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Acid-Base Reactions in Fused Salts. The Dichromate-Bromate Reaction¹

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Abstract

The reaction of a Lewis acid and base, $\text{Cr}_2\text{O}_7^{=}$ and BrO_3^- , in fused KNO_3 - NaNO_3 mixtures has been shown to involve an equilibrium followed by a slow decomposition to gaseous products. The probable mechanism is:

Analysis of the gaseous products shows no oxides of nitrogen. The acidity of BrO_2^+ is much less than that of NO_2^+ , such that no significant amount of NO_2^+ is formed with the bromate present. Also, solubility measurements of BaCrO_4 were carried out in KNO_3 - NaNO_3 mixtures to compute equilibrium constants.

Introduction

Some equilibrium studies of Lewis acids and bases in fused alkali nitrates have been made in which $\text{Cr}_2\text{O}_7^{=}$ was used as an acid, and others in which BrO_3^- was used as a base. In the first case, $\text{Cr}_2\text{O}_7^{=}$ was allowed to react with nitrate to form NO_2^+ .² In the second case, a heavy metal ion was added with BrO_3^- and the decomposition of the metal-bromate

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complex was studied.³ When a divalent metal ion reacts with bromate, the metal-bromate complex, $MBrO_3^+$, is formed and slowly decomposed. This was postulated on the basis that the rate of decomposition varied with metal ion used. However, if one uses $Cr_2O_7^{2-}$ as an acid, no complex is formed, and BrO_2^+ is the probable equilibrium product with bromate present. Thus, a direct comparison of the relative stabilities of BrO_2^+ to NO_2^+ in fused KNO_3 - $NaNO_3$ could be made provided no oxides of nitrogen are formed during the course of the $Cr_2O_7^{2-} + BrO_3^-$ reaction. This turned out to be the case.

Experimental

Materials and Apparatus. - A. C. S. reagent grade chemicals were used. All determinations were performed using a system similar to that described by Duke and Lawrence.³

Procedure. - $K_2Cr_2O_7$ was added to a solution of $Ba(NO_3)_2$ and $NaBrO_3$ in fused KNO_3 - $NaNO_3$ solvent. The rate of reaction was studied by collecting evolved bromine in a sulfite solution and titrating with standard $AgNO_3$ using eosin as an indicator. The reaction was allowed to go to near completion. The rate of appearance of bromine was determined, and from this the rate of disappearance of total bromate (i. e. $T_{Br} = BrO_3^- + BrO_2^+$) may be calculated. The concentrations of dichromate and barium were always in excess of bromate; however, barium ion concentration was varied from run to run to enable separation of the equilibrium constant and rate constant. In all cases concentrations are expressed in molality units.

Results and Discussion

Preliminary runs allowed selection of proper temperature and concentrations for convenient study. The Ba^{++} , because it precipitates

the chromate ion but not the dichromate ion, controls the concentration of chromate through the solubility product. The experimental data gave a first order plot in disappearance of total bromate, indicating decomposition of bromyl ion by some first order mechanism to bromine and oxygen. Varying the rate of the sweep gas, nitrogen, had no effect on the rate of the reaction; therefore, there appears to be no gaseous intermediate as found in the nitrate reaction.²

Upon substituting $[\text{BrO}_3^-] = T_{\text{Br}} - [\text{BrO}_2^+]$ into the equilibrium expression and replacing BrO_2^+ in $-\frac{dT_{\text{Br}}}{dt} = k[\text{BrO}_2^+]$ one obtains an expression:

$$-\frac{dT_{\text{Br}}}{dt} = \frac{kK[\text{Cr}_2\text{O}_7^{=}]}{K[\text{Cr}_2\text{O}_7^{=}] + [\text{CrO}_4^{=}]^2} T_{\text{Br}}.$$

Using the solubility product for BaCrO_4 , K_{sp} , one obtains:

$$-\frac{dT_{\text{Br}}}{dt} = \frac{kK[\text{Cr}_2\text{O}_7^{=}] [\text{Ba}^{++}]^2}{K[\text{Cr}_2\text{O}_7^{=}] [\text{Ba}^{++}]^2 + K_{\text{sp}}^2} T_{\text{Br}}.$$

Since $[\text{Cr}_2\text{O}_7^{=}]$ and $[\text{Ba}^{++}]$ are in excess, $k' = \frac{kK[\text{Cr}_2\text{O}_7^{=}] [\text{Ba}^{++}]^2}{K[\text{Cr}_2\text{O}_7^{=}] [\text{Ba}^{++}]^2 + K_{\text{sp}}^2}$,

the pseudo rate constant, remains constant for a given run.

The reciprocal of k' is: $1/k' = 1/k + \frac{K_{\text{sp}}^2}{kK[\text{Cr}_2\text{O}_7^{=}]} \cdot \frac{1}{[\text{Ba}^{++}]^2}$.

A plot of $1/k'$ vs $1/[\text{Ba}^{++}]^2$ gives a straight line from which k and K are evaluated.

The reaction was studied at 230, 250 and 260°C. The pseudo first order rate constants obtained from $\ln T_{\text{Br}}$ vs time plots are listed in Table I. Solubility data of BaCrO_4 in NaNO_3 - KNO_3 solvent are listed in

TABLE I

T, °C	1/k' (min.)	[Ba ⁺⁺]
230	7.6	0.0020
	10.5	0.0100
	50.8	0.0025
250	5.13	0.0070
	6.65	0.0050
	12.70	0.0030
	22.95	0.0020
	17.18	0.0025
260	3.87	0.0100
	2.17	0.0100
	15.63	0.0020
	8.50	0.0050
	4.17	0.0050

TABLE II

T, °K	Sol'y. (m.)
532	2.0×10^{-3}
522	1.8×10^{-3}
512	1.6×10^{-3}

Table II. The solubility appeared to be independent of the relative amounts of potassium ion and sodium ion present but varied with temperature to give a straight line when the log of the solubility was plotted against reciprocal temperature. Table III lists the temperature dependence of the equilibrium constant and the rate constant to give the heat of reaction as

TABLE III

T, °K	k min. ⁻¹	K mole ⁻¹
503	0.13	1.05×10^{-8}
523	0.33	3.50×10^{-8}
533	0.58	4.80×10^{-8}

65 kcal. and activation energy as 55 kcal. respectively. Also both constants varied with cation ratio of the solvent. The values obtained for variation in solvent are listed in Table IV.

TABLE IV

at 250°C

Cation Ratio (K/Na)	k	K
60/40	0.30 min. ⁻¹	3.2×10^{-8}
50/50	0.33	3.5×10^{-8}
38/62	0.38	4.8×10^{-8}

References

- (1) Contribution No. 1279. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.
- (2) F. R. Duke and M. Iverson, J. Phys. Chem., 62, 417 (1958).
- (3) F. R. Duke and W. W. Lawrence, J. Am. Chem. Soc., 83, 1296 (1959).

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