fig. 1 and 2) and the chemical feature of the influencing phenomenon there is also a typical correspondence. The initial slope of the curve $\nu = \nu(c)$ at $c_I = 0$ evidently seems to be equal to $(\beta - \delta_1)$ which is at the same time the initial slope of the curve $F = F(c_I)$. This means that the reaction order is in the initial stage at $c_I = 0$ in the same meaning increasing or decreasing as the influencing factor. Therefore the change of the reaction order can be characterized by curves of types 1 or 2 depending on whether the influencing begins with catalysis or inhibition, respectively.

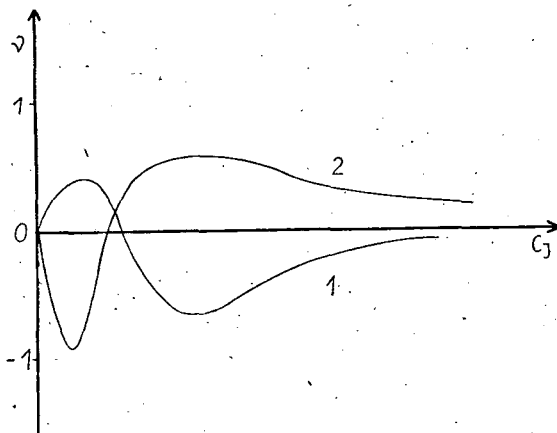


Fig. 2. The change of the order for influencing with extreme. 1 influencing beginning with catalysis, 2 influencing beginning with inhibition

From the variability of ν outlined before, it can be seen that a rough evaluation of the reaction order may lead to a false interpretation of the process. For example, when this order seems in a concentration range to be about $1/2$, then it is a hasty conclusion to regard the reaction as a half order one with respect to the concentration of the influencing substance. And it would be quite wrong to draw extreme conclusions from an unusual concrete value of this order, as *e. g.* to look for a peculiar mechanism in case of an order nearly equal to $1/3$.

To illustrate this establishment as well as to demonstrate the variation of the order defined by (3) let the results of the investigations relating the thermal decomposition of propionic aldehyde, elaborated by SZABÓ and MÁRTA, be considered. According to these authors' statements this decomposition proceeds according to chain reaction developed by C_2H_5 radicals produced in the initiating reaction $C_2H_5CHO \rightarrow C_2H_5 + CHO$ (which is followed by the very fast reaction $CHO + C_2H_5CHO \rightarrow C_2H_5CO + CO + H_2$) and disappearing in the terminating reaction $C_2H_5 + C_2H_5 \rightarrow C_2H_6 + C_2H_4$. If nitrogen monoxide is added to the reaction then stabilized radicals, C_2H_5NO , will be formed also participating in the chain and

terminating reactions as mentioned before and discussed in the papers referred [1], [6] and [7]. Considering these elementary steps, it is easy to show that the rate expressions of the reaction can be given by equations (6) and (6₀) — with the insignificant modification of replacing the constants k_1 and k_2^I by $2k_1$ and $2k_2^I$, respectively. (As a matter of fact, the initiating reaction produces two ethyl radicals and the chain consumes two aldehyde molecules in every step.) As a consequence of these rate formulae the influencing factor and followingly the order can be represented in form of equations (7) and (8)—(9), respectively.

Table I

The variation of the reaction order in the experiments at $t = 515^\circ\text{C}$ with the initial aldehyde pressures $p_{\text{Ald.}}$; $p_0 = 150\text{ mm Hg}$

$\log c_I$	$\log F(c_I)$	$\nu = \frac{\Delta \log F(c_I)}{\Delta \log c_I}$
0,255-1	0,892-1	
0,342-1	0,88 -1	-0,14
0,716-1	0,85 -1	-0,08
0,903-1	0,857-1	+0,037
0,301	0,954-1	+0,23
0,477	0,995-1	+0,24
0,716	0,083	+0,37
1,00	0,19	+0,38
1,23	0,294	+0,45
1,422	0,38	+0,447
1,686	0,506	+0,477
1,792	0,559	+0,50

Table II

The variation of the reaction order in the experiments at $t = 535^\circ\text{C}$ with the initial aldehyde pressures $p_{\text{Ald.}}$; $p_0 = 150\text{ mm Hg}$

$\log c_I$	$\log F(c_I)$	$\nu = \frac{\Delta \log F(c_I)}{\Delta \log c_I}$
0,00 -1	0,924-1	
0,30 -1	0,869-1	-0,18
0,653-1	0,819-1	-0,14
0,813-1	0,819-1	0,00
0,255	0,869-1	+0,11
0,49	0,903-1	+0,144
0,857	0,045	+0,38
1,238	0,182	+0,35
1,556	0,338	+0,49
1,653	0,375	+0,38
1,806	0,435	+0,39

In the following tables (Table I and II) these values are grouped having evaluated them from the experimental data of SZABÓ and MÁRTA [1] by means of (3) and (8) and by replacing the derivatives $d \log F(c_I)/d \log c_I$ by the quotients

$\Delta \log F(c_I) / \Delta \log c_I$. The data are plotted on Figs. 3–6 which contain also the variation of reaction order calculated with the characteristic quantities β , δ_1 and δ_2 of the reaction according to (9), as well as the variation of the influencing factor. (All the curves are given in plotting versus $\log c_I$.)

As it seems immediately the plotting $\log F(c_I)$ versus $\log c_I$ shows in the range $0,6 < \log c < 2,0$ a quite satisfactory linearity with the slope of about $1/2$. (This is demonstrated also by the curves $v = v(c_I)$ the maximum of which lies very near to $1/2$ in a wide concentration range where the variation is extremely slow.) In this way the reaction seems to be of a half order one in the concentration range in question without drawing any further conclusions regarding the mechanism of the reaction.

Table III

The variation of the reaction order in the experiments at $t = 550^\circ \text{C}$ with the initial aldehyde pressures $p_{\text{Ald.}}$; $o = 150 \text{ mm Hg}$

$\log c_I$	$\log F(c_I)$	$v = \frac{\Delta \log F(c_I)}{\Delta \log c_I}$
0,301–1	0,888–1	
0,58 –1	0,83 –1	–0,19
0,81 –1	0,79 –1	–0,17
0,95 –1	0,778–1	–0,10
0,114	0,81 –1	+0,19
0,204	0,83 –1	+0,28
0,58	0,903–1	+0,18
1,215	0,093	+0,29
1,33	0,146	+0,45
1,44	0,19	+0,41
1,78	0,33	+0,40

Table IV

The variation of the reaction order in the experiments at $t = 565^\circ \text{C}$ with the initial aldehyde pressures $p_{\text{Ald.}}$; $o = 150 \text{ mm Hg}$

$\log c_I$	$\log F(c_I)$	$v = \frac{\Delta \log F(c_I)}{\Delta \log c_I}$
0,40–1	0,87 –1	
0,78–1	0,79 –1	–0,16
0,20	0,76 –1	–0,08
0,57	0,82 –1	+0,17
0,70	0,82 –1	+0,24
1,16	0,99 –1	+0,31
1,56	0,155–1	+0,43
1,66	0,22	+0,60
1,78	0,28	+0,51

It seems very probable that the results in HINSELWOOD and coworkers' investigations, according to which the effect of the influencing substance would be summarized in a half order reaction with respect to the influencing species, have similar

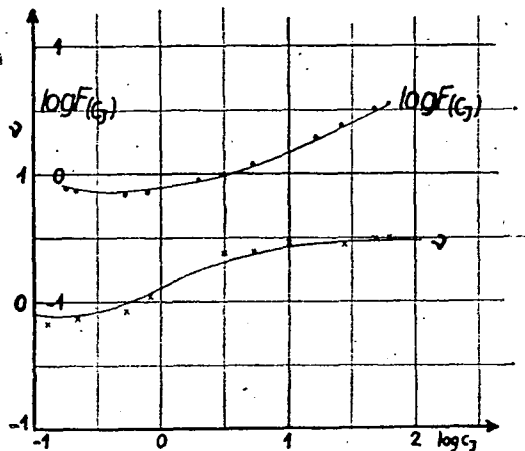


Fig. 3. The variation of the reaction order and the influencing factor in the experiments at $t = 515^\circ\text{C}$ with the initial aldehyde pressure $p_{\text{ald. } 0} = 150 \text{ mmHg}$. Continuous curve: calculated according to equation (7) and (9) with $\beta = 1,3$, $\delta_1 = 4,1$, $\delta_2 = 0,003$. ● and ×: calculated directly from the experimental data

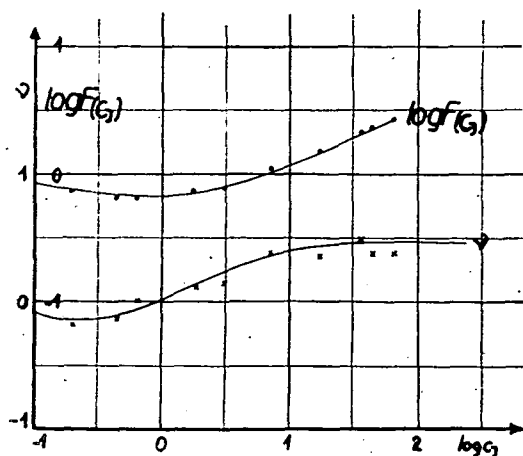


Fig. 4. The variation of the reaction order and the influencing factor in the experiments at $t = 535^\circ\text{C}$ with the initial aldehyde pressure $p_{\text{ald. } 0} = 150 \text{ mmHg}$. Continuous curve: calculated according to equation (7) and (9) with $\beta = 0,85$, $\delta_1 = 3,1$, $\delta_2 = 0,0017$. ● and ×: calculated directly from the experimental data

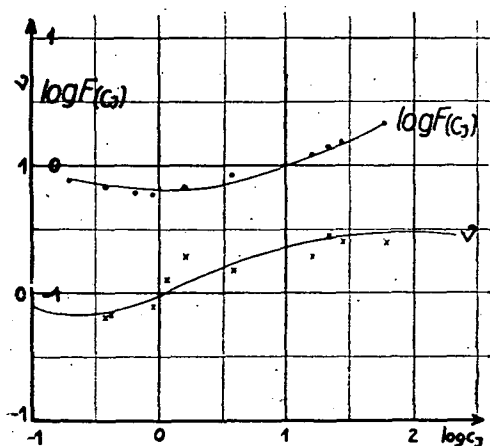


Fig. 5. The variation of the reaction order and the influencing factor in the experiments at $t = 550^\circ\text{C}$ with the initial aldehyde pressure $p_{\text{ald. } 0} = 150 \text{ mmHg}$. Continuous curve: calculated according to equation (7) and (9) with $\beta = 0,65$, $\delta_1 = 2,75$, $\delta_2 = 0,0011$. ● and ×: calculated directly from the experimental data

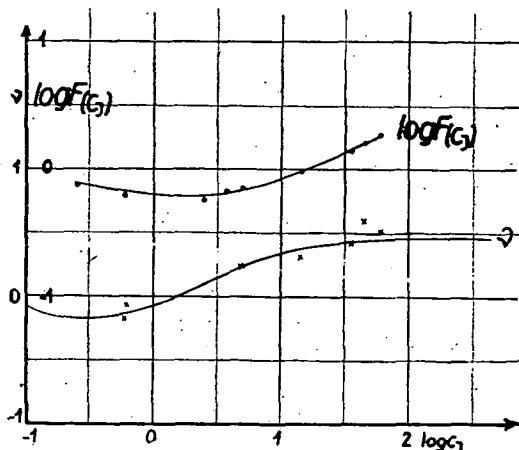


Fig. 6. The variation of the reaction order and the influencing factor in the experiments at $t = 565^\circ\text{C}$ with the initial aldehyde pressure $p_{\text{ald. } 0} = 150 \text{ mmHg}$. Continuous curve: calculated according to equation (7) and (9) with $\beta = 0,50$, $\delta_1 = 2,30$, $\delta_2 = 0,0007$. ● and ×: calculated directly from the experimental data

reason. These authors made their experiments with sufficiently high nitrogen monoxide concentrations under which circumstances the determination of the initial stage of the influencing curve did not occur.

