

The Effect of Cerium(III) and Cerium(IV) on Chromic Acid Oxidations. Elimination of the Chromium(IV)-Alcohol Oxidation¹

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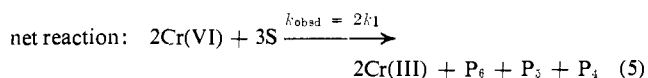
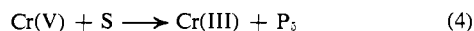
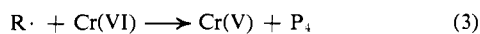
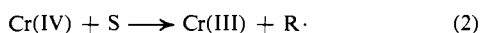
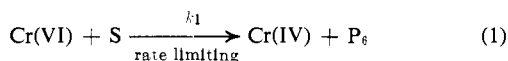
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Abstract: The presence of either cerium(III) or of cerium(IV) reduces the rate of chromic acid oxidations of alcohols and suppresses the cleavage of phenyl *tert*-butyl carbinol. The effect can be observed at cerium concentration as low as 10^{-7} M; it is interpreted by a mechanism in which cerium catalyzes the disproportionation of chromium(IV) to chromium(III) and chromium(VI).

The oxidation of alcohols by chromic acid involves both one-electron and two-electron transfer reactions.² The mechanism of this oxidation involves an initial rate-limiting two-electron oxidation of the alcohol by chromium(VI) with production of an aldehyde or ketone and a tetravalent chromium intermediate. It is now well established, at least in solutions containing some water, that this chromium(IV) reacts in a rapid one-electron oxidation with a molecule of alcohol to yield a free radical and a chromium(III) species.³

The simplest mechanism incorporating these reactions is given in Scheme I. This mechanism predicts

Scheme I



that 33% of the products will be formed through a free-radical intermediate (product P₄). Because two chromium(VI) molecules are reduced for each chromium(VI) reacting in the rate-limiting step, the mechanism further predicts that the observed second-order rate constant, k_{obsd} , should be equal to $2k_1$.

In fact, the reaction mechanism seems to be more complicated. Chromium(V), rather than reacting solely with the substrate, can also undergo a disproportionation to chromium(IV) and chromium(VI) (Scheme II)³ which would lead up to 67% instead of 33% of P₄.

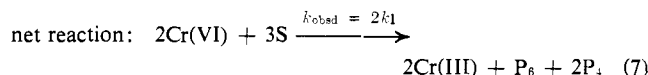
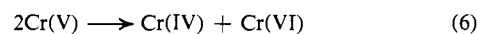
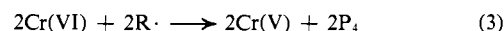
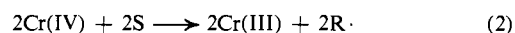
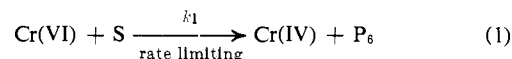
Further, there is experimental evidence that not all the radical formed in reaction 2 undergoes oxidation.

(1) This work was supported by the Petroleum Research Fund, administered by the American Chemical Society, and by the U. S. Army Research Office (Durham).

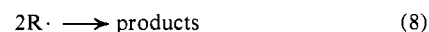
(2) (a) For extensive reviews of chromic acid oxidations, see K. B. Wiberg, "Oxidation in Organic Chemistry," Part A, Academic Press, New York, N. Y., 1965; R. Stewart, "Oxidation Mechanisms: Application to Organic Chemistry," W. A. Benjamin, New York, N. Y., 1964; (b) K. B. Wiberg and H. Schäfer, *J. Amer. Chem. Soc.*, **91**, 927, 933 (1969).

(3) (a) J. Roček and A. E. Radkowsky, *ibid.*, **90**, 2896 (1968); **95**, 7123 (1973); (b) K. B. Wiberg and S. K. Mukherjee, *ibid.*, **93**, 2543 (1973); (c) P. M. Nave and W. S. Trahanovsky, *ibid.*, **92**, 1120 (1970); (d) M. Rahman and J. Roček, *ibid.*, **93**, 5455, 5462 (1971).

Scheme II



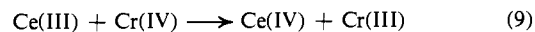
Some of it seems to react by a bimolecular disproportionation or dimerization^{3d}



which will result in an experimental rate constant lower than the value of $2k_1$ required by Schemes I and II. Hence the actual value of the experimental rate constant will lie between the values of k_1 and $2k_1$.

Oxidations involving different valence states of chromium do not always lead to the same products. For example, chromic acid oxidation of phenyl alkyl carbinols produces both the corresponding ketone and benzaldehyde.⁴ The oxidative cleavage reaction has been shown in these systems and in the related cyclobutanol oxidation to be due to a reaction with one-electron oxidants.^{3,5}

If the chromium(IV) species could be removed before it is able to react with alcohol, the one-electron cleavage in chromic acid oxidations would be eliminated. One means of removing chromium(IV) is by reaction with a one-electron reducing agent, such as cerium(III) (eq 9). To be effective, two conditions must be met: (1)



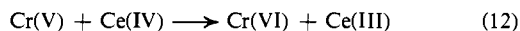
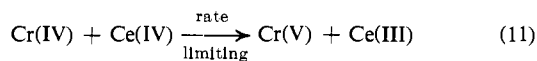
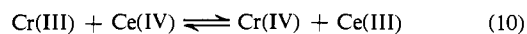
the reducing agent must react more rapidly with Cr(IV) than Cr(IV) can react with alcohol (eq 2), and (2) neither the reducing agent nor its oxidized form should be reactive toward any species other than Cr(VI). In addition, at least 1 equiv of reducing agent is required for eq 6 to be sufficient in removing chromium(IV). Hampton, Leo, and Westheimer have, in fact, used excess amounts of cerium(III) perchlorate to reduce chromium(IV) in the chromic acid oxidation of phenyl *tert*-butyl carbinol.^{4a}

(4) (a) J. Hampton, A. Leo, and F. H. Westheimer, *ibid.*, **78**, 306 (1956); (b) J. J. Cawley and F. H. Westheimer, *ibid.*, **85**, 1771 (1963); (c) W. A. Mosher and F. C. Whitmore, *ibid.*, **70**, 2544 (1948).

