ending processes are important in the combustion wave. Further discussion of these reactions is postponed until more is known about the chemistry of methane oxidation at the high temperatures present in flames.

PRINCETON, NEW JERSEY

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

The Thermal Decomposition of Ethyl Nitrite[1,2]

BY JOSEPH B. LEVY

RECEIVED OCTOBER 21, 1955

The thermal decomposition of ethyl nitrite has been investigated in the gas phase at pressures of 10–50 mm. and temperatures of 161, 181 and 201°. Reaction kinetics have been measured and reaction products analyzed by means of the infrared spectra. Nitrous oxide, acetaldehyde, ethyl alcohol and nitric oxide have been found as products. The yields of acetaldehyde ranged from 60–90%. The addition of large amounts of nitric oxide did not materially affect the reaction rate but boosted the acetaldehyde yield toward a limit of 100% and the nitrous oxide yield to 50%. In the presence of added acetaldehyde the rate increased sharply and nitrous oxide was not a product. A mechanism has been suggested to explain these results.

Introduction

The thermal decomposition of nitrite esters has been the subject of much study[3–7] and has generally been discussed in terms of the following mechanism, written for the ethyl nitrite case, and referred to hereafter as the Steacie–Rice mechanism.

$$C_2H_5ONO \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C_2H_5O\cdot + NO$$

$$C_2H_5O\cdot + C_2H_5ONO \xrightarrow{k_2} C_2H_5OH + CH_3\cdot CHONO$$

$$CH_3\underset{\cdot}{C}HONO \longrightarrow CH_3CHO + NO$$

$$C_2H_5O\cdot \longrightarrow CH_3\cdot + CH_2O$$

$$CH_3\cdot + C_2H_5ONO \longrightarrow CH_4 + CH_3\underset{\cdot}{C}HONO$$

The decomposition reactions have generally been studied kinetically in the temperature range 160–220°. Evidence for the last two steps has been found at temperatures of about 400° and at very low pressures.[4] At the lower temperatures only the first three steps appear to be important. To satisfy the observed first-order kinetics it is necessary in considering these steps to assume that $k_2 >> k_{-1}$. Evidence recently has been found in this Laboratory that not only contradicts this assumption but also indicates that the second step plays no role in the reaction.[8] The thermal decomposition of ethyl nitrite has accordingly been investigated in the temperature range 161–201° at pressures of the order of 10–50 mm. The analytical tool used has been the infrared spectrometer. The results are reported below.

Experimental Part

Chemicals.—The ethyl nitrite was prepared in standard fashion,[3a] distilled and a middle fraction taken. It was stored in sealed ampules in a refrigerator.

In the early experiments the nitric oxide used was purchased from the Matheson Company. It was condensed into a tube on the vacuum line. By warming the tube only slightly it was possible to generate nitric oxide free of nitrogen dioxide. Small amounts of nitrous oxide were observed at times in the nitric oxide, however, and when it became clear that nitrous oxide was a product in some of the decompositions, a different source of nitric oxide was used. This involved the preparation of nitric oxide from potassium nitrate, sulfuric acid and mercury. No nitrous oxide was ever observed in this nitric oxide. This latter source of nitric oxide was used where analyses for nitrous oxide were made.

Acetaldehyde used was Eastman Kodak White Label grade and was taken directly from the bottle. Ethyl alcohol was 100% ethanol U.S.P. grade. The nitrous oxide used was taken directly from the cylinder.

The Analytical Procedure.—The compounds considered in setting up the analytical scheme were ethyl nitrite itself, acetaldehyde and nitrous oxide. Nitric oxide and ethanol were omitted because no suitable peaks for them are available in the infrared region involved.

Ethyl nitrite and acetaldehyde were determined using their absorption peaks at 12.85 and 5.70 μ, respectively. The analysis for nitrous oxide is more difficult because the intensity of the absorption peaks is not independent of the total pressure.[9] For this reason it was necessary to set up a calibration curve using some standard total pressure. The wave length used was 4.50 μ and the total pressure was set at atmospheric and was attained merely by opening the cell stopcock to the air.

The analysis for these three compounds was tested using synthetic mixtures containing all the products, *viz.*, ethyl nitrite, acetaldehyde, nitrous oxide and nitric oxide in amounts corresponding to various stages of reaction. The results indicated that ethyl nitrite, acetaldehyde and nitrous oxide could be determined to ±0.3 mm. In the actual analysis of decomposition runs the procedure was first to analyze for the ethyl nitrite and acetaldehyde. The stopcock to the infrared cell was then opened to the atmosphere and closed and the optical density at the nitrous oxide peak taken.

