perature the vapor pressure of the glycols is very low. Analysis for O^{18} was made by scanning several times through the peak regions of interest and averaging the observed "isotopic" intensity ratios. Typical observed values for natural isobutylene glycol were 61/59 = 32.0/12500 and 77/75 = 8.2/1728. The combination of high intensities and good reproducibility leads us to believe that the final percentage reaction figures of Table V are correct to about ±5%.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Kinetics and Mechanism of the Acid-catalyzed Hydrolysis of Substituted Ethylene Oxides[1]

BY J. G. PRITCHARD AND F. A. LONG

RECEIVED NOVEMBER 17, 1955

The kinetics of the acid-catalyzed hydrolysis of ten simple epoxides have been studied at 0°, by a dilatometric procedure, in aqueous perchloric acid with acid concentrations ranging up to 3.5 molar. The rates vary widely with substituent; at constant acid concentration the rate for isobutylene oxide is faster than that for epibromohydrin by about 10^4. For the seven oxides whose rates could be studied in concentrated solutions of acid, log k_1 was found to increase linearly with $-H_0$. On this basis it is concluded that the hydrolysis goes by an A-1 mechanism involving a carbonium ion intermediate. This conclusion is supported by evidence from several other sources.

The hydrolysis of ethylene oxides in dilute aqueous solution of acids is known from the studies of Brönsted, Kilpatrick and Kilpatrick[2] to lead to the 1–2 glycols and to follow the rate law

$$\frac{-\mathrm{d}C_{\text{oxide}}}{\mathrm{d}t} = k_1 C_{\text{oxide}} \qquad (1)$$

where the first-order rate coefficient, k_1, is directly proportional to the hydrogen ion concentration. As noted in the previous paper of this series,[3] there are two likely mechanisms for this reaction, both of which would agree with the dilute solution kinetics.[4] One is an A-2 mechanism in which the conjugate acid of the oxide undergoes nucleophilic attack by a water molecule. The other is an A-1 mechanism for which the rate-determining step is unimolecular reaction of the conjugate acid of the oxide to give a carbonium ion.

A procedure which can be used to obtain evidence for these mechanisms is to study the hydrolysis in concentrated solutions of strong acids and see whether the rate is proportional to the Hammett acidity function, H_0.[5–10] This paper reports kinetic studies of the acid-catalyzed hydrolysis in aqueous solutions of perchloric acid at concentrations up to 3.5 molar. Still another type of evidence which bears on the mechanism is the effect of substituents on the rates, and to obtain data for this we have studied the hydrolysis of ten different epoxides.

Experimental

Hydrolysis rates were measured dilatometrically at 0° in a water–methanol bath whose temperature could be held constant to ±0.01°. Since the volume change for hydrolysis of epoxides is relatively large, adequate accuracy was obtained by the use of 50-ml. dilatometers of simple design. Epoxide concentrations varied from 0.05 to 0.2 molar. For all experiments pre-cooled epoxide was added to a pre-cooled and degassed solution of perchloric acid present in an upper chamber of the dilatometer, and the mixture was rapidly stirred and then transferred into the working chamber of the dilatometer by compressed air. Rate coefficients were calculated graphically using the Guggenheim procedure; Fig. 1 is a plot of typical data. Units of k_1 are sec.$^{-1}$ in all cases.

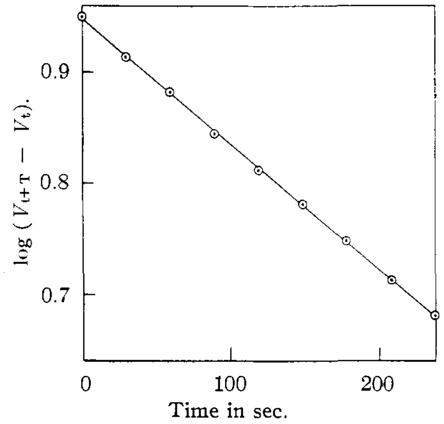

Fig. 1.—Guggenheim plot for reaction of 0.1 M ethylene oxide in 1.86 M aqueous perchloric acid at 0°.