From the explanation the conclusion must be drawn that in the possession of a reaction order of the influencing substance some care must be taken not to overestimate its significance. Apart from the fact that it cannot be regarded as an unequivocal characteristic of the reaction (because it is a locally defined concept) its origin also indicates that it must be regarded with an other view as the reaction order of the reactants. In fact the previously described variation of the influencing factor arises from those interactions by which the influencing species regulates the stationary concentration of the radicals. Thus the order defined for this concentration dependence of the reaction rate can be regarded more precisely not as an order of the reaction, but rather as the order of the influencing phenomenon. This is the proper view of the reaction order with respect to the concentration of the influencing substance which coincides with the essence of the mechanism of the influencing phenomenon and therefore promotes their investigation.

* * *

The authors wish to express their thanks to Professor Z. G. SZABÓ, Fellow of the Hungarian Academy of Sciences, for his kind interest and suggestions.

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ПОРЯДОК РЕАКЦИЙ ПОДВЕРЖЕННЫХ ВОЗДЕЙСТВИЮ

Ф. Марта и П. Хун

Авторы изучали порядок катализированных и ингибированных реакций в функции концентрации c_I влияющего материала на основе $\nu = \partial \log w / \partial \log c_I$.

Для нескольких случаев цепного воздействия авторы дали это выражение имея в виду характеристику реакций, и также установили возможные типы вариантов. Эта интерпретация далее раскрыла связь между порядком и фактором воздействия реакции.

Результаты этих соображений были сравнены с экспериментами.

The following materials were examined as pyrolysis contacts: Iron sponge, coarse powdered aluminium (Al-grits), chamotte pearls, pumice with particle diameter of 0,3 to 1 cm, and pumice impregnated with borax solution. It was found that the nature of the heat transferring contact material had no significant role in the pyrolysis, but the area of the contact surface was of decisive importance. In agreement with the work of PANJUTIN [4], we found that the presence of metals and traces of mineral acids increase the tendency of tar formation. Chamotte pearl,

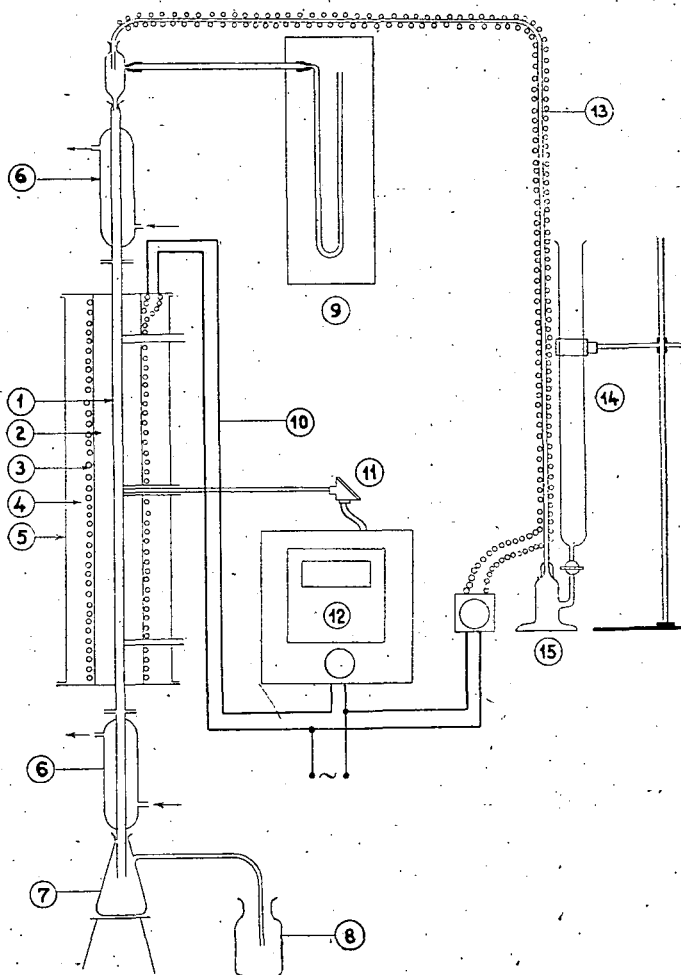


Fig. 1. Tube reactor for the preparation of methyl undecylenate. — 1. Reactor tube packed with contact in the heated zone. 2. Heat transferring aluminium block. 3. Heating filament. 4. Heat insulator (glass wool). 5. Tin-plate mantle. 6. Condenser. 7. Receiver. 8. Gas absorber. 9. Manometer. 10. Electric lines. 11. Thermocouple. 12. Automatic temperature controller. 13. Heated pressure feed line. 14. Feeding burette. 15. Feed pump.

pumice, and pumice impregnated with 10% borax solution were found to be the best contacts for this process among the materials examined and listed above. Yields and conversions, in percentages, of methyl undecylenate production are shown in Figs. 2., 3. and 4., at a feed rate of 200 ml per hour, and with various contacts.

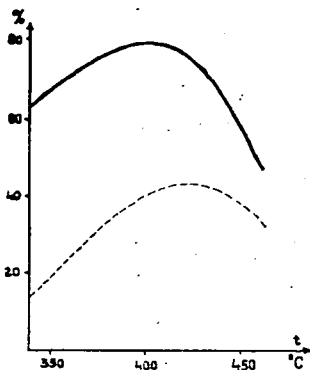


Fig. 2. Contact: Chamotte pearls.
Length (volume) of the bed: 114 cm (157 cu. cm)

These diagrams indicate the following facts:

a) When different contact materials are used, the yields and conversions of methyl undecylenate production remain practically the same.

b) Higher temperatures bring about an increase of conversion and yield up to a certain maximum, then they are decreased with all contacts examined by us. The decrease of the formation of methyl undecylenate above a certain limiting temperature is due to too extensive pyrolysis and formation of tar at these temperatures.

c) When the volume (length of the bed) of the contact is increased, optimum conversions and yields are attained at lower temperatures, as a consequence of increased contact time.

The character of the reaction is primarily influenced by the length of the pyrolysing bed (volume of contact), by the feed rate of the starting material, and by the temperature used. These three factors show close relationship to each other,

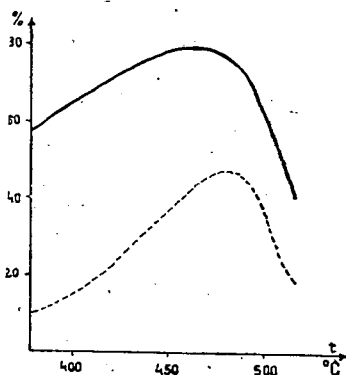


Fig. 3. Contact: Pumice. Length (volume) of the bed: 80 cm (110 cu. cm)

Conversion: -----

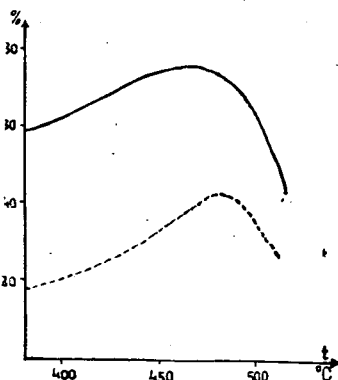


Fig. 4. Contact: Borax on pumice.
Length (volume) of the bed: 80 cm (110 cu. cm)

Yield: _____

as it is seen from the Tables below, which show the variation of the conversions and yields of methyl undecylenate production with different lengths (or volumes) of contact (A), the effects of the temperature (B) and that of the rate of feed (C).

At constant temperature and with a constant rate of feed, the conversion and yield show changes of opposed direction when the length of bed of the contact is increased. Under the conditions specified in Table A, the conversion is increasing, at the same time the yield of methyl undecylenate is decreasing, which is indication of a more extensive over-pyrolysis of the formed products.

Table A

Length of bed (volume) cm (cu. cm)	Conversion %	Yield %
50 (70)	22	80
80 (110)	28	75
114 (157)	37	50

Temperature 430°C. Feed rate 200ml/h.

Table B

Temp. of decompn. °C	Conversion %	Yield %
380	11	58
430	28	75
510	24	45

Feed rate 200 ml/h.
Length of bed (volume) 80 cm (110 cu. cm)

Table C

Feed rate ml/h	Conversion %	Yield %
200	28	75
300	22	65
400	14	56

Length of bed (volume) = 80 cm (110 cu. cm).
Temperature 430°C

When the rate of feed and volume of contacting material are kept constant, lower temperatures produce changes other than required, leading to poorer yields and conversions. Increased temperatures result in improved values until an optimum is reached; above this temperature over-pyrolysis and polymerisation [5] is experienced.

With constant volume of contact material and constant temperature; an increase of the feed rate will bring about a decrease of contacting time; consequently conversions and yields will be decreased. It follows that, for the sake of economy, the temperature of pyrolysis must be increased near to the point of too extensive decomposition in such cases when the feed rate is increased, but the length (or volume) of contacting bed is kept constant.

Relationships among the feed rate of the starting material, temperature, and conversion or yield of methyl undecylenate are shown in the above Tables and in Figs. 5. and 6.

Besides the mentioned interdependence of feed rate and temperature of pyrolysis, the summarizing diagrams well indicate that at higher temperatures better conversions and yields for methyl undecylenate may be obtained if the pumice is impregnated with borax.

