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TOMUS XXI

FASCICULI 1-2

AUSHAF 21 (1-2) 1-84 (1975)

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Adiuvantibus

M. BARTÓK, L. CSÁNYI, P. FEJES, F. GILDE, P. HUHN, L. KETSKEMÉTY,
F. MÁRTA, L. SZALAI et F. SZÁNTÓ

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KOVÁCS KÁLMÁN

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n -ELECTRON ($n=2, 4, 6, 8$) TRIPLETS AS S^2 EIGENFUNCTIONS

By

F. BERENCZ

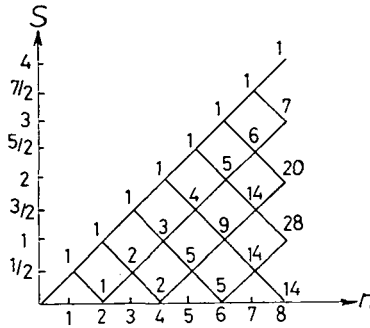
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n -electron ($n=2, 4, 6, 8$) triplets as S^2 eigenfunctions were constructed by the method of spin operators.

Introduction

In previous papers [1—3] using the abstract formulation of the method of branching diagrams, a spin operator was constructed with the so-called S^+ step up and S^- step down spin operator which, when operating on the eigenfunctions of the total S_z spin operator related to maximal projections of total spin, creates each eigen-function of the total S^2 corresponding to its different eigenvalues. The branching diagram has the form:



and the formula of the operator is as follows:

$$\begin{aligned}
 O_{X_1 X_2 X_3 \dots X_{2n-1} X_{2n}} &= \left(\frac{X_1 - X_2 + X_3 - \dots + X_{2n-1} + X_{2n} + 1}{X_1 - X_2 X_3 - \dots + X_{2n-1} + 1} \right)^{1/2} \times \\
 &\times \left(\frac{X_1 - X_2 + X_3 - \dots + X_{2n-3} - X_{2n-2} + 1}{X_1 - X_2 + X_3 - \dots + X_{2n-3} + 1} \right)^{1/2} \times \dots \times \left(\frac{X_1 - X_2 + 1}{X_1 + 1} \right)^{1/2} \times \\
 &\times \sum_{k=0}^{X_{2n}} (-1)^k \frac{(X_1 - X_2 + X_3 - \dots + X_{2n-1} - k)!}{(X_1 - X_2 + X_3 - \dots + X_{2n-1})! k!} (S_{X_1 X_2 X_3 \dots X_{2n-1}}^- S_{X_{2n}}^+)^k \times
 \end{aligned}$$

$$\begin{aligned} & \times \sum_{j=0}^{x_{2n-2}} (-1)^j \frac{(x_1 - x_2 + x_3 - \dots + x_{2n-3} - j)!}{(x_1 - x_2 + x_3 - \dots + x_{2n-3})! j!} (S_{\bar{x}_1}^- S_{x_2}^+ \dots S_{x_{2n-3}}^- S_{x_{2n-2}}^+)^j \times \dots \times \\ & \times \sum_{i=0}^{x_2} \frac{(x_1 - i)!}{x_i! i!} (S_{\bar{x}_1}^- S_{x_2}^+)^i. \end{aligned}$$

In a next paper [4] with the proposed operator technique the n -electron ($n=2, 4, 6, 8$) singlets as S^2 eigenfunctions were constructed.

Since in the investigation of molecules by configuration interaction, by one of the most important method of quantum chemistry, all the states of definite multiplicity for the various configurations are required, in the present paper the n -electron ($n=2, 4, 6, 8$) triplets as S^2 eigenfunctions were constructed.

The n -electron triplets

Let us denote the Slater determinants describing the states of n -electron systems as follows

$$n = 2$$

$$A = |\alpha\alpha|.$$

$$n = 4$$

$$B_1 = |\alpha\alpha\alpha\beta|, \quad B_2 = |\alpha\alpha\beta\alpha|, \quad B_3 = |\alpha\beta\alpha\alpha|, \quad B_4 = |\beta\alpha\alpha\alpha|.$$

$$n = 6$$

$$C_1 = |\alpha\alpha\alpha\alpha\beta\beta|, \quad C_2 = |\alpha\alpha\alpha\beta\beta\alpha|, \quad C_3 = |\alpha\alpha\alpha\beta\alpha\beta|,$$

$$C_4 = |\alpha\alpha\beta\beta\alpha\alpha|, \quad C_5 = |\alpha\alpha\beta\alpha\alpha\beta|, \quad C_6 = |\alpha\alpha\beta\alpha\beta\alpha|,$$

$$C_7 = |\alpha\beta\alpha\alpha\alpha\beta|, \quad C_8 = |\alpha\beta\alpha\alpha\beta\alpha|, \quad C_9 = |\alpha\beta\alpha\beta\alpha\alpha|,$$

$$C_{10} = |\alpha\beta\beta\alpha\alpha\alpha|, \quad C_{11} = |\beta\beta\alpha\alpha\alpha\alpha|, \quad C_{12} = |\beta\alpha\beta\alpha\alpha\alpha|,$$

$$C_{13} = |\beta\alpha\alpha\beta\alpha\alpha|, \quad C_{14} = |\beta\alpha\alpha\alpha\beta\alpha|, \quad C_{15} = |\beta\alpha\alpha\alpha\alpha\beta|.$$

$$n = 8$$

$$D_1 = |\alpha\alpha\alpha\alpha\alpha\beta\beta\beta|, \quad D_2 = |\alpha\alpha\alpha\alpha\beta\beta\beta\alpha|, \quad D_3 = |\alpha\alpha\alpha\alpha\beta\beta\alpha\beta|,$$

$$D_4 = |\alpha\alpha\alpha\alpha\beta\alpha\beta\beta|, \quad D_5 = |\alpha\alpha\alpha\beta\beta\beta\alpha\alpha|, \quad D_6 = |\alpha\alpha\alpha\beta\beta\alpha\alpha\beta|,$$

$$D_7 = |\alpha\alpha\alpha\beta\beta\alpha\beta\alpha|, \quad D_8 = |\alpha\alpha\alpha\beta\alpha\alpha\beta\beta|, \quad D_9 = |\alpha\alpha\alpha\beta\alpha\beta\beta\alpha|,$$

$$D_{10} = |\alpha\alpha\alpha\beta\alpha\beta\alpha\beta|, \quad D_{11} = |\alpha\alpha\beta\beta\alpha\alpha\alpha\beta|, \quad D_{12} = |\alpha\alpha\beta\beta\alpha\alpha\beta\alpha|,$$

$$D_{13} = |\alpha\alpha\beta\beta\alpha\beta\alpha\alpha|, \quad D_{14} = |\alpha\alpha\beta\alpha\alpha\alpha\beta\beta|, \quad D_{15} = |\alpha\alpha\beta\alpha\alpha\beta\beta\alpha|,$$

$$D_{16} = |\alpha\alpha\beta\alpha\beta\beta\alpha\alpha|, \quad D_{17} = |\alpha\alpha\beta\alpha\alpha\beta\alpha\alpha|, \quad D_{18} = |\alpha\alpha\beta\alpha\beta\alpha\alpha\beta|,$$

$$D_{19} = |\alpha\alpha\beta\alpha\beta\alpha\beta\alpha|, \quad D_{20} = |\alpha\beta\alpha\alpha\alpha\alpha\beta\beta|, \quad D_{21} = |\alpha\beta\alpha\alpha\alpha\beta\beta\alpha|,$$

$$\begin{aligned}
 D_{22} &= |\alpha\beta\alpha\alpha\beta\beta|, & D_{23} &= |\alpha\beta\alpha\alpha\beta\beta\alpha|, & D_{24} &= |\alpha\beta\alpha\alpha\beta\alpha\beta|, \\
 D_{25} &= |\alpha\beta\alpha\alpha\beta\alpha\beta|, & D_{26} &= |\alpha\beta\alpha\beta\alpha\alpha\beta|, & D_{27} &= |\alpha\beta\alpha\beta\alpha\alpha\beta\alpha|, \\
 D_{28} &= |\alpha\beta\alpha\beta\alpha\alpha\beta|, & D_{29} &= |\alpha\beta\beta\beta\alpha\alpha\alpha\alpha|, & D_{30} &= |\alpha\beta\beta\alpha\alpha\alpha\alpha\beta|, \\
 D_{31} &= |\alpha\beta\beta\alpha\alpha\alpha\beta\alpha|, & D_{32} &= |\alpha\beta\beta\alpha\beta\alpha\alpha\alpha|, & D_{33} &= |\alpha\beta\beta\alpha\alpha\beta\alpha\alpha|, \\
 D_{34} &= |\alpha\beta\alpha\beta\beta\alpha\alpha\alpha|, & D_{35} &= |\alpha\alpha\beta\beta\beta\alpha\alpha\alpha|, & D_{36} &= |\beta\beta\beta\alpha\alpha\alpha\alpha\alpha|, \\
 D_{37} &= |\beta\beta\alpha\alpha\alpha\alpha\alpha\beta|, & D_{38} &= |\beta\beta\alpha\alpha\alpha\alpha\beta\alpha|, & D_{39} &= |\beta\beta\alpha\alpha\alpha\beta\alpha\alpha|, \\
 D_{40} &= |\beta\beta\alpha\alpha\beta\alpha\alpha\alpha|, & D_{41} &= |\beta\beta\alpha\beta\alpha\alpha\alpha\alpha|, & D_{42} &= |\beta\alpha\alpha\alpha\alpha\alpha\beta\beta|, \\
 D_{43} &= |\beta\alpha\alpha\alpha\alpha\beta\beta\alpha|, & D_{44} &= |\beta\alpha\alpha\alpha\alpha\beta\alpha\beta|, & D_{45} &= |\beta\alpha\alpha\alpha\beta\beta\alpha\alpha|, \\
 D_{46} &= |\beta\alpha\alpha\alpha\beta\alpha\beta\alpha|, & D_{47} &= |\beta\alpha\alpha\alpha\beta\alpha\alpha\beta|, & D_{48} &= |\beta\alpha\alpha\beta\alpha\alpha\alpha\beta|, \\
 D_{49} &= |\beta\alpha\alpha\beta\alpha\alpha\beta\alpha|, & D_{50} &= |\beta\alpha\alpha\beta\alpha\beta\alpha\alpha|, & D_{51} &= |\beta\alpha\alpha\beta\beta\alpha\alpha\alpha|, \\
 D_{52} &= |\beta\alpha\beta\beta\alpha\alpha\alpha\alpha|, & D_{53} &= |\beta\alpha\beta\alpha\alpha\alpha\alpha\beta|, & D_{54} &= |\beta\alpha\beta\alpha\alpha\alpha\beta\alpha|, \\
 D_{55} &= |\beta\alpha\beta\alpha\alpha\beta\alpha\alpha|, & D_{56} &= |\beta\alpha\beta\alpha\beta\alpha\alpha\alpha|.
 \end{aligned}$$

The relating eigenfunctions are as follows

$$n = 2$$

$$\Phi_1^2 = A.$$

$$n = 4$$

$$\Phi_1^4 = O_{X_1 X_2} B_1 = \frac{1}{\sqrt{12}} [3B_1 - (B_2 + B_3 + B_4)];$$

$$\Phi_2^4 = O_{X_1 X_2} B_2 = \frac{1}{\sqrt{6}} [2B_2 - (B_3 + B_4)];$$

$$\Phi_3^4 = O_{X_1 X_2} B_3 = \frac{1}{\sqrt{2}} (B_3 - B_4).$$

$$n = 6$$

$$\begin{aligned}
 \Phi_1^6 = O_{X_1 X_2} C_1 &= \frac{1}{2\sqrt{60}} [12C_1 - 3(C_2 + C_3 + C_5 + C_6 + C_7 + C_8 + C_{14} + C_{15}) + \\
 &+ 2(C_4 + C_9 + C_{10} + C_{11} + C_{12} + C_{13})];
 \end{aligned}$$

$$\Phi_2^6 = O_{X_1 X_2} C_2 = \frac{1}{12\sqrt{2}} [12C_2 - 4(C_4 + C_6 + C_8 + C_9 + C_{13} + C_{14}) + 4(C_{10} + C_{11} + C_{12})];$$

$$\begin{aligned}
 \Phi_3^6 = O_{X_1 \dots X_4} C_3 &= \frac{1}{12} [9C_3 - 3(C_2 + C_5 + C_7 + C_{15}) - 2(C_4 + C_9 + C_{13}) + \\
 &+ 2(C_6 + C_8 + C_{10} + C_{11} + C_{12} + C_{14})];
 \end{aligned}$$

$$\Phi_4^6 = O_{X_1 X_2} C_4 = \frac{1}{2\sqrt{3}} [2C_4 - (C_9 + C_{10} + C_{12} + C_{13}) + 2C_{11}];$$

$$\Phi_5^6 = O_{X_1 \dots X_4} C_5 = \frac{1}{6\sqrt{2}} [6C_5 - 3(C_7 + C_{15}) - 2(C_4 + C_6) - (C_{10} + C_{12}) + C_8 + C_9 + 2C_{11} + C_{13} + C_{14}];$$

$$\Phi_6^6 = O_{X_1 \dots X_4} C_6 = \frac{1}{6} [4C_6 - 2(C_4 + C_8 + C_{14}) - (C_{10} + C_{12}) + C_9 + 2C_{11} + C_{13}];$$

$$\Phi_7^6 = O_{X_1 \dots X_4} C_7 = \frac{1}{2\sqrt{6}} [3(C_7 - C_{15}) - (C_8 + C_9 + C_{10}) + C_{12} + C_{13} + C_{14}];$$

$$\Phi_8^6 = O_{X_1 \dots X_4} C_8 = \frac{1}{2\sqrt{3}} [2(C_8 - C_{14}) - (C_9 + C_{10}) + C_{12} + C_{13}];$$

$$\Phi_9^6 = O_{X_1 \dots X_4} C_9 = \frac{1}{2} [C_9 + C_{12} - (C_{10} + C_{13})].$$

$$n = 8$$

$$\Phi_1^8 = O_{X_1 \dots X_2} D_1 = \frac{1}{10\sqrt{2}} [10D_1 + D_5 + D_6 + D_7 + D_{11} + D_{12} + D_{13} + D_{16} + D_{18} + D_{19} + D_{23} + D_{24} + D_{25} + D_{26} + D_{27} + D_{28} + D_{30} + D_{31} + D_{33} + D_{37} + D_{38} + D_{39} + D_{45} + D_{46} + D_{47} + D_{48} + D_{49} + D_{50} + D_{53} + D_{54} + D_{55} - 2(D_2 + D_3 + D_4 + D_8 + D_9 + D_{10} + D_{14} + D_{15} + D_{17} + D_{20} + D_{21} + D_{22} + D_{42} + D_{43} + D_{44}) - (D_{29} + D_{32} + D_{34} + D_{35} + D_{36} + D_{40} + D_{41} + D_{51} + D_{52} + D_{56})];$$

$$\Phi_2^8 = O_{X_1 X_2} D_2 = \frac{1}{6\sqrt{10}} [12D_2 - 3(D_5 + D_7 + D_9 + D_{15} + D_{16} + D_{19} + D_{21} + D_{23} + D_{25} + D_{43} + D_{45} + D_{46}) + 2(D_{12} + D_{13} + D_{27} + D_{28} + D_{31} + D_{32} + D_{33} + D_{34} + D_{35} + D_{38} + D_{39} + D_{40} + D_{49} + D_{50} + D_{51} + D_{54} + D_{55} + D_{56}) + 3(D_{29} + D_{36} + D_{41} + D_{52})];$$

$$\Phi_3^8 = O_{X_4 \dots X_4} D_3 = \frac{1}{48\sqrt{5}} [72D_3 + 66(D_{13} + D_{28} + D_{32} + D_{33} + D_{34} + D_{35} + D_{39} + D_{40} + D_{50} + D_{51} + D_{55} + D_{56}) + 12(D_{11} + D_{26} + D_{30} + D_{37} + D_{48} + D_{53}) + 6(D_7 + D_9 + D_{15} + D_{19} + D_{21} + D_{25} + D_{44} + D_{46}) - 24D_2 - 18(D_6 + D_{10} + D_{17} + D_{18} + D_{22} + D_{24} + D_{44} + D_{47}) - 12(D_5 + D_{16} + D_{23} + D_{45}) - 3(D_{29} + D_{36} + D_{41} + D_{52}) - (D_{12} + D_{27} + D_{31} + D_{38} + D_{49} + D_{54})];$$

$$\Phi_4^8 = O_{X_1 \dots X_4} D_4 = \frac{1}{40\sqrt{3}} [48D_4 + 6(D_5 + D_{16} + D_{23} + D_{45}) + 4(D_{32} + D_{34} + D_{35} +$$

$$+ D_{40} + D_{51} + D_{56}) + 6(D_{11} + D_{12} + D_{26} + D_{27} + D_{30} + D_{31} + D_{37} + D_{38} + D_{48} + D_{49} + D_{53} + D_{54}) - 9(D_7 + D_8 + D_{18} + D_{19} + D_{24} + D_{25} + D_{46} + D_{47}) + 3(D_9 + D_{10} + D_{15} + D_{17} + D_{21} + D_{22} + D_{43} + D_{44}) - 12(D_2 + D_3 + D_6 + D_{14} + D_{20} + D_{42}) - 6(D_{29} + D_{36} + D_{41} + D_{52}) - 4(D_{13} + D_{28} + D_{33} + D_{39} + D_{50} + D_{55});$$

$$\Phi_5^8 = O_{X_1 X_2} D_5 = \frac{1}{6} [3(D_5 - D_{36}) + D_{29} + D_{32} + D_{33} + D_{39} + D_{40} + D_{41} + D_{52} + D_{55} + D_{56} - (D_{13} + D_{16} + D_{23} + D_{28} + D_{34} + D_{35} + D_{45} + D_{50} + D_{51})];$$

$$\Phi_6^8 = O_{X_1 \dots X_4} D_6 = \frac{1}{6\sqrt{6}} [9D_6 + 2(D_{34} + D_{35} + D_{51}) + D_{12} + D_{13} + D_{16} + D_{19} + D_{23} + D_{25} + D_{27} + D_{28} + D_{29} + D_{32} + D_{40} + D_{41} + D_{45} + D_{46} + D_{49} + D_{50} + D_{52} + D_{56} - (D_{31} + D_{33} + D_{38} + D_{39} + D_{54} + D_{55}) - 3(D_5 + D_7 + D_{18} + D_{24} + D_{34} + D_{35} + D_{36} + D_{47} + D_{51})];$$

$$\Phi_7^8 = O_{X_1 \dots X_4} D_7 = \frac{1}{6\sqrt{3}} [6D_7 + 2(D_{31} + D_{38} + D_{54}) + D_{13} + D_{16} + D_{23} + D_{28} + D_{29} + D_{32} + D_{40} + D_{41} + D_{45} + D_{50} + D_{52} + D_{56} - 3(D_5 + D_{36}) - 2(D_{12} + D_{19} + D_{25} + D_{27} + D_{46} + D_{49}) - (D_{33} + D_{34} + D_{35} + D_{39} + D_{51} + D_{55})];$$

$$\Phi_8^8 = O_{X_1 \dots X_4} D_8 = \frac{1}{48\sqrt{5}} [72D_8 + 2(D_{30} + D_{31} + D_{37} + D_{38} + D_{53} + D_{54}) + 8(D_{13} + D_{28} + D_{34} + D_{35} + D_{50} + D_{51}) + 6(D_{15} + D_{17} + D_{18} + D_{19} + D_{21} + D_{22} + D_{24} + D_{25} + D_{43} + D_{44} + D_{46} + D_{47}) + 4(D_{29} + D_{41} + D_{52}) - 3D_5 - 24(D_{14} + D_{20} + D_{42}) - 28(D_6 + D_7 + D_9 + D_{10}) - 12(D_{11} + D_{12} + D_{26} + D_{27} + D_{36} + D_{48} + D_{49}) - 8(D_{32} + D_{33} + D_{39} + D_{40} + D_{55} + D_{56}) - 4(D_{16} + D_{23} + D_{45})];$$

$$\Phi_9^8 = O_{X_1 \dots X_4} D_9 = \frac{1}{6\sqrt{6}} [9D_9 + 2(D_{31} + D_{33} + D_{34} + D_{35} + D_{38} + D_{39} + D_{51} + D_{54} + D_{55}) + D_{16} + D_{19} + D_{23} + D_{25} + D_{29} + D_{41} + D_{45} + D_{46} + D_{52} - 3(D_5 + D_7 + D_{15} + D_{21} + D_{36} + D_{43}) - 2(D_{12} + D_{13} + D_{26} + D_{28} + D_{32} + D_{40} + D_{49} + D_{50} + D_{56})];$$

$$\Phi_{10}^8 = O_{X_1 \dots X_6} D_{10} = \frac{1}{24\sqrt{3}} [27D_{10} + 6(D_{30} + D_{37} + D_{53}) + 4(D_{33} + D_{34} + D_{35} + D_{39} + D_{51} + D_{55}) + 3(D_7 + D_{15} + D_{18} + D_{21} + D_{24} + D_{43} + D_{47}) - 2(D_{12} + D_{16} + D_{23} + D_{27} + D_{29} + D_{41} + D_{45} + D_{49} + D_{52}) - 9(D_6 + D_9 + D_{17} + D_{22} + D_{44}) - 6(D_5 +$$

$$+ D_{11} + D_{26} + D_{36} + D_{48}) - 4(D_{13} + D_{28} + D_{32} + D_{40} + D_{50} + D_{56}) - 2(D_{31} + D_{38} + D_{54}) - (D_{19} + D_{25} + D_{46});$$

$$\Phi_{11}^8 = O_{X_1 \dots X_4} D_{11} = \frac{1}{24} [12(D_{11} + D_{37}) + 3(D_{36} + D_{41}) + 2(D_{27} + D_{28} + D_{31} + D_{32} + D_{33} + D_{34} + D_{49} + D_{50} + D_{51} + D_{54} + D_{55} + D_{56}) - 6(D_{26} + D_{30} + D_{48} + D_{53}) - 4(D_{12} + D_{13} + D_{35}) - (D_{38} + D_{39} + D_{40})];$$

$$\Phi_{12}^8 = O_{X_1 \dots X_4} D_{12} = \frac{1}{6\sqrt{2}} [4(D_{12} + D_{38}) + D_{28} + D_{32} + D_{33} + D_{34} + D_{50} + D_{51} + D_{55} + D_{56} - 2(D_{13} + D_{27} + D_{31} + D_{35} + D_{39} + D_{40} + D_{49} + D_{54})];$$

$$\Phi_{13}^8 = O_{X_1 \dots X_4} D_{13} = \frac{1}{2\sqrt{6}} [2(D_{13} + D_{32} + D_{34} + D_{39} + D_{51} + D_{56}) - 2(D_{35} + D_{40}) - (D_{28} + D_{33} + D_{50} + D_{55})];$$

$$\Phi_{14}^8 = O_{X_1 \dots X_4} D_{14} = \frac{1}{12\sqrt{10}} [24D_{14} + 6(D_{37} + D_{38}) + 4(D_{13} + D_{16} + D_{35}) + 3(D_{21} + D_{22} + D_{24} + D_{25} + D_{26} + D_{27} + D_{43} + D_{44} + D_{46} + D_{47} + D_{48} + D_{49}) + 2(D_{29} + D_{32} + D_{33} + D_{52} + D_{55} + D_{56}) - 12(D_{20} + D_{42}) - 6(D_{11} + D_{12} + D_{15} + D_{17} + D_{18} + D_{19}) - 4(D_{39} + D_{40} + D_{41}) - 3(D_{30} + D_{31} + D_{53} + D_{54}) - 2(D_{23} + D_{28} + D_{34} + D_{45} + D_{50} + D_{51})];$$

$$\Phi_{15}^8 = O_{X_1 \dots X_4} D_{15} = \frac{1}{6\sqrt{3}} [6D_{15} + 2(D_{38} + D_{39}) + D_{23} + D_{25} + D_{27} + D_{28} + D_{35} + D_{45} + D_{46} + D_{49} + D_{50} - 3(D_{21} + D_{43}) - 2(D_{12} + D_{13} + D_{16} + D_{19} + D_{40} + D_{41}) - (D_{32} + D_{33} + D_{35} + D_{36} + D_{51} + D_{54} + D_{55})];$$

$$\Phi_{16}^8 = O_{X_1 \dots X_4} D_{16} = \frac{1}{6\sqrt{2}} [4(D_{16} - D_{41}) + 2(D_{29} + D_{39} + D_{40} + D_{52}) + D_{28} + D_{34} + D_{50} + D_{51} - 2(D_{13} + D_{23} + D_{35} + D_{45}) - (D_{32} + D_{33} + D_{55} + D_{56})];$$

$$\Phi_{17}^8 = O_{X_1 \dots X_4} D_{17} = \frac{1}{6\sqrt{12}} [18D_{17} + 6D_{37} + 4(D_{35} + D_{39}) + 3(D_{21} + D_{24} + D_{26} + D_{43} + D_{47} + D_{48}) + 2(D_{12} + D_{19} + D_{23} + D_{28} + D_{29} + D_{32} + D_{45} + D_{50} + D_{52} + D_{56}) + D_{31} + D_{54} - 9(D_{22} + D_{44}) - 6(D_{11} + D_{15} + D_{18}) - 4(D_{13} + D_{16} + D_{40} + D_{41}) - 3(D_{30} + D_{53}) - 2(D_{28} + D_{33} + D_{34} + D_{51} + D_{55}) - (D_{25} + D_{27} + D_{46} + D_{49})];$$

