The heat of homolytic dissociation of tetrafluorenylhydrazine appeared to be nearly constant at 16.3 to 17.4 ± 1.2 kcal. in the solvents mentioned above. The heat of dissociation of the N-N bond in tetrafluorenylhydrazine is lower than that in tetraphenylhydrazine by 14 kcal. In the hexarylethane series, no appreciable change in dissociation energy from the 11.5 kcal. for hexaphenylethane was noted upon varying the aryl substituents. According to the theory set forth by Lewis and Lipkin, 1 the two central carbon atoms are essentially neutral in the hexaarylethanes, while each of the two nitrogen atoms in hydrazine derivatives bears a lone pair of electrons and the coulombic repulsion of the high charge density on the nitrogens plays an important role in the dissociation. Tetraphenylhydrazine resonates among the Kekulé structures and the o- and p-quinoid structures in which the withdrawal of the lone pair of electrons on a nitrogen atom into the o- and p- positions of the phenyl rings decrease the coulombic repulsion between the nitrogen and strengthens the N-N bond. However, this type of resonance is not possible in tetrafluorenylhydrazine, the two nitrogens being more negative than those in tetraphenylhydrazine and the coulombic effect diminishing the energy required to dissociate the molecule. It is probable that steric hindrance also influences the dissociation energy of the N-N bond in tetraarylhydrazines.

Acknowledgment.—We wish to thank the Research Corporation of America for the Frederick Gardner Cottrell grants which enabled us to carry out this work.

PITTSBURGH, PA.

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

The Thermal Decomposition of Nitrate Esters. II. The Effect of Additives on the Thermal Decomposition of Ethyl Nitrate 1

BY JOSEPH B. LEVY

RECEIVED APRIL 3, 1954

Introduction

The thermal decomposition of ethyl nitrate has recently been investigated using infrared spectrometry as the analytical tool. 2 An examination of the reaction products found and of the reaction kinetics showed the reaction to be more complex than had earlier been supposed. 3–5 The effect of additives both on the nature of the reaction products and on the kinetics is of great interest and the present paper reports the application of the infrared techniques to the study of these effects.

Experimental Part

Chemicals.—The ethyl nitrate, nitrogen dioxide, oxygen, nitric oxide, acetaldehyde and diethyl peroxide on the thermal decomposition of ethyl nitrate at 181° have been studied. The results of these studies have been examined in the light of a mechanism proposed in an earlier paper and give it strong support. On the basis of the proposed mechanism it has been possible to carry out the thermal decomposition of ethyl nitrate under conditions such that the kinetics were truly first order and the activation energy and frequency factor could be properly related to the step wherein the N-O bond was broken.

The Experimental Procedure.—The methods of making the measurements and manipulating the gas mixture have been described in the previous paper. 3 In the experiments with oxygen it was not possible to condense the oxygen completely into the reaction bulb. Knowing the pressure in the measuring bulb and observing the residual pressure after the bulk of the oxygen had been transferred, it was possible to calculate how much was in the reaction bulb. When nitric oxide was used, it was first condensed into a tube on the vacuum system. The tube was then warmed only enough to give the desired pressure of nitric oxide.

The less volatile nitrogen oxides which are present in small amounts in the nitric oxide were left behind in the tube.

Results

Table I summarizes the results of the studies with nitrogen dioxide, oxygen, ethyl nitrite, nitric oxide, acetaldehyde and diethyl peroxide as additives.

Discussion

In the previous paper 2 the following mechanism was proposed for the thermal decomposition of ethyl nitrate. The results shown in Table I will be discussed in terms of this mechanism.

\[
\begin{align*}
\text{C}_2\text{H}_5\text{ONO}_2 & \xrightarrow{h_1} \text{C}_2\text{H}_5\text{O}^- + \text{NO}_2^- \\
\text{C}_2\text{H}_5\text{OH} & \xrightarrow{k_{-1}} \text{CH}_2 = \text{CHO} \\
[2\text{C}_2\text{H}_5\text{O}^- + 3\text{NO}_2 & \xrightarrow{k_1} 3\text{NO}_2 + 2\text{H}_2\text{O} + \text{CO} + \text{CO}_2 ] \\
[2\text{CH}_2 &= \text{CHO} + 7\text{NO}_2 \xrightarrow{k_1} 7\text{NO}_2 + 3\text{H}_2\text{O} + 2\text{CO}_2 ] \\
\text{C}_2\text{H}_5\text{OH} & \xrightarrow{k_2} \text{C}_2\text{H}_5\text{ONO}_2
\end{align*}
\]

(1) Full experimental details of this work including infrared spectra can be found in J. B. Levy, Navord Report 2899, 1953.

