[CONTRIBUTION FROM THE EXPLOSIVES RESEARCH DEPARTMENT, NAVAL ORDNANCE LABORATORY]

The Decomposition of Diethyl Peroxide in the Presence of Nitric Oxide and Ethyl Nitrite

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The reaction between ethoxyl radicals and nitric oxide at 181° has been studied using the decomposition of diethyl peroxide as the source of ethoxyl radicals. It has been found that ethyl nitrite is formed. The effect of ethoxyl radicals on the decomposition of ethyl nitrite has been examined at 181°. The mechanism of the thermal decomposition of nitrite esters is discussed in terms of the results obtained.

Introduction

The thermal decomposition of nitrite esters has been the subject of much study[1,2] and the following mechanism has been proposed.

$$\mathrm{RCH_2ONO} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{RCH_2O\cdot + NO} \qquad (1)$$

$$\mathrm{RCH_2O\cdot + RCH_2ONO} \xrightarrow{k_2} \mathrm{RCH_2OH + R\underset{\cdot}{\overset{H}{C}}ONO} \qquad (2)$$

$$\mathrm{R\underset{\cdot}{C}HONO \longrightarrow RCHO + NO} \qquad (3)$$

In order to satisfy the observed first-order kinetics of the reaction it is necessary to assume that $k_2\mathrm{RCH_2ONO} >>> k_{-1}\mathrm{NO}$. In the course of other work in this Laboratory this point has been investigated and the results are reported in this paper.

The Basis of the Method.—The decomposition of diethyl peroxide has recently been studied by Harris and Egerton[3] in a static system over a pressure range of 2 to 30 cm. and by Rebbert and Laidler[4] at very low pressures, using a flow system wherein the peroxide was carried along in a large excess of toluene vapor. The evidence indicates that the first step in the diethyl peroxide decomposition is

$$\mathrm{C_2H_5OOC_2H_5 \longrightarrow 2C_2H_5O\cdot}$$

At 181° the half-life of diethyl peroxide as calculated from the data of Harris and Egerton[3] is about 8 sec. while that for ethyl nitrite is about 130 minutes.[1b] By heating a mixture of diethyl peroxide, nitric oxide and ethyl nitrite at 181° for a few minutes it should be possible in essence to generate ethoxyl radicals in the presence of ethyl nitrite and nitric oxide and by measuring the change in ethyl nitrite pressure to get a measure of the comparative velocities of reaction (4) and (5).

$$\mathrm{C_2H_5O\cdot + NO \longrightarrow C_2H_5ONO} \qquad (4)$$

$$\mathrm{C_2H_5O\cdot + C_2H_5ONO \longrightarrow C_2H_5OH + CH_3\underset{\cdot}{\overset{H}{C}}ONO} \qquad (5)$$

Experimental Part

Chemicals.—The ethyl nitrite was prepared in standard fashion,[1b] distilled and a middle fraction taken. It was stored in sealed ampules in a refrigerator.

The nitric oxide used was purchased from the Matheson Co. and was certified as 98% pure. It was used directly from the cylinder but further purification was effected by allowing the tube on the bulb filling apparatus containing the nitric oxide to warm up only enough to generate a sufficient pressure of nitric oxide. In this way the higher nitrogen oxides which are the chief impurity were retained in the tube. When a glass photometric cell was filled this way and analyzed for nitrogen dioxide at 4050 Å. it was found to be completely transparent.

The diethyl peroxide was prepared as described by Harris and Egerton.[3] The final distillation at atmospheric pressure yielded a product boiling at 62.5–63.5°. The mass spectrometer pattern was taken and was very similar to that obtained by Rebbert and Laidler[4] for diethyl peroxide. The presence of a small peak at a mass number of 74 indicated that ethyl ether was present but it was difficult to assess the amount. At any rate, the purity was considered sufficient for the experiments in prospect.

The Analytical Technique.—In Fig. 1, the infrared spectrum of pure ethyl nitrite taken on a Perkin–Elmer model 21 double beam infrared spectrometer is compared to the spectrum of the products obtained when diethyl peroxide is heated with nitric oxide at 181°. It is clear that ethyl nitrite is the product of this reaction. The peak centering at 12.85 μ was that used for the analysis of ethyl nitrite. Diethyl peroxide, its decomposition products and nitric oxide were found to be transparent in this region. The analysis then simply involved measuring the optical density of the decomposition mixtures at this point and dividing it by the Beer's law constant for ethyl nitrite.

