

THE THERMAL DECOMPOSITION OF *n*-PROPYL NITRITE

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A recent investigation of the thermal decomposition of ethyl nitrite has been extended to include the analogous decomposition of *n*-propyl nitrite. The order of the reaction was found to be 1,25, and the overall activation energy 36,6 kcal. The products of the decomposition were found to be nitric oxide, nitrous oxide, propionaldehyde, propanol, water and formaldehyde. The effect of nitric oxide, propionaldehyde, propylene and hydrogen on the rate of the decomposition and on the product-distribution has also been investigated. The results are compared with those of the decomposition of ethyl nitrite and a similar mechanism is suggested which is able to explain the main features of the reaction.

Among various authors there is a general agreement that the alkoxy radicals play an important role in the gas-phase pyrolysis of alkyl nitrites. The authors are of different opinion, however, concerning the reactions of alkoxy radicals. The abstraction of hydrogen atom by these radicals from the parent nitrite molecule postulated by STEACIE and his co-workers [1], RICE and RODOWSKAS [2] can be neglected in the light of LEVY's results [3].

The decomposition of alkoxy radicals has also been postulated by many authors [1, 2, 3, 4, 5]. According to their assumption the aldehyde of lower carbon number than the corresponding alkoxy radical should be present in the products of the decomposition of nitrites. In the case of the decomposition of ethyl nitrite, for instance, the products should contain formaldehyde when the decomposition of ethoxy radicals takes place. This product was found neither by LEVY [6] nor during the experiments carried out in this laboratory [7, 8, 9]. It seems very likely that a fission of alkoxy radicals having higher carbon number than the ethoxy radicals may occur during the pyrolysis of alkyl nitrites. This assumption seems to be supported by LEVY [10] who found formaldehyde in the decomposition products of *n*-propyl nitrite, but detailed analyses of the decomposition products were not made. From this point of view it seemed worth-while investigating the thermal decomposition of *n*-propyl nitrite which was carried out in the temperature range of 190–220°C and at initial pressures of 60–180 torr.

Experimental

The apparatus and the procedures were the same as described earlier [7, 8]. The samples extracted from the reaction vessel were analyzed by a Carlo Erba Fr. Mod. C. Gas Chromatograph on a column of 80 cm long and of 5 mm internal diameter packed with 20% of ethyl cyano ether supported on fire brick of 80 mesh. All the reactants were carefully purified. Propyl nitrite, nitric oxide and propylene were produced and purified as described earlier [7, 8]. Propionaldehyde was produced

by oxidation of propanol with chromic acid. The fraction obtained by several fractional distillation was subjected to repeated distillation at low temperatures under vacuum. Hydrogen taken from a steel flask was deoxygenated with pyrophoric copper on a silica gel carrier [11]. The gas was then transferred into the storing bottle through traps cooled with liquid air.

Results

(a) Effect of initial pressure and of temperature on the decomposition of propyl nitrite

For the investigation of the effect of initial pressure experiments were carried out at 200°C and at pressures of 60, 100, 140, and 180 torr. The results are shown in Fig. 1.

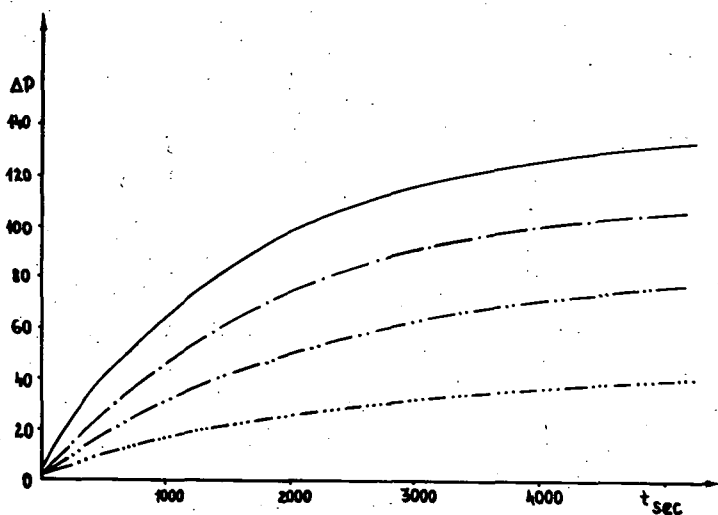


Fig. 1. $\Delta P-t$ curves at 200°C and at initial pressures of 60, 100, 140, 180 torr, — · · · —, — — —, — — —, —, respectively

