Effect of Hyperconjugation on the Decomposition of N-Alkyl-N-nitrosoacetamide

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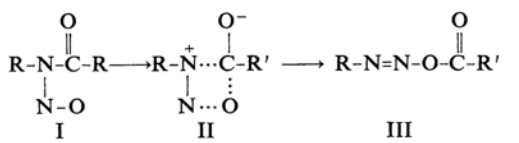
In the decomposition of *N*-alkyl-*N*-nitrosoacetamide, the β-phenyl group has been found, in an earlier paper, to decrease the heat of activation. This decrease in the heat of activation was explained by the stabilization of the transition state, involving second order hyperconjugation.

The effect of the β-phenyl group on the decomposition of *N-sec*-alkyl-*N*-nitrosoacetamide was found to be more pronounced when the alkyl group was cyclohexyl than when it was isopropyl, and the heat of activation of *N*-cyclohexyl-*N*-nitrosoacetamide was smaller than that of *N*-isopropyl-*N*-nitrosoacetamide. Hence the second order hyperconjugation was suggested as more probable for the cycloalkyl group. This hypothesis was supported by a hydrogen deuterium isotope effect experiment in which the rates of decomposition of *N*-cyclohexyl-*N*-nitrosoamides were found to be 1.1 ~2.8 times higher than those of corresponding deuterated homologues.

The thermal decomposition of *N*-alkyl-*N*-nitrosoamide has been known to result either in the formation of nitrogen and ester or in that of nitrogen, carboxylic acid and olefin as in the following equation (1).

$$\mathrm{RN(NO)COR'} \begin{cases} \rightarrow \mathrm{N_2 + ROCOR'} \\ \rightarrow \mathrm{N_2 + R'CO_2H + olefins\ (corresponding\ to\ R)} \end{cases} \quad (1)$$

This decomposition has been considered to proceed through an intermediate, III, diazoester, while the rate-determining step was suggested to involve a four-membered ring, II[1].



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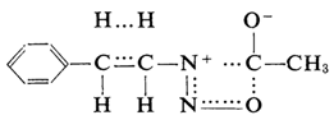
$$\longrightarrow \text{products} \quad (2)$$

In an earlier work[2] we have shown that the rate and the heat of activation of decomposition of *N*-ω-phenyl-*n*-alkyl-*N*-nitrosoacetamide varied with the increase of methylene linkages, and that the heat of activation of *N*-2-phenylethyl-*N*-nitrosoacetamide was smaller than those of *N*-benzyl- and *N*-3-phenyl-*n*-propyl-*N*-nitrosoacetamides. The heat of activation of *N*-2-phenylethyl-*N*-nitrosoacetamide was found to be 3 kcal. smaller than that of *N*-*n*-propyl-*N*-nitrosoacetamide. We suggested that the transition state IV of the decomposition of *N*-2-phenylethyl-*N*-nitrosoacetamide is



IV

more stable than those of the others because the double bonds in the phenyl group can conjugate with the π-electrons in the four-membered ring by means of the second-order hyperconjugation[3].

In this paper, the decompositions of several *N*-alkyl-*N*-nitrosoacetamides are examined in order to confirm our hypothesis and to find the nature of the hyperconjugation which occurs in the alkyl group, especially in the cyclic alkyl group.

Results and Discussion

The rates of decomposition of the *N-n*-alkyl-*N*-nitrosoacetamides were measured in xylene, while those of the *N-sec*-alkyl-*N*-nitrosoacetamides were done in benzene. All the nitrosoamides examined decomposed following first order kinetics. At the same temperature duplicate rate measurements were carried out. The maximum deviation of rate constants obtained in each experiment fell within $\pm 1\%$. Thus, the error of the heat of activation was calculated to be ± 0.2 kcal. per mol.[4]

1) R. Huisgen, *Ann.*, **574**, 184 (1951), and four earlier papers; D. H. Hey, J. Stuart-webb and G. H. Williams, *J. Chem. Soc.*, **1952**, 4657; E. H. White, *J. Am. Chem. Soc.*, **77**, 6014 (1955).

2) M. Murakami and K. Akagi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 532 (1954).

