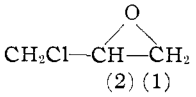
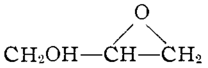
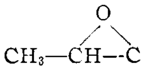
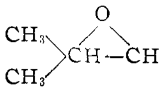
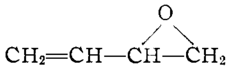
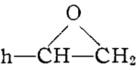
TABLE II

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.

ITHACA, N. Y.

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(19) L. Smith and S. Skyle, *Acta Chem. Scand.*, **4**, 39 (1950).

(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).

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(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.

[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).

technique and by a different method of interpreting the data than that used in reference 4. The present work yields an estimate of the H_2O from the self-dissociation of the HNO_3 and an estimate of how much of the total N_2O_5 from the self-dissociation of HNO_3 has to be in the molecular form in order to explain the kinetics of decomposition of liquid HNO_3 in terms of the unimolecular decomposition of N_2O_5.

The stoichiometry for the decomposition has been established to be[5-7]

$$4HNO_3 \rightleftarrows 4NO_2 + 2H_2O + O_2 \qquad (1)$$

in both the liquid and gas phases. In the present study the evolution of oxygen from the liquid was used to follow the decomposition.

Experimental

Preparation of Materials.—Anhydrous nitric acid was prepared by vacuum distillation at 35° and below of hydrogen nitrate from mixtures of reagent grade potassium nitrate and excess concentrated sulfuric acid. Collection of the water-white acid was made directly in the decomposition cell at −40°. In order to minimize the water content of the acid, as indicated by the reproducibility of the decomposition runs, it was necessary that about 30 ml. of the acid be distilled over into a separate collector before the decomposition sample was collected in the cell. The cell was vented to atmospheric pressure through a liquid nitrogen trap prior to removal from the preparation train. Chlorofluorocarbon grease[8] was the best grease found for use on the stopcocks of the cell. No reaction between the grease and the acid was observed. About 40-g. samples of acid were used during the kinetic runs. All weighings were made with the acid in the decomposition cell.

Apparatus.—The decomposition flask consisted of a 75 ml. long-necked Pyrex flask to which were sealed 2 sidearms with stopcocks and male ball-joints. In the center of the neck of the flask was sealed a cold-finger so that −20° refrigerant could be circulated to decrease the loss of gases other than oxygen from the cell. The cell was mounted on a shaker which agitated the cell in a constant-temperature oil-bath. Temperature of the bath was maintained to ±0.02° by a fixed heater and a proportional controller which was designed around a thermistor bridge circuit in conjunction with a published circuit.[9] Fluctuations of the temperature of the refrigerant in the cold-finger relative to the oil-bath were ±0.05°. The cell was connected to the oxygen collection system through a glass spiral and a glass-wool-sulfuric acid trap, which removed any nitrogen dioxide that escaped from the decomposition cell. The volume of oxygen evolved during a run was measured in a 25-ml. buret to obtain rates and in a 250-ml. buret to obtain total volume. Nitrobenzene was used as the displacement liquid in the burets.

Calculation of the Data.—Results were calculated on the basis that only oxygen escaped from the decomposition cell. Analysis with a mass spectrometer of the gas evolved showed that the assumption was valid. Plots of volume of gas *versus* time showed that about 5 minutes were required to establish thermal equilibrium. Rates were usually constant over the 20 ml. collection periods. Hence, the average rate was associated with the mid-time of the collection period. To correct for thermal expansion effect plots were made of apparent moles of acid and apparent sample weight (calculated from gas evolved assuming that it was all oxygen) *versus* time. Comparison of the extrapolated values at zero time with values based upon the sample weight permitted correction for the gas resulting from thermal expansion. Experimental values for the densities of these solutions were not available and were not determined. Therefore, the results were calculated in terms of molality instead of molarity.

