

The behavior in acetonitrile is quite different. Added HgCl_2 increases k_α and k_e enormously, rates being followed conveniently at 25.0° . The value of k_α is increased from *ca.* $1 \times 10^{-7} \text{ sec}^{-1}$ at 25.0° in the absence of salt^{7b} to $1.1 \times 10^{-3} \text{ sec}^{-1}$ in the presence of $0.01 M \text{ HgCl}_2$. Both k_α and k_e are linear in $[\text{HgCl}_2]$ in the concentration range $0.0015\text{--}0.0135 M$, leading to the second-order rate constants 0.110 and $0.110 M^{-1} \text{ sec}^{-1}$, respectively. This provides a k_{rac}/k_e ratio of 1.00 in line with return to RCl from a racemic ion pair intermediate II where all the chlorine atoms on HgCl_3^- are equivalently labeled.

p-Chlorobenzhydryl chloride racemizes slowly in benzene ($D = 2$) at 25.0° even in the presence of HgCl_2 . The racemization proceeds to completion ($99 \pm 5\%$) with good first-order kinetics as sampled up to 90% reaction, providing the second-order rate constant $1.04 \times 10^{-3} M^{-1} \text{ sec}^{-1}$. Similarly, the rate of exchange between RCl and HgCl_2 is slow in benzene where the dependence of k_e on $[\text{HgCl}_2]$ in the concentration range reported is $4.37 \times 10^{-3} M^{-1} \text{ sec}^{-1}$. The effect of going to this poorly ionizing solvent where the reaction intermediate stability is reduced, is to preferentially reduce that equilibration process in the ion pair which is of higher energy. Since k_α is smaller than k_e , equilibrating the faces of the benzhydryl cation must be more difficult than equilibrating chlorine atoms of HgCl_3^- in the $\text{R}^+\text{HgCl}_3^-$ pair. If the ion pairs in benzene have the same constitution as in acetone, the rate of ionization is $\frac{3}{2}k_e$; thus only 16% of the ionization reactions which give rise to chlorine exchange is accompanied by racemization, providing a *ca.* 1 kcal/mol free energy difference between the two equilibration processes.

The HgCl_2 -promoted ionization of *d*-RCl in acetone ($D = 20$) gives rise to ion pairs so constituted that two chlorine atoms are from the labeled HgCl_2 and one from RCl and only when the ion pair racemizes do all three chlorine atoms become equivalent in the ion pair I thus providing the unique k_{rac}/k_e ratio of $3/2$. The reaction in this solvent of low dielectric constant is accompanied with efficient ion pair return and no detectable dissociation.¹⁴ In the more dissociating solvent, 80% acetone ($D = 26$), the ion pair intermediates still maintain the same constitution observed in acetone, providing the unique k_{rac}/k_e ratio of $3/2$ (1.6 ± 0.16). However, ion pair return is now reduced to 45% and is accompanied by 55% dissociation. Finally, in acetonitrile ($D = 36$) ion pair dissociation is very efficient compared to ion pair return producing a racemic cation which is no longer affiliated with the original HgCl_3^- . Thus, racemic RCl is regenerated by HgCl_3^- which has fully equilibrated the original chlorine atom from RCl with the *total* chlorine atom pool II providing a k_{rac}/k_e ratio of unity.

The unique k_{rac}/k_e ratio of 1.5 observed in acetone⁹ was assigned to a single mechanism and not to fortuitous balancing of two independent reactions with different statistics. The results in 80% acetone indicated that a single mechanism must be involved in anhydrous acetone and 80% acetone because it seems unlikely that

the two independent reactions would show the same solvent sensitivity.

That the transition from acetone to acetonitrile effects the ion pair dissociation constants (k_2) primarily can be demonstrated using $\text{Ph}_3\text{C}^+\text{HgCl}_3^-$ ion pair dissociation (K_{diss}) information as model system. Since ion pair recombination (k_{-2}) is approximately diffusion control, the value of k_2 (sec^{-1}) can be estimated at 140 for acetone and $410,000$ for CH_3CN . The *ca.* 5% average deviation in the measured results provides estimates for the k_2/k_{-1} ratio of $\lesssim 1/20$ in acetone and $\gtrsim 20$ in CH_3CN . It follows then that the rate of ion pair return (k_{-1}) is quite insensitive to solvent variation, increasing from 2800 in acetone to $20,000$ in CH_3CN . By comparison, k_2 increases by three orders of magnitude.