From the results of experiments carried out at different initial pressures the order of the reaction was determined. Applying the van't Hoff's method, the overall order was found to be 1.25. The rate constants calculated on the basis of first and 3/2 order rate equation show a definite trend of decrease and increase resp., as can be seen from Table I. For the characterization of the rates it seemed more reasonable — taking into consideration the observed discrepancies — to use the times belonging to the same stages of the reaction instead of the rate constants.

The effect of temperature has been investigated for all of the already mentioned initial pressures at temperatures of 190, 200, 210, and 220°C. The results of these experiments are illustrated in Fig. 2.

The activation energy was determined from the temperature dependence of one eighth, one quarter and half-times shown in Fig. 3.

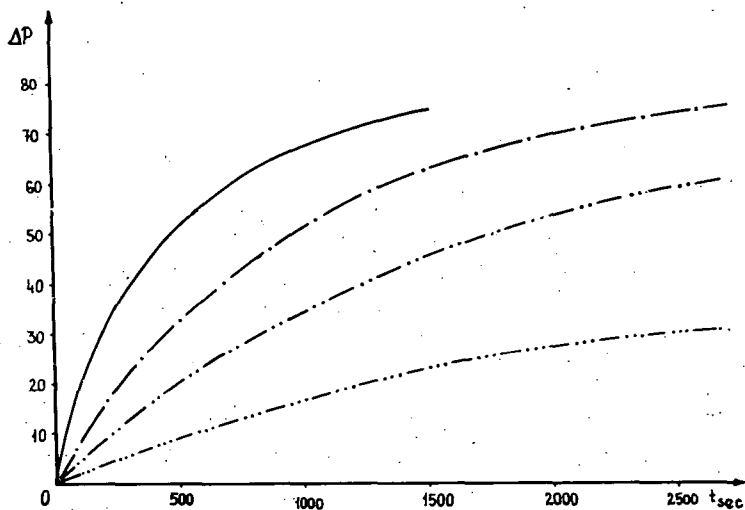


Fig. 2. $\Delta P-t$ curves at an initial pressure of 100 torr and at temperatures:
 190°, - · - · - 200°, - - - 210°, — 220 °C

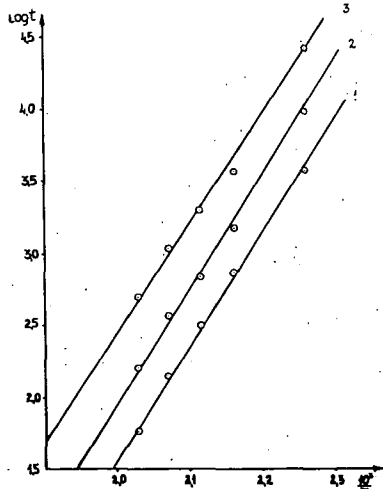


Fig. 3. Dependence of the one eighth (1), one quarter (2), and half times (3) on the temperature

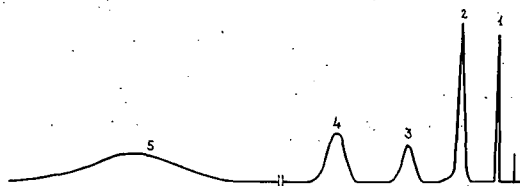


Fig. 4. The chromatogram of the products at a conversion of 94,6%, $P_0=100$ torr; $T_0=200$ °C, carrier gas: helium,

Sensitivities:

(1) NO + N ₂ O	128 mV
(2) propyl nitrite	128 mV
(3) formaldehyde	32 mV
(4) propionaldehyde	32 mV
(5) propyl alcohol	32 mV