At the end of each dilatometer run, the perchloric acid concentration of the reaction mixture was determined by titration of an aliquot with standardized sodium carbonate. Values of H_0 (at 25°) corresponding to the stoichiometric concentration of acid were taken from smoothed plots of the data of Hammett and Deyrup,[11] as corrected by Hammett and Paul.[12]

It is known that epoxides may undergo hydrolysis by a pH independent, "water" reaction. However, from the available data[3,5] it can be safely concluded that the contribution to the hydrolysis from the "water" reaction is negligible for all the experiments of the present study.

Solutions of perchloric acid were made up from reagent grade acid and redistilled water. The more common epoxides were reagent grade materials and were distilled before use. We are indebted to the Shell Development Company for samples of β-methylepichlorohydrin and β-methyl glycidol and to the Carbide and Carbon Chemical Company for

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[1] Work supported by a grant from the Atomic Energy Commission.

[2] J. N. Brönsted, M. Kilpatrick and M. Kilpatrick, THIS JOURNAL, **51**, 428 (1929).

[3] F. A. Long and J. G. Pritchard, *ibid.*, **78**, 2663 (1956).

[4] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 341.

[5] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 273–277.

[6] F. A. Long and M. Purchase, THIS JOURNAL, **72**, 3267 (1950).

[7] F. A. Long, W. F. McDevit and F. Dunkle, *J. Phys. Chem.*, **55**, 813, 829 (1951).

[8] R. W. Taft, Jr., THIS JOURNAL, **74**, 5372 (1952).

[9] D. McIntyre and F. A. Long, *ibid.*, **76**, 3240 (1954).

[10] V. Gold and J. Hilton, *J. Chem. Soc.*, 843 (1955).

[11] L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 2721 (1932).

[12] L. P. Hammett and M. Paul, *ibid.*, **56**, 827 (1934).

isobutylene oxide, *cis*-2,3-epoxybutane and *trans*-2,3-epoxybutane. Some physical properties of these compounds are: β-methylepichlorohydrin, b.p. 122°, $n^{20}\text{D}$ 1.4330; β-methylglycidol, b.p. 74–76° (26 mm.), $n^{20}\text{D}$ 1.427; isobutylene oxide, b.p. 52°, $n^{25}\text{D}$ 1.3700; *cis*-2,3-epoxybutane, b.p. 60–61°, $n^{30}\text{D}$ 1.3770; *trans*-2,3-epoxybutane, b.p. 54°, $n^{30}\text{D}$ 1.3690.

Results and Discussion

For all of the epoxides studied the rates were accurately first order in concentration of epoxide. In all cases the first-order rate coefficient increased with increasing concentration of acid. For two reactants, propylene oxide and isobutylene oxide, the hydrolysis product was isolated and found to be the expected 1,2-glycol and there is no reason to doubt that the same reaction occurs for the other oxides.

Figures 2 and 3 are plots of log k_1 *vs.* the acidity function, H_0, where k_1 is the first-order rate coefficient as defined in equation 1. In both figures it can be seen that log k_1 is linear in $-H_0$ with a slope close to unity. For two of the oxides, epibromohydrin in Fig. 2 and ethylene oxide in Fig. 3, a dotted line shows the predicted curve of log k_1 *vs.* $-H_0$ if log k_1 were actually proportional to log C_{H^+} rather than $-H_0$. It is evident that in concentrated solutions of perchloric acid the rate is not proportional to log C_{H^+}.[13]

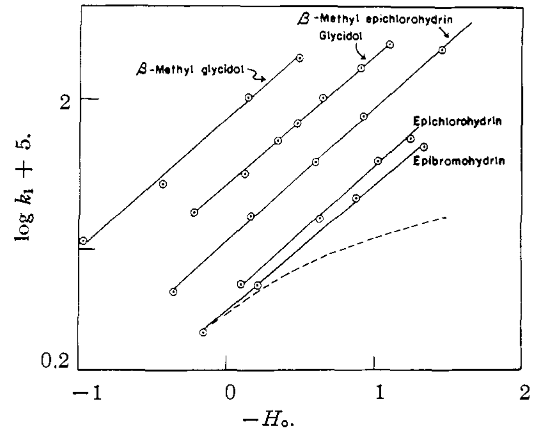

Fig. 2.—Log k_1 at 0° *vs.* the Hammett acidity function (for 25°) for the hydrolysis of ethylene oxide derivatives with polar substituents.

