

## THE THERMAL DECOMPOSITION OF ETHYL NITRITE. II

### The Effect of Reaction Products on the Rate and Analytical Survey of the Products

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The reaction products from the thermal decomposition of ethyl nitrite have been determined by vapor-phase chromatography at various stages of the reaction for initial pressure of 140 torr. The products of the decomposition were found to be nitrogen monoxide, nitrous oxide, acetaldehyde, ethanol, acetal, and water. The yield of the acetaldehyde and that of the nitrous oxide was found to decrease as the reaction proceeded.

The effect of the products on the rate of the decomposition and on the composition of the products have also been examined.

The acetaldehyde increased the rate of the decomposition and the yield of the acetal and the ethanol, while, it decreased the yield of the nitrous oxide. The nitrogen monoxide reduced the rate and the yield of the acetal and increased the yield of the acetaldehyde and the nitrous oxide.

In a previous paper [1], the rate pressure relations of the decomposition of ethyl nitrite were reported. The correlation between the pressure increase and the actual rate of disappearance of nitrite was also given. It was thought reasonable to make an analytical survey of the products, as complete as possible, at the various stages of the reaction. This seemed necessary, because there was a contradiction between the mechanism suggested by various authors [2—5] and the existence of products such as hydrogen, methane, formaldehyde, and carbon monoxide.

#### *Experimental*

The experimental procedure employed for the separation and the determination of the reaction products has been briefly described in a previous paper [1]. The acetaldehyde, ethanol, acetal, water, and nitrite were separated at 50°C on a 160 cm column of 5 mm internal diameter packed with 10% of  $\beta\beta'$ -oxipropionitrile supported on fire brick of 60—80 mesh. Helium at 20 ml/min was used as carrier gas. The oxides of the nitrogen were separated at room temperature in a 160 cm column of 5 mm internal diameter packed with molecular sieve 5A. A column packed with silicone oil was employed before the adsorption column to prevent the organic products from getting into the adsorption column. The determination of the water was carried out at 115°C on a column of 2 meters in length packed with 10% of silicone oil supported on fire brick. The identification of the peaks appearing on the chromatogram was carried out as follows: a known amount of the compound supposed to be present was added to the sample withdrawn from the reaction vessel.

and analysed by a chromatograph. When the increase of the peak in question was proportional to the amount of the added compound then it was accepted as a proof of the fact that the product was identical with the added compound.

### Results

The products of the reaction, as we were able to identify by vapor-phase chromatography, were nitrogen monoxide, nitrous oxide, acetaldehyde, ethanol, acetal, and water. Quantitative analysis of these products were made at different stages of the reaction. Since in the literature there was contradiction between the mechanism of this reaction and the existence of some products we searched very carefully for some other possible products, such as methane, hydrogen, hydrogen cyanide, carbon monoxide, formaldehyde and formaldoxime, but none of these were present in detectable amount. Using helium as carrier gas, it was possible to identify the acetaldehyde, ethanol, acetal, ethyl nitrite, and the sum of nitrogen oxides from one sample as is shown in Fig. 1. The nitrogen oxides were separated and determined on a column packed with molecular sieve 5A as illustrated in Fig. 2. For