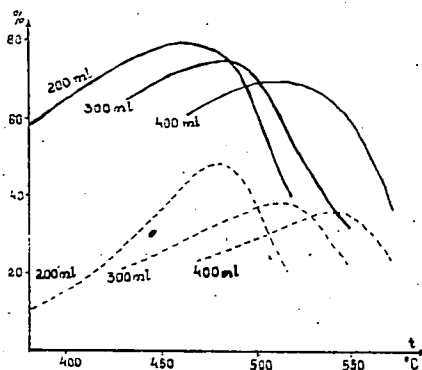


Fig. 5. Contact: Pumice. Length (volume) of the bed: 80 cm (110 cu. cm)
Conversion: -----

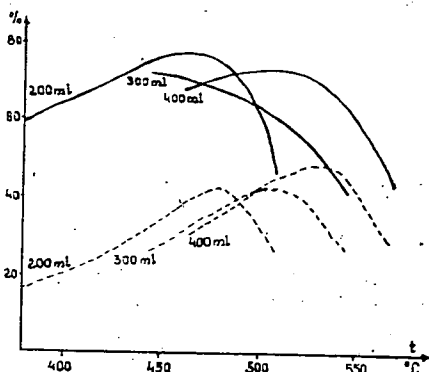


Fig. 6. Contact: Borax on pumice
Yield: _____

The experiments lead to the conclusion that when methyl ricinoleate is pyrolysed in a continuous tube reactor, optimum conversion (40–50%) and yield (75–80%) of methyl undecylenate may be obtained in the temperature ranges shown in Tables D and E, if the length of the contacting bed and the feed rate of the material are as indicated.

Table D

Feed rate ml/h	Optimum pyrolysis temp. °C
100	390–410
200	420–440
300	440–460

Length (volume) of contact bed = 114 cm (157 cu. cm)

Table E

Feed rate ml/h	Optimum pyrolysis temp. °C
100	430–450
200	460–480
300	490–510
400	510–530

Length (volume) of contact bed = 80 cm (110 cu. cm)

2. Pyrolysis of methyl ricinelaideate

The pyrolysis of methyl ricinelaideate was the subject of a study, conducted parallel with that of methyl ricinoleate. Such experiments have not been reported with the former compound. The material was prepared by us from methyl ricinoleate, following the principle of PLAYFAIR's synthesis [6], [7]. The experiments with this trans compound obtained thus, led to the following conclusions.

The course of the pyrolysis is somewhat different from that of methyl ricinoleate, which is explained by the different spatial arrangements and stabilities of the compounds. With chamotte pearl contact and under identical conditions, con-

versions and yields of methyl undecylenate production are lower in the case of the trans compound. This is probably due to the fact that the dehydration and polymerisation reactions of methyl ricinelaide are favoured in the presence of chamotte pearl contact. When pumice, or even more, when pumice impregnated with borax is used, decomposition of methyl ricinelaide to methyl undecylenate and n-heptaldehyde (oenanthole) becomes the main reaction, especially at higher temperatures. A probable explanation of this behaviour is the assumption of a trans-cis rearrangement taking place above some defined temperature (about 450° C); subsequently, the product undergoes pyrolysis. This mechanism of reaction readily explains the fact that conversions and yields are lower with the trans than with the cis compound if lower temperatures are applied, as a consequence of slower isomeric rearrangement. This is shown in the diagrams below.

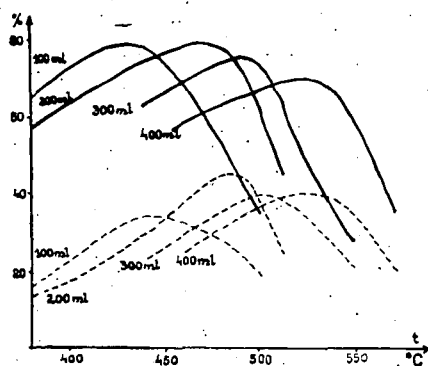


Fig. 7. Pyrolysis of methyl ricinoleate. Conversions and yields. Length (volume) of contact bed: 80 cm (110 cu. cm)
Conversion: -----

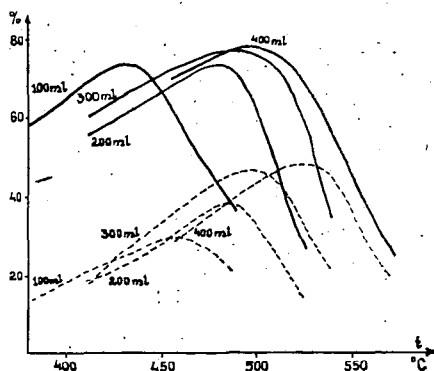


Fig. 8. Pyrolysis of methyl ricinelaide. Conversions and yields

Yield: -----

These figures show the average conversions and yields for methyl undecylenate obtained with pumice and borax on pumice at different feed rates (ml/hour), and as a function of temperature.

The other principal product of the pyrolysis of both methyl ricinoleate and ricinelaide is n-heptaldehyde. Conversions and yields for this compound correspond to the formation of methyl undecylenate until the point of over-pyrolysis is reached. At higher temperatures, due to its higher thermal stability, n-heptaldehyde becomes preponderant in comparison with methyl undecylenate.

Our experiments led to the following main conclusions concerning the preparation of methyl undecylenate by pyrolysis:

1. The most important factor in the pyrolysis is the surface area of the contact.
2. Borax-on-pumice is an advantageous contact for the reaction.
3. When the volume of the contact is increased, optimum pyrolysis temperature becomes lower, as a consequence of increased contact time.
4. With higher feed rates the temperature must be increased in order to maintain good conversions.

5. Optimum pyrolysis temperatures on borax on pumice catalysts for methyl ricinelaide are higher than for methyl ricinoleate, due to the higher thermal stability of the former compound.

6. According to our experiments, when reaction conditions are properly chosen, methyl undecylenate can be prepared with a conversion of 40 to 50%.

Experimental

Methyl ricinoleate

The compound was prepared according to the method of FALKAY and KRÁMER [8].

One part of castor oil was mixed with 0,4 parts of methyl alcohol, and 10% sodium hydroxide was added to adjust a 0,4% alkali hydroxide content in the mixture, calculated for castor oil. The mixture was refluxed for 30—40 minutes with occasional shaking. Then it was neutralized with diluted sulphuric acid and the excess methyl alcohol distilled off. After cooling, the reaction mixture separated to two layers. The lower layer consisted mainly of concentrated glycerol. It was separated, and the methyl ester layer was washed with water until free of mineral acid. Then it was dried by drawing air through the mixture, and finally distilled. B. p. 185—190° C at 2 mm; 209—211° C at 7 mm; 238—242° at 10 mm. The product was a water-white oil. The yield was almost theoretical. Analysis:

	Acid value	Ester value	Iodine value
Required for $C_{19}H_{36}O_3(312,48)$	—	179,58	81,3
Found	4.8—4.9	177,76	87,2

Two hydroxy acids were isolated from the crude methyl ricinoleate with the melting points of 114—115° C (*A*) and 145—147° C (*B*), their structure, however, has not been investigated. Analysis showed the following values: For material *A*, C 69,57%; H 10,66%. Molecular weight 250—270. For material *B*, C 68,75%; H 11,00%. Molecular weight 220—250.

Ricinelaic acid

Ricinelaic acid was prepared by isomerizing ricinoleic acid according to the method of KASS and RADLOVE [7]. The product consisted of pale yellow crystal needles, m. p. 49—51° C.

Methyl ricinelaide

Ricinelaic acid was dissolved in three to five times the calculated amount of methanol, and the solution saturated with dry hydrogen chloride under cooling in ice. The solidified material was filtered and washed until free of mineral acid. B. p. 202—203° C at 4 mm; 211—213° C at 5—6 mm; 250—253° C at 10 mm. Yield of the pale yellow liquid was 70—75%. The product solidified on standing

at room temperature, m. p. 32—33° C. The material had the following characteristics:

	Acid value	Ester value	Iodine value
Required for $C_{19}H_{36}O_3$ (312,48)	—	179,58	81,3
Found (for distilled material)	3,15	168,9	80,5

Analysis after recrystallisation from methanol: $C_{19}H_{36}O_3$ (312,48) requires C 73,03; H 11,61%. Found: C 73,10; H 11,80%.

Pyrolysis of methyl ricinoleate and methyl ricinelaide

Systematic pyrolysis experiments were carried out in a continuous tube reactor of 110 cm length and 1,55 cm diameter. 70—120 g of the raw material was processed in each run, over various contacts. The length (volume) of the bed was 114 cm (157 cu. cm) when chamotte pearl was used, and 80 cm (110 cu. cm) when pumice or borax on pumice was employed. Feed rates of 70, 100, 200, 300, and 400 ml/hour and temperature ranges of 220—550° C were tried. With a given rate of feed, the temperature of pyrolysis was, in general, increased by degrees of 50° C, up to the point when excessive decomposition (fuming) was experienced. Two or three experiments were always carried out under identical conditions. The diagrams and tables show average results.

After switching on the electrical heating and adjusting the automatic temperature controller, the material to be pyrolysed was fed into the reactor tube at an exactly determined rate, by the aid of an automatic feeder.

The product of the pyrolysis was a more or less coloured reddish-brown fluorescent liquid, the colour being dependent on the conditions of the experiment and on the nature of the starting material. The yield varied between 60 and 100%. The pyrolysed material was fractionated by distilling it first under atmospheric, and from above 180° C under reduced pressure. The products could be purified by repeated atmospheric distillation.

The following products were obtained:

- a) Fore-run, to b. p. 70° C.
- b) Aldehyde — n-heptaldehyde fraction, boiling range 70—220° C. The yield varied within wide limits, depending on the reaction conditions. The aldehyd content of the fraction was 40—60%.
- c) Methyl undecylenate fraction, boiling range 230—260° C. Yield 10—52% of the theoretical.

Analysis:

	Acid value	Ester value	Iodine-bromine value
$C_{12}H_{22}O_2$ (198,29) requires	—	282,92	80,6
Found	8—15	245—264	80—96

Repeated fractionated distillation gave uniform methyl undecylenate in a yield of 60—70%. B. p. 248° C at 760 mm.

d) Distillation residue. This material consisted mainly of unreacted methyl ricinoleate and its amount varied between 10 and 85%.

The distillation residue of the trans compound obtained when the pyrolysis was carried out at 430—480° C solidified on cooling, and its distillation gave methyl ricinelaideate. With higher pyrolysis temperatures a residue distilling at the boiling point of methyl ricinoleate was obtained, which, however, has not been identified so far.

* * *

The authors express their thanks to professor Dr. J. KISS for kindly drawing their attention to the subject and for his permanent interest in this research. Thanks are due to Mrs. K. L. LÁNG for carrying out the analyses, as well as to Mr. P. PÉNZES for his kind assistance.

