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Stabilities of Trivalent Carbon Species. 3. Reduction of Organic Cations by Chromous Ion[1]

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Abstract: Several organic cations of various structural types are reduced to their corresponding free radicals or dimers by chromous ion in acidic ethanol. Second-order rate constants (L mol^{-1} s^{-1}) for the reductions in 75% ethanol, 2 N HClO$_4$ at 25 °C vary over a range of 10^4: *N*-methylacridinium, 0.02; 2,4,6-triphenylpyrylium, 0.14; sesquixanthylium, 0.6; tropylium, 2.0; flavylium, 10; 9-phenylxanthylium, 110; 9-phenylthioxanthylium, 400. A comparison of chemical reactivity with reduction potential for the organic cations (Marcus treatment) and substituent effects on the reactivity of flavylium ions suggest an outer-sphere activated complex in the electron-transfer reaction. The rate constants for chromous reductions, as log *k*, combined with pK_{R^+} values are used to determine relative stabilities of free radicals. The mechanism of chromous reduction of these cations is compared to reduction of alkyl halides.

Almost all of the information concerning stabilities of trivalent carbon species has been obtained from equilibrium or rate measurements in which these species have been formed from tetravalent precursors. However, the fundamental importance of electron-transfer processes involving organic cations, anions, and radicals has been recognized, and two types of experiments have been useful: measurement of the ionization potentials of free radicals in the gas phase by mass spectrometry and electrochemical measurement of redox potentials in solution. The first method has generally been limited to simpler species, e.g., allyl and benzyl, while the latter method requires species which are reasonably stable, e.g., triphenylmethyl, and there have been few systems amenable to both types of investigation.

In this paper we present the results of a kinetic study of the one-electron reductions of a series of organic cations of various structure by chromous ion. The reductions proceed through an outer-sphere activated complex, and the rate constants are related simply to the equilibrium constants for the electron-transfer reaction.

$$R^+ + Cr^{2+} \rightarrow R\cdot + Cr^{3+} \tag{1}$$

$$R\cdot \rightleftharpoons 0.5R_2 \tag{2}$$

It is possible, therefore, to use relatively simple kinetic measurements to obtain information about the stabilities of free radicals relative to their corresponding cations.

Conant and his co-workers[4] investigated metal ion reductions of organic cations more than 50 years ago and found the principal organic products to be dimers of the first formed radicals or the radicals themselves if they were sufficiently stable. Conant used the reaction in potentiometric titrations, but he did not measure the rates of the redox reactions.

A review of one-electron reductions of organic cations has been published recently.[5]

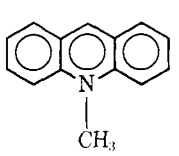
We reported earlier that in aqueous solution tropylium cation is quantitatively reduced to ditropyl by chromous ion,[6] and Okamoto and his co-workers subsequently studied the reaction in detail.[7] Okamoto also investigated the reduction of tropylium cations with zinc[7a,8] and cyclopropenium cations with chromous ion.[9] In their study of the reduction of tropylium and cyclopropenium cations, Okamoto and co-workers used aqueous hydrochloric acid as solvent. They showed that chloride ion acts as a bridging group in the electron transfer and the rate of reduction by chromous ion increases toward a maximum with increasing chloride concentration. They concluded that in the absence of a bridging anion, a water molecule in the coordination sphere of chromous ion serves as a bridge for the electron transfer.[7c]

We have examined the chromous ion reduction of a series of organic cations of differing structures and reactivity in the absence of bridging anions: *N*-methylacridinium, **1**; 2,4,6-triphenylpyrylium, **2**; sesquixanthylium, **3**; tropylium, **4**; flavylium, **5**; 9-phenylxanthylium, **6**; 9-phenylthioxanthylium, **7**.

Table I. Salts of Organic Cations

Cation	Anion	Lit. procedure	Mp, °C	Lit. mp, °C	Ref
1	CH_3OSO_3	*a*	200-204 dec		*b*
2	BF_4	*c*	230	228-229	*c*
4	BF_4	*d*	200 dec	200 dec	*d*
5a	ClO_4	*e*	189-191 dec	186-191 dec	*f*
5b	ClO_4	*g*	203-204 dec	196-197 dec	*g*
5c	ClO_4	*g*	176-177 dec		*h*
5d	ClO_4	*g*	219-221 dec	227 dec	*i*
5e	ClO_4	*g*	199-201 dec		*j*

