[CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Acid–Base Reactions in Fused Salts. II.[1] The Absolute Concentration of NO_2^+ Ion in Fused Nitrate

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The reactions $S_2O_7^{=} + NO_3^- \rightarrow NO_2^+ + 2SO_4^{=}$ and its subsequent reaction $NO_2^+ + NO_3^- \xrightarrow{\text{slow}} 2NO_2 + O$ were studied kinetically at two temperatures. The equilibrium in the first reaction was found to lie sufficiently far to the right so that its equilibrium constant could be determined. Thus, it was possible to establish a scale of acidity in fused nitrates based on the absolute concentration of NO_2^+.

Introduction

Recently Duke and Iverson[2] studied the rate of decomposition of dichromate in a fused alkali nitrate mixture. They found that the reaction consists of two steps: the equilibrium

$$Cr_2O_7^{=} + NO_3^- \rightleftarrows NO_2^+ + 2CrO_4^{=}$$

followed by the slow step

$$NO_3^- + NO_2^+ \xrightarrow{\text{slow}} \text{decomposition products}$$

They obtained values for the product of the equilibrium constant and the rate constant but were unable to separate the two quantities.

Thus, it was felt that a similar study of a stronger acid such as pyrosulfate might be of interest.

Experimental

Materials and Apparatus.—A.C.S. reagent grade chemicals were used. All the rate determinations were carried out in an apparatus similar to that described previously.[2] A test-tube shaped Pyrex reaction vessel was immersed in a constant temperature bath consisting of a mixture of fused alkali nitrates. The temperature was maintained to within one degree of the required level with a chromel–alumel thermocouple controlling a Celectray controller (Weston Electrical Instrument Company).

The reaction vessel was made from a 32 mm. o.d. Pyrex tubing. A 34/45 standard taper ground glass joint was used at the top and was fitted with a gas inlet tube extending to within $^1/_2$ inch from the bottom of the vessel. An outlet tube extended from the cap.

The flow rate of the sweep gas was measured by means of a gas flowmeter.

Procedure.—All chemicals were dried at 100° before being used. The solubility of Na_2SO_4 in KNO_3–$NaNO_3$ eutectic mixture was determined in a manner to be described. Molten solvent in a large test-tube was saturated with Na_2SO_4 at 25° higher than the required temperature. The solution was stirred by bubbling nitrogen gas for at least one hour. After cooling to the desired temperature and allowing the excess Na_2SO_4 to settle, samples were drawn out with a preheated medicine dropper and analyzed.

The rate of decomposition of pyrosulfate was studied by following the change in acid concentration with time. The eutectic mixture and Na_2SO_4 were fused in the reaction vessel. Solid $S_2O_7^{=}$ then was added to the melt. Stirring was accomplished by using nitrogen as a sweep gas. In every case, 100 g. of eutectic solvent and a nitrogen flow rate of 0.21 liter per minute were used. The samples were drawn with a preheated dropper at periodic intervals and were dissolved in water. The acidity of the solution was analyzed by adding excess KIO_3 and KI and titrating with thiosulfate. The water used in the analysis was boiled and stored under Ascarite.

Results and Discussion

Preliminary studies indicated the reaction proceeded very rapidly at 235°. The addition of sulfate retarded the rate, which indicated that a reversible reaction is involved. As in the case of the dichromate reaction, the rate is dependent on the flow rate of the sweep gas. The order in $S_2O_7^{=}$ was one and was independent of the gas flow rate.

