

# Thermal Decomposition of $\beta$ -Propiolactone in the Gas Phase

T. L. James and C. A. Wellington

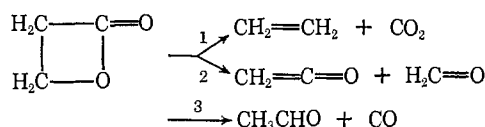
Contribution from the Department of Chemistry, University College of Swansea, Swansea, Glamorgan, Great Britain. Received June 23, 1969

**Abstract:** The thermal decomposition of  $\beta$ -propiolactone was found to be a first-order reaction yielding equal amounts of ethylene and carbon dioxide as the only products. Addition of nitric oxide had no effect on the reaction. From the temperature dependence of the reaction at an average initial pressure of 12 Torr, the activation energy was found to be  $45.81 \pm 0.07$  kcal mole<sup>-1</sup> and the preexponential factor  $(1.17 \pm 0.08) \times 10^{16}$  sec<sup>-1</sup>. Two alternative activated complexes are discussed in terms of the Marcus-Rice quantum theory of unimolecular reactions.

Walters and his coworkers by very careful, precise, and painstaking experiments have shown conclusively that cyclobutane<sup>1</sup> and its derivatives decompose by a homogeneous unimolecular mechanism to form two fragments by the rupture of bonds on opposite sides of the ring. A summary of some of the results is given by Zupan and Walters.<sup>2</sup> The products are always ethylene and a substituted ethylene and where the substituent is unsaturated and can form a conjugated substituted ethylene, the activation energy and  $A$  factor are both low.

From the basis of this careful work it is possible to predict which type of molecule is likely to undergo homogeneous unimolecular decomposition and further, as thermochemical data improve, to provide a rationale as to why two competing processes proceed at different ratios. For example, in the decomposition of *cis*-1,2-dimethylcyclobutane Gerberich and Walters<sup>3</sup> have found that the ring cleavage to give two molecules of propylene has almost the same  $A$  factor as the cleavage to ethylene and 2-butene, but the Arrhenius activation energy is 2.6 kcal mole<sup>-1</sup> lower. This is consistent with the former cleavage having an enthalpy change 8 kcal mole<sup>-1</sup> lower at 700°K than the latter.

$\beta$ -Propiolactone was chosen for study since it was a small molecule and offered the opportunity for following the falloff in unimolecular rate constant with pressure; moreover, it could decompose by three different ring cleavages each giving two stable molecules.



For these cleavages, the difference, (1) - (2), in the enthalpy changes can be calculated to be  $-39.2$  kcal mole<sup>-1</sup>, suggesting that reaction 1 is likely to be predominant. To calculate the enthalpy change for each individual reaction, the heat of formation of  $\beta$ -propiolactone is needed. There is no literature value for this<sup>3a</sup> but in an undergraduate experiment, B. Cox and R. Gammon determined the value independently and obtained values close to  $-79$  kcal mole<sup>-1</sup>. Using

(1) C. T. Genaux, F. Kern, and W. D. Walters, *J. Am. Chem. Soc.*, **75**, 6196 (1953).

(2) M. Zupan and W. D. Walters, *ibid.*, **86**, 173 (1964).

(3) H. R. Gerberich and W. D. Walters, *ibid.*, **83**, 3935 (1961).

(3a) NOTE ADDED IN PROOF. R. H. Linnell and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **72**, 3863 (1950)], however, give a value of  $-71$  kcal mole<sup>-1</sup> for the enthalpy of formation of  $\beta$ -propiolactone.

this value, reaction 1 is exothermic by 2.5 kcal mole<sup>-1</sup>, while reaction 2 is endothermic by 37 kcal mole<sup>-1</sup> and would have an activation energy of at least this value. A third mode of decomposition, forming acetaldehyde and carbon monoxide, is also possible. This would not follow the pattern for the decomposition of four-membered ring compounds outlined above, and it would also involve an  $\alpha$ -hydrogen shift. On thermochemical grounds, it is endothermic by 13 kcal mole<sup>-1</sup>, which suggests that it may be less favorable than process 1.

## Experimental Section

**Materials.** Commercial samples of  $\beta$ -propiolactone (bp 155° at 1 atm pressure) were obtained from B.D.H. Chemical Co. and Aldrich Chemical Co. These were dried over molecular sieve 4A, degassed, and found to be pure<sup>4</sup> by glpc and mass spectrometric analysis.