[a] A. Kaufman and A. Albertini, *Chem. Ber.*, **42**, 1999 (1909); [b] Although this salt is not a new compound (cf. A. Albert, "The Acridines", 2d ed, St. Martin's, New York, N.Y., 1966, p 344), we have not found its melting point in the literature. The UV-visible spectrum of the salt corresponds to that reported for the perchlorate: S. F. Mason, *J. Chem. Soc.*, 2437 (1960). [c] K. Dimroth, *Angew. Chem.*, **72**, 331 (1960). [d] K. Conrow, *Org. Synth.*, **43**, 101 (1963). [e] R. LeFevre, *J. Chem. Soc.*, 2771 (1929). [f] A. Lowenbein, *Chem. Ber.*, **57**, 1517 (1924). [g] C. Michaelidis and R. Wizinger, *Helv. Chim. Acta*, **34**, 1761 (1951). [h] Anal. Calcd for $C_{16}H_{13}O_6Cl$: C, 57.07; H, 3.86; Cl, 10.53. Found: C, 57.15; H, 4.02; Cl, 10.35. [i] M. Mercier, J. Chopin, C. Martzer, Ng. Ph. Buu-Hoi, and N. D. Xuong, *Bull. Soc. Chim. Fr.*, 702 (1958). [j] Anal. Calcd for $C_{15}H_{10}O_5Cl_2$: C, 52.80; H, 2.93; Cl, 20.80. Found: C, 53.02; H, 3.04; Cl, 20.67.



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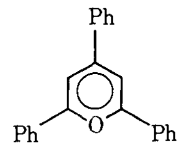

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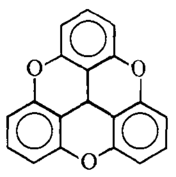

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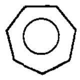

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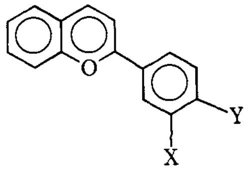
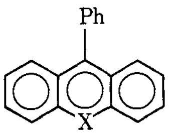


5a, X = H; Y = H
b, X = H; Y = OCH_3
c, X = OCH_3; Y = H
d, X = H; Y = CH_3
e, X = H; Y = Cl



6, X = O
7, X = S

Experimental Section

Organic Cations. Some of the organic cations were prepared as salts and some were generated as perchlorates by dissolving their corresponding alcohols in aqueous or alcoholic perchloric acid. Sesquixanthydrol, mp 200 °C, the precursor of **3**, was kindly provided by Professor J. C. Martin, and 9-phenylxanthydrol, mp 159-160 °C, the precursor of **6**, and 9-phenylthioxanthydrol, mp 102-104 °C, the precursor of **7**, were provided by Dr. N. G. Thame. Table I lists the cations which were prepared as salts.

Organic Products from Cation Reductions. Aqueous acidic solutions of the cations were prepared and added to solutions of $CrCl_2$ or $Cr(ClO_4)_2$ under oxygen-free nitrogen. Cations **1**, **4**, and **5a** yielded dimers which had been reported previously and which were isolated in excellent yield by extraction of the aqueous mixture with ether or pentane. Cation **1** was reduced to 10,10′-dimethyl-9,9′-biacridane, mp 270 °C (lit.[10] 280 °C), **4** was reduced to ditropyl, mp 58-59 °C (lit.[11] 61 °C), and **5** was reduced to 4,4′-bis(flav-2-ene), mp 167-168 °C (lit.[12] 167-168 °C).

Reduction of Cation 7. A solution of 9-phenylthioxanthydryl perchlorate was prepared by dissolving 0.35 g of 9-phenylthioxanthydrol in 25 mL of aqueous perchloric acid. After deaerating the solution with nitrogen, 2.4 mL of 1.05 N $Cr(ClO_4)_2$ was added. A brown precipitate formed which dissolved in ether to give a deep red solution. When air was admitted to the solution, the red color immediately disappeared and white crystals began to form. The product, mp 170 °C dec, is assumed to be di-9-phenylthioxanthydryl peroxide, lit. mp 175-180 °C dec,[13] which had previously been prepared from the chloride and molecular silver (presumably forming the free radical) followed by reaction with oxygen.

Stoichiometry of the Reaction. Chromous perchlorate solutions were prepared from electrolytic chromium chips (Varlacoid Chemical Co.) and analyzed by titration with ceric ammonium nitrate, according to the procedure of Kochi and Buchanan.[14a] Solutions were kept in serum-cap bottles and transferred by syringe. The stoichiometry of the reductions was determined by allowing an excess of $Cr(ClO_4)_2$ to react with the organic salt and titrating excess chromous ion. It was found that 1 mol of organic cation is reduced by 1 mol of chromous perchlorate.