Since the pyrosulfate reaction appears analogous to that of dichromate, one can write the equilibrium

$$S_2O_7^{--} + NO_3^- \rightleftarrows NO_2^+ + 2SO_4^{--}$$

and the slow step

$$NO_3^- + NO_2^+ \longrightarrow 2NO_2 + O$$

The rate law can be written as

$$-\frac{d(T_A)}{dt} = k(NO_2^+) \qquad (1)$$

where T_A is the total acidity as determined from the aqueous titration. Since the sample was analyzed for (H^+), if there is an appreciable amount of NO_2^+ present in the melt, the total acidity at any time would arise from the reactions

$$S_2O_7^{=} + H_2O \longrightarrow 2SO_4^{=} + 2H^+$$

and

$$NO_2^+ + H_2O \longrightarrow NO_3^- + 2H^+$$

Hence

$$T_A = S_2O_7^{=} + NO_2^+ = 2H^+ \qquad (2)$$

The equilibrium constant is

$$K = \frac{[NO_2^+][SO_4^{=}]^2}{[S_2O_7^{=}]} \qquad (3)$$

From equations 2 and 3 one gets

$$-\frac{dT_A}{dt} = \frac{kKT}{K + [SO_4^{=}]^2} = k'T \qquad (4)$$

where the pseudo first-order rate constant is

$$k' = \frac{kK}{K + [SO_4^{=}]^2} \qquad (5)$$

The reciprocal of equation 5 is

$$\frac{1}{k'} = \frac{1}{k} + \frac{[SO_4^{=}]^2}{kK} \qquad (6)$$

If $1/k'$ is plotted against $(SO_4^{--})^2$, the intercept will be $1/k$, the slope $1/kK$ and the intercept divided by the slope will be K. Therefore, if K is large enough, k and K both can be found.

The reaction was studied at 235 and 275°. The pseudo first-order rate constants obtained from log T_A *vs.* time plots are listed in Table I. These constants did not vary with the pyrosulfate ion concentration. The low values for 0.20 *m* SO_4^{--} at 235° and 0.30 *m* SO_4^{--} at 275° probably are due to supersaturation of the melt with SO_4^{--} as the reaction proceeds. Solubility data are listed in Table III.

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[1] Contribution No. 760. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] F. R. Duke and M. L. Iverson, THIS JOURNAL, **80**, 5061 (1958).

TABLE I

VARIATION OF THE PSEUDO-FIRST-ORDER RATE CONSTANT WITH SULFATE ION CONCENTRATION[a]

235°			275°		
$[SO_4^{=}]_m$	$k' \times 10^2$, min.$^{-1}$	n[b]	$[SO_4^{=}]_m$	$k' \times 10^2$	n
0.05	3.7 ± 0.4	2	0.07	8.7 ± 0.4	2
.08	3.2	1	.10	7.7 ± 0	2
.10	2.8 ± .4	3	.15	5.6 ± 3	2
.125	2.2 ± .1	2	.20	4.9 ± 1	2
.15	2.0 ± .1	3	.225	4.2 ± 0	2
.175	1.8 ± .03	2	.25	3.8 ± 4	2
.20	1.5 ± .2	5	.30	3.3 ± 3	2
.21	1.5	1	.34(satd.)	3.5 ± 1	2
.22	1.6	1			
.25(satd.)	1.6 ± 0.1	3			

[a] Initial $S_2O_7^{=}$ concentration 0.01, 0.02, 0.03 *m* at 235°; 0.02 *m* at 275°. Nitrogen flow rate: 0.21 l./min. [b] n = number of runs.

TABLE II

RATE AND EQUILIBRIUM CONSTANT DATA FOR REACTIONS OF PYROSULFATE AND DICHROMATE WITH FUSED NITRATE

k (min.$^{-1}$)	T, °C.	$K_{S_2O_7^=}$	T, °C.	$K_{Cr_2O_7^=}$[a]
0.038	235	0.026	250	8.5×10^{-14}
0.096	275	0.038	300	3.8×10^{-12}
ΔH_a = 13 kcal.		ΔH = 5 kcal.		ΔH = 50 kcal.

[a] From extrapolation of data in ref. 2 and F. R. Duke and M. L. Iverson, *J. Phys. Chem.*, 62, 417 (1958).