Results

The Nature of the Products.—Figure 1 is the spectrum of a sample of ethyl nitrite carried to complete decomposition. Acetaldehyde may be identified by the carbonyl absorption at 5.65 μ and the characteristic aldehyde C–H absorption at 3.5–3.75 μ. The presence of ethyl alcohol is best established by admitting air to the infrared cell. As shown in Fig. 1 this results in the appearance of the ethyl nitrite spectrum coupled with a decrease in the absorption at 9.4 μ, where C–O absorption peak of ethyl alcohol is found. This last peak is not

---

[1] The material reported here was presented in part before the Division of Physical and Inorganic Chemistry at the 126th Meeting of the American Chemical Society, New York, N. Y., September, 1954.

[2] Full experimental details of this work, including infrared spectra can be found in the reference, J. B. Levy, NavOrd 3833, 1954.

[3] (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).

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

[5] N. Kornblum and E. P. Oliveto, *ibid.*, **71**, 226 (1949).

[6] L. P. Kuhn and L. DeAngelis, *ibid.*, **76**, 328 (1954).

[7] P. Gray, *Proc. Roy. Soc.*, (*London*), **A221**, 462 (1953).

[8] J. B. Levy, THIS JOURNAL, **75**, 1801 (1953).

[9] P. C. Cross and F. Daniels, *J. Chem. Phys.*, **2**, 6 (1934).

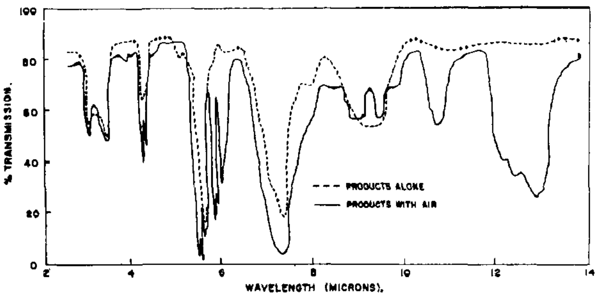

Fig. 1.—Thermal decomposition of ethyl nitrite at 181°.

intense enough to be used for the identification of ethyl alcohol. The ethyl nitrite formation results from the immediate reaction of the ethyl alcohol present with the nitrogen dioxide formed by the air oxidation of the nitric oxide present. The brown color of nitrogen dioxide observed on the admission of air is further confirmation of the presence of nitric oxide in the products.

Acetaldehyde, ethyl alcohol and nitric oxide have been reported[3a] as the products of the thermal decomposition of ethyl nitrite. The small amounts of carbon monoxide also reported would not be detected by the infrared analyses used here. In addition to these compounds the presence of another product is indicated by the peak at 4.5–4.6 μ shown in Fig. 1. The contour, intensity and pressure dependence of this peak are characteristic of nitrous oxide which is thus also a product.

For experiments with large (70 mm.) pressures of ethyl nitrite it was possible to detect traces of hydrogen cyanide in the products by means of the 14.05 μ absorption. Estimates from the peak intensities put the yields of hydrogen cyanide at 2–5% of the initial nitrite ester. These amounts were barely perceptible for the runs at the usual (~20 mm.) pressures. It may be noted that when ethyl nitrite was decomposed in the presence of acetaldehyde the hydrogen cyanide yields were boosted to 5–10% of the original ethyl nitrite.

The double pointed peak at 5.5–5.6 μ in Fig. 1 is due to the presence of nitrosyl chloride, while the large peak at 7–7.5 μ shows that sodium nitrate is present on the cell faces. These products result from the slow reaction of nitrogen dioxide with the sodium chloride cell faces, a reaction much too slow to compete with the nitrogen dioxide–ethanol reaction.

Since a mass spectrographic analysis showed no methane or formaldehyde present it may be assumed that the products indicated above are the only ones present in any amount.

The Source of the Nitrous Oxide.—Nitrous oxide has been observed in trace amounts in the products of the thermal decomposition of methyl nitrite.[10] It also has been found in the products of the photochemical decomposition of ethyl and methyl nitrites.[11] Since painting the reaction vessel black had no effect on the nature of the reaction products it is clear that nitrous oxide is a true product of the thermal decomposition.