Approximately 0.5 g of solid carbon dioxide was put into a small bulb, immersed in liquid air, and evacuated. The liquid air bath was replaced by a solid carbon dioxide-acetone bath and the sample distilled into a trap surrounded by liquid air. The liquid air was replaced by the CO<sub>2</sub>-acetone bath and the sample allowed to evaporate into a storage bulb.

About 100 Torr of ethylene (Phillips research grade 99.98%) was introduced into the vacuum line and purified by bulb-to-bulb distillation.

A sample of nitric oxide from the Matheson Gas Co. (99% pure) was outgassed at  $-186^\circ$  and was allowed to evaporate from a  $-115^\circ$  slush bath into a storage bulb.

**Apparatus.** The apparatus has been described earlier.<sup>5</sup> The section close to the reaction vessel was wound with heating tape and heated to about 100°. This was necessary because of condensation problems due to the low vapor pressure of  $\beta$ -propiolactone at room temperature (2.5 Torr).

Samples were introduced into the reaction vessel by flash vaporization from a cold finger using an oil bath at 150°. Using this apparatus experiments could be conducted up to 20 Torr without condensation.

**Analysis.** On partial decomposition of the material at 250°, the contents of the reaction vessel were completely condensed and transferred to a Perkin-Elmer Fraktometer (Model 116) with a katharometer detector and analyzed on a 6-ft 20% w/w Apiezon L on Silocell 22 column. The only product peaks observed were those corresponding to carbon dioxide and ethylene. This was checked by analysis in a similar manner on a 6-ft activated silica gel column and again only two product peaks were obtained, the retention volumes of which were identical with those of carbon dioxide and ethylene. Using these analytical procedures, the other possible products, ketene, acetaldehyde, and carbon monoxide, would have been detected. No traces of these products were found, which indicated that processes 2 and 3 were not important in the decomposition of  $\beta$ -propiolactone.

(4) D. W. Boone, C. O. Britt, and J. E. Boggs, *J. Chem. Phys.*, **43**, 1190 (1965).

(5) T. L. James and C. A. Wellington, *J. Chem. Soc.*, **A**, 2398 (1968).

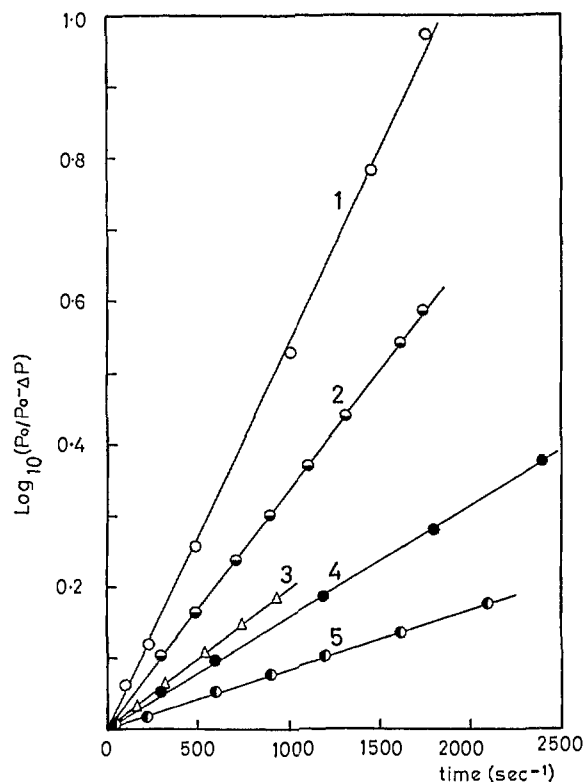


Figure 1. First-order law plots for  $\beta$ -propiolactone at the initial pressures and temperatures, and for the percentage conversions indicated. For each plot, for clarity, only a small number of representative experimental points are shown: (1) 6.14 Torr, 254.5° (90%); (2) 12.84 Torr, 247.1° (74%); (3) 8.33 Torr, 255.2° (35%) (time scale  $\times 5$ ); (4) 10.21 Torr, 239.2° (58%); (5) 11.53 Torr, 215.4° (35%).

