into two bands. However, since this is the only deviation from the selection rules which was observed, it is not possible to assign a lower symmetry, such as C_{2v}, to the nitrate ion in these solutions, although a recent Raman investigation[21] of fused silver nitrate, in which very precise intensity measurements were made, has shown that NO_3^- ions of both symmetries (D_{3h} and C_{2v}) may be present. Frequently the extent of this splitting has been used as a criterion for the magnitude of cation–anion interactions in nitrates.[10,14] The results in Table II indicate that such interactions are present in these solutions and, since the splitting of ν_3 increases with concentration, these interactions occur to a greater extent at higher concentrations.

Acknowledgments. We thank Dr. F. C. Nachod for use of the n.m.r. facility at Sterling Winthrop Research Institute, and for helpful discussions relative to interpretations of these results. This work was made possible, in large part, by financial support received from the U. S. Atomic Energy Commission, Division of Chemistry, Washington, D. C.

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[21] G. E. Walrafen and D. Irish, *J. Chem. Phys.*, **40**, 911 (1964).

Acid-Base Reactions in Fused Salts. The Dichromate–Chlorate Reaction

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(Received July 17, 1964)

Dichromate ion reacts with chlorate ion in fused $NaNO_3$–KNO_3 mixtures to form chlorine and oxygen. Chloride is found to catalyze the reaction. The postulated mechanism includes

$$Cr_2O_7^{2-} + ClO_3^- \overset{K}{\rightleftharpoons} ClO_2^+ + 2CrO_4^{2-} \text{ (rapid equilibrium)}$$

$$ClO_2^+ + Cl^- \xrightarrow{k} Cl_2 + O_2 \text{ (slow step)}$$

Chloride was added in excess so that its concentration would remain essentially constant during the course of the reaction. Barium ion, also in excess, was added to make the reaction proceed at a measurable rate and to control the concentration of the chromate ion. Temperature and solvent effects were also determined.

Introduction

Equilibrium studies of Lewis acids and bases in fused alkali nitrates have been made in which $Cr_2O_7^{2-}$ was the acid and either NO_3^- or BrO_3^- was the base.[1,2] It is of interest to see whether or not the other halates, ClO_3^- and IO_3^-, behave as Lewis bases in a manner similar to BrO_3^-. Bromate reacts with dichromate to form an intermediate which decomposes at a low rate

$$Cr_2O_7^{2-} + BrO_3^- \overset{K}{\rightleftharpoons} BrO_2^+ + 2CrO_4^{2-}$$

$$BrO_2^+ \xrightarrow{k} \text{products}$$

By evaluating the equilibrium constant, K, for each of the halates, the relative acidities of ClO_2^+ and IO_2^+ to BrO_2^+ in fused nitrates could be measured. No oxides of nitrogen were formed, indicating that ClO_3^-

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[1] F. R. Duke and M. Iverson, *J. Am. Chem. Soc.*, **80**, 5061 (1958).

[2] F. R. Duke and J. Schlegel, *J. Phys. Chem.*, **67**, 3487 (1963).

is a sufficiently strong base that the nitrate reaction could be neglected.

Experimental Section

Materials and Apparatus. ACS reagent grade chemicals were used. All determinations were performed using a system similar to that described by Duke and Lawrence.[3]

Procedure. A solution of Ba^{2+} and ClO_3^- in fused $NaNO_3$-KNO_3 was purged with nitrogen for 1 hr. to allow the solution to reach the temperature of the bath and to sweep out any adsorbed water. The solution was kept at a temperature of 260° for several days and periodically checked for possible decomposition of chlorate. Analysis for the appearance of chloride and disappearance of chlorate showed that no decomposition had occurred. Dichromate was added to start the reaction.

The rate of the reaction was studied by collecting evolved chlorine in basic solution. The solution was then acidified, KI was added, and the liberated iodine was titrated with standard thiosulfate solution. The reaction was allowed to go to near completion. In all cases 1 mole of dichromate produced 1 mole of chlorine. The rate of appearance of chlorine was determined, and from this the rate of disappearance of total acid was calculated. The chlorate and barium ions were always in excess; however, their concentrations were varied from run to run to allow separation of the equilibrium constant from the rate constant. Separate runs were made to determine the amount of oxygen evolution. The evolved gases were passed through Ascarite and collected in a gas buret. Chromatographic analysis showed oxygen to be the only gas present in the gas buret along with some nitrogen which was used to purge the system before the reaction.

Results and Discussion

The reaction proceeds at a measurable rate when all of the reactants are in excess of dichromate. The products of the reaction are chlorine, oxygen, and chromate. Barium ion was added to control the concentration of chromate through the solubility product of barium chromate. In all runs, 1 mole of chlorine was recovered for every mole of dichromate consumed. Therefore, the rate of disappearance of total acid, $T_A = [Cr_2O_7^{2-}] + [ClO_2^+]$, may be calculated by following the rate of appearance of chlorine.

A long induction period in the absence of added Cl^- indicates a complex mechanism under these conditions. The addition of sodium chloride before the reaction caused the induction period to disappear. The order in chloride was determined by plotting the logarithm of the pseudo rate constant *vs.* the logarithm of total chloride. The order was found to be 1 in chloride ion, which indicates the rate-determining step to be $ClO_2^+ + Cl^- \rightarrow Cl_2 + O_2$. At an initial chloride ion concentration of 0.30 *m*, chloride produced in the reaction becomes negligible, and the volume ratio of Cl_2 to O_2 is 1 to 1. This concentration is used in all subsequent runs to determine the equilibrium and rate constants.

