

THE THERMAL DECOMPOSITION OF ETHYL NITRITE. I

Rate Pressure Relations

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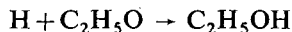
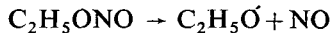
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Facts are described which made the reinvestigation of the thermal decomposition of ethyl nitrite justifiable in spite of the fact that numerous studies have already been carried out in this respect. Some problems concerning the mechanism of the reaction are mentioned. The experimental apparatus, the method of preparation and purification of the substances and the analytical procedure are also described. From the experimental data it follows that the thermal decomposition of ethyl nitrite is a process taking place according to the first order. For the overall activation energy of the process 36,69 kcal was obtained and the value of the activation constant was $4,58 \cdot 10^{13} \text{ sec}^{-1}$.

Introduction

Although the thermal decomposition of alkyl nitrites has been the subject of much study, some very important aspects of the mechanism of the decomposition are still not very clear. Since some steps of the thermal decomposition of organic compounds influenced by nitric oxide occur in the reactions of the decomposition of nitric esters, it might be of relevance to clear up the precise mechanism of the latter in the better understanding of the inhibition of free-radical reactions by nitric oxide.

The first investigations for the thermal decomposition of alkyl nitrites were carried out by STEACIE and SHAW [1—4]. The thermal decomposition of ethyl nitrite has been studied by these authors in a conventional static system in the temperature range 190—240°C at pressures of the order 50—550 torr. The reaction was followed by pressure measurement and by analysis. The main reaction products were found to be nitrogen monoxide, carbon monoxide, acetaldehyde and ethanol. The mechanism suggested by these authors



does not account for the products and the final pressure increase found experimentally. The percentage pressure increase — as it can be seen from Table I — never reached the 100% value as it could be expected on the basis of the mechanism.

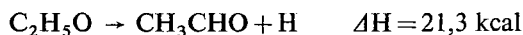
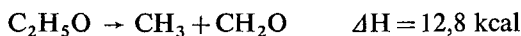
The investigation carried out by RICE and RODOWSKAS [5] STEACIE and CALDER [6], STEACE and KATZ [7], and particularly by GRAY [8] gave more and more evidence for the important role of alkoxy radicals in the decomposition of alkyl nitrites.

Table I
The final pressure increases found by STEACIE
and SHAW [1—4]

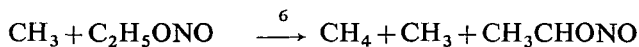
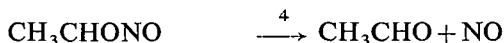
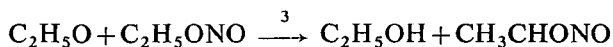
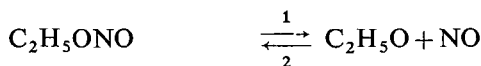
Temperature C°	Initial Pressure cm	Maximum Pressure Increase (per cent)
199,9	238,9	88,7
209,8	134,8	90,3
209,8	184,8	83,3
219,9	284,0	90,7
219,9	333,6	83,3
230,2	228,5	84,2
230,2	232,1	85,3
240,7	279,6	80,7

mean value: $\overline{85,8}$

GRAY's results made it possible to determine the activation energy of the decomposition of C_2H_5O radicals



and on the basis of the activation energies the first type of the decomposition of C_2H_5O radical seems to be more likely than the second one. This assumption was supported by ADLER, PRATT, GRAY [9] who were able to detect the presence of aldehyde of lower carbon number than the corresponding alkoxy radical in the products of the decomposition of nitrites. The results obtained in the study of the decomposition of alkyl nitrites [1—9] led to the proposal of the mechanism — written for the case of the ethyl nitrite — and which became known and referred to later on as the STEACIE—RICE mechanism



Steps (5) and (6) were observed only at temperatures of about 400°C and at very low pressures [5], so at lower temperatures only the first three steps seem to be important. The attention was first called to the existence of step (2) by POLLARD, PEDLER and HARDY [10]. These authors studied the reaction between NO_2 and C_2H_5ONO and found $C_2H_5ONO_2$ in the products. The formation of ethyl nitrate should take place in the $C_2H_5O + NO_2 \rightarrow C_2H_5ONO_2$ reaction. Since the ethyl nitrate decomposes at the temperature applied by the authors (190°C) its concentration varies according to a maximum curve as it is shown in Table II.

