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 hexaarylethane series, no appreciable change in dissociation energy from the 11.5 kcal. for hexaphenylethane was noted upon varying the aryl substituents.[11] According to the theory set forth by Lewis and Lipkin,[4] 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 *ortho* and *para* 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.

(11) R. Preckel and P. W. Selwood, THIS JOURNAL, **63**, 3397 (1941).

[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

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The effects of 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.

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 and nitric oxide were prepared as before.[2] Acetaldehyde was Eastman Kodak White Label Grade and was used directly from the bottle. The oxygen was taken directly from an oxygen cylinder. The diethyl peroxide was prepared as described by Harris and Egerton.[6] The final distillation at atmospheric pressure yielded a product boiling at 62.5–63.5°. It was stored in sealed ampules in a refrigerator. The formaldehyde used was generated by heating a tube containing paraformaldehyde. In the time interval between filling the bulb with formaldehyde and putting it in the bath, no deposit of the formaldehyde in the form of its polymer on the sides of the bulb could be seen.

The Experimental Procedure.—The methods of making the measurements and manipulating the gas mixture have been described in the previous paper.[2] 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. In this way 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

$$C_2H_5ONO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C_2H_5O\cdot + NO_2 \qquad (1)$$

$$C_2H_5O\cdot \longrightarrow CH_3\cdot + CH_2O \qquad (2)$$

$$[2CH_2O + 3NO_2 \longrightarrow 3NO + 2H_2O + CO + CO_2] \qquad (3)$$

$$[2CH_3\cdot + 7NO_2 \longrightarrow 7NO + 3H_2O + 2CO_2] \qquad (4)$$

$$C_2H_5O\cdot + NO \xrightarrow{k_2} C_2H_5ONO \qquad (5)$$

ethyl nitrate. The results shown in Table I will be discussed in terms of this mechanism.

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(1) Full experimental details of this work including infrared spectra can be found in J. B. Levy, Navord Report 2897, 1953.

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

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

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

(5) L. Phillips, Thesis, University of London (1949).

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

TABLE I

THE EFFECT OF ADDITIVES ON THE RATE OF DECOMPOSITION OF ETHYL NITRATE[a]

		Initial Pressure,[b] mm.				
Expt.	Additive	Ethyl nitrate	Additive	t, min.	Decomposition, %	k,[c] min.-1.
1	NO_2	22.0	0	40.0	50.0	
2	NO_2	15.1	2.92	40.0	42.1	
3	NO_2	12.2	6.72	40.0	35.4	
4	NO_2	16.1	30.0	40.0	26.7	
5	NO_2	17.5	52.8	40.0	25.7	
6	O_2	..	0	20.0	28.0[d]	
7	O_2	19.5	55.5	20.0	8.9	
8	O_2	..	0	85.0	83.3[d]	
9	O_2	19.5	52.0	85.0	46.2	
10	C_2H_5ONO	19.2	0	75.0	14.8	
11	C_2H_5ONO	19.2	15.0	75.0	14.8	
12	C_2H_5ONO	19.2	...	150.0	28.8	
13	C_2H_5ONO	19.2	13.0	150.0	26.6	
14	NO	19.9	3.2	20.0	32.2	0.0195
15	NO	22.0	16.6	20.0	55.9	.0405
16	NO	21.2	35.0	20.0	65.5	.0530
17	NO	21.2	60.0	20.0	69.0	.0583
18	NO	19.5	37.4	80.0	94.4	.036
19	CH_3CHO	..	0	10.0	15.5[d]	
20	CH_3CHO	20.0	10.0	10.0	32.0	.038
21	CH_3CHO	19.5	20.0	10.0	43.6	.057
22	CH_3CHO	20.0	30.0	10.0	45.0	.060
23	$(C_2H_5O)_2$	18.9	11.2	10.0	45	.059
24	$(C_2H_5O)_2$	20.2	23.0	10.0	39	.046
25	$(C_2H_5O)_2$	18.9	11.2	20.1	56	.041
26	$(C_2H_5O)_2$	20.2	23.0	20.1	60	.048

[a] Experiments 10–13 were carried out at 161°. All the others were carried out at 181°. [b] Measured at 25°. [c] First-order rate constant. [d] Value interpolated from reaction rate data.[2]

Nitrogen Dioxide.—Phillips[3,5] first reported that nitrogen dioxide lowered the rate of decomposition of ethyl nitrate. His results are confirmed by experiments 1–5. His explanation, that nitrogen dioxide acted to accelerate the back part of step 1, has been incorporated into the above scheme.

Oxygen.—The inhibiting effect of oxygen may be explained on the basis of its oxidation of the nitric oxide formed in steps 3 and 4 to nitrogen dioxide. By keeping the nitrogen dioxide concentration high, the reverse of step 1 is accelerated and by keeping the nitric oxide concentration low, the contribution of step 5 toward carrying the reaction forward is cut down.