3) E. Berliner and F. Berliner, *J. Am. Chem. Soc.*, **71**, 1195 (1949); M. J. S. Dewer, "The Electronic Theory of Organic Chemistry", Oxford Univ. Press, (1950), p. 158; (Later, however, Dewar himself seems to have changed his original thought. See M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959)).

4) T. I. Crowell and L. P. Hammett, *J. Am. Chem. Soc.*, **70**, 3444 (1948); P. M. Dumber and L. P. Hammett, ibid., **72**, 109 (1950); R. K. Brinton, ibid., **77**, 842 (1955).

The Effect of β-Phenyl Group of *N*-2-Phenyl-*sec*-alkyl-*N*-nitrosoacetamide.—A similar effect by the β-phenyl group was observed in the decompositions of both *N*-2-phenyl-isopropyl- and *trans*-*N*-2-phenylcyclohexyl-*N*-nitrosoacetamides in benzene. The results obtained are shown in Table I.

TABLE I. DECOMPOSITION RATE, HEAT AND ENTROPY OF ACTIVATION OF *N*-2-PHENYL-*sec*-ALKYL-*N*-NITROSOACETAMIDE IN BENZENE

RN(NO)COCH$_3$ R	Temp. °C	$10^4 \times k$ sec^{-1}	$\Delta H^{\ddagger}$ kcal. mol^{-1}	$\Delta S^{\ddagger}$ e.u.
sec-Butyl	34.8	0.677	23.9	− 4.5
	44.7	2.35		
	54.9	7.91		
2-Phenyl-isopropyl[2]	50.0	2.53	20.6	−13.5
	60.0	7.08		
	70.0	17.5		
2-Cyclohexyl-isopropyl	34.8	0.408	23.5	− 5.0
	44.7	1.39		
	55.1	4.55		
trans-2-Cyclohexyl-cyclohexyl	34.8	1.30	21.8	− 8.1
	44.7	3.95		
	54.9	12.2		
trans-2-Phenyl-cyclohexyl	34.8	0.642	17.6	−22.5
	44.7	1.34		
	54.9	3.24		

As will be shown in the latter part of this paper, the rate of reaction was found to increase, decreasing the heat of activation by the steric effect of a α-substituent of *N*-alkyl group in the decomposition of nitrosoamide[5].

However, a β-alkyl substituent does not seem to have a steric effect; the heats of activation of *N*-2-cyclohexyl-isopropyl-*N*-nitrosoacetamide and *N*-*sec*-butyl-*N*-nitrosoacetamide were the same as that of *N*-isopropyl-*N*-nitrosoacetamide (23.7 kcal./mol.).

The phenyl group at the β-position apparently decreased the heat of activation of the decomposition. The decrease by the β-phenyl group, which can not be explained by steric effect, is probably caused by the greater stability at the transition state, which involves second order hyperconjugation between the phenyl group and four membered ring.

It is very interesting to note that the effect of β-phenyl on the heat of activation is greater in a cyclohexyl system than in an open chain system. The difference in the heat of activation between *N*-2-cyclohexyl-isopropyl- and *N*-2-phenyl-isopropyl-*N*-nitrosoacetamide was 3 kcal. per mol., while the difference in the heat of activation between *trans*-*N*-2-cyclohexylcyclohexyl- and *trans*-*N*-2-phenylcyclohexyl-*N*-nitrosoacetamides was 4 kcal. per mol.

5) R. Huisgen, *Ann.*, **595**, 55 (1955).

Although all these compounds have one hydrogen atom at the α-carbon atom of the *N*-alkyl group, the β-carbon atom of *N*-2-phenyl-isopropyl-*N*-nitrosoacetamide has two hydrogen atoms which are available for hyperconjugation with the benzene ring in the transition state, while *N*-2-phenylcyclohexyl-*N*-nitrosoacetamide has only one. Therefore, if the magnitude of second order hyperconjugation is dependent on the number of available hydrogen atoms, the effect of β-phenyl could be expected to be larger in the *N*-isopropyl compound than in the *N*-cyclohexyl compound. However, the observed result was contrary to our expection.

We would like to suggest that the magnitude of second order hyperconjugation is not determined by the number of available hydrogen atoms but rather by the structure of the ethylene linkage which is involved. In other words, hyperconjugation would be larger in cyclic alkane than in open chain alkane.