Table II

The variation in the pressure of ethyl nitrate formed in the reaction between NO_2 and $\text{C}_2\text{H}_5\text{ONO}$

Time of Reaction (min)	2,0	2,8	3,5	5,5	7,5	11	15	25	45	60
Pressure of Ethyl Nitrate (mm mercury)	1,8	2,5	3,9	4,4	5,1	5,3	4,6	3,4	0,9	0

On the analogy of this reaction the $\text{C}_2\text{H}_5\text{O} + \text{NO} \rightarrow \text{C}_2\text{H}_5\text{ONO}$ reaction was postulated and experimentally substantiated by LEVY [11] having studied the thermal decomposition of diethyl peroxide in the presence of nitric oxide and ethyl nitrite. As it can be seen from Table III in the reaction between nitric oxide and $\text{C}_2\text{H}_5\text{O}$ radical produced by the decomposition of diethyl peroxide ethyl nitrite formed.

Table III

Product of the decomposition of diethyl peroxide (DEP) in the presence of ethyl nitrite and nitric oxide at 181°C

Experiment	DEP	NO	$\text{C}_2\text{H}_5\text{ONO}$	Time (min)	Final Pressure of $\text{C}_2\text{H}_5\text{ONO}$	$\text{C}_2\text{H}_5\text{ONO}$ Produced	Yield %
1	12	22	—	6,0	14,1	14,1	59
2	11,5	44,0	—	6,0	15,1	15,1	66
3	11,0	22,0	10,5	4,0	22,8	12,3	56
4	11,0	22,0	—	4,0	12,2	12,2	56
5	12,8	—	20,0	4,0	20,2	0,2	—
6	14,0	—	20,0	4,0	20,9	0,9	—

From this study it also became clear that the hydrogen abstraction from the ethyl nitrite molecule by $\text{C}_2\text{H}_5\text{O}$ radical does not take place, so the step (3) postulated in the STEACIE—RICE mechanism should not play a role in the decomposition of ethyl nitrite. To substantiate this assumption the thermal decomposition of ethyl nitrite has been reinvestigated by LEVY [12] in the temperature range $161\text{--}201^\circ\text{C}$, at pressures of the order of 10—50 torr. The principal reaction products found by LEVY were acetaldehyde, nitric oxide, nitrous oxide together with the lesser amount of ethanol, hydrogen cyanide and water; mass spectrographic analysis, however, showed neither methane nor formaldehyde. The most striking result of LEVY's experiments is the appearance of nitrous oxide as a significant reaction product. CARTERS and TRAVERS [13] and PURKIS and THOMPSON [14] observed the formation of nitrous oxide in the decomposition of other nitrites, too. LEVY has studied the effect of reaction products on the decomposition. These results are listed in Table IV. From the data of Table IV it can be seen that added nitric oxide does not bring about a change in the value of specific rates, but added acetaldehyde gives rise to an increase. The effect of added nitric oxide and acetaldehyde on product distribution is shown in Table V, from which it can be seen that added nitric oxide results in an increase in the yield of acetaldehyde towards a limit of 100% and in that of nitrous oxide towards a limit of 50%. The addition of acetaldehyde eliminates