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ПИРОЛИЗ МЕТИЛ-РИЦИНОЛАТА И ЕТИЛ-РИЦИНЕЛАИДАТА. ЭКСПЕРИМЕНТЫ ИЗОЛИРОВАНИЯ МЕТИЛ-УНДЕЦИЛЕНАТА

И. Кобор, Л. Месарош и Л. Хакл

Авторами было исследовано соотношение между склонностью к крекированию метилового эфира рициноловой и рицинелайдиновой кислот и изомерией цис и транс.

THE SYNTHESIS AND REDUCTION OF 3-INDOLYLACETONITRILE

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(Received March 30, 1960)

The important plant growth hormone, indolylacetonitrile was successfully prepared by the authors in various ways. Reduction by lithium aluminium hydride of the compound gave tryptamine, an important intermediate of tryptophane metabolism.

The activity of indolylacetic acid as a plant growth hormone was demonstrated first by KÖGL et al. [1].

Later, plant growth promoting effect was experienced also with other compounds having the indole skeleton. Thus, *e. g.*, in 1952 a group of English researchers [2], [3] succeeded in isolating indolylacetonitrile from pumpkin by means of chromatographic methods.

The present paper deals with the methods tried by us in synthesising indolylacetonitrile and for the reduction of this compound to the corresponding amine:

1. The first authors reporting about natural 3-indolylacetonitrile gave also a method for its synthesis which was accomplished by route I, described in the experimental part.

2. A second route was found in quaternizing the corresponding MANNICH base, isolating the quaternary salt and boiling the product with potassium cyanide; this method, however, gave but moderate yields (Route II) [4].

3. Condensation with formaldehyde and potassium cyanide may also become a practical way of synthesis (Route III) [5].

4. The work of several authors revealed another possibility for the preparation of indole-3-acetonitrile (Route IV); in comparison with the rest of the methods, this synthesis appears to be the best [6].

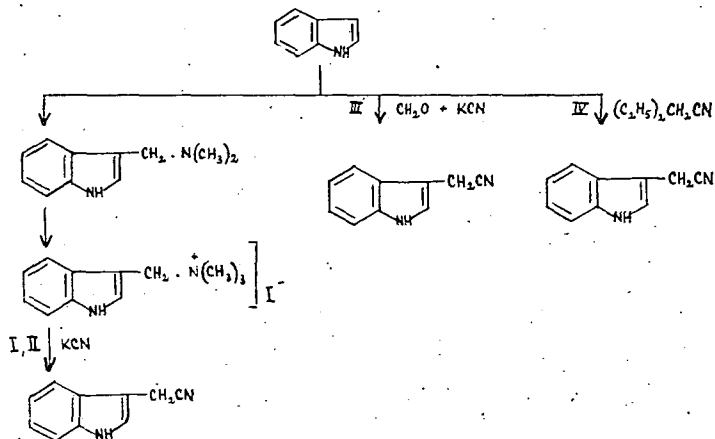
A consideration of these syntheses clearly reveal that yields are always lower in the processes where the nitrilo-group is formed in several steps than in the cases where this reaction consists of one single step. The only difference between route I and II is that the quaternary product is not isolated in the latter case. The synthesis according to route III could be realized only with a poor yield.

On the other hand, indole-3-acetonitrile could be prepared in a good yield according to route IV, when proper temperature control was applied.

Freshly distilled indole-3-acetonitrile gave tryptamine on reduction with lithium aluminium hydride or with sodium borohydride.

* Institute of Plant Physiology, The University, Szeged

The above routes of synthesis may be outlined as follows:



Experimental

The materials used were of the following grade and origin:

Indole, „rein”, „Gesellschaft für Teerverwertung” m. b. H. Duisburg—Meiderich.

Formaldehyde, pro anal., 35% aqueous solution, Fine Chemicals Factory, Reanal, Budapest.

Diethylamine aqueous solution, Fine Chemicals Factory, Reanal, Budapest.

Potassium cyanide „Kalium cyanatum, Ph. H. IV” material was used.

Diethylaminoacetonitrile was prepared as described in *Organic Syntheses* [7].

The synthesis of indolylacetonitrile in various ways, and the reduction of this product are described in detail below. It should be noted that the synthesis according to route III is suitable primarily for the preparation of the potassium salt of indolylacetic acid.

The starting material of the synthesis according to route II was gramine or ethylgramine [8]. In both cases trimethyl or diethylmethyl skatyl ammonium methylsulphate had to be synthesized first, from which compounds the quaternary iodides were made [9].

Diethylmethylskatylammoniummethylsulphate was a new compound of this series; it was prepared from diethylgramine by means of dimethyl sulphate in anhydrous tetrahydrofuran [9]. The product was recrystallized from anhydrous ethanol, m. p. 156—157°C.

Analysis: Calculated for $(\text{C}_{14}\text{H}_{21}\text{N}_2) \cdot (\text{CH}_3\text{O}_4\text{S})$ (328,4): C 51,19; H 7,35%. Found: C 51,62; H 7,49%.

When an aqueous solution of this compound was treated with potassium iodide, the quaternary iodide was obtained, which gave recrystallization from methanol-ether (1:1) a material of m. p. 170—172°C.

$(\text{C}_{14}\text{H}_{21}\text{N}_2)\text{I}$ (340,2) requires I 37,30%. Found I 38,00%.

0,1 mol of the isolated quaternary iodide was refluxed in aqueous solution for 10 hours with 0,1 mol of KCN. The product was extracted with five 100 ml portions of ether, the ethereal layer was washed with water, dilute sulphuric acid and sodium carbonate solution, finally it was dried over anhydrous sodium sulphate. The ether was evaporated, and the remaining nitrile was distilled in good vacuum. B. p. 165—169° C at 0,5 mm.

$C_{10}H_8N_2$ (157,19) requires C 76,9; H 5,15%. Found C 77,1; H 5,50%.

The picrate was precipitated by treatment with a calculated amount of 5% picric acid solution in ethanol, m. p. 120° C. $C_{16}H_{11}O_7N_5$ (385,29) requires N 18,19%. Found 18,75%.

It should be noted that indole could be recovered at the end of the distillation; it was isolated in the form of its picrate, m. p. 181° C. $C_{14}H_{10}O_7N_4$ (346,25) requires N 16,18%. Found N 16,40%.

According to route I, indolylacetonitrile could be prepared without isolating the quaternary salt [3].

The synthesis according to route IV, developed in 1953 [6] should be described more detailed, since this method was proved to be the simplest way of preparing indolylacetonitrile.

0,1 mol indole and 0,2 mol of diethylaminoacetonitrile was refluxed under nitrogen atmosphere for 6 hours at 170° C (measured in the mixture). The condensation took place, and after a time the indolylacetonitrile could be isolated in a good yield. Proper control of temperature is absolutely necessary during this reaction.

Then the excess diethylaminoacetonitrile was evaporated in the vacuum of a water-pump, then the residue was distilled at 0,2 mm, b. p. 160—165° C.

The product was converted into the corresponding picrate for the purpose of identification.

The fore-run of the distillation gave indole and another crystalline material having m. p. 150° C. This material gave the following analysis: C 82,49; H 6,32; N 12,0%.

Treatment with an alcoholic solution of picric acid gave the picrate of the unknown material, m. p. 158—159° C. Found: N 20,94%.

It follows from these results that the unknown compound must be of the indole structure, containing some unsaturated side chain. The elucidation of its structure would afford valuable support concerning the detailed mechanism of the reaction.

The indolylacetonitrile was converted to tryptamine in anhydrous ether solution by reduction with $LiAlH_4$ [10]. The tryptamine was then isolated in the form of its hydrochloric acid salt, m. p. 246—247° C. The base had m. p. 116° C.

The reduction could be carried out in a similar way in aqueous medium with sodium borohydride. The isolation and purification of the final product was again possible in the form of the hydrochloride.

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СИНТЕЗ И РЕДУКЦИЯ 3-ИНДОЛИЛАЦЕТОНИТРИЛА

Б. Маткович, Л. Ференци и Ш. Фельдеак

Применением различных методов удалось получить важнейший растительный гормон рожта — индолацетонитрил. Восстановление его алюминиевым гидридом лития привело к тритамину, являющемуся важным промежуточным продуктом обмена веществ триптофана.

A MODIFIED SYNTHESIS OF THIAMIN PYROPHOSPHATE AND DIHYDROXYACETONE MONOPHOSPHATE

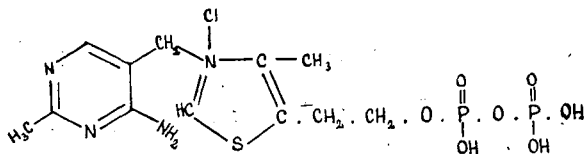
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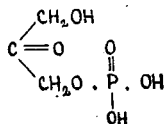
Improved procedures for synthesising the biochemically important materials, thiamin pyrophosphate and dihydroxyacetone monophosphate, are described. The former compound was successfully purified by precipitation with styphnic and phosphotungstic acids.

Organic phosphorus compounds, containing the O—P bond, may be divided, according to their biochemical behaviour, into two general categories: 1. Compounds containing so-called high-energy phosphate bonds and 2. those having low-energy phosphate bonds. A most typical representative of the first group is adenosine triphosphoric acid (ATP); the second group includes such compounds as, *e. g.*, the phosphates of glucose and fructose.

The objects of the syntheses described in this paper were thiamin pyrophosphate (TPP), which belongs to the group of esters containing high-energy bonds, and dihydroxyacetone monophosphate (DAP), a compound having low-energy phosphate bond.



TTF = TPF = thiamin trifoszfát



DOAF = dioxiacetonfoszfát

According to present knowledge, the pyrophosphoric acid ester of thiamin has an important role in biological decarboxylation processes; the compound is regarded

as the prosthetic group of carboxylase systems, therefore it is also named cocarboxylase [1]–[6]. On the other hand, in the opinion of other authors [7], this compound is important as a phosphate donor. Later it was found that TPP occurred also in various animal tissues [8]. The role of TPP in decarboxylation and transketolation processes is dealt with in detail by WIESNER and VALENTS [9].

The biosynthesis of TPP may be readily effected from thiamin in the presence of yeast cells [10].

The chemical synthesis has the serious drawback that besides the required thiamin pyrophosphate or thiamin triphosphate (TTP) it gives various by-products, such as thiamin diphosphate (TDP), monophosphate (TMP), and possibly even thiamin tetraphosphate [11]. Several methods have been developed for eliminating by-product formation during the preparation of TPP and for the purification of the product [12]–[15].

We have applied a combination of WEIJLARD's purification procedure [13] with the method of preparation of BIGLINO and SEGRE [14]. The principle of our synthesis was heating of thiamin hydrochloride and phosphorus pentoxide in a medium of orthophosphoric acid and final purification of the product by precipitating with styphnic and phosphotungstic acids. Details of the procedure are given in the experimental part.