Decomposition of *N*-*n*-Alkyl-, *N*-*sec*-Alkyl- and *N*-Cycloalkyl-*N*-nitrosoacetamides.—There were large differences in the rate and the heat of activation in decompositions of *N*-*n*-propyl-, *N*-*sec*-butyl- and *N*-cyclohexyl-*N*-nitrosoacetamides. The decompositions of some *N*-*n*-alkyl-, *sec*-alkyl- and cycloalkyl-*N*-nitrosoacetamides were also examined in order to find if the reactivity of the nitrosoamide is affected by hyperconjugation which is caused by π-electrons in the four-membered ring at the transition state. The results obtained are shown in Tables II, III and IV.

The heats of activation on *N*-*n*-alkyl-*N*-nitrosoacetamides, as shown in Table II, had no correlation with the number of hydrogen atoms available for hyperconjugation, all

TABLE II. DECOMPOSITION RATE, HEAT AND ENTROPY OF ACTIVATION OF *N*-*n*-ALKYL-*N*-NITROSOACETAMIDE IN XYLENE

RN(NO)COCH$_3$ R	Temp. °C	$10^4 \times k$ sec^{-1}	$\Delta H^{\ddagger}$ kcal. mol^{-1}	$\Delta S^{\ddagger}$ e.u.
Methyl	80.0	0.165	27.5	−5.3
	90.2	0.525		
	100.2	1.46		
Ethyl	70.2	0.313	27.0	−3.4
	80.0	0.975		
	90.2	2.925		
n-Propyl[a]	70.0	0.365	28.5	−1.2
	90.0	3.85		
n-Butyl	70.1	0.349	27.7	−0.9
	80.1	1.10		
	90.0	3.45		
Isobutyl	59.9	0.229	27.1	−1.0
	70.0	0.793		
	80.0	2.43		
	90.2	7.75		

a) Ref. 2

Table III. Decomposition rate, heat and entropy of activation of *N*-*sec*-alkyl-*N*-nitrosoacetamide in benzene

RN(NO)COCH$_3$ R	Temp. °C	$10^4 \times k$ sec^{-1}	$\Delta H^{\ddagger}$ kcal. mol^{-1}	$\Delta S^{\ddagger}$ e.u.
Isopropyl	24.9	0.235	23.7	−2.6
	34.8	0.848		
	44.7	3.04		
sec-Butyl	34.8	0.677	23.9	−4.2
	44.6	2.35		
	54.9	7.91		
1-Ethyl-propyl	25.0	0.212	24.3	−0.2
	35.0	0.809		
	45.0	2.95		

Table IV. Decomposition rate, heat and entropy of activation of *N*-cycloalkyl-*N*-nitrosoacetamide in xylene

RN(NO)COCH$_3$ R	Temp. °C	$10^4 \times k$ sec^{-1}	$\Delta H^{\ddagger}$ kcal. mol^{-1}	$\Delta S^{\ddagger}$ e.u.
Cyclobutyl	30.0	0.245	21.5	−11.2
	45.0	1.38		
	55.0	4.01		
Cyclopentyl	24.9	0.406	21.7	− 8.3
	34.8	1.27		
	44.7	4.26		
Cyclohexyl	24.9	0.712	20.8	−10.3
	34.8	2.16		
	44.7	6.76		
Cycloheptyl	24.9	0.283	22.6	− 5.9
	34.8	1.04		
	44.7	3.32		
	54.9	10.32		
Cyclooctyl	29.3	0.406	23.8	− 6.2
	34.8	0.860		
	44.7	3.01		
	54.9	9.78		

substances giving almost the same value (within the bounds of experimental error) except for the *N*-*n*-propyl compound. In the decomposition of *N*-*sec*-alkyl-*N*-nitrosoacetamides (Table III), the differences in heats of activation were very small, although there seems to be a trend for the heat of activation to increase with the decrease in the number of the available hydrogen atoms for the second order hyperconjugation. (All these compounds have one hydrogen atom for the first order hyperconjugation.) Therefore, in the decomposition of *N*-normal and *sec*-alkyl-*N*-nitrosoacetamides, the effect of hypercojugation is not large enough to effect the heat of activation. However, the situation was different when the *N*-alkyl group was cyclic. The heat of activation of *N*-cycloalkyl-*N*-nitrosoacetamides changed with the change in the ring size, the *N*-cyclohexyl compound being the most reactive.