(5) (a) K. Meyer and J. Roček, *ibid.*, **94**, 1209 (1972); (b) J. Roček and A. E. Radkowsky, *J. Org. Chem.*, **38**, 89 (1973).

Cerium(IV) also reacts with chromium(IV). King and Tong have shown that in the cerium(IV) oxidation of chromium(III) three one-electron transfer reactions are involved (Scheme III) with the oxidation of chro-

Scheme III



mium(IV) being the rate-limiting step.⁶ We have previously communicated that both cerium(IV) and cerium(III) may be used to trap chromium(IV) in chromic acid oxidations of alcohols and that the amount of cerium used can be significantly less than 1 equiv, based on chromic acid used.⁷ In this paper further results are reported that show that cerium(IV) and cerium(III) effectively remove chromium(IV) when used in catalytic amounts.

Results

Table I presents a summary of the second-order rate

Table I. Chromic Acid Oxidation of 2-Propanol in Aqueous Media at 25.0° in the Presence of Cerium(IV) and Cerium(III)^a

[Ce(IV)] ₀ , M ^b	10 ³ k _{obsd} , M ⁻¹ sec ⁻¹	[Ce(III)] ₀ , M	10 ³ k _{obsd} , M ⁻¹ sec ⁻¹	[Cr(VI)] ₀ / [Ce] ₀
0	4.33 ^{c,d}	0	4.33 ^{c,d}	
6.00 × 10 ⁻⁸	4.37	6.00 × 10 ⁻⁸	4.22	1.00 × 10 ⁵
1.20 × 10 ⁻⁷	4.38	1.20 × 10 ⁻⁷	4.13	5.00 × 10 ⁴
3.00 × 10 ⁻⁷	4.22	3.00 × 10 ⁻⁷	3.56	2.00 × 10 ⁴
6.00 × 10 ⁻⁷	4.30	6.00 × 10 ⁻⁷	4.00	1.00 × 10 ⁴
1.20 × 10 ⁻⁶	3.88	1.20 × 10 ⁻⁶	3.53	5.00 × 10 ³
3.00 × 10 ⁻⁶	3.32	3.00 × 10 ⁻⁶	3.08	2.00 × 10 ³
6.00 × 10 ⁻⁶	3.08	6.00 × 10 ⁻⁶	2.88	1.00 × 10 ³
1.20 × 10 ⁻⁵	2.78	1.20 × 10 ⁻⁵	2.78	5.00 × 10 ²
3.00 × 10 ⁻⁵	2.72	3.00 × 10 ⁻⁵	2.70	2.00 × 10 ²
6.00 × 10 ⁻⁵	2.67	6.00 × 10 ⁻⁵	2.60	1.00 × 10 ²
1.20 × 10 ⁻⁴	2.45	1.20 × 10 ⁻⁴	2.42	50.0
3.00 × 10 ⁻⁴	2.38			20.0
6.00 × 10 ⁻⁴	2.38	6.00 × 10 ⁻⁴	2.17	10.0
1.20 × 10 ⁻³	2.22	1.20 × 10 ⁻³	2.26 ^f	5.00
3.00 × 10 ⁻³	2.10			2.00
6.00 × 10 ⁻³	2.07	6.00 × 10 ⁻³	2.98	1.00
1.20 × 10 ⁻²	1.97	1.20 × 10 ⁻²	2.84	0.500
3.00 × 10 ⁻²	1.60 ^e	3.00 × 10 ⁻²	2.88 ^e	0.200

^a [Cr(VI)]₀ = 6.00 × 10⁻³ M; [(CH₃)₂CHOH]₀ = 0.615 M; [H₂SO₄]₀ = 0.90 M. ^b Contained cerium(III): [Ce(IV)]₀/[Ce(III)]₀ = 18.4. ^c Average of three determinations; precision ±0.04 × 10⁻³. ^d For [Cr(VI)]₀ = 6.87 × 10⁻³ M, [(CH₃)₂CHOH]₀ = 0.200 M, and [H₂SO₄]₀ = 0.90 M, k_{obsd} = 4.23 × 10⁻³ M⁻¹ sec⁻¹. ^e Average of two determinations; precision ±0.02 × 10⁻³. ^f Through the first 20% of reaction, k_{obsd} = 2.84 × 10⁻³ M⁻¹ sec⁻¹.

constants for the chromic acid oxidations of 2-propanol in aqueous media in the presence of cerium(IV) and cerium(III). The rate of reaction was measured by observing the rate of production of chromium(III) at 580 nm; good pseudo-first-order plots were obtained in all kinetic experiments through at least 2 half-lives. Under the same reaction conditions the second-order rate constant for cerium(IV) oxidation of 2-propanol was 1.35 × 10⁻⁵ M⁻¹ sec⁻¹, about 1/300 as great as that for chromic acid oxidation. In the aqueous sul-

(6) J. Y.-P. Tong and E. L. King, *J. Amer. Chem. Soc.*, **82**, 3805 (1960).