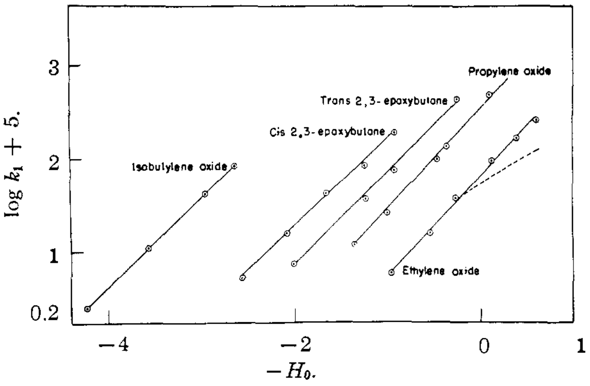

Fig. 3.—Log k_1 at 0° *vs.* the acidity function for the hydrolysis of ethylene oxide derivatives with methyl substituents.

The last column of Table I, which summarizes the rate data, gives slopes of the log k_1 *vs.* $-H_0$ plots. Although in all cases the slopes are close to unity there is a clear division into two groups. For the oxides of hydrocarbons the slopes range from 0.95 to 1.06 whereas for the oxides with polar substituents the slopes are in the range 0.85 to 0.90. The explanation of these departures from unity is presumably similar to that recently discussed for the acid-catalyzed hydrolysis of methylal.[14]

As Table I illustrates, the rate of epoxide hydrolysis is influenced markedly by substituents in the specific sense that the rate is increased by electron releasing groups and decreased by electron attracting groups. Taft[15] has recently shown that it is possible to arrive at substituent constants (σ^*-values) for use with aliphatic reactions in the same way as the Hammett σ-values can be applied to reactions of *meta* and *para* substituted benzene derivatives. Furthermore, Taft has shown that in cases where steric and resonance effects are constant, rates will vary with substituent according to the simple equation

$$\log k = \rho^*\sigma^* + \text{constant} \qquad (2)$$

TABLE I

HYDROLYSIS RATES OF ETHYLENE OXIDE DERIVATIVES IN AQUEOUS SOLUTIONS OF PERCHLORIC ACID AT 0°

No.	Oxide	Concn. range of $HClO_4$, m./l.	$10^5 k_1$, sec.$^{-1}$ at $H_0 = 0$	Slope, log k_1 *vs.* $-H_0$
1	Epibromohydrin	0.2–3.5	3.8	0.86
2	Epichlorohydrin	1.0–3.3	4.8	.87
3	β-Methylepichlorohydrin	0.4–2.6	11.5	.89
4	Glycidol	0.6–3.0	26.6	.89
5	β-Methylglycidol	0.1–1.6	75	.89
6	Ethylene oxide	0.5–2.2	63	1.06
7	Propylene oxide	0.8–2.5	350	1.06
8	*trans*-2,3-Epoxybutane	0.01–0.5	770[a]	1.01[b]
9	*cis*-2,3-Epoxybutane	3×10^{-3}–0.1	1480[a]	0.95[b]
10	Isobutylene oxide	5×10^{-5}–2×10^{-3}	33000[a]	0.98[b]

[a] Extrapolated value. [b] Slope of plot of log k_1 *vs.* log C_{H^+}.

Figure 4 gives the results of application of equation 2 to our data for acid-catalyzed epoxide hydrolysis using the Taft values of σ^*. We have used different symbols to distinguish three groups of reactants; monosubstituted oxides, 1,1-disubstituted oxides and 1,2-disubstituted oxides. For the latter group we have actually plotted log (k_1/2) rather than log k_1. This has been done under the assumption that, in accord with the conclusions of the previous paper,[3] reaction of unsymmetrical oxides will take place almost entirely at one site in the molecule and hence that reaction of symmetrical oxides will be relatively faster by a statistical factor of two. It appears from Fig. 4 that equation 2 works quite well with the monosubstituted oxides and that the 1,2-disubstituted oxides, after statistical correction, fit the curve for the monosubstituted oxides. Actually one of the 1,2-disubstituted oxides, *cis*-2,3-epoxybutane, does not fit. However, it is plausible that the *cis* configuration is less stable than the *trans* and hence it is not surprising that only the *trans* should fit the curve of Fig. 4 and that the *cis*

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[13] It should be noted that only at concentrations of perchloric acid above about 1 molar is it possible to distinguish between $-H_0$ and log C_{H^+}.

