

with the Pb placed equidistant from the carbon atoms should not exist since the acceptor 6p orbital of Pb(II) would not belong to the same symmetry species as the donor π orbitals of the olefin. No such complexes are known, and we have not yet succeeded in synthesizing them with either Sn(II) or Pb(II). On the other hand, such a complex should be possible with the Pb(II) placed equidistant between carbons 2 and 3 of butadiene. Experiments are currently underway to prepare such compounds.

In this structure Pb-Cl bonds are weakened to form the fourth Al-Cl bond in AlCl_4^- . On this basis one would expect anhydrous PbCl_2 to behave as a moderating cocatalyst in AlCl_3 -catalyzed alkyl halide Friedel-Crafts reactions but have little effect in AlCl_3 -catalyzed acyl halide reactions.

(34) If the aromatic-metal interaction is considered alone the binding can be considered in terms of charge-transfer theory; see R. S. Mulliken, *J. Amer. Chem. Soc.*, **74**, 811 (1952).

Unfortunately, there is no direct experimental data on this point either way.³⁵

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Registry No. $\pi\text{-C}_6\text{H}_6\text{Pb}(\text{AlCl}_4)_2 \cdot \text{C}_6\text{H}_6$, 52003-11-9.

Supplementary Material Available. A listing of structure factors will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-2429.

(35) G. A. Olah, "Friedel Crafts and Related Reaction," Vol. 1, G. A. Olah, Ed., Interscience, New York, N. Y., 1963, p 259.

Contribution from the Chemistry Department,
Nuclear Research Centre Negev, Beer Sheva, Israel

Chromium-Carbon Bonds in Aqueous Solutions. A Pulse Radiolytic Study

H. COHEN and D. MEYERSTEIN*

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The specific rates of reaction of 16 aliphatic radicals with $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ were determined. The absorption spectra due to the chromium-carbon bonds in the products of these reactions were measured. The specific rates of aequation of these complexes as a function of pH were determined. The effects of the structure of the aliphatic radicals on these spectra and specific rates of reactions are discussed in detail. It is shown that chromium induces water elimination when a β -hydroxyl group is present.

The products of reaction of a series of carbon free radicals with several transition metal complexes in their lower oxidation states were shown to contain carbon-to-metal bonds.¹ The specific rates of reaction of several aliphatic radicals with $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ in aqueous solutions were recently measured, using the pulse radiolytic technique.² It was suggested that a major factor in determining the specific rate of this reaction is the probability of locating the unpaired electron on a given carbon atom. It seemed of interest to check this conclusion by measuring the specific rates of reaction of a larger series of free radicals with $\text{Cr}(\text{H}_2\text{O})_6^{2+}$.

Further it seemed that the pulse radiolytic technique might permit observation of the uv spectra of such chromium-carbon compounds $\text{Cr}^{\text{III}}(\text{H}_2\text{O})_5\text{RH}$. Because of the experimental techniques used in other studies,^{1b,f} the spectra of only relatively stable compounds were reported, and for most of them, only at $\lambda > 300$ nm. We hoped that measurement of a large series of such compounds would help in elucidating the origin of the bands due to the chromium-carbon bonds.

Finally, it seemed of interest to study the kinetics of the

cleavage reaction of the chromium-carbon bonds. The data available suggest that the mechanism of this reaction is heterolytic or homolytic for different chromium-carbon compounds.^{1c,f,3}

Experimental Section

Materials. All organic solutes used were reagent grade chemicals, supplied by Fluka, Merck, or Hopkin Williams, and were used without further purifications. The perchloric acid used, 70% HClO_4 Pro-analysis, was supplied by Merck. All the water used was triply distilled.

Chromium(II) perchlorate solutions were prepared by dissolution of Spectrograde chromium metal, Johnson Matthey, in 1.0 M HClO_4 under an argon atmosphere. When solutions at pH > 2 were required, excess chromium metal was introduced into 0.2 M HClO_4 . These solutions were diluted after no further hydrogen evolution was observed. The pH's of the latter solutions were measured under an argon atmosphere. The vessel used is shown in Figure 1. The argon used was bubbled through a washing bottle containing a concentrated $\text{Cr}(\text{ClO}_4)_2$ solution before it entered the reaction vessel. The argon was bubbled through the 5/20 ground joint A into the solution while stopcock B was closed and stopcock C was open. The solutions thus prepared contained $(2-100) \times 10^{-3}$ M $\text{Cr}_{\text{aq}}^{2+}$ and less than 5% of $\text{Cr}_{\text{aq}}^{3+}$ as determined by the epr technique.

Procedure. The chromium(II) solutions were transferred into 100-ml all-glass syringes (joined to the preparation vessel at the ground joint A) by applying argon pressure through stopcock B while stopcock C was closed. Portions of 5-20 ml of these chromium(II) solutions were transferred into another 100-ml syringe containing a deaerated argon-saturated solution of the required organic solute and perchloric acid. These solutions were transferred into the irradiation cells.