(7) M. P. Doyle, R. J. Swedo, and J. Roček, *ibid.*, **92**, 7599 (1970).

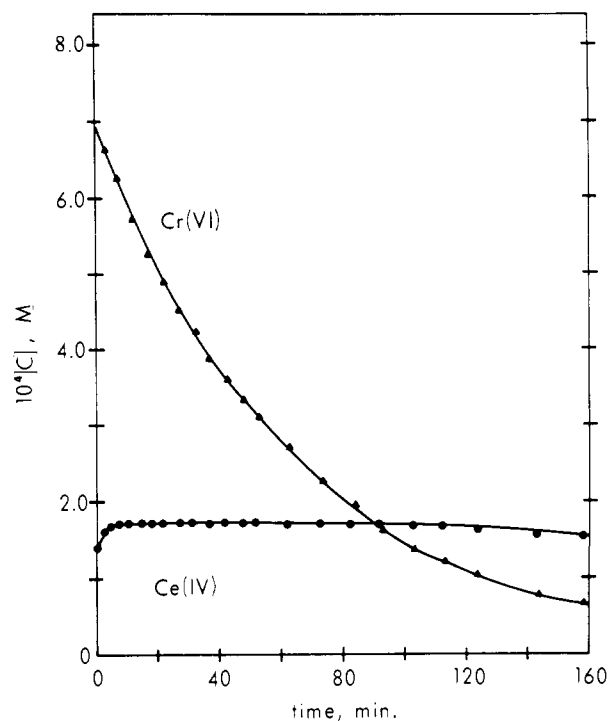


Figure 1. Concentration of chromium(VI) (●) and cerium(IV) (▲) vs. time. [Cr(VI)]₀ = 6.87 × 10⁻⁴ M, [Ce(IV)]₀ = 1.45 × 10⁻⁴ M, [Ce(III)]₀ = 0.31 × 10⁻⁴ M, [(CH₃)₂CHOH]₀ = 0.100 M, [H₂SO₄] = 0.90 M, temperature = 25.0°.

furic acid medium we were not able to observe complex formation between cerium(IV) and 2-propanol using the procedure previously described by Trahanovsky and Young.⁸

The effect of cerium(IV) and cerium(III) on the rate of reaction is comparable except at [Cr(VI)]₀/[Ce]₀ ratios less than 2:1. A reduction in the rate constant is first observed when the concentration of cerium is only 0.0001 times that of the chromic acid. With increasing cerium concentration the second-order rate constant for the chromic acid oxidation of 2-propanol approaches a value of one-half the rate constant for the same oxidation without added cerium. When the cerium concentration approaches and exceeds that of the chromium(VI), the effect of cerium(IV) does not parallel that of cerium(III). At cerium(IV) concentrations greater than 0.5 times that of chromium(VI) the rate constant for chromic acid oxidation shows a continual drop. With cerium(III), on the other hand, the rate constants go through a minimum value and with further increasing cerium(III) concentration reach a higher approximately constant value. Hampton, Leo, and Westheimer observed a similar effect of high cerium(III) concentrations on the rate of chromic acid oxidation.^{4a}

In a separate experiment involving the chromic acid oxidation of 2-propanol using cerium(IV) and cerium(III), the change in the concentrations with time of both chromium(VI) and cerium(IV) were determined (Figure 1). Oxidation of cerium(III) occurs in a rapid reaction until the sum of the initial concentrations of cerium(IV) and cerium(III) represents the total cerium(IV) concentration. After this initial production of cerium(IV), the concentration of cerium(IV) remains

(8) L. B. Young and W. S. Trahanovsky, *ibid.*, **91**, 5060 (1969).

Table II. Oxidation of Chromium(III) by Cerium(IV) in Aqueous Sulfuric Acid Solutions at 25.0°

$10^3[\text{Ce(IV)}],$ M	$10^3[\text{Ce(III)}],$ M	$10^3[\text{Cr(III)}],$ M	$[\text{H}^+]^b$	$[\text{HSO}_4^-]^b$	$[\text{SO}_4^{2-}]^b$	$10^3k,$ $M^{-1} \text{sec}^{-1}$
11.4	0.617	5.82	1.15	0.65	0.25	4.2
22.8	1.24	5.82	1.15	0.65	0.25	4.2
28.5	1.55	5.82	1.15	0.65	0.25	4.0
0.9-9.3	0.007-7.9	4.4-8.7	1.30	0.65	0.11	5.0 ^c
0.9-23.3	0.007-55.3	4.3-42.6	0.24	0.39	0.51	4.8 ^c
0.5-9.3	0.003-0.013	4.3-21.8	1.06	0.29	0.29	5.8 ^c

^a $[\text{H}_2\text{SO}_4] = 0.90 M$. ^b Calculated by assuming $K_2 = [\text{H}^+][\text{SO}_4^{2-}]/[\text{HSO}_4^-] = 0.42$. ^c Data of King and Tong.⁶

constant through more than 2 half-lives for the chromic acid oxidation of 2-propanol. It is noteworthy that the increase in the concentration of Ce(IV) through the initial phase of the reaction (first 10 min) corresponds to the same change in the chromic acid concentration, *i.e.*, 1 mol of cerium(III) is oxidized for each mole of chromium(VI) reduced.