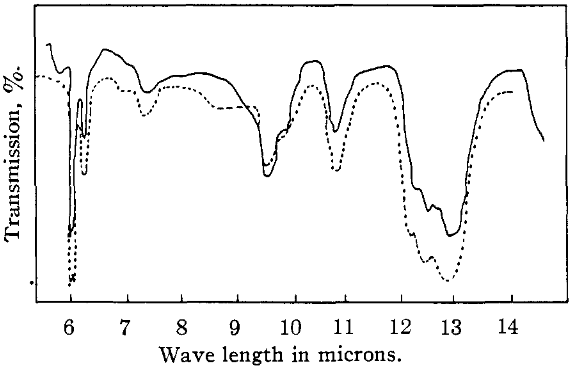

Fig. 1.—Spectrum of: ———, product of $\mathrm{C_2H_5OOC_2H_5}$–NO reaction; --------, pure $\mathrm{C_2H_5ONO}$ (curve displaced downward).

The cells used for the analyses were 52 mm. long. Measurements of optical density were taken for various pressures of ethyl nitrite ranging from 4.5 to 30.1 mm. When the optical density was plotted *vs.* pressure a straight line was obtained. The slope as determined by least squares was 0.0441 ± 0.0009.

The Experimental Measurements.—The experiments were carried out by immersing bulbs filled with the appropriate gases in a constant temperature bath for the appropriate time. The reaction was stopped by immersing the bulbs in cold water.

The bulbs were attached through stopcocks to a vacuum line bearing a manometer and a tube containing the ethyl nitrite. When a suitable pressure of ethyl nitrite had been admitted to a bulb, its stopcock was closed, the contents frozen in the bottom of the bulb by means of liquid nitrogen and the bulb pulled off below the stopcock with a hand torch.

To prepare mixtures of gases, each gas was measured into one bulb and then condensed with liquid nitrogen into the

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[1] (a) E. W. R. Steacie and G. T. Shaw, *Proc. Roy. Soc.* (*London*), **A146**, 388 (1934); (b) *J. Chem. Phys.*, **2**, 345 (1934); (c) **3**, 394 (1935); (d) *Proc. Roy. Soc.* (*London*), **A151**, 685 (1935); (e) E. W. R. Steacie and W. McF. Smith, *J. Chem. Phys.*, **4**, 504 (1936).

[2] F. O. Rice and E. L. Rodowskas, THIS JOURNAL, **57**, 350 (1935).

[3] E. G. Harris and A. C. Egerton, *Proc. Roy. Soc.* (*London*), **A168**, 1 (1938).

[4] R. E. Rebbert and K. J. Laidler, *J. Chem. Phys.*, **26**, 574 (1952).

reaction bulb. When ethyl nitrite was one of the gases, it was measured into an infrared cell at the same time as it was introduced into the bulb. The pressure was then measured by taking the optical density of the gas in the cell at 12.85 μ. This gave a more accurate pressure measurement since the Beer's law constant is calculated on the basis of a large number of pressure measurements and hence is more accurate than a direct pressure reading on the manometer would be.

The reaction bulbs were equipped with a side arm which had been previously pulled out to a thin tip. It was then possible to transfer the bulb contents to an infrared cell by means of the usual break-off techniques.

Results.—The experimental results are summarized in Table I.

TABLE I

PRODUCTS OF THE DECOMPOSITION OF DIETHYL PEROXIDE (DEP) IN THE PRESENCE OF ETHYL NITRITE AND NITRIC OXIDE AT 181°

Expt.	Initial pressure,[a] mm. DEP	NO	C_2H_5-ONO	Time, min.	Final pressure[a] of C_2H_5-ONO	C_2H_5-ONO produced	Fractional yield[b] of C_2H_5-ONO
1	11.0	22.0	..	1.0	3.7	3.7	0.17
2	10.0	42.0	..	1.0	5.5	5.5	.28
3	10.0	75.0	..	1.0	3.9	3.9	.19
4	11.0	22.0	..	2.0	3.7	3.7	.17
5	11.0	23.0	..	4.0	13.4	13.4	.61
6	13.8	23.5	..	4.3	16.0	16.0	.58
7	12.0	22.0	..	6.0	14.1	14.1	.59
8	11.5	44.0	..	6.0	15.1	15.1	.66
9	11.0	22.0	10.5	4.0	22.8	12.3	.56
10	11.0	22.0	..	4.0	12.2	12.2	.56
11	12.8	..	20.0	4.0	20.2	0.2	..
12	14.0	..	20.0	4.0	20.9	0.9	..

[a] Measured at 25°. [b] Based on a theoretical yield of 2 moles of ethyl nitrite per mole of ethyl peroxide.

Harris and Egerton[3] have reported a slight induction period for the decomposition of diethyl peroxide. This period is lengthened by the addition of nitric oxide. Thus 30% nitric oxide increased it from 6 sec. to about 2 min. at 170°. The low yield in expt. 1–4 is attributed to incomplete decomposition of the diethyl peroxide due to this effect. The lower yield in expt. 3 as compared to expt. 2 is attributed to the greater inhibition in expt. 3 due to the greater amount of nitric oxide. Judging from expts. 4, 5, 6 and 7 a period of four minutes of heating was sufficient to give the maximum yield for the given pressures.