Kinetics. The rates of the reductions were measured spectrophotometrically, under oxygen-free conditions. A solution of the organic salt in 75% ethanol, 2 N $HClO_4$ was deaerated by bubbling oxygen-free nitrogen through the solution for 30 min. The solution was then introduced into a weighed cylindrical spectrophotometer cell (1- or 10-cm path length) which was stoppered with a self-sealing serum cap. The cell was placed in the thermostated cell compartment of a Cary 14 spectrophotometer and allowed to come to thermostatic equilibrium (25.0 °C). The serum cap was fitted with a venting needle to allow introduction of the $Cr(ClO_4)_2$ solution. The required volume of standardized $Cr(ClO_4)_2$ solution, which was at the same temperature as the cell, was added to the cell with a calibrated syringe. After the solution was added, the venting needle was removed and the cell was shaken well and returned to the cell compartment. The entire addition and mixing procedure was completed within 10 s. In all cases, a large excess of $Cr(ClO_4)_2$ was used and the disappearance of absorption of the organic cation was recorded. After the reaction was complete, the filled cell was weighed and the density of the solution determined. The volume of the solution and the concentration of chromous ion were calculated. Pseudo-first-order kinetics was observed in all cases and second-order rate constants were calculated.

The kinetics measurements were carried out at the following wavelengths (nm): **1**, 415, 445; **2**, 380, 410; **3**, 450, 475; **4**, 280; **5a**, 398; **5b**, 443; **5c**, 385; **5d**, 405; **5e**, 395; **6**, 375; **7**, 385.

Reduction Potentials. The reduction potentials of the cations were measured by means of rapid-scan triangular wave cyclic voltammetry by Dr. W. C. Flythe, using a Chemtrix Model SSP-2 instrument.[15] The cations were reduced at a hanging mercury drop electrode in the same solvent used for the rate measurements, and potentials are referred to a $Hg|Hg_2SO_4$-17 M H_2SO_4 electrode. A platinum wire counter electrode was used. With the exception of cation **3**, the reductions at high scan rates (100 V/s) approached reversibility.

Results and Discussion

The reaction of chromous ion with cations **1**,[10] **4**,[11] and **5**[12] in aqueous acid produces dimers which were previously obtained by using other reducing agents (e.g., metallic zinc). Conant and Sloan reported that free radicals were produced from cations **2** and **6** by the action of chromous chloride.[4] Martin and his co-workers[16] have reported that cation **3** is converted to a dimer by reduction by chromous ion in sulfuric-acetic acid mixtures. Cation **7** was reduced with chromous ion in aqueous acid to give a substance whose ether solution was deep red and which reacts rapidly with oxygen to give white crystals whose decomposition point agrees with that of di-9-phenylthioxanthyl peroxide.[13] We assumed that this behavior, in analogy to the behavior of the structurally related ion **6**, indicated the formation of the 9-phenylthioxanthyl free radical and its subsequent reaction with oxygen. However, recently Price and his co-workers[17] investigated one-electron reductions of **7** in nonaqueous media and obtained a red oil which gave a green oil by elution with benzene through an alumina column. The green oil is evidently a dimer with a sulfur-sulfur linkage. Although we cannot account for the difference in reduction products, we assume that chromous ion reduces cation **7** via a one-electron reduction, as it does with cations **1-6**.

Table II. Reduction of Organic Cations by $Cr(ClO_4)_2$ in 75% Ethanol, 2 N $HClO_4$, 25 °C

Cation	$[R^+]$, M	$[Cr(ClO_4)]$, M	k, $M^{-1}\ s^{-1}$	k_{av}, $M^{-1}\ s^{-1}$	Log k	$-E$[a]	Log K_5	pK_{R^+}
1	4.1×10^{-5}	4.1×10^{-2}	0.020	0.020 ± 0.003	−1.70	0.92[b]	0	9.75[c]
	4.1×10^{-5}	4.1×10^{-2}	0.017					
	4.1×10^{-5}	2.9×10^{-2}	0.023					
2	3.5×10^{-5}	8.3×10^{-3}	0.13	0.14 ± 0.01	−0.87	0.83	1.51	
	3.5×10^{-5}	1.7×10^{-2}	0.15					
3	6.7×10^{-6}	3.4×10^{-3}	0.59	0.60 ± 0.03	−0.22	0.68	4.03	9.05[d]
	6.7×10^{-6}	5.1×10^{-3}	0.63					
4	1.2×10^{-4}	9.3×10^{-3}	2.0	2.0	+0.30	0.69	3.87	4.7[e]
5	4.3×10^{-6}	1.7×10^{-3}	11	10 ± 1	+1.00	0.60	5.38	
	4.3×10^{-6}	1.4×10^{-3}	9.1					
	4.3×10^{-6}	8.4×10^{-4}	10					
6	2.1×10^{-6}	5.8×10^{-4}	109	110 ± 1	2.04	0.48	7.39	1.10[f]
	2.6×10^{-6}	8.6×10^{-4}	110					
	4.4×10^{-6}	3.9×10^{-4}	109					
7	4.7×10^{-6}	3.4×10^{-4}	474	404 ± 70	2.60	0.44	8.06	0.10[g]
	4.2×10^{-6}	3.4×10^{-4}	405					
	4.2×10^{-6}	3.4×10^{-4}	332					