Results

In Fig. 1 is shown a plot of rate of decomposition *versus* concentration of nitric acid at two temperatures. The data at 70° comprise 5 experimental runs and the data at 65° comprise 4 runs. The curves through the data were established by visually adjusting a spline to give a good fit. The order of the rate with respect to nitric acid, as obtained in a log–log plot, was found to be between 35 and 40. The order also varied with concentration. The value for the rate of decomposition of HNO_3 at 70° was found to be 13.3×10^{-8} mole/sec./g. as shown in Fig. 1 for a value of acid concentration of 1.5868×10^{-2} mole/g. (100% HNO_3). Using a value of 1.424 for the density of HNO_3,[10] the rate has a value of 19×10^{-5} mole/sec./l., in comparison with a value of 16.1×10^{-5} mole/sec./l. at 71.1° given by Robertson, *et al.*[4] The somewhat higher value obtained in the present work may be the result of slightly more anhydrous acid being used.

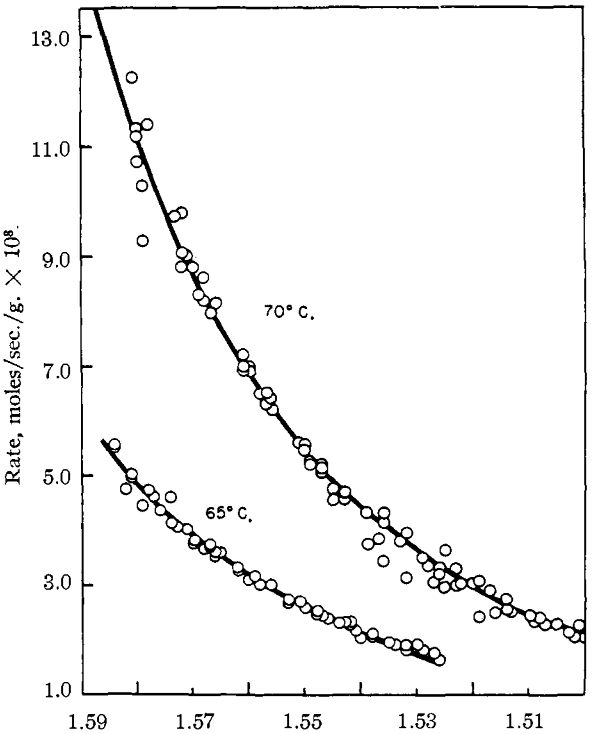

Fig. 1.—Variation of rate of decomposition of liquid nitric acid with concentration of the acid.

Because of the known self-dissociation of nitric acid under some conditions into water, nitronium ion and nitrate ion,[11] an attempt was made to represent the rate data in terms of a first-order decomposition of dinitrogen pentoxide. The self-dissociation can be represented by equation 2.

$$2HNO_3 \rightleftarrows N_2O_5 + H_2O \qquad (2)$$

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[5] H. H. Franck and W. Schirmer, *Z. Elektrochem.*, **54**, 254 (1950).

[6] H. S. Johnston, L. Foering, Y. Tao and G. H. Messerly, THIS JOURNAL, **73**, 2319 (1951).

[7] H. S. Johnston, L. Foering and R. J. Thompson, *J. Phys. Chem.*, **57**, 390 (1953).

[8] Experimental Polymer S-6 Grease, manufactured by M. W. Kellogg Co., P. O. Box 469, Jersey City 3, New Jersey.

[9] R. H. McFee, *Rev. Sci. Instr.*, **23**, 52 (1952).

[10] This value is based on an extrapolation of density data given in reference 3.

[11] C. K. Ingold and D. J. Millen, *J. Chem. Soc.*, 2612 (1950).