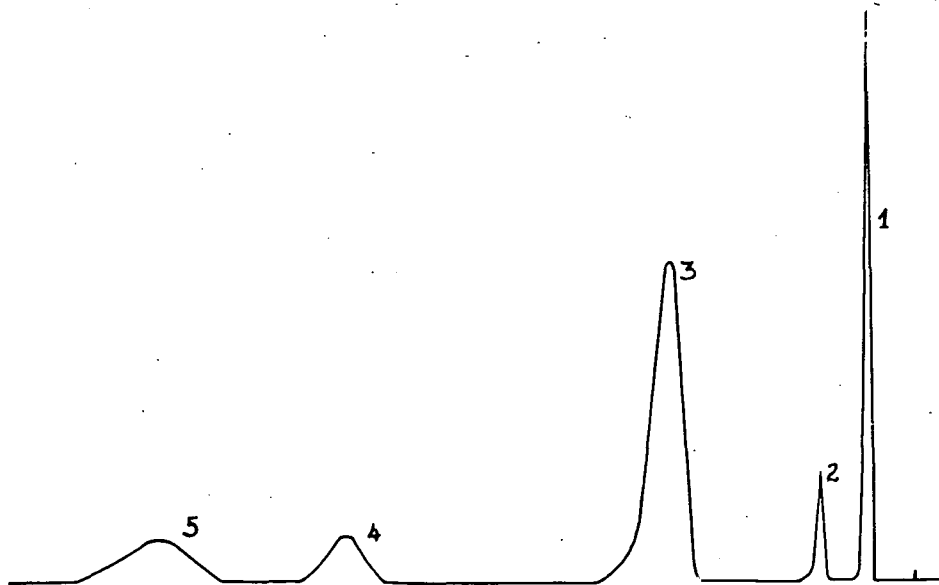


Fig. 1. The chromatogram of the products of the decomposition of ethyl nitrite,  $P_0=140$  torr,  $T=210^\circ\text{C}$ ; Sensitivities: 1.  $\text{NO}+\text{N}_2\text{O}$  256 mV 2. Ethyl Nitrite 64 mV 3. Acetaldehyde 64 mV 4. Acetal 64 mV 5. Ethyl Alcohol 64 mV

a longer period, we could not identify the peak appearing between the acetaldehyde and the ethanol, because this peak was produced by none of the possible products reported so far. In an effort to establish the product which brings about the peak in question, the assumption was made that it must have come about, in some way, in a reaction involving the other products. Therefore, different artificial mixtures of the products were prepared in the same ratio and quantity as they were found

in the analysis of the products of the decomposition of ethyl nitrite. Each of these mixtures was introduced into the reaction vessel, the temperature of which was maintained at where the decomposition of nitrite was investigated, and after a period

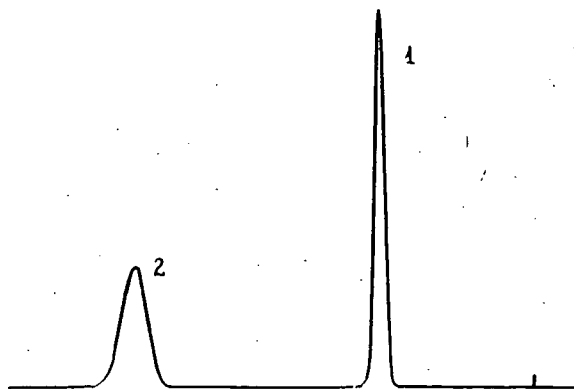


Fig. 2. The separation of nitrogen oxides formed in the reactions  $P_0=140$  torr;  $T=210$  °C; Sensitivities: 1. NO 1280 mV 2.  $N_2O$  320 mV

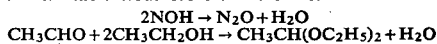
of time samples were taken and analyzed. Of all the mixtures (a)  $NO + CH_3CHO + C_2H_5OH$ , (b)  $NO + CH_3CHO$ , (c)  $NO + C_2H_5OH$ , (d)  $CH_3CHO + C_2H_5OH$  only the mixtures of (a) and (b) gave the peak in question. Taking into account the possible reactions between the acetaldehyde and the ethanol, we came to the conclusion that this product must correspond to the acetal. To substantiate this assumption, acetal was synthesized, and the described procedure of identification was carried out which proved that the assumption had been correct. From the results of the analysis it was possible to determine the material balance of the products of the decomposition of ethyl nitrite as is shown in Table I. The difference observed

Table I

Material balance of the decomposition products of ethyl nitrite,  $P_0=140$  torr;  $T=210$  °C;

Nitrogen monoxide	118,4 torr
Nitrous oxide	10,1 „
Acetaldehyde	66,0 „
Acetal	11,2 „
Alcohol	16,7 „
Water*	21,3 „
Residual Ethyl nitrite	6,1 „
Total:	249,8 torr
Monometrically measured	260,3
Deviation	4,0%

\* Water formed together with the nitrous oxide and the acetal



was determined only qualitatively.

does not exceed the limit of experimental error, and can be explained by the assumption that some of the higher boiling products formed condensed during the sampling. The appearance of a yellowish deposit was actually observed in the glass tubes, which may account for the theoretically expected lower value of the final pressure increase.