(2) J. B. Levy, THIS JOURNAL, 76, 3254 (1954).

(3) (a) L. Phillips, Nature, 165, 564 (1950); (b) 160, 753 (1947).


3790

JOSEPH B. LEVY

Vol. 76
July 20, 1954

EFFECT OF ADDITIVES ON THERMAL DECOMPOSITION OF ETHYL NITRATE

Table I

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Additive</th>
<th>Initial Pressure, mm.</th>
<th>Decomposition, %</th>
<th>k, min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NO₂</td>
<td>22.0</td>
<td>0</td>
<td>40.9</td>
</tr>
<tr>
<td>2</td>
<td>NO₂</td>
<td>15.1</td>
<td>2.92</td>
<td>40.0</td>
</tr>
<tr>
<td>3</td>
<td>NO₂</td>
<td>12.2</td>
<td>6.72</td>
<td>40.0</td>
</tr>
<tr>
<td>4</td>
<td>NO₂</td>
<td>16.1</td>
<td>30.0</td>
<td>40.0</td>
</tr>
<tr>
<td>5</td>
<td>NO₂</td>
<td>17.5</td>
<td>52.8</td>
<td>40.0</td>
</tr>
<tr>
<td>6</td>
<td>NO₂</td>
<td>0</td>
<td>20.0</td>
<td>28.0</td>
</tr>
<tr>
<td>7</td>
<td>NO₂</td>
<td>19.5</td>
<td>55.5</td>
<td>20.0</td>
</tr>
<tr>
<td>8</td>
<td>NO₂</td>
<td>0</td>
<td>20.0</td>
<td>28.0</td>
</tr>
<tr>
<td>9</td>
<td>NO₂</td>
<td>19.5</td>
<td>52.0</td>
<td>40.0</td>
</tr>
<tr>
<td>10</td>
<td>CH₃ONO</td>
<td>19.2</td>
<td>0</td>
<td>70.0</td>
</tr>
<tr>
<td>11</td>
<td>CH₃ONO</td>
<td>19.2</td>
<td>15.0</td>
<td>70.0</td>
</tr>
<tr>
<td>12</td>
<td>CH₃ONO</td>
<td>19.2</td>
<td>22.5</td>
<td>20.0</td>
</tr>
<tr>
<td>13</td>
<td>CH₃ONO</td>
<td>19.2</td>
<td>30.0</td>
<td>20.0</td>
</tr>
<tr>
<td>14</td>
<td>CH₃ONO</td>
<td>19.0</td>
<td>3.2</td>
<td>30.0</td>
</tr>
<tr>
<td>15</td>
<td>NO</td>
<td>22.0</td>
<td>16.6</td>
<td>20.0</td>
</tr>
<tr>
<td>16</td>
<td>NO</td>
<td>21.2</td>
<td>35.0</td>
<td>20.0</td>
</tr>
<tr>
<td>17</td>
<td>NO</td>
<td>21.0</td>
<td>20.0</td>
<td>60.0</td>
</tr>
<tr>
<td>18</td>
<td>NO</td>
<td>19.5</td>
<td>37.4</td>
<td>20.0</td>
</tr>
<tr>
<td>19</td>
<td>CH₂CHO</td>
<td>0</td>
<td>10.0</td>
<td>15.4</td>
</tr>
<tr>
<td>20</td>
<td>CH₂CHO</td>
<td>0</td>
<td>10.0</td>
<td>32.0</td>
</tr>
<tr>
<td>21</td>
<td>CH₂CHO</td>
<td>19.5</td>
<td>20.0</td>
<td>43.6</td>
</tr>
<tr>
<td>22</td>
<td>CH₂CHO</td>
<td>20.0</td>
<td>30.0</td>
<td>45.0</td>
</tr>
<tr>
<td>23</td>
<td>CH₃ONO</td>
<td>18.9</td>
<td>11.2</td>
<td>10.0</td>
</tr>
<tr>
<td>24</td>
<td>CH₃ONO</td>
<td>20.2</td>
<td>23.0</td>
<td>10.0</td>
</tr>
<tr>
<td>25</td>
<td>CH₃ONO</td>
<td>18.9</td>
<td>11.2</td>
<td>20.1</td>
</tr>
<tr>
<td>26</td>
<td>CH₃ONO</td>
<td>20.2</td>
<td>23.0</td>
<td>20.1</td>
</tr>
</tbody>
</table>

