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

The Thermal Decomposition of Nitrate Esters. I. Ethyl Nitrate[1]

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The thermal decomposition of gaseous ethyl nitrate has been studied at 161–201° at pressures of a few cm. An analytical technique has been developed using the absorption spectra in the infrared and visible regions which has made it possible to follow the disappearance of ethyl nitrate directly. It has been found that ethyl nitrite is a major product of the reaction and that methyl nitrite and nitromethane are formed in minor amounts. The formation of nitrogen dioxide and nitric oxide as reported by others has also been observed using the optical techniques. The variations with time of ethyl nitrate, ethyl nitrite and nitrogen dioxide have been followed quantitatively. Some semi-quantitative data have also been found for nitric oxide and nitromethane. The mechanism for nitrate ester decomposition is examined in the light of the results found and some revisions suggested.

Introduction

The thermal decomposition of nitrate esters in the gas phase has been the subject of much kinetic study by manometric techniques.[2–6] Because of the complex nature of the reaction it was felt that the study of it by a technique which yielded more detailed information about the reaction would be worthwhile. This paper describes the application of infrared and visible spectrophotometric techniques to the study of the thermal decomposition of ethyl nitrate.

Experimental Part

Apparatus.—Two infrared spectrometers were used. For all the actual analyses of the gas mixtures a Perkin-Elmer Model 12-C instrument was used. For qualitative examination of different spectra a Perkin-Elmer Model 21 Double Beam Recording Spectrometer was used. Both instruments were equipped with rock salt optics.

The infrared cells used consisted of 52.0 mm. sections of 47 mm. Pyrex tubing having vacuum stopcocks sealed on to the body. Rock salt cell faces were sealed to the cell ends using paraffin wax which was found to be resistant to the action of nitrogen dioxide as well as inert to the other possible components. The nitrogen dioxide was measured in Pyrex cells 50.0 mm. long and having faces 35 mm. in diameter.

Chemicals.—Ethyl nitrate was Eastman Kodak white label grade which was redistilled. A fraction boiling at 87.5–87.8° was used. The ethyl nitrite was prepared in a standard fashion.[7] It was distilled before use and the middle third of the distillate used. It was stored in a sealed ampule in a refrigerator. The nitrogen dioxide (Matheson Co., purity 98%) was distilled into the vacuum system through a tube of anhydrous calcium sulfate. The nitric oxide (Matheson Co., purity 98%) was used without further treatment.

The Infrared Measurements.—The measurements made on the Perkin-Elmer Model 12-C infrared spectrometer were carried out using the "cell in-cell out" technique. The compounds determined were always present at pressures well within the range covered in the Beer's law measurements. In the calculation of the constant for nitrogen dioxide, allowance was made for the association equilibrium using the data of Verhoek and Daniels.[8]

The Experimental Measurements.—The preparation and analysis of the gas mixtures and the actual kinetic runs were carried out as described in an earlier paper.[9] Several bulbs were filled simultaneously and the initial pressure of ethyl nitrate was obtained optically by transferring the contents of one bulb to an infrared cell without any heating period.

Time was counted from the immersion of the bulbs in the thermostat to their quenching in the cold water-bath. Both operations took only a few seconds. The time required for the bulbs to attain bath temperature was measured at 181° by immersing a bulb filled with air at about 40 mm. in the bath. By means of an attached manometer it was observed that the pressure had attained its maximum value by 0.5 minutes. On plunging the bulb into cold water it is the initial cooling which is important in quenching the reaction and this would obviously take much less time. Any time error arising in this way should be a constant absolute amount less than 0.5 minute and would be taken care of in the statistical treatment of the data.

Results

The Nature of the Reaction Products.—From the infrared spectra of the reaction products it was found that ethyl nitrite, nitromethane and methyl nitrite were formed. The presence of nitrogen dioxide was established by its color and the presence of nitric oxide by the intensification of the nitrogen dioxide color when air was admitted to the mixture. Ethyl nitrite was a major product and was readily identified by direct comparison of the products' spectra with that of pure ethyl nitrite. Nitromethane and methyl nitrite were minor products, the latter being detectable only in the late stages of the reaction. The absorption peaks of both compounds were obscured by ethyl nitrite peaks. It was possible to effect a quantitative separation of the nitromethane (b.p. 101.5°) from the ethyl nitrite (b.p. 17°) using a system of cold traps. The spectrum of the less volatile fraction checked exactly with that of pure nitromethane. For methyl nitrite the procedure was to observe the difference spectrum resulting when a cell containing a decomposition mixture was compared in the double beam infrared spectrometer with one containing ethyl nitrite to duplicate the amount in the mixture. Comparison of the resultant spectrum with that of pure methyl nitrite established the presence of this compound in the products.