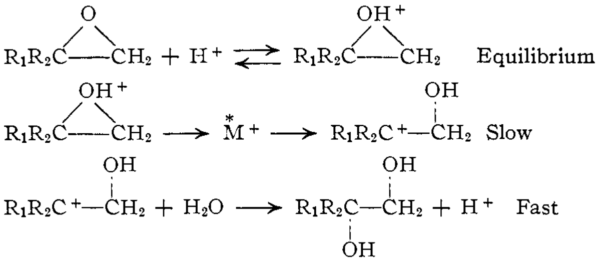
[14] F. A. Long and D. McIntyre, THIS JOURNAL, **76**, 3243 (1954).

[15] R. W. Taft, Jr., *ibid.*, **74**, 3120 (1952); **75**, 4231 (1953).

should give a faster rate. For all three of the 1,1-disubstituted oxides, the agreement with the curve of Fig. 4 is poor and at present we have no explanation for this.

From Fig. 4 the value of ρ^* for this epoxide hydrolysis reaction is -1.95 indicating that the rate is favored by electron releasing substituents. For comparison, Taft quotes ρ^*-values of -3.65 for hydrolysis of monosubstituted diethyl acetals[16] and $+1.72$ for ionization of carboxylic acids.[15]

Mechanism of the Hydrolysis.—On the basis of the O^{18} studies of the previous paper[3] it was concluded that the most likely course for the acid-catalyzed hydrolysis is an A-1 mechanism as



The alternate, A-2, mechanism differs in that the postulated rate step is a bimolecular attack on the conjugate acid by a water molecule, with the result that the activated complex includes a water molecule. It has been found experimentally that for the A-2 mechanism, rates closely parallel concentration of hydrogen ion and not the acidity function. In contrast, both general theory and studies with other systems lead one to believe that for the A-1 mechanism the rate will parallel the acidity function. In the present case the rate of the reaction may be written as

$$\begin{aligned}\text{Rate} &= k_1 C_{\text{oxide}} \\ &= k_{\text{bi}} C_{\text{oxide}} C_{\text{H}^+} \\ &= k^\circ_{\text{bi}} C_{\text{oxide}} \frac{C_{\text{H}^+} f_{\text{H}^+} f_{\text{oxide}}}{f^*_{\text{M}^+}}\end{aligned}$$

where k°_{bi} is a true constant and f_{H^+}, f_{oxide} and $f^*_{\text{M}^+}$ are activity coefficients of hydrogen ion, oxide and activated complex, respectively. Hence

$$\log k_1 = \log \frac{C_{\text{H}^+} f_{\text{H}^+} f_{\text{oxide}}}{f^*_{\text{M}^+}} + \text{Constant} \qquad (3)$$

The acidity function is defined as

$$H_0 = -\log \frac{C_{\text{H}^+} f_{\text{H}^+} f_{\text{B}}}{f_{\text{BH}^+}} \qquad (4)$$

where f_{B} and f_{BH^+} are activity coefficients of the neutral and conjugate acid forms of the Hammett indicator which is used to determine H_0. Addition of equations 3 and 4 gives

$$\log k_1 = -H_0 + \log \frac{f_{\text{oxide}}}{f^*_{\text{M}^+}} - \log \frac{f_{\text{B}}}{f_{\text{BH}^+}} + \text{Constant}$$

Noting that all activity coefficients reduce to the value unity in dilute solutions, the experimental fact that log k_1 varies linearly with $-H_0$ with unit slope leads to the conclusion that

$$\frac{f_{\text{oxide}}}{f^*_{\text{M}^+}} = \frac{f_{\text{B}}}{f_{\text{BH}^+}}$$

This is quite reasonable for the A-1 mechanism since the activated complex is structurally very close to the conjugate acid of the reactant oxide.

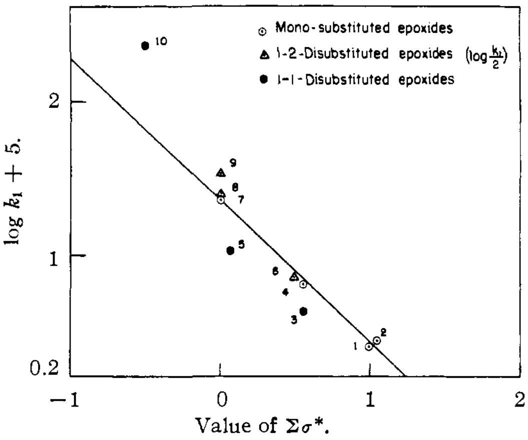


Fig. 4.—Plot of log k_1 *vs.* Taft σ^* values, referred to 0 for one methyl substituent. Numbers alongside points refer to the oxides of Table I.