Dihydroxyacetone monophosphate (DAP), a component of the enzyme aldolase, may be synthesised in two ways.

1. Dihydroxyacetone is treated with phosphorus oxychloride in anhydrous quinoline at low temperatures. The product is finally isolated in the form of its calcium salt [16].

2. In the other synthesis, ethyl metaphosphate is used for introducing the phosphate group. The product is isolated in the form of its barium salt [17].

In the course of the present investigation both methods of preparation have been used and the details of the procedures established, as shown in the experimental part.

Experimental

Dihydroxyacetone: The product of the I. G. Farbenindustrie Aktiengesellschaft, Frankfurt a. Main, Höchst, was used.

Thiamin pyrophosphate

Phosphorus pentoxide (50 g) was dissolved at 110–120° C in 50 ml of 85% orthophosphoric acid and 13.0 g of thiamin hydrochloride was added in small portions. The addition was completed in about 30 minutes. The solution was allowed to stand 24 hours, then 60 ml of 2*N* phosphoric acid and 200 ml of water were added. After treating with decolourising carbon and filtration, anhydrous acetone was added until the solution became slightly turbid. The mixture was allowed to stand overnight in a refrigerator. A white crystalline precipitate was obtained which was filtered, and the mother liquor was again treated with acetone as described.

The first crop of crystals was dissolved in 2*N* hydrochloric acid, and the TPP precipitated again by treatment with acetone. A repetition of this procedure afforded a pure product with correct values of combustion analysis.

Final purification of the material could, however, be effected only by precipitation with styphnic acid (1,3-dihydroxy-2,4,6-trinitrobenzene) and with phosphotungstic acid. For this purpose, 1 g of the material was dissolved in 5 ml of water, 5 ml of 8% styphnic acid solution was added, then the mixture was treated with anhydrous acetone until it became turbid. A powdery precipitate separated on standing in a refrigerator, which was filtered and dried under infrared light.

1 g of the product obtained as described, was dissolved then in 50 ml of 2*N* hydrochloric acid, and precipitated with 20 ml of 25% phosphotungstic acid. The formed precipitate could be filtered off and analysis showed it to be identical with TPP.

Analysis: $C_{12}H_{19}O_7N_4SP \cdot 3 H_2O$ (479,37) requires: C 33,85; H 4,46; N 13,17; P 14,58%. Found: C 33,97; H 5,02; N 13,34; P 14,50%.

Calcium dihydroxyacetone monophosphate

A solution of 1 g dihydroxyacetone in 30 ml anhydrous quinoline was cooled to -15 to $-20^\circ C$, and it was dropwise added to a cooled solution of 2 g $POCl_3$ in 10 ml quinoline. During the whole addition the mixture was kept at the temperature specified above. In about half an hour the material solidified to a thick crystalline mass. It was diluted with an equal volume of ice-water and 5 ml of 25% calcium acetate solution was added. Then the solution was neutralized by means of sodium hydroxide until it was only slightly acidic to litmus, centrifuged to separate the quinoline and calcium phosphate, and finally the calcium salt of dihydroxyacetone phosphate was precipitated by admixing three volumes of alcohol.

The purity of the product may be checked by analysing a sample for inorganic, hydrolysable and total phosphate contents. If the presence of significant amounts of dihydroxyacetone diphosphate is detected, the product may be purified by hydrolysis in 2 *N* HCl, and subsequent precipitation with alcohol.

Ethyl metaphosphate

Phosphorus pentoxide (200 g) was refluxed in excess diethylether, which had been previously dried over sodium, until the P_2O_5 was converted to a viscous syrup. This process required about 60 hours. The supernatant ether was separated, the material was dissolved in 400 ml of chloroform and filtered. The solution was refluxed for 5 hours in the steam bath, when the difficultly soluble components separated. After filtering from the solids, the ethyl metaphosphate was precipitated by the addition of two volumes of anhydrous ether.

A thick white syrup was obtained which tends to turn brown on standing. The material is not stable during storage. It can be stored for a while in chloroform, however on contact with air it turns rapidly brown in this case, too. If the solvent is separated from the freshly prepared syrup, the material may be used directly for the preparation of dihydroxyacetone monophosphate.

Barium dihydroxyacetone monophosphate

Crystalline dihydroxyacetone (0,945 g) was dissolved in a small amount of water and the solvent was repeatedly evaporated in an exsiccator over concentrated sulphuric acid, until the original weight was obtained. The procedure was repeated several times. The material was then thoroughly mixed with 0,9 g of ethyl metaphosphate syrup; this process resulted in the formation of a pure white material.

Unreacted ethyl metaphosphate was removed from the product by repeated extractions with ether.

After having evaporated the chloroform, the residue was dissolved in water and filtered. The filtrate was carefully neutralized with 15 ml of saturated $\text{Ba}(\text{OH})_2$ solution. The mixture was allowed to stand overnight, and the small amount of precipitated barium phosphate was filtered.

The barium salt of dihydroxyacetone monophosphate was precipitated from the filtrate by the addition of anhydrous ethanol. Sometimes an amorphous precipitate was obtained; it could be transformed into crystalline material by dissolving in water and reprecipitating with ethanol.

Uniformity of the product was checked by paper chromatography, in butanol-acetic acid-water solvent with detection by ammonium molybdate and SnCl_2 [18].

When excess ethyl metaphosphate was employed, the principal product was dihydroxyacetone diphosphate.

When in the above procedure, neutralization was carried out by means of $\text{Ca}(\text{OH})_2$ instead of $\text{Ba}(\text{OH})_2$, calcium dihydroxyacetone phosphate was obtained. It has the advantage over the barium salt that it can be decomposed by as mild an agent as 1N oxalic acid; this behaviour is common with that of calcium salts of phosphate esters in general, e. g., calcium 1,6-fructose diphosphate. Centrifuging of the insoluble calcium oxalate and repetition of the procedure several times, gave the pure ester. On the other hand, decomposition of the barium salt requires the use of sulphuric acid, consequently in this case a certain degree of decomposition of the product may be involved, too.

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МОДИФИЦИРОВАННЫЙ СИНТЕЗ ТИАМИН ПИРОФОСФАТА
И ДИОКСИ-АЦЕТОНФОСФАТА

Б. Магкович, П. Пэнзеш и Ш. Фельдеак

Известны различные методы для введения фосфатной группы или фосфатных групп в органические вещества. Здесь должны быть выдвинуты лишь два из них, служащие для фосфорилирования гидроксильных групп первичных спиртов. Различие между двумя методами состоит в том, что в то время как в случае диокси-ацетон-фосфата образуется эфирная связь в случае тиамина создается пиррофосфатная связь.

**AN INVESTIGATION OF THE CONNECTION BETWEEN
PHYSIOLOGICAL ACTIVITY AND CHEMICAL STRUCTURE
OF NEW DRUGS ACTING ON THE CENTRAL NERVOUS SYSTEM II**

Synthesis of cyclic tertiary aminopropionic esters and "reversed" esters

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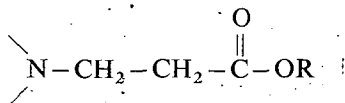
Physiological Institute of the Medical University, Szeged

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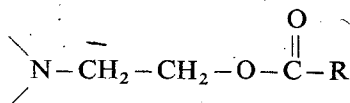
The methyl, ethyl, butyl and benzyl esters of piperidine, pyrrolidine and morpholine and their methiodides have been prepared. The action of these compounds on the central nervous system was examined, and from the results some conclusions were drawn concerning the connection between pharmaceutical effect and chemical structure.

In our previous publication on similar subject (1) we had stated that in experiments with animals tertiary aminoacetates showed nicotin-like action, except for the benzyl ester, which produced in large doses slight anti-nicotinic effects. In our experiments described in the present paper we studied whether anti-nicotinic activity could be increased by lengthening the alkyl chain connecting the carboxyl groups with the tertiary amine.

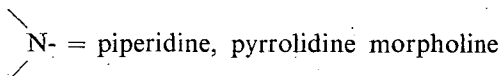
To this end cyclic tertiary aminopropionic esters and so-called "reversed" esters were prepared. By this latter name we mean the esters of tertiary aminoalcohols with aliphatic or aromatic carboxylic acids. Their structure is the following:



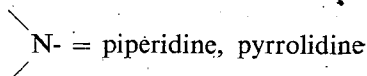
R ester of tertiary amino-
propionic acid



„reversed” ester

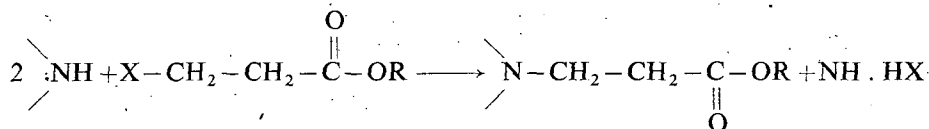


R = methyl, ethyl, butyl,
benzyl



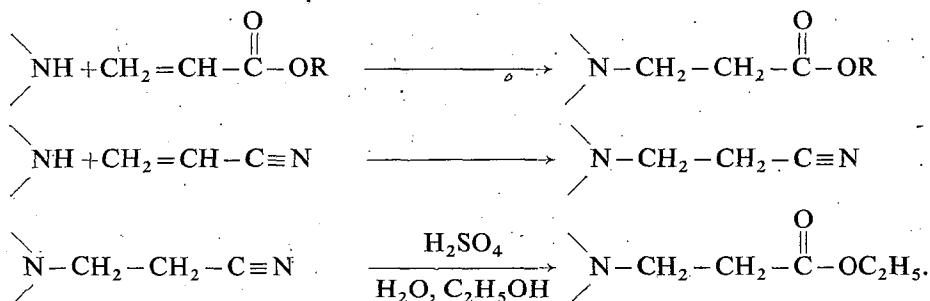
R = phenyl, methyl

For the synthesis of tertiary aminopropionates, first WEDEKIND'S (2) method was applied, viz. β -iodopropionates were reacted with the secondary amine in the molar ratio 1:2, in a medium of anhydrous benzene. In our case this method did not give satisfactory yields of the required products. According to our experiments, best yields were obtained by carrying out the condensation with chloro- or bromopropionic esters (3). The reaction scheme is:



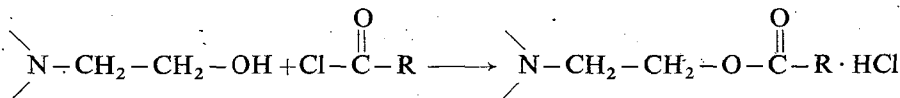
X = Cl, Br, I.