$$\begin{aligned} \Phi_{18}^8 = O_{X_1 \dots X_3} D_{18} = \frac{1}{12\sqrt{3}} [12D_{18} + 6D_{37} + 3(D_{26} + D_{48}) + 2(D_{12} + D_{13} + D_{23} + D_{25} + \\ + D_{29} + D_{40} + D_{45} + D_{46} + D_{52}) + D_{31} + D_{33} + D_{34} + D_{51} + D_{54} + D_{55} - 6(D_{11} + D_{24} + \\ + D_{47}) - 4(D_{16} + D_{19} + D_{41}) - 3(D_{30} + D_{53}) - 2(D_{35} + D_{38} + D_{39}) - (D_{27} + D_{28} + \\ + D_{32} + D_{49} + D_{50} + D_{56})]; \end{aligned}$$

$$\begin{aligned} \Phi_{19}^8 = O_{X_1 \dots X_6} D_{19} = \frac{1}{6\sqrt{6}} [8D_{19} + 4D_{38} + 2(D_{13} + D_{23} + D_{27} + D_{29} + D_{31} + D_{40} + D_{45} + \\ + D_{52} + D_{55}) + D_{33} + D_{34} + D_{50} - 4(D_{12} + D_{16} + D_{25} + D_{41} + D_{46}) - 2(D_{35} + D_{39} + \\ + D_{49} + D_{54}) - (D_{28} + D_{32} + D_{50} + D_{55} + D_{56})]; \end{aligned}$$

$$\begin{aligned} \Phi_{20}^8 = O_{X_1 \dots X_4} D_{20} = \frac{1}{12\sqrt{5}} [12(D_{20} - D_{42}) + 3(D_{43} + D_{44} + D_{46} + D_{47} + D_{48} + D_{49} + \\ + D_{53} + D_{54}) + 2(D_{23} + D_{28} + D_{29} + D_{32} + D_{33} + D_{34}) - 3(D_{21} + D_{22} + D_{24} + D_{25} + \\ + D_{26} + D_{27} + D_{30} + D_{31}) - 2(D_{45} + D_{50} + D_{51} + D_{53} + D_{55} + D_{56})]; \end{aligned}$$

$$\begin{aligned} \Phi_{21}^8 = O_{X_1 \dots X_4} D_{21} = \frac{1}{6} [3(D_{21} - D_{43}) + D_{29} + D_{32} + D_{34} + D_{45} + D_{46} + D_{49} + D_{50} + \\ + D_{54} + D_{55} - (D_{23} + D_{25} + D_{27} + D_{28} + D_{31} + D_{33} + D_{51} + D_{52} + D_{56})]; \end{aligned}$$

$$\begin{aligned} \Phi_{22}^8 = O_{X_1 \dots X_6} D_{22} = \frac{1}{12\sqrt{2}} [9(D_{22} - D_{44}) + 3(D_{43} + D_{47} + D_{48} + D_{53}) + 2(D_{29} + D_{32} + \\ + D_{34} + D_{45} + D_{50} + D_{55}) + D_{25} + D_{27} + D_{31} - 3(D_{21} + D_{24} + D_{26} + D_{29}) - 2(D_{23} + \\ + D_{28} + D_{33} + D_{51} + D_{52} + D_{56}) - (D_{46} + D_{49} + D_{54})]; \end{aligned}$$

$$\begin{aligned} \Phi_{23}^8 = O_{X_1 \dots X_4} D_{23} = \frac{1}{2\sqrt{6}} [2(D_{23} + D_{29} - D_{45} - D_{52}) + D_{50} + D_{51} + D_{55} + D_{56} - \\ - (D_{28} + D_{32} + D_{33} + D_{34})]; \end{aligned}$$

$$\begin{aligned} \Phi_{24}^8 = O_{X_1 \dots X_6} D_{24} = \frac{1}{12} [6(D_{24} - D_{47}) + 3(D_{48} + D_{53}) + 2(D_{29} + D_{45} + D_{46}) + D_{27} + \\ + D_{28} + D_{31} + D_{33} + D_{51} + D_{56} - 3(D_{26} + D_{30}) - 2(D_{23} + D_{25} + D_{52}) - (D_{32} + D_{34} + \\ + D_{49} + D_{50} + D_{54} + D_{55})]; \end{aligned}$$

$$\begin{aligned} \Phi_{25}^8 = O_{X_1 \dots X_6} D_{25} = \frac{1}{6\sqrt{2}} [4(D_{25} - D_{46}) + 2(D_{29} + D_{45} + D_{49} + D_{54}) + D_{28} + D_{33} + \\ + D_{51} + D_{56} - 2(D_{23} + D_{27} + D_{31} + D_{52}) - (D_{32} + D_{34} + D_{50} + D_{55})]; \end{aligned}$$

$$\Phi_{26}^8 = O_{X_1 \dots X_6} D_{26} = \frac{1}{4\sqrt{3}} [3(D_{26} - D_{30} - D_{48} + D_{53}) + D_{31} + D_{32} + D_{33} + D_{49} + D_{50} + D_{51} - (D_{27} + D_{28} + D_{34} + D_{54} + D_{55} + D_{56})];$$

$$\Phi_{27}^8 = O_{X_1 \dots X_6} D_{27} = \frac{1}{2\sqrt{6}} [2(D_{27} - D_{31} - D_{49} + D_{54}) + D_{32} + D_{33} + D_{50} + D_{51} - (D_{29} + D_{34} + D_{55} + D_{56})];$$

$$\Phi_{28}^8 = O_{X_1 \dots X_6} D_{28} = \frac{1}{2\sqrt{2}} [D_{28} + D_{32} + D_{51} + D_{55} - (D_{33} + D_{34} + D_{49} + D_{56})].$$

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n-ЭЛЕКТРОН (*n*=2, 4, 6, 8) ТРИПЛЕТЫ КАК СОБСТВЕННЫЕ ФУНКЦИИ S^2

Ф. Беренц

n-электрон (*n*=2, 4, 6, 8) триплеты, как собственные функции S^2 были созданы методом спиновых операторов.

НЕОДНОРОДНОЕ СПЕКТРАЛЬНОЕ УШИРЕНИЕ СПЕКТРОВ α И β ФОСФОРЕСЦЕНЦИИ КРАСИТЕЛЕЙ

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Показано, что для некоторых исследованных органических красителей в твёрдых растворах при комнатной и низкой температурах и в полярных растворителях при низких температурах может наблюдаться смещение спектров фосфоресценции в красную сторону, с увеличением длины волны возбуждающего света на длинноволновом краю полосы поглощения, то есть наблюдается bathochromная фосфоресценция. При повышении температуры величина bathochromного сдвига спектров уменьшается и сам эффект постепенно исчезает. Эти результаты свидетельствуют о существовании неоднородного уширения триплетных уровней энергии молекул красителей в твёрдых и полярных растворителях при комнатной и ещё больше при низкой температурах.

Введение

При анализе спектроскопических свойств полярных растворов необходимо рассматривать элементарную ячейку (ЭЯ) раствора, состоящую из молекул красителя и молекул растворителя, окружающих её и непосредственно взаимодействующих с ней (сольватная оболочка) [1, 4].

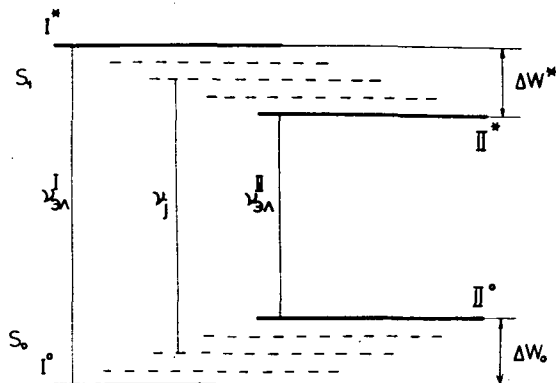


Рис. 1. Схема уровней элементарной ячейки (ЭЯ) полярного раствора

Из-за тепловых движений молекул (при $T > 0$), ЭЯ раствора обладают различной полной энергией и следовательно имеют отличающиеся по энергии системы электронно-колебательных уровней. Для дипольных молекул в полярных растворах наиболее сильное смещение электронно-колебательных уровней связано с энергией ориентационного взаимодействия молекул в ячейках раствора. Вследствие этого, электронно-колебательные уровни красителей в полярном растворе являются ориентационно-уширенными.

Как видно из приведённой на рис. 1 схемы ЭЯ, каждое элементарное состояние является ориентационно-уширенным. Величины ΔW_0 и ΔW^* определяют ориентационное уширение в основном и возбуждённом состояниях и являются важными характеристиками полярного раствора. Электронные переходы красителя сопровождаются изменениями ориентационной и колебательной энергией ЭЯ и поэтому связанные с ними спектры следует рассматривать как электронно-колебательно-ориентационные.

В спектрах флуоресценции красителей при наличии ориентационного уширения наблюдаются интересные специфические закономерности [1, 4, 8]. Они связаны с возможностью их перехода от состояния однородного ориентационного спектрального уширения при выполнении неравенства

$$f = \frac{\tau_p}{\tau^*} \ll 1 \quad (1)$$

к неоднородному в случае нарушения этого соотношения. В неравенстве (1) f -фактор ориентационной спектральной однородности, τ_p -время ориентационной релаксации молекул ЭЯ, τ^* -время жизни молекул красителя в возбуждённом электронном состоянии.

Неравенство (1) несложно нарушить, так как τ_p зависит от вязкости среды и может изменяться в широких пределах от 10^{-10} сек до бесконечности при охлаждении среды от 300 до 77 °К, или при переходе от жидких растворов к полимерным матрицам [2]. Неоднородное ориентационное уширение является причиной нарушения универсального соотношения Степанова и выражается в появлении зависимости спектра флуоресценции от частоты возбуждения [1, 4, 5, 8]. Нарушение однородности ориентационного уширения спектров наблюдается в эксперименте в спиртовых и глицериновых растворах красителей при низких температурах [1], в полимерных матрицах при $T=293$ °К [1], неравенство (1) не выполняется из-за увеличения времени ориентационной релаксации среды, и при тушении люминесценции посторонними примесями и в сильном поле световой волны, когда нарушение (1) связано с сокращением времени жизни возбуждённого состояния [8].

Во всех случаях неоднородное ориентационное спектральное уширение наблюдалось лишь в спектрах флуоресценции красителей [1—5, 8]. В данной работе впервые сообщается об экспериментальном обнаружении неоднородного спектрального уширения спектров α - и β -фосфоресценции органических красителей.

Материалы и методы

Из ряда диоксиксантеновых красителей использовались эритрозин В и зозин У. У этих веществ, при комнатной температуре обе замедленного излучения, можно исследовать и время затухания этих излучений, которое пор-

ядка мсек. Третьим исследованным веществом являлся акридиновый оранжевый, так как в этом случае при высокой температуре наблюдается только α компонент фосфоресценции и время жизни его триплетного состояния больше, чем у вышеупомянутых красителей.

В одном случае в качестве растворителя использовался поливиниловый спирт (ПВС), так как при комнатной температуре он является твёрдым и в этой стеклообразной среде тушащим действием кислорода можно пренебречь [6]. Другим растворителем служил глицерин, из которого кислород удалялся пропусканием пузырьков азота, чтобы избавиться от тушащего действия триплетного состояния [7].

Концентрации растворов красителей были $1 \cdot 10^{-3}$ г/г, когда использовался раствор ПВС, и $1 \cdot 10^{-4}$ моль/л в случае глицерина. При этих концентрациях красителей, судя по форме спектров поглощения и люминесценции, димеризация ещё не наступила.

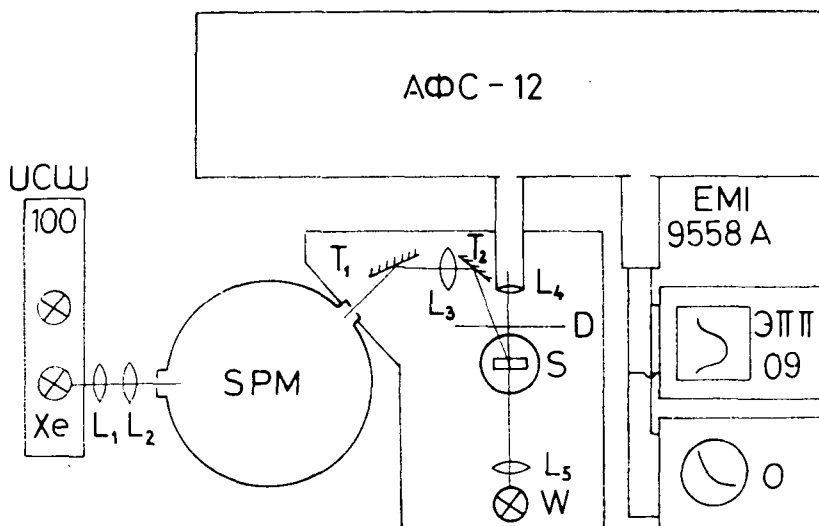


Рис. 2. Блок-схема экспериментальной установки

Спектры поглощения и люминесценции измерялись на одной и той же установке (рис. 2). Образцы были помещены в сосуд Дюара S , где низкая температура достигалась с помощью жидкого азота. Буквами L_1, \dots, L_5 , и T_1, T_2 обозначены линзы и зеркала. Для измерения спектров поглощения служила вольфрамовая лампа W . Возбуждающей установкой спектрофлуориметра использовалась ксеноновая лампа Xe , типа XBO 450 и призмный монохроматор $SPM-1$. Для разложения спектров поглощения, флуоресценции и фосфоресценции служил высокочувствительный дифракционный спектрофотометр ДФС-12. Сигнал фотоумножителя типа ЭПМ 9558 А регистрировался электронным потенциометром типа ЭПП-09. Спектры фосфоресценции были получены при помощи дискового фосфороскопа D .

При измерениях времени затухания источником света служила импульсная лампа типа ИСШ—100, которую можно было помещать вместо ксеноновой лампы. Кривые затухания были сняты на экране осциллоскопа *O*.

Экспериментальные результаты и их обсуждение

Все исследованные красители обладают интенсивными бесструктурными полосами α - и β -фосфоресценции, причём спектры эозина *Y* и эритрозина *B* в поливиниловом спирте даже при комнатной температуре ($T=298$ °К) содержат α и β компоненты (рис. 3). Эти свидетельства о малой величине S_1-T_1 энергетического интервала и высоком выходе фосфоресценции.

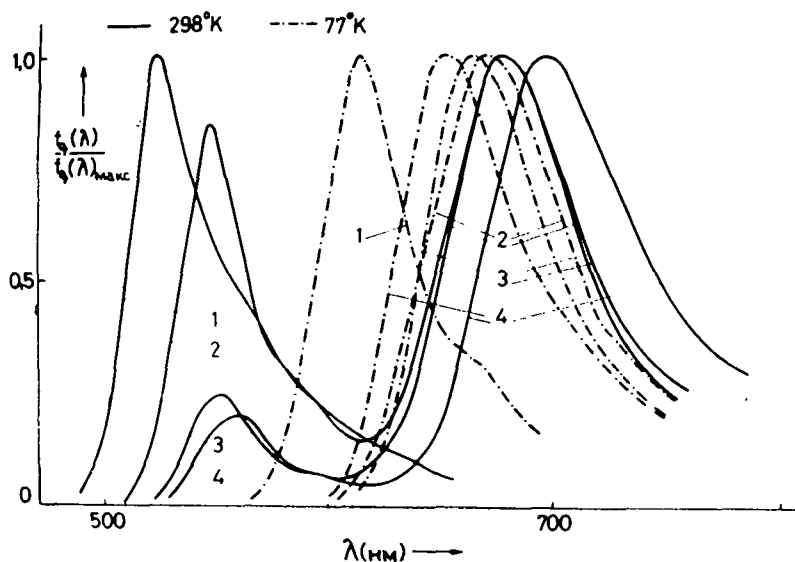


Рис. 3. Спектры фосфоресценции красителей ($\lambda_{\text{возб}}$ лежит в стоксовой области спектра поглощения) при комнатной (сплошная линия) и при температуре 77 °К (пунктир); 1 — акридиновый оранжевый в ПВС, 2 — эозин *Y* в ПВС, 3 — эритрозин *B* в ПВС, 4 — эритрозин *B* в глицерине (без O_2)

При повышении T от 77 °К, спектры α и β компонентов расширялись и смещались в красную сторону (рис. 3). Например, для эритрозина *B* величина смещения максимума β фосфоресценции составляет 12 нм, а полуширина растёт на 10 нм от 60 нм до 70 нм. Характерно отметить, что при $T=298$ °К в обескислороженном глицериновом растворе эритрозина *B* полоса α фосфоресценции не совпадает с полосой суммарного свечения, хотя в ПВС эти полосы идентичны (рис. 4).

Во всех исследованных красителях как при комнатной температуре, так и при $T=77$ °К наблюдались отчётливые зависимости положения α и β ком-

понтентов флюоресценции от длины волны возбуждающего света, при возбуждении в области длиноволнового края полосы поглощения (рис. 5). Во всех случаях, с увеличением длины волны возбуждения, спектры флюоресценции:

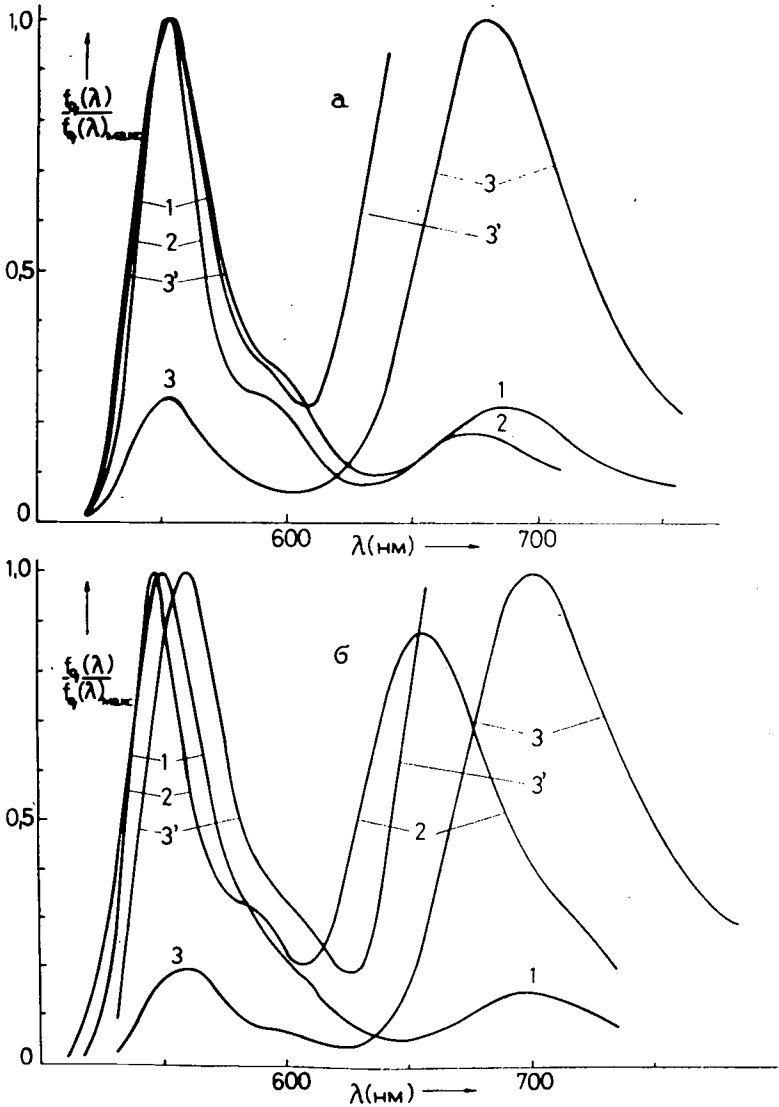


Рис. 4. Спектры суммарного и замедленного излучений эритрозина В: а — $1 \cdot 10^{-3}$ г/г эритрозин В в ПВХ, б — $1 \cdot 10^{-4}$ моль/литр эритрозина В в глицерине, 1 — спектр суммарного излучения при $T=298$ °К, $\lambda_B=500$ нм; 2 — спектр суммарного излучения при $T=77$ °К, $\lambda_B=500$ нм; 3 и 3' спектр флюоресценции при $T=298$ °К, $\lambda_B=500$ нм

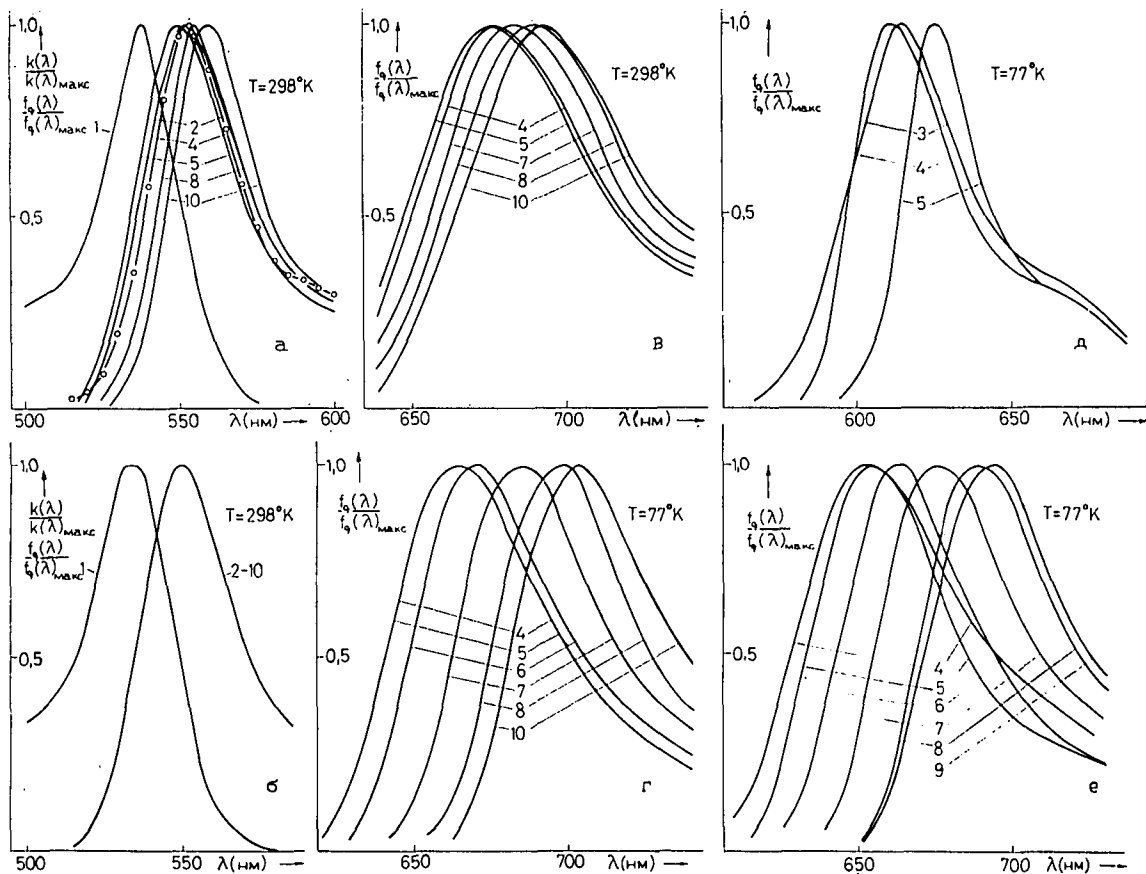


Рис. 5. Спектры поглощения, суммарного и замедленного свечений эритрозина В (а, б, в, г, е рисунки) и акридин оранжевого (д рисунок), $c = 1 \cdot 10^{-3}$ г/г в ПВС; 1 — спектр поглощения; 2 — спектр суммарного излучения, $\lambda_B = 500$ нм; 3—10 спектр α и β фосфоресценции λ_B : 3 — 480 нм, 4 — 500 нм, 5 — 520 нм, 6 — 530 нм, 7 — 540 нм, 8 — 550 нм, 9 — 555 нм, 10 — 560 нм; а, б, в — $T = 298$ °К, г, д, е — 77 °К

последовательно и пропорционально с ростом $\lambda_{\text{возб}}$ смещаются в красную сторону. Кроме ряда возможных толкований, из-за предыдущих явлений, по аналогии с батохромной флуоресценцией [1], полученный эффект можно назвать батохромной фосфоресценцией. При повышении температуры величина батохромного сдвига спектров фосфоресценции уменьшается. Соответственно этому на рис. 6. приведены зависимости максимумов β компонента эозина Y и эритрозина B от $\lambda_{\text{возб}}$ для различных температур. Из этого рисунка видно, что самые сильные зависимости $\lambda_{\text{макс}}^{\text{фосф}}$ от $\lambda_{\text{возб}}$ наблюдаются при $T=77^\circ\text{K}$. С ростом T они уменьшаются и после 323°K например у эозина Y полностью исчезают.

