taining the tracer only, as expected.[11] When corrections are made for the increase in (Na^+) and decrease in (NaR) in equation 2 because of the presence of macro concentration of Co, the values of K_d, cor. become equal to the corresponding K_d for tracer only.

(C) Co(II) and Zn(II) Complexes of Imidazole.—Li, *et al.*,[3] mention that in ion-exchange experiments with Co-60 complex of imidazole, the values of $1/K_d$ for imidazole concentrations varying from 0.01–0.80 *M* were always smaller than the value of $1/K_d^0$. We have repeated the ion-exchange experiments for the zinc complex of imidazole at $\mu = 0.16$ and *p*H 7.1 and have found that for imidazole concentrations varying from 0.01–0.40 *M*, $1/K_d$ remains practically constant at only 8% of the value of $1/K_d^0$. The zinc–imidazole complex with a double positive charge, like the Co–imidazole complex, must therefore also have been taken up by the cation exchanger as is the uncomplexed cation. The greater affinity of the larger imidazole complex relative to the uncomplexed cation of the same charge presumably is caused by van der Waals forces.[12]

Direct visual evidence of the uptake of an imidazole complex ion by "Dowex-50" cation exchanger was obtained. A solution of Cu(II)–imidazole complex ion was passed through a column of a special light-colored sample of resin ("Dowex-50 W"), and a dark blue band of the complex ion was observed at the top of the resin bed. The complex is decomposed by the passage of dilute hydrochloric acid through the resin, whereupon the imidazole is washed away, leaving an olive green band of uncomplexed Cu(II). Similar observations have been reported for other positively charged metal complexes as, for example the uptake of the ammonia complexes of Cu(II), Ni(II) and Zn(II) by a cation exchanger.[13]

Solvent-extraction experiments with imidazole complexes should behave normally in that the value of $1/K_d$ should increase with increasing concentration of imidazole and should always be greater than $1/K_d^0$. This is brought out by the data of Table V.

TABLE V

SOLVENT-EXTRACTION EXPERIMENT ON Co(II) COMPLEX OF IMIDAZOLE

*p*H 5.45, $\mu = 0.15$, 25°

Total imidazole, *T*, *M*	(Imidazole)[a]	$1/K_d$	$\frac{(K_d^0/K_d) - 1}{\text{(imidazole)}}$[b]
0.032	0.00067	1.58	168
.048	.00101	1.62	137
.064	.00134	1.78	191
.080	.00168	1.84	174
		Av.	168

[a] In calculating (imidazole) from *T* and *p*H of 5.45, *p*H of imidazole is taken to be 7.12. [b] A plot of $1/K_d$ *vs.* (imidazole) is linear and the extrapolated value of $1/K_d^0$ is 1.42.

The average value for log k_1 of the Co(II)–imidazole complex is calculated to be 2.23. This is a reasonable value for the formation constant of Co–imidazole complex, inasmuch as log K_1 of Co(II) complex of NH_3 is 2.0.[14,15]

A solvent-extraction experiment on the Zn(II)–imidazole complex also shows that $1/K_d$ is greater than $1/K_d^0$ and increases when the concentration of imidazole increases. The value of log k_1 for Zn–imidazole complex is calculated to be 2.6, in good agreement with the value log k_1 = 2.58 reported by Edsall, *et al.*[15] The imidazole complexes therefore furnish excellent examples of how ion-exchange and solvent-extraction experiments can complement each other in the study of metal complexes.

LEMONT, ILLINOIS

---

[11] J. Schubert, in "Ion Exchange Theory and Application," Ed. F. C. Nachod, Academic Press, Inc., New York, N. Y., 1949, pp. 167–221.

[12] T. R. E. Kressman and J. A. Kitchener, *J. Chem. Soc.*, 1208 (1949).

[13] R. Nelson and H. F. Walton, *J. Phys. Chem.*, **48**, 406 (1944).

[14] J. Bjerrum, "Metal Ammine Formation in Aqueous Solutions," P. Haase and Sons, Copenhagen, 1941.

[15] J. T. Edsall, G. Felsenfeld, D. S. Goodman and F. R. N. Gurd, THIS JOURNAL, **76**, 3054 (1954).

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

The Thermal Decomposition of Liquid Nitric Acid. II[1]

BY H. F. CORDES, N. R. FETTER AND J. A. HAPPE

RECEIVED MARCH 8, 1958

The thermal decomposition of liquid nitric acid has been studied at 55, 65 and 75°. The rate of decomposition can be expressed in terms of the water produced by the decomposition. $-d(HNO_3)/dt = (HNO_3)^2/[f_0^0 + S(H_2O)]$. "Activation energies" have been determined for f_0^0 and *S*. They are −38.7 and −27.8 kcal., respectively. The rate expression shows dependence upon the addition of some inorganic materials to the acid. The ionic mechanism, previously proposed for the decomposition, is discussed and found to be inadequate to explain the effects of the additives. An alternative free radical mechanism is proposed. This mechanism is found to be more satisfactory than the ionic mechanism and furnishes a correlation between the liquid phase and gas phase decompositions.