Experiments 9 and 10 are a direct measure of the relative reactivity of nitric oxide and ethyl nitrite with the ethoxyl radical. In expt. 10 as much ethoxyl reacted with nitric oxide in the presence of an amount of ethyl nitrite equal to the nitric oxide as did in expt. 9 where no ethyl nitrite was present. This indicates that the ethoxyl–nitric oxide reaction is much more rapid than the ethoxyl–ethyl nitrite reaction at this temperature. Experiments 11 and 12 are even more decisive. On the basis of two moles of ethoxyl radical per mole of diethyl peroxide more than enough diethyl peroxide was present to decompose all the ethyl nitrite in each experiment. Instead no decomposition occurred. The slight increases observed may be attributed in part to the analytical error and in part to the possible formation of ethyl nitrite from small amounts of nitric oxide present in the ethyl nitrite.

It is not clear what happens to the ethoxyl radicals in expt. 11 and 12. An examination of the infrared spectrum of the products from expt. 11 shows only minor absorption at the acetaldehyde carbonyl absorption at 5.65 μ. Due to the tendency of formaldehyde to polymerize to paraformaldehyde its vapor pressure is too low to allow any conclusions to be reached on its presence by means of the infrared spectrum.

It is somewhat puzzling that the maximum yield of ethyl nitrite was only about 0.66. If this were due to a competition between (4) and some other reaction of the ethoxyl radical it would seem that doubling the nitric oxide pressure, expt. 6 and 7, would increase the yield more than it did. It is possible alternatively that this is due in part to an impurity in the diethyl peroxide. The mass spectrograph pattern indicated the presence of ethyl ether, although the amount is uncertain. When a sample of diethyl peroxide was heated by itself to complete decomposition a pressure increase of 104% was obtained. Harris and Egerton[3] reported a pressure increase of about 117% for their samples so that it would seem that by this test the material used here was of comparable purity. Since in any case a substantial yield of ethyl nitrite could be obtained it was possible to test the point at issue and this aspect of the experimental work was not pursued further.

The Mechanism of the Decomposition of Alkyl Nitrites.—In considering a mechanism for this reaction, the following observations made by Steacie may be considered. Nitric oxide was a major product. On the basis of one nitric oxide molecule per molecule of nitrite decomposed, the yields were about 90%. In addition varying small amounts, 1–10%, of carbon monoxide were present as well as small amounts of inert gases. The analyses used by Steacie and Shaw[1b] to establish the presence of alcohols and aldehydes as the products were not quantitative but it is quite certain that these products were present in more than trace amount. (Kornblum and Oliveto[5] have recently reported the formation of 2-octanol in 80% yield in the pyrolysis of liquid 2-octyl nitrite.)

It is doubtful whether any arguments can be based on the pressure increases observed during the reaction. These varied from 60% for *n*-butyl nitrite to 100% for *n*-propyl nitrite. The final pressures were not constant in any case. The presence of tarry materials in the case of *n*-propyl and *n*-butyl nitrites is another complicating factor.

It seems quite likely that the first step in the reaction is (1). The steps suggested by Rice and Rodowskas to give the alcohol and aldehyde must, in the light of the results of Table II, be incorrect. The only plausible route left for these is

$$C_2H_5O\cdot + C_2H_5O\cdot \longrightarrow C_2H_5OH + CH_3CHO \quad (6)$$

Steps like (6) have been proposed before for alkoxyl radicals[6,7] but (2) has been preferred to (6) because of the much higher concentration of the

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(5) N. Kornblum and E. P. Oliveto, THIS JOURNAL, **71**, 226 (1949).

(6) G. K. Adams and C. E. H. Bawn, *Trans. Faraday Soc.*, **45**, 494 (1949).

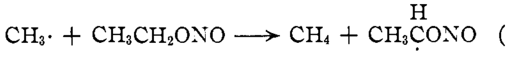
(7) A. Appin, J. Chariton and O. Todes, *Acta Physicochim.*, **5**, 655 (1936).

alkyl nitrite as compared to the alkoxyl radical. This factor is apparently offset by the much lower activation energy of (6). Step (6) is probably accompanied by the reaction suggested by Rice and Rodowskas

$$C_2H_5O\cdot \longrightarrow CH_3\cdot + CH_2O \qquad (7)$$

Since (6) is bimolecular and (7) is unimolecular, it will be seen that lower pressures will favor (7) and the yield of ethyl alcohol and acetaldehyde as compared to formaldehyde would depend on the pressure and temperature. Since as mentioned earlier the infrared spectrum of the products in expt. 11 indicates that little acetaldehyde was formed, it appears that at these pressures and at this temperature (7) predominates over (6). In the other extreme, the pyrolysis of 2-octyl nitrite in the liquid phase, the high yield of alcohol and ketone is consistent with the relatively high concentration of alkoxyl radicals.