Полученные результаты, на наш взгляд, свидетельствуют о существовании неоднородного уширения триплетных уровней энергии молекул красителей в ПВС и глицерине. Это неоднородное уширение может быть связано как с различной ориентацией всех молекул красителей, так и с отличием локальных полей, в которых они находятся. Уширение триплетного состояния ΔW_T вследствие этих причин может быть довольно значительным (рис. 7). Поль-

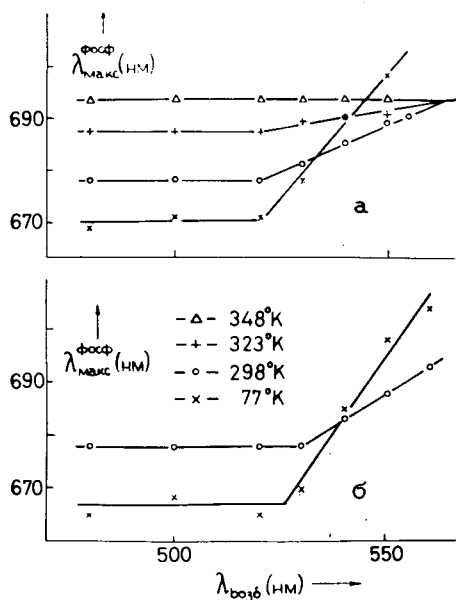


Рис. 6. Зависимости максимумов β фосфоресценции эозина Y (а) и эритрозина B (б) от $\lambda_{\text{возб}}$ при различных температурах; Δ — 348°K , $+$ — 323°K , \circ — 298°K , \times — 77°K .

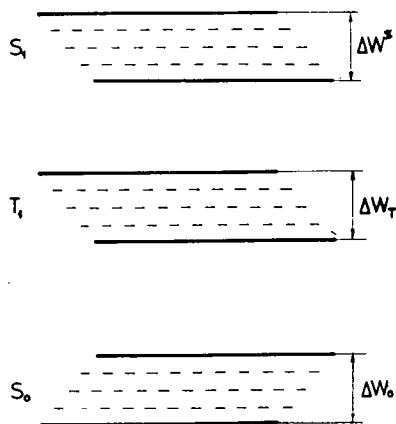


Рис. 7. Схема уровней молекул красителя в полимерном растворе

зуюсь ранее предложенным методом для определения величин ориентационного уширения электронных состояний мы определили, что для эритрозина B $\Delta W_T = 880 \text{ см}^{-1}$. С ростом температуры неоднородное уширение исчезает (рис. 6). Это можно объяснить усилением с ростом температуры обмена энергией молекул красителя с матрицей, вследствие чего однородный спектр каждой

молекулы красителя уширяется так, что его ширина становится сравнимой с величиной неоднородного уширения ΔW_T .

Для более точного выяснения полученного нами эффекта, необходимы ещё измерения истинных люминесцентных характеристик. Более подробный расчёт спектроскопических свойств модели красителя в полимерной матрице будет представлен в следующей нашей работе.

* * *

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INHOMOGENEOUS SPECTROSCOPIC BROADENING OF α AND β PHOSPHORESCENCE SPECTRA OF DYES

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A shift of phosphorescence spectra of organic dyes in solid solution has been found at room and low temperatures, as well as in frozen polar solvents at low temperatures, when increasing the excitation wavelength at the long wavelength side of the absorption band. We call this effect bathochromic phosphorescence. The bathochromic shift is decreasing with increasing temperature. These results prove the appearance of inhomogeneous broadening of the triplet energy-level of dye molecules in solid and polar solvents at room temperature, and even more at low temperatures.

DENSITOMETRIC EVALUATION OF INTERFERENCE PATTERNS DUE TO COHERENT LIGHT ON THE BASE OF CALIBRATION CURVES DETERMINED WITH INCOHERENT LIGHT

By

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The calibration of ORWO NP 27 (Wolfen) films was performed with spontaneous or induced luminescence light emission of an alcoholic rhodamine 6G solution excited by a flash lamp. The shape of the blackening curves measured with both methods proved to be the same within the error of measurement.

Introduction

The first order spatial coherence of a dye laser excited by a flash lamp was determined with the aid of an interferometer of Young type [1], by photographing the interference pattern and calculating the visibility from the densitometric data obtained.

One of the central problems of our measurements was the calibration of the ORWO NP 27 film used.

During our work the question emerged whether the blackening of the film depends on the coherence properties of the incident light, *i.e.* whether the blackening curve produced by incoherent light can be used for evaluating the interference pattern obtained with coherent laser light.

Some publications concerning this problem, both theoretical and experimental, are available in literature.

ROSENBLUM [2] summarized the state of knowledge concerning the functioning of photoemulsions and the photon statistics of laser and thermal light. On this basis, completed with some suppositions on the photoemulsions, he calculated the shape of the blackening curve. According to his calculations the steepness of the blackening curve should be less for thermal light than for laser light, if the time of exposition is less than or equal to the coherence time. This difference between the densities can be attributed to the fundamental difference between the photon statistics of laser and thermal light, respectively.

Prior to the publications of ROSENBLUM's paper, AUSSNEG and KREINER [3] published experimental results concerning the problem. Studying red-sensitive and orthochromatic plates, they found the sensibility for rubin-laser ($\lambda = 6943 \text{ \AA}$; half-width 10^{-7} sec) to be higher than in the case of excitation by thermal source.

POLOVTSEVA *et al.* [4] determined the blackening curves of some photographic plates for quasithermal and thermal light. They found differences both in the gradation and in the inertia of the plates.

As these theoretical and experimental investigations did not give a satisfactory and unequivocal solution of the problem, we found necessary to perform further measurements seeming important from our point of view, for determining the blackening curve both with laser light and with thermal light.

Methods of measurement

Our aim was to compare the shape of the non-linear part pertaining to low intensities of the blackening curves of the film used in our studies in the case of illumination with coherent and with incoherent light. (The part pertaining to higher blackening was not necessary, as such blackenings did not occur during our investigations.) As a light detector of sufficient sensitivity and accuracy, theoretically independent of coherence, was not available, the dependence on coherence of the inertia of the photographic plates could not be studied. This, however, does not imply a problem because in order to calculate the visibility it is sufficient to know the ratio of the intensities, and for determining this ratio it is not necessary to know the position of the blackening curve along the energy axis.

Homogeneous illumination of the grey filter of seven grades was obtained by the arrangement seen in Fig. 1a.

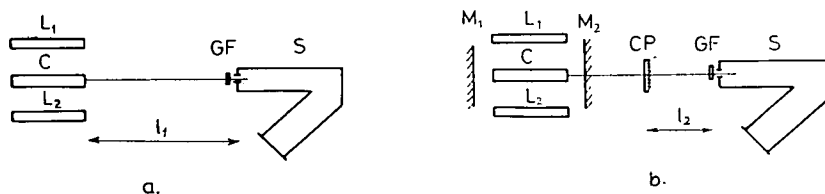


Fig. 1. L_1, L_2 : flash lamps; C : cuvette; M_1, M_2 : mirrors; CP : clouded plexiglass plate; GF : grey filter; S : spectrograph.

Incoherent light was produced by spontaneous luminescence of an active dye-stuff solution (rhodamine 6G in ethanol) in a cylindrical cuvette of 10 cm length and 0.8 cm inner diameter. Excitation of the dye-solution was produced by two xenon flash-lamps type IFP—800, L_1 and L_2 . The end-windows of the cuvette were not parallel within an accuracy of 1'; the intensity of the exciting light was low enough to secure the thermal character of the luminescence.

As the decay-time of the dye-solution was in the nsec range, the changes in intensity of the luminescence followed with good accuracy the changes in intensity of the flash pulses, which were of μsec -order. The axis of the cylindrical cuvette was coincident with the optical axis of the Steinheil spectrograph S of stigmatic image. In our measurements, the distance l_1 was 100 cm; according to our experience, the illumination of the grey filter was homogeneous in this case.

In order to perform the calibration with a laser, the arrangement described was modified by placing the cylindrical cuvette in an optical resonator consisting of

the mirrors M_1 and M_2 (Fig. 1b) and by raising the exciting energy above the threshold energy of the laser.

Homogeneous illumination and decreased intensity of the illuminating light was achieved by placing a clouded plexiglass plate CP at a distance $l_2=50$ cm from the grey filter. The grey filter was calibrated for 590 nm wavelength, corresponding to the wavelength of the laser light.

Results of measurements

We made photographs of the graded grey filter on ORWO NP 27 film with coherent and incoherent light using the arrangements described above. To secure the identity of the conditions of development, all photographs were developed at the same time in a developer FORTE 22, consisting of methol 5 g, sulphite (anhydrous) 100 g, water *ad* 1000 ml. The time of development was 12 minutes, the temperature of the developer 18.0 ± 0.2 °C; fixation lasted 15 minutes. With regard to the circumstance that our grey filter, despite its seven grades, decreased the light intensity only by 1.5 orders of magnitude, the wide range of light intensities necessary for obtaining different blackenings was produced by changing the pumping energy. The developed films were evaluated using a semiautomatic Zeiss densitometer.

The blackening curves were obtained by plotting the \bar{D} values of the blackening compared with that of the background, as a function of the transmissions of the grey filter. The shape of the blackening curves obtained with spontaneous and with induced emission, respectively, were compared by fitting both curves at the point where the error of measurements was comparatively the smallest (point A in Fig. 2).

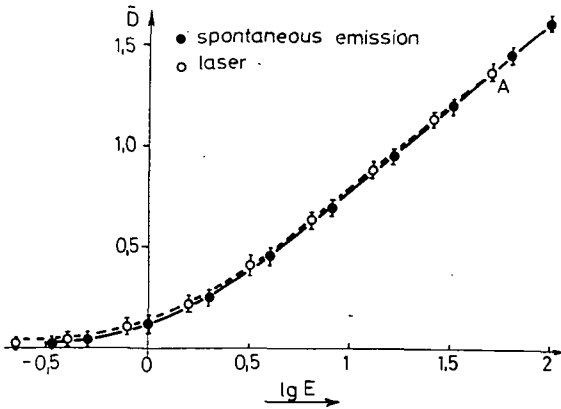


Fig. 2

It can be seen from the figure that the shape of both curves is identical within the errors of measurements.

As it is only necessary to know the ratios of the light intensities for determining the visibility and, irrespective of an additive constant, this ratio is unequivocally determined by the course of the blackening curves; therefore the results of our

experimental research mean that, in the case of the light sources investigated, the degree of visibility is independent of the circumstance whether the blackening curve of the film was determined whith spontaneous or induced luminescence.

* * *

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О ДЕНСИТОМЕТРИЧЕСКОЙ ОБРАБОТКЕ ИНТЕРФЕРЕНЦИОННОЙ КАРТИНЫ КОГЕРЕНТНОГО СВЕТА С ПОМОЩЬЮ ГРАДУИРОВОЧНОЙ КРИВОЙ, ПОЛУЧЕННОЙ НЕКОГЕРЕНТНЫМ СВЕТОМ

Л. Визе, Ф. Пинтер, Л. Гати, Й. Юнг

Определена градуировка пленки ORWO NP 27 (Wolfen) с помощью спонтанного и вынужденного излучения раствора родамина 6Ж в этиловом спирте при возбуждении импульсными лампами. Кривые почернения, снятые этими двумя методами, в пределах ошибки измерения, совпадают.

ИЗУЧЕНИЕ ОПТИЧЕСКИХ СВОЙСТВ СИСТЕМ КРАСИТЕЛЬ-ДЕТЕРГЕНТ ОТ ВРЕМЕНИ ОСВЕЩЕНИЯ

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Для *in vitro* моделирования фотосинтезирующих организмов весьма подходящими являются растворы детергентов, содержащие различные органические красители. Зависимость физических а также оптических свойств модельной системы от освещения и особенно от длительности времени освещения указывает меру возможности использования этих систем. В данной работе установлено, что стабильность исследованных систем по мере освещения значительно падает и интенсивность поглощения и люминесценции с ростом времени освещения сильно уменьшается. Очень интересным и отличающимся от остальных является поведение систем, содержащих метиленовый голубой.

Для *in vitro* моделирования фотосинтезирующих организмов оказываются очень подходящими системы краситель-детергент, которые по структуре сходны с структурой хлоропласта [1—3]. При использовании данной модельной системы необходимо знать её поведение и стабильность при различных внешних факторах. Поэтому применяемая модель в ходе исследований подвергается различным внешним воздействиям, так, например, нагревается, хранится длительное время и освещается.

Ранее были исследованы оптические свойства систем краситель-детергент от температуры и длительности хранения в темноте [4, 5]. В данной работе приведены результаты исследования по стабильности модельной системы краситель-детергент в зависимости от освещения.

Исследуемые системы и методика исследований

Состав применяемой модельной системы подробно описан в нашей ранней работе [4]. Исследовали спектры поглощения и люминесценции при различной длительности освещения [5] систем тионин-натрий-лаурилсульфат (Th + SLS), родамин 6Ж-натрий-лаурилсульфат (Rh 6Ж + SLS) и метиленовый голубой-натрий-лаурилсульфат (MB + SLS). Для освещения использовалась лампа накаливания типа TUNGSRAM—LARGIPHOT 125 W. Растворы находились от источника света примерно на 25 см, где интенсивность освещения была 1500 люксов. Растворы держались при постоянной температуре (70 °C), которая во время измерений обеспечивалась с помощью ултратермостата типа U—10 Höppler.

Спектры поглощения измерялись на спектрофотометре CF—4 DR Optica Milano, а спектры люминесценции на спектрофлуориметре ДФС—12.

Результаты измерений

1. Системы Th+SLS

В табл. I приведены основные результаты измерений спектров поглощения и люминесценции. Из данных табл. I видно, что по мере освещения интенсивность поглощения значительно падает, и 96 часовое освещение вызывает полное обесцвечивание при концентрации детергента ниже критической концентрации мицеллообразования (ККМ). При концентрациях выше ККМ происходит 50%-ое уменьшение поглощения после 96 часового освещения. Убывание поглощения красителя объясняется фотохимическим превращением тионина под влиянием освещения.

Таблица I

Значения интенсивности и положения максимумов спектров поглощения и люминесценции системы Th+SLS

$C_{SLS} \cdot 10^3$ (моль/л)	$k(\lambda)_{\text{МАКС}} (\text{CM}^{-1})$			$f_q(\lambda)_{\text{МАКС}} (\%)$		
	$\lambda_{\text{МАКС}} (\text{NM})$			$\lambda_{\text{МАКС}} (\text{NM})$		
	Длительность освещения (в часах)					
	0	24	96	0	24	96
0	0,596	0,057	0	100	40,7	0
	597,0	596,0	—	619,0	621,5	—
2	0,208	0,158	0,044	53,9	32,3	28,3
	602,0	600,0	600,0	622,0	622,0	622,0
2,5	0,291	0,200	0,042	58,9	37,0	5,1
	600,0	600,0	600,0	621,5	621,0	622,0
3	0,415	0,288	0,040	62,6	36,0	0
	601,0	600,0	600,0	621,5	620,5	—
3,5	0,527	0,347	0,119	71,2	48,6	31,5
	601,0	600,0	600,0	620,5	620,5	621,5
4	0,583	0,366	0,105	81,8	57,2	38,3
	601,0	600,5	603,0	620,0	620,0	621,0
6	0,622	0,520	0,204	134,9	122,9	80,8
	601,0	600,5	601,0	620,0	621,0	621,5
8	0,685	0,547	0,337	143,6	134,1	103,7
	600,5	600,5	601,5	619,5	619,5	621,0

Из табл. I видно также, что более сильно выражена степень уменьшения интенсивности люминесценции и самое меньшее изменение достигает 30%-ов. Из данных спектров поглощения можно было бы ожидать, что при меньших концентрациях детергента тионин потеряет способность излучения. Видно также, что после 96 часового освещения водный раствор тионина и раствор содержащий $3 \cdot 10^{-3}$ моль/л детергента совсем не показывают люминесценцию.

2. Системы Rh 6Ж + SLS

По данным измерений спектров поглощения и люминесценции систем Rh 6Ж + SLS (табл. II) под влиянием освещения видно, что после 24 часового освещения интенсивность поглощения незначительно растет, потом под влия-

Таблица II
Значения интенсивности и положения максимумов спектров поглощения и люминесценции системы Rh 6Ж + SLS

$C_{SLS} \cdot 10^3$ (моль/л)	$k(\lambda)_{\text{МАКС}} (\text{CM}^{-1})$			$f_q(\lambda)_{\text{МАКС}} (\%)$		
	$\lambda_{\text{МАКС}} (\text{NM})$			$\lambda_{\text{МАКС}} (\text{NM})$		
	Длительность освещения (в часах)					
	0	24	96	0	24	96
0	0,819	0,837	0,776	100	119,5	142,6
	527,0	525,5	524,0	553,5	549,5	544,5
2	0,767	0,749	0,741	16,3	8,8	12,0
	534,5	533,0	527,0	555,0	553,0	551,0
2,5	0,783	0,785	0,721	19,2	14,9	22,7
	535,0	533,0	529,0	557,5	555,5	551,0
3	0,794	0,810	0,726	35,9	23,4	30,4
	534,0	533,0	529,0	559,5	557,5	557,0
3,5	0,822	0,819	0,750	45,9	32,2	38,5
	534,0	533,0	529,5	559,5	558,5	557,0
4	0,826	0,839	0,730	61,3	45,8	49,9
	534,0	532,5	526,5	558,0	558,5	556,0
6	0,847	0,879	0,825	71,9	71,9	73,4
	534,0	532,0	530,5	557,0	557,5	556,5
8	0,844	0,883	0,855	74,4	72,4	78,7
	534,0	532,0	530,5	556,0	556,5	555,5

МВ

○ 0 моля/л SLS Δ 2·10⁻³ моля/л SLS × 2,5·10⁻³ моля/л SLS □ 3,5·10⁻³ моля/л SLS + 8·10⁻³ моля/л SLS

t = 70°C

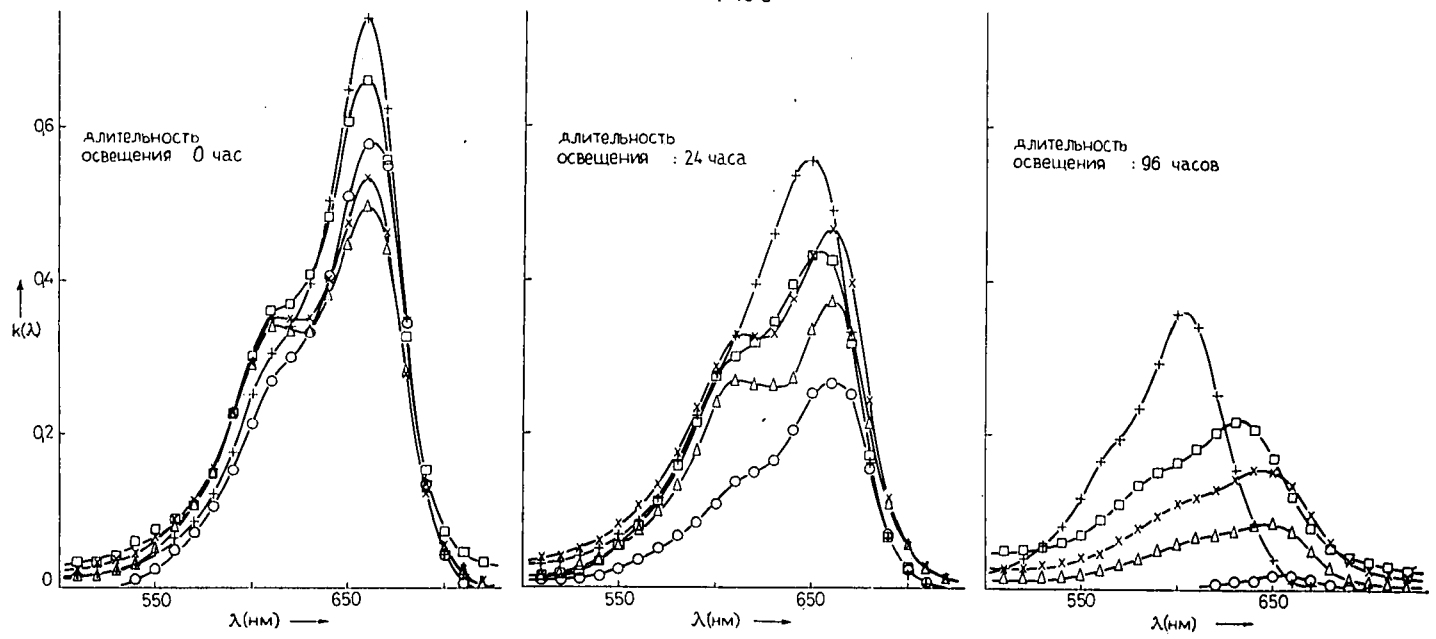


Рис. 1

нием более длительного освещения — уменьшается. Положение максимумов спектров поглощения и люминесценции по мере освещения сдвигаются на 3—9 нм в сторону коротких длин волн.

3. Системы MB+SLS

На рис. 1 показаны спектры поглощения этих систем в зависимости от времени освещения. Видно, что водный раствор MB под влиянием длительного освещения полностью обесцвечивается. Значительно уменьшается интенсивность поглощения растворов, содержащих детергент, однако степень убывания интенсивности поглощения с ростом концентрации детергента SLS уменьшается.

На рис. 1 хорошо видно, что положение максимума α -полосы сильно сдвинуто в сторону коротких длин волн. Значение смещения этой полосы под влиянием освещения с ростом концентрации детергента увеличивается. Зависимость значения сдвига от концентрации детергента объясняется довольно сильным взаимодействием метиленового голубого и детергента.

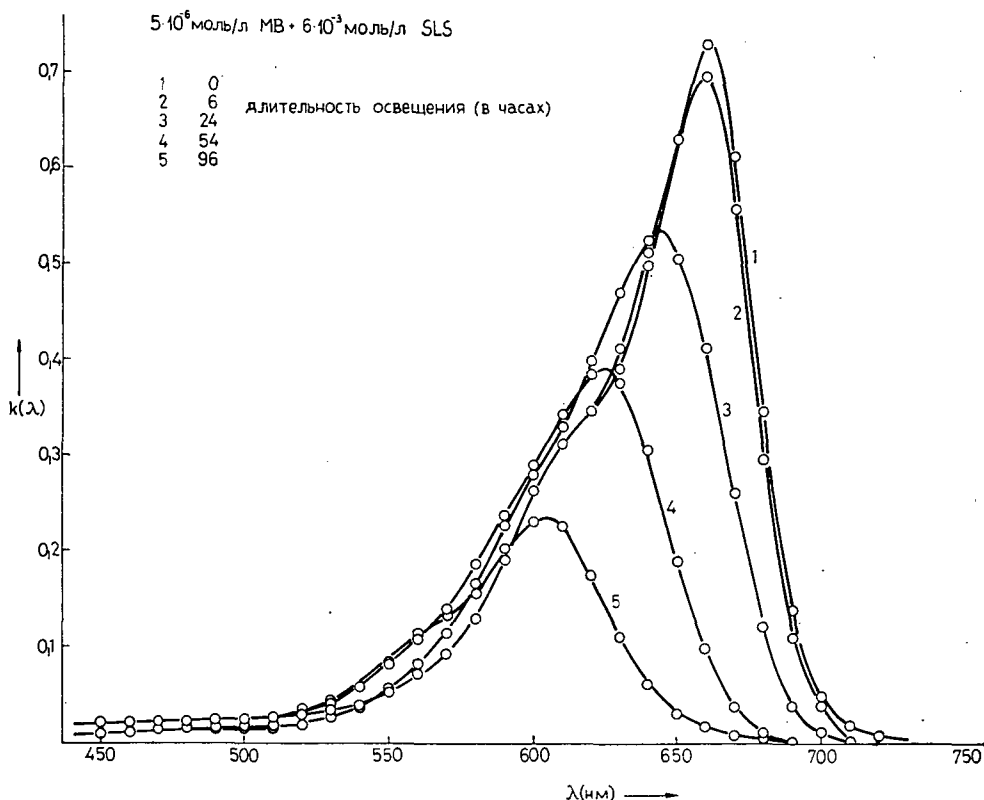


Рис. 2

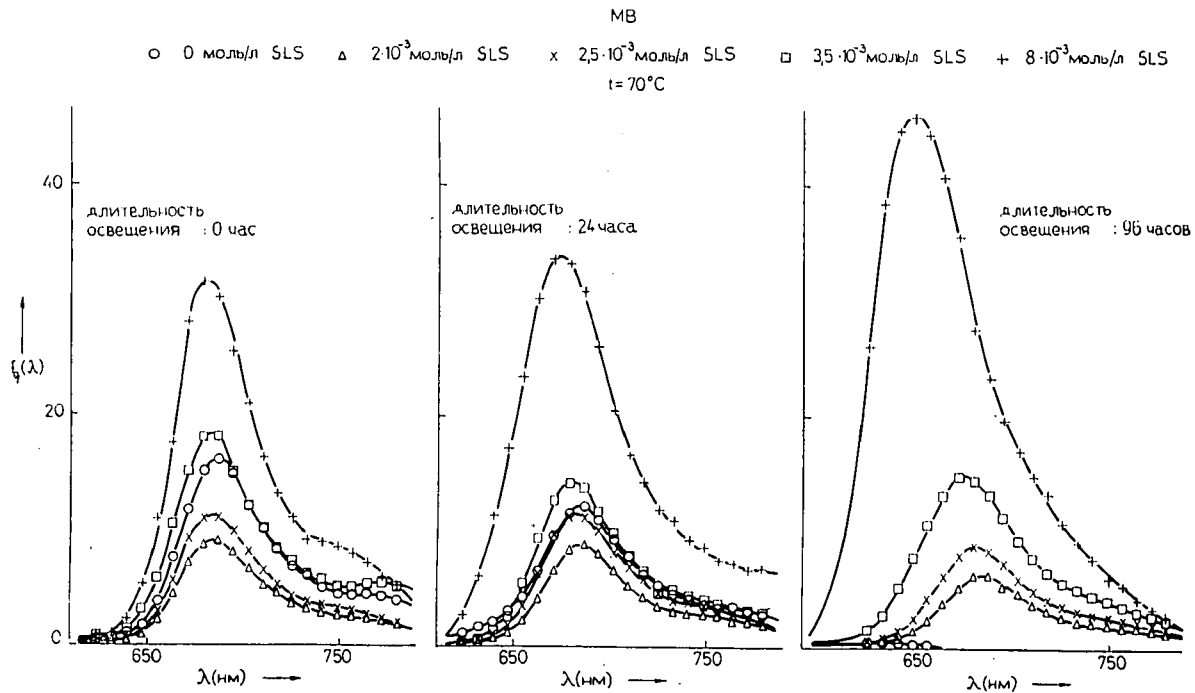


Рис. 3

Рис. 2 показывает положение и интенсивность α -полосы растворов MB, содержащих $6 \cdot 10^{-3}$ моль/л SLS в зависимости от времени освещения. Хорошо видно, что под влиянием освещения происходит примерно 60%-ое уменьшение и спектры на 55 нм сдвинуты в сторону коротких длин волн.