Introduction

Previous papers have reported on the thermal decomposition of liquid nitric acid.[2,3] These papers raised questions about the mechanism of the decomposition. It was felt that some further information might be obtained from a detailed study of the effect of several additives on the decomposition rate, and the present work was undertaken with this view in mind. One of the previous articles[2] contained some information about the effect of several

---

[1] Section 1 appeared in THIS JOURNAL, **78**, 2670 (1956).

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

[3] C. W. Tait, J. A. Happe, R. W. Sprague and H. F. Cordes, THIS JOURNAL, **78**, 2670 (1956).

additives on the rate. The concentrations were quite high (1–2 *m*) and they were not varied. In addition to investigating the effect of additives, the data concerning the activation energy of the reaction have been improved. The present paper also establishes that water is the prime inhibiting species for the decomposition and corrects a previous interpretation of the data. It is shown that the mechanism for the gas phase decomposition of nitric acid can be used to explain the data for the liquid decomposition as satisfactorily as the ionic mechanisms previously proposed. The decompositions were all carried out at constant pressure and the degree of decomposition was determined by the amount of oxygen evolution according to the stoichiometric equation

$$2HNO_3 \longrightarrow 2NO_2 + H_2O + 1/2O_2$$

Experimental

Apparatus.—With the exception of one change, the apparatus was the same as that described in an earlier report.[3] The shaking device described in that report was replaced by a Kel-F coated magnetic stirring bar and a rotating magnet was placed in the constant temperature bath directly beneath the reaction vessel. This method of agitation was found to give steadier gas evolution than had been obtained previously. The temperature of the bath was controlled to ±0.05° during an individual decomposition.

Preparation of Materials.—HNO_3—the preparation of the nitric acid has been described elsewhere.[3] H_2O—the water was ordinary laboratory distilled water. $KFSO_3$—the potassium fluorosulfonate was prepared by adding dropwise a slight excess of fluorosulfonic acid to 0.1 mole of potassium chloride. After reaction had occurred the hydrogen chloride gas was pumped off and the reaction mixture was filtered by suction to remove the excess fluorosulfonic acid. The resulting cake was washed with cold water and recrystallized from slightly alkaline hot water. The final product was free of chloride and sulfate ions. NO_2FSO_3—The nitronium fluorosulfonate was prepared according to the method of Goddard, Hughes and Ingold.[4] KNO_3—the potassium nitrate was reagent grade material and it was used as it was obtained from the manufacturer. N_2O_4—the dinitrogen tetroxide was obtained commercially. It was purified with oxygen to remove any nitric oxide but was not dried.

Results

Treatment of the Data.—From a record of evolved oxygen as a function of time, rates of evolution were computed for each 2 cc. of gas evolved. The change in rate over a 10-cc. volume was found to be less than the scatter between the 2-cc. intervals and the rates were averaged in groups of five. Using the stoichiometric equation for the decomposition together with the gas formula, the rates were converted to moles of nitric acid decomposed per 1000 g. of nitric acid per second. Molal concentrations were used since the densities of these solutions are not known. The integral volume of evolved oxygen at the mid-point of each 10-cc. interval was converted to the equivalent molal water concentration in the solution.

As was discussed in a previous paper,[3] the most convenient method of examining the data is to compute the quantity *f*. A quantity enclosed in parentheses will denote a molal concentration.

$$\frac{(HNO_3)^2}{\dfrac{-d(HNO_3)}{dt}} = f$$

f is then plotted as a function of the water concentration; a typical plot is shown in Fig. 1. In all cases the plots were found, visually, to be straight lines up to 0.3 *m* in water of decomposition. The data for each individual run were fitted by least squares to the line

$$f = f_0^0 + S(H_2O)$$

The initial concentration of nitric acid remains nearly constant, even for those runs containing additives, and hence f_0^0 will be proportional to the reciprocal of the initial rate of decomposition for a given mixture. The first two or three points usually showed a deviation from the least square line. Temperature records during this time indicate that the deviations were due to lack of thermal equilibrium with the bath and to expansion of gas in the reaction cell. These first points were not employed in determining the least square parameters.

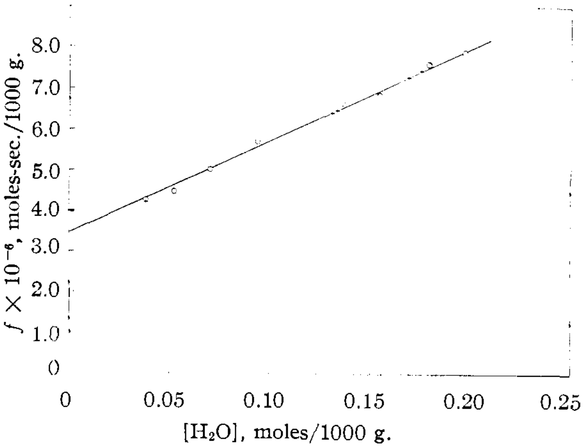

Fig. 1.—Dependence of *f* on water on decomposition at 338.15°K.