The β -chloropropionates were prepared from chloropropionic acid and the corresponding alcohol (4,5) in the presence of sulphuric acid. This method could not be applied for the preparation of benzyl ester; this synthesis can be achieved by starting with β -chloropropionyl chloride (6). Tertiariation with acrylates is more limited in scope, however, it gives very good results here: *E. g.*, the reaction of a secondary amine with methyl acrylate in the molar ratio of 1:1, gave an almost quantitative yield of the corresponding tertiary methyl aminopropionate (7). Carrying out this reaction by using acrylonitrile, subsequent saponification gave also very high yields of the tertiary amino-carboxylic acid or, when alcohol and sulphuric acid were used, of the corresponding ester:



Methyl pyrrolidino, piperidino and morpholidinopropionates were prepared by this method, too.

Mention should be made here of the general procedure of synthesizing reversed esters, which were prepared by reacting the corresponding acid chloride with the tertiary aminoethanol:



From among the reversed esters, the piperidino- β -ethyl esters of benzoic acid and of acetic acid have been prepared so far.

The hydrochlorides, picrates — and with a few exceptions — the methiodides of all the bases have been prepared.

In view of the experimental results obtained so far, the relationship between chemical structure and action exerted on the central nervous system can be summarized as follows:

1. It is known that certain tertiary aminocarbonic esters, besides other advantageous therapeutic properties, can hinder nicotinic convulsions even in very small doses. Parpanit (diethylaminoethyl ester of 1-phenylcyclopentane-1-carboxylic acid) belongs to this group. This observation turned our attention to the group of amino esters. In connection with the classes of compounds synthesized by us, the following observations were derived:

a) The methyl, ethyl and butyl esters of piperidinoacetic acid show nicotin-like effect, while benzyl esters have antinicotinic action, when administered in large doses.

b) The same holds true for derivatives of pyrrolidinoacetic acid but their nicotin-like activity is more pronounced.

c) Esters of morpholinoacetic acid have no antinicotinic action. A similar grouping of propionic esters reveal the following observations:

a) With piperidinopropionic esters, nicotin-like effect is decreased when the number of the carbon atoms of the esterifying alcohol is increased a weak antinicotinic action appears in the butyl ester, while the benzyl ester definitely hinders the spasms caused by nicotine.

b) Pyrrolidino derivatives show even stronger nicotin-like activity except for the benzyl ester which even in this series possess antinicotinic action. Preparation of the methiodides from pyrrolidinoacetic and propionic esters having nicotin-like action increases this effect.

c) In the series of morpholinopropionic esters both effects are practically suspended.

It follows generally from the above mentioned facts that esters containing aliphatic substituents with smaller radical-weight have nicotin-like action while homologous esters with a higher number of carbon atoms and those which contain aromatic substituents show antinicotinic activity. The nature of the tertiary base modifies the effect only partly, while in the case of morpholine the activity in both directions is considerably decreased:

2. In the series of "reversed esters", e. g., with piperidino- β -ethyl benzate, where the "carbonyl" function is in reversed position in comparison with the previous type, of esters, increased antinicotinic action is revealed.

3. Quaternary derivatives of tertiary aminopropionic esters show ganglion-blocking effect running parallel with the appearance of the antinicotinic effect of the bases.

Experimental

β -chloropropionic acid was prepared by the addition of hydrogen chloride to acrylonitrile; the hydrolysis of the product gave β -chloropropionic acid (7, 8). B. p. 150–160° C at 40 mm; M. p. 41° C.

The esters of β -chloropropionic acid were prepared in the usual way of esterification with the corresponding alcohol in the presence of sulphuric acid (4, 5).

For the preparation of the methyl ester, HROMATKA's method (7) was found to be the best: 0,27 mol methyl acrylate was reacted with 0,27 mol piperidine under

cooling and stirring (the time of the addition of piperidine was 25 to 30 min). After complete addition, stirring was continued for 3 hours and the mixture was refluxed on a water-bath over a period of 8 hours. B. p.: 72° C, at 2 mm.

β -chloroethyl benzoate was obtained from ethylene chlorohydrin and benzoylchloride (8). Freshly distilled β -chloroethyl benzoate was added to piperidine in anhydrous benzoene. The reaction was very slow, therefore the mixture had to be refluxed for 2 or 3 hours on a water-bath. After cooling benzene was distilled off and the viscous residual oil was fractionated. B. p.: 141° C, at 2 mm. The hydrochloride was separated from the product in ether solution by a calculated amount of hydrogen chloride dissolved in ether. M. p. 184° C.

Analysis ($C_{14}H_{20}O_2NCl$) Calculated: C 62,31 H 7,47 Cl 13,15
Found: C 62,21 H 7,53 Cl 13,40%.

Preparation of cyclic amino-propionic esters. All the cyclic aminopropionic esters have been prepared under similar conditions by condensing halocarboxylic esters with secondary amines, therefore the method of preparing all these products is given in the general description below. Data for the products are to be found in Table I (on page 64).

A three-necked flask with ground-glass joints, immersed into ice-water, was equipped with a mechanical stirrer, reflux condenser, carrying a calciumchloride tube and with a dropping funnel. 2 X mol of the freshly distilled anhydrous amine was dissolved in 2,5 mol of anhydrous benzene, and introduced into the flask and 1 X mol halocarboxylic acid dissolved in 2,5 mol of anhydrous benzene was added dropwise through the funnel under constant stirring. After having completed the addition of the halocarboxylic acid solution, stirring was continued for half an hour, meanwhile the temperature was raised by heating the water-bath to attain 70—80° C. Then the mixture was allowed to stand 2 or 3 hours. The precipitate was filtered, washed with some benzene, the combined benzene solutions were dried over anhydrous sodium sulphate, the solvent was evaporated, and the residual oil fractionated. Amine ester hydrochlorides were prepared from the produced tertiary aminoesters in ether solution with the calculated amount of hydrogen chloride dissolved in ether, while quaternary salts were precipitated in anhydrous ethanol solution by means of methyl iodide.



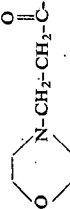
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Table I

	R =	Empirical formula	b. p., °C m. Hg.	Analysis		Picrate			Metiodide			Hydrochloride M. p. °C
				Nitrogen %		M. p. °C	Nitrogen %		M. p. °C	Iodine		
				Calc.	Found		Calc.	Found		Calc.	Found	
	methyl	C ₉ H ₁₇ O ₂ N	72/2	8,19	8,30	164	14,00	13,98	147-148	40,07	40,70	189
	ethyl	C ₁₀ H ₁₉ O ₂ N	102- 103/5	7,56	7,43	131,5	13,52	14,20	—	—	—	169
	butyl	C ₁₂ H ₂₄ O ₂ N	124- 125/6	6,51	6,76	108-109	12,26	12,10	110	42,43	41,70	164,7
	benzyl	C ₁₅ H ₂₁ O ₂ N	149- 150/1	5,66	5,89	113	11,49	11,95	—	—	—	193,5
	methyl	C ₈ H ₁₅ O ₂ N	76/5	8,91	8,72	147	14,51	14,55	166	42,47	43,10	125
	ethyl	C ₉ H ₁₇ O ₂ N	85/6	8,19	8,30	114	14,00	14,30	—	—	—	146
	butyl	C ₁₁ H ₂₁ O ₂ N	106- 108/5	7,02	7,12	97	13,08	13,38	—	—	—	74-75
	benzyl	C ₁₄ H ₁₉ O ₂ N	138- 139/1	6,00	5,88	102	12,12	12,54	154	33,96	34,28	152
	methyl	C ₉ H ₁₅ O ₃ N	82/2	8,13	8,23	129	13,93	14,12	151	40,32	39,65	203
	ethyl	C ₉ H ₁₇ O ₃ N	108/6	7,87	7,94	108	13,52	14,01	—	—	—	188-189
	butyl	C ₁₁ H ₂₁ O ₃ N	131- 132/6	6,51	6,81	150	12,67	13,05	115	35,57	35,66	173
	benzyl	C ₁₄ H ₁₉ O ₃ N	154/1	5,62	5,83	125	11,68	11,73	—	—	—	189-190

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ИССЛЕДОВАНИЕ СВЯЗИ ФАРМАКОЛОГИЧЕСКОГО ЭФФЕКТА
И ХИМИЧЕСКОЙ СТРУКТУРЫ В СЛУЧАЕ НОВЫХ ЛЕКАРСТВ
ВЛИЯЮЩИХ ЦЕНТРАЛЬНУЮ НЕРВНУЮ СИСТЕМУ

Б. Маткович, Ш. Фельдеак и Н. Порсас

Бензильные, метильные, этильные и бутильные эфиры и метойодиды приперидино, пирролидино и морфолино — пропионной кислоты были приготовлены. Эффект этих примесей на центральную нервную систему был также исследован. Из результатов авторы делают выводы на связь между химической структурной и фармакологическим эффектом.

THE ADDITION OF HYDROGEN CHLORIDE TO ALLYL DIMETHYLAMINE IN THE MOLTEN STATE

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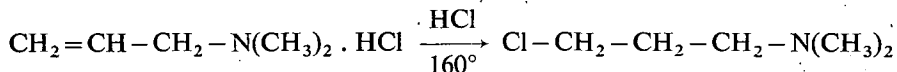
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(Received April 5, 1961)

When a benzene solution of dimethylamine carbonate was acted upon by allyl chloride, the product was allyl dimethylamine; addition of hydrogen chloride into the molten hydrochloride of the latter compound furnished 3-chloropropyl dimethylamine.

The hydrogen halide addition to N-substituted allylamine systems has been investigated by KHARASCH and FUCHS (1) under various conditions. The addition of gaseous hydrogen chloride to the molten hydrochloride of allyl diethylamine resulted in the formation of an isomeric mixture of 2- and 3-chloropropyl diethylamine. This method gave a higher yield of the 3-chloropropyl diethylamine isomer than the method of using concentrated aqueous hydrochloric acid under pressure.



In the present work the HCl addition to molten allyl dimethylamine-hydrochloride was attempted. The preparation of allyl dimethylamine as described by WESTON and his coworkers (2) as well as by COPE and TOWLE (3), consisted of reacting dimethylamine with allyl chloride under pressure. Furthermore, the base was prepared from allyl bromide by PARTHELL and BROICH (4), and from allyl iodide by KNORR and ROTH (5).

In our experiments, allyl dimethylamine was prepared in a satisfactory yield from allyl chloride by reacting it either with the benzene solution of dimethylamine carbonate or with aqueous dimethylamine solution without pressure.

The addition of hydrogen chloride to molten allyl dimethylamine hydrochloride resulted in the formation of 3-chloropropyl dimethylamine. According to the method of KHARASCH, the addition is carried out by passing dry hydrogen chloride over the surface of the melt instead of this procedure, however, it seemed more suitable to bubble the gas through molten material, thus ensuring a larger contacting surface of the components of the heterogeneous reaction mixture.