[a] Reduction potential, volts vs. $Hg|Hg_2SO_4$–17 M H_2SO_4, scan rate 100 V/s. [b] Extrapolated value from measurements in 90% ethanol, 0.5 N $HClO_4$. [c] R. J. Goldacre and J. N. Phillips, *J. Chem. Soc.*, 1724 (1949). [d] J. C. Martin and R. G. Smith, *J. Am. Chem. Soc.*, **86**, 2252 (1964). [e] W. V. E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954). [f] R. A. Diffenbach, Ph.D. Thesis, The Pennsylvania State University, 1966. [g] N. G. Thame, Howard University, Ph.D. Dissertation, 1970.

The simplest scheme which accounts for the formation of free radicals and dimeric products is the electron-transfer reaction (eq 1) and the radical association (eq 2). However, an alternative mechanism is suggested by the elegant experiments of Kochi and Davis[14b] on the chromous ion reduction of benzyl halides. In aprotic media, the only reduction product is dibenzyl, and an organochromium ion is a reaction intermediate. In the reductions described here, dimers could arise from an organochromium ion as follows:

$$R^+ + Cr^{2+} \rightarrow R\cdot + Cr^{3+} \qquad \text{slow}$$

$$R\cdot + Cr^{2+} \rightarrow RCr^{2+} \qquad \text{fast}$$

$$RCr^{2+} + R^+ \rightarrow RR + Cr^{3+} \qquad \text{fast}$$

The presence of an organochromium ion as an intermediate is not reasonable in our experiments because, as Kochi and Davis have shown, the principal product (>98%) of chromous ion reduction of benzyl halides in protic solvents is toluene, formed from protonolysis of the organochromium ion:

$$RCr^{2+} + H^+ \rightarrow RH + Cr^{3+} \qquad \text{fast}$$

Since no R–H was observed, even in highly acidic solutions, an organochromium ion intermediate cannot be responsible for the formation of R–R.

Kinetics Measurements. The solvent which was used for the kinetics measurements, 75% ethanol (by volume), 2 N $HClO_4$, was chosen because all reactants and products are sufficiently soluble and the cations are not converted to alcohols or ethers. The exact coordination of the chromous or chromic ions is not known in this solvent system.

The second-order rate constants for the chromous ion reductions of cations **1**–**7**, which vary over a range of 10^4, are listed in Table II. The rate constant for cation **7**, about 400 $M^{-1}\ s^{-1}$, is probably the maximum which could be determined using our spectrophotometric technique.

The reduction potentials of the cations were determined by rapid-scan triangular wave cyclic voltammetry, and the potentials are listed in Table II. All of the reduction potentials (midpoint of cathodic and anodic maximum) were measured in the same solvent system as the rate measurements, with the exception of cation **1**. In 2 N $HClO_4$, the cyclic voltammograms indicate that the *N*-methylacridinyl radical is protonated before reoxidation and a reversible reduction potential for **1** cannot be measured. However, reversible behavior was observed in 90% ethanol, 0.5 N $HClO_4$, and the potential observed in that solvent was extrapolated to 75% ethanol, 2 N $HClO_4$ by comparing the shifts in potential for cations **2** and **4** in the two solvent systems and assuming that a similar shift would be seen for cation **1** in the absence of protonation of the radical. Because of the slow electron-transfer reaction, the chromous–chromic potential could not be measured by cyclic voltammetry.

It seems reasonable to assume that the reductions proceed via an outer-sphere activated complex because there are no ligands on the cations which could be involved in bridging with the chromous ion. According to Marcus' theory of electron-transfer reactions which proceed via an outer-sphere activated complex[18] an approximate relation between k, the rate constant for chromous ion reduction of an organic cation, and the self-exchange rate constants k_R and k_{Cr}

$$R^+ + R\cdot \xrightarrow{k_R} R\cdot + R^+$$

$$Cr^{2+} + Cr^{3+} \xrightarrow{k_{Cr}} Cr^{3+} + Cr^{2+}$$

and equilibrium constant for the electron-transfer reaction K is given by

$$k = (k_R k_{Cr} K)^{1/2} \tag{3}$$

None of the terms on the right side of eq 3 have been measured directly in the solvent used for the cation reductions, but some reasonable estimates can be made. The only reported value of k_R is for the triphenylmethyl cation–radical exchange in CF_3CO_2H-CH_3CO_2H mixture at 25 °C, $1.3 \times 10^8\ M^{-1}\ s^{-1}$.[19] This value is similar to other electron exchange reactions of organic molecules which have extended π-electron systems, such as aromatic hydrocarbons and their corresponding radical ions. The "intrinsic barrier" to electron transfer[20] is very small in these systems because the molecular geometries of the reduced and oxidized species are presumably identical. On the other hand, k_{Cr} is small, $2 \times 10^{-5}\ M^{-1}\ s^{-1}$ in water, 1 N $HClO_4$,[21] as considerable molecular reorganization accompanies the electron transfer.