To determine if the rate law for oxidation of chromium(III) by cerium(IV) given by King and Tong⁶ (Scheme II) held under our reaction conditions we repeated the oxidation of chromium(III). These data are reported in Table II. The rate expression, $d[\text{Cr(VI)}]/dt = k[\text{Cr(III)}][\text{Ce(IV)}]^2/[\text{Ce(III)}]$, held in each case studied; and the rate constants that we obtained compared favorably with those previously reported.⁶ Addition of 2-propanol to mixtures of cerium(IV), cerium(III), and chromium(III), under conditions similar to those given in Table II, had a negligible effect on the initial rate. As much as a 1000-fold excess of 2-propanol over either Cr(III) or cerium reagents was added with no noticeable change in the rate of appearance and yield of chromium(VI).⁹

The effect of cerium on chromic acid oxidations in aqueous acetic acid is similar to that observed in aqueous solutions (Table III). Good pseudo-first-order

Table III. Chromic Acid Oxidation of 2-Propanol in 70% Aqueous Acetic Acid at 25.0° in the Presence of Cerium(IV) and Cerium(III)^a

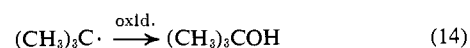
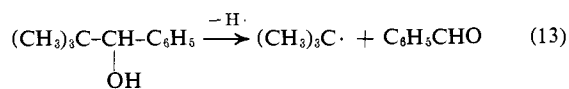
$[\text{Ce(IV)}]_0,$ M^b	$10^2k_{\text{obsd}},$ $M^{-1} \text{sec}^{-1}$	$[\text{Ce(III)}]_0,$ M	$10^2k_{\text{obsd}},$ $M^{-1} \text{sec}^{-1}$	$[\text{Cr(VI)}]_0/$ $[\text{Ce}]_0$
0	2.80 ^c	0	2.80 ^c	
		5.95×10^{-9}	2.75	1.06×10^6
6.00×10^{-8}	2.83	5.95×10^{-8}	2.79 ^d	1.05×10^6
1.20×10^{-7}	2.77	1.19×10^{-7}	2.45	5.24×10^4
6.00×10^{-7}	2.40	5.95×10^{-7}	2.37	1.05×10^4
1.20×10^{-6}	2.27	1.19×10^{-6}	2.28	5.24×10^3
6.00×10^{-6}	1.93	5.95×10^{-6}	1.91	1.05×10^3
1.20×10^{-5}	1.78	1.19×10^{-5}	1.80	5.24×10^2
6.00×10^{-5}	1.64	5.95×10^{-5}	1.63	1.05×10^2
1.20×10^{-4}	1.65	1.19×10^{-5}	1.63	52.4
		3.57×10^{-4e}	1.58 ^f	17.6
6.00×10^{-4}	1.87 ^f			10.5
1.20×10^{-3g}	1.87 ^f			5.24

^a $[\text{Cr(VI)}]_0 = 6.29 \times 10^{-3} M$; $[(\text{CH}_3)_2\text{CHOH}]_0 = 0.0524 M$; $[\text{H}_2\text{SO}_4]_0 = 0.18 M$. ^b Quantitative determination of $[\text{Ce(IV)}]$ showed less than 0.1% Ce(III) was present. ^c Average of three determinations; precision $\pm 0.03 \times 10^{-2}$. ^d Average of two determinations; precision $\pm 0.10 \times 10^{-2}$. ^e Limit of cerium(III) solubility under these conditions. ^f Average of two determinations; precision $\pm 0.02 \times 10^{-2}$. ^g Limit of cerium(IV) solubility under these conditions.

(9) If chromium(IV), produced from chromium(III) by cerium(IV) oxidation, reacted with 2-propanol, a decrease in the yield of chromium(VI) should be observed.

rate plots were observed through at least 2 half-lives. Under the same reaction conditions the cerium(IV) oxidation of 2-propanol has a second-order rate constant of $3.83 \times 10^{-6} M^{-1} \text{sec}^{-1}$, about 1/7000 of that for chromic acid oxidation. The change in the observed rate constant for chromic acid oxidation with increasing cerium concentration is nearly the same as that found in aqueous solution. As in aqueous solution the rate constant is reduced by about 25% when the cerium concentration is less than 0.001 times that of the chromic acid. In the acetic acid solution at $[\text{Cr(VI)}]_0/[\text{Ce(IV)}]_0$ of 10 or less, the rate constant is reduced by about 40%. Due to the insolubility of the cerium(III) sulfate, similar data could not be obtained at high cerium(III) concentrations.

Cerium could reduce the rate of the chromic acid oxidation by reacting either with chromium(IV) or with the radical produced by one-electron oxidation of alcohol by chromium(IV) (Scheme I). In order to distinguish between these alternatives, we studied both the kinetics and the composition of reaction products formed in the oxidation of phenyl *tert*-butyl carbinol in the presence of cerium. This alcohol is known to undergo oxidative cleavage with one-electron oxidants.^{4,10} Therefore, the yield of cleavage products (benzaldehyde and *t*-BuOH, eq 13 and 14) from the



chromic acid oxidation in the presence of cerium should be a good measure of our ability to trap chromium(IV). Data for the chromic acid oxidation of phenyl *tert*-butyl carbinol in 70% aqueous acetic acid in the presence of either cerium(IV) or cerium(III) are given in Table IV. Good pseudo-first-order rate plots were obtained through more than 2 half-lives. The yields of products were determined directly from the reaction solution immediately after the reaction had completed 10 half-lives. We found that under the reaction conditions specified in Table IV, the second-order rate constants for the oxidation of benzaldehyde by chromic acid is $7.94 \times 10^{-4} M^{-1} \text{sec}^{-1}$ and by cerium(IV) $5.09 \times 10^{-4} M^{-1} \text{sec}^{-1}$. Benzaldehyde thus was not oxidized further by either chromic acid or cerium(IV) in the presence of the large excess of phenyl *tert*-butyl carbinol used in this series of experiments.