In an effort to establish the mode of formation of the nitrous oxide the assumption was made that the nitrous oxide arose in some way by a reaction involving nitric oxide. Mixtures of nitric oxide with ethyl nitrite, acetaldehyde or ethyl alcohol were heated for appropriate periods of time. The reaction of nitric oxide and ethoxyl radical was investigated by heating a mixture of nitric oxide and diethyl peroxide. Of all of these only the last named gave nitrous oxide. In a sample experiment 11.6 mm. of diethyl peroxide was heated with 46 mm. of nitric oxide at 181° for six minutes. The yield of ethyl nitrite found was 69% and that of nitrous oxide 2–4%. The chief product of this reaction thus is ethyl nitrite,[8] but apparently nitric oxide and ethoxyl radical also react to give nitrous oxide in small amounts.

The Reaction Kinetics.—Reaction rates were measured at 161, 181 and 201°. The results for 181°, which are typical, are plotted for a first-order reaction in Fig. 2. Experiments were carried out on the decomposition of ethyl nitrite alone and in the presence of added nitric oxide, acetaldehyde and ethyl alcohol.

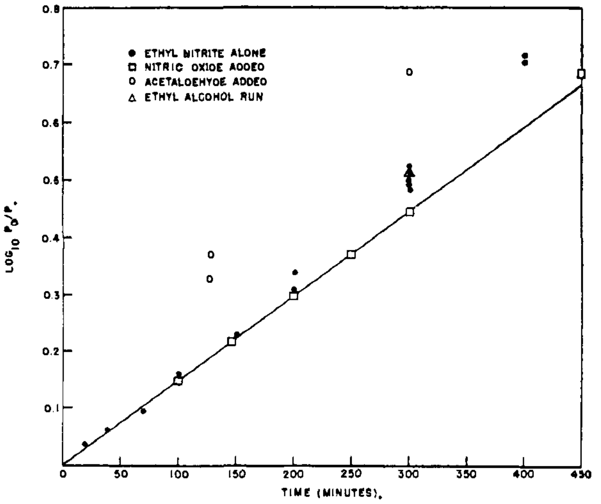

Fig. 2.—The thermal decomposition of ethyl nitrite at 181°.

As Fig. 2 shows, for ethyl nitrite by itself the curve obtained is fairly linear at the start of the reaction but after about 50% reaction the points bend up and away from a straight line. In the presence of added nitric oxide the curve is linear over the entire reaction course and coincides with the initial linear portion of the curve for ethyl nitrite alone.

It can also be seen that added ethyl alcohol has no effect on the reaction while acetaldehyde causes marked acceleration. Some of the pertinent data are shown in Table I.

It can be seen from experiments 1, 2, 6, 7 and 9 that the apparent first-order rate constant is increasing as the reaction proceeds. In the presence of added nitric oxide the rate remains constant at about 57×10^{-5} sec.$^{-1}$ even though the nitric oxide added varies by a factor of almost seven, experiments 3, 4 and 5.

The rate expression calculated from the experiments in the presence of nitric oxide at 161, 181 and 201°, is $k = 6.1 \times 10^{13} \exp(-37{,}500 \pm 550/$

---

(10) A. G. Carter and M. W. Travers, *Proc. Roy. Soc.* (*London*), **A158**, 495 (1937).

(11) C. H. Purkis and H. W. Thompson, *Trans. Faraday Soc.*, **32**, 1466 (1936).

TABLE I

THE KINETICS OF THE THERMAL DECOMPOSITION OF ETHYL NITRITE AT 181°

Expt.	Initial pressures (mm.) C_2H_5ONO	Additive	Time, min.	Reaction, %	10^5k^a (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 CH_3CHO	126	52.6	97.0
12	31.0	50 CH_3CHO	126	57.0	110.3

[a] First order rate constant, $2.303/t \log (P_0/P)$.

RT) sec.$^{-1}$. The accuracy indicated for the activation energy is that calculated from those of the individual rate constants. These were calculated by the method of least squares. This value for k is in good agreement with that reported by Steacie and Shaw[3a] of $k = 1.39 \times 10^{14}$ exp. $-37{,}000/RT$ sec.$^{-1}$.

The Product Composition.—Product analyses for the 201° experiments are shown in Table II.

TABLE II

THE PRODUCTS OF THE THERMAL DECOMPOSITION OF ETHYL NITRITE AT 201°

Expt.	Time, min.	Initial pressure C_2H_5-ONO	Additive	Reaction, %	Yield,[a] % CH_3CHO	N_2O[b]
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 ± 0.5
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	56 ± 5
11	45	20.6	29 NO	59.0	86 ± 3	48 ± 3
12	45	18.2	101 NO	57.2	96 ± 4	....
13	76	33.5	32 NO	77.6	81 ± 2	49 ± 1
14	15	20.0	24.5 CH_3CHO	47.0	.....	0
15	30	20.0	58.0 CH_3CHO	78.4	.....	0

[a] The yield uncertainties are calculated using ordinary probable error formulas[12] and assuming the analyses for nitrous oxide and acetaldehyde are good to ±0.3 mm. [b] 2(moles nitrous oxide found ÷ moles ethyl nitrite reacted).