Изменения спектров люминесценции под влиянием освещения для систем MB+SLS показаны на рис. 3. Видно, что при концентрациях детергента ниже ККМ происходит значительное уменьшение интенсивности люминесценции. В случае растворов содержащих $8 \cdot 10^{-3}$ моль/л (и $6 \cdot 10^{-3}$ моль/л) SLS интенсивность люминесценции под влиянием освещения возрастает. Видно также, что при увеличении концентрации детергента положения максимумов люминесценции смещены в сторону более коротких волн.

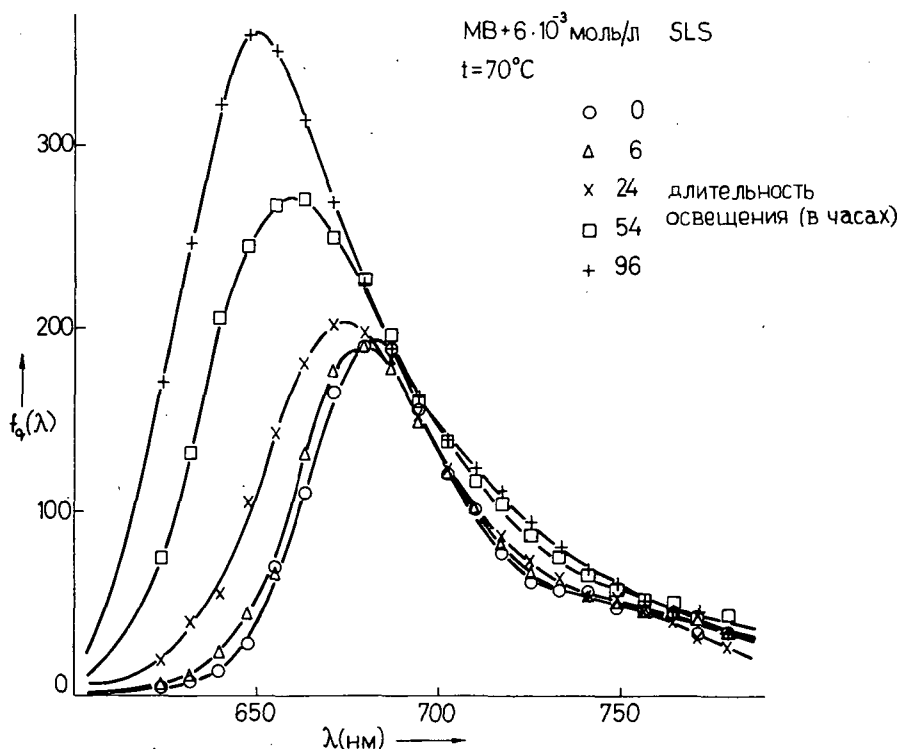


Рис. 4

Изменения люминесценции растворов MB содержащих $6 \cdot 10^{-3}$ моль/л SLS под влиянием освещения показаны на рис. 4. Хорошо видно, что с увеличением длительности освещения возрастает способность к излучению и увеличивается сдвиг максимумов люминесценции в сторону коротких длин волн. После 96 часового освещения происходит примерно 100%-ое возрастание интенсивности люминесценции и 34 нм-ый сдвиг максимума.

Заключение: Под влиянием освещения стабильность систем краситель-детергент значительно уменьшается. Сравнительно высокая стабильность под действием освещения наблюдается у системы родамина 6Ж. После длительного освещения растворы тионина и метиленового голубого при концентрациях детергента ниже ККМ обесцвечиваются и практически не показывают люминесценции. Для систем МВ + SLS под влиянием освещения характерно смещение положения максимумов поглощения и люминесценции в сторону коротких длин волн. Причиной нестабильности исследованных систем, вероятно, является фотохимическое превращение красителей под влиянием длительного освещения.

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DEPENDENCE ON ILLUMINATION OF OPTICAL PROPERTIES OF DYE-DETERGENT SYSTEMS

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Detergent systems containing organic dyes are very useful as models of photosynthesizing organisms. The dependence of the physical (optical) properties of the model system is a measure of the applicability of the system. It could be stated that the stability of the systems studied decreases by illumination, the values of their absorption and luminescence maxima are strongly diminished by increasing the period of illumination. The behaviour of the system containing methylene blue is especially interesting and shows differences with respect to the other systems studied.

TIME STABILITY OF DETERGENT (MICELLE) SYSTEMS CONTAINING ORGANIC DYES

By

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Micelle systems containing organic dyes are often used as *in vitro* models to study physical processes of photosynthesis. Time stability is an important characteristic of the applicability of this model. In this paper the dependence of optical properties of dye-detergent systems on the duration of keeping the system in dark is investigated. It can be stated on the basis of our measurements that the dye systems studied, kept in the dark for a longer period, especially below critical micelle concentration (c.m.c.) and at higher temperatures, fade and seem to become "exhausted", *i.e.* their absorption maxima and fluorescence intensities decrease.

Introduction

Micelle systems containing organic dyes are often used as *in vitro* models of chloroplasts, as they approximate well the structure of chloroplasts well [1—3], which play an important role in photosynthesis. The model system being exposed to various external influences during the investigation, its stability against these influences is at the same time a measure of its applicability.

The temperature dependence of the stability of micelle systems has been investigated earlier [4]. The present paper describes the influence on stability exerted by holding the system in dark for a longer period.

Composition of the systems. Experimental methods

The composition of the model used was the same as described earlier [4]. Absorption and emission properties of three dye-detergent systems, namely thionin + sodium laurylsulphate (Th + SLS); Rhodamine 6G + sodium laurylsulphate (Rh 6G + SLS); methylene blue + sodium laurylsulphate (MB + SLS) were studied at three different temperatures (30 °C, 50 °C, 70 °C), holding the systems in the dark. Absorption and emission spectra were measured at the time of preparation of the solutions as well as 6, 24, 54, and 96 hours later. This choice of the times of measurement was determined partly by the circumstance that we wished to follow the changes in the spectral characteristics after different times spent in the dark, and partly by practical (technical) conditions of the measurements.

Darkness and constant temperature were secured by placing the systems examined in a light-tight thermostat.

A recording spectrophotometer Optica Milano Type CF 4 DR was applied for absorption measurements, a recording spectrophotometer Type DFS—12 for measuring the emission. During the measurements the temperature was held constant by cuvette holders the temperature of which was regulated by a Höppler thermostat Type U—10.

Results and discussion

1. Absorption measurements

The degree of stability of the micelle system clearly depends on the changes in the absorption properties of the system produced by holding it in the dark at constant temperature for different times.

The dependence of the micelle system on these parameters is presented in Table I for the α absorption band of thionin. It can be seen that above c.m.c. the sys-

Table I
Values and location of $k(\lambda)_{\max}$ of the α absorption band of Th + SLS systems

t (°C)	T (hours)		$C_{SLS} \cdot 10^3$ (M/l)					
			0	2	3	3.5	4	8
30	0	$k(\lambda)_{\max}$ (cm ⁻¹)	0.610	0.126	0.324	0.594	0.670	0.706
		λ_{\max} (nm)	600.0	601.0	603.0	603.5	602.0	603.5
	24	$k(\lambda)_{\max}$ (cm ⁻¹)	0.592	0.104	0.240	0.407	0.648	0.731
		λ_{\max} (nm)	600.0	604.0	602.0	603.0	603.0	603.0
	96	$k(\lambda)_{\max}$ (cm ⁻¹)	0.611	0.101	0.214	0.329	0.616	0.706
		λ_{\max} (nm)	600.5	600.0	603.0	603.0	603.5	603.5
50	0	$k(\lambda)_{\max}$ (cm ⁻¹)	0.564	0.155	0.348	0.581	0.645	0.695
		λ_{\max} (nm)	598.0	602.5	601.0	601.5	601.0	601.0
	24	$k(\lambda)_{\max}$ (cm ⁻¹)	0.559	0.123	0.281	0.421	0.625	0.695
		λ_{\max} (nm)	597.5	600.0	601.0	600.5	601.0	601.5
	96	$k(\lambda)_{\max}$ (cm ⁻¹)	0.537	0.125	0.260	0.366	0.614	0.692
		λ_{\max} (nm)	597.0	599.0	600.5	601.0	601.0	601.0
70	0	$k(\lambda)_{\max}$ (cm ⁻¹)	0.596	0.208	0.415	0.527	0.583	0.685
		λ_{\max} (nm)	597.0	602.0	601.0	601.0	601.5	600.5
	24	$k(\lambda)_{\max}$ (cm ⁻¹)	0.575	0.197	0.330	0.434	0.523	0.673
		λ_{\max} (nm)	595.5	598.0	598.0	600.0	600.5	600.5
	96	$k(\lambda)_{\max}$ (cm ⁻¹)	0.492	0.178	0.283	0.373	0.489	0.636
		λ_{\max} (nm)	595.5	598.0	600.0	601.0	600.5	600.5

tem Th+SLS is very stable, even after a longer period (96 hours) in the dark. At low detergent concentrations, however, the maxima of the α -band significantly decrease with increasing duration of the dark period, even at lower temperatures. At 70 °C, even systems found to be stable above c.m.c. do not show such stability; at this temperature an important decrease in absorption is found even at higher detergent concentrations. It can also be seen that at low detergent concentrations, especially at 50 °C and 70 °C, the maximum of the α -band is slightly shifted towards shorter wavelengths; above c.m.c. this shift cannot be observed.

Table II

Values and location of $k(\lambda)_{\max}$ of the α absorption band of Rh 6G+SLS systems

t (C°)	T (hours)		$C_{SLS} \cdot 10^3 (M/l)$					
			0	2	3	3,5	4	8
30	0	$k(\lambda)_{\max}$ (cm ⁻¹)	0.789	0.764	0.850	0.880	0.895	0.940
		λ_{\max} (nm)	528.0	536.5	535.5	535.5	535.5	535.0
	24	$k(\lambda)_{\max}$ (cm ⁻¹)	0.916	0.735	0.828	0.875	0.885	0.920
		λ_{\max} (nm)	527.5	535.5	535.0	535.0	535.0	535.0
	96	$k(\lambda)_{\max}$ (cm ⁻¹)	0.843	0.738	0.836	0.862	0.886	0.892
		λ_{\max} (nm)	526.0	534.0	535.0	535.0	535.0	535.0
50	0	$k(\lambda)_{\max}$ (cm ⁻¹)	0.840	0.800	0.845	0.851	0.849	0.850
		λ_{\max} (nm)	526.0	534.0	534.0	534.0	534.0	534.0
	24	$k(\lambda)_{\max}$ (cm ⁻¹)	0.811	0.776	0.835	0.854	0.860	0.890
		λ_{\max} (nm)	526.5	535.0	534.5	534.0	534.0	533.5
	96	$k(\lambda)_{\max}$ (cm ⁻¹)	0.855	0.756	0.830	0.850	0.856	0.897
		λ_{\max} (nm)	526.5	534.5	535.0	535.0	534.5	533.5
70	0	$k(\lambda)_{\max}$ (cm ⁻¹)	0.819	0.767	0.794	0.822	0.826	0.844
		λ_{\max} (nm)	527.0	534.5	534.0	534.0	534.0	534.0
	24	$k(\lambda)_{\max}$ (cm ⁻¹)	0.806	0.735	0.765	0.810	0.803	0.860
		λ_{\max} (nm)	526.5	534.5	534.5	534.5	534.5	534.0
	96	$k(\lambda)_{\max}$ (cm ⁻¹)	0.815	0.721	0.797	0.819	0.812	0.867
		λ_{\max} (nm)	526.0	534.0	533.0	533.5	533.5	532.0

Table II shows the changes in the absorption maxima of the system Rh 6G+SLS, caused by holding the system in the dark. It can be seen that the influence of the dark period on the absorption of the system is less important, the changes remain generally below 5%; at higher temperatures, the changes are somewhat more significant.

Concerning the changes in absorption of MB+SLS systems due to longer periods in the dark, the same can be said as for Th+SLS systems.

2. Emission measurements

The changes in emission caused by longer dark periods are presented in Table III. It can be seen that, up to $4 \cdot 10^{-3}$ M/l SLS concentration, the luminescence intensity at 30 °C decreases due to the dark period, while at higher concentrations it remains constant. At 50 °C and 70 °C a significant decrease in intensity is observed even at

Table III

Values and location of emission maxima ($f_q(\lambda)_{\max}$) of Th+SLS systems

t (°C)	T (hours)		$C_{\text{SLS}} \cdot 10^3$ (M/l)					
			0	2	3	3.5	4	8
30	0	$f_q(\lambda)_{\max}$ (%)	100.0	17.3	42.3	76.4	146.4	179.0
		λ_{\max} (nm)	619.0	618.5	621.5	621.0	621.0	620.5
	24	$f_q(\lambda)_{\max}$ (%)	104.0	11.3	29.9	50.5	137.4	184.3
		λ_{\max} (nm)	620.0	621.5	620.0	622.0	621.0	620.5
	96	$f_q(\lambda)_{\max}$ (%)	76.2	9.6	24.8	40.5	133.3	179.8
		λ_{\max} (nm)	619.0	621.5	622.5	621.0	620.	620.0
50	0	$f_q(\lambda)_{\max}$ (%)	100.0	32.0	42.6	73.2	121.3	166.7
		λ_{\max} (nm)	620.0	621.5	621.0	620.5	619.5	620.0
	24	$f_q(\lambda)_{\max}$ (%)	98.5	26.3	43.2	59.3	103.5	151.7
		λ_{\max} (nm)	620.0	621.5	621.0	620.5	620.0	620.0
	96	$f_q(\lambda)_{\max}$ (%)	90.9	12.6	32.9	46.7	69.4	104.7
		λ_{\max} (nm)	620.0	621.5	622.0	621.5	620.5	620.5
70	0	λ_{\max} (nm)	100.0	53.9	62.6	71.2	81.8	143.6
		$f_q(\lambda)_{\max}$ (%)	619.0	622.0	621.5	620.5	620.0	619.5
	24	λ_{\max} (nm)	93.2	49.4	55.0	64.5	69.8	137.6
		$f_q(\lambda)_{\max}$ (%)	619.5	621.5	621.5	621.0	620.0	619.5
	96	$f_q(\lambda)_{\max}$ (%)	95.6	41.4	49.1	57.0	71.8	133.4
		λ_{\max} (nm)	620.0	622.0	621.0	621.5	620.5	620.0

higher detergent concentrations. This shows that the systems seem to become "exhausted", especially at higher temperatures.

Table IV shows the changes caused by the dark period in fluorescence intensity of the Rh 6G+SLS systems. It can be seen that at detergent concentrations below c.m.c. the values of $f_q(\lambda)_{\max}$ significantly decrease at all three temperatures; above c.m.c. a less significant increase is found.

Concerning the changes in fluorescence intensity due to the dark period of systems containing MB, the same can be said as in the case of thionin.

Table IV

 Values and location of emission maxima ($f_q(\lambda)_{\max}$) of Rh 6G+SLS systems

t (°C)	T (hours)		$C_{\text{SLS}} \cdot 10^3$ (M/l)					
			1	2	3	3,5	4	8
30	0	$f_q(\lambda)_{\max}$ (%)	100.0	21.2	71.5	82.1	84.8	81.9
		λ_{\max} (nm)	552.0	558.5	559.0	559.5	559.0	557.0
	24	$f_q(\lambda)_{\max}$ (%)	101.5	7.5	48.0	79.2	85.4	73.6
		λ_{\max} (nm)	553.0	558.5	561.0	561.0	560.0	558.5
	96	$f_q(\lambda)_{\max}$ (%)	124.6	6.9	43.2	87.1	101.9	93.8
		λ_{\max} (nm)	553.0	557.5	560.5	559.5	559.0	557.5
50	0	$f_q(\lambda)_{\max}$ (%)	100.0	29.3	56.6	66.5	75.4	74.3
		λ_{\max} (nm)	552.5	561.0	560.5	560.0	559.0	558.0
	24	$f_q(\lambda)_{\max}$ (%)	104.8	24.7	53.8	71.8	80.0	64.6
		λ_{\max} (nm)	553.0	560.0	560.5	560.0	558.5	557.0
	96	$f_q(\lambda)_{\max}$ (%)	104.4	13.1	44.4	58.5	71.0	71.4
		λ_{\max} (nm)	553.0	560.5	559.5	559.5	558.5	558.0
70	0	$f_q(\lambda)_{\max}$ (%)	100.0	16.3	35.9	45.9	61.3	74.4
		λ_{\max} (nm)	553.5	555.0	559.5	559.5	558.0	557.0
	24	$f_q(\lambda)_{\max}$ (%)	111.7	16.2	35.7	56.3	61.9	95.2
		λ_{\max} (nm)	554.0	557.5	561.0	560.0	560.0	557.5
	96	$f_q(\lambda)_{\max}$ (%)	103.2	11.5	39.8	49.2	56.7	83.8
		λ_{\max} (nm)	554.0	558.5	560.0	560.0	559.5	556.0

Summarizing the results, it can be stated that below c.m.c. the systems studied significantly fade by being kept in the dark. Good stability above c.m.c. is found in Rh 6G+SLS systems. In Th+SLS and MB+SLS systems above c.m.c., slight decreases in absorptions intensity can be observed at higher temperatures. The systems seem to become "exhausted" by the dark period, their ability of emission decreases.

Below c.m.c., *i.e.* before the formation of an ordered structure, the three dye-detergent systems studied are instable, while above c.m.c. they are more stable at all temperatures.

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ЗАВИСИМОСТЬ СТАБИЛЬНОСТИ СИСТЕМ КРАСИТЕЛЬ-ДЕТЕРГЕНТ ОТ ВРЕМЕНИ

Я. Хевеши и М. Молнар

В работе исследовалась зависимость оптических свойств систем краситель-детергент от длительности хранения в темноте. Экспериментальные результаты показывают, что исследованные системы при постоянных температурах после длительного времени хранения в темноте, главным образом при концентрациях ниже критической концентрации мицеллообразования (ККМ), и при повышенных температурах выцветают, значения максимумов поглощения и интенсивности флуоресценции уменьшаются.

PHOTOCHEMICAL METHODS IN CHEMICAL ANALYSIS

1. Literature review

By

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Recent development in the field of analytical photochemistry is reviewed and systematized. The essential characteristics of methods such as photometry, photocatalytic method, photogravimetry, end point detection by photochemical indicator reaction, methods based on photodissociation, etc. are elucidated by typical examples.

To date photochemical reactions have found little application in chemical analysis. Until twenty years ago, to the best of our knowledge there was only a single method based on a photochemical reaction [1]. In contrast, a number of references drawing attention to the negative role of photochemical reactions could be found: the photosensitivity of many substances (their fading or change in colour) leads to a positive or negative error in their determination, and to poor reproducibility of the measurements.

Research during the past twenty years has produced an increasing number of data proving that photochemical reactions can be more than simply a source of error; they can also provide new possibilities for chemical analysis. This is not surprising if it is remembered that photochemical reactions have a number of favourable features not possessed by ordinary chemical reactions. For example, the nature of the reagent in photochemical reactions, the photon, can readily be changed by variation of the wavelength of the light used for irradiation, and by this means the selectivity of a reaction can be increased. The rate of a photochemical reaction can be influenced by regulating the intensity of the photon current. Another advantage is that addition of the reagent can be completed by stopping the irradiation; in this way one may avoid the reagent excess which arises in traditional analysis and which may bring about further transformation of the reaction product. A further substantial advantage results from the fact that photochemical reactions are in general fairly sensitive and accordingly permit the determination of microcomponents, too.

Since these advantages of photochemical reactions have been increasingly utilized in recent years, we considered it timely to compile a brief review of the results attained in this developing field of analysis, in spite of the fact that two monographs were published not too long ago [2, 3]. One of these was not written from a purely analytical aspect, and accordingly it does not present all the principles of measurement. The other monograph is definitely analytical in outlook, and gives a faithful picture

of the relevant results up to roughly the end of 1972. This monograph has the added value that it also deals with those photochemical reactions which the authors consider might possibly be used as basis for future analytical procedures. Even though these monographs have appeared, we consider publication of our review to be justified, for our conceptions differ from those of the authors mentioned as regards the analytical evaluation and the classification of the photochemical reactions employed.

From the aspect of chemical analysis the procedures based on photochemical reactions can be classified in the following way.

1. Photonometry, photochemical production of the reagent

The essence of this method is that the reagent is produced in a solution of the substance to be determined, by irradiation of a suitable auxiliary reagent with light of constant intensity; the reagent produced then reacts instantaneously with the substance to be measured. According to the Bunsen—Roscoe law, the amount of substance formed in a photochemical reaction is proportional to the product of the light intensity and the duration of the irradiation, and thus the amount of the substance to be determined can be obtained by measuring the duration of the irradiation. This can be done in several ways. One possibility is to observe the appearance of the product of the photochemical reaction. This can be followed directly if this substance is coloured, while if it is not, or not sufficiently, coloured, then it is converted to a coloured substance with a suitable reagent and observed in this way. If the substance to be determined is coloured, the end-point of the photochemical titration can be established by measuring the decrease in its absorption. Naturally, not only optical, but other end-point indicating methods, too, may be possible. It is clear that this method is analogous to the indirect, or reagent-developing coulometric method. This principle was employed by YOKOYAMA and IKEDA [4] in the following way for the determination of thallium(III). A uranium(VI) salt and lactic acid were added to the thallium(III) solution to be analyzed, the solution was irradiated with light of constant intensity, and the appearance of the uranium(IV) band was observed spectrophotometrically. When irradiated, uranium(VI) is reduced by lactic acid to uranium(IV), which in turn reduces thallium(III). The end-point of the reaction is indicated by the appearance of a uranium(IV) excess.

BRICKER and SCHONBERG [5] determined chromate and vanadate by irradiating these compounds in the presence of iron(III) and oxalic acid. The iron(II) formed in the photolysis of iron(III)+oxalate reduces chromate to chromium(III), and vanadate to vanadium(IV). The increases in the amounts of chromium(III) and vanadium(IV) were followed spectrophotometrically.

SMITH and FITZGERALD [6] used the tungsten(V) formed on the photolysis of tungsten(VI) and glucose for the titration of vanadate, chromate and ferricyanide. The end of the titration was indicated by the appearance of the blue colour of the tungsten(V). The above determinations were performed with the aid of calibration curves (amount of substance *vs.* time).

2. Photocatalytic procedures

The procedures listed under this heading can be carried out in two ways. In one possibility a reaction which is slow under normal conditions is made to take place at a rate suitable for analytical measurements by adding a photocatalyst (photon-carrier, sensitizer) to the solution and irradiating the system.

With appropriate selection of the experimental conditions, a possibility arises for the determination of the amount of the photocatalyst. Irradiation is performed with light of constant intensity for a definite period, and the extent of the transformation of the substance used for the measurement is determined; this is proportional to the amount of the photocatalyst.

With the aim of the determination of chromium(VI), ALMÁSSY *et al.* [7, 8] accelerated the slow reaction between chromate and methyl orange by irradiating with ultraviolet light. This was achieved by adding an iron(III)-oxalate photon-carrier system to the solution under examination. In this case the chromate can be titrated directly with a methyl orange solution. In addition to the direct determination of chromium(VI), this procedure was also applied for the indirect measurement of the iron(II) ion and hydrogen peroxide. In the latter two cases chromate was added in excess, and the excess was titrated with methyl orange solution.

SIERRA *et al.* [9, 10] employed photocatalysis to accelerate the reactions between peroxydisulphate and iron(II) or mercury(I). The peroxydisulphate was titrated with iron(II) solution during irradiation, in the presence of erythrosin-B as photon-carrier, together with silver and iodide ions. Erythrosin-B dye was employed as photocatalyst on titration with mercury(I) solution. A 160 watt tungsten lamp was used as light source.