If all values of k_R are identical in the group of cations studied here, then eq 3 can be recast as eq 4.

$$\log k = 0.5 \log K + \text{constant} \tag{4}$$

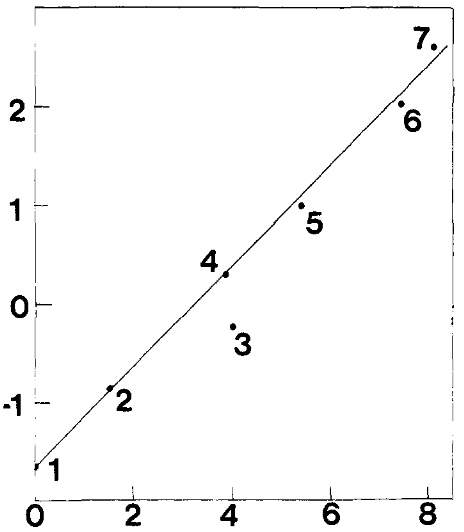


Figure 1. Marcus plot for reduction of organic cations: abscissa, log K_5; ordinate, log k. Numbers for points correspond to cations as denoted in text.

Table III. Reduction of Substituted Flavylium Cations by $Cr(ClO_4)_2$ in 75% Ethanol, 2 N $HClO_4$, 25 °C

Cation	Concn cation × 10^6 M	Concn Cr^{II} × 10^3 M	k, M^{-1} s^{-1}	Av k	σ^{+a}
5a	4.3	1.4	9.10	9.62	0
		1.4	9.87		
		0.84	9.90		
5b	3.3	1.4	1.81	1.67	−0.78
		2.2	1.67		
		2.8	1.57		
5c	3.3	0.77	10.4	10.8	+0.047
		1.2	11.1		
5d	4.7	1.4	4.17	4.0	−0.31
		2.8	4.04		
		0.83	3.76		
5e	4.1	8.4	15.2	14.6	+0.114
		1.1	14.1		
		1.7	12.4		
		0.78	16.5		

[a] H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

In order to test this equation in the absence of the Cr^{2+}-Cr^{3+} potential, equilibrium constants K_5 were calculated for reaction 5 from the cation reduction potentials.

$$R^+ + \mathbf{1}\cdot \overset{K_5}{\rightleftharpoons} R\cdot + \mathbf{1}^+ \qquad (5)$$

Values of log K_5 are listed in Table II, and the correlation between log k and log K_5 is shown in Figure 1. The slope of the correlation line, 0.52 ± 0.03, is in excellent agreement with the theoretical value of 0.5. The agreement with Marcus' equation suggests that the reductions proceed through an outer-sphere mechanism and that the values of k_R are similar in the series of cations. The deviation of cation **3** from the linear correlation is ascribed to the error in its reduction potential. The observed deviation is expected if the radical formed by electrochemical reduction dimerizes rapidly so that R^+-$R\cdot$ equilibrium is not established.

Substituent Effects on Reduction of Flavylium Ions. The series of flavylium cations **5a–e** (as perchlorates) was reduced with chromous ion, and the second-order rate constants were determined spectrophotometrically. The 4′-nitro derivative (**5**, X = H; Y = NO_2) reacts with chromous ion with apparent reduction of the nitro group rather than reductive dimerization of the cation. The second-order rate constants are listed in Table III, and a linear correlation of log k vs. σ^+ is shown in Figure 2. The modest value of ρ, 1.03, seems reasonable, since most of the positive charge is delocalized in the benzopyryium ring system and the effect of substituents in the phenyl ring is relatively unimportant.[22]

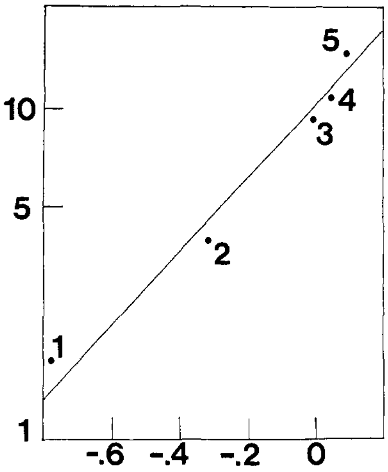


Figure 2. Substituent effects in reduction of flavylium ions: abscissa, σ^+ values; ordinate, k, plotted logarithmically. Numbers for points correspond to cation **5** as follows: 1 = **5b**; 2 = **5d**; 3 = **5a**; 4 = **5c**; 5 = **5e**.