Discussion

The main points which emerge from the results reported here and in the earlier paper[8] may be listed and considered in terms of the Steacie–Rice mechanism. They are: (a) nitrous oxide is a significant reaction product and its formation depends on a reaction between nitric oxide and ethoxyl radical. This cannot be explained on the basis of the Steacie–Rice mechanism. (b) Acetaldehyde is found in yields of 60–90% when ethyl nitrite is decomposed by itself, runs 1–5, Table II. The Steacie–Rice mechanism requires a yield of 50% for acetaldehyde. (c) Despite the fact that the reaction of ethoxyl radical with nitric oxide to give ethyl nitrite is a fast reaction[8] the rate of thermal decomposition of ethyl nitrite is not lowered by added nitric oxide, at least during the first 50% of reaction. For longer periods of reaction the effect of nitric oxide is to lower the rate to the limiting initial value. (d) The pressure of added nitric oxide results in increases in the acetaldehyde yield toward a limit of 100% and in the nitrous oxide yield to 50%. (e) The addition of acetaldehyde accelerates the reaction and eliminates nitrous oxide as a product. Points (c), (d) and (e) cannot be explained in terms of the Steacie–Rice mechanism.

The above points may be considered in terms of the following sequence of steps.

$$C_2H_5ONO \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C_2H_5O\cdot + NO \qquad (1)$$

$$C_2H_5O\cdot + NO \xrightarrow{k_2} NOH + CH_3CHO \qquad (2)$$

$$2NOH \xrightarrow{k_3} N_2O + H_2O \qquad (3)$$

$$C_2H_5O\cdot + NOH \xrightarrow{k_4} C_2H_5OH + NO \qquad (4)$$

Point (a) is satisfied in that the formation of nitrous oxide in step 3 depends on a reaction between nitric oxide and the ethoxyl radical in step 2. There is supporting evidence for the reaction of step 3 in the literature.[13] The acetaldehyde yield, point (b), in the above sequence depends on the relative importance of steps 3 and 4. If the reaction proceeds solely *via* steps 1, 2 and 3 a 100% yield of acetaldehyde would result, while if only steps 1, 2 and 4 occurred the yield would be 50%. The observed yields of 60–90% are thus readily accommodated.

To consider point (c) it is necessary to include the kinetic aspects of the above sequence. If the steady-state assumption is made for ethoxyl radical the expression resulting is

$$\frac{-\,d \ln (C_2H_5ONO)}{dt} = \frac{k_1(k_2(NO) + k_4(NOH))}{(k_{-1} + k_2)(NO) + k_4(NOH)}$$

The kinetic situation is quite complicated during the later stages of the decomposition of ethyl nitrite by itself. In the early stages or in the presence of excess nitric oxide, it is simpler. Here the acetaldehyde yields are close to 100% and the rate is independent of nitric oxide. Under such conditions it is evident that $k_2(C_2H_5O\cdot)(NO) >> k_4(C_2H_5O\cdot)(NOH)$, hence that $k_2(NO) >> k_4(NOH)$ and that $(k_{-1} + k_2)(NO) >> k_4(NOH)$. The above expression thus reduces to

$$\frac{-d \ln (C_2H_5ONO)}{dt} = \frac{k_1k_2}{k_{-1} + k_2}$$

and the requirement of point (c) is met.

The effect of nitric oxide on the product distribution, point (d), can be considered in the following way. Increasing the nitric oxide concentration, in essence, acts to lower the stationary concentration of the ethoxyl radical. In the presence of added nitric oxide this stationary concentration is equal to $k_1(C_2H_5ONO)/(k_{-1} + k_2)(NO)$. From

---

(12) F. Daniels, J. H. Mathews and J. W. Williams, "Experimental Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 450.