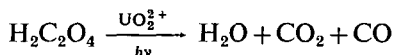
The other possibility of photocatalysis was discovered by KHARLAMOV, MANTSEVICH and DODIN [11], who made use of the iron(III)-catalyzed photooxidation of organic dyes for the determination of iron(III). It was stated that when the organic matter—metal ion system is subjected to light, electron-transfer occurs from the organic substance to the metal ion acceptor. If the solution also contains oxygen, then under suitably selected conditions the oxygen assumes the role of the electron-acceptor, while the metal ion becomes a catalyst. Under favourable concentration conditions the relation between the extent of decolouration of the dye and the metal ion concentration is linear. The method was employed to determine the iron contents of nickel and cobalt.

For the determination of micro amounts of uranium, NEMODRUK and BEZROGOVA [12] added ethanol and methylene blue to a solution containing uranium(VI), and irradiated the system. If oxygen is excluded, the uranium(IV) formed in the photo-reduction reduces the methylene blue to the colourless leuco compound, which in the process is reoxidized to uranium(VI). This is again reduced to uranium(IV), which reduces a further molecule of methylene blue, and so on. Thus, the loss of colour of the dye in a definite time is proportional to the uranium(VI) concentration.

The microdetermination of uranium can also be performed in ethanolic medium in the presence of oxygen. The primary products in the photoreduction are then uranium(IV) and acetaldehyde. In the presence of oxygen, however, peroxide derivatives, too, are produced in the course of the irradiation, and these oxidize uranium(IV) to uranium(VI). This is capable of oxidizing a further alcohol molecule to aldehyde,

and so on. Thus, measurement of the aldehyde concentration provides a sensitive method for the determination of uranium [13].

Although the mechanism of the photochemical reactions taking place in the oxalic acid+uranyl ion system is by no means clarified as yet, it can nevertheless be effectively used for analytical purposes. The reaction can be characterized as the uranyl ion-sensitized photodecomposition of oxalic acid:



According to PEIGE *et al.* [14], under suitable conditions the rate of consumption of oxalic acid is a function of the uranyl ion concentration. The excess of oxalic acid can be determined by permanganate titration. TAYLOR *et al.* [15] employed the above reaction for the determination of uranium by measuring the pressure of the gaseous products.

3. Application of photochemical indicator reactions

In certain cases the reaction between the titrant solution and the photocatalyst can be utilized to indicate the end-point of a titration. SIERRA *et al.* [16] used the reaction between EDTA and dyes of thiazine type as an indicator reaction. It has long been known that thionine or methylene blue in oxygen-free solution oxidizes EDTA if the system is illuminated. This is somewhat surprising, for EDTA is fairly resistant to even the stronger inorganic oxidants. The leuco dye can be measured voltammetrically on a Pt anode. This can be utilized to indicate the end-point in the titration of certain metal ions (*e.g.* lead(II), copper(II), magnesium(II), etc.) with EDTA. During the titration the solution is illuminated with a tungsten lamp, and the formation of the leuco form is observed with the aid of anodically polarized rotating Pt and saturated calomel electrodes. Originally only a residual current is observed, as no free EDTA is present in the solution. However, when the equivalence point is exceeded, the excess EDTA reduces the thionine and the anode current commences. The amperometric end-point can readily be detected. The method is fairly slow, as it is necessary to wait at least 2 minutes after each addition of titrant solution for a well-perceivable current effect to develop.

4. Photogravimetric methods

In these procedures the component to be determined is subjected to a photochemical reaction either directly or *via* a suitable developing reagent; by this means the substance is converted to a precipitate of well-defined composition, the weight of which is measured after the customary operations.

SINGH and PATNAIK [17] solved the determination of uranium(VI) in the presence of iron(III) and vanadium(V) by prolonged irradiation of the solution in question, after addition of ethanol and ammonium fluoride. In the presence of ethanol, uranium(VI) is transformed to uranium(IV), which reacts with the fluoride to give a

poorly-soluble precipitate of composition $\text{NH}_4\text{F} \cdot \text{UF}_4 \cdot \text{H}_2\text{O}$. This conception was used, too, for the separation of uranium from beryllium and zirconium [18].

With the aim of the precipitation of uranium, DIENERT and VILLEMARINE [19], as well as SPITZIN [20] irradiated a uranyl nitrate solution in the presence of hypophosphite. On irradiation the hypophosphite reduces the uranium(VI) and immediately reacts with the uranium(IV) produced to give a precipitate, $\text{U}(\text{H}_2\text{PO}_2)_4$.

For the gravimetric determination of mercury(II) SAKURABA and IKEYA [21—23] irradiated the solution in question in the presence of manganese(II) oxalate in hydrochloric acid medium, and weighed the mercury(I) chloride thus precipitated.

5. Indirect photochemical analytical methods

Photochemical reactions provide fairly extensive possibilities for chemical analysis if the photolysis is used to bring the component to be determined into a measurable form. The substance is subjected to exhaustive photolysis ("reagent" excess) directly or in the presence of an appropriate photon-carrier, and the product is determined (directly or indirectly).

RAO *et al.* [24] demonstrated that uranium(VI) undergoes reduction on the action of light in the presence not only of ethanol, but also of other primary and secondary alcohols; tertiary alcohols, however, exhibit weaker effects. The uranium(IV) formed was titrated with sodium vanadate.

RAO and SANTOPPA [25] used formaldehyde as reductant and similarly titrated the uranium(IV) produced with sodium vanadate, in the presence of N-phenylanthranilic acid or diphenylbenzidine as indicator.

NEMODRUK and BEZROGOVA made a detailed study of the photochemical reduction of uranium(VI) in the presence of ethanol in media of sulphuric acid [26] and phosphoric acid [27]. They examined the effects exerted on the photoreduction by the duration of the irradiation, the temperature, the sulphuric acid or phosphoric acid concentration and the amount of ethanol. The uranium(IV) resulting from the reaction was determined by titration with ammonium vanadate. If the phosphoric acid concentration of the starting mixture was higher than 2.5 M, more ammonium vanadate was consumed than the amount corresponding to the uranium(VI) content. In our view, this is due to the circumstance that at higher phosphoric acid concentrations in the presence of oxygen the ethanol gives rise not only to acetaldehyde, but also to peroxy derivatives, and these latter consume vanadate. This assumption is supported by the fact that a product which can be titrated with ammonium vanadate is obtained even if an acetaldehyde solution is subjected to prolonged irradiation in the absence of uranium [28].

The microdetermination of uranium can be carried out only in oxygen-free medium if the uranium(IV) produced by photoreduction in 0.5—1.0 N sulphuric acid is determined with arsenazo(III). In the presence of oxygen the measurements are subject to a negative error, for the uranium(IV) is partially reoxidized to uranium(VI). The finding that, in contrast with the micro method, the macrodetermination of uranium does give an acceptable result in the presence of oxygen [29] can be explained by the fact that the vanadate solution does not only react selectively with the uranium(IV); it rather gives a measure of the overall reducing capacity of the mixture. The uranium(IV) deficiency in the acid concentration range 1.2—2.5 M

is compensated by the equivalent amount of peroxy compounds formed by oxidation with oxygen, for these peroxy compounds also consume vanadate.

The photochemical reduction of molybdenum(VI) was studied by TANANAEV and LOKHVITSKAYA [30]. Their work served as a basis of a determination of molybdenum by PRASAD and SURYANARAYANA [31]. Molybdenum(VI), in its photoreduction with thiocyanate ion in hydrochloric acid medium, is transformed to molybdenum(V). The molybdenum(V) reacts with the thiocyanate excess to form a stable, coloured complex, which is suitable for the spectrophotometric determination of molybdenum.

KHARLAMOV and KOROBOVA [32] carried out the photoreduction of molybdenum(VI) in the presence of tartaric acid, and similarly measured the molybdenum(V) in the form of its thiocyanate complex. They assumed that on irradiation an excited tartaric acid molecule is formed; a hydrogen atom can then easily split off and give rise to the reduction. We consider it more probable that the photolysis of the molybdenum tartarate complex, which is fairly stable in the pH range 2–5 [33, 34] leads to the photoreduction of the molybdenum(VI). This assumption is supported by the finding that the photoreduction of molybdenum(VI) is complete in the pH range 1–6, while from pH 7 to pH 8 the efficiency of the photoreduction decreases rapidly. NEMODRUK and BEZROGOVA [35] employed ethanol for the photoreduction of molybdenum(VI). The photoreduction was faster in oxygen-free medium than in the presence of oxygen (the molybdenum(V) formed is very stable on standing in air). The molybdenum(V) was determined in the form of its thiocyanate complex.

The photoreduction of rhenium(VII) was investigated by the above authors in media of hydrochloric acid [36] and sulphuric acid [37]. In the presence of ethanol in hydrochloric acid solution, with the exclusion of oxygen, ultraviolet light causes rhenium(VII) to be reduced first to rhenium(V), and then to rhenium(IV) (rhenium(IV) and rhenium(V) are sensitive to the oxygen of the air!). The absorption of the rhenium(IV) itself was used for its spectrophotometric determination. In sulphuric acid medium thiourea was employed as reductant and the rhenium(IV) formed was determined spectrophotometrically in the form of its thiourea complex.

The photoreduction of neptunium(VI) and the possibility of its quantitative determination in this way were investigated by NEMODRUK and BEZROGOVA in perchloric acid [38] and hydrochloric acid [39]. It was found that irradiation of neptunium(VI) and neptunium(V) in the presence of ethanol (with suitably chosen experimental parameters) results in rapid and quantitative reduction to neptunium(IV). The neptunium(IV) was measured spectrophotometrically in the form of its complex with arsenazo(III). Formic acid, too, appeared suitable for the photoreduction of neptunium(VI) in the presence of ethanol.

The contradicting views in the literature with regard to the photochemical reduction of tungsten(VI) were clarified by NEMODRUK and BEZROGOVA [40]. In the presence of ethanol, tungsten(VI) undergoes quantitative photochemical reduction to tungsten(V) if 4 M phosphoric acid is applied for the acidification. The tungsten(V) can be determined spectrophotometrically in the form of its thiocyanate complex, or by titration with ammonium vanadate.

Numerous organic substances are suitable for the photochemical reduction of iron(III). RAO *et al.* [41, 42] studied the photoreduction of iron(III) in the presence of oxalic, lactic, citric and amygdalic acids, and NOVÁK [43] also used oxalic acid. The iron(II) formed was determined by titration with sodium vanadate, with di-

phenylbenzidine or diphenylsulphonic acid as indicator, or spectrophotometrically, in the form of its complex with *o*-phenanthroline. NOVÁK and AREND [44] carried out the determination of iron(III) traces in sodium citrate and sodium tartrate by immediate irradiation of solutions of these materials in the presence of *o*-phenanthroline, with measurement of the intensity of the colour of the resulting iron(II) complex.

RAO and ARAVAMUDAN made use of the photosensitivities of the iron(III)-oxalate [45] and the cerium(IV)-oxalate [46] systems for the quantitative determination of oxalic acid. In the case of the former system iron(II) is formed in an amount equivalent to the oxalate and was determined with sodium vanadate. In the cerium(IV)-oxalate system the excess of cerium(IV) after irradiation was determined by titration with iron(II).

RAO and RAMACHARLU [47, 48] utilized the photoreaction of mercury(II) chloride with sodium oxalate for the volumetric determination of mercury. The photoreduction of mercury(II) in the presence of the oxalate ion is very slow. The application of uranyl nitrate or iron(III) chloride as a photosensitizer leads to the photoreduction proceeding more rapidly, and the mercury(I) chloride can be measured iodometrically.

It is known that the yellow heteropolyacids of silicic acid and phosphoric acid with molybdcic acid can be reduced with tin(II) chloride or sodium sulphite to silico- or phosphomolybdenum blues. The absorptions of these latter can be used to determine even microgramme quantities of silicon and phosphorus. The chemical reduction has the disadvantage that the reduced heteropolyacids are not stable, their absorptions varying with time. If the reduction is carried out photochemically, then the "blue compound" formed on irradiation exhibits an extinction decrease of only 3% in 24 hours. This can presumably be attributed to the fact that on the cessation of the irradiation the reductant disappears from the solution. NEMODRUK and BEZROGOVA [49] used tartaric acid and formic acid for the photoreductions of silicomolybdcic acid and phosphomolybdcic acid, respectively. The reduction was performed in 2N sulphuric acid, at which acid concentration it was found that the molybdcic acid itself was not reduced [32]. The spectra of solutions of silicomolybdenum blue and phosphomolybdenum blue obtained by chemical reduction with tin(II) chloride and by photoreduction coincide, with a maximum at 800 nm.

ALIMARIN *et al.* [50] used the above findings as the basis of the determination of arsenic in the form of molybdenum arsenate. Formaldehyde was employed as reagent for the photoreduction, and the arsenomolybdenum blue produced was measured spectrophotometrically at 825 nm.

Another determination which can be included here is that of the nitrate ion. When methyl orange is subjected to ultraviolet irradiation in the presence of nitrate, the colour fades strongly. This reaction was utilized by DODIN *et al.* [51] for the determination of nitrate in the presence of other oxyanions.

6. Procedure based on photochemical dissociation

Such a procedure is suitable for the determination of compounds which undergo photochemical decomposition to yield a product measurable with satisfactory accuracy. This possibility was employed by DAIBER and PREUSMANN [52] to deter-

mine N-nitroso compounds, amines and amides. On photolysis, these compounds give rise to an equivalent amount of nitrite, which can be measured spectrophotometrically by means of the Griess—Ilosvay reagent.

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ФОТОХИМИЧЕСКИЕ МЕТОДЫ В ХИМИЧЕСКОМ АНАЛИЗЕ

1. Литературный обзор

А. Петер, Л. Й. Чани

В работе рассматривается современное развитие аналитических методов, основанных на фотохимических реакциях. На некоторых примерах рассмотрены свойства таких важнейших методов, как фотонометрии, фотокаталитического метода, фотогравиметрии, применения фотохимических реакций для обозначения конечных точек титрования и метода, основанного на фотодиссоциации.

UV ABSORPTION SPECTRA OF *para*-SUBSTITUTED *trans*-BENZOYL-PHENYL-ETHYLENE OXIDES

By

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The UV spectroscopical examination of the compounds prepared previously by Darzens condensation [1, 2] is described.

In our previous work the preparation of several *p*-substituted benzoyl-phenyl-ethylene oxides has been achieved by Darzens condensation. By NMR spectroscopy these compounds proved to be of *trans* configuration [3]. In the present work UV spectroscopical examination of the compounds has been carried out.

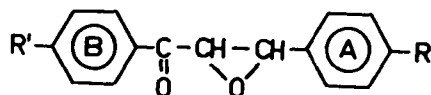
According to several authors, the epoxide-ring is able to conjugate with unsaturated groups, *e.g.* carbonyl group [4, 5]. Other authors agree that this conjugation effect is weaker than in the case of the ethylenimine-ring [6—9]. There is some experimental evidence that in substituted chalcones the conjugation extends to the whole molecule [10—13]. Such an evidence would be that *p*-substitution in any phenyl-ring results in either bathochromic or hypsochromic shift in the UV spectra. Another evidence is that the main absorption bands are found to be at higher wavelengths than in the case of similarly substituted benzaldehydes or acetophenones. The UV spectral data of *para*-substituted benzoyl-phenyl ethylene oxides can be found in Table I.

From the UV spectral data of *p*-substituted benzoyl-phenyl-ethylene oxides listed in Table I the following facts can be established.

1. The main absorption of the unsubstituted epoxy-ketone occurs at much smaller wave length (250 m μ) than in chalcone (312 m μ).
2. Substituents in the *p*-position of the B-ring result in remarkable bathochromic shift in the UV spectrum.
3. The same substituents in the A-ring, with the only exception of the nitro group, cause no shift.
4. Substituents in the *p*-position of both rings show the same shift as that of the B-ring, again with the exception of the nitro group.

From these facts the conclusion may be drawn that the conjugation does not extend to the whole molecule of epoxy-ketones. This may indicate that the epoxide-ring is able to conjugate only with the carbonyl group or not to conjugate at all. The only exception, the slight bathochromic shift of the nitro group can be explained with its own absorption.

Table I

UV absorption of *p*-substituted *trans*-benzoyl-phenyl-ethylene oxides

R'	R	μ
H	H	250 (247) [14]
OMe	H	287
Me	H	260 (262) [14]
Br	H	264
Cl	H	260 (261) [14]
NO ₂	H	276, 227 [14]
H	OMe	250, 230 [14]
H	Me	251 (251) [14]
H	Cl	250 (250) [14]
H	NO ₂	256
OMe	Me	288, 220
OMe	NO ₂	290, 219
Me	Me	260
Me	NO ₂	265
Br	Cl	264
Br	NO ₂	270
Cl	Cl	260 (261) [14]
Cl	NO ₂	266
NO ₂	NO ₂	270

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УЛЬТРАФИОЛЕТОВЫЙ СПЕКТР ПОГЛОШЕНИЯ
ПАРА-ЗАМЕЩЕННЫХ ОКИСЕЙ ТРАНС-БЕНЗОИЛФЕНИЛЭТИЛЕНА

Д. Шипош, И. Чех, Г. Сепеш

Соединения, приготовленные Дарzens-конденсацией [1, 2], изучены методом ультрафиолетовой спектроскопии.

**STUDY OF THE TRANSFORMATION
OF 1,3-DIOXACYCLOALKANES ON A PLATINUM CATALYST.
EXPERIMENTAL RESULTS AND DISCUSSION**

(Review article)

By

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The experimental results of the isomerization and hydrogenolysis of 1,3-dioxacycloalkanes (about 60 compounds) on a platinum catalyst are reviewed, and an account is given of new reaction directions determined by the structures of the compounds and by the experimental conditions, and of the main parameters affecting these.

Introduction

Of the 1,3-dioxacycloalkanes, we have dealt mainly with the transformation of the 1,3-dioxanes in the presence of heterogeneous catalysts [1—8], for these stand out within this family of compounds from both theoretical and practical aspects. Investigation of homologues with five, seven or eight atoms in the ring was considered as a part of our task only in so far as it was necessary to prove the general nature of new regularities revealed in the case of the 1,3-dioxanes [9]. This gave the possibility of studying the change of certain reaction types depending on the number of atoms in the ring.

The first reviews on the chemistry of the 1,3-dioxanes appeared in 1952 [10, 11]; these were supported by a considerable number of experimental results, and drew attention to this type of compounds. In recent years, interest in the chemistry of the 1,3-dioxanes has increased significantly; this is proved not only by the practical application of this family of compounds, but also by the increasing number of publications dealing with the 1,3-dioxanes. The reviews published more recently focus attention also on the theoretical aspects of the chemistry of the 1,3-dioxanes, *e.g.* on their stereochemistry and on their heterogeneous catalytic transformations [12, 13].

The practical importance of the 1,3-dioxanes has not yet attained the level which would be expected on the basis of the comparatively ready availability of these compounds. For instance, direct transformation (Prins reaction) [14] of the great amounts of olefins produced by the petrol-chemical industry is a cheap source of 1,3-dioxanes. It should be noted, however, that the use of 1,3-dioxanes is continuously increasing (solvents, antidetonators, intermediates in the organic chemical industry, starting and auxiliary materials in drug syntheses, plastics monomers,

etc.). From this respect 4,4-dimethyl-1,3-dioxane should be stressed as it has acquired great importance because of its role in the manufacture of isoprene.

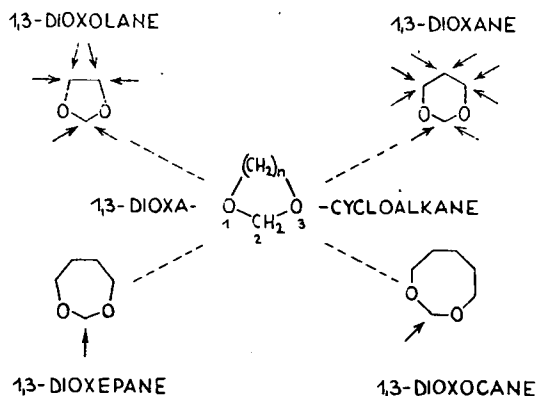
The 1,3-dioxacycloalkanes can be considered as cyclic derivatives of bifunctional diols with oxo compounds (cyclic acetals and ketals), and those can similarly be regarded as bifunctional systems. It is known that bifunctional systems undergo special chemical transformations which are not characteristic of the individual isolated functions. Thus, the new isomerization reactions observed in the heterogeneous catalytic transformations of 1,3-dioxacycloalkanes form in our view, an extremely interesting part of the chemistry of cyclic systems containing two hetero atoms.

A systematic survey of literature dealing with this family of compounds indicates that the heterogeneous catalytic transformations of the 1,3-dioxanes can be classified in three main groups [13]:

- (a) transformation of 1,3-dioxanes to conjugated dienes;
- (b) isomerization of 1,3-dioxanes to β -alkoxyoxo compounds;
- (c) hydrogenolysis of 1,3-dioxanes to primary alcohols, 1,3-diols and 1,3-diol monoethers.

In the study of the first two processes, heterogeneous catalysts with various electrophilic characters, mainly phosphates, oxides and silicates have been used. The catalytic hydrogenolysis has been investigated in a static system, in the liquid phase, at high pressure, in the presence of various metals and copper(II)-chromium(III) oxide. The 1,3-dioxanes and their cyclic homologues with different numbers of ring atoms have not been examined in the vapour phase in the presence of metal catalysts.

Accordingly, we set out to investigate the transformations of mono-, di- and polysubstituted 1,3-dioxanes and of some 1,3-dioxolane, 1,3-dioxepane and 1,3-dioxocane derivatives on the action of metal heterogeneous catalysts.



Of the 1,3-dioxacycloalkanes presented in the scheme, a study was made of about sixty compounds from the derivatives containing a substituent (primarily an alkyl group) on the carbon atom denoted by an arrow.

A large proportion of the model compounds were prepared as described previously [15], while some stereoisomeric 1,3-dioxanes were made available by the Department of Organic Chemistry, State University, Odessa.

The isomerization and hydrogenolysis of these compounds on a platinum catalyst were examined at atmospheric pressure. Experiments were also carried out on other metal catalysts, and procedures were elaborated for the liquid-phase catalytic hydrogenolysis of certain dioxanes under pressure [16], and for their transformation to oxacyclobutanes on a catalyst of acidic character [17].

The aim of our experiments was to establish the reaction directions on platinum catalysts of the transformations of 1,3-dioxacycloalkanes containing different numbers of atoms, and to examine the variation of the reaction directions as a function of the structure of the starting material. A study was further made of the effects of the nature, number and ring-position of the substituents with regard to the stability of the ring. The changes in the extent and main directions of the transformation were determined as a function of the individual reaction parameters. A thermolite-supported catalyst containing 10% platinum (in the following Pt/T) was mainly employed [18, 19]. The experiments were performed with a microreactor built into a gas-chromatograph with impulse injection, in a carrier gas stream of hydrogen or helium [18, 19]. Examinations were also made on a Pt/C catalyst, and on ammonia-poisoned catalysts.

The chemical processes were followed qualitatively and quantitatively by analytical and preparative gas-chromatography, as well as by IR spectrophotometry, together with the other generally used methods of separation and identification. In some cases investigations of a preparative nature, too, were carried out in a continuous-operation reactor. Experiments were also performed to establish the mechanisms and stereochemical courses of the new processes discovered.

Relative stabilities of 1,3-dioxacycloalkanes in their transformations on Pt/T in the presence of hydrogen

Already the preliminary experiments drew attention to some novel changes: hitherto unobserved directions of transformation of 1,3-dioxacycloalkanes in the presence of various heterogeneous catalysts; these made the topic under examination even more interesting, and underlined its importance. On the basis of the appropriate thermodynamic data, it was possible to assume the isomerization of 1,3-dioxanes to esters. However, it was not expected to find the considerable selectivity determined by the number of atoms in the rings and by the positions and numbers of the substituents, nor the fact that in certain cases isomerization leading to the formation of esters would become the characteristic reaction direction.

Already at the beginning of the experimental work it was found that for isomerization to the ester the combined presence of both platinum and gaseous hydrogen is necessary. Thus, the thermolite support in the presence of hydrogen, and the Pt/T in the absence of hydrogen, did not prove active under similar experimental conditions [1]. As regards the open-chain acetals, ester formation could not be observed in the transformation of acetaldehyde diethylacetal in the presence of hydrogen.

The degrees of transformation of the dioxacycloalkanes as a function of temperature are shown in Figs 1—6, which indicate the relative stability or reactivity of the above compounds under the given experimental conditions.

The experimental data ([1—4, 9], Figs 1—6) permit the following main conclusions.