Further, at 250° a sample of  $\beta$ -propiolactone was decomposed almost completely and the contents of the reaction vessel completely condensed in a trap. To the trap a small volume of distilled water was added, and the resulting solution was tested for formaldehyde by the phenylhydrazine method.<sup>6</sup> A blank result was obtained showing that, if the reaction producing formaldehyde and ketene were present at all, its contribution must be less than 0.05% of the total. This result was checked at 255 and 247° with precautions taken to ensure that formaldehyde would not have polymerized in the apparatus, and in each case no trace of formaldehyde could be detected.

Using the silica gel column the gas chromatograph was calibrated for carbon dioxide and ethylene by injecting known amounts of the compounds separately and integrating the peaks produced with a Kent Chromalog integrator. From these calibrations the absolute amount of the two compounds produced in any experiment could be determined. The reaction was also followed by pressure change using a wide-bore mercury manometer and a P.T.I. cathetometer, reading to 0.01 mm and estimating to 0.001 mm, focused on the meniscus. From the pressure change the amounts of carbon dioxide and ethylene could be calculated, after suitable correction for the dead-space volume had been made, on the basis of the following stoichiometry.



## Results

Results of the chromatographic analyses are given in Table I.  $P_0$  is the initial pressure of reactant and  $\Delta P_c$  the corrected pressure increase when the contents

(6) K. Mueller, Ph.D. Thesis, University of Rochester, 1951; Matsukawa, *J. Biochem. (Tokyo)*, **30**, 386 (1939); C. A. Wellington, Ph.D. Thesis, University of St. Andrews, 1960.

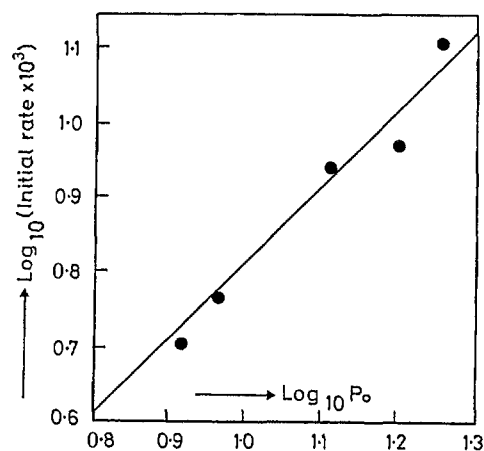


Figure 2. Plot  $\log$  (initial rate of reaction) against  $\log$  (initial pressure) for decomposition of  $\beta$ -propiolactone.

of the reaction vessel was analyzed. The ratios of the absolute yields of ethylene and carbon dioxide to those calculated from pressure changes are shown in columns 4 and 5. Furthermore, in some experiments, the total yield of  $\text{CO}_2$  and  $\text{C}_2\text{H}_4$  (fraction of products volatile at  $-78^\circ$ ) was measured using a gas buret, and the ratio of the total  $\text{CO}_2 + \text{C}_2\text{H}_4$  yield to that expected on the basis of pressure change is given in column 6. From these results the stoichiometric ratios for ethylene and carbon dioxide are 1.00 and 0.99, respectively, with standard deviations of 0.01.

Table I. Results of the Gas Chromatographic Analyses

$P_0$ , Torr	$\Delta P_c$ , Torr	Temp, °C	$\text{CO}_2$	$\text{C}_2\text{H}_4$	$\text{CO}_2 + \text{C}_2\text{H}_4$
3.65	1.81	254.9	0.96	1.04	
8.33	2.81	255.2	0.97	1.02	
12.03	6.77	248.1			0.97
10.19	5.15	247.2			0.97
8.19	3.90	247.4	1.03	1.06	
10.79	4.27	247.4			1.04
10.10	2.47	247.4	0.93	0.98	
12.84	8.53	247.1			0.98
15.49	7.62	247.4			0.96
8.78	4.14	231.2	0.97	1.03	
12.13	4.33	223.5	1.04	1.04	
11.53	3.77	215.4			1.05
			Av values		0.99 $\pm$ 0.01
					$\text{C}_2\text{H}_4$ 1.00 $\pm$ 0.01

Figure 1 shows the first-order law plots of the pressure data for the experiments at 255.2, 247.1, and 215.4°. At 254.4° the increase in pressure on "completion" of the reaction (6.08 Torr) was within 1% of the initial pressure of reactant (6.14 Torr).

Thus the pressure increase is a quantitative measure of the extent of the reaction and was used, with suitable dead space corrections, to determine the kinetic parameters for the reaction.