$$\text{RCl} + \text{HgCl}_2 \xrightleftharpoons[k_{-1}]{k_1} \text{R}^+\text{HgCl}_3^- \xrightleftharpoons[k_{-2}]{K_{\text{diss}}/k_2} \text{R}^+ + \text{HgCl}_3^-$$

Solvent	$10^6 K_{\text{diss}}, M^{15}$	k_2, sec^{-1}	k_{-1}, sec^{-1}
Acetone	0.14	140	$\lesssim 2,800$
CH_3CN	410.0	410,000	$\gtrsim 20,000$

While the earlier literature contains some indications of ion pair phenomena in the salt-promoted reactions of alkyl chlorides,¹⁶ a study directed toward the elucidation of the intrigued mechanism has not been reported. This paper is the second in a series on the study of ion pair behavior in salt-promoted reactions.

(15) The dissociation constants for the solutions of trityl chloride plus mercuric chloride were measured spectrophotometrically as described by J. W. Bayles, A. G. Evans, and J. R. Jones, *J. Chem. Soc.*, 1020 (1953).

(16) (a) K. Heald and G. Williams, *ibid.*, 362 (1954); (b) D. R. Read and W. Taylor, *ibid.*, 679 (1940).

(17) Deceased, Nov 23, 1969.

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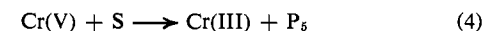
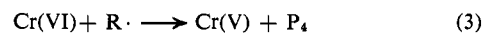
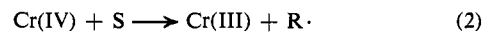
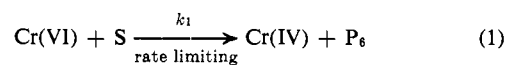
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Pure Chromium(VI) Oxidations. The Effective Removal of Chromium(IV) from Interference in Oxidations by Chromic Acid

Sir:

The chromic acid oxidation of alcohols is a multistep process involving the formation of chromium(IV) and chromium(V) intermediates.¹ We have recently shown that reaction Scheme I best explains all data available

Scheme I



(14) The k_α/k_e ratio is not changed to unity by the presence of added LiHgCl_3 , suggesting the absence of significant ion pair dissociation. Ion pair dissociation will inevitably give rise to HgCl_3^- exchange providing a k_α/k_e ratio of 1 .

(1) (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).

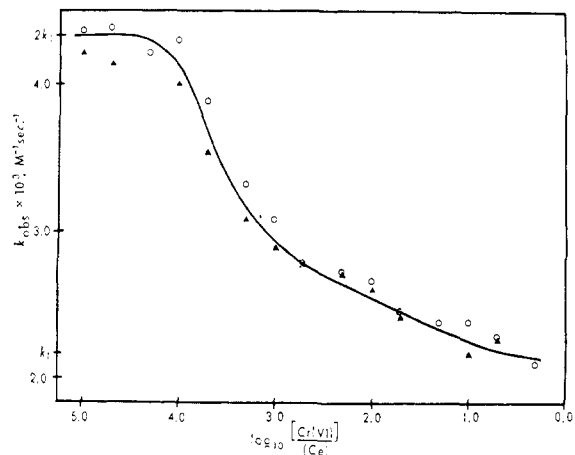
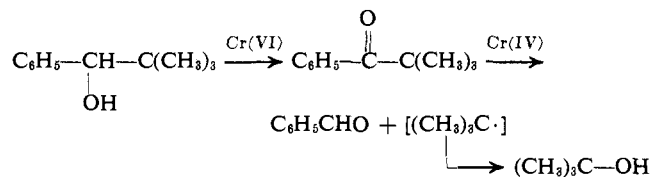


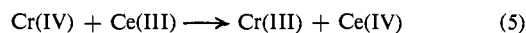
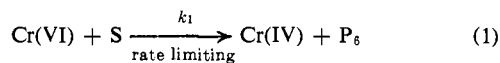
Figure 1. Effect of cerium(IV), O, and cerium(III), \blacktriangle , on the rate of chromic acid oxidation of 2-propanol: $[\text{Cr(VI)}]_0 = 6.000 \times 10^{-3} \text{ M}$; $[(\text{CH}_3)_2\text{CHOH}]_0 = 0.6148 \text{ M}$; $[\text{H}_2\text{SO}_4] = 0.90 \text{ M}$; 25.0° ; aqueous solution.

at this time.² Since a second molecule of chromium(VI) is used in a rapid oxidation of the radical (eq 3) formed from chromium(IV) oxidation,³ the overall rate, expressed as $-d[\text{Cr(VI)}]/dt$, has twice the value of the rate of the rate-limiting step (eq 1). Substrates which can undergo oxidative cleavage reactions to yield a relatively stable radical usually give a mixture of two products:⁴ a "normal" product, formed by chromium(VI) oxidation,^{4b} and a cleavage product, which we believe results from the reaction of the substrate with chromium(IV), e.g.