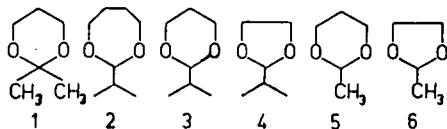
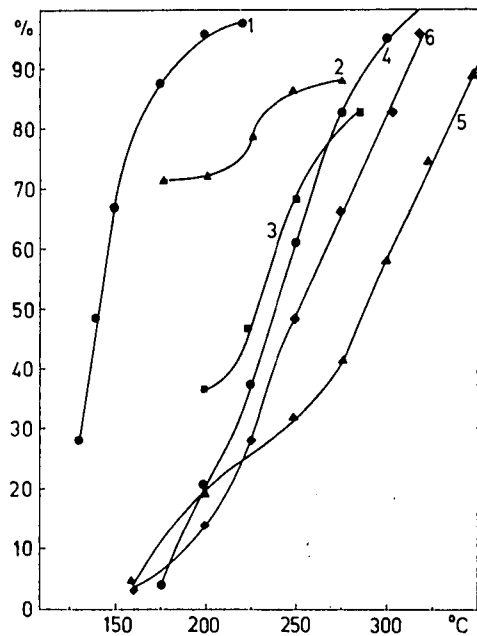


Fig. 1

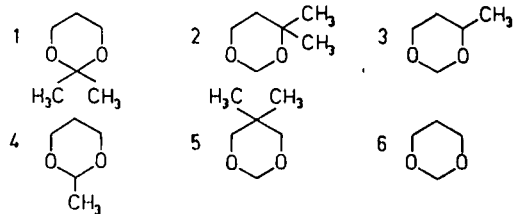
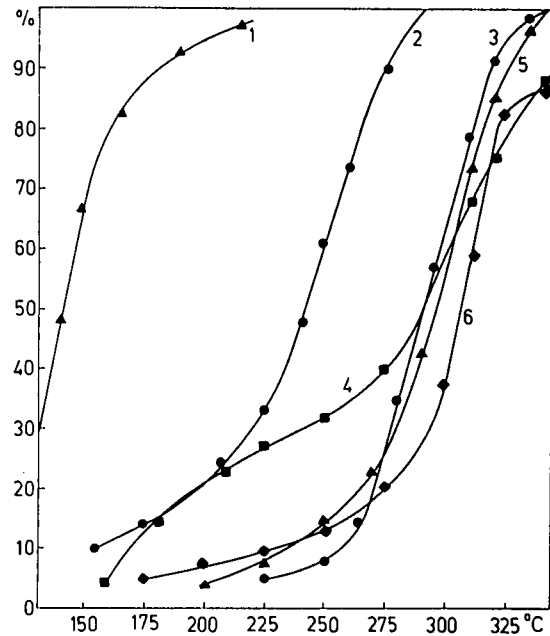


Fig. 2

Figs 1—6. Variation of the conversion in the transformations of 1,3-dioxacycloalkanes on Pt/T, as functions of the number of ring atoms, the nature, position and number of the substituents and the temperature.

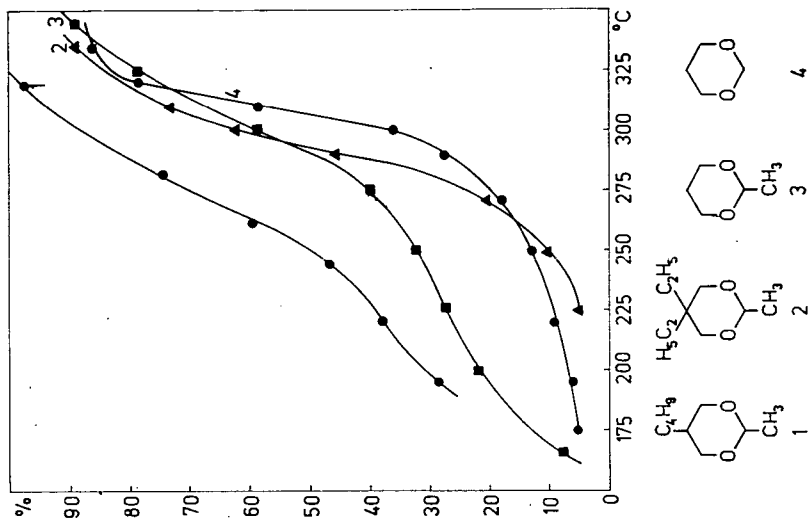


Fig. 4

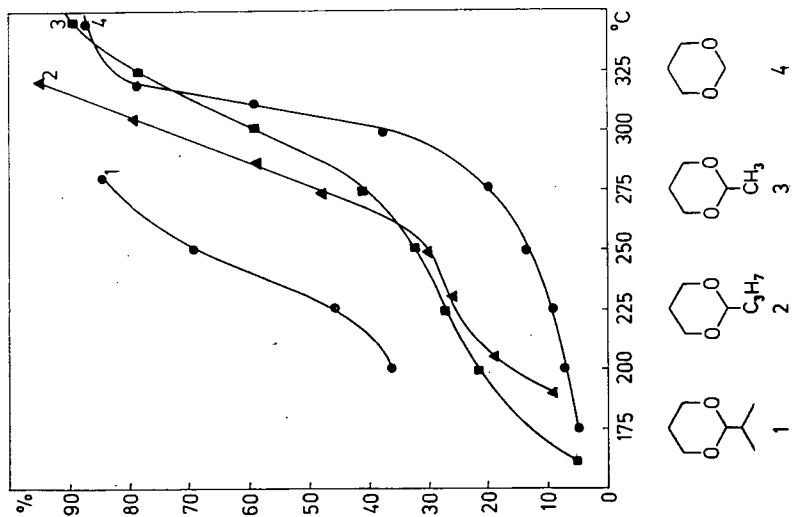


Fig. 3

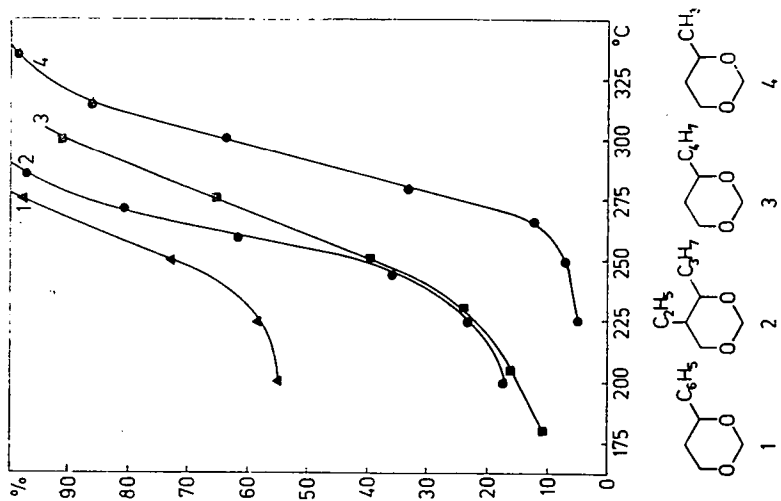


Fig. 5

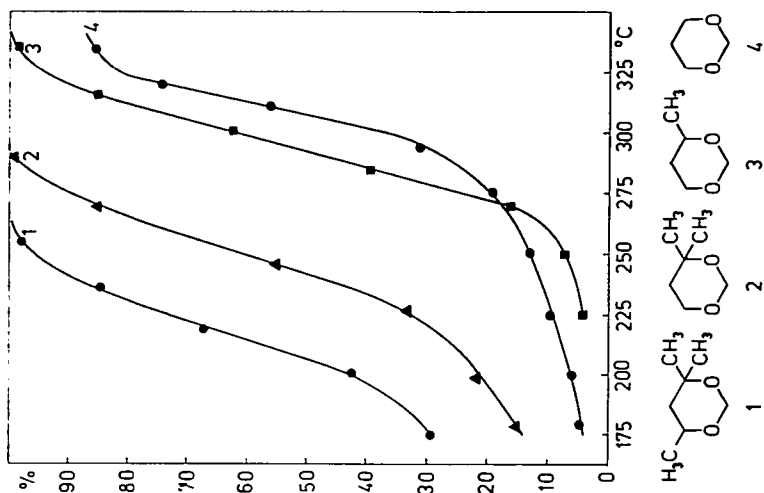


Fig. 6

On a Pt/T catalyst the stability of the 1,3-dioxacycloalkanes as a function of the number of atoms in the ring exhibits the following sequence: $8 \sim 7 < 6 \sim 5$ (Fig. 1). As it will be seen later, the differences in the rates of decomposition of the dioxacycloalkanes are brought about primarily by the differences in reaction direction, these depending on the number of atoms in the ring and on the substituents.

The stability of the 1,3-dioxanes as a function of the number of C_2 substituents varies as follows: formal > acetal > ketal (Fig. 2). The stability series for the alkyl-substituted 1,3-dioxanes is: $2- < 4- < 5-$ alkyl-1,3-dioxanes.

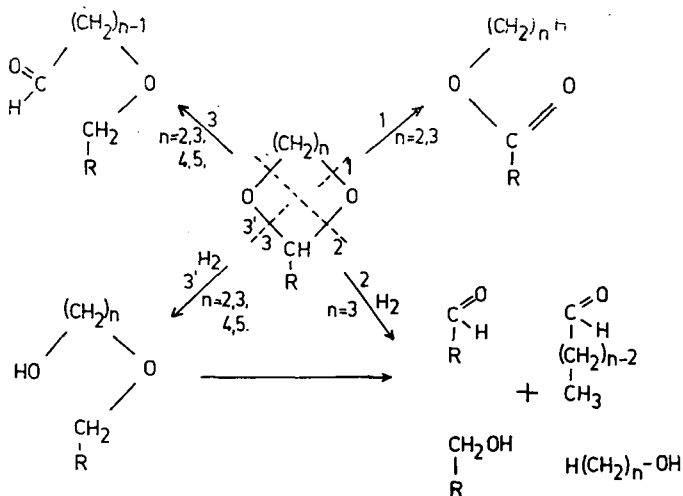
The stability of the 1,3-dioxanes depends on the number of substituents on C_5 in the following way: 5,5-dialkyl-1,3-dioxane > 5-alkyl-1,3-dioxane (Fig. 3).

Alkyl substituents at a given position in the ring affect the stability of the 1,3-dioxanes in the sequence of their +I effects (possibly on the basis of their effects on the adsorption of the substrate molecules) (Figs. 4 and 5). The reactivity of the 1,3-dioxanes increases proportionally to the number of substituents on C_4 (Fig. 6). The C_2 isopropyl group increases the reactivity of the 1,3-dioxanes more than that of the other studied members of the 1,3-dioxacycloalkanes.

As already mentioned, the differences in stability of the 1,3-dioxacycloalkanes can be explained decisively by the transformation directions; these will be reported in detail later. In the case of the acetals we shall discuss the characteristics of the transformations of five-, six-, seven- and eight-membered 1,3-dioxacycloalkanes on Pt/T. Since formals and ketals were prepared only from 1,3-diols, it can be understood that in these sub-sections only the corresponding dioxanes will be involved. A special account is given of the transformations of the derivatives of 1,3-dioxadecalin, and 5-alkoxyalkyl-1,3-dioxane stereoisomers of known structure.

Transformation of 1,3-dioxacycloalkanes of acetal type

The main transformation directions observed can be seen in the following process scheme on the example of the non-substituted cyclic acetals:



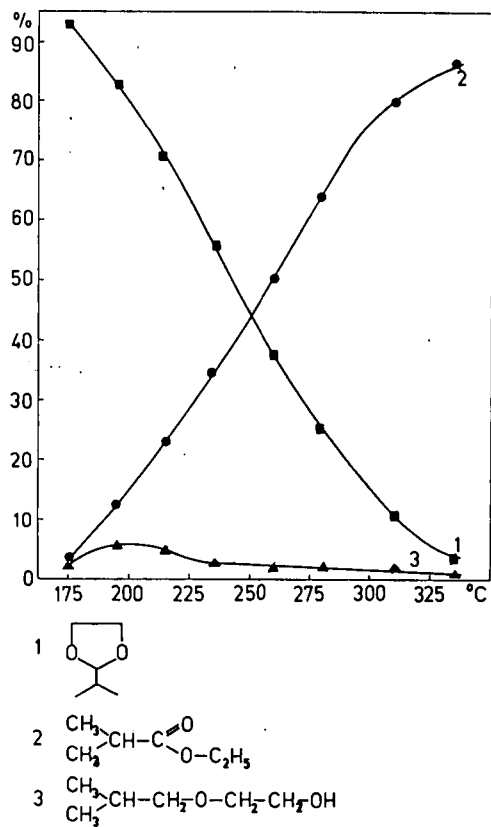


Fig. 7

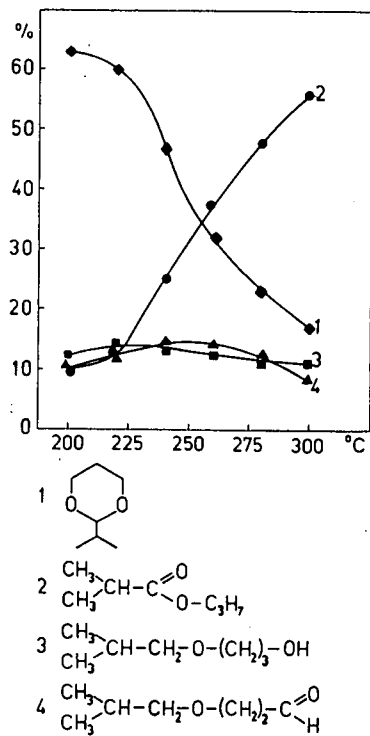


Fig. 8

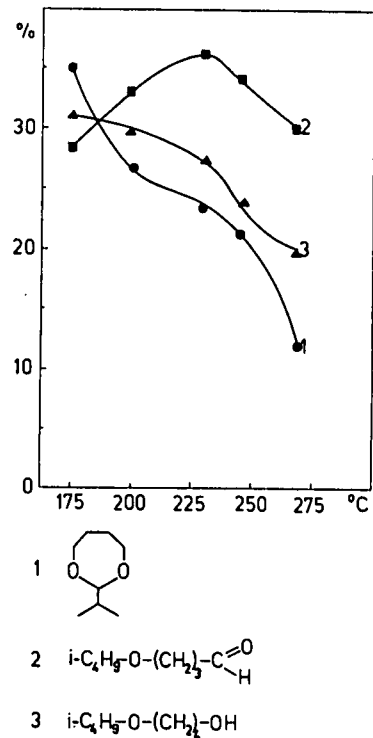


Fig. 9

Figs 7—12. Variation of the product composition as a function of temperature in the transformation of some 1,3-dioxacycloalkanes on Pt/T.

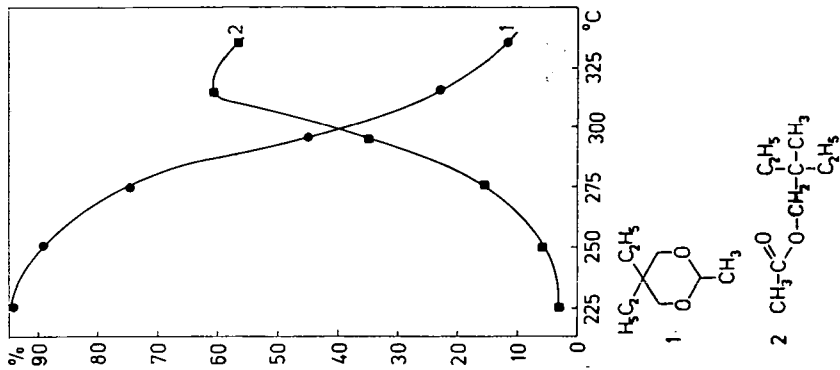


Fig. 12

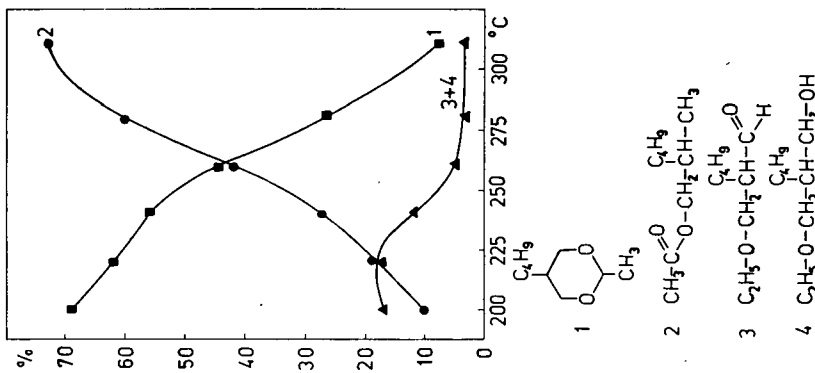


Fig. 11

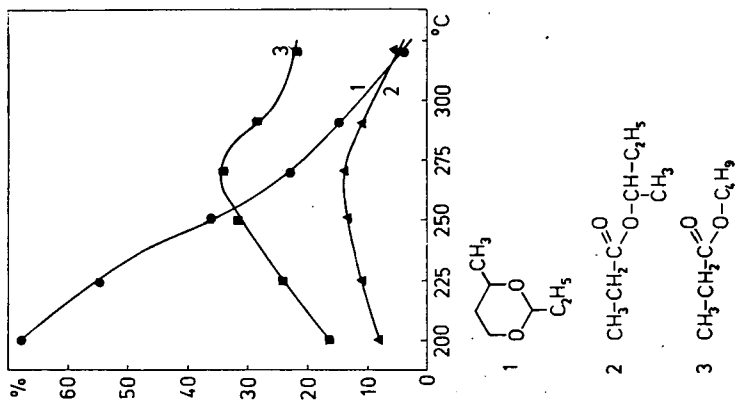


Fig. 10

Of the four main reaction directions, two are isomerizations, one is hydrogenolysis, and one is a fragmentation process. The extents of these main processes are determined decisively by the number of ring atoms, but other factors exerting an effect are the ring substituents and the reaction parameters (predominantly the surface state of the catalyst and the temperature). Before giving a more detailed treatment of the experimental results [1—4, 9], the temperature-dependent variation of the composition of the catalysate is plotted for a number of model compounds in Figs 7—12.

On Pt/T in the presence of hydrogen, the 2-alkyl-1,3-dioxolanes mainly undergo isomerization to the corresponding esters. Conversion to the ester may reach even

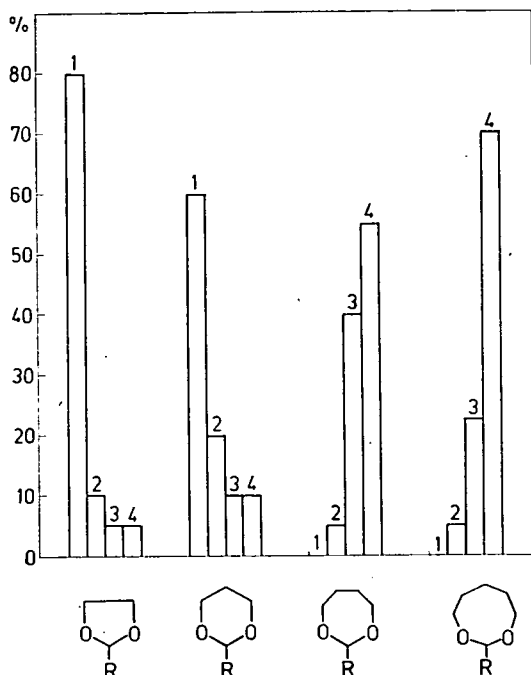


Fig. 13. Average yields of products formed in the transformations of cyclic acetals with various numbers of ring atoms on Pt/T (1: esters; 2: products of fragmentation; 3: alkoxyoxo compounds; 4: diol monoethers)

85—90%. Under the same experimental conditions the 2-alkyl-1,3-dioxanes are similarly isomerized to the corresponding esters. The selectivity of ester formation is somewhat lower, but in favourable conditions attains 80% in these systems, too. As a consequence of the splitting of the C₂-O bond under similar experimental conditions, the 2-alkyl-1,3-dioxepanes and 2-alkyl-1,3-dioxocanes are isomerized to

the corresponding alkoxyaldehydes, and as a result of hydrogenolysis are transformed to the 1,4- and 1,5-diol monoethers. The two reaction directions together make up as much as 95%. Esters were not found among the reaction products, even in traces.

Thus, on the basis of the extents of the main transformation processes outlined above, the 2-alkyl-1,3-dioxacycloalkanes can be arranged in the following series (Fig. 13):

Based on the yield of ester formation: 1,3-dioxolanes > 1,3-dioxanes (1,3-dioxepanes = 1,3-dioxocanes = 0).

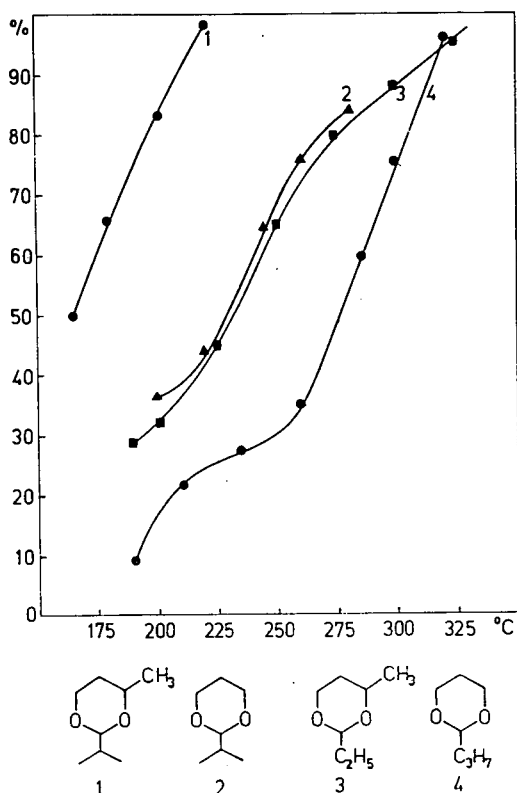


Fig. 14. Effect of the C_2 -isopropyl group on the extents of transformation of 1,3-dioxanes on Pt/T.

Based on transformation to alkoxyaldehydes and diol monoethers: 1,3-dioxolanes < 1,3-dioxanes \ll 1,3-dioxepanes \sim 1,3-dioxocanes.

Fragmentation processes occur as a consequence of the higher temperature. Of course, at higher temperature the main processes are also followed by various secondary changes due to decomposition [5].

The substituents affect the relative extent of the main reaction directions. As a function of the substituent on C₂, the degree of ester formation varies according to the following sequence: 2-isopropyl->2-methyl->2-phenyl-1,3-dioxolane; 2-isopropyl-<2-propyl->2-ethyl->2-methyl-1,3-dioxane.

The presence of the C₂-phenyl group promotes the fragmentation processes *via* the splitting of the C₂-O bond, but it also accelerates the hydrogenolysis. The C₂-isopropyl group increases both the rate of decomposition and the extent of ester formation in the dioxolanes, but in the dioxanes it decreases the rate of ester formation in favour of the hydrogenolysis; in asymmetric dioxanes it affects the direction of ester formation [4]; in the case of dioxepanes it increases the rate of hydrogenolysis at the expense of fragmentation [9].

These experimental facts can be explained by the "shielding" effect of the isopropyl group on the C₂-H bond. Thus, owing to its spatial shielding effect, the isopropyl group inhibits the dissociative chemisorption of the substrate accompanied by the splitting of its C₂-H bond, which is very probably a condition for isomerization to the ester. Naturally, at the same time this promotes the hydrogenolysis (the competing, parallel process), as proved by the experimental data.

As a result of the asymmetry of 4-substituted 1,3-dioxanes, transformation accompanied by ring-opening leads to two series of products. The C₄ substituent promotes isomerization proceeding with splitting of the O₃-C₄ bond. Accordingly, the rate of formation of esters of primary alcohols is higher than that of the esters of secondary alcohols.

On the basis of what has been said above, it may be easily seen that the differences in the rates of decomposition of 1,3-dioxacycloalkanes can be explained by the differing reaction possibilities. The 1,3-dioxacycloalkanes decompose at the highest rate, undergoing the greatest extent of hydrogenolysis. Thus, the rate of decomposition of 1,3-dioxacycloalkanes is determined in the long run not by the number of ring atoms, but by the decomposition direction depending on the structure of the compound.

This finding is well illustrated in Fig. 15. It can be seen that the highest rate of transformation is that of 2,2-dimethyl-1,3-dioxane, from which products formed by splitting of the C₂-O bond are obtained in a yield of 85%.

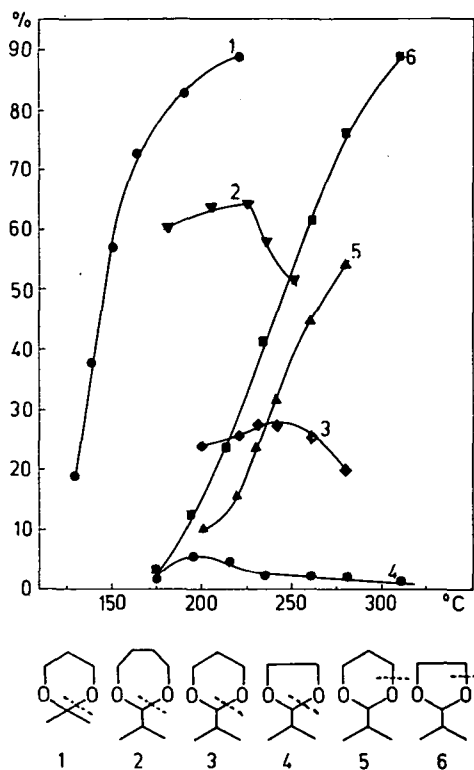
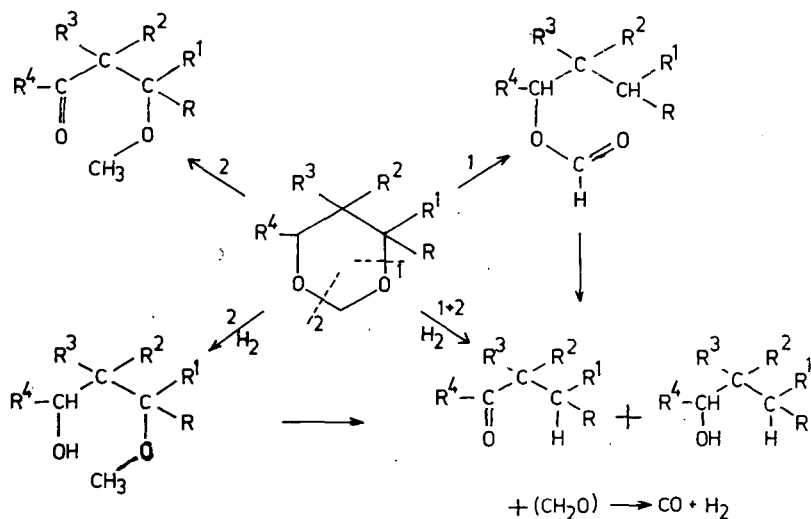


Fig. 15. Variation as a function of temperature of the yields of products formed by splitting of the C₂-O₃ and O₃-C₄ bonds in the transformation of 1,3-dioxacycloalkanes on Pt/T.