Now let us look at the differences in the heat of activation (Table V) which appeared clearly in three alkyl series, *n*-alkyls, *sec*-alkyls, and cycloalkyls that are smaller than the seven-membered ring.

Table V. Heat of activation of *n*-alkyl-, *sec*-alkyl- and cycloalkyl-nitrosoacetamide

RN(NO)COCH$_3$ R	$\Delta H^{\ddagger}$ kcal. mol^{-1}
n-Alkyl	27.0～28.5
sec-Alkyl	23.7～24.3
Cycloalkyl	20.8～22.6

Huisgen[5] explained the difference between *N*-*n*-alkyl- and *N*-*sec*-alkyl-*N*-nitrosoamides as follows: the energy level of the ground state of *N*-*sec*-alkyl-*N*-nitrosoamide is higher than that of *N*-*n*-alkyl-*N*-nitrosoamide because the former has some steric strain as a result of the interaction of the branched alkyl group and the nitroso group, but the latter has not, while the energy levels of the transition states of the two compounds are the same.

While the difference in heat of activation between *N*-*n*-alkyl- and *N*-*sec*-alkylnitrosoamides can be accounted for by such a steric strain of the ground state, the difference between the heat of activation of *N*-*sec*-alkylnitrosoamide and that of *N*-cyclic alkyl nitrosoamide is hard to explain by a similar steric strain, because the acetamide group of the cyclic compound is at the equatrial position, thus causing no change in the steric strain.

Here again the second order hyperconjugation seems to offer a better explanation, because quasi-π-bond formation would be more favored in puckered cycloalkyl groups than in open chain compounds.

Decomposition of *N*-1- or 2-Deuterated Cyclohexyl-*N*-nitrosoacetamides.—If the assumption dercribed above is correct, it can be expected that the decomposition rate of *N*-cyclohexyl-*N*-nitrosoacetamide will decrease when 1- or 2-hydrogen atoms of cyclohexyl are replaced by deuterium atoms. The results obtained are exactly as expected and are presented in Table VI:

Table VI. Decomposition rates of *N*-cyclohexyl- and *N*-1- or 2-deuterated cyclohexyl-*N*-nitrosoacetamide in benzene

RN(NO)COCH$_3$ R	$10^4 \times k$ sec^{-1}	D atoms per molecule
Cyclohexyl	6.76	
1-Deuterated cyclohexyl	6.08	0.297
2-Deuterated cyclohexyl	2.43	2.54

The rate of acetolysis of cyclopentyl tosylate is known to be retarded[6] by the sustitution

6) A. Streitwieser, Jr., R. H. Jagow and S. Suzuki, *J. Am. Chem. Soc.*, 77, 6713 (1955).

of deuterium at the 2-position. The difference in free energy of activation per a deuterium atom was found to be ca. 100 cal. From this value it would be adequate to assume that the second order hyperconjugation can explain the decreased reactivities of *N*-deuterated cyclohexyl-*N*-nitrosoacetamides, because the second order hyperconjugation might be of the same order of magnitude as the first order hyperconjugation[7].

Experimental

Preparation of Amines.—Methyl-, ethyl-, *n*-propyl-, *n*-butyl-, isobutyl-, and cyclohexyl-amines were all commercially available products. *trans*-2-Phenylcyclohexylamine[8] (b. p. 116~118°C/6 mmHg., hydrochloride m. p. 247°C), *trans*-2-cyclohexyl-cyclohexylamine[8] (b. p. 110~110.5°C/4 mmHg), *sec*-butylamine[9] (b. p. 63°C), cyclopentylamine (b. p. 104~106°C) and cycloheptylamine (b. p. 85°C/75 mmHg, hydrochloride m. p. 245~246°C) were prepared from the corresponding oximes by reduction, using sodium and absolute ethanol[8]. Cyclooctylamine[9] (b. p. 72°C/12 mmHg, picrate m. p. 191~192°C), and 2-cyclohexyl-isopropylamine[10] (b. p. 85~87°C/21 mmHg, n_D^{20} 1.4615) were prepared by catalytic reduction from cyclooctanoneoxime and 2-phenylisopropylamine respectively. 1-Ethyl-*n*-propylamine (b. p. 90°C, picrate m. p. 167~168°C) and cyclobutylamine (b. p. 80~81°C) were prepared by the Schmidt reaction from α-ethylbutyric acid and cyclobutanecarboxylic acid respectively.