Phenyl *tert*-butyl carbinol is quantitatively cleaved by cerium(IV) as well as by chromium(IV).¹⁰ However, under the same conditions as those given in Table IV,

(10) W. S. Trahanovsky and J. Cramer, *J. Org. Chem.*, **36**, 1890 (1971).

Table IV. Chromic Acid Oxidation of Phenyl *tert*-Butyl Carbinol in 70% Aqueous Acetic Acid at 25.0° in the Presence of Cerium(IV) and Cerium(III)^a

[Ce(IV)] ₀ , <i>M</i>	10 ² <i>k</i> _{obsd} , <i>M</i> ⁻¹ sec ⁻¹	% cleavage ^b	[Ce(III)] ₀ , <i>M</i>	10 ² <i>k</i> _{obsd} , <i>M</i> ⁻¹ sec ⁻¹	% cleavage ^b	[Cr(VI)] ₀ / [Ce] ₀
0	9.75 ^c	40	0	9.75 ^c	40	
1.20 × 10 ⁻¹⁰	9.86	36				3.27 × 10 ⁷
1.20 × 10 ⁻⁹	9.63	28				3.27 × 10 ⁶
			6.00 × 10 ⁻⁸	9.45		6.55 × 10 ⁶
1.20 × 10 ⁻⁸	8.23	30				3.27 × 10 ⁶
1.20 × 10 ⁻⁷	8.17	29	1.20 × 10 ⁻⁷	9.60	25	3.27 × 10 ⁴
1.20 × 10 ⁻⁶	7.24	18	1.20 × 10 ⁻⁶	7.26	29	3.27 × 10 ³
6.00 × 10 ⁻⁶	6.24		6.00 × 10 ⁻⁶	6.53	12	655
1.20 × 10 ⁻⁵	6.22	8	1.20 × 10 ⁻⁵	6.23	11	327
6.00 × 10 ⁻⁵	6.08	7	6.00 × 10 ⁻⁵	6.27	10	65.5
1.20 × 10 ⁻⁴	5.47	6	1.20 × 10 ⁻⁴	6.13	5	32.7
6.00 × 10 ⁻⁴	5.28	5	6.00 × 10 ⁻⁴	6.33	4	6.55
1.20 × 10 ⁻³ ^d	6.44 ^e	7	1.20 × 10 ⁻³ ^d	6.32 ^f	4	3.27

^a [Cr(VI)]₀ = 3.93 × 10⁻³ *M*; [C₆H₅CHOHC(CH₃)₂]₀ = 5.70 × 10⁻² *M*; [H₂SO₄]₀ = 0.18 *M*. ^b Yield of benzaldehyde based on glpc analyses using an internal standard. Duplicate runs show the precision of analysis to be within ±2%. ^c Average of two determinations; precision ±0.04 × 10⁻². ^d Limit of cerium solubility. ^e Average of three determinations; precision ±0.23 × 10⁻². ^f Average of three determinations; precision ±0.01 × 10⁻².

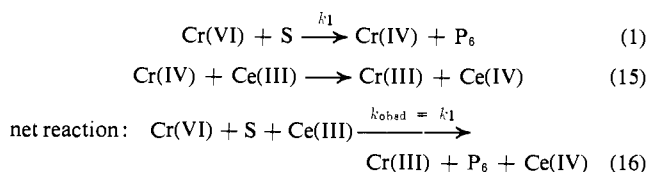
the second-order rate constant for oxidation of phenyl *tert*-butyl carbinol by cerium(IV) was 6.45 × 10⁻⁴ *M*⁻¹ sec⁻¹, only 1/100 of that for the corresponding chromic acid oxidation. Under our experimental conditions we estimate that less than 3% of cleavage product would be produced from ceric oxidation at the highest cerium(IV) concentration listed in Table IV, an estimate borne out by the difference in per cent cleavage product for chromic acid oxidation with 1.2 × 10⁻³ *M* cerium(IV) and cerium(III).

From Table IV it is evident that cerium(IV) and cerium(III) effect both a decrease in the observed rate of oxidation and in the amount of cleavage product, benzaldehyde. The yields of pivalophenone, not given in Table IV, show a corresponding increase when cerium is added. To reduce the amount of cleavage product to one-half of that found in the "normal" chromic acid oxidation requires only a comparably small amount of either cerium(IV) or cerium(III), less than 0.001 times that of chromic acid. Both cerium(III) and cerium(IV) at concentrations of 1.2 × 10⁻³ *M* reduce the second-order rate constants for the chromic acid oxidation of phenyl *tert*-butyl carbinol by more than 40%.

Discussion

The decrease of the observed oxidation rate, as well as the suppression of the cleavage reaction in the oxidation of phenyl *tert*-butyl carbinol, indicates that cerium reacts with the chromium(IV) formed in the rate-limiting step of the oxidation (eq 1). The ability of stoichiometric amounts of cerium(III) to reduce chromium(IV) was known and the mechanism well understood (Scheme IV).⁴ This mechanism leads to a reduction of the

Scheme IV



rate from a value of *k*_{obsd} lying between *k*₁ and 2*k*₁ (and considerably closer to 2*k*₁) to *k*₁.