* Experiments 10–13 were carried out at 181°. All the others were carried out at 181°. b Measured at 25°. c First-order rate constant. d Value interpolated from reaction-rate data.

Nitrogen Oxide.—Phillips3,4,5 first reported that nitrogen oxide lowered the rate of decomposition of ethyl nitrate. His results are confirmed by experiments 1–5. His explanation, that nitrogen dioxide lowered the rate of decomposition of step 1, is supported by equation 9. The results found here for nitrogen oxide in the reaction mixture explains the low rate constant calculated for experiment 18 in Table II.

Ethylnitrate.—Experiments 10–13 show that the addition of ethyl nitrite does not affect the rate of decomposition of ethyl nitrate. If this inhibiting effect of nitrogen dioxide were due to its oxidation of ethyl nitrite the addition of the latter would have resulted in inhibition. The absence of this inhibition supports Phillips’ original explanation for the effect of nitrogen dioxide in the absence of added oxygen.

Nitric Oxide.—Experiments 14–17 show that nitric oxide addition results in a sharp rate increase. It has recently been suggested6 that nitric oxide reacts directly with ethyl nitrate via

\[ \text{NO} + \text{CH₃ONO} \rightarrow \text{NO}_2 + \text{CH₃ONO}_2 \tag{9} \]

If this were so the addition of increasing amounts of nitric oxide would bring about a continual increase in the reaction rate. It is clear from Table I that this is not so. The increase in initial nitric oxide pressure from 35 to 60 mm. in experiments 16 and 17 results in only a 3.5% increase in percentage reaction. This is inconsistent with a direct attack of nitric oxide on ethyl nitrate but fits in very well with the mechanism written earlier. In the presence of excess nitric oxide this mechanism reduces to steps 1 and 6. A kinetic treatment of steps 1 and 5 yields the expression

\[ \frac{d\ln C_{\text{CH₃ONO}}}{dt} = \frac{k_1}{1 + \frac{k_2}{k_3} (\text{NO})} \tag{10} \]

This expression predicts that with the addition of nitric oxide the rate should approach a limiting value corresponding to \(k_1\). This limit is reached when step 5 has been so accelerated that the reverse of step 1 is negligible. The constants listed in Table I do approach a limiting value of about 0.058 min⁻¹ which thus may be logically interpreted as a rough value for \(k_1\).

A further result of the addition of nitric oxide is the formation of larger amounts of nitrogen dioxide and ethyl nitrite than in its absence. Pollard, Marshall and Pedler6 reported the increased amount of nitrogen dioxide found and explained their results via equation 9. The results found here for nitrogen dioxide and ethyl nitrite confirm their results but are equally well explained by the mechanism written. The accumulation of nitrogen dioxide in the reaction mixture explains the low rate constant calculated for experiment 18 in Table II.

Table II

<table>
<thead>
<tr>
<th>Fraction of ethyl nitrate decomposition at 181°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield of ethyl nitrite³</td>
</tr>
<tr>
<td>0.49</td>
</tr>
<tr>
<td>.86</td>
</tr>
<tr>
<td>.82</td>
</tr>
</tbody>
</table>

³ Moles formed per mole ethyl nitrate decomposed. 
² Ethyl nitrate alone.

