Electrochemical Company and were purified before use by fractional distillation and crystallization. Compounds I and II were prepared by the method of Ponderman and Girardet,[2] and compound III was obtained by using the procedure of Rouche.[9]

Procedure.—The absorption spectra were determined in 95% ethanol solutions by means of a Beckman DU spectrophotometer. Where indicated in the accompanying figures small volumes of the stock solutions were diluted with standard solutions of alcoholic hydrogen chloride and the absorption curves were then read without delay. The spectral properties of the compounds reported in this paper are summarized in Table I.

TABLE I

THE ULTRAVIOLET ABSORPTION SPECTRA OF SOME BENZOTRIFLUORIDES

Benzotrifluoride	Absorption maxima			
	λ (mμ)	$\epsilon \times 10^{-3}$	λ' (mμ)	$\epsilon' \times 10^{-3}$
2-NO_2, 3-NH_2	233.5[a]	14.9[a]	395[a]	2.58[a]
3-NH_2, 4-NO_2	232.5[a]	21.2[a]	390–400[a]	4.50
	232[b]	8.70[b]	410[b]	1.20
2-NO_2, 5-NH_2	234.5[a]	7.42[a]	370	11.6[a]
	245[b]	4.94[b]		
3-NH_2	241.5[a]	10.12[a]	300[a]	2.01[a]
	241[c]	1.20[c]		
3-NO_2	247[a]	6.90[a]		
2-Cl, 5-NO_2	263[a]	9.33[a]		

[a] In 95% ethanol. [b] In 10 *M* alcoholic hydrogen chloride. [c] In 0.1 *M* alcoholic hydrogen chloride.

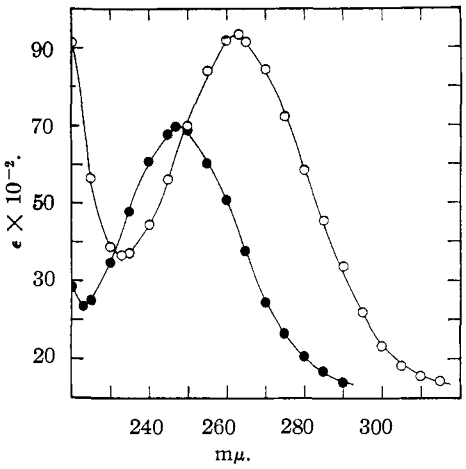

Fig. 6.—Absorption spectra in 95% ethanol: ○, 2-chloro-5-aminobenzotrifluoride; ●, 3-nitrobenzotrifluoride.

PITTSBURGH, PENNSYLVANIA

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[9] H. Rouche, *Bull. Sci. Acad. Roy. Belg.*, **13**, 346 (1927).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

A Spectrophotometric Study of the Homolytic Dissociation of Tetrafluorenylhydrazine[1]

BY TING LI CHU AND THEODORE J. WEISMANN

RECEIVED MARCH 8, 1954

Tetrafluorenylhydrazine undergoes homolytic and ionic dissociations in solution; however, only homolytic dissociation takes place in non-polar solvents. The extent of homolytic dissociation of tetrafluorenylhydrazine in benzene, dioxane, pyridine, tetrahydrofuran and toluene has been determined spectrophotometrically at several temperatures and concentrations. The dissociation constants in different solvents vary noticeably; however, the heat of dissociation appears to be nearly constant at 16.2 to 17.4 ± 1.2 kcal. The heat of dissociation of the N–N bond in tetrafluorenylhydrazine is about 14 kcal. less than that in tetraphenylhydrazine. This difference is explained by the coulombic repulsion of the high charge density on the two nitrogen atoms as set forth by G. N. Lewis and D. Lipkin.

The tetraarylhydrazines resemble the hexaarylethanes in their ability to dissociate yielding diarylamino free radicals. While tetraphenylhydrazine dissociates in solution only at relatively high temperatures (above 90°),[2] some of its derivatives show appreciable dissociation at room temperature and have been studied qualitatively by ebulliometric and colorimetric methods.[3] The dissociation of tetraarylhydrazines appears to be affected by steric and resonance effects; however, Lewis and Lipkin[4] asserted that the coulombic repulsion of the high charge density on the two nitrogens is also an important factor in the dissociation.