There is another way in which the addition of oxygen can result in a lowered reaction rate. Ogg[7] has recently reported that at room temperature in the presence of oxygen, nitrogen dioxide oxidizes ethyl nitrite to ethyl nitrate. The reaction does not occur in the absence of oxygen.

$$2C_2H_5ONO + NO_2 + O_2 \longrightarrow C_2H_5ONO_2 + NO_2$$

If this reaction is also important at 181° it would serve as an additional explanation for the effect of oxygen.

The question now arises as to whether this is also the mechanism whereby nitrogen dioxide inhibits the reaction in the absence of added oxygen or whether Phillips' explanation is valid. This point can be settled by considering the effect of ethyl nitrite on the reaction.

Ethyl Nitrite.—Experiments 10–13 show that the addition of ethyl nitrite does not affect the rate of decomposition of ethyl nitrate. If the 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 suggested[8] that nitric oxide reacts directly with ethyl nitrate *via*

$$NO + C_2H_5ONO_2 \longrightarrow NO_2 + C_2H_5ONO \quad (9)$$

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 of 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 5. A kinetic treatment of steps 1 and 5 yields the expression

$$\frac{-\mathrm{d}\ \ln\ C_2H_5ONO}{\mathrm{d}t} = \frac{k_1}{1 + \frac{k_{-1}(NO_2)}{k_5(NO)}} \quad (10)$$

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 Pedler[8] 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

TABLE II

YIELDS OF ETHYL NITRATE AND NITROGEN DIOXIDE IN ETHYL NITRATE DECOMPOSITION AT 181°

Fraction of ethyl nitrate dec.	Yield of ethyl nitrite[a]		Yield of Nitrogen dioxide[a]	
0.49	1.0[b]	0.66[c]	1.0[b]	0.16[c]
.66	0.85[b]	.75[c]	0.79[b]	.11[c]
.82	0.93[b]	.68[c]	0.48[b]	.09[c]

[a] Moles formed per mole ethyl nitrate decomposed. [b] Nitric oxide added. [c] Ethyl nitrate alone.

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(7) R. A. Ogg, Jr., at "The Chemistry of the Oxides of Nitrogen," Symposium sponsored by the Office of Ordnance Research, Chicago, Illinois, September 3 and 4, 1953.

(8) F. H. Pollard, H. S. B. Marshall and A. E. Pedler, *Nature*, **171**, 1154 (1953).

I. The rate expression 10 reveals that it is the ratio NO_2/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.[9,10] 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

$$C_2H_5O\cdot + C_2H_5ONO_2 \longrightarrow C_2H_5OH + CH_3\underset{\cdot}{C}HONO_2 \quad (11)$$

written in the original mechanism[3,4] has been rejected[2] on the basis of a study of the effect of the diethyl peroxide decomposition on ethyl nitrite. 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*

$$C_2H_5OOC_2H_5 \longrightarrow 2C_2H_5O\cdot$$

in a few minutes.[6] 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

$$C_2H_5O\cdot + C_2H_5OOC_2H_5 \longrightarrow C_2H_5OH + CH_3CHO + C_2H_5O\cdot$$

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

$$CH_3\underset{\cdot}{C}HONO_2 \longrightarrow CH_3CHO + NO_2$$
$$C_2H_5O\cdot + NO_2 \longrightarrow C_2H_5ONO_2$$

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

The Mechanism of the Reaction.—Insofar as the results in the Table can be plausibly explained in terms of the mechanism written they offer support for it.

In the writing of this mechanism[2] it was pointed out that an alternative to steps 2–4 would be furnished by the sequence

$$C_2H_5O\cdot + NO_2 \longrightarrow CH_3CHO + HONO \quad (11)$$
$$[CH_3CHO + NO_2 \longrightarrow NO + \text{products}] \quad (12)$$

The incorporation of this sequence would mean that ethoxyl radical and nitrogen dioxide would be reacting both to slow the reaction down by reversing step 1 and to carry it forward *via* step 11. The kinetic consequence of this would be that the addition of nitrogen dioxide would not affect the rate. The fact that the addition of nitrogen dioxide slows the reaction down considerably is support for the choice of steps 2–4.

The Kinetics of the Reaction.—It has been pointed out[2] that since the ethyl nitrate decomposition yields such complex kinetic data, attempts[3,4] 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

THE THERMAL DECOMPOSITION OF ETHYL NITRATE IN THE PRESENCE OF NITRIC OXIDE AND ACETALDEHYDE

	161°	171°	181°
Rate constant, min.$^{-1}$	0.00752 ± 0.00002	0.0218 ± 0.0002	0.0611 ± 0.0009

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

$$k = 10^{16.85}\, e\, \frac{-41{,}230 \pm 495}{RT}\ \text{sec.}^{-1}$$

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 min.$^{-1}$ in excellent agreement with the measured rate.

