The Decomposition of Chlorate in a Dichromate Solution of Fused Nitrates

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The reaction of dichromate with chlorate in fused alkali nitrates has been previously studied at high chloride and chlorate ion concentrations,¹ the over-all reaction being

$$Cr_2O_7^{2-} + ClO_3^{-} + Cl^{-} = Cl_2 + O_2 + 2CrO_4^{2-}$$
 (1)

Barium ion was added to control the concentration of the chromate ion and to drive the equilibrium to the right so that the reaction proceeds at a measurable rate. The postulated mechanism for this reaction includes

$$\operatorname{Cr}_{2}O_{7}^{2-} + \operatorname{ClO}_{3}^{-} \xrightarrow{K}$$

 $\operatorname{ClO}_{2}^{+} + 2\operatorname{CrO}_{4}^{2-} \mathrm{m} \text{ (rapid equilibrium)} \quad (2)$

$$\operatorname{ClO}_2^+ + \operatorname{Cl}^- \xrightarrow{k} \operatorname{Cl}_2^+ + \operatorname{O}_2^-$$
(3)

and the rate law is

$$-\frac{\mathrm{d}T_{\mathrm{A}}}{\mathrm{d}t} = \frac{kK[\mathrm{ClO}_{3}^{-}][\mathrm{Cl}^{-}][\mathrm{Ba}^{2+}]^{2}}{K[\mathrm{ClO}_{3}^{-}][\mathrm{Ba}^{2+}]^{2} + K_{\mathrm{sp}^{2}}} T_{\mathrm{A}} = k'T_{\mathrm{A}} \quad (4)$$

where T_A is total acidity, $[Cr_2O_7^{2-}] + [ClO_2^+]$, K_{sp} is the solubility product of BaCrO₄ in fused KNO₃-NaNO₃, and k' is the pseudo-first-order rate constant.

Additional information about the mechanism of reaction 1 has now been obtained by studying this reaction at low initial chloride ion concentration. According to reaction 3 of the previously postulated mechanism, one would expect the chloride ion concentration to decrease during the reaction. However, it is now found that the chlorine produced acts as a catalyst for the decomposition of ClO_3^- to Cl^- and O_2 , thus increasing the amount of Cl^- .

Experimental Section

The apparatus, material, and general procedure were essentially the same as previously described.¹ The initial addition of chloride was varied from run to run and after the reaction was complete, chloride was determined in the melt. An aliquot portion of the melt was taken to determine the concentration of ClO_3^- . Bromide in the presence of 7.5 N hydrochloric acid was used to reduce the chlorate. The bromine obtained was determined iodometrically. If the oxygen volume was desired, a duplicate run was performed and the oxygen released by the reaction was collected in a gas buret.

A solution of approximately 1 m ClO_3^- and 0.3 m Ba²⁺ in 100 g of fused KNO₃-NaNO₃ was purged with nitrogen for several hours at 260°. To check for possible decomposition of ClO₃⁻, this solution was kept at 260° for several days and periodically checked for ClO₃⁻, ClO₄⁻, Cl⁻, and gaseous products such as oxides of nitrogen and chlorine. Recovery of all of the ClO_3 ⁻ and the absence of Cl^- , ClO_4^- , and gaseous products confirmed the stability of the solution. Dichromate (0.5 mmole) was added to start the reaction. In all runs, 1 mole of chlorine was recovered for every mole of dichromate consumed. Therefore, the rate of disappearance of total acid, $T_{\rm A} = [\operatorname{Cr}_2 \operatorname{O}_7^{2-}] + [\operatorname{ClO}_2^+]$, can be calculated by following the rate of appearance of chlorine. The method of determining the rate constants has been described and their values have been tabulated.¹

Results and Discussion

The data in Figure 1 show that even when chloride ion was not deliberately added, the reaction followed pseudo-first-order kinetics after an induction period. The length of this induction period was found to be in-



Figure 1. First-order plot of the disappearance of total acid at different initial chloride concentrations: O, 0.00 m; Δ , 0.02 m; \Box , 0.04 m; \bullet , 0.08 m.

(1) J. M. Schlegel, J. Phys. Chem., 69, 3638 (1965).

versely dependent on the initial concentration of chloride ion in the melt, becoming negligibly small at a chloride ion concentration of $0.20 \ m$. In all cases, analysis of the melt showed a significant increase in the concentration of chloride ion during the reaction. This observation indicates the presence of a reaction path which produces chloride ion in efficient competition with reaction 3 which consumes chloride ion. This increase in chloride ion concentration shall be referred to as additional chloride.