(13) (a) P. Harteck, *Ber.*, **66**, 423 (1923); (b) H. A. Taylor and C. Tanford, *J. Chem. Phys.*, **12**, 47 (1944).

this it follows that the rate of step 2 is independent of the nitric oxide concentration. Since the rate of production of the nitroxyl species *via* step 2 is unchanged, it may be assumed that the stationary nitroxyl concentration is not changed appreciably. The addition of nitric oxide should thus lower the rate of step 4. The decrease in the rate of step 4 relative to that of step 2 results in an increase in the acetaldehyde yield toward a limit of 100%. Similarly the addition of nitric oxide favors step 3 over step 4 and the nitrous oxide yield should increase, as observed. The nitrous oxide yield should approach 100% as a limit, however, rather than the 50% observed. This suggests that the nitroxyl species may be reacting in a fashion other than that of steps 3 and 4. The inclusion of the step

$$2NOH \longrightarrow 2NO + H_2 \qquad (5)$$

seems a reasonable explanation for the discrepancy between the expected and the observed nitrous oxide yields. Mass spectrographic analyses of the products for hydrogen are planned as a test for this point.

The effect of acetaldehyde on the reaction, point (e), also requires the postulate of additional steps. The steps

$$C_2H_5O\cdot + CH_3CHO \xrightarrow{k_6} C_2H_5OH + CH_3\underset{\cdot}{C}O \qquad (6)$$

$$CH_3\underset{\cdot}{C}O \longrightarrow CH_3\cdot + CO \qquad (7)$$

$$CH_3\cdot + NO \longrightarrow CH_3NO \longrightarrow CH_2{=}NOH \longrightarrow HCN + H_2O \qquad (8)$$

furnish a reasonable explanation for the carbon monoxide reported as a product in low yield (~4%) by Steacie and Shaw[3a] and for the small amounts of hydrogen cyanide found here. Incorporation of steps 6–8 in the kinetic treatment leads to the expression

$$\frac{-\mathrm{d}\ln(C_2H_5ONO)}{\mathrm{d}t} = k_1\left(1 - \frac{k_{-1}(\mathrm{N})\mathrm{O}}{(k_{-1} + k_2)(\mathrm{NO}) + k_4(\mathrm{NOH}) + k_6(\mathrm{CH_3CHO})}\right)$$

As the acetaldehyde concentration gets larger the fraction within the parentheses gets smaller and the over-all rate increases. Actually it is easy to see that it is the ratio $(CH_3CHO)/(NO)$ that determines the rate and not (CH_3CHO) alone. Experiments like runs 11 and 12 of Table I thus are not suitable for a quantitative determination of the effect of acetaldehyde but do illustrate the qualitative nature of the effect.

The explanation for the effect of acetaldehyde in eliminating nitrous oxide as a product[14] may lie in the higher stationary concentration of methyl radicals found in the presence of acetaldehyde due to step 7. These may well compete successfully for the nitroxyl species *via*

$$CH_3\cdot + NOH \longrightarrow CH_4 + NO$$

The above mechanism is thus capable of explaining the main features of the reaction.

The effect of the above ideas on the interpretation of the activation energy may be noted. It appears that equating the activation energy to the O–N bond energy is incorrect. If the rate constant $k_1k_2/(k_{-1} + k_2)$ is approximated to k_1k_2/k_{-1} on the assumption that $k_{-1} >> k_2$, the observed activation energy becomes $E_1 + E_2 - E_{-1}$. Since E_{-1} refers to the recombination of two rather simple radicals it may be equated to zero and $E_{\mathrm{act}} = E_1 + E_2$. It is not possible to evaluate E_2. It seems reasonable to set $E_6 \approx 7.5$ kcal./mole the value found for the similar reaction between methyl radical and acetaldehyde.[15] Since $k_2 >> k_6$ it seems a good guess that $E_2 < E_6$ and is probably of the order of a few kcal./mole.

A good way to get at the true value of E_1 and at the same time to get a good test of the mechanism would be to heat mixtures of ethyl nitrite and nitric oxide enriched with N^{15}. According to the above mechanism exchange of nitric oxide should occur at a rate much faster than that of reaction. Experiments have been carried out along these lines. Unfortunately the results have been highly erratic, variable amounts of exchange having been observed at room temperature even with the most stringent precautions. These experiments have accordingly been halted.

Acknowledgment.—This work was carried out under a task assignment from the Bureau of Ordnance, Department of the Navy.

WHITE OAK, MARYLAND

---

(14) Purkis and Thompson[11] have suggested that the nitroxyl species oxidizes acetaldehyde to acetic acid. No evidence of acetic acid was found in the products here. The possibility that nitrous oxide might be oxidizing acetaldehyde was disproved experimentally.

(15) D. W. Volman and R. K. Brinton, *J. Chem. Phys.*, **20**, 1764 (1952).