At high chloride ion concentrations, the reactions involved are

$$Cr_2O_7^{2-} + ClO_3^- \overset{K}{\rightleftharpoons} ClO_2^+ + 2CrO_4^{2-} \quad \text{(fast equilibrium)}$$

$$ClO_2^+ + Cl^- \xrightarrow{k} Cl_2 + O_2 \text{ (slow step)}$$

The rate law can be written $-dT_A/dt = k[ClO_2^+] \times [Cl^-]$, where $T_A = [Cr_2O_7^{2-}] + [ClO_2^+]$. Substitute $[Cr_2O_7^{2-}] = T_A - [ClO_2^+]$ and $[CrO_4^{2-}] = K_{sp}/[Ba^{2+}]$ into the equilibrium expression to obtain

$$[ClO_2^+] = \frac{K[ClO_3^-][Ba^{2+}]^2}{K[ClO_3^-][Ba^{2+}]^2 + K_{sp}^2}$$

The rate expression will then be

$$-dT_A/dt = \frac{kK[ClO_3^-][Cl^-][Ba^{2+}]^2}{K[ClO_3^-][Ba^{2+}]^2 + K_{sp}^2}T_A$$

This equation reduces to a pseudo-first-order rate equation when the concentrations of the ions are high with respect to dichromate, $-dT_A/dt = k'T_A$. The reciprocal of the pseudo rate constant is

$$1/k' = \frac{1}{k[Cl^-]} + \frac{K_{sp}^2}{kK[ClO_3^-][Cl^-][Ba^{2+}]^2}$$

The equilibrium constant and the rate constant were separated by plotting $1/k'$ *vs.* $1/[Ba^{2+}]^2$ (Figure 1). The rate constant was obtained from the ordinate intercept, $1/k[Cl^-]$, in which the chloride ion concentration was always 0.30 *m*. Note that the abscissa intercept is equal to $-K[ClO_3^-]/K_{sp}^2$. The solubility of barium chromate in fused nitrates and its temperature dependence have been determined.[2] The concentration of chlorate was 0.94 *m* in all cases. Making the appropriate substitutions, the equilibrium constant can be obtained. Table I lists the values of the equilibrium constants and rate constants at several temperatures.

Lux suggested that for oxide systems an acid may be defined as any material which gains oxide ions.[4] Flood[5]

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[3] F. R. Duke and W. Lawrence, *J. Am. Chem. Soc.*, 83, 1269 (1961).

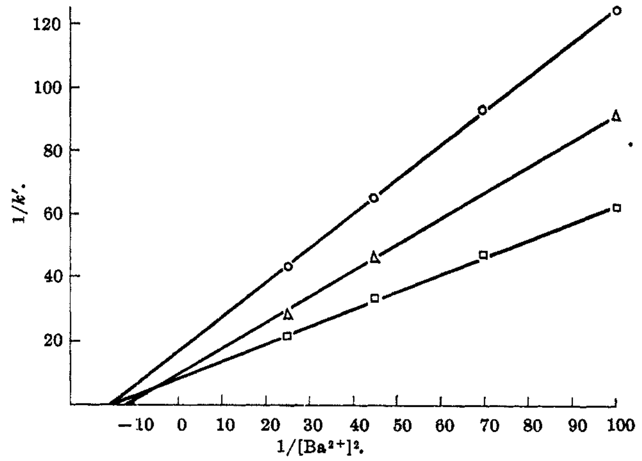

Figure 1. Variation of $1/k'$ as a function of $1/[Ba^{2+}]^2$ at 250° (○), 260° (△), and 270° (□).

Table I: Equilibrium Constants and Rate Constants for the $Cr_2O_7^{2-}$–ClO_3^- Reaction at Several Temperatures

T, °C.	k, M^{-1} min.$^{-1}$	$K \times 10^{10}$, M
250	0.208	1.64
260	0.333	2.46
270	0.417	3.31

extended the Lux concept and pointed out that in such systems acid strengths may be compared by comparing the magnitude of equilibrium constants defined as $K = a_{acid}a_{O^{2-}}/a_{base}$. Therefore, the equilibrium constants obtained from the dichromate–halate reactions determine the relative strength of the acids, BrO_2^+, ClO_2^+, and IO_2^+, in fused alkali nitrates. Table II lists the equilibrium constants at 250° for three acid–base reactions. The strengths of the acids increase in the order BrO_2^+, ClO_2^+, NO_2^+. Although the equilibrium constant for the dichromate–nitrate reaction was determined indirectly,[6,7] its value is included as a comparison.

If no anomalies exist, one would expect the iodyl ion, IO_2^+, to be the weakest acid. Preliminary studies of the dichromate–iodate reaction indicate that iodate is not as reactive as the other halates. This observation does not mean that the equilibrium constant for this reaction is smaller than for the other halates, making iodyl ion the strongest acid. The iodyl ion may be more stable. Experiments are now in progress to establish the relative acidity of IO_2^+.

Table II: Equilibrium Constants for Three Acid–Base Reactions

Reaction	K, M^{-1}
$Cr_2O_7^{2-}$–BrO_3^-	3.5×10^{-8}
$Cr_2O_7^{2-}$–ClO_3^-	1.6×10^{-10}
$Cr_2O_7^{2-}$–NO_3^-	8.5×10^{-14}

Acknowledgment. The author is grateful to the Research Council of Rutgers, The State University, for support of this work.

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(5) H. Flood and T. Forlund, *Acta Chem. Scand.*, **1**, 592 (1947).

(6) F. R. Duke and M. Iverson, *J. Phys. Chem.*, **62**, 417 (1958).

(7) F. R. Duke and S. Yamamoto, *J. Am. Chem. Soc.*, **81**, 6378 (1959).