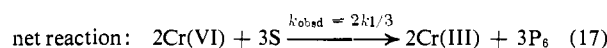
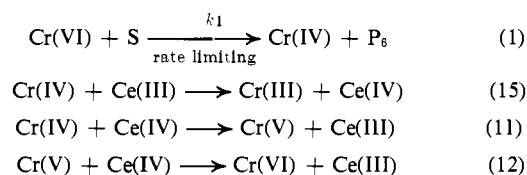
Our results, however, led to the astonishing finding

that cerium(III) is active in reducing the overall reaction rate and in suppressing cleavage reaction at concentrations several orders of magnitude lower than those required by Scheme IV. Reduction of the rate constant by about 25% occurs in both aqueous and 70% aqueous acetic acid solutions when the [Cr(VI)]₀/[Ce]₀ ratio is approximately 3000:1; at this same ratio the amount of cleavage product in the chromic acid oxidation of phenyl *tert*-butyl carbinol is reduced to one-half that found in the chromic acid oxidation without added cerium.¹¹

Further, cerium(III) and cerium(IV) affect the reaction equally at low cerium concentrations, while at high cerium concentrations the overall reaction rate is reduced more by cerium(IV) than by cerium(III).

In order to explain these experimental findings the reaction mechanism must provide for an interconversion between the two valence states of cerium which would lead to the establishment of a quasi-equilibrium between cerium(III) and cerium(IV). The mechanism must further explain the removal of chromium(IV) and the reduction of the oxidation rate. A mechanism which satisfies these requirements is given in Scheme V.

Scheme V



The reduction of Cr(IV) by cerium(III) (reaction 15) is obviously much faster than the oxidation of chromium(IV) by cerium(IV) (reactions 11 and 12). Con-

(11) Although not all cleavage product is eliminated from the chromic acid oxidation of phenyl *tert*-butyl carbinol (Table IV), the constant amount of benzaldehyde found at high cerium concentrations must be formed in some other manner than by chromium(IV) oxidation since cerium has no further effect at ratios of [Cr(VI)]₀/[Ce]₀ less than approximately 100. Since oxidation of alcohol by Cr(IV) (eq 2) is competitive with oxidation or reduction of Cr(IV) by Ce(IV) (eq 8) or Ce(III) (eq 6), an increase in the concentration of cerium at constant alcohol and chromic acid concentrations should give a decrease in the yield of cleavage product. Other processes, including two-electron oxidative cleavage may be responsible for as much as 7% of the cleavage products under our reaction conditions.

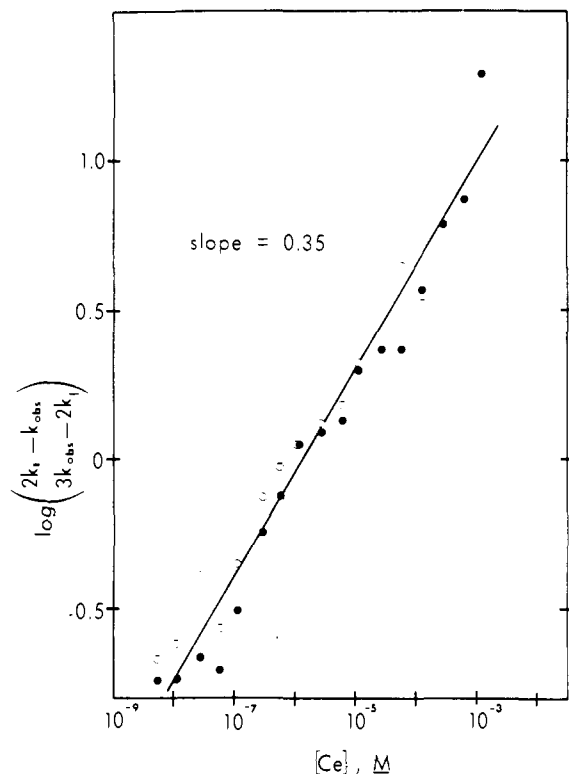
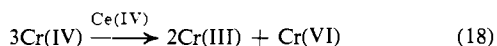


Figure 2. Dependence of rates in the oxidation of 2-propanol by chromic acid on the concentration of cerium(IV) (●) and cerium(III) (○). Plot according to eq 24; k_1 is the second-order rate constant for the oxidation of 2-propanol by chromium(VI) (reaction 1); note text for comments on the choice of the value for k_1 .

sequently, at lower cerium concentrations, almost all cerium is converted into cerium(IV) and stays in this form as long as chromium(VI) is present (Figure 1).

In the mechanism given in Scheme V, cerium acts as a catalyst for the disproportionation of chromium(IV) (eq 18). Since from every three chromium(IV) species



formed in the rate-limiting step one chromium(VI) is re-formed, the observed second-order rate constant for this process is expected to be $2k_1/3$, a value which is 33% lower than that predicted from Scheme IV. This can explain the difference in the effect of cerium(III) and cerium(IV) at high concentration. At low cerium concentrations all cerium is rapidly converted into cerium(IV), regardless of the form in which it was initially introduced into the reaction, and therefore will exert the same effect on the reaction by the mechanism given in Scheme V. The same mechanism will be operative at high cerium(IV) concentrations. However, at high concentrations of cerium(III) only reaction 10 will take place, and, consequently, mechanism IV rather than V will become operative. Under these conditions no oxidation of chromium(IV) back to chromium(VI) (via reactions 11 and 12) should take place and k_{obsd} should become equal to k_1 rather than to $2k_1/3$ as derived from Scheme V. Thus, with increasing cerium(III) concentration, the oxidation rate should decrease, ideally to reach the value of $0.67k_1$, then increase again to the value of k_1 . No such effect should be observed for cerium(IV). The experimental data given in Table I are in full agreement with this conclusion.