After having completed the addition, the base could be liberated from the formed 3-chloropropyl dimethylamine hydrochloride by concentrated sodium hyd-

roxide solution. It is noteworthy that while similar treatment of allyl diethylamine (1) gave a mixture of 2- and 3-chloroisomers, allyl dimethylamine yielded in our experiments only the 3-chloroisomer, and a single fractionated distillation of the base on a usual column afforded a product of satisfactory purity.

Experiments of hydrogen chloride addition were attempted also in dimethylformamide solution in the presence of benzoyl peroxide, but under such conditions no addition took place, and only the unreacted starting material could be recovered.

Experimental

Allyl dimethylamine hydrochloride. 50 g (47 ml, 0,66 mol) allyl chloride was mixed with 384 ml of a benzene solution of dimethylamine carbonate, containing 60 g (1,33 mol) of dimethylamine. After having allowed the mixture to stand half an hour, it was gently refluxed for an hour on a steam-bath. After 24 hours' standing at room temperature, the separated crystals were filtered off and washed with some anhydrous benzene. The combined filtrate and washing liquid were distilled in a water-bath under atmospheric pressure. The distillate was extracted with 200 ml of 2 N HCl in several portions and the combined aqueous extract was evaporated to dryness under reduced pressure. The yield was 61,2 g (77%) of hygroscopic allyl dimethylamine hydrochloride.

Allyl dimethylamine (base). a) 26,6 g (25 ml 0,35 mol) of allyl chloride and 208 ml of a benzene solution of dimethylamine carbonate (15,43 g) dimethylamine in 100 ml benzene were mixed; after standing 24 hours, the mixture was glutly refluxed, then after cooling again 52 ml dimethylamine solution of the above concentration was added, and the mixture was allowed to stand 24 hours at room temperature. The separated crystals were filtered, and washed with some anhydrous benzene. The filtrate was combined with the washing liquid, and distilled under atmospheric pressure on a water-bath. The distillate was fractionally extracted with 200 ml of 2 N HCl. The combined aqueous extracts were evaporated to dryness under reduced pressure, and treated with 100 ml 50% NaOH solution. The separated organic layer after drying over anhydrous sodium sulphate was fractionated at atmospheric pressure. B. p. 60—64°; 10,5 g. (40%), $n_D^{25,3} = 1,3980$

(Data in literature: b. p. 61—64° C (2); $n_D^{25} = 1,3981(3)$.)

Analysis: (C ₅ H ₁₁ N)	Calculated	C 70,53	H 13,02	N 16,45;
	Found	C 70,62	H 13,10	N 16,61.

b) 50 g of allyl chloride (47 ml, 0,66 mol) and 150 ml of aqueous dimethylamine solution (40 g dimethylamine in 100 ml) were mixed under cooling. The reaction mixture was homogenized by adding 40 ml ethanol in portions and shaking. After 24 hours' standing the reaction mixture was refluxed for an an hour, then allowed again to stand 24 hours. After filtration the mixture was acidified with concentrated hydrochloric acid under intensive cooling then the acidic solution was evaporated under reduced pressure. The obtained syrupy residue was treated with 150 ml 50% NaOH, the organic layer separated, and after drying (Na₂SO₄ sicc.) fractionated under atmospheric pressure.

B. p. 60°, $n_D^{22} = 1,3991$ 22,6 g (41%).

3-chloropropyl dimethylamine (base) a) 51,4 g. of allyl dimethylamine hydrochloride was melted at 155–160°, and a stream of dry hydrogen chloride was passed through it for 24 hours. Weight increase was 7 g. The substance thus obtained was dissolved in 25 ml water, saturated with K_2CO_3 , and filtered. The filtrate was extracted with 10 × 100 ml ether, while the salt remaining on the filter was previously washed with the single ether portions. After drying over anhydrous Na_2SO_4 , the combined ether extracts were fractionated.

B. p. t_{50} : 51–53°, 12,1 g. (23%), $n_D^{20} = 1,4314$

(Data in literature: b. p. t_{50} : 51–53° (6), $n_D^{20} : 1,4313$ (7).

Analysis ($C_5H_{12}NCl$)	Calculated	C 49,38	H 9,94	N 11,52	Cl 29,15
	Found	C 49,47	H 9,87	N 11,69	Cl 29,23

Picrate prepared in the usual way in abs. ethanol solution. M. p. 109–110° (Data in literature 109,8–110,1° [6]).

Analysis ($C_{11}H_{15}O_7N_4Cl$)	Calculated	C 37,66	H 4,31	N 15,97
	Found	C 37,70	H 4,42	N 16,08.

b) Dry hydrogen chloride was introduced into 49,7 g allyl dimethylamine base under cooling. The reaction mixture became considerably warm, then it froze to give a white crystalline mass. Thereafter it was heated to 155–160° while continuing the introduction of HCl gas. After 12 hours of gas-introduction the increase of weight was 40,6 g (95,1%). The cooled product was dissolved in 50 ml water, treated with decolorizing carbon, and mixed with 100 ml 50% NaOH while cooling in icewater. The organic layer was separated, dried over Na_2SO_4 and fractionated.

B. p. t_{50} : 51–54°, 20,6 g. (30%) $n_D^{21} : 1,4310$

Picrate prepared in the above way. M. p. 109–110°.

Attempted HCl-addition in dimethylformamide solution

100 g of allyl dimethylamine hydrochloride was dissolved in 200 ml of freshly distilled dimethylformamide. Dry HCl-gas was bubbled through the cooled solution for 6 hours. Then dimethyl formamide was distilled off at 10 mm pressure, and the crystalline residue treated with 200 ml 50% NaOH solution. The organic layer was separated, dried over Na_2SO_4 , and fractionated under atmospheric pressure. B. p. 61–64°, 22,6 g. (37%), $n_D^{23} : 1,3993$ corresponding to the properties of the allyl dimethylamine base. No 3-chloropropyl dimethylamine could be isolated.

* * *

The authors wish to express their thanks to KORNÉLIA L. LÁNG and GIZELLA B. BOZÓKI for the analyses, and to the United Pharmaceutical Works for financial support of this research.

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ПРИСОЕДИНЕНИЕ ХЛОРИСТОГО ВОДОРОДА К АЛЛИЛДИМЕТИЛАМИН
В ПЛАВАХ

М. Халмош, Т. Мохачи и Дь. Ченгери

Реакция аллилхлорида с бензольным раствором диметиламинкарбоната ведет к аллилдиметиламину. Путем присоединения хлористого водорода в плавах гидрохлорида последнего 3-хлорпропилдиметиламин получается.

FRIES REARRANGEMENT OF 3-NITROPHENYL BENZOATE

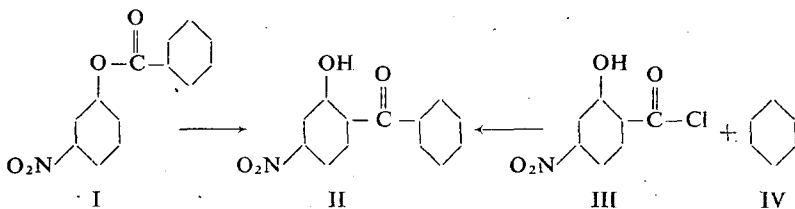
By Á. FURKA and T. SZÉLL

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(Received 17 March, 1961)

The aluminium chloride catalysed FRIES isomerisation of 3-nitrophenyl benzoate in the absence of a solvent gave the unknown 4-nitro-2-hydroxy-benzophenone, the structure of which was proved by the FRIEDEL—CRAFTS reaction of 4-nitro-2-hydroxy-benzoyl chloride with benzene.

It has been reported [1] that our attempts to realize the FRIES rearrangement of 3-nitrophenyl benzoate in nitrobenzene had been unsuccessful. The isomerisation, however, could be carried out without using a solvent. Thus 3-nitrophenyl benzoate (I) underwent FRIES reaction by fusing it with molar quantity of aluminium chloride at 170—175° C for two hours giving the unknown 4-nitro-2-hydroxy-benzophenone (II) with a yield of 11%, while 23% of the ester remained unchanged. In order to prove the structure, II was synthesized from 4-nitro-2-hydroxy-benzoyl chloride (III) and benzene (IV) by FRIEDEL—CRAFTS reaction, in nitrobenzene at 110° C with a yield of 60%. II was characterized by its sodium salt, phenylhydrazone and 2,4-dinitrophenylhydrazone.



Experimental¹

FRIES reaction of 3-nitrophenyl benzoate. Ester, prepared as previously described [1] (15 g, 62 millimoles) was thoroughly mixed with powdered anhydrous aluminium chloride (8,22 g, 62 millimoles), introduced into a flask equipped with a guard tube and heated in an oil bath. The temperature of the bath was slowly raised to 170° C (during an hour) and kept at it for further two hours. The cooled, solidified mixture was dissolved in 50 ml of hot ethanol, made acid by adding 10 ml of concent-

¹ Melting points are uncorrected.

rated hydrochloric acid and poured into 600 ml of water at 30° C. The oil separated was freed from water and boiled with 250 ml of tetrachloro-ethane for 12 hours, filtered through cotton and shaken with 3 × 40 ml of 4% sodium hydroxyde solution. From the residual tetrachloro-methane solution 3,5 g of 3-nitrophenyl benzoate was recovered. On acidifying the combined alkaline extract a black material has been separated which was extracted with 5 × 10 ml of hot ligroin. By removing ligroin 1,65 g crude 4-nitro-2-hydroxy-benzophenone was obtained (yield: 11%). Recrystallization from ethanol gave yellow needles melting at 112—113° C. (Found: N 6,0%, $C_{13}H_9O_4N = 243,2$ calculated: N 5,8%). The yellow sodium salt of this ketone precipitated on adding ethanol solution of sodium ethylate to the benzene- or nitrobenzene solution of 4-nitro-2-hydroxy-benzophenone. The phenylhydrazine was prepared by boiling the ketone with a calculated amount of phenylhydrazine in 60% ethanol. Orange needles, m. p. 188—189° C (Found: N 12,7, $C_{19}H_{15}O_3N_3 = 333,3$ calculated: N 12,9%. 2,4-dinitrophenylhydrazine was prepared by adding a solution of 2,4-dinitrophenylhydrazine (1g dissolved in 100ml of concentrated sulphuric acid) to the solution of the ketone in 50% aqueous ethanol. Orange yellow crystals, m. p. 280—283° C (Found: N 16,2%, $C_{19}H_{13}O_7N_5 = 423,3$ calculated: N 16,5%).