Table IV
The kinetics of the thermal decomposition of ethyl nitrite at 181 °C

Expt.	C ₂ H ₅ ONO	Initial Pressures (mm) Additive	Time (min.)	Reaction %	10 ⁵ ·k sec ⁻¹ *
1	16,7	— — — —	150	40,5	57,8
2	23,0	— — — —	200	50,8	59,3
3	19,7	93,0 NO	145	39,0	57,0
4	30,1	14,0 NO	200	49,2	56,5
5	30,1	34,0 NO	200	49,2	56,5
6	26,8	— — — —	300	68,1	63,6
7	18,8	— — — —	300	67,1	62,0
8	44,7	20,5 NO	300	64,3	57,3
9	44,7	— — — —	400	80,2	67,7
10	35,0	34,0 NO	450	79,4	57,3
11	31,0	30,0 CH ₃ CHO	126	52,6	97,0
12	31,0	50,0 CH ₃ CHO	126	57,0	110,3

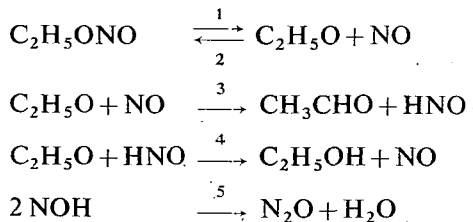
* First order rate constant, 2,303/t ln P₀/P

Table V
The products of the thermal decomposition of ethyl nitrite at 201 °C

Expt.	Time (min)	Initial Pressures		Reaction %	Yield %	
		C ₂ H ₅ ONO	Additive		CH ₃ CHO	N ₂ O *
1	10	29,6	—	20,0	83 ± 5	25 ± 5
2	15	29,6	—	27,5	87 ± 5	22 ± 4
3	30	29,6	—	51,4	70 ± 3	21 ± 2
4	76	29,6	—	84,2	62 ± 1	19 ± 1
5	245	59,5	—	100,0	60 ± 1	19,5 ± 5
6	10	21,2	33 NO	16,0	100 ± 8	50 ± 7
7	15	19,2	39 NO	26,6	89 ± 5	—
8	15	18,2	101 NO	24,1	100 ± 5	—
9	20	20,6	29 NO	34,5	87 ± 6	51 ± 5
10	30	33,5	33 NO	42,0	97 ± 3	48 ± 3
11	45	20,6	29 NO	59,0	86 ± 3	48 ± 3
12	45	18,2	101 NO	75,2	96 ± 4	—
13	76	33,5	32 NO	77,6	81 ± 2	49 ± 1
14	15	20,0	24,5 CH ₃ CHO	47,0	—	—
15	30	20,0	58,0 CH ₃ CHO	78,4	—	—

* 2 (moles nitrous oxide found/moles ethyl nitrite reacted)

nitrous oxide as a product. To account for these results, the mechanism for the pyrolysis of ethyl nitrite suggested by LEVY is:



which gives a rate expression for the disappearance of the ethyl nitrite:

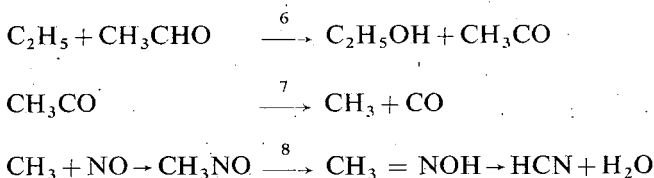
$$-\frac{d \ln [\text{C}_2\text{H}_5\text{ONO}]}{dt} = k_1 \frac{k_3[\text{NO}] + k_4[\text{NOH}]}{(k_2 + k_3)[\text{NO}] + k_4[\text{NOH}]}$$

In the presence of added nitric oxide — assuming that $k_3[\text{NO}] \gg k_4[\text{NOH}]$ and $(k_2 + k_3)[\text{NO}] \gg k_4[\text{NOH}]$ — the rate expression becomes

$$-\frac{d \ln [\text{C}_2\text{H}_5\text{ONO}]}{dt} = \frac{k_1 k_3}{k_2 + k_3}$$

i. e. the rate independent of the concentration of the nitric oxide which is in agreement with LEVY's experiments. The mechanism is able to account for the effect of added nitric oxide on the product distribution, however, not for the yield of nitrous oxide. The yield of the latter should reach 100% in the presence of added nitric oxide on the basis of LEVY's mechanism. To explain the yield of 50% found experimentally, LEVY has taken into consideration the consumption of HNO radical in the step $2 \text{NOH} \rightarrow 2 \text{NO} + \text{H}_2$, too. The fact that LEVY could not detect H_2 in the products contradicts the assumption of this step.