The change in the yields of the reaction products was determined as the function of time on the basis of analytical results. In the case of acetaldehyde the results are shown in Fig. 3., where the partial pressure of acetaldehyde is plotted against time. Plotting the logarithm of the partial pressure of acetaldehyde against time we did not get a straight, which indicated that as the reaction proceeded the

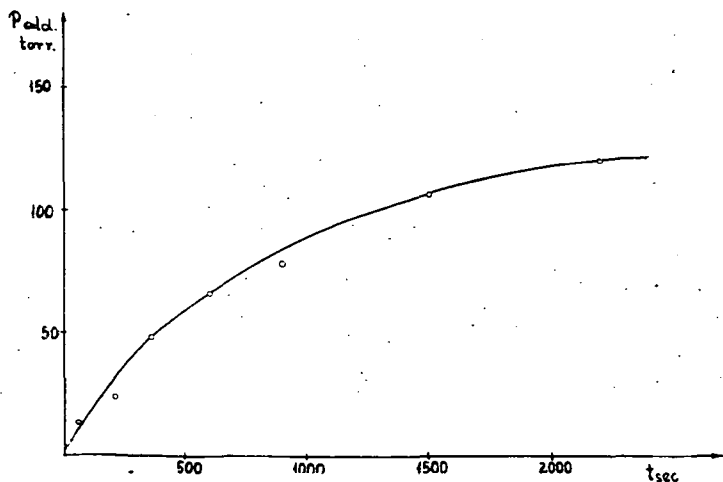


Fig. 3. The change of the partial pressure of acetaldehyde with time

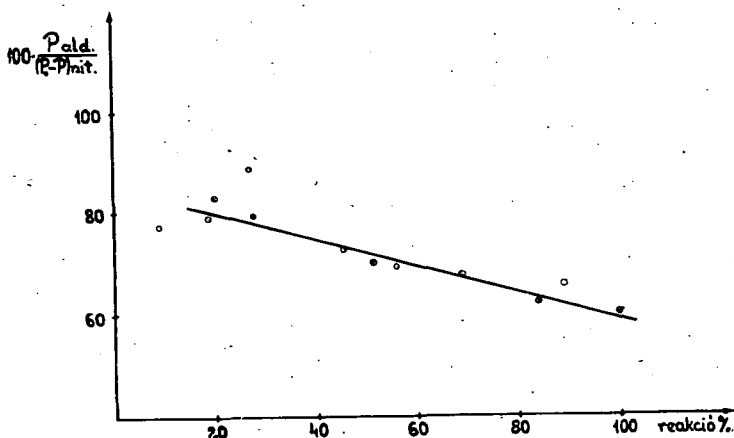


Fig. 4. The change in the yield of acetaldehyde with the proceeding of the reaction,  $\odot$  Own measurements;  $\bullet$  LEVY'S data