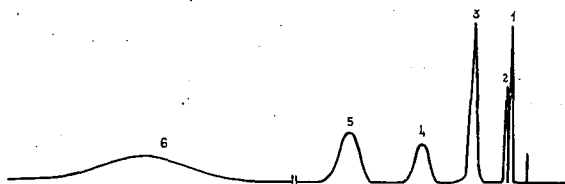


Fig. 5. The chromatogram of the products at a conversion of 94,6%, $P_0=100$ torr, $T_0=200$ °C, carrier gas: nitrogen,

Sensitivities:

(1) NO	32 mV
(2) N ₂ O	32 mV
(3) propyl nitrite	32 mV
(4) formaldehyde	4 mV
(5) propionaldehyde	4 mV
(6) propanol	4 mV

Table I
Rate constants calculated according to first
and 3/2 orders

t_{sec}	% decomp.	$10^{-4} \cdot k_1$	$10^{-5} \cdot k_{3/2}$
404	15	4,05	4,21
509	18	3,94	4,21
622	21	3,85	4,08
826	27	3,84	3,80
1105	33	3,52	3,89
1586	43	3,56	4,02
1905	48	3,45	4,08
2675	59	3,34	4,22
3087	64	3,28	4,31
3578	68	3,18	4,28
4581	75	3,02	4,36

The values of activation energy and that of the activation constant were found to be 36,6 kcal and $3,16 \times 10^{13}$ resp., in good agreement with the data to be found in the literature.

(b) *The products of the reaction and their effect on the decomposition*

The products of the reaction we were able to identify gas chromatographically were nitric oxide, nitrous oxide, propionaldehyde, propanol, formaldehyde and water. With the exception

of water quantitative analyses of these products were made at different stages of the reaction. Using helium as carrier gas it was possible to determine the yield of propionaldehyde, propanol, formaldehyde, propyl nitrite and the sum of nitrogen oxides from one sample as is shown in Fig. 4.

Nitrogen oxides could be separated and determined on a column packed with molecular sieve 5A, and on the column mentioned earlier but using nitrogen as carrier gas. The chromatogram obtained in the latter case is shown in Fig. 5.

The changes in the partial pressures of the products and of propyl nitrite determined from the analysis are shown in Fig. 6. From the results of the analysis the material-balance of the products of the decomposition was determined and listed in Table II.

The effect of products such as nitric oxide and propionaldehyde as well as that of hydrogen and propylene on the decomposition of propyl nitrite has also been studied.

Table II
Material balance of the decomposition
products of propyl nitrite
 $P_0 = 100$ torr; $T = 200^\circ\text{C}$

Product	Partial pressure
Nitrous oxide	6,1
Nitric oxide	89,1
Residue of propyl nitrite	5,4
Formaldehyde	5,8
Propionaldehyde	49,3
Propyl alcohol	16,4
Water	6,1

Total: 178,2
Manometrically measured 186,0
Diviation 4,5%

Table III
The Effect of nitric oxide
on the values of half-times

P_{NO} torr	$t_{1/2}$ sec
0	2100
5	2250
10	2380
20	2700
30	3400

The results of the experiment carried out in the presence of added nitric oxide may be summarized as follows:

- The order of the reaction was not influenced by added nitric oxide
- The final pressure change slightly decreased increasing the amount of nitric oxide
- The rate of the decomposition decreased as can be seen from Table III.
- The yield of nitrous oxide and propionaldehyde increased and that of formaldehyde and propanol decreased as can be seen from Table IV.

Table IV
Material balance of products in the presence of added nitric oxide and propionaldehyde of 100 torr

Product	Partial pressure of products in the presence of	
	Nitric oxide	propionaldehyde
Nitrous oxide	10,2	3,1
Nitric oxide	72,1	92,1
Residual propyl nitrite	5,4	4,2
Formaldehyde	1,0	6,1
Propylaldehyde	52,1	47,9
Propyl alcohol	14,8	16,3
Water	10,2	3,1
	Total:	
Manometrically measured	165,8	172,8
Diviation	4,2%	6,1%