**Order of Reaction.** In a series of experiments at 243° the initial pressure ( $P_0$ ) of  $\beta$ -propiolactone was varied from 8 to 18 mm. The initial rates were determined, a method of iterative least squares was used to analyze the data, and the order of reaction was found to be  $1.06 \pm 0.08$  (Figure 2).

Moreover, for any reaction at the higher pressures used, a first-order plot of the data gave a straight line, and it was concluded that the reaction was of first order above 6 Torr (Figure 1).

Rate constants were calculated from pressure-time data by an iterative least-squares procedure using a computer program for an I.C.L. 1905 computer. The results are given in Table II. The standard deviations obtained were used to weigh each rate constant when used in the Arrhenius expression to obtain the activation energy of the reaction.

Table II. First-Order Rate Constants for  $\beta$ -Propiolactone

Temp, °C	$P_0$ , Torr	$k_1 \times 10^6$ , sec <sup>-1</sup>	Std dev of $k_1 \times 10^6$
211.1	20.39	2.343	0.003
211.5	13.55	2.606	0.006
215.2	8.91	3.807	0.015
215.4	11.78	3.693	0.006
223.9	9.10	8.305	0.014
223.5	12.47	7.441	0.101
231.3	11.50	15.75	0.02
231.2	8.97	16.39	0.03
239.2	9.58	32.94	0.05
239.3	10.30	34.02	0.05
237.3	3.56	59.68	0.31
247.5	8.24	57.51	0.14
247.2	9.25	66.20	0.15
247.4	10.17	76.83	0.52
247.4	10.90	72.90	0.22
248.1	12.17	78.41	0.18
247.1	12.91	72.87	0.14
247.4	15.70	58.64	0.09
247.4	17.80	66.79	0.09
253.6	11.48	104.2	0.2
253.6	9.47	104.4	0.3
255.2	8.31	131.4	1.1
255.4	8.03	135.1	0.8
240.4	16.66 <sup>a</sup>	36.61	0.05

<sup>a</sup> 2.60 Torr of NO added.

**Effect of Adding Nitric Oxide.** When nitric oxide was added to the system no significant change in the rate of reaction was observed. For example, the results at 240.4° with the addition of 2.60 Torr of nitric oxide to 16.66 Torr of  $\beta$ -propiolactone is shown in Figure 3.

**Temperature Dependence.** Figure 3 gives the Arrhenius plot for the first-order rate constant in the temperature range 205–255° and the pressure range 10–18 Torr, the bulk of the results being obtained at 12 Torr. The activation energy was determined by an iterative least-squares analysis of the weighted rate constant-temperature data to be  $45.81 \pm 0.07$  kcal mole<sup>-1</sup> with a corresponding  $A$  factor of  $(1.17 \pm 0.08) \times 10^{16}$  sec<sup>-1</sup>. From the latter value the entropy of activation was calculated to be 12.45 cal deg<sup>-1</sup> mole<sup>-1</sup>.

**Variation with Initial Pressure.** The Arrhenius parameters were determined at an average pressure of 12 Torr which would not correspond to infinite pressure conditions. A series of rate constants at 247.2° were determined at initial pressures from 18 to 1.3 Torr and these extrapolated on a  $\log k$  vs.  $1/p^{1/2}$  plot to  $1/p^{1/2} = 0$ . The extrapolated value was about 15% higher than the values at 12 Torr. From the extrapolated results the Arrhenius factor ( $A_\infty$ ) was found to be  $1.57 \times 10^{16}$  sec<sup>-1</sup>, and the entropy of activation, 12.48 cal deg<sup>-1</sup> mole<sup>-1</sup>. These values were used in the RRKM calculations which follow.

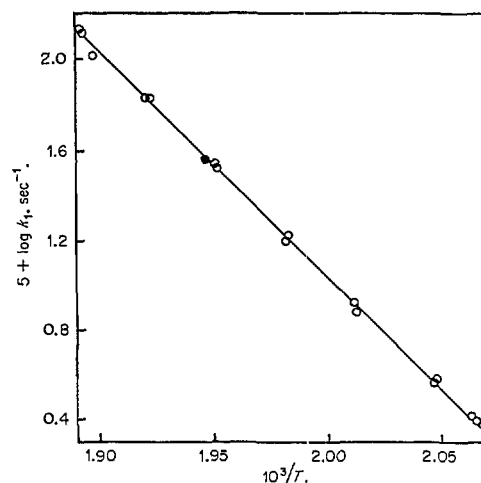


Figure 3. Arrhenius plot for  $\beta$  propiolactone; O,  $\beta$ -propiolactone; ●, NO added.