The increase in vapor pressure of the solution while thermal equilibrium was being reached and expansion of any gas in the flask caused the apparent total oxygen evolved to be in error. This effect prevented a direct extrapolation of the *f vs.* (H_2O) curve to obtain a value of *f* at zero water concentration. The extrapolation was accomplished by picking a point of known time on the *f vs.* (H_2O) curve and extrapolating to zero time to obtain a value of f_0^0. The corrections were small and any error introduced by not correcting the rate during the warm up period was negligible.

Decomposition of Pure Acid and the Activation Energy for the Reaction.—The decomposition of the pure acid was studied at 55, 65 and 75° The values of f_0^0 and S were found to be temperature dependent. The data are listed in Table I. Plots of either $\log f_0^0$ or $\log S$ *vs.* the reciprocal of the absolute temperature were straight lines. The data were least squared to equations of the Arrhenius form and the activation energies and pre-exponential factors were obtained. The results are

$$f_0^0 = 10^{-18.43\pm0.58}\, e^{38.66\pm0.92/RT} \times 10^3 \frac{\text{mole-sec.}}{1000\text{ g.}}$$

$$S = 10^{-10.57\pm0.62}\, e^{27.78\pm0.96/RT} \times 10^3 \text{ sec.}$$

This gives an activation energy of 38.66 ± 0.92 kcal. for the initial rate. This value is slightly

---

(4) D. R. Goddard, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2559 (1950).

TABLE I

f_0^0 AND S AS A FUNCTION OF ABSOLUTE TEMPERATURE T

T, °K. (0°C. = 273.16°K.)	f_0^0, mole-sec./1000 g. × 10^{-6}	S, sec. × 10^{-7}
326.54	27.12	7.92
327.21	26.32	9.48
327.57	23.72	12.78
328.05	25.53	8.84
328.05	18.84	11.38
336.68	4.05	2.27
336.95	3.98	2.09
337.54	4.09	2.15
338.15	3.57	2.32
338.54	3.08	2.07
343.14	1.74	1.14
347.45	0.799	0.812
347.71	0.905	.688
347.81	1.05	.829
347.83	0.798	.749
347.85	.718	.751
347.94	.711	.862
347.98	.767	.712
348.05	.508	.777
348.09	.677	.888
348.23	.517	.730

TABLE II

EFFECT OF ADDITIVES ON THE PARAMETER f_0^0 AT 65.00°

The spread is ± one standard deviation.

Additive	Dependence on additional concn.	Least square evaluation, $\frac{\text{moles-sec.}}{\text{1000 g.}} \times 10^{-6}$
H_2O	$f_0^0 = (f_0^0)_0 + S^1(H_2O)$	$(f_0^0)_0 = (3.85 \pm 0.43)$ $S^1 = (2.11 \pm 0.23) \times 10^7$ sec.
KNO_3	None	(f_0^0) av. $= (3.82 \pm 1.01)$
N_2O_4	None	(f_0^0) av. $= (3.55 \pm 0.71)$
$KFSO_3$	None	(f_0^0) av. $= (2.79 \pm 0.46)$
NO_2FSO_3	None	(f_0^0) av. $= (2.33 \pm 0.70)$
Pure acid (interpolated)	....	$(f_0^0) = (3.62 \pm 0.50)$
Av. of all values of f_0^0		$(f_0^0) = (3.33 \pm 0.57)$

TABLE III

EFFECT OF ADDITIVES ON THE PARAMETER S AT 65.00°

The spread is ± one standard deviation.

Additive	Dependence on additive concn.	Least square evaluation
H_2O	None	(S) av. $= (2.69 \pm 0.32) \times 10^7$, sec.
KNO_3	$S = S_0 + P(KNO_3)$	$S_0 = (2.10 \pm 0.13) \times 10^7$, sec. $P = (1.84 \pm 0.48) \times 10^7$, $\frac{\text{sec. 1000 g.}}{\text{mole}}$
N_2O_4	$S = S_0 + P(N_2O_4)$	$S_0 = (1.50 \pm 0.09) \times 10^7$, sec. $P = (2.32 \pm 0.19) \times 10^7$, $\frac{\text{sec. 1000 g.}}{\text{mole}}$
NO_2FSO_3	$\frac{1}{S} = \frac{1}{S_0} + R(NO_2FSO_3)$	$S_0 = (2.22 \pm 0.51) \times 10^7$, sec. $R = (2.37 \pm 0.58) \times 10^7$, $\frac{\text{sec.}^{-1}\text{ 1000 g.}}{\text{mole}}$
$KFSO_3$	None	(S) av. $= (2.03 \pm 0.29) \times 10^7$, sec.
Pure acid (interpolated)	....	$S = (2.36 \pm 0.33) \times 10^7$, sec.
Av. all values of S	....	$S = (2.14 \pm 0.34) \times 10^7$, sec.

higher than previous ones,[2,3] which were nearer to 32 kcal. The difference is not large and it is felt that the present method of estimating f_0^0 is an improvement over the previous methods. The activation energy for the inhibition constant S is -27.78 ± 0.96 kcal. It should be noted that both f_0^0 and S have the units of reciprocal rates and hence their activation energies will have opposite sign from the normal Arrhenius equation.