This conclusion, that the mechanism is of the A-1 type with formation of a carbonium intermediate, is supported by several other experimental results. The large increase in rate caused by electron releasing groups (leading, as noted earlier, to a ρ^*-value of -1.95) is the expected result for a unimolecular rate-determing step but is not expected for a bimolecular rate-determining step.[17] The fact that the simple Taft $\sigma^*\rho^*$ relation fits most of the data also argues for a unimolecular rate step. A rate step involving nucleophilic attack of a water molecule would be expected to involve some steric hindrance in which case the simple $\sigma^*\rho^*$ relation would be less likely to hold.

Another item which lends support to the A-1 mechanism is the observed relative rates for the acid catalyzed, hydroxide ion catalyzed and *p*H independent or "water" hydrolysis of isobutylene oxide. From the data of the previous paper[3] the relative values of the second-order rate coefficients for these three reactions are

$$k_{\text{H}^+} : k_{\text{OH}^-} : k_{\text{w}} = 5 \times 10^8 : 5 \times 10^3 : 1$$

A consideration of the relative nucleophilic activities of hydroxide ion and the water molecule makes it unlikely that the rapid acid-catalyzed reaction proceeds by the direct nucleophilic attack of a water molecule on the protonated oxide. Indirectly this favors the A-1 mechanism.

A final item concerns data on the relative amounts of isomers formed by reaction of nucleophiles with substituted ethylene oxides in acid solution.[18] Table II gives the data of several workers and where available we have also listed our rate coefficient for the perchloric acid hydrolysis at $H_0 = 0$ (0.87 *M* acid). It is apparent that the percentages of 2-chloro and 2-alkoxy isomers parallel strikingly the increases in k_1. This can be interpreted on the basis of a competition between a direct nucleophilic attack on the epoxide or its conju-

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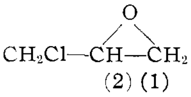
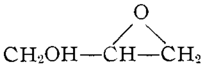
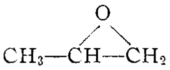
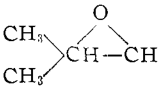
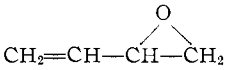
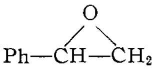
[16] M. M. Kreevoy and R. W. Taft, Jr., private communication.

[17] Ref. 4, p. 335.

[18] A detailed discussion of the directions of opening of epoxide rings is given by S. Winstein and R. B. Henderson in Vol. I of Elderfield's "Heterocyclic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950.

TABLE II

COMPARISON OF AQUEOUS HYDROLYSIS RATES WITH OBSERVED PERCENTAGES OF 1- AND 2-ISOMERS FROM REACTION WITH NUCLEOPHILES

Substrate molecule	% of 1-Isomer From Cl^- (HCl)	From alcohols (with acid)	$10^5 k_1$ at $H_0 = 0$
Epichlorohydrin: 	100^{19}	98^{20}	4.8
Glycidol: 	90^{19}	78^{21}	27
Propylene oxide: 	75^{19}	50^{22}	350
Isobutylene oxide: 	40^{23}	40^{24}	33000
Butadiene monoxide 	0^{25}	0^{26}	Fast
Styrene oxide: 	0^{27}	0^{28}	Fast

gate acid, and an A-1 mechanism terminated by addition of chloride ion or alcohol. As noted in the previous paper which gave similar data on the addition of O^{18}-labeled water, direct nucleophilic attack is expected to give the 1-isomer whereas carbonium ion formation is expected to give the 2-isomer.

These various results constitute strong evidence for an A-1, carbonium ion mechanism. However, it should be noted that several of the supporting items really refer to substituted oxides and hence do not give very direct evidence about the mechanism for ethylene oxide itself. Since for this case a carbonium ion if formed will be primary, the A-1 mechanism seems less likely. The two items which do suggest an A-1 mechanism even for ethylene oxide are the fact that its hydrolysis in perchloric acid solutions follows H_0 (Fig. 3) and the fact that the relative rate for this hydrolysis fits satisfactorily the σ^* plot of Fig. 4. Hence we tentatively conclude that even for this case the A-1 mechanism holds. Further experiments on these hydrolyses are in progress.