By combining Schemes I and V one can derive a rate law (eq 19 and 20). Assuming that the rates of reactions

$$-d[\text{Cr(VI)}]/dt = k_{\text{obsd}}[\text{Cr(VI)}][\text{S}] = k_1[\text{Cr(VI)}][\text{S}] + k_3[\text{R}\cdot][\text{Cr(VI)}] - k_{12}[\text{Cr(V)}][\text{Ce(IV)}] \quad (19)$$

$$k_{\text{obsd}}[\text{Cr(VI)}][\text{S}] = k_1[\text{Cr(VI)}][\text{S}] + k_2[\text{Cr(IV)}][\text{S}] - k_{11}[\text{Cr(IV)}][\text{Ce(IV)}] \quad (20)$$

2 and 3 and those of reactions 11 and 12 are equal, one obtains the steady-state concentration of chromium(IV) and of cerium(III), as given by eq 21 and 22. By com-

$$[\text{Cr(IV)}] = \frac{k_1[\text{Cr(VI)}][\text{S}]}{k_2[\text{S}] + k_{10}[\text{Ce(III)}] + k_{11}[\text{Ce(IV)}]} \quad (21)$$

$$[\text{Ce(III)}] = \frac{2k_{11}[\text{Ce(IV)}]}{k_{10}} \quad (22)$$

binning eq 20, 21, and 22 and putting $[\text{Ce(IV)}] = [\text{Ce}]$ (where $[\text{Ce}]$ is the total cerium concentration), one obtains eq 23

$$k_{\text{obsd}} = \frac{2k_1(k_2[\text{S}] + k_{11}[\text{Ce}])}{k_2[\text{S}] + 3k_{11}[\text{Ce}]} \quad (23)$$

This equation can be rearranged to

$$\frac{2k_1 - k_{\text{obsd}}}{3k_{\text{obsd}} - 2k_1} = \frac{k_{11}[\text{Ce}]}{k_2[\text{S}]} \quad (24)$$

Figure 2 gives a logarithmic plot of the left-hand side of eq 24 vs. $[\text{Ce}]$. A fairly good straight line over the whole concentration range, covering more than five orders of magnitude, is obtained. The plot is quite sensitive to the value of k_1 : a good straight line is obtained if one uses the k_1 value from measurements of high cerium(III) concentrations ($k_{\text{obsd}} = k_1 = 2.86 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$).¹² A surprising and rather puzzling result is that the slope of the straight line is 0.35 instead of 1.0 as required by eq 24. This indicates that the observed rate very approximately depends on $[\text{Ce}]^{1/3}$ rather than on $[\text{Ce}]$. This result would seem to indicate that the species responsible for the disproportionation of chromium(IV) is not the prevalent form in which cerium(IV) is present, but rather some "active" species the concentration of which is approximately proportioned to the cube root of the analytical cerium concentration. We are unable to identify this "active" species. It should, however, be noted, that the experimental data would fit a mechanism involving an equilibrium between a monomeric and trimeric form of cerium with only the monomeric form being an active catalyst of the chromium(IV) disproportionation. Unfortunately, we are unaware of any supporting evidence for such an interpretation.

Experimental Section

Materials. 2-Propanol and benzaldehyde were of reagent grade quality and used without further purification. Phenyl *tert*-butyl carbinol was prepared from benzaldehyde and *tert*-butylmagnesium chloride¹³ followed by isolation and purification through an F&M

(12) This value is about 32% higher than one-half of k_{obsd} in the absence of cerium. It thus can be estimated that about one-third of the free radicals formed in reaction 2 undergo bimolecular dimerization or disproportionation (reaction 8), whereas two-thirds are oxidized by chromium(VI) (reaction 3).

(13) J. B. Conant and H. Blatt, *J. Amer. Chem. Soc.*, 50, 551 (1928).

Prepmaster Junior gas chromatograph using a 2 in. \times 80 in. 20% Carbowax 20M column. The white solid collected in this manner was recrystallized from hexane, mp 42.0–42.5° (lit.¹⁴ mp 44–45°). Pivalophenone was prepared from pivaloyl chloride and phenylmagnesium bromide¹⁴ followed by isolation and purification by glpc as mentioned above. Volatile compounds were checked for purity on a F&M 5750 Research Chromatograph. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected.

Baker Analyzed reagents, potassium chromi-um sulfite and potassium dichromate, were used without prior purification. Cerium(III) sulfate octahydrate, cerium(IV) ammonium nitrate (analyzed reagent grade), and sulfatoceric acid were from G. F. Smith Co.

Stock Solutions. Cerium(IV) and cerium(III) solutions were prepared by dissolving the cerium reagent in 0.90 M sulfuric acid. No effect of the source of ceric ion on the rates of reaction was observed when either sulfatoceric acid or ceric ammonium nitrate was used;¹⁵ analytical reagent cerium(IV) ammonium sulfate was generally used to prepare stock solutions. Concentrations of cerium(IV) solutions were determined both by titration with analytical reagent iron(II) ammonium sulfate using a ferroin indicator¹⁶ and spectrophotometrically.⁵ The concentrations of cerium(III) solutions were determined spectrophotometrically for concentrations above 10^{-5} M. For reactions in aqueous media, 2-propanol, chromic acid, and cerium solutions were similarly prepared in 0.90 M sulfuric acid; for reactions in aqueous acetic acid, chromic acid and 2-propanol solutions in water were prepared. A solution of phenyl *tert*-butyl carbinol in 80% aqueous acetic acid was prepared prior to each kinetic run. Acid concentrations of the sulfuric acid solutions were determined by titration with standard sodium hydroxide.

