

THE THERMAL DECOMPOSITION OF ETHYL NITRITE. III

The Effect of Propylene and the Mechanism of the Reaction

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(Received April 10, 1966)

The effect of propylene on the decomposition of ethyl nitrite and on the composition of the reaction products has been examined. According to the experimental results propylene has not any influence on the composition of the reaction products. The rate of decomposition in the presence of propylene was slightly increased.

A mechanism has been suggested which is able to account for the experimental results described in the previous two papers and in the present one. This mechanism can explain the main features of the reaction and the product distribution influenced by nitric oxide and acetaldehyde.

In previous papers [1, 2] the rate pressure relations of the decomposition and the effect of the products on the rate and on the composition of products were reported.

Having found that the nitric oxide exerts an inhibiting effect on the decomposition of ethyl nitrite and that it gives rise to a great change in the composition of reaction products, we decided to investigate the effect of propylene on the decomposition reaction.

The results of the experiments carried out in the presence of different amount of propylene showed that the rate of the decomposition and the final pressure-change were slightly increased as it can be seen from Table I.

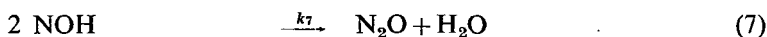
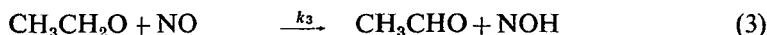
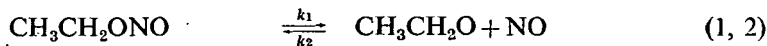
Table I
The effect of propylene on the rate of the reaction
T = 209,1°C; P₀ = 140 torr

Propylene _{torr}	$\tau_{1/2}$ sec	ΔP_{torr}
0	880	120,3
50	840	119,8
100	800	126,7
200	790	127,6

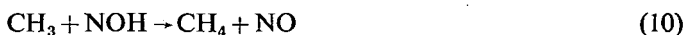
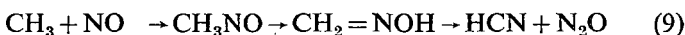
From the analysis of the products, it turned out that the propylene had not appreciable effect neither on the yield nor on the composition of the products found in the absence of propylene. This experimental fact indicates that the interaction between the propylene and the radical formed in the decomposition reaction may be neglected. This result is surprising, because it could have been expectable that the ethoxyl radicals abstracted hydrogen from propylene and, consequently, the yield of ethanol would have been increased.

The overall mechanism of the reaction

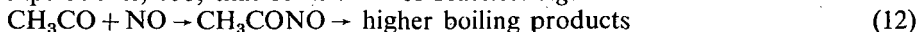
The experimental results described in the previous papers [1, 2] may be interpreted by the following sequence of steps:



which are very similar to those proposed by LEVY [3] and can explain the main features of the reaction. We did not take into consideration the steps:



suggested by LEVY, because CO, CH₄, H₂ and HCN could not be detected at the present work. The steps (10) and (11) were assumed by LEVY to explain the yield of nitrous oxide found in the presence of added acetaldehyde and nitric oxide. If, however, the change observed in the yield of nitrous oxide was due to these steps, then methane and hydrogen should be formed in the quantity proportional to the difference found in the yield of nitrous oxide. The absence of carbon monoxide, hydrogen cyanide and formaldoxime in the products makes the existence of steps (8) and (9) very unlikely. On the other hand, however, it is true, on the basis of our experiments, too, that some kind of reaction *e.g.*



between the species CH₃CO and NO should be taken into consideration. Our assumption is that this reaction step must be responsible for the appearance of the higher boiling product observed in our experiments and which is also referred to by BROMBERGER and PHILLIPS [4]. We observed that the formation of this yellowish product became more appreciable in the presence of excess of acetaldehyde when step (5) and, consequently, step (12) were more dominant.

In the presence of added acetaldehyde a significant deficiency in nitrogen balance, as well as a decrease in the final pressure-change were observed. All these experimental facts seem to be interpreted by the assumption of a reaction involving species CH₃CO and NO.

The product, having found and being identified as acetal, comes from the reaction involving ethanol and acetaldehyde in step (6).

Although on the basis of the experiments there is no doubt about the formation of the acetal [2], nevertheless, it seems somewhat strange how this product can be formed under such an experimental condition and in such a significant quantity.