Additives.—It was felt that the addition of several compounds to pure nitric acid might alter the rate of decomposition and shed some light on the details of the mechanism. A number of decompositions were carried out on solutions of various inorganic substances in nitric acid. In all of the decompositions, the rates were found to behave qualitatively the same as those for pure nitric acid; that is, the parameter f was found to be a linear function of the water of decomposition. In some cases, the values of f_0^0 and S were found to be functions of the additive concentrations. A summary of the data is given in Tables II and III. If the value of the parameter was not found to be a function of the additive concentration, the average value is listed. In the cases where dependence was found, the empirical equation for the dependence is listed along with a least square fit of the data to the equation. All of the decompositions carried out on solutions containing additives were done near 65°. The activation energies for f_0^0 and S were assumed to be independent of the additives and the values of these activation energies for the pure acid were used to correct all data to 65.00°.

H_2O.—Seven decompositions were carried out with solutions of water in nitric acid. The values of S obtained from the rate data were found to be independent of the concentration of added water and within experimental error had the same value as the parameter S obtained from rate data from the pure acid. The values of f_0^0 from the individual runs were plotted as a function of added water. The plot is shown in Fig. 2. It can be seen that the curve is linear. Respectively, the slope of this line and the value of f_0^0 extrapolated to pure acid are within experimental error of being the same as S and f_0^0 obtained from the individual decompositions using pure acid and are listed as S^1 and $(f_0^0)_0$ in Table II.

These data furnish a justification for treating f as a function of water of decomposition during a run. Without these data, the independent variable used in analyzing the rate data could be considered no more than a measure of the degree of advancement of the reaction and might as easily have been identified with the dinitrogen tetroxide concentration as with the water concentration.

N_2O_4.—Ten decompositions were made using solutions of dinitrogen tetroxide in nitric acid. The values of f_0^0 obtained from these rate data were independent of the amount of additive and essentially the same as for the pure acid. The parameter S was found to be a linear function of the amount of added dinitrogen tetroxide. This dependence is slight and would not be expected to be observed as a change in S during a run. The dependence is shown in Fig. 3. The effect of added dinitrogen tetroxide is to increase the inhibition of the rate of

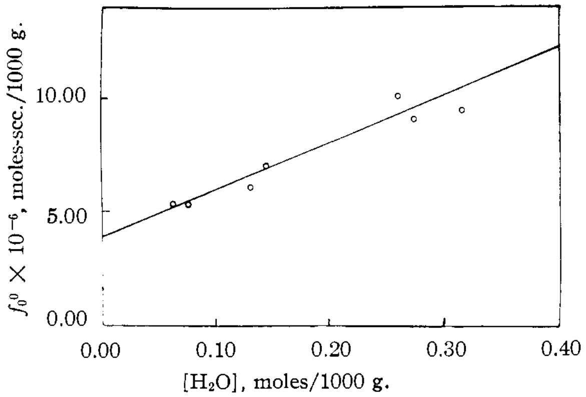

Fig. 2.—Dependence of f_0^0 on added water.

decomposition. This inhibition by dinitrogen tetroxide is contrary to the effect predicted by Robertson, *et al.*[2] They predicted an increase in the decomposition rate at low nitrate concentrations. The value of S when extrapolated to zero dinitrogen tetroxide concentration is somewhat lower than the value of S obtained from the pure acid. This deviation is almost outside the expected limits of experimental error. There seems to be no simple explanation for this deviation. The lack of dependence of f_0^0 and the very slight dependence of S on the dinitrogen tetroxide concentration further justify the treatment of the rate during a single run as a strong function of only one product—water.

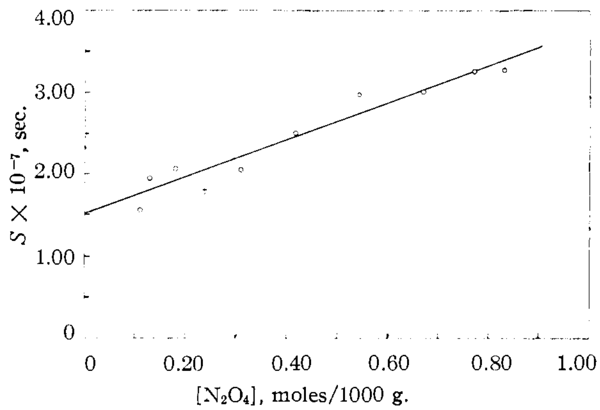

Fig. 3.—Dependence of S on added dinitrogen tetroxide.