## Discussion

The decomposition of  $\beta$ -propiolactone would seem from the results to be a first-order, molecular process yielding ethylene and carbon dioxide in equal amounts as the only products. Although surface effects have not been studied directly, the reproducibility of the results suggests that surface effects would not be important. The products are those expected on thermochemical grounds, the lower energy process taking place exclusively.

The energy of activation is considerably lower than that for similar processes in other four-membered ring compounds. In the oxetane series, in which the ring includes a single oxygen atom, the activation energies<sup>7</sup> are of the order of 60 kcal mole<sup>-1</sup>. For the decomposition of cyclobutanecarboxaldehyde<sup>8</sup> the activation energy (53.3 kcal mole<sup>-1</sup>) is the lowest for the cyclobutane ring series.<sup>2</sup> If both the present compound and the cyclobutanecarboxaldehyde decompose by a diradical mechanism, the activated complexes have similarities, but for the latter case, resonance stabilization due to a semiconjugated structure is possible, e.g.,  $\text{CH}_2 \cdots \text{CH}_2 - \text{CH}_2 \cdots \text{CHCH}=\text{O}$  which are not possible in the former, e.g.,  $\text{CH}_2 \cdots \text{CH}_2 - \text{O} \cdots \text{C}=\text{O}$ . It is probable, then, that low activation energy reflects the weakness of the bonds in the  $\beta$ -propiolactone ring compared with those in cyclobutyl and oxetane compounds.

The very large entropy of activation suggests that the activated complex must be a very "loose" one which might be thought to favor a diradical type of structure. To test the implications of the large positive entropy of activation, Marcus-Rice quantum mechanical calculations were made with different complexes. Complex A was based on the assumption of a simultaneous rupture of the  $-\text{CH}_2-\text{C}=\text{O}$  and  $-\text{CH}_2-\text{O}-$  bonds while complex B corresponded to a diradical complex which was formed by the initial rupture of the  $-\text{CH}_2-\text{C}=\text{O}$  bond. A diradical intermediate could, of course, be formed by rupture of the  $\text{CH}_2-\text{O}$  bond, but the choice of complex B was made to consider the loosest possible type of intermediate.

(7) G. F. Cohoe and W. D. Walters, *J. Phys. Chem.*, **71**, 2326 (1967);  
D. A. Bittker and W. D. Walters, *J. Am. Chem. Soc.*, **77**, 1429 (1955).  
(8) B. C. Roquiltte and W. D. Walters, *ibid.*, **84**, 4049 (1962).

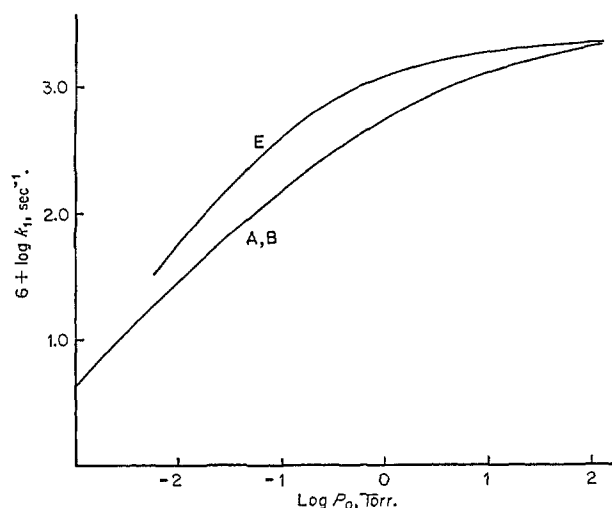
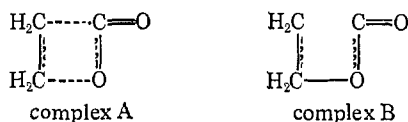


Figure 4. Unimolecular falloff for  $\beta$ -propiolactone at 259°: E = experimental; A, B = RRKM calculated curve for complexes A and B.