Application of the steady-state treatment to the mechanism described above gives rise to the following expression for the concentration of ethoxyl radical:

$$[\text{C}_2\text{H}_5\text{O}] = \frac{k_1[\text{C}_2\text{H}_5\text{ONO}]}{(k_2 + k_3)[\text{NO}] + k_4[\text{NOH}] + k_5[\text{CH}_3\text{CHO}]} \quad (13)$$

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

$$-\frac{d[\text{C}_2\text{H}_5\text{ONO}]}{dt} = k_1[\text{C}_2\text{H}_5\text{ONO}] - k_2[\text{C}_2\text{H}_5\text{O}][\text{NO}] \quad (14)$$

into which if (13) is substituted the resulting rate expression will be:

$$-\frac{d[\text{C}_2\text{H}_5\text{ONO}]}{dt} = k_1[\text{C}_2\text{H}_5\text{ONO}] \left\{ 1 - \frac{k_2[\text{NO}]}{(k_2 + k_3)[\text{NO}] + k_4[\text{NOH}] + k_5[\text{CH}_3\text{CHO}]} \right\} \quad (15)$$

and after rearrangement:

$$-\frac{d \ln [\text{C}_2\text{H}_5\text{ONO}]}{dt} = k_1 \left\{ 1 - \frac{k_2}{k_2 + k_3 + k_4 \frac{[\text{NOH}]}{[\text{NO}]} + k_5 \frac{[\text{CH}_3\text{CHO}]}{[\text{NO}]}} \right\} \quad (16)$$

From the rate expression (16) it can be seen that the rate of the reaction depends on the ratio of $\text{CH}_3\text{CHO}/\text{NO}$; and on increasing the concentration of acetaldehyde or that of nitric oxide the rate of the reaction increases or decreases respectively.

The mechanism, consisting of the sequence of steps (1—7), is also suitable for the explanation of the product distribution influenced by nitric oxide and acetaldehyde.

In the presence of greater amount of acetaldehyde the rates of steps (5) and (6) increase bringing about the disappearance of the ethoxyl radicals mainly by step (5) instead of step (3); its consequence being the decrease in the yield of nitrous oxide and an increase in that of acetal in agreement with the experiments. Under this experimental condition — taking into consideration that

$$(k_2 + k_3)[\text{NO}] + k_4[\text{NOH}] \ll k_5[\text{CH}_3\text{CHO}] \quad (17)$$

the rate expression (16) is simplified to

$$-\frac{d \ln [\text{C}_2\text{H}_5\text{ONO}]}{dt} = k_1 \left\{ 1 - \frac{k_2[\text{NO}]}{k_5[\text{CH}_3\text{CHO}]} \right\} \quad (18)$$

showing an increase in the rate as compared to equation (15).

In the presence of added nitric oxide the rate of step (2) is increased and this plays part in the lowering of the stationary concentration of the ethoxyl radicals. The rates of steps (3) and (7) remain essentially unchanged, because the decrease in the concentration of ethoxyl radicals is compensated by the increase in the concentration of nitric oxide. However, the rates of steps (4), (5), (6), decrease, and

consequently the yield of ethanol and that of acetal decreases. This means that the ethoxyl radicals are consumed mainly by step (3) bringing about an increase in the yield of acetaldehyde and nitrous oxide. Under such conditions the inhibiting effect of nitric oxide can be interpreted by the equation (16). On applying high concentration of nitric oxide it is evident that in the rate equation (16)

$$(k_2 + k_3) \gg k_4 \frac{[\text{NOH}]}{[\text{NO}]} + k_5 \frac{[\text{CH}_3\text{CHO}]}{[\text{NO}]} \quad (18)$$

and that the rate expression (16) is reduced to

$$-\frac{d \ln [\text{C}_2\text{H}_5\text{ONO}]}{dt} = k_1 \left\{ 1 - \frac{k_2}{k_2 + k_3} \right\} \quad (19)$$

which accounts for the limiting value of inhibition at the very high concentration of nitric oxide as found by LEVY.

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The authors are indebted to Mrs. TAKÁCS for her assistance in carrying out the experiments.

References

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ТЕРМИЧЕСКОЕ РАЗЛОЖЕНИЕ ЭТИЛНИТРИТА. ЧАСТЬ III. ЭФФЕКТ ПРОПИЛЕНА И МЕХАНИЗМ РЕАКЦИИ

Ф. Марта и Л. Шереш

Авторами изучалось влияние пропилена на скорость реакции разложения этилнитрита и на состав продукта реакции. По опытным результатам пропилен не оказал влияния на состав продуктов реакции. Скорость реакции разложения в присутствии пропилена немного увеличилась.

Предложен механизм, по которому может толковать опытные данные описанные в настоящей статье и также в предыдущих двух частях. По этому механизму толкуются основные черты реакции и разделение продуктов под влиянием окиси азота и ацетальдегида.