Hampton, Leo, and Westheimer have shown that the chromium(IV), formed in the rate-limiting step, can be rapidly reduced by cerium(III).^{4b} The reaction proceeds according to Scheme II. Introduction of ce-

Scheme II



rium(III) thus results both in a reduction of the rate to one-half the original value and in suppression of the cleavage reaction. Scheme II requires that cerium(III) be present in at least the same amount as chromium; and, in fact, Westheimer and coworkers always employed a rather large excess of cerium(III).

Cerium(IV) is known to oxidize chromium(IV) to chromium(VI). King and Tong have shown that the oxidation of chromium(III) to chromium(VI) involves three successive one-electron transfer reactions as shown in Scheme III.⁵ Chromium(IV) reacts much

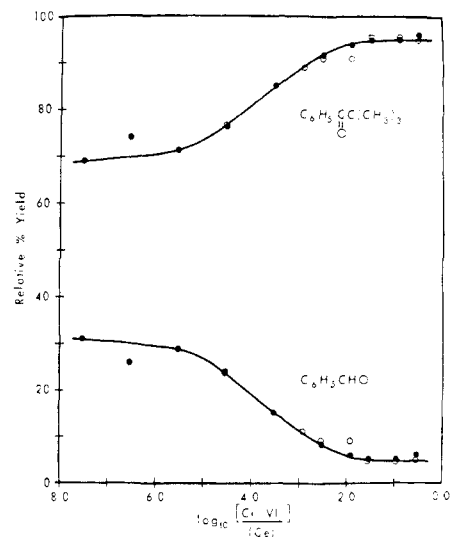
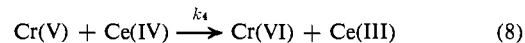
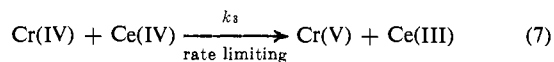
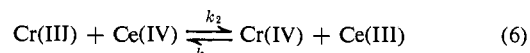


Figure 2. Effect of cerium(IV), \bullet , and cerium(III), O, on the product composition in the chromic acid oxidation of phenyl-*tert*-butylcarbinol: $[\text{Cr(VI)}]_0 = 3.933 \times 10^{-3} \text{ M}$; $[\text{C}_6\text{H}_5\text{CHOHC}(\text{CH}_3)_3]_0 = 5.740 \times 10^{-2} \text{ M}$; $[\text{H}_2\text{SO}_4] = 0.18 \text{ M}$; 25.0° ; 70% aqueous acetic acid.

more rapidly with cerium(III) than with cerium(IV) (i.e., $k_{-2}[\text{Ce(III)}] \gg k_3[\text{Ce(IV)}]$).

Scheme III



We would like to report the surprising observation that cerium(IV) affects rates and product compositions in chromic acid oxidations of alcohols in the same way as cerium(III). Moreover, both cerium(III) and cerium(IV) are effective in concentrations well below that of chromium.

Figure 1 shows the effect of cerium(IV) and cerium(III) on the rate of the chromic acid oxidation of 2-propanol.⁶ From these data it is evident that both valence states of cerium are about equally effective in reducing the rate of oxidation. This necessitates the assumption that both cerium(IV) and cerium(III) can react rapidly with either chromium(IV) or the radical and thus prevent the reduction of the second molecule of chromium(VI). The amount of cerium needed to have a pronounced effect on the reaction rate is very low: a noticeable influence on the rate can be already observed with the cerium concentration as low as 0.0001 times that of the chromium(VI). To reduce the rate to a value just halfway between the usual rate and the limiting rate requires a $[\text{Ce}]$ to $[\text{Cr(VI)}]$ ratio of only 1:2000.

When cerium(III) is added initially, the rapid production of cerium(IV) can be observed spectrophotometrically as chromium(VI) reacts with 2-propanol. The concentration of cerium(IV) then remains at the level of the total cerium ion concentration until well

(6) The second-order rate constant for oxidation of 2-propanol by cerium(IV) was over 300 times less than that for the corresponding chromic acid oxidation under identical conditions.