The equilibrium constant for the dissociation would be

$$K_D = [N_2O_5][H_2O]/[HNO_3]^2 \tag{3}$$

It has also been established[11] that under some conditions N_2O_5 is essentially completely ionized in HNO_3 according to equation 4

$$N_2O_5 \rightleftarrows NO_2^+ + NO_3^- \tag{4}$$

The equilibrium constant for the ionization would be

$$K_i = [NO_2^+][NO_3^-]/[N_2O_5] \tag{5}$$

If the assumption is made that molecular N_2O_5 is the active decomposing species in liquid HNO_3, it follows that

$$-d[HNO_3]/dt = -2d\,[N_2O_5]/dt \tag{6}$$

Since the decomposition of N_2O_5 in the gas phase and in inert solvents[12] is a first-order reaction in N_2O_5, equation 6 becomes

$$-d[HNO_3]/dt = 2k[N_2O_5] \tag{7}$$

Substitution of the value for N_2O_5 from equation 3 into equation 7 leads to the result that

$$-d[HNO_3]/dt = 2kK_D[HNO_3]^2/[H_2O] \tag{8}$$

The experimental technique used in the present work involved measuring the rate of evolution of O_2 from the solution and using the stoichiometry according to equation 1 to calculate $d[HNO_3]/dt$, $[HNO_3]$ and $[H_2O]$. The water calculated in this fashion involves the water generated during decomposition and does not take into account the water present initially in HNO_3 from the self-dissociation equilibrium. The assumption was made that the water from the self-dissociation, w_0, was a constant. Under this assumption, equation 8 becomes

$$-d[HNO_3]/dt = 2kK_D[HNO_3]^2/(w_0 + [H_2O]) \tag{9}$$

Rearrangement of equation 9 yields the expression

$$w_0/2kK_D + [H_2O]/2kK_D = [HNO_3]^2/(-)\,d[HNO_3]/dt = f \tag{10}$$

In Fig. 2 is shown a plot of f *versus* the water generated during decomposition. The particular values shown in Fig. 2 were calculated from the curves drawn through the data of Fig. 1. In the initial portion of the decomposition the data in Fig. 2 can be fit by a straight line. Evaluation of the slopes and intercepts yields values of w_0 = 0.189 molal and $kK_D = 2.18 \times 10^{-8}$ sec.$^{-1}$ at 65° and w_0 = 0.156 molal and $kK_D = 4.41 \times 10^{-8}$ sec.$^{-1}$ at 70°. The ΔE for kK_D is 32.4 kcal./mole, which agrees well with the value obtained by Robertson, *et al.*[4]

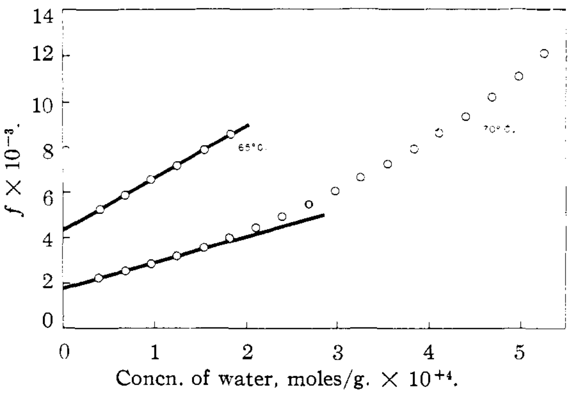

Fig. 2.—Variation of ratio, $f = [HNO_3]^2/d[HNO_3]/dt$, with concentration of water generated during decomposition.

Discussion

In earlier work with Raman spectra of liquid nitric acid,[11] an estimate of 0.23 molal was obtained for the water from the self-dissociation of nitric acid at −15°. Cryoscopic measurements in nitric acid[13] yielded a value of 0.27 molal. It is believed that the values obtained in the present kinetic study are in good agreement with the results from these other studies.

In order to evaluate the specific rate constant, k, from the values of kK_D obtained from the kinetic data, it would be desirable to have an experimental determination of the concentration in nitric acid of molecular dinitrogen pentoxide. Then values of K_D, the dissociation constant, and hence values of k could be calculated from the decomposition of the liquid acid for comparison with the specific rate constant obtained from the decomposition of pure dinitrogen pentoxide.