Kinetic Measurements. For chromic acid oxidation of 2-propanol and phenyl *tert*-butyl carbinol the rate of appearance of chromium(III) as a function of time was followed at 580 nm using a thermostated Cary 15 spectrophotometer. Stock solutions were thermally equilibrated at 25° prior to introduction into the spectrophotometric cell (quartz, 10.0 cm) also at 25.0°. The initial measurement of absorbance was made within 2 min after mixing. The rates of cerium(IV) oxidation of 2-propanol were followed at 500 and 520 nm in aqueous solution and at 465 nm in 70% aqueous acetic acid; with phenyl *tert*-butyl carbinol the rate of disappearance of cerium(IV) was observed at 465 nm. The oxidation of chromium(III) by cerium(IV) was followed by observing the rate of disappearance of chromium(III) at 580 nm.

Absorbance Indices. The absorbance indices for individual solutions were measured at each wavelength employed in the kinetic study using the standard stock solutions. At 580 nm the absorbance indices of chromium(VI), chromium(III), and cerium(IV) in 0.90 M sulfuric acid were 0.203, 14.8, and $0.178 M^{-1} \text{ cm}^{-1}$, respectively. Cerium(III) is transparent at 580 nm. No correction was made for the absorption of chromium(VI) and cerium(IV) at 580 nm; an introduction of less than 1% error in the rate constant results by not making this correction. The absorbance indices of each solution from the chromic acid oxidation of 2-propanol in aqueous media was determined at the infinite measurement assuming that chromium(III) was the only absorbing species; the range observed in these measurements was $15.6 \pm 0.8 M^{-1} \text{ cm}^{-1}$.

(14) J. H. Ford, C. D. Thompson, and C. S. Marvel, *J. Amer. Chem. Soc.*, **57**, 2619 (1935).

(15) E. L. King and M. L. Pandow, *ibid.*, **75**, 3063 (1953).

(16) G. F. Smith, G. Frank, and A. E. Kott, *Ind. Eng. Chem., Anal. Ed.*, **12**, 268 (1940).

Similar measurements were obtained in aqueous acetic acid with a smaller range in absorbance indices.

In aqueous solution the observed absorbance of cerium(IV)–chromium(VI) solutions was greater than the sum of the absorbances of the individual solutions in accordance with the observations of King and Tong in perchloric acid media.¹⁷ Representative data are given in Table V. No attempt was made to measure an

Table V. Representative Absorbance Data for Chromium(VI)–Cerium(IV) Solutions^a

λ , nm	$10^4[\text{Ce(IV)}], M$	$10^4[\text{Cr(VI)}], M$	Calcd A_T^b	Obsd A_T^c	ΔA_T^d
315	0.726	3.43	0.513	0.521	0.008
315	1.45	0.344	0.667	0.725	0.058
315	1.45	3.43	0.847	0.923	0.076
315	2.90	3.43	1.408	1.698	0.290
350	1.45	6.87	1.069	1.080	0.011

^a Aqueous solution; 25.0°; $[\text{H}_2\text{SO}_4] = 0.90 M$. ^b Calculated total absorbance. Determined using the individual absorbance indices of chromium(VI) and cerium(IV). ^c Observed total absorbance. ^d Difference between observed and calculated values.

equilibrium constant or measure the amount of the expected chromium(VI)–cerium(IV) complex, as has been done previously.¹⁷ No effect on the spectrum of chromium(VI) by cerium(III) was observed.

Determination of the simultaneous change in concentration of chromium(VI) and cerium(IV) with time, as shown in Figure 1, was made by measurement of the change in absorbance at 315 and 350 nm. The concentrations of cerium(IV) and chromium(VI) at particular times were calculated according to eq 25 and 26, where

$$[\text{Ce(IV)}] = \frac{\epsilon^{315}_{\text{Cr(VI)}} A_T^{350} - \epsilon^{350}_{\text{Cr(VI)}} A_T^{315}}{\epsilon^{350}_{\text{Ce(IV)}} \epsilon^{315}_{\text{Cr(VI)}} - \epsilon^{315}_{\text{Ce(IV)}} \epsilon^{350}_{\text{Cr(VI)}}} \quad (25)$$

$$[\text{Cr(VI)}] = \frac{\epsilon^{315}_{\text{Ce(IV)}} A_T^{350} - \epsilon^{350}_{\text{Ce(IV)}} A_T^{315}}{\epsilon^{315}_{\text{Ce(IV)}} \epsilon^{350}_{\text{Cr(VI)}} - \epsilon^{350}_{\text{Ce(IV)}} \epsilon^{315}_{\text{Cr(VI)}}} \quad (26)$$

ϵ is the absorbance index of the individual species and A_T is the total absorbance of the solution. The absorbance indices of chromium(VI) and cerium(IV) were 524 and $4469 M^{-1} \text{ cm}^{-1}$ (315 nm) and 1095 and $3167 M^{-1} \text{ cm}^{-1}$ (350 nm), respectively. The λ_{max} of cerium(IV) and chromium(VI) were at 315 and 350 nm, respectively; the contribution to the total absorbance from chromium(III) and cerium(III) was negligible.

Product Analyses in Phenyl *tert*-Butyl Carbinol Oxidations. After 10 half-lives in the chromic acid oxidation of phenyl *tert*-butyl carbinol, a 2.00-ml aliquot was removed and mixed with 0.1 g of sodium acetate. An internal standard (nitrobenzene) was added to this aliquot and the solution analyzed directly on an F&M Model 5750 gas chromatograph using a 10 ft \times $1/8$ in. 10% Carbowax 20M column. Response factors for the individual components were 0.97 (benzaldehyde), 0.57 (pivalophenone), and 0.70 (phenyl *tert*-butyl carbinol). Per cent yields were based on the reaction stoichiometry (eq 5). Similar measurement of product yields using ether extraction provided comparable relative per cent yields; however, isolated yields were low.

(17) J. Y.-P. Tong and E. King, *J. Amer. Chem. Soc.*, **76**, 2132 (1954).