Cain and Wiselogle[5] studied the rate of dissociation of tetraphenylhydrazine by measuring the rate of absorption of nitric oxide and obtained 30 kcal. as the heat of activation. Lewis and Lipkin[4] observed that diphenylamino radicals combine instantaneously at 100°K., indicating that the activation energy for association must be less than 1 kcal. Therefore, the heat of dissociation of tetraphenylhydrazine is presumably equal to the 30 kcal. found for the heat of activation. This value was confirmed by Cole and Gilbert[6] from heat of combustion data. The heat of dissociation of other tetraarylhydrazines has not been determined experimentally.

Goldschmidt[7] observed that tetrafluorenylhydrazine shows a green color in solution at room temperature due to dissociation and found colorimetrically that the degree of dissociation increases in the series of solvents: ether, acetone, toluene, benzene, pyridine.

It is the purpose of this work to study the homolytic dissociation of tetrafluorenylhydrazine in solution at several temperatures and at several concentrations in order to evaluate the equilibrium constants, the heats and the entropies of this dissociation. The solvents employed were benzene, dioxane, pyridine, tetrahydrofuran and toluene.

Experimental

Materials.—Tetrafluorenylhydrazine was prepared by the oxidation of 9-aminofluorene[7] which was obtained from

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[1] Taken in part from the M.S. thesis of T. J. Weismann, Duquesne University, 1954.

[2] H. Wieland, *Ber.*, **39**, 1500 (1906).

[3] H. Wieland, *Ann.*, **392**, 130 (1912).

[4] G. N. Lewis and D. Lipkin, THIS JOURNAL, **63**, 3232 (1941).

[5] C. K. Cain and F. Y. Wiselogle, *ibid.*, **62**, 1163 (1940).

[6] L. G. Cole and E. C. Gilbert, *ibid.*, **73**, 5423 (1951).

[7] S. Goldschmidt, *Ann.*, **456**, 161 (1927).

9-fluorenone by conversion into its oxime[8] and subsequent reduction.[9] It was found that tetrafluorenylhydrazine is stable in the solid state but decomposes rapidly in solution when exposed to air, hence further purification of the hydrazine was carried out under vacuum. The crude material was treated with anhydrous tetrahydrofuran, the solution filtered through a sintered glass disk and concentrated by evaporating part of the solvent. Anhydrous methanol was distilled in to precipitate the hydrazine, which, after filtration, was washed with methanol several times and dried, m.p. 185-186° (vac.).

Anal. Calcd. for $C_{52}H_{36}N_2$: C, 90.70; H, 5.23; N, 4.07. Found: C, 89.52; H, 5.41; N, 3.98.

Goldschmidt purified this compound by dissolving it in boiling benzene followed by reprecipitation with methanol and obtained a product which melted about 243°. Obviously, the tetrafluorenylhydrazine was decomposed when treated in this manner because of the instability of its solution in air, particularly at higher temperatures. In the present investigation, the residue after the tetrahydrofuran extraction melted at 241-243° (vac.) with decomposition and was very insoluble. The absorbancy of its solutions at 4680 Å. (this absorption is characteristic of the difluorenylamino free radical) showed only very slight temperature dependence while that of solutions of the lower melting product was much more pronounced.

The solvents used for spectrophotometric measurements were purified according to standard procedures. Mallinckrodt A.R. grade benzene and toluene were dried over sodium-potassium alloy. Mallinckrodt A.R. grade pyridine was dried over potassium hydroxide and distilled. Eastman Kodak tetrahydrofuran was fractionally distilled, b.p. 65-66°, and dried over sodium-potassium alloy. Dioxane was purified by prolonged refluxing with sodium, followed by fractional distillation, b.p. 101-101.5°, and drying over sodium-potassium alloy.

Spectrophotometric Measurements.—Spectrophotometric measurements were made using a Beckman Model DU spectrophotometer.

For quantitative absorbancy measurements in the visible region (4680 Å.), 1.0-cm. Pyrex cells were used. The cell was connected to a glass tubing equipped with ground joint through which it could be attached to, or sealed-off from, the vacuum line. In order to permit accurate measurements on relatively concentrated solutions, the cells were fitted with four Vycor plates (each plate being about 2 mm. thick) to reduce the light path through the solution. All Pyrex cells were calibrated against a 1.000-cm. quartz cell in the conventional manner and the appropriate corrections were applied to the observed absorbancy obtained with each cell.