Experimental determinations of molecular dinitrogen pentoxide in nitric acid are not available. In the absence of experimental values, estimates of K_D were obtained by using values for k from the gas-phase decomposition of dinitrogen pentoxide.[14] In this fashion estimates were obtained of the concentration of molecular dinitrogen pentoxide needed to explain the kinetics of decomposition of liquid nitric acid.

The activation energy for the decomposition of dinitrogen pentoxide is essentially constant for the decomposition in the gas phase and in several solvents.[13] The specific rate constants also agree fairly well under these various conditions. These results suggest that the same mode of decomposition is involved in the gas phase and in solution. It has also been reported[15] that in some solvents, *e.g.*, nitric acid, although the decomposition is first order the activation energy is increased and the specific rate constant is decreased significantly over the values obtained in the gas-phase decomposition. This result suggests that either a different mode of decomposition is involved in nitric acid as a solvent or that there has occurred a reduction in the concentration of the active decomposing species, presumably by ionization of the dinitrogen pentoxide.

In the case of the present data, values of k were calculated from the data on the gas-phase decomposition of dinitrogen pentoxide.[13] A value of 24.7 kcal./mole was used for the activation energy and a value of 1.65×10^{-5} sec.$^{-1}$ was used for k at 20°. Use of these numbers yields values of 4.64×10^{-3} sec.$^{-1}$ for k at 65° and 7.97×10^{-3} sec.$^{-1}$ at 70°. These values for k yield values of $K_D = 4.70 \times 10^{-6}$ at 65° and $K_D = 5.54 \times 10^{-6}$ at 70° from the values of kK_D determined from the present kinetic study. The value of ΔE for K_D over this tempera-

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(12) H. Eyring and F. Daniels, This Journal, **52**, 1472 (1930).

(13) R. J. Gillespie, E. D. Hughes and C. K. Ingold, *ibid.*, 2552 (1950).

(14) H. Eyring and F. Daniels, *ibid.*, **52**, 1472 (1930).

(15) H. Eyring and F. Daniels, *ibid.*, **52**, 1486 (1930).

ture interval is 7.5 kcal./mole. Use of values for w_0 in conjunction with the calculated values for K_D with the assumption that the total concentration of dinitrogen pentoxide, *i.e.*, molecular plus ionized, is equal to the concentration of water as evaluated by w_0 shows that the present rate data can be accounted for in terms of a first order decomposition of dinitrogen pentoxide if 3.2% of the dinitrogen pentoxide from the self-dissociation of the acid is in the molecular form at 65° and if 5.4% is in the molecular form at 70°.

In regard to the question of identifying molecular dinitrogen pentoxide in liquid nitric acid, Raman spectra[11] at $-15°$ gave no clear cut indication of lines for this species, although lines for nitronium ion and nitrate ion were evident. In order to see whether this Raman result is compatible with interpretation of the present kinetic data, a calculation was made for the equilibrium constant, K_i, for the ionization of dinitrogen pentoxide into nitronium and nitrate ions according to equations 4 and 5. Calculation of K_i was made assuming again that the total concentration of dinitrogen pentoxide was equal to w_0 as obtained from the kinetic studies. The concentration of the molecular species was obtained from the values of w_0 and K_D, the self-dissociation constant for nitric acid, as listed above. It was calculated in this fashion that at 65° K_i = 5.61 molal and at 70° K_i = 2.54 molal. The ΔE from these values for K_i is -36.6 kcal./mole. From these values K_i was calculated at $-15°$ and it was found that, although molecular dinitrogen pentoxide may exist in liquid nitric acid at elevated temperatures, at $-15°$ it should be essentially completely ionized. The result of this calculation, then, is compatible with the experimental result that the molecular species was not identified in Raman spectra for nitric acid solution at $-15°$. The calculations also suggest, however, that Raman spectra should be obtained at higher temperatures in order to identify the molecular species. Such work should be attempted in order to test experimentally the estimates of the molecular species calculated from the present kinetic study.