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

[10] L. C. Browning, private communication.

It may be noted that the activation energy found here is higher than the values reported by others which ranged from about 36 kcal.[3b] to 39.9 kcal.[4] Because of the techniques employed here it is felt that the value 41,290 kcal. is the correct value for this reaction and that it may with justification be equated to the N–O bond energy in ethyl nitrate. The value for this bond energy has generally been taken as 34–37 kcal. per mole on the basis of studies on the nitrite esters. However the nitrite ester studies have met with some criticism[11] and the activation energies for the decomposition of these esters are still in some doubt.

The frequency factor found here, $10^{16.85}$ sec.$^{-1}$ is substantially higher than the value generally associated with first order reactions which is 10^{13} sec.$^{-1}$. In terms of the transition state theory this implies a high positive value for the entropy of activation, in this case a value of about 15 cal./mole. It has recently been reported by Szwarc[12] that frequency factors for many first order dissociations are of the order of 10^{14} to 10^{16} sec.$^{-1}$, so that there is no reason to consider the present case anomalous.

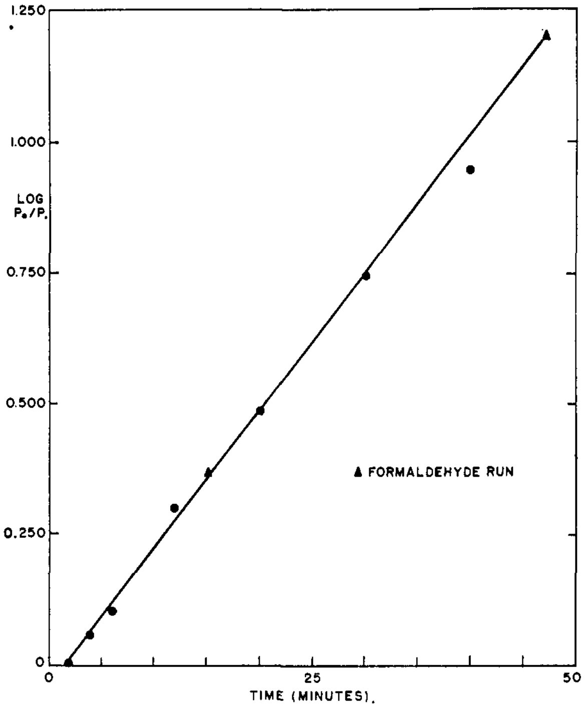

Fig. 1.—The rate of decomposition of ethyl nitrate at 181° in presence of nitric oxide and acetaldehyde.

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[11] M. Szwarc, *Chem. Rev.*, **47**, 75 (1950).

[12] M. Szwarc, *Disc. Faraday Soc.*, **14**, 125 (1953).

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

The Thermal Decomposition of Chloroform. I. Products[1a]

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The pyrolysis of gaseous chloroform has been investigated from 450 to 525°. 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 $CCl_3H \rightarrow CCl_2H\cdot + Cl\cdot$ (1), $Cl\cdot + CCl_3H \rightleftarrows HCl + CCl_3\cdot$ (2), $CCl_2H\cdot + CCl_3H \rightarrow CCl_2H_2 + CCl_3\cdot$(3), followed by displacement reactions, recombinations, disproportionations and dehydrochlorinations. The isotope exchange reaction of chloroform-*d* with hydrogen chloride was found to be rapid under conditions comparable to the pyrolysis experiments.

The thermal decomposition of chloroform was studied by Lessig.[2] He reported that the pressure–time curve was very irregular, and observed the formation of a "yellow crystalline material together with a tar." Verhoek[3] 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[4] 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[5] (carbonized) by the equivalent of about one hundred runs.

The products in the exit gases were frozen out in a series

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[1] (a) Part of a Ph.D. dissertation submitted by G.P.S. to the Graduate School of Illinois Institute of Technology; (b) Lamp Development Laboratory, General Electric Co., Cleveland, Ohio; (c) University of Michigan, Ann Arbor, Michigan.

[2] E. T. Lessig, *J. Phys. Chem.*, **36**, 2325 (1932).

[3] F. H. Verhoek, *Trans. Faraday Soc.*, **31**, 1525 (1935).

[4] C.P. chloroform was purified according to the procedure in Vogel, "Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1948. Mass spectral and infrared examination of the product revealed no detectable impurities. For certain check experiments the chloroform was prepared directly from chloral, with identical results. Chloroform-*d* was synthesized from chloral and sodium deuteroxide. It was found to contain 1.6 ± 0.2% chloroform with no other impurities.

[5] R. J. Williams, *J. Chem. Soc.*, 113 (1953).