The above compounds accounted for all the peaks observed in the 2–15 μ region except for a small peak around 5.7 μ. This is the region where carbonyl absorption is found and suggests the possible presence of acetaldehyde or formaldehyde. Since the peak was always small it was not possible to establish whether either or both of these compounds were present.

Previous workers[4–6] using standard analytical techniques have reported nitric oxide, nitrogen dioxide, carbon dioxide and carbon monoxide as

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[1] Complete experimental details including infrared spectra can be found in J. B. Levy, Navord Report 2313, June 12 (1952).

[2] S. Roginsky, *Phys. Z. d. Sowjetunion*, **1**, 640 (1932).

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

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

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

[6] L. Phillips, Thesis, University of London (1949).

[7] E. W. R. Steacie and G. T. Shaw, *J. Chem. Phys.*, **2**, 345 (1934).

[8] F. H. Verhoek and F. Daniels, THIS JOURNAL, **53**, 1250 (1931).

[9] J. B. Levy, *ibid.*, **76**, 1801 (1954).

products present in substantial amounts accompanied by very small amounts of nitrogen and nitrous oxide. The presence of water as a product also has been reported although no analyses for it were made.

The Analysis of the Reaction Mixtures.—The mixtures were analyzed quantitatively for ethyl nitrate and ethyl nitrite using the peaks at 11.73 and 12.85 μ, respectively. Nitrogen dioxide was determined quantitatively in the quartz spectrophotometer using the absorption at 4050 Å. The estimates for nitric oxide were made by admitting air to the glass cell and measuring the increase in the absorption. Separate experiments with pure nitric oxide established that this analysis was accurate to better than 5%. The admission of atmosphere to a cell containing only nitrogen dioxide did not affect the absorption.[10] This method of analyzing for nitric oxide was not tested with synthetic mixtures. For this reason the values found have been used only to indicate the general course of the nitric oxide variation. The estimates made for nitromethane used the absorption intensity at the 6.30 μ peak after the separation from the ethyl nitrate had been made as described above.

In Table I are given the Beer's law constants required for the analyses.

TABLE I

BEER'S LAW CONSTANTS (UNIT PRESSURE = 1 MM., UNIT CELL LENGTH = 1 MM.) PRESSURE RANGE 0–30 MM.

Wave length, μ	Ethyl nitrate	Ethyl nitrite	Nitrogen dioxide
5.70	0.000021 ± 0.000006	....	....
11.73	.00108 ± .00004m	0.000046 ± .000006	....
12.85	.00003 ± .000002	.000919 ± .000008[a]	....
0.4050	....	....	0.000888 ± 0.000014

[a] Above 15 mm. pressure this curve deviated from linearity and a calibration curve was used. This deviation is not due to pressure broadening but is probably due to the fact that the light beam was not monochromatic.

The analytical technique was tested in two ways. Synthetic mixtures were made up containing ethyl nitrate, ethyl nitrite, nitrogen dioxide and acetaldehyde in varying amounts and analyzed for the first three components. The accuracy of the analyses was 3–4% for ethyl nitrate and ethyl nitrite, and 5–6% for nitrogen dioxide. This was considered sufficient for the purpose. Further testing of the analytical technique was accomplished in the following way. Samples of ethyl nitrate were carried to varying degrees of decomposition and analyzed. Synthetic mixtures were made up containing ethyl nitrate and ethyl nitrite in amounts to duplicate the analysis. The spectrum of the synthetic mixture was compared to that of the decomposition mixture. The agreement was excellent at all of the peaks of these two compounds, confirming the validity of the analysis.