(2) J. Roček and A. E. Radkowsky, *J. Amer. Chem. Soc.*, **90**, 2986 (1968).

(3) M. Rahman and J. Roček, manuscript in preparation.

(4) (a) P. M. Nave and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, **92**, 1120 (1970); (b) J. Hampton, A. Leo, and F. H. Westheimer, *ibid.*, **78**, 306 (1956); (c) W. A. Mosher and F. C. Whitmore, *ibid.*, **70**, 2544 (1948).

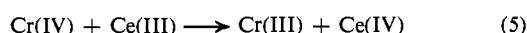
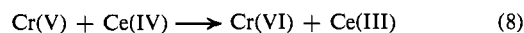
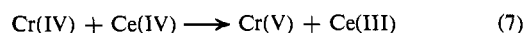
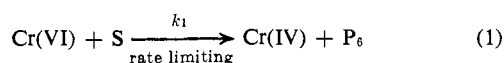
(5) J. Y. -P. Tong and E. L. King, *ibid.*, **82**, 3805 (1960).

after ten half-lives for the chromic acid oxidation has passed.

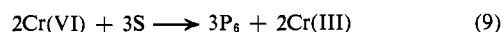
Figure 2 shows the effect of cerium(III) and cerium(IV) on the product composition in the oxidation of phenyl-*tert*-butylcarbinol⁷ by chromium(VI). In the absence of added cerium ion, chromic acid oxidation of this substrate produces both the normal product, pivalophenone (64%), and cleavage products, benzaldehyde (36%) and *tert*-butyl alcohol. When the amount of cerium is approximately 50 times less than that of the chromium(VI), the amount of cleavage product is reduced to the minimal amount of 5%. Reduction of the cleavage reaction to one-half that without cerium present requires a [Cr(VI)] to [Ce] ratio of 10,000.

These results show that the reactive chromium(IV) species, formed in the rate-limiting step in chromic acid oxidations, can be effectively removed by reaction with very small amounts of either cerium(IV) or cerium(III). Scheme IV adequately explains our data.

Scheme IV



The combination of steps 7 and 8 with three times reaction 1 and two times reaction 5 gives eq 9, according



to which chromium(VI) is the only oxidant reacting with the organic substrate. The added cerium compounds thus act as a catalyst effecting the disproportionation of the intermediate chromium species chromium(IV) and chromium(V) into the stable valence states of chromium.

Further work is in progress and will be reported in detail.

Acknowledgment. The assistance of Mrs. Ruth Hartwick in these studies is acknowledged. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the U. S. Army Research Office (Durham) for their support of this work.

(7) Under identical conditions the second-order rate constant for oxidation of phenyl-*tert*-butylcarbinol by cerium(IV) was 150 times less than that for the corresponding chromic acid oxidation. Both benzaldehyde (62%) and pivalophenone (38%) were produced in the cerium(IV) oxidation.

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π - π^* Region Cotton Effects of Cyclic Conjugated Dienes and Enones. Interpretation in Terms of Allylic Axial Chirality Contributions¹

Sir:

Although the Cotton effects of optically active 1,3-cyclohexadienes² and heteroannular transoid con-

jugated dienes³ in the 230–280-nm (π - π^* transition) region correlate well with the helicity or chirality of the chromophore (positive when the planes of the two double bonds are skewed in a right-handed helix; negative when left-handed),⁴ heteroannular cisoid conjugated dienes apparently have had to be excluded from this treatment.⁵ Likewise, while optical rotatory dispersion (ORD) and circular dichroism (CD) curves of transoid α,β -unsaturated cyclic ketones in the same spectral region generally conform⁶ to the transoid diene chirality rule,³ they are frequently complicated by strong overlapping optical transitions of opposite sign.⁷

Similarly, a proposed extension^{6a} of the homoannular cisoid diene chirality rule² to cisoid conjugated enones, while evidently widely accepted,^{6b,7,8} has not been firmly validated. Indeed, nmr⁹ and even other ORD-CD data^{8b} (for the longer wavelength n - π^* transition) are available showing that such an extension is probably incorrect for at least two of the cases (cholest-5-en-4-one and cholest-4-en-6-one) originally cited^{6a} to illustrate it.