The additional chloride can only come from chlorate. If chlorate is decomposing to chloride and oxygen

$$\text{ClO}_3^- \longrightarrow \text{Cl}^- + \frac{3}{2}\text{O}_2$$
 (5)

then the ratio of chlorine gas to oxygen gas is not 1:1 as indicated by reaction 3. The amount of evolved oxygen was measured and found to vary depending upon the half-life of the reaction. The same dependence was found to hold true for additional chloride ion. Table I shows the relationship between oxygen evolution and additional chloride. As predicted by eq 5, 1.5 moles of oxygen are evolved for every mole of chloride formed, after correcting for the chloride consumed and oxygen produced by reaction 3. It can be argued that Cl^- catalyzes the decomposition of $ClO_3^$ to Cl^- and O_2 . A similar behavior has been reported by Duke and Shute.² They observed that the decomposition of BrO_3^- to Br^- and O_2 is catalyzed by Br^- at 350°. Solutions of ClO_3^- and Cl^- in fused alkali nitrates at 260° are stable for several days; therefore reaction 5 must involve a catalyst other than C1-.

Table I:	Relationship	between	Chloride	Ion	and
Oxygen Pr	roduced at 26	0°°			

Addl Cl ⁻ , mmoles	Cor addl Cl-, mmoles	O2, mmoles	Cor O2, mmoles	Ratio O2/Cl-
2.93	3.18	5.00	4.75	1.49
2.03	2.28	3.64	3.39	1.49
2.00	2.25	3.24	2.99	1.33
1.60	1.85	3.07	2.82	1.52

 a Each run represents 0.25 mmole of $K_2 Cr_2 O_7$ and 20 mmoles of Ba[NO_3]_2 in 100 g of solvent.

A catalyst for the decomposition of chlorate was found to be Cl_2 . Chlorine is slightly soluble in fused alkali nitrates, imparting a pale green color to the solvent. In the presence of Cl_2 , ClO_3^- was found to undergo decomposition according to eq 5. The decomposition could be stopped by carefully sweeping out all the dissolved chlorine. The solution thus obtained was again indefinitely stable toward decomposition.

Mechanistically the chlorine-catalyzed decomposition of chlorate can proceed by the sequence of reactions

$$Cl_2 + ClO_3^- \longrightarrow Cl_2O_3 + Cl^- \tag{6}$$

$$Cl_2O_3 \longrightarrow Cl_2 + \frac{3}{2}O_2$$
 (7)

Although Cl_2O_3 has not been prepared and isolated, it may exist as an intermediate. Attempts were made to isolate such an intermediate by sweeping the gaseous products out of the melt and allowing them to condense in a Dry Ice-acetone trap. No oxides of chlorine were found. Once the molecule Cl_2O_3 is formed, it decomposes to Cl_2 and O_2 .

In summary, the decomposition of ClO_3^{-1} in the presence of $\text{Cr}_2\text{O}_7^{2-}$ can proceed by two reaction paths. A trace of chloride present as an impurity is enough to start the reaction. At very low chloride ion concentrations, only the reactions shown by eq 6 and 7 which produce chloride ion are important; but as the chloride ion concentration increases, the equilibrium concentration of the postulated intermediate, Cl_2O_3 , is repressed while the rate of the competitive reaction 3 is enhanced. At high chloride ion concentration, only the reaction sequence given by eq 2 and 3 contributes significantly to the observed decomposition and can be expressed by the pseudo-first-order reaction, eq 4.

(2) F. R. Duke and E. A. Shute, J. Phys. Chem., 66, 2114 (1962).

Anisotropy in Physical Adsorption on Graphite

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This note examines the possibility that the strong anisotropy of graphite may be responsible for two distinct arrays of sites for physical adsorption. Dispersion attraction depends on the polarizabilities of the interacting species. Since that of graphite is high *parallel* to basal plane and virtually zero *perpendicular* to it,² we expect that an approaching adatom will be subjected to considerably different electronic environments depending upon the direction of its approach to

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⁽²⁾ E. R. Lippincott and J. M. Stutman, J. Phys. Chem., 68, 2926 (1964).