The Variation of the Products.—The variation of the products over the course of the reaction is shown for 181° in Fig. 1. The data are plotted as P/P_0, the partial pressure of the particular component divided by the initial ethyl nitrate pressure. This was necessary since the initial ethyl nitrate pressure was chosen so that the pressure of ethyl nitrate in the mixture to be analyzed would be at an appropriate value—*i.e.*, 5–10 mm. The results at 161 and 201° were similar. For nitromethane, estimates made at 40 and 80% reaction indicated yields of 8 and 9%, respectively, based on the amount of ethyl nitrate decomposed. An estimate made on a sample carried to complete decomposition gave a yield of 9% for nitromethane. These points are not shown in Fig. 1.

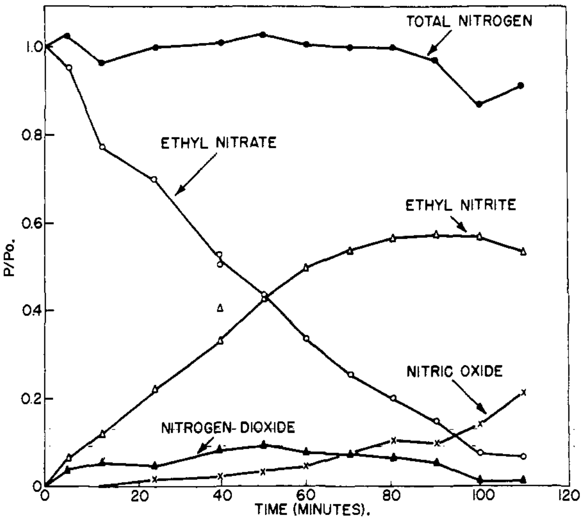

Fig. 1.—Thermal decomposition of ethyl nitrate at 181°.

The importance of ethyl nitrite as a product is clearly shown in Fig. 1. It reaches a maximum of $P/P_0 = 0.6$ at a point where about 80% of the ethyl nitrate has decomposed. This corresponds to a yield of ethyl nitrite of 75% based on the ethyl nitrate decomposed.

The observation[4,6] that the nitrogen dioxide formed passes through a maximum is confirmed by Fig. 1, although the maximum is very flat and quite low. The nitric oxide pressure begins to become important only in the late stages of the reaction. The observation of large amounts of nitric oxide by other workers[4–6] is due to the fact that in those cases the reaction times were long enough to allow substantial decomposition of the ethyl nitrite. The effects of this decomposition can be seen in the upswing in the nitric oxide curve toward the end of the reaction.

To get the points for the total nitrogen curve in Fig. 1 the values for nitric oxide, nitrogen dioxide, ethyl nitrite, ethyl nitrate and nitromethane were summed up. The nitromethane values were calculated assuming it is formed in 8.5% yield over the entire reaction. This is admittedly crude but since the amounts of nitromethane were quite small, errors in it would not affect the total nitrogen value very much. No analyses for methyl nitrite were carried out. Over most of the reaction the total nitrogen curve plotted in Fig. 1 is close to a value of one. Toward the end of the reaction it drops down

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(10) Similar results are reported for the effect of nitrogen: T. C. Hall, Jr., and F. E. Blacet, *J. Chem. Phys.*, **20**, 1745 (1952).

due to the neglect of methyl nitrite. This behavior of the curve is strong support for the assumption that all the nitrogen-containing compounds present in the gas mixtures have been accounted for.

The Kinetics of the Reaction.—Previous workers have treated the thermal decomposition of ethyl nitrate as a first order reaction although when the data were so plotted the curves were not simple straight lines. Phillips[5,6] neglected the initial part of the rate curves and used a later linear portion to calculate rate constants. Adams and Bawn[4] in effect used initial slopes. The data obtained here at 181° are plotted as if the reaction were first order in Fig. 2. It is clear that the points fall on a curve of increasing slope rather than on a straight line. It was possible to draw a fairly good straight line through an initial part of the curve and a line of greater slope through a later part. Similar results were obtained at 161°. At 201° the scatter in the points was greater and only one line could be drawn through the points. Rate constants were calculated from the different parts of the curves at 161 and 181°. The activation energies and frequency factors calculated from these constants were compared in Table II to those reported by the earlier workers.