Okamoto and co-workers found a similar correlation for the chromous reduction of substituted phenyltropylium ions in aqueous HCl. In this system, a better correlation was found when σ values, rather than σ^+ values, were used, and ρ = +1.31.[7e] In zinc reduction of tropylium ions in which substituents are bonded directly to the ring, log k_{rel} correlates fairly well against σ_p and poorly against σ^+, with ρ = +4.0.[8a] The greater reaction constant for substituents connected directly to the tropylium ring is expected, but it is not clear why different substitent constants are needed for the tropylium and flavylium ions.

It should be noted that a similar substituent effect has been observed by Sutin and his co-workers[23] in the oxidation of 5-substituted tris-1,10-phenanthrolineiron(II) by Ce(IV), and the reduction of 5-substituted tris-1,10-phenanthrolineiron(III) by Fe(II). The positive charge resides mainly on the central metal atom and adjacent nitrogen atoms, and ρ values, obtained by correlation with σ_p values and corrected for the presence of three equivalent substituents, are −0.63 in the former reaction and 0.62 in the latter. Thus the reductions of the flavylium and tropylium cations bear a close resemblance to the reactions of metal ions which are known to proceed via an outer-sphere mechanism. In contrast, the rate constants for reduction of substituted benzyl halides by chromous ion,[14b] which involves ligand transfer and the oxidation of substituted tris-1,10-phenanthrolineiron(II) by peroxydisulfate,[24] which does not proceed via an outer-sphere mechanism, do not show correlation with substituent constants.

Significance of Log *k*. The rate constants for chromous ion reduction of organic cations reflect the free-energy differences between the cations and their corresponding free radicals, as indicated by the Marcus plot (Figure 1).[25] By comparing log k with estimations of cation stabilities, it is possible to derive relative stabilities of free radicals.[26] If it is assumed that precursor alcohols have the same energy, the pK_{R^+} values[27] may be used as a measure of relative cation stabilities, and eq 5 may be compared to eq 6.

$$R^+ + \mathbf{1}OH \overset{K_6}{\rightleftharpoons} ROH + \mathbf{1}^+ \qquad (6)$$

$$\log K_6 = pK_{R^+}(\mathbf{1}) - pK_{R^+}(R)$$

It can be seen that if all of the free radicals had the same energy, log k and log K_5 would also reflect cation stability and log k would be proportional to pK_{R^+} (from eq 4 and 5, log $k = -(0.5)$pK_{R^+} + constant). The data in Table II indicate that the free radicals have greatly differing stabilities, as there is no correlation between log k and pK_{R^+}. Especially noteworthy is the destabilized (antiaromatic) triphenylcyclopropenyl radical, already discussed by Breslow,[28] and the stabilized sesquixanthydryl radical.

The pK_{R^+} values for tropylium (4.7) and triphenylcyclopropenyl cations (3.2) differ by 1.5, but the difference in log k for chromous reduction in 10% aqueous HCl is 5.4[9] because of the high energy of the triphenylcyclopropenyl radical relative to the tropyl radical. Information about the sesquixanthydryl radical is difficult to obtain because of its propensity to dimerize, even at high temperature.[16] The rapid dimerization precludes accurate reduction potential measurements for **3** or other measurements on the free radical itself. However, a comparison of log k with pK_{R^+} yields information about the relative stability of this radical. For example, if the sesquixanthydryl radical had the same energy as the tropyl radical, log k would reflect the difference in pK_{R^+} values (0.5×4.30) and log k for **3** would be 2.15 units more negative than log k for **4**. It is only 0.52 units more negative, and the difference, $2.15 - 0.52 = 1.63$ units, in log k is equivalent to a difference in log K_5 of 3.26, which at 25 °C is a difference in radical stability of 4.2 kcal/mol, favoring sesquixanthydryl radical. Thus, within the limits of the assumptions concerning the pK_{R^+} values and the approximate Marcus equation, information about the relative stability of the sesquixanthydryl radical may be obtained easily from standard kinetics techniques. Obviously, such information can only by derived for those cations for which pK_{R^+} can be measured, so that **2** and **5**, which do not form alcohols reversibly, cannot be compared with the other cations.

A discussion of the interrelation of kinetic and thermodynamic measurements of stabilities of trivalent carbon species in the gas phase and in solution will be presented soon.