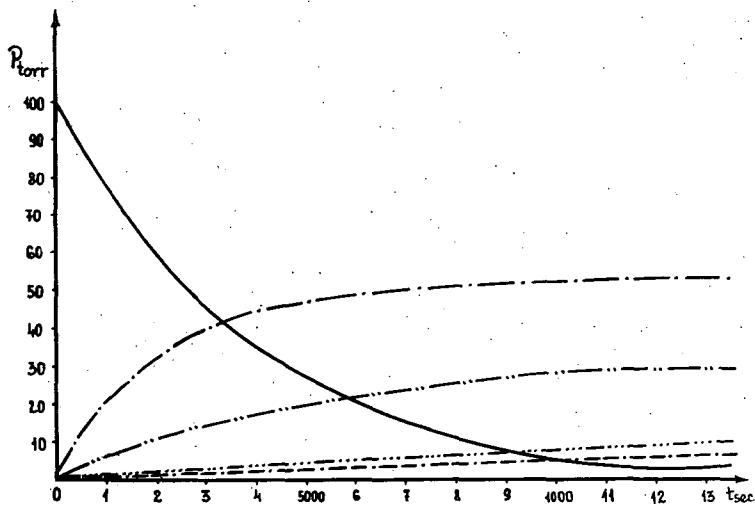


Fig. 6. Plot of the partial pressure of the products against time — propyl nitrite; - - - NO; - . . - propionaldehyde; . . . - propanol; - - - formaldehyde

In the experiments carried out in the presence of added propionaldehyde it was found that

- (a) The order of the reaction remained unchanged
- (b) The final pressure change was roughly the same as in the absence of propionaldehyde
- (c) The rate of the decomposition increased as is shown in Table V.
- (d) The yield of the products altered only slightly with the exception of nitrous oxide the yield of which was reduced as can be seen from Table IV.

Table V
The effect of propionaldehyde
on the values of half-times

$P_{\text{propionaldehyde}}$ torr	$t_{\frac{1}{2}}$ sec
0	2100
5	1900
10	1650
20	1500
50	1340
100	1010

The hydrogen and propylene had not any appreciable effect on the rate and on the order of the decomposition; their effect on the product-distribution is illustrated in Table VI.

During the pyrolysis the formation of tarry products was observed and this was greatly increased in the presence of added propylene. The analysis of these tarry products led to the following results regarding their composition: C=47,91%, H=5,37%, N=13,97%, O=32,75%.

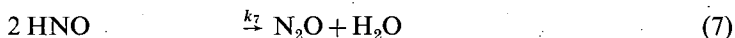
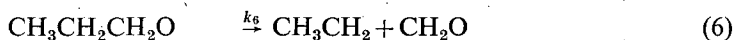
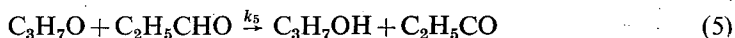
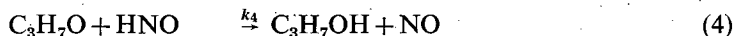
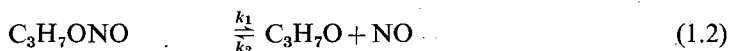
Table VI
Effect of propylene and hydrogen on the yields of products
at 25% conversion

Products	—	Propylene (100 torr)	Hydrogen (100 torr)
Nitrous oxide and Nitric oxide	9,5	10,8	10,0
Propyl nitrite	82,5	82,4	87,8
Formaldehyde	1,5	1,0	0,2
Propionaldehyde	4,8	2,4	2,4
Propyl alcohol	1,9	1,8	2,0

Discussions

From the results described above it appears that nitrous oxide is a significant product of the reaction. This result is in an apparent disagreement with the results of LEVY [10] who found that nitrous oxide appears as a product only in the presence of added nitric oxide. The kinetic feature of the decomposition of *n*-propyl nitrite is very similar to that of ethyl nitrite with the difference that formaldehyde becomes a product due to the decomposition of propoxyl radical.