Since tetrafluorenylhydrazine is stable in the solid state, it was weighed directly on an Ainsworth microbalance and placed in the absorption cell. The cell was then attached to the vacuum line and thoroughly evacuated. A known volume (about 10 ml.) of pre-dried solvent, measured in a pipet, was distilled in and the cell sealed off while under vacuum.

In order to accommodate the additional height of the Pyrex cells in the cell compartment of the spectrophotometer, a special cover made of a hollow aluminum box approximately 6" high was used. The cell compartment was thermostated by circulating water through the double wall of the compartment from a constant temperature bath, and insulated from the lamp housing by asbestos cloth to avoid the slight temperature gradient between the front and rear of the compartment. The temperature inside the compartment could be maintained within ±0.2°. The absorption cells were placed in the constant temperature bath for about 20 minutes before being placed in the cell compartment where they remained for a similar period of time before the absorbancy measurements were made. The absorbancy of the solutions at 4680 Å. was measured at several temperatures ranging from 15 to 40°, first at the lower temperatures and then at various intervals to the highest temperature, after which the solution was cooled and the low temperature measurements checked. The results were reproducible in most cases over a period of about 8 hours, indicating the stability of the difluorenylamino free radical.

The absorption spectrum of the difluorenylamino anion in the visible region also was studied. A weighed amount of tetrafluorenylhydrazine was placed in the Pyrex cell and a small piece of freshly cut sodium placed above a constriction approximately 10 cm. from the bottom of the cell. The cell was evacuated and a known volume of solvent distilled in, the sodium melted and allowed to pass through the constriction (surface impurities on the sodium remained above the constriction) to a position on the side of the tube slightly above the solution. The cell was sealed off at the constriction. The reaction between sodium and tetrafluorenylhydrazine took place readily on shaking and the extent of the reaction could be controlled.

Results and Discussion

Goldschmidt's qualitative estimate of the dissociation of tetrafluorenylhydrazine appears to be erroneous. Solutions of tetrafluorenylhydrazine in non-polar solvents are light yellow. In polar solvents, the solutions range in color from green to greenish-blue, depending on the solvent used. The absorption spectra of tetrafluorenylhydrazine in benzene, pyridine and tetrahydrofuran in the visible region are given in Fig. 1. All solutions show a common absorption band at 4680 Å. which is temperature-dependent and is attributed to the difluorenylamino free radical. The additional absorption bands in polar solvents at 6150 and 7900 Å. are temperature-independent within experimental error. Their intensities depend on the polarity of the solvent, indicating a possible ionic dissociation in addition to the homolytic dissociation. In order to confirm this viewpoint, the absorption spectrum of the difluorenylamino anion was studied (Fig. 2). The absorption bands at 4680 and 7900 Å., present in the tetrahydrofuran solution of tetrafluorenylhydrazine disappear and the absorption at 6150 Å. becomes exceptionally intense. Thus, the ionic dissociation of tetrafluorenylhydrazine in polar solvents is evident. The absorption band at 6150 Å. is characteristic of the anion and that at 7900 Å. is probably characteristic of the cation. It is probable that solvation plays an important role in the stabilization of the cation. Because of the experimental difficulties in obtaining the molar absorbancy of the difluorenylamino anion, no quantitative data on the ionic dissociation could be obtained. We estimated that 10^{-3} to 10^{-4} M tetrafluorenylhydrazine solutions in pyridine or tetrahydrofuran undergo less than 2% ionic dissociation and so this effect is neglected in subsequent calculations for the homolytic dissociation.

In determining the homolytic dissociation of tetrafluorenylhydrazine, the absorbancy of its solution at 4680 Å. was used as a measure of the concentration of difluorenylamino free radical. The observed absorbancy is the sum of the absorbancies of the hydrazine and the free radical: $D = 2C\alpha\epsilon + C(1 - \alpha)\epsilon'$. Where D is the observed absorbancy of a C molar solution of tetrafluorenylhydrazine at 4680 Å., α is the apparent degree of dissociation, ϵ is the true molar absorbancy of the difluorenylamino free radical and ϵ' is the molar absorbancy of tetrafluorenylhydrazine. The equilibrium constant, expressed in terms of concentration, for the dissociation of tetrafluorenylhydrazine at a given temperature is

$$K = \frac{4C\alpha^2}{1 - \alpha} = \frac{4(D - C\epsilon')^2}{(2C\epsilon - D)(2\epsilon - \epsilon')}$$

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(8) J. Schmidt and J. Söll, *Ber.*, **40**, 4257 (1907).