KNO_3.—The results obtained from the rate data on the potassium nitrate solutions are nearly identical with the results derived from the dinitrogen tetroxide solutions. The values of f_0^0 are independent of the potassium nitrate concentration and are within experimental error of the values of f_0^0 obtained from the pure acid. The variation of S with potassium nitrate concentration is nearly the same as the variation with dinitrogen tetroxide. The value of S extrapolated to zero potassium nitrate concentration is in agreement with the value of S obtained from the pure acid. The quantitative similarity of the effects of potassium nitrate and dinitrogen tetroxide indicates that the primary effect of either additive is caused by some common unit, probably the nitrate ion. Potassium nitrate would be expected to be highly ionized in nitric acid. If the effect of dinitrogen tetroxide is to be the same as for potassium nitrate, then the former should also be a highly ionized 1-1 electrolyte. This conclusion is in agreement with spectral data obtained by Millen and Watson.[5] Their data indicate that dinitrogen tetroxide in nitric acid is highly ionized to nitrosonium ions and nitrate ions.

NO_2FSO_3.—Eight decompositions were made with solutions of nitronium fluorosulfonate in nitric acid. This additive was chosen because the nitronium ion has been postulated as one of the important species in the decomposition mechanism.[2,3] No trend of f_0^0 with the nitronium fluorosulfonate concentration could be found. Within experimental error, the average value of f_0^0 obtained from these solutions is identical with the value of f_0^0 obtained from the pure acid data.

The reciprocal of the parameter S was found to be a linear function of the nitronium fluorosulfonate concentration. A plot of the data is shown in Fig. 4. The value of S extrapolated to zero nitronium fluorosulfonate concentration is essentially the same as the value of S obtained from the pure acid decompositions.

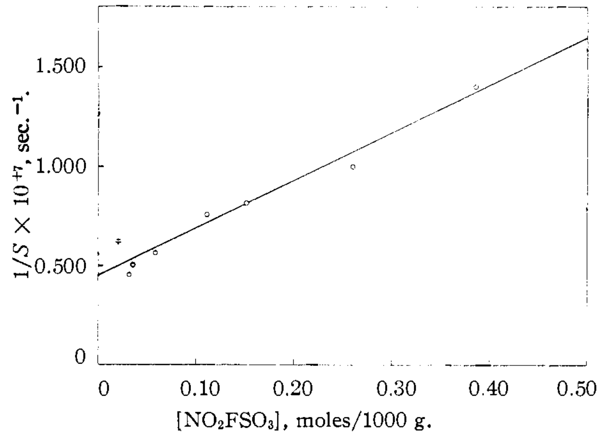

Fig. 4.—Dependence of S on added nitronium fluorosulfonate.

$KFSO_3$.—It was thought that changes in the ionic strength from one solution to another might account for some of the effects observed when the solutions containing additives were decomposed. To test this possibility, a series of decompositions was made on solutions of potassium fluorosulfonate in nitric acid. Potassium fluorosulfonate is a strong electrolyte similar to potassium nitrate, nitronium fluorosulfonate and dinitrogen tetroxide, and any data obtained from potassium fluorosulfonate solutions should indicate the general order of magnitude of the inert salt effect. The values of f_0^0 and S showed no dependence on the concentration of potassium fluorosulfonate. The average values of these parameters are within experimental error of the values for the corresponding parameters obtained from the pure nitric acid. These data indicate that either there are no important reactions taking place between charged species or that the ionic strength of the medium is so high that the

---

(5) D. J. Millen and D. Watson, *J. Chem. Soc.*, 1369 (1957).

addition of up to 0.3 molal of a 1-1 electrolyte has no effect on the activity coefficients of the reacting species.

Other Additives.—Decomposition studies were made on solutions of nitrosonium fluorosulfonate and on solutions of nitronium fluorosulfonate-potassium nitrate mixtures. The rate data were erratic, irreproducible and lacking in any correlation with the concentration of the additives.

Some decompositions were carried out on solutions of potassium perchlorate in nitric acid. The studies were discontinued when it was discovered that chlorine containing gases were being evolved by the solutions during decomposition.

Discussion

Earlier papers have contained discussions of the mechanisms of the decomposition of liquid nitric acid. These mechanisms have involved the species dinitrogen pentoxide as an intermediate.[2,3] Eyring and Daniels[6] and Franck and Schirmer[7] have studied the decomposition of dinitrogen pentoxide in nitric acid and found that this decomposition followed the same rate law as the gas phase reaction but with a much lower empirical first-order rate constant. This lower rate constant can be explained in terms of an ionization of the dinitrogen pentoxide.[8,9]

$$N_2O_5 \rightleftharpoons NO_2^+ + NO_3^- \qquad (1)$$

This ionization is reported to be very nearly complete.[8] Self-ionization of liquid nitric acid has been shown to exist. The evidence comes from conductivity and spectral measurements.[10,11] The ionization can be described in terms of the two equilibria[10]

$$2HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^- \qquad (2)$$

$$H_2NO_3^+ \rightleftharpoons NO_2^+ + H_2O \qquad (3)$$

The equilibria (1, 2, 3) together with the decomposition step

$$N_2O_5 \longrightarrow NO^+ + NO_3^- + {}^1/_2O_2 \qquad (4)$$

constitute a possible mechanism for the decomposition of the acid. Step 4 is presumed to follow the gas phase mechanism.[12,13]

In a previous paper from this Laboratory, the simpler mechanism composed of steps 1, 4 and 5 was proposed.