The FRIEDEL—CRAFTS reaction of 4-nitro-2-hydroxy-benzoyl chloride with benzene

5,5 g of 4-nitro-2-hydroxy-benzoic acid (30 millimoles, m. p. 220—223° C), prepared according to literature [2], and 8,0 g of thionyl chloride (66 millimoles) were dissolved in 30 ml of nitrobenzene, and refluxed for two hours in an oil bath of 120° C. In order to remove thionyl chloride completely, the solution was diluted with 30 ml of benzene and distilled (the endtemperature of the oil bath was 142° C). This operation was repeated twice. To the thionyl chloride free nitrobenzene solution 25 ml of benzene, and 8,0 g of aluminium chloride (60 millimoles) were added, and the solution kept in an oil bath of 100—110° C, for two hours and a half. The excess of the benzene was then removed by distillation continued until the temperature of the oil bath reached 145°, the residue cooled to room temperature and decomposed by pouring it into the mixture of 30 g of ice and 15 ml of concentrated hydrochloric acid. The organic layer was washed successively five times with 70 ml of 2 N hydrochloric acid, five times with 70 ml of cold water and finally with four 50 ml portions of hot water (70° C). From the combined aqueous extract 0,4 g of 4-nitro-2-hydroxy-benzoic acid was extracted with chloroform. The dark nitrobenzene layer was washed four times with 50 ml of 1 N sodium hydroxyde, the combined alkaline extract acidified, cooled in ice, and filtered to give 4,4 g 4-nitro-2-hydroxy-benzophenone, m. p. 99—100° C. Yield: 60%. After recrystallization from 35 ml of ethanol the m. p. was 110—112° C, which was un-depressed on admixture with the ketone, obtained by the FRIES reaction of 3-nitro-phenyl benzoate.

* * *

The present work was supported by the Hungarian Academy of Sciences, which is gratefully acknowledged. The authors are indebted to KORNÉLIA L. LÁNG and GIZELLA B. BOZÓKI (Inst. of Org. Chem. Univ. Szeged) for the microanalyses.

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ПЕРЕГРУППИРОВКА 3-НИТРОФЕНИЛ-БЕНЗОАТА ПО ФРИСУ

А. Фурка и Т. Селл

Изомеризация ФРИС без растворителя 3-нитрофенилбензоата, катализируемая хлористом алюминием, дала неизвестный 4-нитро-2-гидроксибензофенон, структура которого доказывалась реакцией ФРИДЕЛЕ — КРАФТС 4-нитро-2-гидроксихлорного бензола и бензола.

AN INSTRUMENT FOR THE DEMONSTRATION OF COUNTERCURRENT CONTINUOUS PROCESSES

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and

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(Received January 15, 1961)

An instrument made of glass has been described for the demonstration and study of counter-current continuous processes.

§ 1. Introduction

The importance of countercurrent continuous reactions and processes is well known. The simple device, shown below, is one of those apparatuses which are suitable for the demonstration of the principle of countercurrent and continuity, as well as for the laboratory exercises of students in chemistry. Thus, the instrument may be used in high schools and universities, both for demonstration and experimenting in connection with chemical engineering operations as well as with the instruction of chemical technology.

§ 2. Description of the apparatus

The apparatus consists of 5—10 reactor-units, made of glass (Fig. 1). Fig. 2 shows a set-up of five units. The liquid of a relatively low density is fed from the separating funnel, placed on a higher level, and the liquid passes in conformity with the principle of the communicating vessels, through the heat exchanger coil (which may be omitted in certain given cases) and the reactor-units. The material of higher density, fed from the other separating funnel, runs by gravitation. The reactors may also be made in such a manner (Fig. 3), as to permit to fill it with glass beads or RASCHIG rings, in order to make the mixing of the two phases still more complete.

§ 3. Some examples of the practicability of the apparatus

a) With the apparatus, e. g., the countercurrent continuous extraction may be demonstrated. Obviously, a great number of pairs of materials is suitable for the demonstration of the liquid-liquid extraction. Thus, may conveniently be used,

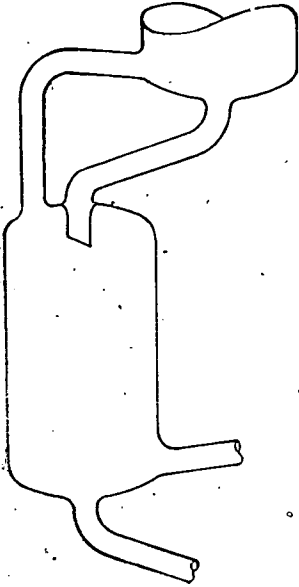


Fig. 1

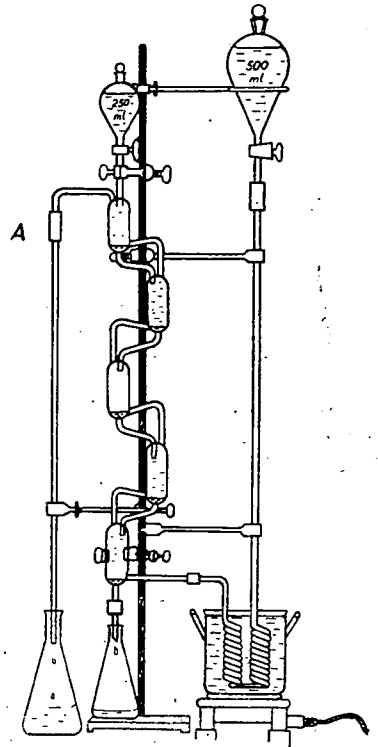


Fig. 2

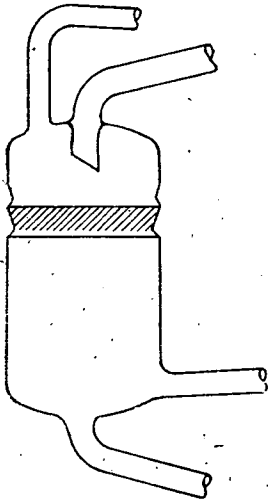


Fig. 3

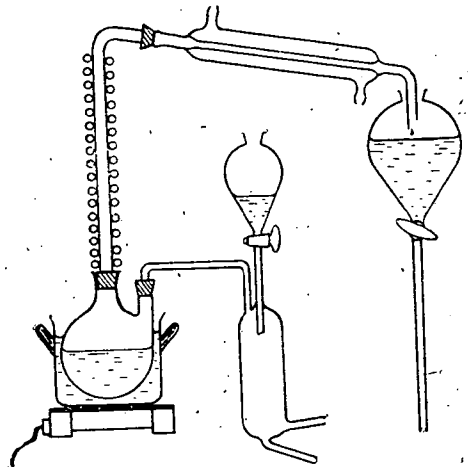


Fig. 4

e. g., picric acid, dissolved in benzene (1 g per litre) together with 1 N aqueous solution of NaOH. The fading of the hue of the yellow benzene solution and the turning yellow of the caustic — at the beginning colourless — solution (sodium picrate), may be easily followed with naked eyes or by means of colorimetry. An example of industrial character is the extraction of phenols from gasworks liquor, previously neutralized and coloured violet with ferric chloride, by means of esters (ethyl- or butyl-acetate). Here, the gradual discolouration of the heavier aqueous part may be observed in consequence of the dissolution of phenols.

b) The apparatus may be used for carrying out countercurrent *reaction*, too. Thus, e. g., sulfuric acid refining of crude benzene and tar or petroleum products, as well as other heterogeneous liquid-liquid reactions may be carried out with this device.

As a typical example, we shall further on expose the continuous sulfonation of benzene, which will demonstrate at the same time the operation of the apparatus as well.

§ 4. *Manufacture of benzene sulfonic acid*

This process is a well known industrial procedure in its *continuous* form, too [1], although benzene sulfonic acid may also be produced by a batch type reaction without any difficulty [2].

The benzene gets into the apparatus through a spiral, plunged into a water bath of 75° C, while at the same time a 12—20 percent oleum is fed from the smaller funnel at such a rate as to ensure the formation of a 8—12 mm thick permanent seal of oleum in the bottom reactor. It is, of course, important that the outflow of the oleum at the bottom be of the same rate as its feeding above. At equal length of time about three times as much ml of benzene should pass through the apparatus as oleum. The oleum may repeatedly be used as long as its concentration does not drop to 2 or 3 per cent. The oleum dissolves the sulfonic acid better than benzene does, therefore, it is more expedient — for the sake of realizing better conditions of distribution — to use such oleum which already has a content of sulfonic acid, *i. e.*, which had already passed through the apparatus. The ageing of oleum may be controlled with the help of a densitometer. The benzene solution, containing some tenth part of per cent of benzene-sulfonic acid is made flown — advantageously, at a rapid pace of dropping, as shown by Fig. 4 — into the flask which is joined at spot „A” to the apparatus, shown by Fig. 2. The solvent is then removed from the flask by means of electric heating (open flame would mean a fire hazard!), at such a rate as it is required. As it is also shown in Fig. 4, the benzene obtained in the course of distillation takes part again in the process, while the sulfonic acid becomes concentrated in the flask. In order to obtain the product, one may either follow the semi-continuous procedure described below or else carefully evaporate the benzene and make the residue flow into an ice-cold saturated NaCl solution, when — after allowing to stand for about 2 hours in a refrigerator — the PhSO_2ONa crystallizes in the form of small platelets [2].

Semi-continuous procedure: If, for any reason, the modification sketched by Fig. 4 is not at disposal, then benzenesulfonic acid may be produced in the original setting, in a more primitive way, too. In this case the benzene flowing through (400 ml) is made pass six or seven times again through the apparatus, while the

oleum (200 ml) is replenished about four times. The benzene, flowing out at the end of the test is then washed with 4×20 ml of water, 3 g NaCl are added to the combined aqueous extract, and following the dissolution it is concentrated to a volume of 10 ml. The solution thus obtained, practically saturated regarding NaCl is placed in a refrigerator, where PhSO_2ONa crystallizes in about two hours. The benzene washed out, may be used again, after drying (Na_2SO_4).

From time to time, a part of the spent acid must be taken away, while stronger oleum (e. g. a 20 per cent) shall be added to the spent sulfonating acid in the required proportion, the thus obtained oleum will be again utilized. The oleum taken away, is flown into a saturated ice cool NaCl solution of about a 3,5-fold volume. This way, from each 10 ml part of oleum a further yield of 2—6 g of PhSO_2ONa may be obtained in a way identical with the above described one.

In the first experiment, the production is somewhat smaller, since at the beginning the apparatus is filled with pure benzene, while in the consecutive tests, the benzene in the apparatus already contains sulfonated products, too.

* * *

The authors wish to express their gratitude to Á. FURKA for his helpful suggestions.

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СРЕДСТВО ДЛЯ ИЛЮСТРАЦИИ БЕЗПРЕРЫВНЫХ ПРОЦЕССОВ ПРОТИВНОГО ТЕЧЕНИЯ

Т. Селл и Л. Шаму

Для изучения и иллюстрации процессов непрерывного противного течения было написано одно стеклянное средство.

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