(9) J. Schmidt and H. Stützel, *ibid.*, **41**, 1243 (1908).

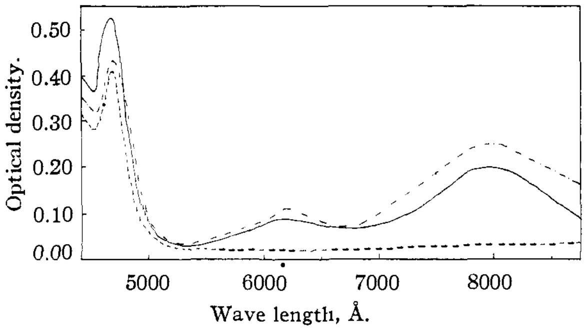

Fig. 1.—Absorption spectra of tetrafluorenylhydrazine in visible region: ———, 5 × 10^{-4} M tetrahydrofuran solution; - - - -, 4 × 10^{-4} M benzene solution; - - - - -, 3.4 × 10^{-4} M pyridine solution; cell thickness, 1.00 cm.; temp., 21°.

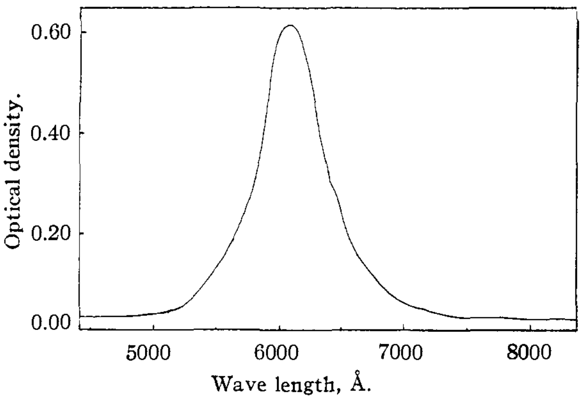

Fig. 2.—Absorption spectrum of approximately 10^{-5} M difluorenylamino anion in tetrahydrofuran.; cell thickness, 1.00 cm.; temp., 20°.

Upon measuring the absorbancy of three solutions of different concentration at 4680 Å., one obtains three simultaneous equations from which the parameters ϵ, ϵ' and K can be evaluated. Solution of the above equations for three benzene solutions, of tetrafluorenylhydrazine at 25° gives the values $\epsilon = 1167$ and $\epsilon' \sim 14$. In view of its small magnitude, ϵ' may be neglected and the expression for the equilibrium constant is reduced to $K = 2D^2/\epsilon(2C\epsilon - D)$.

TABLE I

EQUILIBRIUM CONSTANTS FOR THE HOMOLYTIC DISSOCIATION OF TETRAFLUORENYLHYDRAZINE

Solvent	ϵ, ±20	Temp., °C., ±0.2	Concn. range, moles	$K \times 10^4$
Benzene	1167	13.5	4.1×10^{-4} to 2.5×10^{-3}	2.56 ± 0.08
		19.2	4.7×10^{-4} to 1.7×10^{-3}	4.29 ± .1
		25.7	8.2×10^{-4} to 3.4×10^{-3}	8.52 ± .15
		33.5	3.9×10^{-4} to 1.4×10^{-3}	16.0 ± .3
Dioxane	1170	17.3	5.6×10^{-4} to 9.4×10^{-4}	2.24 ± .06
		26.2	4.3×10^{-4} to 2.3×10^{-3}	5.73 ± .15
		29.4	2.9×10^{-4} to 9.1×10^{-3}	7.37 ± .15
		37.7	3.8×10^{-4} to 1.2×10^{-3}	16.0 ± .3
Pyridine	1175	14.1	4.3×10^{-4} to 1.4×10^{-3}	3.6 ± .1
		23.0	3.3×10^{-4} to 1.5×10^{-3}	9.7 ± .2
		26.2	4.3×10^{-4} to 1.4×10^{-3}	12.2 ± .3
		35.8	2.3×10^{-4} to 1.3×10^{-3}	30.6 ± .5
Tetrahydrofuran	1175	17.3	3.8×10^{-4} to 8.6×10^{-4}	4.37 ± .1
		27.2	3.8×10^{-4} to 3.8×10^{-3}	11.7 ± .2
		35.0	5.3×10^{-4} to 2.5×10^{-3}	24.0 ± .3
Toluene	1167	14.0	4.4×10^{-4} to 1.8×10^{-3}	3.16 ± .08
		25.0	4.3×10^{-4} to 1.8×10^{-3}	8.96 ± .15
		33.4	4.3×10^{-4} to 1.2×10^{-3}	18.8 ± .3

