In the case of synergism with TBP, where the magnitude of the synergistic constant was independent of the element involved, it was reasoned that the TBP must be bound to the TTA and not to the metal.[8] Consequently, we might have predicted that the synergistic constants for thorium and americium should be equal. There is, however, a basic difference in the case of TBP, where only thorium forms a species containing one TBP per ThT_4 and all other elements investigated form species containing two molecules of synergist.[9] Although it might be possible for an additional molecule of amine, in the form of R_3NHCl, to be attached to a TTA molecule on each of the americium products of synergism, the extent of this reaction must be very small.

We feel that the argument in the case of TBP should now be modified to the extent that one of the molecules is bound to the TTA and the second bound to the metal. In a benzene system the TBP is bound to TTA with a formation constant of $10^{4.7}$ and to the element with a constant of $\sim 10^{1.9}$ (derived from the values of $10^{6.6} \times 10^{-4.7}$ in Table 1, ref. 8).

It is now reasonable that thorium, the only element which was coordinately saturated by the TTA, should be the only element which does not show evidence for the formation of a species containing two molecules of TBP. Synergism in the case of TBP is therefore governed mainly by a reaction involving binding with a TTA which is attached to a metal, whereas in the amine system the synergism is governed mainly by a reaction involving binding directly with the element which has TTA attached. It is now also reasonable that differences between elements could not be observed in the case of TBP, since the contribution from that part of the reaction is very small. This modifies the previous conclusion which implied that differences between elements could not be observed because both molecules of TBP were bound to molecules of TTA. In the amine system where synergism arises mainly from reactions involving binding with the element, it would be most interesting in future works to explore whether differences between elements can be detected.

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The Kinetics of Formation of Blue Peroxychromic Acid in Aqueous Solution[1a]

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The formation of blue peroxychromic acid, $CrO_5(aq)$, has been investigated spectrally by the stopped-flow technique. Over a limited range of reactant concentrations, $d[CrO_5(aq)]/dt = k[H^+][H_2O_2][HCrO_4^-]$, $k = 10^{7.6 \pm 0.2} \exp(-4500 \pm 200/RT)$, and at 25°, $k = 2.0 \times 10^4\ M^{-2}\ sec^{-1}$. Two possible mechanisms are suggested, both involving protonation preequilibria.

Introduction

Blue peroxychromic acid is formed when hydrogen peroxide is added to acidified solutions of dichromate. The formula is now well established as CrO_5[2,3] although in aqueous solution it might better be regarded as $CrO_5 \cdot H_2O$.[4] The predominant equilibrium in dilute aqueous solution is

$$HCrO_4^- + 2H_2O_2 + H^+ \rightleftharpoons CrO_5 + 3H_2O \qquad (1)$$

with an equilibrium constant of 5.4×10^7 at 10° and ionic strength 0.09.[3] The blue species decomposes readily and in a complex manner to chromium(III) species.[5,6] It may be stabilized, however, by extraction into a variety of complexing organic solvents such as ether or ethyl acetate[7] or by conversion to solid complexes of nitrogen bases, *e.g.*, pyridine ($CrO_5 \cdot py$)[8] and phenanthroline ($CrO_5 \cdot phen$).[3]

Although the formation of blue peroxychromic acid in aqueous solution has been variously described as "virtually instantaneous,"[3] "immediate,"[6] and "very rapid,"[9] in fact, Chance[10] in 1940 showed its formation to be in the flow range of study while testing his stopped-flow apparatus with spectral monitoring. He found a second-order rate constant of $1.9 \times 10^3\ M^{-1}\ sec^{-1}$ in 0.005 M H_2SO_4 at 18°.

We have examined the formation of $CrO_5(aq)$ in detail, and the over-all order of the reaction (not established by Chance) and the Arrhenius parameters have been obtained.

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Experimental Section

Materials.—Analar potassium dichromate and 100 volume hydrogen peroxide were used. The latter (3 ml) was diluted (250 ml) to give an approximately 0.1 *M* solution. This stock solution was standardized immediately before use with BDH standard ceric sulfate.

Kinetic Runs.—The Gibson stopped-flow apparatus was that used in previous studies.[11] In most cases the formation of CrO_5(aq) was followed at 580 mμ where the blue species absorbs (ϵ_m 450)[3,7] and the oxy anions of chromium(VI) have negligible absorption.[12] Some runs were at 375 mμ where the loss of chromium(VI) was followed. The optical density changes observed at various wavelengths in the stopped-flow apparatus corresponded very well with those expected from the published spectra. The kinetic runs were carried out with pseudo-first-order conditions, nitric acid and hydrogen peroxide being in large excess over chromium(VI). Complete formation of CrO_5(aq) was expected and spectrally observed with the conditions used (eq 1). The subsequent decomposition of peroxychromic acid was usually slow enough not to interfere with the formation measurements although at higher acidities the decomposition rate was enhanced and "infinity" readings had to be taken immediately as the formation was complete. Attempts to measure the rate of formation of CrO_5 in high acidities (up to 2 *M* H^+) were thwarted by its rapid decomposition.