Acknowledgments.—It is a pleasure to acknowledge the assistance given this study by several members of the laboratory. D. Moore designed the thermistor bridge circuit for the constant temperature bath and Helen R. Young and A. V. Jensen carried out the mass spectrometric analysis of the decomposition gases. Mrs. Ethel Kaufman assisted with some of the kinetic runs.

CHINA LAKE, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Mechanism of Substitution Reactions of Complex Ions. VIII. Hydrolysis of *cis*- and *trans*-Chlorohydroxo-bis-(ethylenediamine)-cobalt(III) Complexes[1,2]

BY RALPH G. PEARSON, ROBERT E. MEEKER AND FRED BASOLO

RECEIVED DECEMBER 5, 1955

The rates of reaction of *cis*- and *trans*-chlorohydroxo-bis-(ethylenediamine)-cobalt(III) complexes with water are reported. They are considerably faster than those of the corresponding dichloro complexes. A discussion is given of the products of reaction of one mole of hydroxide ion with one mole of *cis*- or *trans*-$[\mathrm{Coen_2Cl_2}]^+$.

An examination of the literature showed that there was no report of a direct measurement of the rate of aquation of a chlorohydroxo complex ion of cobalt(III). These compounds are, in fact, unknown in the solid form and can only be prepared in solution where they have a limited life-time. It is necessary therefore to study their reaction *in situ* directly after formation.

We have made several chlorohydroxo complexes in solution by adding a limited amount of alkali to an aqueous solution of the corresponding chloroaquo or dichloro complex. The rate of aquation of the remaining chloro group was then determined immediately by potentiometric titration. The *cis*-isomer of chloroaquobis-(ethylenediamine)-cobalt(III) is known but it has not been possible to isolate the *trans*-form.[3] It is assumed that a proton transfer on adding one equivalent of alkali leaves the configuration unchanged and thus readily furnishes the *cis*-chlorohydroxo in solution

$$cis\text{-}\mathrm{Coen_2ClH_2O^{+2}} + \mathrm{OH^-} \longrightarrow cis\text{-}\mathrm{Coen_2ClOH^+} + \mathrm{H_2O} \quad (1)$$

To prepare and study the *trans*-chlorohydroxo complex it is necessary to start with a dichloro complex.

When one equivalent of hydroxide ion is added to a solution of a dichloro complex a very complicated system results. Initially hydroxide ion is consumed according to equation 2 to form the chlorohydroxo complex. Both the *cis*- and *trans*-chlorohydroxo complexes may be formed.

$$[\mathrm{Coen_2Cl_2}]^+ + \mathrm{OH^-} \xrightarrow{k_1} [\mathrm{Coen_2ClOH}]^+ + \mathrm{Cl^-} \quad (2)$$

These products then compete with the dichloro complex for the remaining hydroxide ion, forming the *cis*- and *trans*-dihydroxo complexes, as illustrated in equation 3. Reaction (3) is nearly as rapid as reaction (2), as shown by a comparison of rate constants k_1 and k_2 in reference 1

$$[\mathrm{Coen_2ClOH}]^+ + \mathrm{OH^-} \xrightarrow{k_2} [\mathrm{Coen_2(OH)_2}]^+ + \mathrm{Cl^-} \quad (3)$$

so that an appreciable concentration of the dihydroxo complex is formed.

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(1) For previous papers in this series see R. G. Pearson, R. E. Meeker and F. Basolo, THIS JOURNAL, **78**, 709 (1956).

(2) This investigation supported by the U. S. Atomic Energy Commission under Contract AT(11-1)89, Proj. No. 2.

(3) A. Werner, *Lieb. Ann.*, **386**, 17 (1912).