---

I. The rate expression 10 reveals that it is the ratio NO₂/NO which determines the rate. In the late stages of reaction this ratio is much larger than at the beginning and a lowered rate constant results.

**Acetaldehyde.**—Acetaldehyde is known to react rapidly with nitrogen dioxide although the mechanism and the nature of the reaction products are still unsettled. Since nitric oxide accelerates the reaction by reacting with ethoxyl radicals to pull equilibrium 1 to the right, it was felt that acetaldehyde should do the same. Experiments 19-22 show that it does. Moreover the apparent limiting rate constant has a value of 0.060 min⁻¹, in good agreement with that found with nitric oxide.

**Diethyl Peroxide.**—The reaction

\[
\text{C}_2\text{H}_5\text{O}_2 + \text{C}_2\text{H}_5\text{ONO}_2 \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{CH}_3\text{CHO} + \text{C}_2\text{H}_5\text{O}_2
\]

written in the original mechanism has been rejected on the basis of a study of the effect of the diethyl peroxide decomposition on ethyl nitrate. The results of the addition of diethyl peroxide to ethyl nitrate are shown in experiments 22-26. The main point of these experiments was that the rate of decomposition of diethyl peroxide is such that all the diethyl peroxide would have decomposed via

\[
\text{C}_2\text{H}_5\text{OOCH}_2 \rightarrow 2\text{C}_2\text{H}_5\text{O}_2
\]

in a few minutes. In all the above experiments there would have been sufficient radicals generated to bring about complete decomposition of the ethyl nitrate via 11, but there is no indication that reaction 11 occurred at all. The rates observed are intermediate between those found in the absence of any additive and those found when acetaldehyde or nitric oxide was added. This may well be explained by the reduction of the nitrogen dioxide by the formaldehyde arising from the ethoxyl radicals through step 3 of the mechanism.

The above experiments are open to some objections. It might be argued that the ethoxyl radicals are used up rapidly in the reaction with the diethyl peroxide

\[
\text{C}_2\text{H}_5\text{O}_2 + \text{C}_2\text{H}_5\text{OOCH}_2 \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{CH}_3\text{CHO} + \text{C}_2\text{H}_5\text{O}_2
\]

and never get a chance to react with the nitrate ester. This would require the formation of large amounts of acetaldehyde. The absorption in the acetaldehyde carbonyl region was small however and hence this objection has been ruled out. On the same grounds it is possible to rule out the suggestion that 11 does occur and is a fast reaction followed by the fast reactions

\[
\begin{align*}
\text{CH}_2\text{CHO}_2\text{ONO}_2 & \rightarrow \text{CH}_3\text{CHO} + \text{NO}_2 \\
\text{C}_2\text{H}_5\text{O}_2 + \text{NO}_2 & \rightarrow \text{CH}_2\text{CHO}_2\text{ONO}_2
\end{align*}
\]

The rejection of 11 as a step in the mechanism is thus supported by the results here.

**The Kinetics of the Reaction.**—It has been pointed out that since the ethyl nitrate decomposition yields such complex kinetic data, attempts to treat it as a first-order reaction and to interpret the heats and entropies of activation so obtained in terms of some specific step in the mechanism can lead to no meaningful result. The foregoing experiments however suggest that a suitable adjustment of experimental conditions should lead to simple first-order kinetics which could be interpreted unambiguously. The additions of nitric oxide and acetaldehyde have both tended to reduce the equilibrium of step 1 to the forward step. If the reverse step could be eliminated completely then the rate of disappearance of ethyl nitrate would measure directly the rate of the initial N-O bond cleavage. This has been accomplished by carrying out the decomposition of ethyl nitrate in the presence of nitric oxide and acetaldehyde together. The nitric oxide serves to react with the ethoxyl radical while the acetaldehyde serves to destroy the nitrogen dioxide as it is formed. The reaction was studied in this way at 161, 171 and 181°. The results at 181° are typical and are shown in Fig. 1. It is clear that under these experimental conditions good adherence to first-order kinetics is observed over the entire course of the reaction. The rate constants, as calculated by the method of least squares, are shown in Table III.