Mechanisms of Chromous Ion Reductions of Ionic and Covalent Organic Compounds. Castro[29] concluded that Conant's reductions of polyarylcarbonium ions by chromous chloride were in fact reductions of polyarylcarbinyl chlorides. This conclusion was based on the failure of $CrSO_4$ to reduce the cation derived from 1,1-diphenylethylene or diphenylmethylcarbinol unless halide ion was added. Slaugh and Raley,[30] however, found that $CrSO_4$ did reduce diphenylcarbinol and triphenylcarbinol in concentrated acid to tetraphenylethane and "hexaphenylethane" (isolated as ditrityl peroxide) in the absence of halide ion, although the reaction was facilitated by the addition of halide ion. The stereochemistry of the dimers formed by chromous ion reduction of α-phenylethyl halides suggested that free radicals were produced which coupled immediately, according to Castro and Kray,[31] but Slaugh and Raley[30] were unable to trap free radicals in similar reductions. The experiments of Kochi and co-workers[14] indicate that the most likely mechanism for the reduction of benzyl halides by chromous ion involves the organochromium ion as shown:

$$ArCH_2X + Cr(II) \xrightarrow{\text{slow}} ArCH_2\cdot + CrX^{2+}$$

$$ArCH_2\cdot + Cr(II) \xrightarrow{\text{fast}} ArCH_2Cr^{2+}$$

$$ArCH_2Cr^{2+} + H^+ \rightarrow ArCH_3 + Cr(III)$$

$$ArCH_2Cr^{2+} + ArCH_2X \rightarrow ArCH_2CH_2Ar + CrX^{2+}$$

The intermediate benzylchromium ion was detected spectrophotometrically, but a corresponding organochromium ion could not be detected in the reactions of α-phenylethyl chloride, trityl chloride, or 1-bromotrypticene.[14b]

In contrast to the reductions of benzyl halides, the reductions of organic cations described above indicate an outer-sphere mechanism for the electron transfer step (lack of RH product in acidic solution). We briefly investigated the effect of added chloride ion on the reduction of sesquixanthydryl cation **3**, because the chloride of this extremely stable cation is ionic[32] and the possibility of reduction of a covalent chloride is remote in this case. At 30 °C, the second-order rate constant for the reduction of **3** (generated from the carbinol, 6×10^{-6} M in acidic ethanol) by $Cr(ClO_4)_2$ (5.5×10^{-3} M) is 0.73 ± 0.02 $M^{-1}\,s^{-1}$ with added $LiClO_4$ (5×10^{-3} M) and 3.2 ± 0.2 $M^{-1}\,s^{-1}$ with added LiCl (5×10^{-3} M). The fourfold increase in rate constant is not unusual for outer-sphere electron transfer reactions between cations for which catalysis by halide ion has been observed.[33] As noted earlier, the same effect of rate acceleration by chloride ion was observed by Okamoto in the reduction of tropylium ion.[7c] It is of interest that added chloride ion actually retards the rate of formation of benzylchromium ion from benzyl chloride, while added $LiClO_4$ has little effect.[14b]

In summary, it appears that chromous ion reduces "free" cations by an outer-sphere mechanism with rate constants directly depending on cation-free radical free energy differences. On the other hand, covalent halides are reduced via an inner-sphere mechanism, with halide transfer from carbon to chromium. It is reasonable that benzhydryl and trityl systems may react via both mechanisms, depending on the relative concentrations of cation and covalent halide present and the rate constants for reduction of R^+ and RX. The stability of the free radical evidently determines the reactions subsequent to the electron transfer: aliphatic and benzyl radicals react with chromous ion to give organochromium ions, but more stable radicals apparently do not react with chromous ion. Inherent in this argument is the assumption that organochromium ions are readily cleaved by acid to give RH, and the absence of RH product in acidic solution implies the absence of organochromium ions.

$$\begin{tikzcd} RX \arrow[r, rightleftharpoons] \arrow[d, "Cr(II)"] & R^+ + X^- \arrow[d, "Cr(II)"'] \\ R\cdot + CrX^{2+} & R\cdot + Cr^{3+} \end{tikzcd}$$

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Oxygen Exchange Reactions of $H_2{}^{18}O$ with the Hexacarbonyl Cations of Manganese and Rhenium

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Abstract: The reactions of $[Mn(CO)_6]^+$ and $[Re(CO)_6]^+$ with labeled water are described. The carbonyl ligands in these cationic carbonyl derivatives are found to undergo facile oxygen exchange reactions with $H_2{}^{18}O$, presumably through a hydroxycarbonyl intermediate, $[M(CO)_5C(O)OH]$, to afford $[M(C^{16}O)_{6-n}(C^{18}O)_n]^+$ species. In the manganese derivative β-hydrogen transfer in the intermediate is noted with the formation of oxygen-18 enriched $HMn(C^{16}O)_{5-n}(C^{18}O)_n$ derivatives. The relative frequency for β-hydrogen transfer vs. oxygen exchange was found to be dependent on the nature of the metal center, with hydrogen transfer being retarded in the more electron-rich metal carbonyl centers such as $[Mn(CO)_5L]^+$ (L = phosphine, pyridine, CH_3CN) and $[Re(CO)_6]^+$.