Rice and Rodowskas have written as a further reaction of the methyl radical



$$CH_3\cdot + CH_3CH_2ONO \longrightarrow CH_4 + CH_3\underset{\cdot}{\overset{H}{C}}ONO \qquad (8)$$

Since in expt. 11 and 12 there was no induced decomposition of the ethyl nitrite, it appears that here the true fate of the methyl radicals is

$$2CH_3\cdot \longrightarrow C_2H_6 \qquad (9)$$

This result is similar to one found by Rebbert and Laidler in the diethyl peroxide decomposition. Despite the presence of a large excess of toluene the major product was ethane and only small amounts were found of methane and dibenzyl, products of

$$CH_3\cdot + C_6H_5CH_3 \longrightarrow CH_4 + C_6H_5CH_2\cdot$$
$$2C_6H_5CH_2\cdot \longrightarrow C_6H_5CH_2CH_2C_6H_3$$

The presence of carbon monoxide in the products can be explained here, as it was in the case of diethyl peroxide,[3,4] on the basis of a radical-induced decomposition of the aldehydes.

It thus appears that a satisfactory picture of the alkyl nitrite decomposition is represented by equations (1), (6), (7) and (9) with the sequence (1), (6) predominating at higher pressures and (1), (7), (9) taking over at lower pressures.

In other reactions where ethoxyl radicals are involved, *e.g.*, the decompositions of diethyl peroxide and ethyl nitrate[6,8] the tendency has been to write mechanisms involving steps like step (2). It seems quite likely that ethyl nitrate and diethyl peroxide are not particularly good chain breakers and that steps like step (6) and (7) are more important.

NOTE ADDED IN PROOF.—Style and Mortlock[9] have recently reported the formation of ethyl nitrite from diethyl peroxide–nitric oxide mixtures at room temperature. To check this apparent discrepancy with the results reported here, two bulbs were filled with mixtures similar to that of experiment 8, Table I. Both bulbs were kept at room temperature in the dark for a week. Examination of the contents of one at that time showed only the original components present and no ethyl nitrite. The other was then heated for six minutes at 181° and gave the same results as reported for experiment 8. In a private communication, Dr. Style suggests that the formation of ethyl nitrite in his and Mortlock's work may be due to catalysis by quite special surfaces. He also suggests the possibility of a photochemical reaction in a part of the apparatus which was exposed.

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[8] L. Phillips, *Nature*, **165**, 564 (1950)

[9] D. W. G. Style and H. N. Mortlock, *ibid.*, **170**, 706 (1953).

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Ferromagnetic Alloys in the System Copper–Manganese–Indium

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An investigation of the copper-rich portion of the ternary ferromagnetic alloy system copper–manganese–indium has been made using thermal, microscopic and magnetic methods. Approximate limits of the α- and β-phases have been determined, and appear to be extensions of the corresponding α- and β-phases in the copper–indium system. The single-phase β region does not include the point Cu_2MnIn. Ferromagnetic Curie temperatures were obtained for the alloys as prepared, after quenching from solidus temperatures and after subsequent aging at 100°. For freshly quenched alloys the highest Curie temperatures, between 250 and 300°, were found in the vicinity of the Cu_2MnIn composition. Aging any of the alloys at 100° generally increased the Curie temperature, probably because of ordering of the structure.

The existence of ferromagnetism in the ternary alloy system copper–manganese–indium has been previously reported by several workers.[1–4] Ferromagnetic alloys composed of copper and manganese, with Al or Sn as the third metal, have been known for some time,[5] and it is found in each case that these properties are associated with a phase possessing an ordered body-centered cubic lattice.[6,7] It is also found that the largest value of magnetic

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[1] S. Valentiner, *Naturwissenschaften*, **4**, 123 (1947).

[2] F. A. Hames and D. S. Eppelsheimer, *Nature*, **162**, 968 (1948).

[3] B. R. Coles, W. Hume-Rothery and H. P. Myers, *Proc. Roy. Soc.* (*London*), **A196**, 125 (1949).

[4] R. R. Grinstead and D. M. Yost, *Phys. Rev.*, **75**, 984 (1949).

[5] Fr. Heusler, W. Stark and E. Haupt, *Verh. deuts. phys. Ges.*, **5**, 219 (1903).

[6] A. J. Bradley and J. W. Rogers, *Proc. Roy. Soc.* (*London*), **144**, 340 (1934).

[7] L. A. Carapella and R. Hultgren, Metals Technology, T. P. 1405 (Oct. 1941).