$$2HNO_3 \rightleftharpoons N_2O_5 + H_2O \qquad (5)$$

Steps 1 and 5 were presumed to remain near equilibrium. From this mechanism and the rate data an estimate of the water of self-dissociaton of nitric acid was obtained. This value was in the neighborhood of 0.15 molal at 65°. If the ionization constants as determined by conductivity data[11] are extrapolated to 65° using a plot of the logarithm of the equilibrium constant against the reciprocal of absolute temperature, a value of 0.15 molal in water is obtained. The calculation of the equilibrium constant assumes that the ionization can be represented by

$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O$$

The following discussion will, however, cast doubt that 0.15 molal is the correct value for the water concentration. The rate expression derived from steps 1, 4 and 5 is

$$\frac{(HNO_3)^2}{\frac{-d(HNO_3)}{dt}} = f = \frac{(H_2O)}{2k_4K_5}$$

In this treatment k_i will be the rate constant for the ith reaction as written and K_i will be the corresponding equilibrium constant. A negative subscript will refer to the reverse of the reaction as written. The concentration of water due to decomposition, or separate addition, was between 0.01 and 0.4 molal. If the equilibrium expression for (5) is examined using the proposed value for the equilibrium concentration of water, assuming that the dinitrogen pentoxide is completely ionized, one is forced to conclude that the true water concentration in the acid will not be a linear function of the formal water concentration in the range of 0.01 to 0.4 molal. Empirically f is found to be a linear function of the latter. Hence, this simple mechanism must be discarded. The observed linearity of f as a function of the formal water suggests that the true water concentration should be a linear function of the formal water concentration, regardless of the mechanism. If a mobile equilibrium involving water exists in nitric acid, a linear dependence between these water concentrations could hold only if the water of dissociation were very much larger or very much smaller than the formal water concentration. If the water of dissociation were much larger than the formal water concentration, then the rate of decomposition would not be expected to be a strong function of the formal water concentration. It does appear possible, in principle, to imagine a mechanism involving a large water of dissociation which would fit the observed rate data. However, it is felt that it is simpler to assume a very small amount of water of dissociation. In order to explain the conductivity data for absolute nitric acid, it is sufficient to consider that steps 2 and 3 constitute the ionization mechanism and that the equilibrium for step 3 lies far enough to the left, so that the water of dissociation is less than 0.01 molal. A steady state treatment of the mechanism composed of steps 1, 2, 3 and 4 leads to the rate expression

$$\frac{(HNO_3)^2}{\frac{-d(HNO_3)}{dt}} = f = \frac{1}{2k_2} + \frac{\{k_{-1} + k_4\}k_{-2}k_3}{2k_1k_2k_3k_4}(H_2O) + \frac{k_{-2}}{2k_2k_3}(NO_3^-)$$

The last term in this expression involves an inhibition by nitrate ion. This term predicts an increase of $f_0{}^0$ with added nitrate ion. This effect is not observed. If it is assumed that this term containing the nitrate dependence is small compared to the other terms, so that it can be neglected,

---

[6] H. Eyring and F. Daniels, This Journal, **52**, 1472 (1930).

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

[8] R. J. Gillespie, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2552 (1950).

[9] J. D. S. Goulden and D. J. Millen, *ibid.*, 2620 (1950).

[10] E. G. Taylor, L. M. Lyne and A. C. Follows, *Can. J. Chem.*, **29**, 439 (1951).

[11] W. H. Lee and D. J. Millen, *J. Chem. Soc.*, 4463 (1956).

[12] R. A. Ogg, Jr., *J. Chem. Phys.*, **15**, 337, 613 (1947).

[13] R. A. Ogg, Jr., *ibid.*, **18**, 572 (1950).

then the resulting rate expression is of the same form as the empirical rate expression for the pure acid decompositions. This rate expression also properly predicts the effect of added water on the rate. The effect of added nitrate on the parameter S is not accounted for by this mechanism.

This mechanism also fails to account for the observed catalysis by the nitronium fluorosulfonate. It was shown above that equilibrium 3 must lie far to the left in order that the water of dissociation be less than 0.01 molal. The steady-state nitronium ion concentration can be no larger than the water of dissociation and all of the additions of nitronium fluorosulfonate would then be much larger than this steady-state value. Under these circumstances the initial oxygen evolution from the nitronium fluorosulfonate solutions should be the result of the nitrate catalyzed decomposition of nitronium ion. This would involve steps 1, 2 and 4. After the large initial rate of oxygen evolution the rate would then be expected to approach the pure acid rate as the nitronium ion was consumed. The observed effect is independent of the amount of oxygen evolved. The excess oxygen evolved by the nitronium fluorosulfonate solutions, as compared to the pure acid, is enough to cause appreciable depletion of the nitronium ion if this were the source of the excess. If the nitronium ion concentration were changing one would not expect the effect to remain constant during a decomposition.

Various reasonable modifications of this mechanism fail to lead to any improvement in the predictions concerning the effects of added nitrate or nitronium ion. In addition it is difficult to see how this ionic mechanism could yield a rate that was independent of the ionic strength as is observed. It may well be that the active intermediate is not dinitrogen pentoxide as has been postulated. The various data concerning the nature of liquid nitric acid may be misleading in that they direct attention to ionic phenomena when the decomposition may be proceeding by a free radical mechanism.