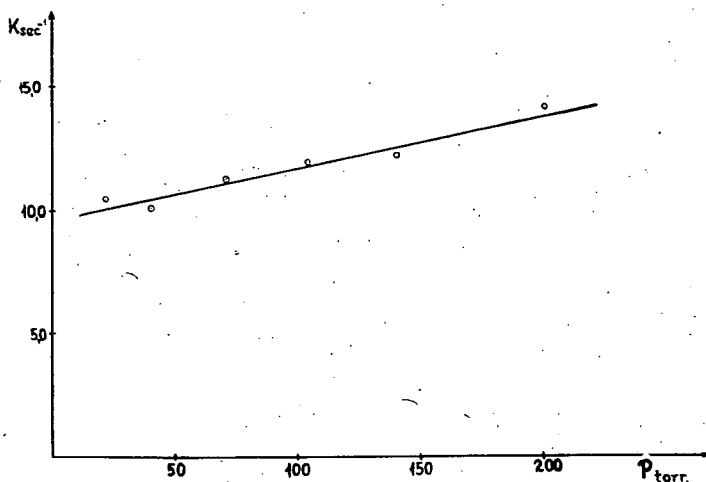


Fig. 5. The effect of acetaldehyde on the rate of the reaction

yield of acetaldehyde decreased. To prove this, the yield of acetaldehyde in percentages of the pressure of nitrite was plotted against the decomposition percentages of nitrite in Fig. 4, showing a decrease in the yield of the acetaldehyde. Fig. 4. also contains LEVY's [4] data obtained by infrared spectroscopy, showing good agreement with ours. It is worth-while to mention that LEVY did not pay attention to this experimental fact, although this is the one which proves the validity of the step  $\text{CH}_3\text{CHO} + \text{C}_2\text{H}_5\text{O} \rightarrow \text{C}_2\text{H}_5\text{O} + \text{CH}_3\text{CO}$  postulated in his mechanism.

The change in the yields of nitrous oxide and ethanol was found to be similar, to a certain extent, to that of acetaldehyde.

From the results described above it seemed worth-while studying in somewhat more detail the effect of products such as nitric oxide, acetaldehyde, and ethanol, as well as that of the surface/volume ratio on the decomposition of ethyl nitrite. Accordingly, experiments were carried out in the presence of different amount of these products. The results of the experiments, carried out in the presence of added acetaldehyde, may be summarized as follows:

(a) The rate of the decomposition increased as shown in Fig. 5. in agreement with LEVY's results.

(b) The final pressure change decreased as can be seen from Table II increasing the amount of acetaldehyde.

(c) The order of the reaction is not influenced by added acetaldehyde as it is proved by the first order rate constants listed in Table III.

Table II  
Effect of acetaldehyde on the decomposition of ethyl nitrite

$T = 110^\circ\text{C}$ ;  $P_0 = 140$  torr;

$P_{\text{aldehyde}}$ torr	$\Delta P_{\text{torr}}$	$\tau_{1/2}$ sec
0	121,3	800
5	112,2	795
100	105,3	635
200	75,5	498

Table III

Effect of acetaldehyde on the decomposition of ethyl nitrite  
 $T=210^{\circ}\text{C}$ ;  $P_0=140$  torr;  $P_{\text{acetaldehyde}}=100$  torr

$t$ sec	$\Delta P$ torr	Reaction %	$k \cdot 10^3 \text{ sec}^{-1}$
117	12,6	12,9	1,179
169	18,2	18,6	1,221
262	26,8	27,3	1,220
418	39,1	39,9	1,219
512	45,4	46,3	1,224
600	51,0	52,0	1,226
808	61,8	63,1	1,237
1077	72,2	73,7	1,230
1462	81,7	83,4	1,231
2374	92,7	94,6	1,240
3240	97,7	99,7	0,813

Table IV

The material balance of the products in the presence of  
 acetaldehyde,  $P_0=140$  torr;  $P_{\text{aldehyd}}=140$  torr  
 $T=210^{\circ}\text{C}$

Nitrogen monoxide	114,3 torr
Nitrous oxide	5,7 "
Acetaldehyde	36,6 "
Acetal	20,2 "
Alcohol	23,0 "
Water	25,9 "
Residual nitrite	3,0 "
Total:	368,7 torr
Manometrically measured	366,8 "
Deviation	0,5%

Table V

The effect of nitric oxide on the rate constant  
 $T=209,8^{\circ}\text{C}$ ;  $P_0=140$  torr;  $P_{\text{NO}}=140$  torr

$t$ sec	$\Delta P$ torr	Reaction %	$k \cdot 10^4 \text{ sec}^{-1}$
232	12,0	12,4	5,686
449	23,8	24,6	6,302
569	29,5	30,6	6,408
699	34,8	36,1	6,389
866	41,2	42,7	6,425
1027	47,5	49,2	6,592
1378	57,6	59,7	6,585
1834	68,3	70,8	6,690
2444	78,1	80,9	6,671
3660	87,8	90,9	6,559
5462	92,8	96,2	5,946

(d) The yield of ethanol and acetal was increased, as it appears from the comparison of Table IV and Table I.