1-Deuterated Cyclohexylamine.—It has been reported that only 1-hydrogen atoms were exchanged by deuterium in the treatment of carboxylic acid with D_2SO_4. A mixture of 12 g. of cyclohexanecarboxylic acid (b. p. 113°C/6 mmHg, m. p. 29~30°C) and 18 g. of ice-cooled D_2SO_4 in a sealed tube was kept at 50°C for 300 hr. The resultant dark-brown mixture was poured into ice-water. The acid was extracted with ether and then was dissolved in a diluted aqueous sodium hydroxide solution. This solution was acidified with sulfuric acid and extracted with ether again. After drying the extract and removing the ether, the residue was distilled under reduced pressure, and 10.6 g. of 1-deuterated cyclohexanecarboxylic acid (b.p. 135°C/25 mmHg) was obtained. This substance has an absorption at 2195 cm^{-1} for carbon-deuterium bond. From 7.5 g. of this acid, 5 g. of 1-deuterated cyclohexylamine (b. p. 134°C) was obtained by the Schmidt reaction, using sulfuric acid. This amine has an absorption at 2170 cm^{-1} for carbon-deuterium bond.

2-Deuterated Cyclohexylamine.—2-Deuterated cyclohexanone was prepared by the method described in a previous work[12]. Twenty grams of cyclohexanone was added to ice-cooled D_2SO_4 (40 g.), and the mixture was kept at 20°C for 90 min. The resultant mixture was poured into ice-water and then extracted with ether. From the extract 5.2 g. of 2-deuterated cyclohexanone was obtained. This substance has an absorption at 2190 cm^{-1} for carbon-deuterium bond. From this ketone 2.2 g. of 2-deuterated cyclohexylamine (b. p. 133~134°C) was obtained by the usual oximation method, using

TABLE VII. *N*-ALKYLACETAMIDES, $RNHCOCH_3$

R	Formula	B.p./mmHg or m.p., °C	C, %		H, %		N, %	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
Methyl	C_3H_7NO	65/8						
Ethyl	C_4N_9NO	80~82/5						
n-Propyl	$C_5H_{11}NO$	122/25						
Isopropyl	$C_5H_{11}NO$	82/9						
n-Butyl	$C_6H_{13}NO$	110/3					12.16	12.00
Isobutyl	$C_6H_{13}NO$	93/2	62.57	62.81	11.38	10.84	12.16	12.15
sec-Butyl	$C_6H_{13}NO$	87/3	62.57	62.32	11.38	11.07	12.16	11.93
1-Ethyl propyl	$C_7H_{15}NO$	66	65.07	65.15	11.70	11.54	10.84	10.34
Cyclobutyl	$C_6H_{11}NO$	44	63.68	64.01	9.80	9.78	12.39	11.98
Cyclopentyl	$C_7H_{13}NO$	143/16	66.10	65.79	10.30	10.15	11.09	10.93
Cyclohexyl	$C_8H_{15}NO$	107	68.04	68.12	10.71	10.46	9.92	9.99
Cycloheptyl	$C_9H_{17}NO$	147~148/3	69.63	69.55	11.04	10.80	9.02	8.68
Cyclooctyl	$C_{10}H_{19}NO$	162/4					8.28	8.05
2-Cyclohexylisopropyl	$C_{11}H_{21}NO$	97					7.64	7.95
trans-2-Phenyl-cyclohexyl	$C_{14}H_{19}NO$	135	77.38	77.34	8.81	8.69	6.45	6.32
trans-2-Cyclo-hexylcyclohexyl	$C_{14}H_{25}NO$	147	75.28	75.63	11.28	11.33	6.27	6.12