(1) (a) F. A. L. Anet and E. Leblanc, *J. Amer. Chem. Soc.*, **79**, 2649 (1957); (b) J. K. Kochi and D. D. Davis, *ibid.*, **86**, 5264 (1964); (c) J. K. Kochi and D. Buchanan, *ibid.*, **87**, 853 (1965); (d) R. G. Coombes, M. D. Johnson, and N. Winterton, *J. Chem. Soc. A*, 7029 (1965); (e) R. G. Coombes and M. D. Johnson, *ibid.*, 177 (1966); (f) W. Schmidt, J. H. Swinehart, and H. Taube, *J. Amer. Chem. Soc.*, **93**, 1117 (1971); (g) T. S. Roche and J. F. Endicott, *ibid.*, **94**, 8622 (1972); (h) J. Halpern and J. P. Maher, *ibid.*, **87**, 5361 (1965); (i) H. E. DeLa Mare, J. K. Kochi, and F. F. Rust, *ibid.*, **85**, 1437 (1963).

(2) H. Cohen and D. Meyerstein, *J. Chem. Soc., Chem. Commun.*, 320 (1972).

(3) A. R. Schmidt and T. W. Swaddle, *J. Chem. Soc. A*, 1927 (1970).

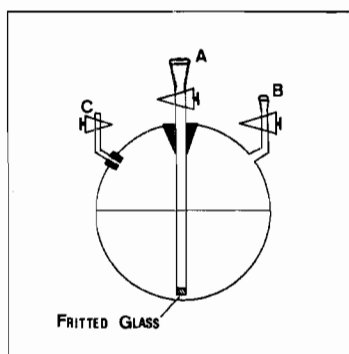


Figure 1. The vessel used for $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ preparations.

Irradiations. The pulse radiolytic experiments were carried out using 0.1–1.0- μsec , 5-MeV, 200-mA pulses from the linear electron accelerator at the Hebrew University of Jerusalem. The dose per pulse was $(1-10) \times 10^{20}$ eV l^{-1} . The irradiation cell was 4 cm long, the analyzing light passing three times through the cell. The experimental setup in Jerusalem and the method used for evaluating the results have been described elsewhere in detail.⁴⁻⁶

The absorption spectra of all the $\text{Cr}^{\text{III}}(\text{H}_2\text{O})_5\text{RH}$ compounds were measured by the pulse radiolytic technique. The absolute molar absorption coefficients were determined by assuming that the yield of the $\text{Cr}^{\text{III}}(\text{H}_2\text{O})_5\text{RH}$ formed is equal to the $\text{Fe}(\text{CN})_6^{3-}$ yield formed by an identical pulse in 1×10^{-3} M $\text{K}_4\text{Fe}(\text{CN})_6$ solutions saturated with N_2O . The latter yield was determined by measuring the absorption at 420 nm where $\epsilon^{420}_{\text{Fe}(\text{CN})_6^{3-}}$ is $1000 \text{ M}^{-1} \text{ cm}^{-1}$.

The rates of formation of the $\text{Cr}^{\text{III}}(\text{H}_2\text{O})_5\text{RH}$ compounds were measured at different wavelengths, chosen so that the difference in the molar absorption coefficients between the product and the radical would be as big as possible. The kinetics of decomposition of the chromium-carbon compounds were measured by the pulse radiolytic technique only for those compounds which have a half-life shorter than 50 sec.

The γ irradiations were carried out using a ^{60}Co source with a dose rate of 2300 rads/min. The solutions were irradiated in a 4 cm long spectrophotometric Suprasil cell filled under argon atmosphere. An identical cell filled with the same solution was used as reference. The spectra of the products with half-lives longer than 5 min were thus determined by using a Cary 17 spectrophotometer. The location of the maxima by this method is more accurate than by the pulse radiolytic technique. However, the absolute absorption coefficients cannot be determined by this technique because of the partial decomposition of the compounds before the start of the measurements.

The specific rates of decomposition of the products with a half-life longer than 1 min were also determined by using the Cary 17.

Epr Measurements. Samples irradiated by a total dose of $(0.6-2) \times 10^{20}$ eV l^{-1} were transferred under argon into an epr flat quartz cell. The measurements were carried out in an X-band Varian 4500 epr spectrophotometer.

Analysis. The concentration of $\text{Cr}_{\text{aq}}^{2+}$ in the different solutions was determined by atomic absorption. A Perkin-Elmer Model 303 spectrophotometer was used. Because of the effect of the organic solutes on the results, standard amounts of $\text{Cr}_{\text{aq}}^{3+}$ were added to portions of each solution. Thus the accuracy of the determinations was kept at $\pm 5\%$.

Temperature. All the experiments were carried out at room temperature $22 \pm 2^\circ$.

Results

Spectroscopic Data. Argon-saturated solutions containing 0.15–1.0 M organic solute, 0.1–1.0 M HClO_4 , and $(1-15) \times 10^{-4}$ M $\text{Cr}_{\text{aq}}^{2+}$ were irradiated by a short electron pulse from the linear accelerator. For all the solutes studied the formation of a product, with an absorption spectrum in the 250–450-nm spectral range, was observed within several microseconds after the pulse.