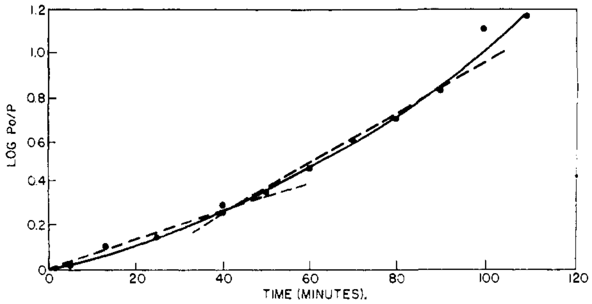


Fig. 2.—Rate of decomposition of ethyl nitrate at 181°.

TABLE II

RATE OF THERMAL DECOMPOSITION OF ETHYL NITRATE

Frequency factor, sec.$^{-1}$	Activation energy, kcal./mole	Source
$10^{13.86}$	36.0	Phillips
$10^{14.44}$	36.6	k_{later}[a]
$10^{15.8}$	39.9	Adams and Bawn
$10^{15.1}$	39.3	k_{initial}[b]

[a] Calculated from slopes of later parts of curves. The 201° constant was consistent with this group. [b] Calculated from slopes of initial parts of curves.

The above results suggest strongly that Phillips and Adams and Bawn were working with different sections of the same rate curves.

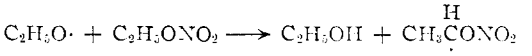
Discussion

The Reaction Products.—Ethyl nitrite has been reported as a product of this reaction by Thiele.[11] No experimental details were given and this report has generally been discounted.[5] The reason other investigators[4,6] failed to observe it is probably due to the reagents used to determine nitrogen dioxide. In both cases the reagents would have given positive tests with ethyl nitrite so that it would have shown up as nitrogen dioxide. The same is true for methyl nitrite while nitromethane probably was undetected because of its low concentration.

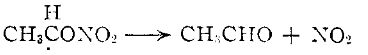
Adams and Bawn and Phillips both reported the formation of small amounts of nitrous oxide and traces of nitrogen. No nitrous oxide was detected in this work in the decomposition of ethyl nitrate. For samples heated long enough to allow substantial decomposition of the ethyl nitrite formed the infrared spectra contained peaks due to nitrous oxide. It has recently been found in this Laboratory[12] that nitrous oxide is a product of the thermal decomposition of ethyl nitrite and it seems quite certain that this is the way it arises here as well. At present no explanation for the nitrogen suggests itself.

The Mechanism of the Reaction.—The following mechanism has been proposed on the basis of the manometric studies[4–6]

$$C_2H_5ONO_2 \rightleftarrows C_2H_5O\cdot + NO_2 \qquad (1)$$



$$C_2H_5O\cdot + C_2H_5ONO_2 \longrightarrow C_2H_5OH + CH_3\overset{H}{\underset{\cdot}{C}}ONO_2 \qquad (2)$$



$$CH_3\overset{H}{\underset{\cdot}{C}}ONO_2 \longrightarrow CH_3CHO + NO_2 \qquad (3)$$

The carbon monoxide, carbon dioxide, water and nitric oxide observed are explained by the further reaction of the products of 3.[13,14]

Because of the absence of methane in the reaction products the steps

$$C_2H_5O\cdot \longrightarrow CH_3 + CH_2O \qquad (4)$$

$$CH_3\cdot + C_2H_5ONO_2 \longrightarrow CH_4 + CH_3\underset{\cdot}{C}HONO_2 \qquad (5)$$

have been excluded. The above mechanism is patterned after that written for nitrite ester decomposition.[15] Step (1) above has been made reversible to account for the observed[5,6] inhibition of the reaction by nitrogen dioxide.

Of the results reported here the chief one that the above mechanism must explain is the formation of ethyl nitrite in such large amounts. The most obvious explanation is the known reaction of nitrogen dioxide and ethyl alcohol[16] *via*

$$2NO_2 + C_2H_5OH \longrightarrow C_2H_5ONO + HONO_2 \qquad (6)$$

One objection to this route is that it would set a limit of 50% on the yield of ethyl nitrite based on the ethyl nitrate decomposed. Actually the yields were of the order of 75%. Another objection is that if the nitrogen dioxide reacted in this way there would not be enough left to oxidize much of the acetaldehyde and substantial yields of the acetaldehyde would have been observed. The absorption observed in the region where the acetaldehyde carbonyl absorption occurs showed that at most only small amounts of acetaldehyde could have been present.

These objections rule out 6 as the sole source of ethyl nitrite but not as a contributing source. There

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(11) H. Thiele, *Angew. Chem.*, **A65**, March (1948).