A free radical mechanism which fits the data more satisfactorily than the ionic mechanism can be devised.

$$HNO_3 \rightleftarrows OH + NO_2 \qquad (6)$$

$$OH + HNO_3 \rightleftarrows H_2O + NO_3 \qquad (7)$$

$$NO_3 + NO_2 \longrightarrow NO + NO_2 + O_2 \qquad (8)$$

$$NO + NO_3 \longrightarrow 2NO_2 \qquad (9)$$

$$2NO_2 \rightleftarrows NO^+ + NO_3^- \qquad (10)$$

These steps, with the exception of the last equilibrium and the reverse of step 7, have been proposed to explain the gas phase decomposition of nitric acid[14-16] A steady state treatment for the species OH, NO_3 and NO leads to the expression for f

$$f = \frac{(HNO_3)}{2k_6} + \frac{k_{-7}k_{-6}}{4k_7k_8k_6}(H_2O) + \frac{k_{-6}\{(NO^+)(NO_3^-)\}^{1/2}}{2k_6k_7(K_{10})^{1/2}}$$

As in the case of the ionic mechanism, the term involving the nitrate ion is not of the proper form to account for the observed effect of either potassium nitrate or dinitrogen tetroxide. If this term is small enough to be neglected then the form of the rate expression becomes identical with that derived from the ionic mechanism. In this case, however, the rate would be expected to be independent of the ionic strength. The first term in this expression can be identified with f_0^0. The concentration of nitric acid is a molal concentration and is therefore independent of the temperature. This means that f_0^0 should have the negative of the activation energy for k_6. The value of the activation energy for k_6 obtained from the low pressure gas phase data is 38.3 kcal.[16] This compares very favorably with the value of 38.7 obtained in the present work. The constant k_6 is a unimolecular rate constant and is concentration dependent.[14-16] In order to compare the gas phase pre-exponential factor of k_6 with the present value, the limiting high pressure gas phase data are needed but are not now available. The pre-exponential factor obtained from the present data is $10^{19.33\pm0.58}$ sec.$^{-1}$; this places some doubt on the interpretation of k_6 as a unimolecular rate constant since most unimolecular rate constants have pre-exponential factors nearer to 10^{15} sec.$^{-1}$.

If this free radical mechanism is to fit the observed data, it must be true, as for the ionic mechanism, that the self-ionization of nitric acid produces very little water, otherwise the true water concentration will not be a strong, linear function of the formal water concentration. If it should be that either the conductivity data concerning the ionization of nitric acid or the procedure for extrapolating the data to 65° are in error, then the degree of ionization may be much less than is supposed.[17] If the ionization gives products of less than 0.01 molal concentration and reaction 3 lies far to the right, the observed catalysis by nitronium fluorosulfonate can be explained. Consider the free radical mechanism quoted above plus the following reactions involving nitronium ion

$$NO_2^+ + OH \longrightarrow NO_3 + H^+ \qquad (11)$$

$$H^+ + HNO_3 \longrightarrow H_2NO_3^+ \qquad (12)$$

$$H_2NO_3^+ \longrightarrow NO_2^+ + H_2O \qquad (3)$$

Using a steady-state treatment for OH, NO_3, NO, H^+ and $H_2NO_3^+$, assuming that the concentrations of H^+ and $H_2NO_3^+$ are negligible as compared to the nitronium ion concentration and assuming that no reaction can occur *via* dinitrogen pentoxide, an expression for f can be derived

$$f = \frac{(HNO_3)}{2k_6} + \frac{k_{-7}k_{-6}(H_2O)}{4k_6k_7k_8 + k_6k_8k_{11}}\frac{(NO_2^+)}{(HNO_3)}$$

In deriving this expression, a term involving nitrate ion was neglected as in the case without added nitronium ion. The nitronium ion concentration, by this mechanism, remains constant and for small amounts of decomposition the nitric acid concentration is nearly constant and hence this derived expression is of the same form as the observed expression for f.

---

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

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

(16) H. S. Johnston, L. Foering and J. R. White, THIS JOURNAL, **77**, 4208 (1955).

(17) A somewhat lower value for this dissociation is obtained if the vapor pressure data of L. Lloyd and P. A. H. Wyatt, *J. Chem. Soc.*, 4268 (1957), are extrapolated to 65°.

It has been shown that two simple mechanisms, one ionic and the other free radical, can be devised to explain partially the thermal decomposition of nitric acid. Neither mechanism will explain the observed effect of added nitrates upon the rate. Both mechanisms will explain the rate behavior for the decomposition of the pure acid and of dilute solutions of water in nitric acid. Only the free radical mechanism is consistent with the observed absence of an ionic strength effect. The free radical mechanism can be modified to explain the effect of added nitronium ion. The activation energy for the initial rate of the liquid phase decomposition can be predicted, on the basis of the free radical mechanism, from gas phase kinetic data. This prediction is upheld. Further study concerning the nature and the amounts of the species present in liquid nitric acid is necessary if the kinetic data are to be evaluated more thoroughly.