The main features of the reaction may be interpreted by the following sequence of steps:



Application of the steady-state treatment to this mechanism gives rise to the following expression for the concentration of propoxyl radical:

$$[\text{C}_3\text{H}_7\text{O}] = \frac{k_1[\text{C}_3\text{H}_7\text{ONO}]}{(k_2 + k_3)[\text{NO}] + k_4[\text{HNO}] + k_5[\text{C}_2\text{H}_5\text{CHO}] + k_6} \quad (8)$$

The rate of disappearance of propyl nitrite is given by the expression:

$$-\frac{d[\text{C}_3\text{H}_7\text{ONO}]}{dt} = k_1[\text{C}_3\text{H}_7\text{ONO}] - k_2[\text{NO}][\text{C}_3\text{H}_7\text{O}] \quad (9)$$

if expression (8) is substituted into expression (9) the resulting rate expression will be:

$$\begin{aligned} & -\frac{d[\text{C}_3\text{H}_7\text{ONO}]}{dt} = \\ & = k_1[\text{C}_3\text{H}_7\text{ONO}] \left\{ 1 - \frac{k_2[\text{NO}]}{(k_2 + k_3)[\text{NO}] + k_4[\text{HNO}] + k_5[\text{C}_2\text{H}_5\text{CHO}] + k_6} \right\} \end{aligned} \quad (10)$$

and by rearrangement of (10)

$$-\frac{d \ln [\text{C}_3\text{H}_7\text{ONO}]}{dt} k_1 \left\{ 1 - \frac{k_2}{k_2 + k_3 + k_4 \frac{[\text{HNO}]}{[\text{NO}]} + k_5 \frac{[\text{C}_2\text{H}_5\text{CHO}]}{[\text{NO}]} + \frac{k_6}{[\text{NO}]}} \right\} \quad (11)$$

From rate expression (11) it can be seen that the overall rate of the reaction is determined by the ratio of $[\text{C}_2\text{H}_5\text{CHO}]/[\text{NO}]$; on increasing the concentration of propionaldehyde or that of nitric oxide the rate of the decomposition increases or decreases resp., as it was found experimentally.

Since neither ethane nor carbon monoxide were found among the products, one has to assume that the species C_2H_5 and $\text{C}_2\text{H}_5\text{CO}$ together with NO and CH_2O must have disappeared in the reaction leading to the formation of tarry products.

Comparing the decomposition of ethyl nitrite and that of propyl nitrite it turns out that the nitric oxide has roughly the same effect on the product-distribution in both cases, but the propionaldehyde has much smaller influence on the product-distribution than the acetaldehyde had in the case of ethyl nitrite. The mechanism is suitable for the explanation of the product-distribution influenced by nitric oxide but not for that of propionaldehyde.

In the presence of added nitric oxide the rate of step (2) is increased and this results in the decrease of the stationary concentration of the propoxyl radical. The rates of step (3) and (7) remain essentially unchanged, because the decrease in the concentration of propoxyl radicals is compensated by the increase in the concentration of nitric oxide. The rates of steps (4), (5) and (6), however, decrease and consequently the yield of propanol and formaldehyde decreases. The rate of step (6) is decreased mainly because the higher pressure due to the presence of nitric oxide does not favour the unimolecular decomposition of propoxyl radicals. This assumption is proved by the fact that hydrogen results in the decrease of the yield of formaldehyde, too. These circumstances lead to the consequence that the propoxyl radicals are consumed mainly by step (3) bringing about an increase in the yield of propionaldehyde and nitrous oxide.

According to the mechanism the rate of step (5) should increase in the presence of added propionaldehyde bringing about the disappearance of the propoxyl radicals mainly by step (5) instead of step (3) and (6), and resulting in a decrease in the yield of nitrous oxide and formaldehyde and an increase in that of propanol.

During the experiments, however, it was found that while the yield of nitrous oxide was reduced in agreement with the mechanism the yield of formaldehyde and that of propanol was essentially not altered in apparent disagreement with the mechanism. Further experiments are needed to elucidate this discrepancy.

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ТЕРМИЧЕСКОЕ РАЗЛОЖЕНИЕ *n*-ПРОПИЛНИТРИТА

Ф. Марта и Л. Сиравица

Авторы включали в серию изучения термического разложения этилнитрита подобный процесс разложения *n*-пропилнитрита. Порядок реакции оказался 1,25 а среднее значение энергии активации 36,6 ккал. Продукты разложения были окись и двуокись азота, пропиональдегид, пропанол, вода и формальдегид. Изучалось влияние двуокиси азота, пропиональдегида, пропилена и водорода на скорость разложения и на перераспределение продуктов. Полученные результаты сравнивались с теми же разложения этилнитрита и авторы предлагают подобный механизм объяснить главные черты реакции.