The effect of added acetaldehyde on the product distribution is explained by adding the following steps to the scheme:



It was found that added acetaldehyde increased the yield of hydrogen cyanide from 2% to 5—10%. It is rather surprising that LEVY could not detect carbon monoxide, all the more, since its yield, according to the mechanism, should be roughly equal to that of hydrogen cyanide.

The questions that arise in connection with the mechanism suggested by LEVY and other authors may be listed as follows:

a) LEVY's mechanism does not satisfactorily account for the 50% limiting yield of nitrous oxide in the presence of added nitric oxide; it should be 100%.

b) It is difficult to reconcile the mechanism suggested with the degree of pressure change observed experimentally.

c) On the basis of LEVY's mechanism the elimination of the nitrous oxide production by acetaldehyde cannot be explained.

d) There is a contradiction between the mechanism suggested and the existence of products such as hydrogen, methane, formaldehyde, and carbon monoxide.

The above mentioned problems made it desirable to reinvestigate the thermal decomposition of ethyl nitrite which was carried out in the temperature range of 200—230°C and at pressures in the order of 20—220 torr.

Experimental

The experiments were carried out in a conventional static system. The cylindrical Pyrex reaction vessel of 250 ml capacity was enclosed in an electrically heated furnace, the temperature of which was controlled to within $0,2^{\circ}\text{C}$. The reaction was followed by pressure measurements and by determination of the nitrite concentration gas chromatographically. The products of the reaction were analyzed by means of a Carlo Erba Fr. Mod. C gas chromatograph containing a thermal conductivity and a flame ionizing detector. The samples extracted from the reaction vessel by means of a rotary sampling valve were analyzed on two columns. One of them was packed with molecular sieve 5A and was used for the analysis of light-components of the products, the other was packed with $\beta\beta'$ -oxypropionitrite supported on fire brick and was used for the analysis of the remaining products. Dry nitrogen and helium were used as carrier gases.

All the reactants were carefully purified. *Ethyl nitrite* was produced by the method of STEACIE and SHAW and was dried over CaCl_2 for several days and finally distilled. The middle fraction of the distillation was collected and subjected to repeated trap-to-trap distillation under vacuum and stored in a bulb (temperature maintained at -5°C) connected to the vacuum apparatus. *Nitric oxide* was produced by the method of WINKLER from KNO_2 and HJ. The evolving gas was bubbled through traps containing sulfuric acid and KOH respectively, and after repeated distillation at low temperature under vacuum the product was introduced into the storing bulb. *Acetaldehyde and Ethanol*. P. a. productions of Reanal were used and purification was performed by the same procedure as described above. *Propylene* was produced by dehydration of isopropyl alcohol taking place at the temperature of 390°C in a tube reactor containing activated alumina. The evolving propylene was led through four traps; the temperature of the first trap and that of the third was maintained at -45°C , the second trap and the fourth contained 50% KOH solution, and P_2O respectively. The gas purified in this manner was subjected to repeated distillation under vacuum.

Results

a) *Effect of changes in the initial pressure on the decomposition of ethyl nitrite.*