The equilibrium constants, calculated in this manner, for solutions of tetrafluorenylhydrazine in benzene, dioxane, pyridine, tetrahydrofuran and toluene at several temperatures are summarized in Table I.[10]

The dissociation constants of tetrafluorenylhydrazine in solution were used to estimate the ΔH of dissociation. In Fig. 3, log K was plotted *versus* $1/T$ and the slope of the best straight line was used for the calculations. ΔF^0 and ΔS^0, calculated according to thermodynamic relations, are summarized in Table II together with ΔH^0.

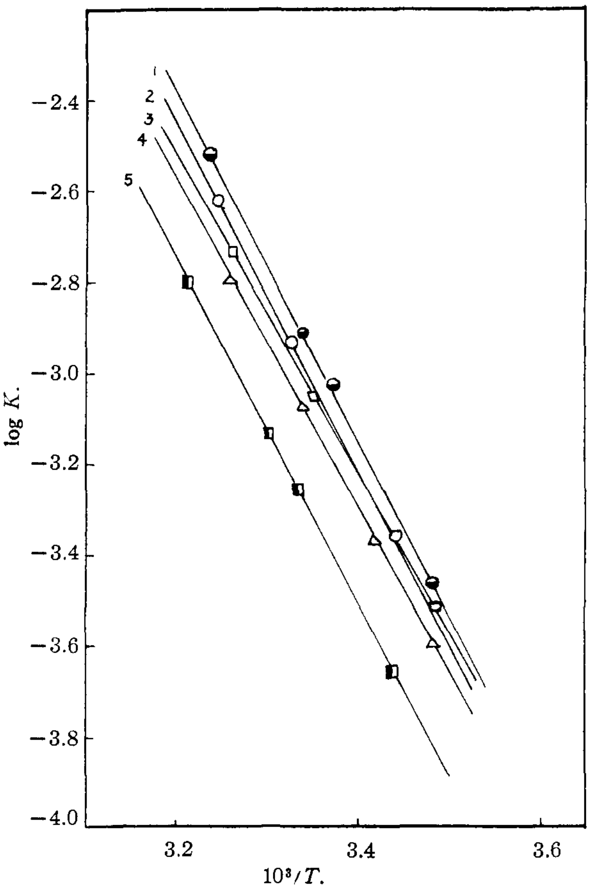

Fig. 3.—The effect of temperature on the dissociation constant of tetrafluorenylhydrazine: ◒, pyridine solutions; ○, tetrahydrofuran solutions; □, toluene solutions; △, benzene solutions; , dioxane solutions.

TABLE II

SUMMARY OF THERMODYNAMIC FUNCTIONS FOR THE HOMOLYTIC DISSOCIATION OF TETRAFLUORENYLHYDRAZINE AT 25°

Solvent	ΔH^0 ± 1.2, kcal.	ΔF^0 ± 0.02, kcal.	ΔS^0 ± 2, cal.
Benzene	16.3	4.25	40.4
Dioxane	17.4	4.52	43.2
Pyridine	17.4	4.05	44.8
Tetrahydrofuran	17.3	4.13	44.2
Toluene	16.2	4.16	40.4

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[10] In these calculations, the volume of solvent was approximated as that of the solution and the change in concentration of the solutions at various temperatures was estimated from the change in density of the solvent. Data are given in detail in the M.S. thesis of T. J. Weismann deposited in the library of Duquesne University.

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.

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[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

RECEIVED APRIL 3, 1954

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).