7) M. M. Kreevoy and H. Eyring, ibid., **79**, 5121 (1957).
8) D. V. Nightingale, J. D. Kerr, J. A. Gallagher and M. Maienthal, *J. Org. Chem.*, **17**, 1017 (1952).
9) E. Rohrmann and H. A. Shonle, *J. Am. Chem. Soc.*, **66**, 1516 (1944).
10) B. L. Zenitz, E. B. Macks and M. L. Moore, ibid., **69**, 1117 (1947).
11) V. N. Setkina and E. V. Byova, *Doklady Acad. Nauk. S.S.S.R.*, **92**, 341 (1953); *Chem. Abstr.*, **49**, 164 (1955).
12) D. N. Kursanov and V. N. Setkina, *Doklady Akad. Nauk. S.S.S.R.*, **94**, 69 (1954); *Chem. Abstr.*, **49**, 844 (1955).

hydroxylamine hydrochloride, and reduction of the resultant oxime, using sodium and absolute ethanol. This amine has a strong absorption at 2175 cm^{-1} for carbon-deuterium bond.

Preparation of Acetamides.—Acetamides were prepared by acetylating the amines with acetic anhydride in ether. After washing with water, aqueous potassium carbonate solution, and water successively the mixture was dried over magnesium sulfate. Removal of the ether and distillation under reduced pressure gave the expected products. Recrystallization from a mixture of ligroin and chloroform gave the products in a pure form. Table VII lists the boiling points or the melting points and analytical data of the acetamides.

Water obtained from the combustion of 1- or 2-deuterated cyclohexyl acetamides contained 1.96 atom % and 16.5 atom % of deuterium respectively.

Nitrosation[13] of Amides.—Into an ice-cooled mixture of 0.01 mol. of acetamide and 0.03 mol. of anhydrous sodium acetate in carbon tetrachloride, a solution of 0.015 mol. of nitrogen tetraoxide in carbon tetrachloride, cooled to $-10\sim-15$°C, was stirred. After 30~60 min. at 0°C, the mixture was poured into ice-water. The carbon tetrachloride layer was washed with water, 5% aqueous solution of potassium carbonate, and water successively and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure at 0°C to give nitrosoacetamide, as yellow or reddish-yellow oil. Since nitrosoamide decomposes very easily, it was used immediately, without further purification, for the measurement of the rate.

Table VIII. Rate constant for the decomposition of *N*-methyl-*N*-nitrosoacetamide in xylene at 100.2°C

Time sec.	$V_\infty - V_t$ cc.	$10^4 \times k$ sec^{-1}
0	87.73	
300	83.91	1.49
600	80.43	1.45
900	77.01	1.44
1200	73.78	1.45
1500	70.55	1.45
1800	67.56	1.43
2100	64.92	1.47
2400	61.70	1.45
2700	59.29	1.45
3000	56.73	1.46
3300	54.27	1.46
3600	51.85	1.46
3900	49.65	1.46
4200	47.47	1.46
4500	45.47	1.47
4800	43.44	1.47
5100	41.52	1.45
Average value		1.46±0.01

Table IX. Rate constant for the decomposition of *N*-cycloheptyl-*N*-nitrosoacetamide in benzene at 24.9°C

Time sec.	$V_\infty - V_t$ cc.	$10^4 \times k$ sec^{-1}
0	103.21	
1800	98.10	0.282
3000	94.45	0.281
4200	91.68	0.283
5400	88.59	0.283
6180	86.68	0.283
6600	85.65	0.283
8400	81.34	0.283
10200	77.33	0.283
11400	74.73	0.283
12600	72.22	0.283
13920	69.53	0.284
15000	67.34	0.285
20280	58.02	0.284
25200	50.45	0.284
32100	41.22	0.285
Average value		0.283±0.001

Kinetic Studies.—The decomposition rates were measured volumetrically. A 50 cc. azotometer and 50% aqueous solution of potassium hydroxide were used for the measurement of the volume of nitrogen evolved from a solution of 0.004~0.007 mol. of nitrosoacetamide in 100 cc. of benzene or xylene. The thermostat was adjusted so as to maintain the temperature within ±0.01°C. The first order rate constant was calculated according to the following equation;

$$k = 2.303/t \cdot \log\{V_\infty/(V_\infty - V_t)\}$$

in which V_t and V_∞ are the volumes having evolved at time t and at the time when the decomposition ceased, usually ten-fold half the life of the reaction. The energy and entropy of activation were calculated by the least square method. Rate data for typical determination are shown in Tables VIII and IX.

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13) E. H. White, *J. Am. Chem. Soc.*, 77, 6008 (1955).