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(20) (a) A. Fairbourre, G. P. Gibson and D. W. Stephens, *J. Chem. Soc.*, 1965 (1932); (b) S. Winstein and L. Goodman, THIS JOURNAL, **76**, 4368 (1954).

(21) J. D. Ingham and P. L. Nichols, *ibid.*, **76**, 4477 (1954).

(22) (a) A. A. Petrov, *J. Gen. Chem.* (*U.S.S.R.*), **14**, 1038 (1944); *C. A.*, **40**, 7153 (1946); (b) H. C. Chitwood and B. T. Freure, THIS JOURNAL, **68**, 680 (1946).

(23) (a) A. A. Petrov, *J. Gen. Chem.* (*U.S.S.R.*), **15**, 690 (1945); *C. A.*, **40**, 5698 (1946); (b) H. Nilson and L. Smith, *Z. physik. Chem.*, **166A**, 136 (1933).

(24) (a) C. E. Sparks and R. E. Nelson, THIS JOURNAL, **58**, 671 (1936); (b) A. A. Petrov, *J. Gen. Chem.* (*U.S.S.R.*), **10**, 981 (1940); *C. A.*, **35**, 3603 (1941).

(25) A. A. Petrov, *J. Gen. Chem.* (*U.S.S.R.*), **11**, 991 (1941); *C. A.*, **37**, 1699 (1943).

(26) R. G. Kadesch, THIS JOURNAL, **68**, 41 (1946).

(27) C. Golumbic and D. L. Cottle, *ibid.*, **61**, 996 (1939).

(28) Ref. 18, p. 38.

ITHACA, N. Y.

[CONTRIBUTION FROM THE INORGANIC CHEMISTRY BRANCH, RESEARCH DEPARTMENT, U. S. NAVAL ORDNANCE TEST STATION]

Kinetics of Thermal Decomposition of Liquid Nitric Acid

BY C. W. TAIT,[1] J. A. HAPPE, R. W. SPRAGUE AND H. F. CORDES

RECEIVED JANUARY 23, 1956

The decomposition of liquid HNO_3 at temperatures of 65 and 70° was studied by observing the rate of evolution of O_2 from the system at atmospheric pressure. The rate data were interpreted in terms of a unimolecular decomposition of molecular N_2O_5, which results from the self-dissociation of HNO_3 into N_2O_5, NO_2^+, NO_3^- and H_2O. Estimates of the H_2O from the dissociation obtained from this kinetic study agree with estimates obtained by other experimental techniques. Calculations based upon the parameters for the gas-phase decomposition of N_2O_5 indicate that the liquid-phase decomposition of HNO_3 can be explained if 3.2% of the total N_2O_5 from the self-dissociation is in the molecular form at 65° and 5.4% is in the molecular form at 70°.

Introduction

A study has been in progress at this Laboratory for several years on the physical[2,3] and chemical properties of nitric acid solutions. Work on the kinetics of thermal decomposition of liquid nitric acid was difficult to interpret because of the erratic nature of the data. We would like to report that we have now obtained reproducible data and have devised a way of interpreting the data which gives promise of assisting in the elucidation of the mechanism of the decomposition.

While the present report was being submitted for publication, an extensive study of the kinetics of the liquid-phase decomposition of nitric acid solutions was published.[4] In that work it was shown that the decomposition is a homogeneous liquid-phase reaction with an apparent energy of activation of 32 to 37 kcal./mole, depending upon the additives present. Based upon the effect of several additives on the rate of decomposition, Robertson, *et al.*, suggested that the unimolecular decomposition of N_2O_5 plays a significant role in the rate-determining step, although a rate mechanism experimentally indistinguishable involves the product $(NO_2^+)(NO_3^-)$. Results reported in the present work were obtained by a different experimental

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[1] Wyandotte Chemicals Corporation, Wyandotte, Michigan.

[2] R. W. Sprague and Ethel Kaufman, *Ind. Eng. Chem.*, **47**, 458 (1955).

[3] R. W. Sprague, *ibid.*, **47**, 2396 (1955).

[4] G. D. Robertson, Jr., D. M. Mason and W. H. Corcoran, *J. Phys. Chem.*, **59**, 683 (1955).