For the investigation of the effect of initial pressure experiments were carried out at 210°C and at pressures of 20, 60, 100, 140, 180 and 220 torr. The results are shown in Fig. 1. It seemed necessary to check whether the reaction rate determined on the basis of the pressure increase corresponds to the rate of disappearance of the nitrite. This seemed questionable on the strength of the data from literature, since the final pressure change — as was reported by the majority of the authors — varied between 80—90%. For this purpose the concentration of ethyl nitrite has been determined at different stages of the reaction by a gas chromatograph and the results were plotted in Fig. 2. Since the final pressure change according to our experiments was found to be 85,1% with good reproducibility, it was concluded that the decomposition of 1,176 torr nitrite gives rise to a pressure change of 1 torr. On the basis of this assumption the concentration of nitrite was calculated at different stages of the reaction and the results were plotted in Fig. 2 in which the measured and

calculated values showed good agreement. From the results of the experiments carried out at different initial pressures the order of the reaction was determined. To check the validity of the first order stated by many authors, the $\log P-t$ values were plotted in Fig. 3. Fig. 3 clearly shows that the reaction is of first order up to

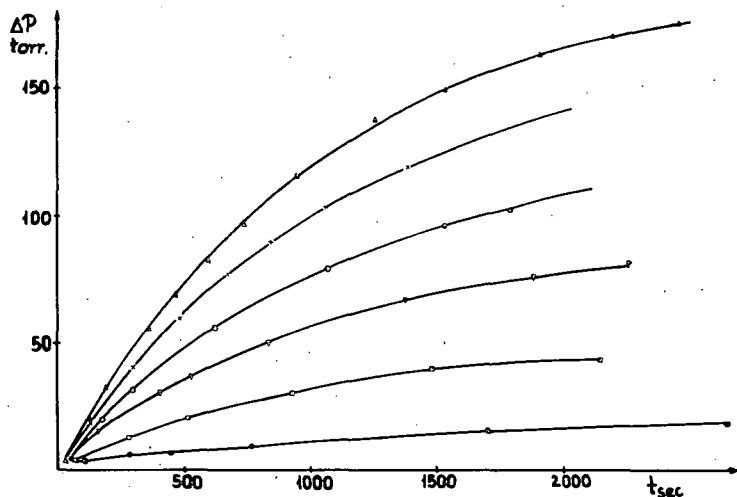


Fig. 1. $\Delta P-t$ curves at 210°C
 Δ 220 torr; \times 180 torr; \odot 140 torr; ∇ 100 torr;
 \square 60 torr; \otimes 20 torr;

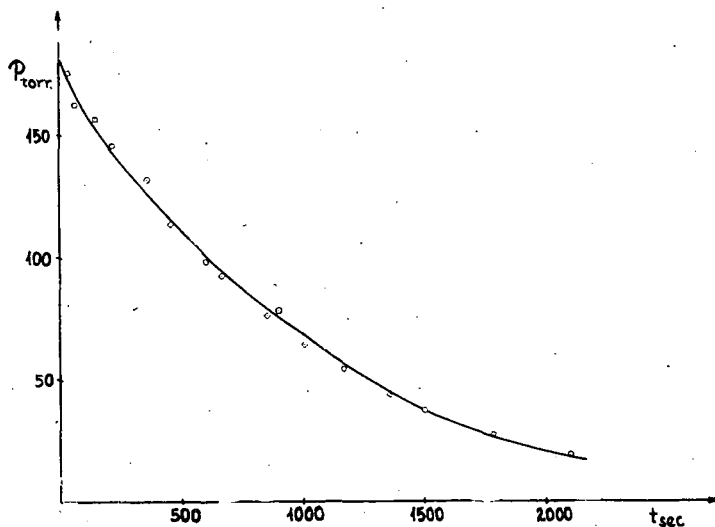


Fig. 2. Calculated and measured nitrite pressures plotted against time, $P_0=180$ torr; $T=210^\circ\text{C}$;
 \odot gas chromatographically measured
 \square calculated from pressure measurements

the point where 60—70% of the nitrite decomposes. This can also be seen from Table VI, where the rate constants calculated by first order are given. The graphically determined rate constants from the different initial pressures from Fig. 3 and those of the calculated ones are given in Table VII.