It is interesting to note that the yield of acetaldehyde is nearly half of that without added acetaldehyde.

The inhibition effect of nitric oxide was observed in the decomposition of alkyl nitrite, too. In the case of the decomposition of ethyl nitrite, however, LEVY found that the rate was not altered in the presence of added nitric oxide. In our experiments, carried out in the presence of added nitric oxide, it was found that:

(a) the rate of the decomposition decreased increasing the amount of nitric oxide,

(b) the order of the reaction remained unchanged. Table V shows that there is no tendency indicating any change, within the same reaction, in the values of the first order rate constants,

(c) the final pressure change is greater,

(d) the yield of the nitrous oxide and that of the acetaldehyde increased,

(e) the yield of the products identified by us as acetal and ethanol was reduced. The results are summarized in Table VI., and illustrated in Fig. 6.

The experiments carried out in the presence of added ethanol showed that neither the rate nor the final pressure increase was influenced by ethanol; this observation being in full agreement with that of LEVY's. The effect of ethanol is illustrated in Fig. 7. together with that of nitric oxide and acetaldehyde.

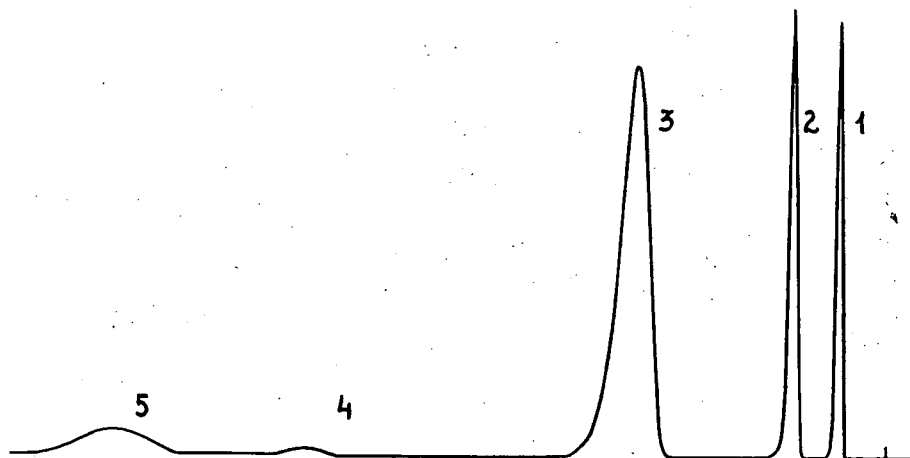


Fig. 6. Effect of nitric oxide on the decomposition of ethyl nitrite  $P_0=140$  torr;  $P_{NO}=140$  torr;  $T=210$  °C; sample was taken after 40 minutes of the beginning of the reaction Sensitivities: 1. NO+N<sub>2</sub>O 64 mV 2. Ethyl Nitrite 160 mV 3. Acetaldehyde 64 mV 4. Acetal 64 mV 5. Ethyl Alcohol 64 mV