Reactions of parent metal carbonyl species with hydroxide ion have been known for some time to result in the production of metal carbonyl hydride derivatives. In this manner $[HFe(CO)_4]^-$ and $[Cr_2H(CO)_{10}]^-$ have been prepared from the reaction of $Fe(CO)_5$ and $Cr(CO)_6$ with hydroxide, respectively.[1] Activated metal carbonyl derivatives similarly are reactive toward water. For example, $[Mn(CO)_6]^+$ readily reacts with water according to the overall reaction

$$[Mn(CO)_6]^+ + H_2O \rightarrow HMn(CO)_5 + H^+ + CO_2 \quad (1)$$

It has been proposed that this reaction proceeds via reduction of $[Mn(CO)_6]^+$ to $[Mn(CO)_5]^-$ which in turn hydrolyzes to $HMn(CO)_5$.[1] On the other hand, $[Re(CO)_6]^+$ is perfectly stable in water. Nevertheless, Muetterties has observed that this species exchanges oxygen with oxygen atoms in water, probably through nucleophilic attack of ^-OH on the carbonyl carbon atom to give the intermediate $Re(CO)_5COOH$.[2] Recently we have extended these studies to include stereospecific incorporation of oxygen-18 into manganese and rhenium pentacarbonyl derivatives.[3,4]

$$M(CO)_5L^+ + H_2{}^{18}O \rightarrow \{M(CO)_4(L)C(=O)^{18}OH\} \rightarrow M(CO)_4(C^{18}O)L^+ \quad (2)$$

(M = Mn, Re; L = phosphine, pyridine, CH_3CN)

Presumably proton exchange readily occurs between the two oxygen atoms in the hydroxycarbonyl intermediate species which is in chemical equilibrium with the starting material.[5]

In an effort to define more precisely the nature of these metal-bound carbon monoxide oxygen exchange reactions with water, we have studied the reactions of $[Mn(CO)_6]^+$ and $[Re(CO)_6]^+$ with $H_2{}^{18}O$.

Experimental Section

Material and Equipment. Reagent grade acetonitrile (Matheson Coleman and Bell) was purified by distillation from sodium hydride or calcium sulfate. Similarly, reagent grade hexane (Matheson Coleman and Bell) was purified by refluxing over calcium sulfate and distilled prior to use. $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ were purchased from Strem Chemical Co. $H_2{}^{18}O$ (96.5% by weight oxygen-18) was obtained from Monsanto Research Corp., Mound Laboratory, Miamisburg, Ohio.

Preparations. $[Mn(CO)_6][BF_4]$ was prepared by the published procedure of Beach and Gray.[6] Similarly, $[Re(CO)_6][BF_4]$ was synthesized in an analogous manner. $Re_2(CO)_{10}$ (1.0 g, 1.9 mmol) dissolved in 20 mL of THF was reduced under nitrogen with an excess of sodium amalgam. After stirring for 30 min the orange solution was filtered under N_2 into 5 mL of ethyl chloroformate and the solution was stirred for an additional 2 h. The cloudy orange solution was filtered under N_2 to remove the NaCl precipitate. BF_3 was slowly bubbled into the filtrate for 15 min causing a white precipitate to form. (Alternatively, an excess of $BF_3 \cdot Et_2O$ was added to the solution which was stirred for 15 min to obtain the white precipitate.) The product was filtered, washed with 20 mL of THF, and vacuum dried. The purified yield was 0.30 g or 44%.

Reactions of $[Mn(CO)_6]^+$ and $[Re(CO)_6]^+$ with H_2O. $[Mn(CO)_6][BF_4]$ (0.103 g, 0.331 mmol) was dissolved in 8.0 mL of dry acetonitrile under nitrogen and an initial infrared spectrum in the $\nu(CO)$ region was obtained in a 0.1-mm sealed solution cell. To the stirred solution at room temperature was added 0.05 mL (2.5 mmol) of 95% $H_2{}^{18}O$ using a microsyringe. The reaction was monitored by periodically withdrawing samples and observing the $\nu(CO)$ infrared spectra. A similar reaction was carried out with $[Re(CO)_6][BF_4]$. Control reactions employing $H_2{}^{16}O$ were simultaneously performed.

A heterogeneous reaction was carried out between $[Mn(CO)_6][BF_4]$ and $H_2{}^{18}O$ by adding 1.0 mL of dry hexane to a degassed sample of $[Mn(CO)_6][BF_4]$ (0.203 g, 0.65 mmol) followed by the addition of 0.10 mL (5.0 mmol) of 95% $H_2{}^{18}O$. The extent of oxy-