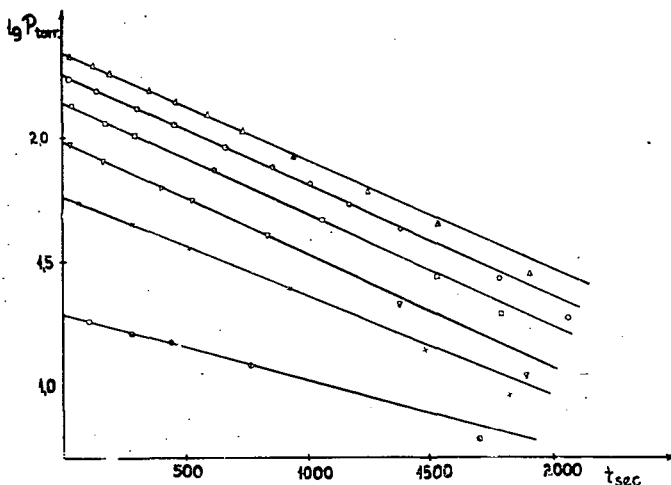


Fig. 3. The plot of the logarithm of pressures of nitrite against time; $T=210^{\circ}\text{C}$; Initial Pressures: 220, 180, 140, 100, 60, 20 torr

Table VI

First order rate constant, $T=210,2^{\circ}\text{C}$, $P=220$ torr

t_{sec}	ΔP_{torr}	Reaction %	$k \cdot 10^3 \text{ sec}^{-1}$
24	4,2	2,255	0,948
118	20,8	11,16	1,005
194	33,1	17,78	1,208
358	56,4	30,27	1,006
467	69,8	37,48	1,005
593	83,6	44,89	1,001
533	97,9	52,57	1,017
944	116,2	67,65	1,036
1234	135,3	72,65	1,036
1536	150,6	80,87	1,070
1909	164,5	88,33	1,119
2199	171,7	92,2	1,152
2465	177,0	95,05	1,219

mean value: 1,0478

b) *Effect of temperature on the rate of the decomposition*

The effect of temperature has been investigated for all of the already mentioned initial pressures at temperatures 200, 210, 220 and 230°C. The effect of the temperature

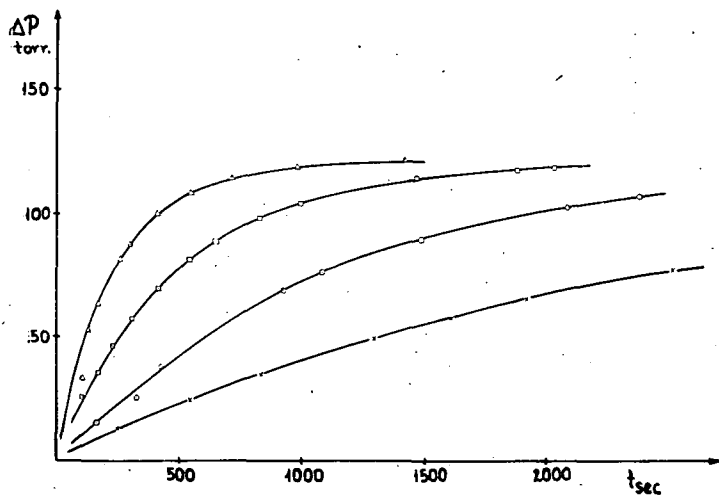


Fig. 4. Effect of temperature on the rate of the reaction,
 $P_0 = 140$ torr, $T = 200^\circ \times$, $210^\circ \circ$, $220^\circ \square$, $230^\circ \triangle$