In this report, on the basis of new plus existing data,^{2,3,6,7} we wish to propose a fundamentally different approach to the interpretation of the π - π^* region Cotton effects of these various systems utilizing the olefin chirality concept of Yogeve, Amar, and Mazur.¹⁰ Rather than the inherent dissymmetry or chirality of the chromophore (when nonplanar), this approach considers *asymmetric perturbations of the double bond components of the chromophore through excited-state interactions with their allylic axial or pseudoaxial bonds as the primary factor controlling the sign of the Cotton effect* (but not necessarily its magnitude).¹¹

(2) (a) A. Moscovitz, E. Charney, U. Weiss, and H. Ziffer, *J. Amer. Chem. Soc.*, **83**, 4661 (1961); (b) A. W. Burgstahler, H. Ziffer, and U. Weiss, *ibid.*, **83**, 4660 (1961); (c) H. J. C. Jacobs and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, **84**, 932 (1965); (d) U. Weiss, H. Ziffer, and E. Charney, *Tetrahedron*, **21**, 3105 (1965); (e) E. Charney, *ibid.*, **21**, 3127 (1965); (f) H. Ziffer, U. Weiss, and E. Charney, *ibid.*, **23**, 3881 (1967).

(3) E. Charney, H. Ziffer, and U. Weiss, *ibid.*, **21**, 3121 (1965).

(4) A possible exception to the cisoid diene chirality rule has been reported recently by S. Bory and C. R. Engel, *Bull. Soc. Chim. Fr.*, 3043 (1970). See also P. Crabbé, *Proc. Nat. Acad. Sci. U. S. A.*, **66**, 4 (1970).

(5) Reference 2d, p 3107, and private communication from Dr. Weiss.

(6) (a) C. Djerassi, R. Records, E. Bunnenberg, K. Mislow, and A. Moscovitz, *J. Amer. Chem. Soc.*, **84**, 870 (1962); (b) J.-C. Bloch and S. R. Wallis, *J. Chem. Soc. B*, 1177 (1966); (c) cf. W. B. Whalley, *Chem. Ind. (London)*, 1024 (1962).

(7) (a) L. Velluz, M. Legrand, and R. Viennet, *C. R. Acad. Sci., Paris*, **261**, 1687 (1965); (b) K. Kuriyama, M. Moriyama, T. Iwata, and K. Tori, *Tetrahedron Lett.*, 1661 (1968); (c) H. Ziffer and C. H. Robinson, *Tetrahedron*, **24**, 5803 (1968).

(8) (a) R. E. Ballard, S. F. Mason, and G. W. Vane, *Discuss. Faraday Soc.*, **35**, 43 (1963); (b) G. Snatzke, *Tetrahedron*, **21**, 413, 439 (1965); (c) P. Crabbé, "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," Holden-Day, San Francisco, Calif., 1965, pp 194–196; (d) L. Velluz, M. Legrand, and M. Grosjean, "Optical Circular Dichroism," Academic Press, New York, N. Y., 1965, pp 131–134; (e) J. H. Brewster, *Top. Stereochem.*, **2**, 64 (1967); (f) C. W. Deutsche, D. A. Lightner, R. W. Woody, and A. Moscovitz, *Annu. Rev. Phys. Chem.*, **20**, 419 (1969).

(9) D. Lavie, S. Greenfield, Y. Kashman, and E. Glotter, *Israel J. Chem.*, **5**, 151 (1967); cf. R. F. Zürcher, *Helv. Chim. Acta*, **46**, 2054 (1963).

(10) A. Yogeve, D. Amar, and Y. Mazur, *Chem. Commun.*, 339 (1967). Although certain obvious limitations in connection with nonconjugated exomethylene steroids have been found [M. Fétizon and I. Hanna, *ibid.*, 462 (1970)] for this rule and its octant counterpart [A. I. Scott and A. D. Wrixon, *Tetrahedron*, **26**, 3695 (1970)], it has proved extremely useful for a number of endocyclic applications [e.g., see A. W. Burgstahler, J. N. Marx, and D. F. Zinkel, *J. Org. Chem.*, **34**, 1550, 3716 (1969)].

(11) The comparatively large amplitudes reported^{2a,c,d} for the ORD curves of such dienes as pyro- and isopyrocalfiferol, which molecular models indicate have a nearly planar chromophore, seem to contradict the proposed^{2e,8f} dependence of the intensity of the Cotton effect on the

(1) Part of a presentation at the 1970 Midwest Regional American Chemical Society Meeting, Lincoln, Neb., Oct 28–30, 1970.