This finding is well illustrated in Fig. 15. It can be seen that the highest rate of transformation is that of 2,2-dimethyl-1,3-dioxane, from which products formed by splitting of the C₂-O bond are obtained in a yield of 85%.

Transformation of 1,3-dioxanes of formal type

The main reaction directions observed on the basis of the experimental results [2, 3, 5, 6] can be summarized in the following reaction scheme: (For purposes of clarity the transformations accompanied by splitting of the C₆-O₁ bond have not been included in this scheme.):



Similarly as for the acetals, in the case of the cyclic formals, too, the same four main transformation directions are observed (two isomerizations, one hydrogenolysis, and one fragmentation process).

With regard to their stabilities and transformation directions under the conditions of examination, the six-membered cyclic formals can be divided into two main groups: 4-aryl-, 4,4-dialkyl-, 4,6-polysubstituted-1,3-dioxanes; and 4-alkyl-, 5-mono-, 5,5-disubstituted-1,3-dioxanes.

The cyclic formals belonging to the first group behave similarly to the acetals as regards both their stabilities and their transformations (in connection with their stabilities see Figs 5 and 6). On Pt/T they are isomerized, mainly to the corresponding formic acid esters. Since the transformation temperature is relatively low, the formates are not further converted and thus their formation can be readily followed. With the 4-aryl- and 4,4-disubstituted-1,3-dioxanes, it is only possible to observe the formation of products obtained by splitting of the C-O bond adjacent to the substituents.

The cyclic formals in the second group have higher decomposition temperatures and stabilities than those of the cyclic acetals. However, the higher temperature favours the fragmentation processes. Here we must consider not only the primary processes, but also the secondary changes following the other three primary processes; these lead to the formation of the same fragments, as shown in the Figure. The proportions of the primary and secondary processes were not investigated. For the transformation of these cyclic formals on Pt/T in the presence of hydrogen, the

fragmentation processes are the more characteristic. In the course of these processes, oxo compounds and alcohols containing one carbon atom less than the starting dioxane are formed, in principle by the elimination of formaldehyde or methanol or by some other secondary processes. The combined amount of these products varies in the range 10—60%, depending on the temperature, and on the nature, position and number of the substituents in the ring. In addition to the fragmentation processes, the isomerization of these cyclic formals to esters is also appreciable (8—20%), but the secondary transformation of the formates produced considerably decreases the amount of esters observed. Under the experimental conditions applied, the formic acid esters (and particularly the esters of formic acid with secondary alcohols) are labile compounds, as can be clearly seen from the experiments with the individual formates (under the same conditions as for the 1,3-dioxanes) (Fig. 16). A comparison of Figs 2 and 16 readily reveals that the decomposition of the 2-butyl

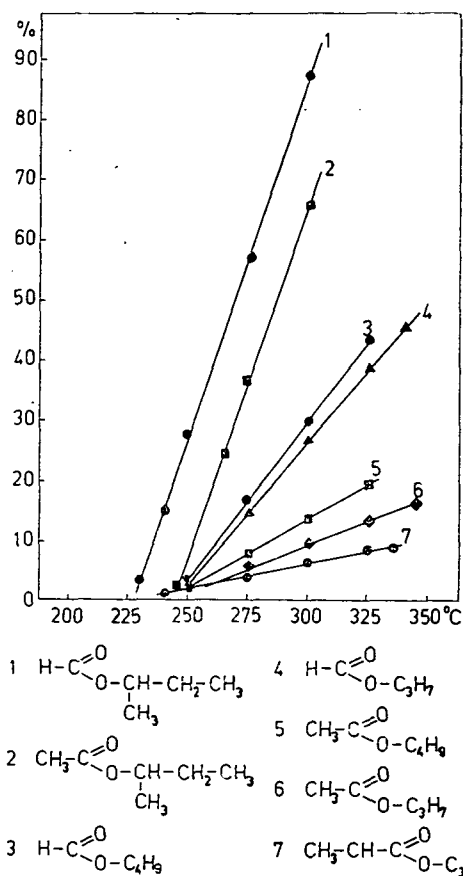
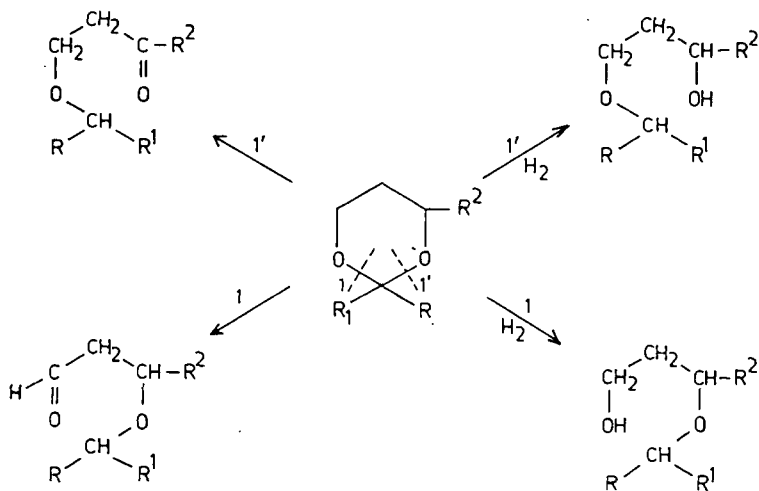


Fig. 16. Variation of the conversions of various esters on Pt/T as a function of the temperature.

formate is faster than that of 4-methyl-1,3-dioxane. The other two processes outlined in the scheme are of minor importance in the case of the formals: 1,3-diol monoethers can be found only in traces among the reaction products, and the maximum amount of β -methoxypropionaldehyde is also only $\sim 1\%$.

Transformation of 1,3-dioxanes of ketal type

The main reaction directions established on the basis of the experimental data [2, 4] are summarized in the following scheme:



The transformations of cyclic ketals on Pt/T in the presence of hydrogen are characterized by hydrogenolysis and by an isomerization process accompanied by splitting of the C_2-O bonds. These two processes lead to the β -alkoxyoxo compounds and to the corresponding 1,3-diol monoethers. A detailed study of the relative extents of the processes indicated by *I* and *I'*, and of the factors affecting these, was not dealt with. Fig. 17 shows a plot of the conversion of a model compound, 2,2-dimethyl-1,3-dioxane, to the two main products, 3-isopropoxypropionaldehyde and 3-isopropoxypropanol, as a function of temperature.

The examined representatives of the 1,3-dioxanes (cyclic ketals) exhibit considerable reactivity even at a comparatively low temperature. Being more readily deformed, compounds containing open-chain substituents at C_2 are more reactive (90% conversion at 220°C) than those containing cyclic substituents (60% conversion at 250°C). The cyclic ketals of cyclohexanone are more reactive than the same derivatives of cyclopentanone; this can be satisfactorily explained by the differences in stereostructural properties of the two rings. The less stable axial $C-O$ bond is more rapidly hydrogenolyzed, and therefore under the conditions of the hydrogenolysis the cyclohexanone ketals are the more reactive. The cyclic structure of C_2 substituents on the dioxane ring has no substantial effect on the reaction directions.

The experimental fact that the cyclic ketals of the 1,3-diols exhibit considerable reactivity on a platinum catalyst in the presence of hydrogen draws attention to the preparative applications of the reaction. Thus, the literature data referring to the hydrogenolysis of dioxanes describe the use of high pressures (>100 atm).

Transformation of *cis*- and *trans*-1,3-dioxadecalin homologues

By means of the examination of the *cis*- and *trans*-1,3-dioxadecalin homologues, a possibility arose for the study of the reactivities of the geometric isomers of 1,3-diol formals, acetals and ketals, and of the stereochemistry of the chemical transformations already described [7]. At the same time, these experimental observations also provide data which help to understand the mechanisms of the processes. The transformation directions described above for the formals, acetals and ketals are also characteristic for the derivatives of 1,3-dioxadecalin, with the following

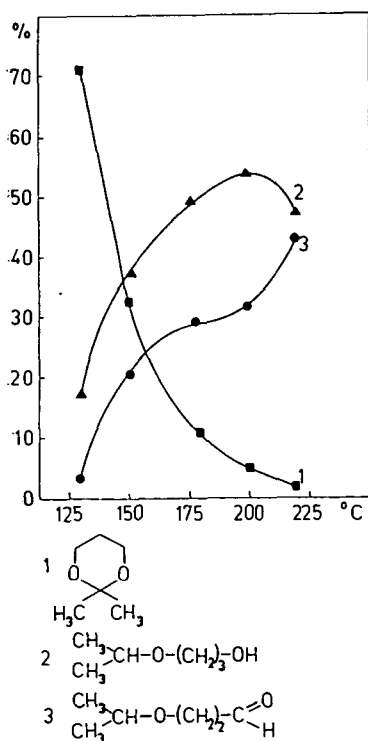


Fig. 17. Variation of the product composition in the transformation of 2,2-dimethyl-1,3-dioxane on Pt/T.

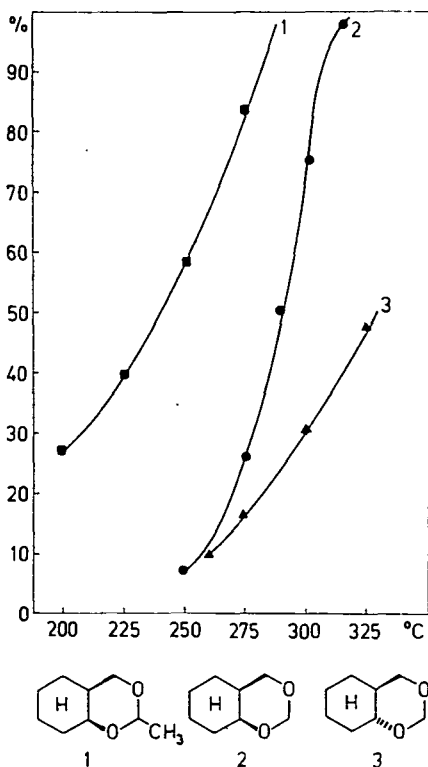
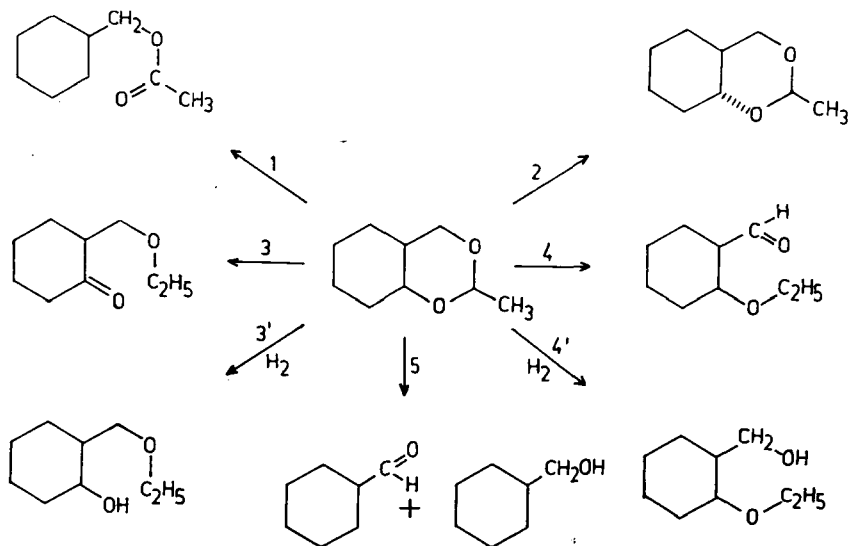


Fig. 18. Variation of the conversion of 1,3-dioxadecalins on Pt/T as a function of the temperature.

additions. The *cis*-isomers are significantly more reactive than the *trans*-isomers (Fig. 18).

Apart from the four main transformation directions discussed earlier, *cis-trans* isomerization, too, is observed with 1,3-dioxadecalin and 2-methyl-1,3-dioxadecalin. This phenomenon was also observed in the course of the investigation of the transformation of decalin on Pt/T in the presence of hydrogen.

The transformation directions in the case of *cis*-2-methyl-1,3-dioxadecalin are presented in the following scheme:

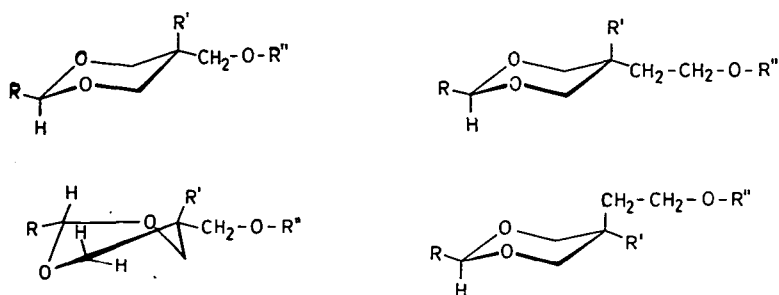


The relative extents of the reaction directions outlined in the scheme at *e.g.* 254 °C (60% conversion) are as follows: reaction direction 1 40%; reaction direction 5 25%; reaction directions 3+3'+4+4' 25%; reaction direction 2 10%. Other theoretically possible ester-formation was not observed. The fact that *trans*-1,3-dioxadecalin and *trans*-2-methyl-1,3-dioxadecalin are of significantly lower reactivity than the *cis*-isomers is shown by the decrease of the ester-formation reaction being minimal. In the case of 2,2-dimethyl-1,3-dioxadecalin only the reaction directions 3, 3' and 4, 4' can be observed. Processes beginning with the splitting of the C₂-O bond take place at very high rate. There is no substantial difference between the reaction rates of the *cis*- and *trans*-stereoisomers.

Transformation of stereoisomeric 5-alkoxyalkyl-1,3-dioxanes

According to structural examinations to date, some of the 5-alkoxyalkyl-1,3-dioxanes are stereoisomers with different conformations, while in another group the

isomers are compounds with the same conformation, *viz.* stereoisomers in the symmetric chair conformation:



R	CH ₃	<i>i</i> -C ₃ H ₇
R'	C ₂ H ₅	C ₂ H ₅
R''	<i>i</i> -C ₃ H ₇	<i>i</i> -C ₃ H ₇

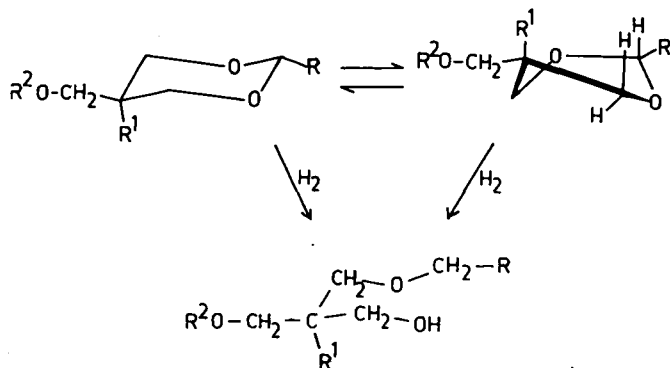
R	CH ₃	<i>i</i> -C ₃ H ₇	CH ₃
R'	CH ₃	C ₂ H ₅	<i>i</i> -C ₃ H ₇
R''	CH ₃	CH ₃	C ₂ H ₅

The stereostructures of the compounds examined were established by measurement of the dipole moments and by study of the IR and NMR spectra (described in [20]).

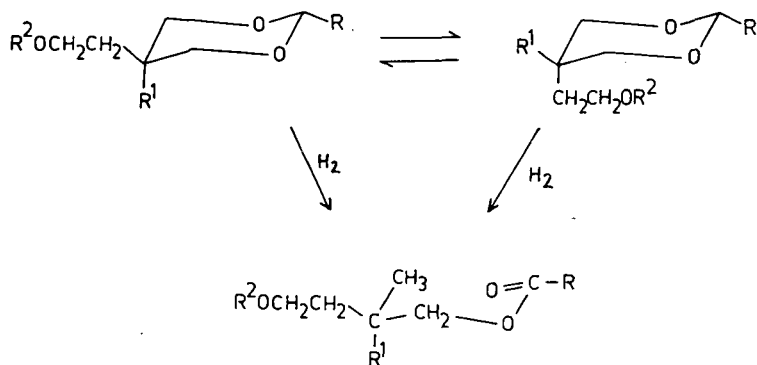
As regards the rates of transformation of the compounds, it can be stated that the *trans*-isomers are more stable than the *cis*-isomers. This finding refers mainly to the stereoisomers in different conformations; clearly, this difference in stability is less significant in the case of stereoisomers with the same conformation.

The main directions of transformation of 5-alkoxyalkyl-1,3-dioxanes on Pt/T in the presence of hydrogen are [8]: isomerization accompanied by the formation of esters; interconversion of the isomers (configurational isomerization); hydrogenolysis to the corresponding triol diethers; fragmentation.

The characteristic reaction directions for the transformations of stereoisomer pairs with different conformations are hydrogenolysis and isomerization. Ester formation is not observed:



In the case of stereoisomer pairs in the same (*l.e.* chair) conformation, the main process is isomerization accompanied by ester formation. It should be noted that, here too, isomerization of the stereoisomers takes place:



At higher temperature, or in the case of a longer contact time, the primary process resulting in the formation of the alkoxy esters in these compounds is accompanied by the hydrogenolysis of the ether bonds as a secondary process. The formation of products involving hydrogenolysis of the β -alkoxy group could also be observed.

During the study of the transformations of these compound types, therefore, interesting stereoselective catalytic processes were discerned, which at the same time also provide valuable data for the investigation of the mechanisms of transformation of dioxanes.

The substantial difference between the retention times of stereoisomers with different conformations draws attention to the applicability of gas-liquid chromatography in the conformational analysis.

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**ИЗУЧЕНИЕ ПРЕВРАЩЕНИЙ 1,3-ДИОКСАЦИКЛОАЛКАНОВ
В ПРИСУТСТВИИ ПЛАТИНОВОГО КАТАЛИЗАТОРА.
ЭКСПЕРИМЕНТАЛЬНЫЕ РЕЗУЛЬТАТЫ И ДИСКУССИЯ. ОБЗОР**

М. Барто́к, Й. Аньо́к

В настоящем обзоре обсуждаются и обобщаются экспериментальные результаты изомеризации и гидрогенолиза 1,3-диоксациклоалканов (60 соединений), выявляются новые направления превращений, определяющиеся структурой исходных соединений и другими параметрами реакций.

MECHANISM OF TRANSFORMATION OF 1,3-DIOXACYCLOALKANES ON A PLATINUM CATALYST

By

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The paper reviews the experimental results relating to the mechanisms of the platinum-catalysed isomerization and hydrogenolysis of 1,3-dioxacycloalkanes, and the conclusions drawn from these. The formation of alkoxyoxo compounds as a result of isomerization can be attributed to active sites of an electrophilic character on the Pt/thermolite catalyst, and can be interpreted by an intramolecular mechanism.

Isomerization to the ester, configurational isomerization and hydrogenolysis are due to the platinum catalyst and the hydrogen chemisorbed on it, and the mechanisms of the processes are thus probably of an intermolecular character.

According to the results of our investigations performed so far in the field of the chemistry of the 1,3-dioxacycloalkanes, we have identified new heterogeneous catalytic isomerizations and certain characteristic features of their mechanisms.

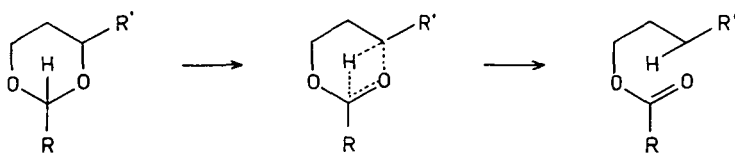
Introduction

In the course of our experimental work it was proved in the case of many compounds (reviewed in [1]) that on a Pt/thermolite (Pt/T) catalyst in the presence of hydrogen, the five- and six-membered cyclic acetals undergo isomerization to esters with very good yields. The more surprising it is that the transformation is selective for the 1,3-dioxolanes, the less surprising the fact that isomerization accompanied by ester formation does not take place in the case of the 1,3-dioxepanes and the 1,3-dioxocanes from the homologous series of cyclic acetals, isomerization involving opening of the C₂-O bond occurring instead, together with hydrogenolysis. Ester formation cannot be observed under similar conditions in the transformation of open chain acetals either.

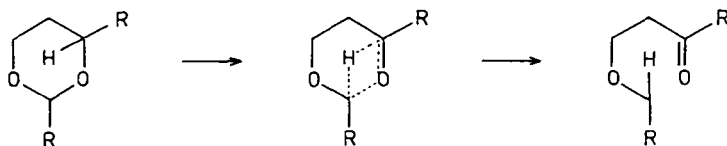
In the liquid phase, under conditions suitable for radical reactions (UV light, presence of peroxides), the five- and six-membered cyclic acetals, and the open-chain acetals, too, undergo transformations accompanied by the formation of esters [2—9], but the selectivity is substantially poorer than that in heterogeneous catalytic isomerization. It was assumed earlier that under similar conditions the 1,3-dioxepanes, too, can be induced to undergo analogous transformations. From this aspect our examinations proved unavailing, for under similar conditions the 1,3-dioxepanes polymerized. Publications can also be found relating to the vapour-phase thermal isomerization of 1,3-dioxanes, where the formation of esters is reported [10—12]. Although the C₄-O and C₆-O bonds are conjugated with double bonds (allyl-type

conjugation) in some of the listed cases, nevertheless the authors discussing the mechanism of the reaction state without exception that the initial step in the reaction is the radical-type loss of hydrogen from C₂. In the final analysis, the non-occurrence of isomerization to the ester in the case of the 1,3-dioxepanes, the 1,3-dioxocanes and the open-chain acetals on Pt/T may bear witness to the fact that the structure of the substrate determines the direction of the processes taking place within one compound type.

If an intramolecular character is attributed to both types of isomerizational transformation of 1,3-dioxacycloalkanes on Pt/T, the two processes can be regarded as 1,3-hydrogen migration, and can be formally interpreted according to the doublet mechanism of the multiplet theory [13]. In the case of ester formation, the H atom is transferred from C₂ to C₃ via a four-membered transition state:



In the case of the formation of alkoxyoxo compounds the direction of hydrogen atom transfer is the reverse of the above:



On this basis, *i.e.* considering the changes only formally, in the classification scheme of BALANDIN [13] the two processes can be listed among reactions with the index II K₁₇³ CO HC.

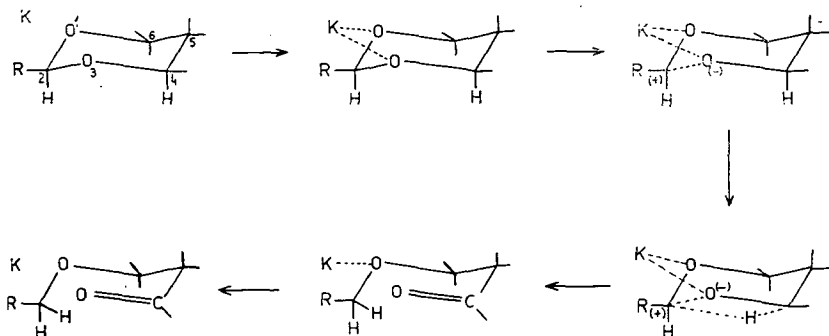
However, our experimental observations to date indicate that the two isomerization processes do not take place by mechanisms of similar type: the formation of the alkoxyoxo compounds is very probably of an intramolecular character, whereas the formation of the esters seems to be a process with an intermolecular mechanism.

Only comparative data of a qualitative nature are available concerning the thermodynamic driving force of the process (the stability of the corresponding esters, but mainly of the cyclic acetals). These data show that, in their thermal decompositions and heterogeneous catalytic transformations, the esters exhibit higher stability than the cyclic acetals [14]. Thus, it may be assumed that in their heterogeneous catalytic transformations the formation of the transition complex necessary for the isomerization of the otherwise reactive 1,3-dioxepanes and 1,3-dioxocanes to esters is prevented by adsorption inhibitions decisively not attributable to energetic reasons, but to reasons closely related with the stereostructures of the rings, *i.e.* to geometric reasons. As regards the mechanisms of the processes observed in the transformation of 1,3-dioxacycloalkanes, further complex experiments are required. The large

amount of hydrogen chemisorbed on the surface of the platinum can take part in complex surface transformations, and in our view it is this circumstance which determines the mechanisms of the processes in most cases. Thus, on Pt/T and Pt/C in helium atmosphere isomerization to the ester does not occur, and other, non-catalytic, but mainly pyrolytic processes are observed.