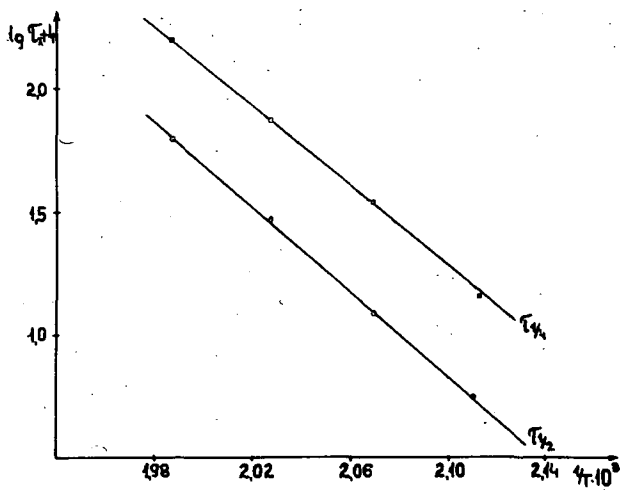


Fig. 5. The temperature dependence of half-times

is illustrated in Fig. 4. The temperature dependence of the reciprocals of half-times is shown in Fig. 5 and that of the calculated rate constants in Fig. 6. The activation energies were determined from the slopes of the straights of Fig. 5. and Fig. 6. The values of action constants (A) and that of the activation energies (ΔH) determined by

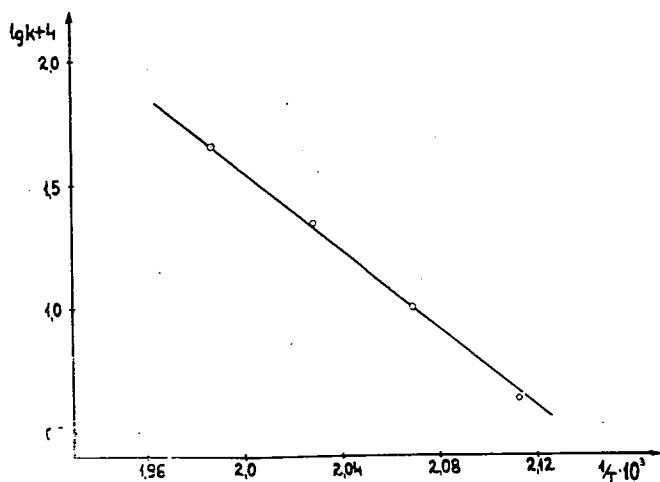


Fig. 6. The temperature dependence of rate constants

Table VII

First order rate constants at various initial pressures $T=210^\circ\text{C}$

P_0 torr	$k \cdot 10^3 \text{ sec}^{-1}$ graphically	$k \cdot 10^3 \text{ sec}^{-1}$ calculated
220	1,006	1,011
180	1,031	1,020
140	1,020	1,038
100	1,043	1,023
60	0,938	1,023
mean value:	1,008	1,0154

the method of the least squares are:

	ΔH	A
From the temperature dependence of k :	36,60 kcal	$3,38 \cdot 10^{13} \text{ sec}^{-1}$
From the temperature dependence of $t_{1/2}$:	36,78 kcal	$5,78 \cdot 10^{13} \text{ sec}^{-1}$
mean value:	<u>36,69 kcal</u>	<u>$4,58 \cdot 10^{13} \text{ sec}^{-1}$</u>

These values are in good agreement with LEVY's 37,5 kcal and $6,10 \cdot 10^{13} \text{ sec}^{-1}$ values obtained for the activation energy and action constant.

The complete form of the rate constant of the overall process is:

$$k = 4,58 \cdot 10^{13} \exp(-36,69/1,98T) \text{ sec}^{-1}.$$

Studying the effect of temperature of the value of final pressure increase, no differences were found in the data of measurements taken at various temperatures.

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ТЕРМИЧЕСКОЕ РАЗЛОЖЕНИЕ ЭТИЛНИТРИТА. I

Соотношения скорости и давления

Ф. Марта и Л. Шэрзи

Описываются факты которые поддерживают важность изучения термического разложения этилнитрита, несмотря на факт что значительное число работ были уже выполнены здесь. Упоминаются некоторые проблемы о механизме реакции.

Оборудование, метод приготовления и очищения веществ а также аналитический процесс определения продуктов также приведены.

Из данных экспериментов видно что термическое разложение этилнитрита является процессом протекающим по первому порядку. Общее значение энергии активации 36,69 ккал и константа реакции: $4,58 \cdot 10^{13} \text{сек}^{-1}$.