The assignment of grouped frequencies to these complexes was made so that the number of vibrational complexions could be calculated by the use of Fowler polynomials.<sup>9</sup> The individual frequencies were based,



as far as possible, on known vibrational frequencies for a particular bond and thereafter adjustments made to fit the entropy increase of 12.48 cal deg<sup>-1</sup> mole<sup>-1</sup>. For the reactant molecule the assignment of Durig<sup>10</sup> was used and included the ring puckering frequency of 113 cm<sup>-1</sup> instead of the remeasured value of 160 cm<sup>-1</sup>.<sup>4</sup>

(9) R. H. Fowler, "Statistical Mechanics," 2nd ed, The Macmillan Co., New York, N. Y., 1936.

(10) J. R. Durig, *Spectrochim. Acta*, **19**, 1225 (1963).

The newer value would change the calculation somewhat, making it easier to allow for the large entropy increase.

For complex B it was necessary to introduce two torsional modes of 50 cm<sup>-1</sup>, the reaction coordinate in both complexes being assumed to be the 1093-cm<sup>-1</sup> C-O ring stretching model. The grouped frequencies for complex B were thus (50)<sup>2</sup>(200)(300)<sup>2</sup>(400)(800)<sup>2</sup>(900)(1200)<sup>6</sup>(1700)(3000)<sup>4</sup>, and on this basis the entropy of activation was 12.72 cal deg<sup>-1</sup> mole<sup>-1</sup>.

In spite of the geometrical form of complex A, it was possible to allow for the large entropy of activation by a reasonable reassignment of frequencies. The ring breathing (1006), stretching (891), and deformation (746 cm<sup>-1</sup>) had all to be reduced sharply, each to 100 cm<sup>-1</sup>. This seems not unreasonable for a ring with two very weak bonds. Otherwise, the frequencies of the complex were similar to the stable molecule. An entropy of activation of 12.64 cal deg<sup>-1</sup> mole<sup>-1</sup> was calculated with the following frequencies for the complex: (100)<sup>4</sup>(300)<sup>1</sup>(500)<sup>1</sup>(800)<sup>2</sup>(1000)<sup>1</sup>(1200)<sup>4</sup>(1500)<sup>2</sup>(1700)<sup>1</sup>(3000)<sup>4</sup>.

It was not possible to make any decision between these two alternatives on the basis of the unimolecular falloff, since for the two complexes an almost identical variation of log (rate constant) - log (initial pressure) curve was obtained. The falloff for both complexes is shown as a single curve (A, B) in Figure 4, along with the experimentally determined curve (E).

To obtain a better correlation with the experimental curve, a reassignment of the frequencies would seem necessary, especially with respect to the reaction coordinate. It is perhaps also necessary to choose a different value for the rate constant for the deactivation of the activated complex, where a bimolecular collision theory value has been used with a collision diameter of 5.3 Å. Especially for complex B, it is unlikely that deactivation and recombination would take place on a simple collision with another molecule.

**Acknowledgment.** One of us (T. L. J.) is grateful to S. R. C. for the award of a research studentship.

## Communications to the Editor

### Kinetic Isotope Effects and CD<sub>3</sub> vs. CH<sub>3</sub> Migration

Sir:

In rearrangement reactions in which two or more equivalent methyl groups can migrate, comparison of kinetic isotope effects with the extent of CH<sub>3</sub> vs. CD<sub>3</sub> migration would provide a direct means of determining whether or not the step of methyl migration corresponds to the rate-controlling step. For this approach to be practical, it is first necessary to establish whether CH<sub>3</sub> and CD<sub>3</sub> have a sufficiently different migratory aptitude and to experimentally check the theoretical correlation between kinetic isotope effects and extent of CH<sub>3</sub> vs.

CD<sub>3</sub> migration in a reaction in which the rate-controlling step does correspond to the migration step.

Methyl migration in the rate-controlling step appeared likely for the acid-catalyzed rearrangement of 1,1-diphenyl-2-methyl-1,2-propanediol, reported to yield only the methyl migration product.<sup>1-4</sup> We observed 11-12% phenyl migration as well. Rate plots were linear for at least three half-lives. Data over an

(1) H. Meerwein, *Ann.*, **396**, 259 (1913).

(2) W. Parry, *J. Chem. Soc.*, 107, 108 (1915).

(3) M. Ramart-Lucas and F. Salmon-Lagagneur, *Compt. Rend.*, **188**, 1301 (1929).

(4) T. Szeki, *Magyar Chem. Lapja*, **1**, 25 (1946).