(12) J. B. Levy, unpublished results.

(13) C. A. MacDowell and J. H. Thomas, *Trans. Faraday Soc.*, **46**, 1030 (1950).

(14) Recent studies, L. C. Browning, private communication, have shown that this reaction is more complex than originally supposed, nitromethane, methyl nitrate and methyl nitrite being observed in the products at 100–140°.

(15) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, N. Y., 1946, p. 141.

(16) A. D. Yoffe and P. Gray, *J. Chem. Soc.*, 1112 (1951).

is evidence however against the actual occurrence of step 2. Recent work in this laboratory[9] on the thermal decomposition of ethyl nitrite has shown that the analogous reaction is not important in that case and there is no reason why that conclusion cannot be extended to the nitrate case. To this may be added the observation in this laboratory that *t*-butyl nitrite is formed in substantial amount in the decomposition of *t*-butyl nitrate.[17] For this ester a step like 2 is impossible.

Another possible source for the ethyl nitrite is the reaction

$$C_2H_5O\cdot + NO \longrightarrow C_2H_5ONO \qquad (7)$$

which has recently been demonstrated experimentally.[9] For this reaction to be a satisfactory explanation it is necessary to show that sufficient nitric oxide can be formed to give the observed yields of ethyl nitrite without at the same time destroying too much of the hydrocarbon residue. One sequence of equations that fulfills these requirements and which in addition offers a plausible explanation for the other observed products is as follows[18]

$$[2CH_2O + 5NO_2 \longrightarrow CO + CO_2 + 2H_2O + 5NO] \qquad (8)$$

$$[7NO_2 + 2CH_3\cdot \longrightarrow 2CO_2 + 3H_2O + 7NO] \qquad (9)$$

$$CH_3\cdot + NO_2 \longrightarrow CH_3NO_2 \qquad (10)$$

$$CH_3\cdot + NO_2 \longrightarrow CH_3O\cdot + NO \qquad (11)$$

$$CH_3O\cdot + NO \longrightarrow CH_3ONO \qquad (12)$$

The formaldehyde and methyl radicals involved in 8 and 9 arise *via* step 4. Step 4 has been ruled out by Adams and Bawn[4] because they found no methane in the reaction products. This is a valid reason for ruling out step 5 but the absence of the methane can as well be explained by the assumption that the methyl radicals formed react much more rapidly by reactions 9–11 than by 5. Step 8 is a fast reaction at thse temperatures.[19] It is easy to show that the above sequence yields all the products in their proper amount. It may be noted here that an alternative to 8 and 9 can be written wherein the nitrogen dioxide reacts directly with the ethoxyl radical. A decision between these possibilities must await the result of further studies.

The thermal decomposition of nitrate esters is thus a more complex reaction than had previously been supposed. Certainly the kinetic behavior is too complex for the simple treatments used in the past. The situation is especially difficult because the mechanisms of the reactions of the primary products such as steps 8 and 9, as well as of the thermal decomposition of ethyl nitrite are either unknown or at least unsettled.[9,19] Other reactions such as

$$CH_3\cdot + NO \longrightarrow CH_3NO \longrightarrow \text{products}$$

about which little is known may also play a part.[20] Although a final complete mechanism thus cannot be written at this time the one discussed here has been suggested because it does give a coherent picture of the reaction and points out approaches for further study. The results of such studies will be reported in the near future.

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[17] J. B. Levy and F. J. Adrien, unpublished results.

[18] The sequence 11 and 12 is used for the formation of methyl nitrite because it was observed principally in the late stages of the reaction where the nitric oxide concentration becomes large. A one step direct union analogous to 10 would require methyl nitrite to be formed steadily over the whole reaction period as was nitromethane. A theoretical justification for this sequence may be presented. If methyl nitrite were formed in one step by a direct reaction of methyl radical and nitrogen dioxide an activated molecule would result which would have a great excess of energy (the C–O bond energy of 77.1 kcal./mole), much more than would be required to cleave the O–N bond (35–40 kcal.). The net result would be that of step 11.

[19] F. H. Pollard and R. M. H. Wyatt, *Trans. Faraday Soc.*, **45**, 760 (1949).

[20] I am indebted to one of the referees for suggesting this point.