TABLE III

SOLUBILITY OF Na_2SO_4 IN $NaNO_3$–KNO_3 EUTECTIC

T, °C.	Solubility (m) $\times 10^2$
235	25 ± 1
250	28.2 ± 0.7
275	34.2 ± .8
300	42.1 ± .5

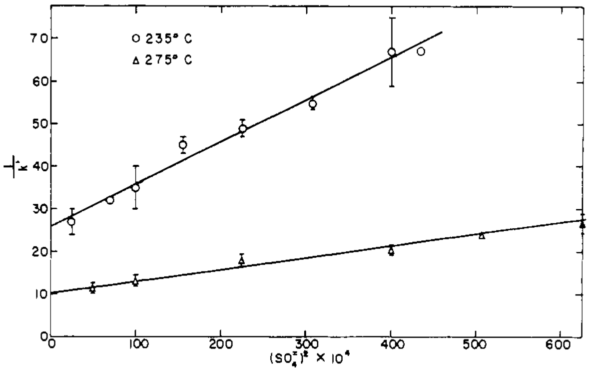

Fig. 1.—Plot of reciprocal rate data *vs.* $[SO_4^-]^2$ to determine *k* and *K*.

The plots of equation 7, $1/k'$ *vs.* the square of the initial sulfate ion concentration, are shown in Fig. 1. It should be noted that the sulfate ion concentration increases during the reaction and, therefore, the values for K obtained from these graphs may be slightly smaller than the true value.

Comparison with the Dichromate–Nitrate Reaction.—Since the dichromate and the pyrosulfate reactions have the same slow step and were studied under similar conditions, the rate constant obtained in this study can be used to calculate the equilibrium constant for the former. The result (see Table II) shows that $Cr_2O_7^{--}$ is a much weaker acid than $S_2O_7^{--}$. The rate of the dichromate reaction was brought into the measurable range by adding heavy metal ions to precipitate the chromate as it is formed. The large over-all apparent activation energy for the dichromate reaction (*ca.* 63 kcal.) is partly compensated by the increase in solubility of these chromate salts with temperature.

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Kinetics of Discharge of Metal Ion Complexes with Preceding Chemical Reaction

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The kinetics of discharge of complexes with preceding formation of an intermediate by a purely chemical reaction are treated for faradaic impedance measurements and the galvanostatic and potentiostatic methods. Contributions from charge transfer and the preceding chemical reaction can be separated from experimental data. Analysis is given (a) for variations of the faradaic resistance (series equivalent circuit) and faradaic capacity with $1/\omega^{1/2}$ ($\omega = 2\pi f$, f = frequency), (b) for potential–time curves, and (c) for current–time curves. The contribution from chemical kinetics vanishes for $1/\omega^{1/2} \rightarrow 0$ or $t = 0$, and the exchange current density can be computed from simple equilibrium considerations. The chemical kinetics component of the faradaic resistance is constant for large values of $1/\omega^{1/2}$ or t.

It is now well established[2] that discharge of certain metal ion complexes is preceded by a purely chemical reaction of the type

$$MY_p^{+(n-pz)} \rightleftarrows MY_\nu^{+(n-\nu z)} + (p-\nu)Y^{-z} \quad (1)$$

the exchange current for direct discharge being so low that reaction 1 followed by discharge of $MY_\nu^{+(n-\nu z)}$ is faster. The intermediate complex composition can be determined from variations of the exchange current with concentration of complexing agent, all other concentrations remaining constant. This method, which is similar to reaction order determination in chemical kinetics, was extended to electrode processes by Vetter[3] and Gerischer.[4] These authors assumed that chemical equilibrium is achieved but this assumption, while

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[1] (a) Research Associate, 1958–1959; on leave from the Government Chemical Industrial Research Institute, Tokyo. (b) Predoctoral fellow, 1957–1959.

[2] For a review see, for instance, P. Delahay, *Ann. Rev. Phys. Chem.*, **8**, 229 (1957)

[3] (a) For a review see K. J. Vetter, *Z. Elektrochem.*, **59**, 596 (1955). (b) Also K. J. Vetter, "Transactions of Symposium on Electrode Processes," Philadelphia, May 1959, in course of publication.

[4] (a) For instance, H. Gerischer, *Z. Elektrochem.*, **57**, 604 (1953). (b) For a review see H. Gerischer, *Anal. Chem.*, **31**, 33–39 (1959).