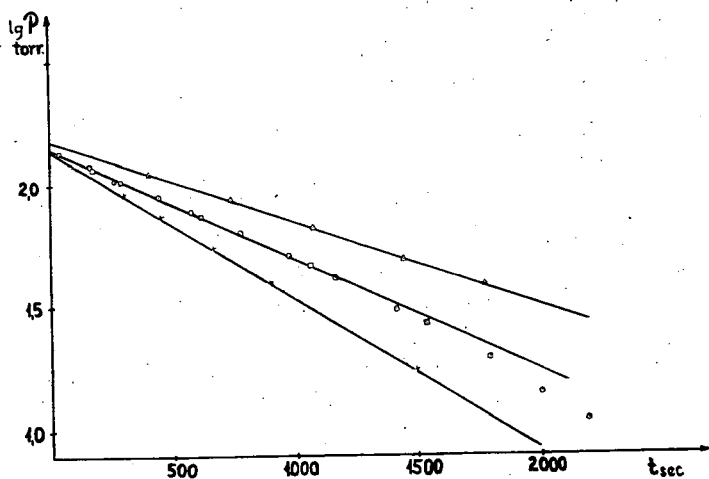


Fig. 7. The effect of the reaction products on the decomposition of ethyl nitrite  
 ○ Ethyl Nitrite alone;                      △ Nitrogen Monoxide (140 torr);  
 □ Ethyl Alcohol (30 torr);                      × Acetaldehyde (140 torr)

Table VI

The material balance of the products in the presence of nitric oxide,  $P_0 = 140$  torr;  $P_{NO} = 140$  torr;  
 $T = 210^\circ\text{C}$

Nitrogen monoxide	84,9 torr
Nitrous oxide	20,0 „
Acetaldehyde	105,0 „
Acetal	4,1 „
Alcohol	13,4 „
Water	24,1 „
Residual nitrite	15,1 „
Total:	406,6 torr
Manometrically measured	421,0 „
Deviation	3,4%

For the sake of comparison with LEVY's experimental data, we summarized in Table VII the changes in products distribution — given in mole % — in the presence of acetaldehyde and nitrogen monoxide.

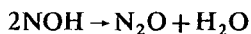
Table VII

Material balances of the decomposition of ethyl nitrite at conversion of 97%

Additive	NO	N <sub>2</sub> O	acetaldehyde	ethyl alcohol	acetal
—	86,3±2	17,4±5	47,3±3	10,1±4	25,1±4
acetaldehyde 140 torr	81,2±2	4,5±3	26,1±4	15,7±6	43,2±5
nitrogen monoxide 140 torr	68,0±2	32,0±5	84,1±2	10,7±4	9,8±4

For the above analysis the samples were taken from the reaction of the decomposition of ethyl nitrite at initial pressure of 140 torr and at temperature 210°C. At the calculations it was taken into consideration that at the decomposition of 1 mole of ethyl nitrite 1 mole of NO or 1/2 mole of N<sub>2</sub>O and 1 mole of acetaldehyde or 1 mole of ethyl alcohol or 1/3 mole of acetal formed, *i. e.* twofold of the pressure quantities obtained for N<sub>2</sub>O and threefold of the values obtained for acetal were taken as the basis of the % calculation.

For the study of the effect of the surface on the reaction, experiments were carried out in a reaction vessel having a surface/volume ratio of 3,27 instead of 1,1. It was found that the increase in the value of S/V had no effect on the rate in agreement with the experiments of STEACIE and SHAW [2]. BENSON [6] assumed that the step of the formation of nitrous oxide



must be heterogeneous. Since it was not possible to observe any change in the yield of N<sub>2</sub>O increasing the S/V ratio, this step also seemed to be homogeneous.



## References

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## ТЕРМИЧЕСКОЕ РАЗЛОЖЕНИЕ ЭТИЛНИТРИТА. II

Влияние продуктов реакции на скорость и данные  
анализа продуктов

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Продукты реакции термического разложения этилнитрита изучались методом хроматографии в паровой фазе в различных стадиях реакции и при начальном давлении 140 тор.

Следующие продукты разложения были получены: окись азота, закись азота, ацетальдегид, этанол, ацетал и вода. Выход ацетальдегида и закиси азота уменьшался с прогрессом реакции.

Влияние продуктов на скорость разложения и состав продуктов также изучались.

Ацетальдегид увеличил скорость реакции и выход ацетала и этанола, а уменьшил выход закиси азота. Окись азота уменьшил скорость и выход ацетала и увеличил тот же ацетальдегида и закиси азота.