CHINA LAKE, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR STUDIES, CORNELL UNIVERSITY]

The Activity Coefficients of Strong Electrolytes. The Halide Salts[1]

BY R. M. DIAMOND

RECEIVED MAY 28, 1958

The idea of "localized hydrolysis," suggested by Robinson and Harned to explain the order of the activity coefficients of the alkali metal hydroxides, fluorides, formates and acetates,[2] is extended to the consideration of other alkali and alkaline earth salts and is shown to give a reasonable explanation for certain anomalies in the order of the activity coefficients of the halides, in particular, for the usual order $Cl < Br < I > ClO_4$. The water structure-breaking and structure-tightening properties of ions are also considered to explain and to predict various other features of the orders of the activity coefficients of large relatively unhydrated ions.

There have been numerous attempts to modify or to extend by means of additional terms the Debye–Hückel expression[3] for the mean activity coefficient of a strong electrolyte so as to obtain an expression usable from the very dilute solution range to concentrations above one molal.[2,4–9] These have resulted in qualitative or quantitative expressions for handling the necessary ion–ion and ion-solvent interactions. (With the latter can also be included the changes in the solvent–solvent interactions caused by the presence of the ions.) The former category obviously includes the electrostatic interaction of an ion with its ion atmosphere[3] and also the possibility of association of an ion with oppositely charged neighbors.[4] The latter category involves particularly the hydration of the ions[8,10] but also the effects of hydration on the dielectric constant[5] and structure of the water solution.[11] However, in spite of the considerable progress made (some in a more or less empirical fashion), there are still difficulties in explaining, even qualitatively, the complete behavior of the activity coefficients of such a simple group of salts as the alkali halides. Such a qualitative explanation is the purpose of this paper.

The alkali metal chlorides, bromides and iodides have activity coefficients which, for a particular halide, decrease in the order $Li > Na > K > Rb > Cs$ at any fixed concentration. The coefficient for a particular salt initially decreases, passes through a minimum and then increases (Fig. 1 and Table I). Both of these features usually are ascribed to the effects of hydration of the cations. The (crystallographically) smaller ions are the more highly hydrated, giving the opposite order for the size of the hydrated alkali cations and for their distance of closest approach to the halide ion, $\mathring{a}$. In dilute solution, the observed activity coefficient order for these alkali halides is correctly given by the Debye–Hückel expression using the above mentioned order

TABLE I

ACTIVITY COEFFICIENTS FOR 1.0 m SOLUTIONS[12] AT 25°[13]

	OH	$C_2H_3O_2$	F	Cl	Br	I	ClO_4
H				0.809	0.871	0.963	0.823
Li	0.554	0.689		.774	.803	.910	.887
Na	.678	.757	0.573	.657	.687	.736	.629
K	.756	.783	.645	.604	.617	.645	
Rb		.792		.583	.578	.575	
Cs	.771	.802		.544	.538	.533	
Mg		.307		.570	.723	.892	.946
Ca				.500	.597	.741	.754
Sr				.461	.535	.680	.643
Ba		.325		.395	.469	.649	.512

	Formate	Acetate	Propionate	Butyrate
Na	0.661	0.757	0.808	0.868

$$\ln \gamma_{\pm} = -\frac{A|Z_1Z_2|\sqrt{I}}{1 + B\mathring{a}\sqrt{I}}$$

of $\mathring{a}$ for the alkali ions, that is, by the limitation on how close the oppositely charged ion atmosphere can approach the central ion. But the increasing magnitude of the differences in the values of $\gamma_{\pm}$ for the different alkalies and the occurrence of a minimum and then a rise in the value of the activity coefficient with increasing concentration (the great-

---

(1) This work was supported in part by the U. S. Atomic Energy Commission.

(2) R. A. Robinson and H. S. Harned, *Chem. Revs.*, **28**, 419 (1941).

(3) P. Debye and E. Hückel, *Physik. Z.*, **24**, 185 (1923).

(4) N. Bjerrum, *K. danske vidensk. Selsk.*, **7**, No. 9 (1926); "Selected Papers," Einar Munksgaard, Copenhagen, 1949.

(5) E. Hückel, *Physik. Z.*, **26**, 93 (1925).

(6) G. Scatchard, *Chem. Revs.*, **19**, 309 (1936).

(7) H. S. Frank, THIS JOURNAL, **63**, 1789 (1941).

(8) R. H. Stokes and R. A. Robinson, *ibid.*, **70**, 1870 (1948).

(9) E. Glueckauf, *Trans. Faraday Soc.*, **51**, 1235 (1955).

(10) N. Bjerrum, *Z. anorg. Chem.*, **109**, 275 (1920).

(11) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

(12) It should be noted that for all other concentrations for which data are available, *i.e.*, 0.1 to several molal, see reference 13, the same orders of the activity coefficients hold.

(13) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," appendix 8.10, Butterworths Scientific Publications, London, 1955.