**Table III**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Rate constant, k (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>161</td>
<td>0.00752 ± 0.00018</td>
</tr>
<tr>
<td>171</td>
<td>0.00090 ± 0.00002</td>
</tr>
<tr>
<td>181</td>
<td>0.00009 ± 0.00009</td>
</tr>
</tbody>
</table>

At 161 and 181° experiments wherein formaldehyde replaced the acetaldehyde were carried out and yielded results which fell exactly on the rate curves. The general rate expression calculated from these data is

\[
\frac{d[\text{NO}_2]}{dt} = 10^{14.86} e^{-41,230 \pm 495 / R T} \text{sec}^{-1}
\]

This expression is calculated from the two extreme values and the error in the activation energy is calculated from the error in these two rate constants. The precision of the data may be shown by the calculation of the 171° rate using the above expression. The rate calculated is \( k = 0.0221 \text{ min}^{-1} \) in excellent agreement with the measured rate.
July 20, 1954

THERMAL DECOMPOSITION OF CHLOROFORM

GEORGE P. SEMELUK AND RICHARD B. BERNSTEIN

The Thermal Decomposition of Chloroform. I. Products

BY GEORGE P. SEMELUK AND RICHARD B. BERNSTEIN

RECEIVED JANUARY 6, 1954

The pyrolysis of gaseous chloroform has been investigated from 450 to 825°. The major products are hydrogen chloride and tetrachloroethylene. A variety of other chlorinated hydrocarbons have been identified and their relative abundances determined, using infrared techniques. Their genesis can be adequately described with a free-radical mechanism

\[
\text{CCl}_3 + \text{HCl} \rightarrow \text{CCl}_2\text{H} + \text{Cl} \quad (1)
\]

followed by displacement reactions, disproportionations and dehydrochlorinations. The rate of decomposition of ethyl nitrate at 181° in presence of nitric oxide and acetaldehyde, carried out under Task Assignment Re2d-02-1 of the Bureau of Ordnance, was studied by Lessig. He reported that the pressure-time curve was very irregular, and observed the formation of a "yellow crystalline material together with a tar." Verhoek measured the pressure increase due to the pyrolysis of chloroform at 452 and 512°. He identified only hydrogen chloride as a product, but suspected the presence of hexachloroethane.

The present investigation consisted of a detailed study of the products of the thermal decomposition of chloroform. A concurrent investigation of the kinetics has been carried out; these results will be presented in paper II.

Experimental

A known quantity (approximately three millimoles) of purified chloroform was introduced at a constant known rate into a carrier stream of purified helium gas and passed through a Vycor reaction chamber, packed with Vycor rings, which had previously been conditioned (carbonized) by the equivalent of about one hundred runs. The products in the exit gases were frozen out in a series of tests.

The thermal decomposition of chloroform was studied by Lessig. He reported that the pressure-time curve was very irregular, and observed the formation of a "yellow crystalline material together with a tar." Verhoek measured the pressure increase due to the pyrolysis of chloroform at 452 and 512°. He identified only hydrogen chloride as a product, but suspected the presence of hexachloroethane.

The present investigation consisted of a detailed study of the products of the thermal decomposition of chloroform. A concurrent investigation of the kinetics has been carried out; these results will be presented in paper II.

Experimental

A known quantity (approximately three millimoles) of purified chloroform was introduced at a constant known rate into a carrier stream of purified helium gas and passed through a Vycor reaction chamber, packed with Vycor rings, which had previously been conditioned (carbonized) by the equivalent of about one hundred runs. The products in the exit gases were frozen out in a series of tests.

Acknowledgments

I would like to express my appreciation to Mr. Archie E. Davis for his help with some of the experimental work, to Dr. Robert M. Talley of the Solid State Division of this Laboratory for making a Perkin-Elmer Model 21 Double Beam Infrared Spectrometer available to me, and to Dr. Evan C. Noonan and Professor K. J. Laidler for helpful discussions on this work, which was carried out under Task Assignment Re2d-02-1 of the Bureau of Ordnance.

Silver Spring, Maryland

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]