The formation of peroxychromic acid measured at 580 mμ gave good first-order rate plots. The corresponding experiments at 375 mμ gave small initial curvatures and then straight line plots for about three half-lives with rate constants in good agreement with the values from the 580-mμ data. The curvature was less pronounced with runs at lower initial chromium(VI) concentrations, and this suggested that it might arise from a small amount of $Cr_2O_7^{2-}$ in the solutions. At least 90% of the chromium is present as $HCrO_4^-$ in the kinetic runs. All experiments were carried out at an ionic strength of 0.1 *M* adjusted with potassium nitrate. The results are collected in Table I; k_{obsd} is the pseudo-first-order constant, and *k* is the calculated third-order rate constant given by $d[CrO_5]/dt = k[H^+][H_2O_2]\cdot[HCrO_4^-]$. The $[H^+]$ and $[H_2O_2]$ were varied by a factor of 5 and the [Cr(VI)] was varied by a factor of 2.5 with no significant change in the values of *k*.

TABLE I

KINETIC DATA FOR BLUE PEROXYCHROMIC ACID FORMATION ($I = 0.1\ M$)

Temp, °C	$[H^+]$,[a] m*M*	$[H_2O_2]$,[a] m*M*	k_{obsd},[b] sec^{-1}	*k*, $M^{-2}\ sec^{-1}$
25.0	9.8	9.5	1.8	1.9×10^4
25.0[c]	9.9	9.8	1.8	1.9×10^4
25.0	9.8	29.5	5.9	2.0×10^4
25.0	9.8	49.5	9.5	2.0×10^4
25.0	29.8	9.5	5.1	1.8×10^4
25.0	49.8	9.5	9.6	2.0×10^4
12.7	29.8	9.5	4.0	1.4×10^4
0.8	29.8	9.5	2.9	1.0×10^4

[a] Average of maximum and final concentrations, allowing for very small reactant consumption during reaction. [b] Mean value for three or four runs with each condition. [c] [Cr(VI)] = 0.2 m*M* run at 375 mμ. All other runs [Cr(VI)] = 0.5 m*M* at λ 580 mμ.

Results and Discussion

We were able to examine the formation of blue peroxychromic acid in only a limited range of concentrations of reactants. These limits were governed by (a) the equilibrium constant of reaction 1, (b) the rapid decomposition of CrO_5(aq) in higher acidities, and (c) the formation of violet and other peroxy compounds at a pH much above 2.[13] With the conditions used, the reaction was beautifully third order over-all, first order in $[H^+]$, $[H_2O_2]$, and $[HCrO_4^-]$. The third-order rate constant obeyed the Arrhenius expression, $k = 10^{7.6\pm0.2} \exp(-4500 \pm 200/RT)\ M^{-2}\ sec^{-1}$, and had the value $2.0 \times 10^4\ M^{-2}\ sec^{-1}$ at 25.0°. The value at 18.0° is $1.7 \times 10^4\ M^{-2}\ sec^{-1}$, and this is in good agreement with the single value ($1.9 \times 10^4\ M^{-2}\ sec^{-1}$) computed from the result of Chance.[10]

It is impossible from the kinetics to distinguish between two likely mechanisms for the reaction. In one, $H_3O_2^+$ is formed rapidly[14] in extremely small amounts,[15] and this then reacts with $HCrO_4^-$ in a rate-determining step. In the other mechanism, H_2CrO_4 reacts with H_2O_2 in the slow step

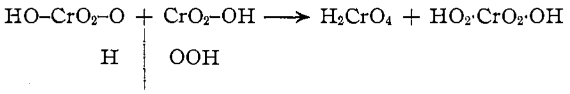
$$HCrO_4 + H^+ \rightleftharpoons H_2CrO_4 \quad (K_B)$$

$$H_2CrO_4 + H_2O_2 \longrightarrow H_2CrO_5 + H_2O$$

$$H_2CrO_5 + H_2O_2 \longrightarrow CrO_5\cdot H_2O + H_2O \quad \text{(fast)}$$

Since $K_B = 0.02$–0.25,[16,17] a limiting rate might be expected in high acidities, but this could not be observed since CrO_5(aq) did not appear in acidities above about 0.5 *M*. We reject a radical mechanism because of the simple kinetic equations and since no evidence for a lower oxidation state of chromium occurs in the formation of CrO_5.

Tuck and Walters[9] have studied the formation of blue peroxychromic acid in tri-*n*-butyl phosphate–cyclohexane mixture where the reaction is much slower than in water. The reaction was also first order in chromium(VI) and H_2O_2 and acid catalyzed. The rate-controlling step was considered the attack of H_2O_2 on the Cr–O–Cr link in $H_2Cr_2O_7$, the reacting species in the nonaqueous solvent



$$\underset{H}{HO\text{–}CrO_2\text{–}O} + \underset{OOH}{CrO_2\text{–}OH} \longrightarrow H_2CrO_4 + HO_2\cdot CrO_2\cdot OH$$

We intend to examine the formation of other peroxy compounds of the transition metals.

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