Mechanism of the formation of alkoxyoxo compounds

In the course of the investigations on the transformations of 1,3-dioxanes, 1,3-dioxepanes and 1,3-dioxocanes on platinum catalysts, the formation of alkoxyoxo compounds was observed in the case of the acetals and the ketals. Although a number of solutions are possible in principle with regard to the mechanism of the process, the formation of the alkoxyoxo compounds can be interpreted in accordance with the RONDESTVEDT mechanism [16], reported in detail previously [15]. On the basis of our experimental data, therefore, the formation of the alkoxyoxo compounds must be attributed to active sites of an electrophilic character on the Pt/T catalyst, and may thus be interpreted by means of 1,3-hydride anion migration according to an intramolecular mechanism:

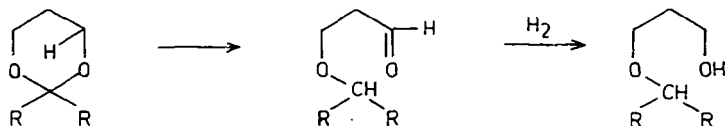


From the results to date of investigations on individual diol monoethers and alkoxyoxo compounds, under the same experimental conditions as for the corresponding dioxacycloalkanes, it may be concluded that two processes accompanied by splitting of the C_2-O bond take place in parallel: namely the formation of alkoxyoxo compounds and the formation of diol monoethers. Otherwise, the primary process character of the isomerizational transformation accompanied by formation of the alkoxyoxo compounds is proved by the fact that it can also be observed at a comparatively low temperature, when the dehydrogenation of the diol monoethers does not yet proceed. Its intramolecular character is proved by the facts that it also takes place in the absence of hydrogen, and that the presence of ammonia inhibits the isomerization, in contrast to the other two main processes (hydrogenolysis, ester formation). At the same time, these latter experimental data indicate that the occurrence of this isomerizational change can be attributed to active sites of an electrophilic character on the Pt/T. Further it should be noted that on Pt/C the isomerization of 1,3-dioxanes to β -alkoxyoxo compounds cannot be observed, which similarly supports the above conclusions.

Hydrogenolysis of 1,3-dioxacycloalkanes

In the course of our experimental work it was found that under the experimental conditions applied in the impulse technique, the acetal-type derivatives of the seven- and eight-membered 1,3-dioxacycloalkanes, and also the six-membered cyclic ketals, very readily undergo splitting on the action of hydrogen in the presence of Pt/T.

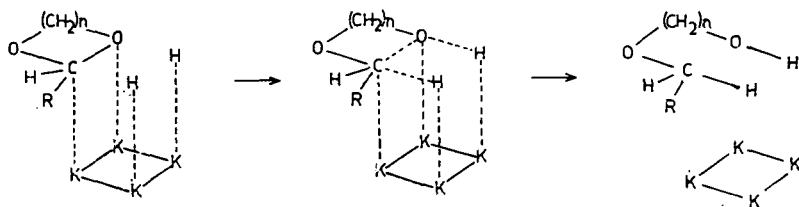
It is understandable that an intermolecular and unconditionally primary character must be attributed to the process of hydrogenolysis, although in principle the formation of the diol monoethers can also be explained by means of consecutive processes: the hydrogenation of the alkoxyoxo compounds formed as intermediates:



However, it is necessary to take into consideration the above statements indicating the parallel nature of the two processes, and that in certain cases the hydrogenolysis proceeds also at low temperatures at which isomerization accompanied by formation of the alkoxyoxo compounds is not observed at all; the primary nature of the hydrogenolysis involving formation of the diol monoethers is then clear-cut.

The high rate of the hydrogenolysis points to a low activation energy (calculated from our experimental results as ~ 4 kcal/mole), in contrast to the isomerization processes accompanied by splitting of the C-H bonds, which have a significantly higher activation energy (18—20 kcal/mole), and therefore they proceed optimally at higher temperatures.

Of the hypotheses relating to the mechanism of the hydrogenolysis, those assuming one- or two-point adsorption of a substrate molecule with simultaneous or consecutive uptake of the two chemisorbed hydrogen atoms can be regarded as most probable. One of the possibilities is illustrated in the following scheme:



Mechanism of isomerization of the 1,3-dioxacycloalkanes to esters

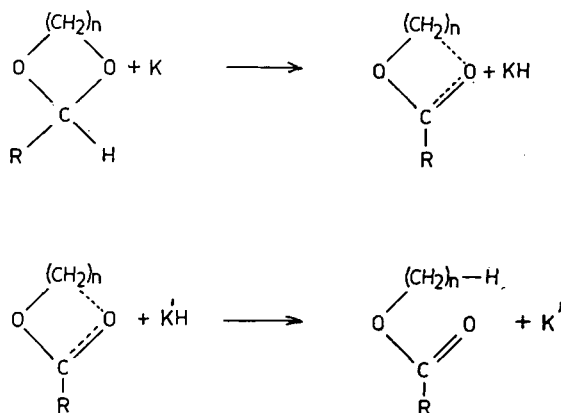
Our experimental data show that of the 1,3-dioxacycloalkanes on Pt/T in the presence of hydrogen, mainly the five- and six-membered acetals are isomerized readily to esters, the stereostructures of which permit the adsorption of the "entire ring". The envelope or half-chair conformation of the 1,3-dioxolanes and the chair conformation of the 1,3-dioxanes each allow the carbon atoms (as the centres affected

in the reaction) adjacent to the oxygen atoms to arrange themselves (in a plane parallel to the imaginary plane of the catalyst in adsorption with a preferred direction). In the case of the above conformations the C_2 -H, C_4 -H and C_6 -H atoms have axial orientations. This state permits dissociative chemisorption of the C_2 -H bond, which in our view is the condition for ester formation. The ready, flexible deformation of the six-membered ring systems with distorted conformations, and also of the seven- and eight-membered ring systems, does not favour the development of the adsorption state with the above-mentioned fixed structure, with the consequence that the ester is not formed.

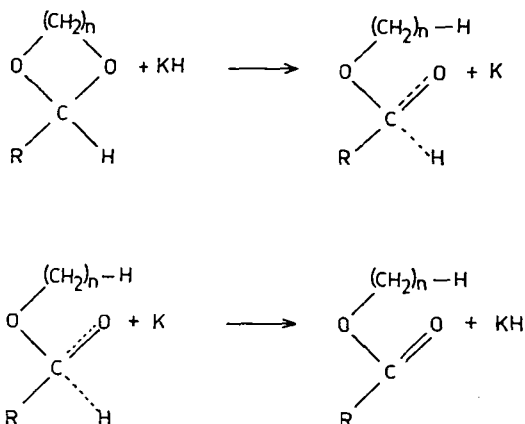
An experimental fact worth of note in the interpretation of the stereochemistry of the transformations is that, in *trans*-1,3-dioxadecalin, *i.e.* in the case of equatorial C-O annellation, the ester formation is an inhibited process.

It has already been mentioned that the mechanism of the ester formation process differs fundamentally from the mechanism of isomerization of the dioxanes involving the formation of alkoxyoxo compounds; an intramolecular character has been attributed to the latter mechanism on the basis of our experimental data obtained so far. The difference can be seen in the fact that the two isomerization processes react in different ways to the same external effect: in a carrier gas stream of helium the ester formation process does not take place, and it is not inhibited by the presence of ammonia; it similarly takes place on other catalysts capable of chemisorbing hydrogen, such as Rh/T, but on Cu/Al there is no ester formation. Therefore, according to our experimental data, isomerization to the ester is achieved with the participation of hydrogen sorbed on the catalyst. Several reaction schemes can be written for this; two essentially different possibilities are given below.

The process starting with splitting of the C_2 -H bond comes to an end with the binding of the sorbed hydrogen to C_4 , which results in the formation of the corresponding ester:



Alternatively, the hydrogen sorbed on the catalyst opens the ring at C_4 , the transition state produced being stabilized in the process of ester formation by the splitting off the hydrogen from C_2 :



The detailed study of the validity of the two mechanisms outlined is now in course, with the application of isotope tracer techniques and IR examinations.

As regards the adsorption of the substrate molecules, it must be unfavourable for hydrogenolysis, *i.e.* the oxygen atoms may not be near the surface of the catalyst. In the absence of kinetic data it naturally cannot be said what part-processes or what step of the transformation can be regarded as rate-determining, but it can be seen that the direction of the transformations is significantly affected by the stereostructure of the molecule of a cyclic acetal, and by the spatial arrangement of the substituents. The non-occurrence of isomerization in the dioxepanes, the considerable difference between the reactivities of the stereoisomeric dioxadecalins, and the behaviour of stereoisomers with different conformations, clearly prove the role of the steric factors.

As regards the reactivity of the 1,3-dioxacycloalkanes it is necessary to single out the substituents on C_2 and C_4 , since these act directly on the C-O and C-H bonds undergoing splitting in the transformation, the bond strengths of which play an important role in the directions and rates of the transformations. In the case of formals the H atoms on C_2 are less mobile, and consequently less reactive. The alkyl groups on C_2 promote the transformation of the dioxanes in the sequence of their positive inductive effects. However, the substituents promote the splitting of the C_2 -H bond and accordingly the isomerization to the ester not only by weakening the strength of the C_2 -H bond, but also by means of their effect on the direction of adsorption of the molecule. The effects of the substituents at C_4 on the rates and directions of transformation of the dioxanes can be interpreted in a similar way. The reason is that the substituents on C_4 affect the strength of the C_4 -O₃ bond. Consequently, the rate of formation of the esters of primary alcohols in the transformation of 4-monosubstituted 1,3-dioxanes is higher than that of the formation of the esters of secondary alcohols produced by splitting of the C_6 -O₁ bond.

The fastest transformation is that of cyclic acetals containing the C_2 -phenyl group; this follows from the special structural features of the molecule (the aromatic ring is in conjugation with the C_2 -O bond), and from the capability of the phenyl group for adsorption. Thus, the presence of the phenyl group can result in transition.

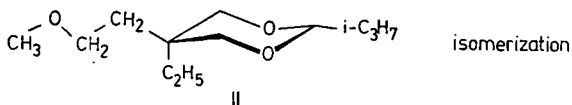
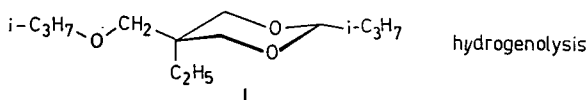
states with structures which favour the splitting of the C₂-O bond, and hence the formation of the corresponding diol monoether and the alkoxyoxo compound. It is possible to interpret in a similar way the rate-increasing effect of the phenyl group at C₄ as regards ester formation.

The determining role of the substituents is best illustrated by the reaction rate sequence, formal < acetal << ketal, observed in the case of the 1,3-dioxanes, and also the various reaction direction affecting this sequence.

Although the studies with stereoisomers of different conformations are still in the initial stage, since establishment of the mechanisms of the processes occurring on the action of the catalysts requires the solution of many part-problems, we consider that even the results available up to now permit a clear interpretation of the processes involved.

The interpretation of the transformation of 1,3-dioxacycloalkanes on Pt/T in the presence of hydrogen requires the establishment of the most fundamental factors which affect the course of the two parallel main processes, the hydrogenolysis and the isomerization to esters.

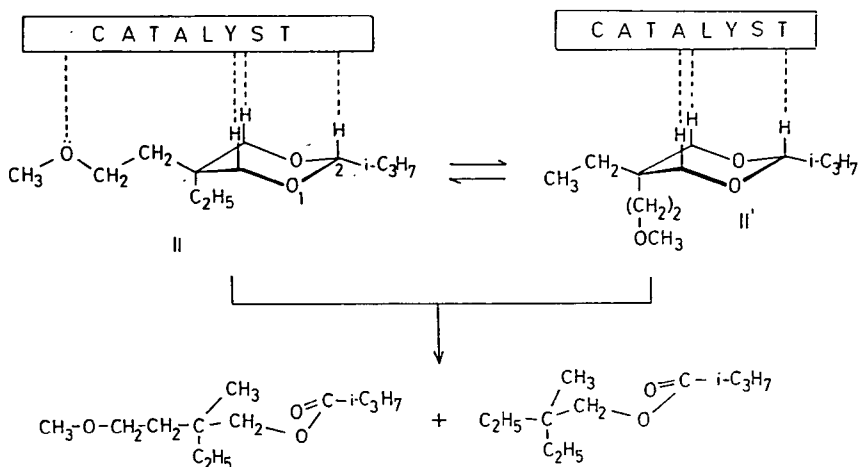
The causes for the two main reactions to occur which can be ascribed to the structure of the molecule can be seen quite clearly in model compounds I and II, for instance:



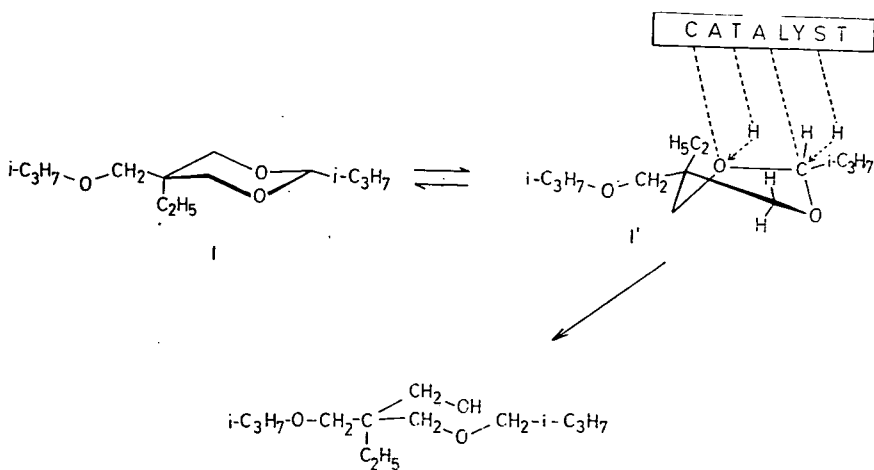
The experimental data obtained on approximately identical Pt/T catalysts in a carrier gas stream of hydrogen show that hydrogenolysis proceeds with great selectivity in the case of I, and ester formation in the case of II. In our view, the different behaviours can be attributed to the fact that, as a result of their different stereostructures, the two molecules are chemisorbed in different geometrical arrangements on the surface of the catalyst.

II may be bonded to the surface along the axial hydrogens of the dioxane ring. This arrangement of the molecule may be promoted by the 5 β -alkoxy group (by means of the non-bonded electron-pair of the oxygen atom). Adsorption of the molecule in such a situation decreases the probability of hydrogenolysis by keeping the C₂, O₁ and O₃ atoms of the dioxane ring away from the surface of the catalyst. At the same time, isomerization to the ester is promoted by means of splitting of C₂-H bond. The above-mentioned oriented adsorption of II is strongly suggested not only by the ester formation, but also by the experimental fact that in the case of compounds containing the equatorial 5 β -alkoxy group, in contrast to compounds containing the 5 α -alkoxy substituent, it was also possible to observe the formation

of products involving hydrogenolysis of the β -alkoxy group:

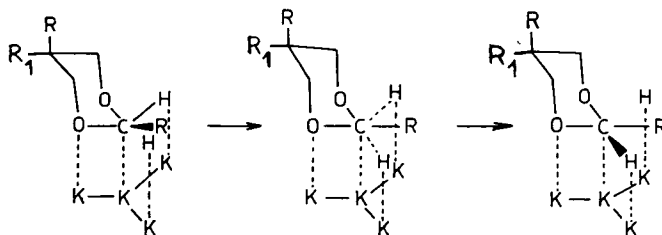


The adsorption of molecule I in a similar way to that of II can be hindered by two factors: (i) its configurational isomerization to the asymmetric isomer with the twisted boat conformation (which, on the basis of our experiments and in the knowledge of the main reaction kinetic parameters of transformations of a similar character observed in the case of alicyclic hydrocarbons [17], is a very fast process), and (ii) the absence of the surface-fixing effect of the *trans* side-chain. The molecule probably undergoes adsorption along the C_2 -O bond, a consequence of which is the hydrogenolysis of the molecule:



Interpretation of the configurational isomerization

Prior to the commencement of our investigations, we found no literature data describing the configurational isomerization of the 1,3-dioxacycloalkanes. Recently, however, two research groups (ELIEL *et al.* [18] and BOGATSKII *et al.* [19]) reported that the 1,3-dioxanes undergo configurational isomerization in the presence of electrophilic catalysts. In the present case the transformation was induced under substantially different conditions, *viz.* on the action of Pt/T. In the process of configurational isomerization the determining role must similarly be attributed to the chemisorbed hydrogen; for under otherwise similar experimental conditions, but in the absence of hydrogen, the occurrence of this isomerizational change cannot be observed. The appearance of isomerization can be ascribed to the configurational change occurring at C₂ on the action of hydrogen, and thus can be interpreted similarly as for S_N2 reactions. Of course, in the process of isomerization the tetrahedral orientation of C₂ is deformed.



This mechanism is supported by the relatively low activation energy of the process (6—8 kcal/mole).

The isomerization in the opposite direction, *i.e.* the isomerization of the asymmetric stereoisomer with the twisted boat conformation, proceeds in an analogous manner. In the long run equilibrium might be established between the two stereoisomers if this were not affected by other, consecutive processes (in this case, isomerization to the ester, or hydrogenolysis).

Understandably, the mechanism of the isomerization process *cis*-1,3-dioxadecalin → *trans*-1,3-dioxadecalin differs essentially from the above, since a change takes place also in the annellation of the two six-membered rings. The different nature of the isomerization is revealed by the fact that, in contrast to the above, the opposite process, *i.e.* the transformation of *trans*-2-methyl-1,3-dioxadecalin to some *cis* isomer, could not be observed. Later investigations in this field must aim at the separation of further stereoisomers, and at the examination of the transformations of these stereoisomers on Pt/T. Study of the above-outlined mechanism of the configurational isomerization is also justified, for adsorption on several points of the substrate molecule is not unconditionally necessary for the occurrence of isomerization.

The experimental results observed so far in connection with 1,3-dioxacycloalkanes on Pt/T are summarized below.

The reaction directions determined by the structures of the compounds and by the experimental conditions have been recognized to be effected by the main parameters. The formation of alkoxyoxo compounds is attributed to active sites of

an electrophilic character on the Pt/T, and interpreted by an intramolecular mechanism.

The roles of the platinum catalyst and the hydrogen on it are confirmed by the occurrence of hydrogenolysis, ester formation and configurational isomerization, and thus the mechanisms of the processes are probably of an intermolecular character.

Several factors resulting from the structures of the substrate molecules and affecting the main processes have been discerned, e.g. the number of ring atoms, the nature, number, position and configuration of the substituents, the direction of adsorption on the substrate molecule, the bond strengths of the bonds of the substrate molecule, etc. In order to understand the details of the mechanism, it is necessary to carry out complex examinations of the system catalyst — hydrogen — substrate by various methods [20].

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МЕХАНИЗМ ПРЕВРАЩЕНИЙ 1,3-ДИОКСАЦИКЛОАЛКАНОВ В ПРИСУТСТВИИ ПЛАТИНОВОГО КАТАЛИЗАТОРА

М. Барток, Й. Апюк

В сообщении подводятся итоги изучения механизма изомеризации и гидрогенолиза 1,3-диоксациклоалканов с обсуждением экспериментальных результатов.

Образование алкокси-оксосоединений при изомеризации 1,3-диоксациклоалканов можно истолковывать по механизму внутримолекулярного характера, посредством электрофильных центров катализатора Pt/T. Изомеризация в сложные эфиры, конфигурационная изомеризация и гидрогенолиз происходят только в присутствии хемосорбированного водорода, следовательно, механизм этих процессов носит межмолекулярный характер.

CONTACT CATALYTIC REACTIONS WITH CO-CATALYTIC PARTICIPATION OF HYDROGEN

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(Received February 17, 1975)

On the basis of our experiments, the co-catalytic role of the hydrogen was extended to different types of carbon compounds.

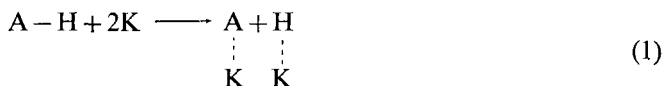
The purpose of this report is to generalize a correlation concerning the co-catalytic role of hydrogen. This generalization has been achieved through demonstrations of several new catalytic reactions taking place in the presence of hydrogen, some of which are described in the literature, and some were studied by us.

In several papers [1—9] there are some references to the fact that, in the case of hydrocarbons, chemisorbed hydrogen has an important role in the catalytic processes taking place on certain metal catalysts. This role exists even when the participation of hydrogen as a reactant cannot be directly observed in the stoichiometry of the reaction. The literature is not consistent in this respect; namely, sometimes it affords a view on detailed investigations but in some other cases, no remark concerning the role of hydrogen is made.

In cases of chemical transformations on catalysts sorbing hydrogen, according to our hypothesis, hydrogen has a determinant role even when its participation cannot be observed stoichiometrically in the chemical process. We had supposed earlier [10] and later also proved experimentally in several cases [11, 12], the co-catalytic role of the chemisorbed hydrogen.

Our hypothesis concerning an $A-H \rightarrow B-H$ reaction scheme (where $M_{A-H} = M_{B-H}$) is given below — without a claim of going into details here.

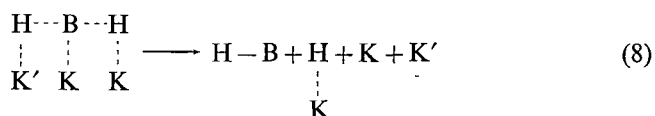
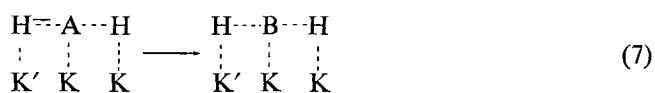
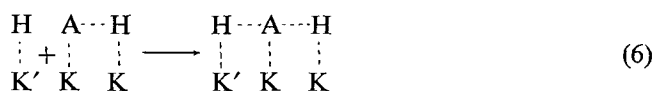
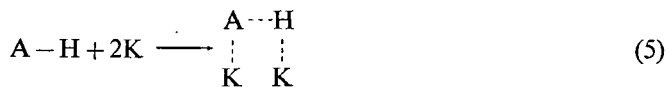
In case of a dissociative mechanism:





K, K' denote centres of the catalyst participating in the reaction.

In case of an associative mechanism:



Some experimental results described in the literature also served as basis of the above generalization relating to the role of hydrogen. According to these results, the participation of hydrogen in certain processes is experimentally proved on different metal catalysts capable of chemisorbing hydrogen, both with and without carriers. These are:

1. Isomerization of saturated and alicyclic hydrocarbons [5, 7—9, 13, 14];
2. Racemization of saturated hydrocarbons [15];
3. Dehydrocyclization and aromatization of saturated hydrocarbons [16—19];
4. Configurational isomerization of alicyclic hydrocarbons [6, 20, 21];
5. *Cis-trans* isomerization of olefins [22];
6. Migration of the double bond in olefins [23—25];
7. Configurational isomerization of the daminocyclohexanes [26];
8. Cyclodehydration of aminoalcohols, and de-amination of polyamines [27, 28].

The mechanism of the isomerization of unsaturated hydrocarbons and that of some of their derivatives can also be interpreted in the same way, under homogeneous catalytic conditions, in the presence of transition metal complexes [29].

We have studied the transformations of heterocyclic compounds containing oxygen, taking place under the influence of platinum metals. In the course of this investigation, we have proved hydrogen participation in the chemical processes during the isomerization of the following types of compounds: isomerization of oxacycloalkanes to oxo compounds [12, 30], isomerization of 1,3-dioxolanes and 1,3-dioxanes to esters [31, 32], and configurational isomerization of 1,3-dioxanes [11].

In the absence of hydrogen, these transformations fail to take place on the metal catalysts investigated. The mechanism of the above processes can be explained according to the general scheme sketched previously.

We reviewed the co-catalytic role of hydrogen in the heterogeneous catalysis, in spite of EIDUS' more general view [33] regarding the role of stoichiometric components — and not only about that of hydrogen. We found this necessary for two reasons. On the one hand, we showed several reactions in which the co-catalytic participation of hydrogen was previously unknown; on the other hand, our purpose was to emphasize the general character of the phenomenon. This generalization concerns the isomerization reactions of all kinds of carbon compounds as well as a number of catalysts chemisorbing hydrogen which are, at the same time, capable of performing dissociative chemisorption of the substrates involving hydrogen splitting.

Our further aim is to study some general correlations concerning the co-catalytic role of hydrogen, on certain types of catalysts and compounds not investigated so far. It is also necessary to examine what types of hydrogen species play roles in the case of each catalyst and substrate.

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КОНТАКТНО-КАТАЛИТИЧЕСКИЕ РЕАКЦИИ
С СОКАТАЛИЗАТОРНЫМ УЧАСТИЕМ ВОДОРОДА

М. Барток

На основании полученных экспериментальных данных, сокаталитическое участие водорода распространено на реакции различных органических соединений.

A kiadásért felelős: Dr. Leindler László
1975

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