(4) D. Meyerstein and W. A. Mulac, *J. Phys. Chem.*, **72**, 784 (1968).
 (5) Internal report of the accelerator laboratory, Hebrew University, Jerusalem, 1968.

(6) H. Cohen and D. Meyerstein, *J. Amer. Chem. Soc.*, **93**, 4179 (1971).

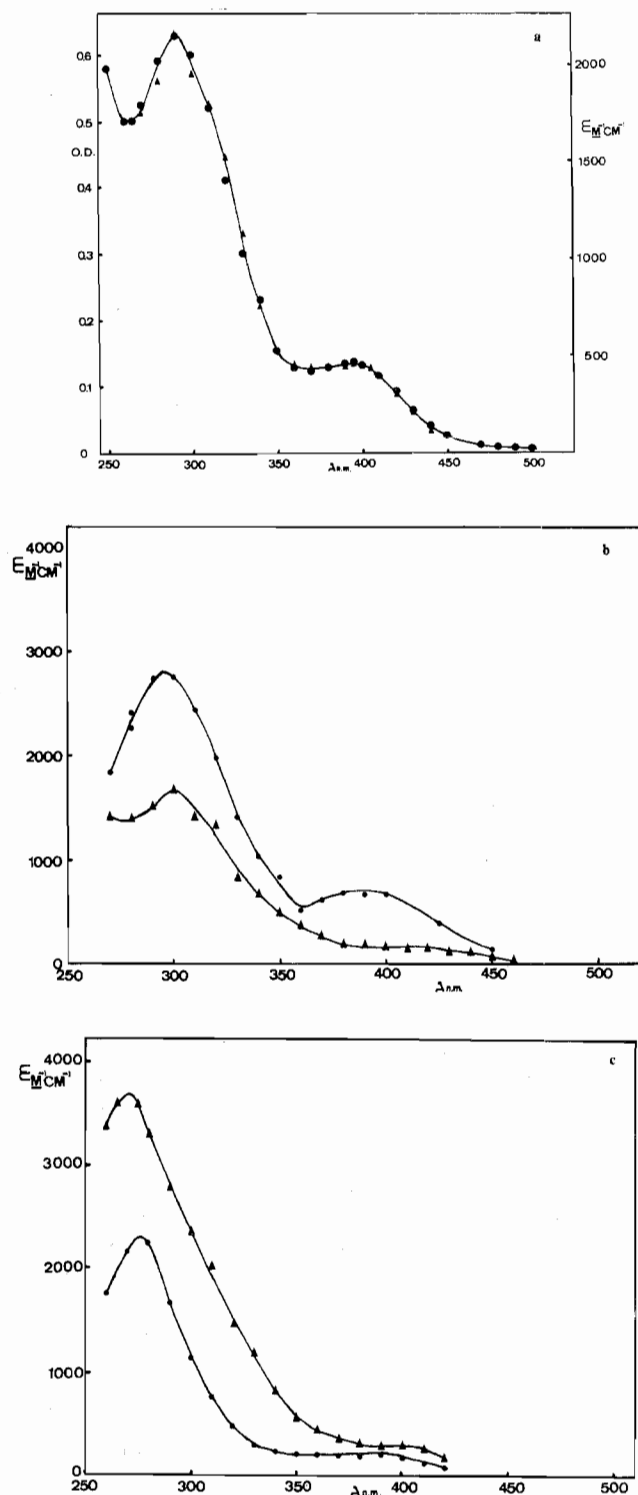
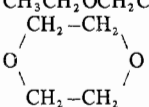
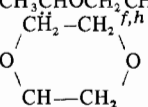


Figure 2. Absorption spectra of some chromium-carbon compounds: (a) spectrum of $(\text{H}_2\text{O})_5\text{CrCH}(\text{CH}_3)\text{OCH}_2\text{CH}_3^{2+}$; \bullet , obtained by irradiation in a ^{60}Co γ source; \blacktriangle , obtained by pulse radiolysis; (b) \bullet , spectrum of $(\text{H}_2\text{O})_5\text{CrCH}(\text{CH}_3)\text{OH}^{2+}$ obtained by the pulse radiolytic method; \blacktriangle , spectrum of $(\text{H}_2\text{O})_5\text{CrCH}(\text{OH})\text{CO}_2\text{H}^{2+}$ obtained by the pulse radiolytic method; (c) \bullet , spectrum of $(\text{H}_2\text{O})_5\text{CrCONH}_2^{2+}$ obtained by pulse radiolysis; \blacktriangle , spectrum of $(\text{H}_2\text{O})_5\text{CrCH}_2\text{N}(\text{CH}_3)\text{CONH}_2^{2+}$ obtained by pulse radiolysis.

The spectra for all the compounds studied are composed of two absorption bands. The first has its maximum, λ_{max}^1 , in the 250–310-nm range with a relatively high molar absorption coefficient ($450 < \epsilon_{\text{max}}^1 < 4000 \text{ M}^{-1} \text{ cm}^{-1}$). The second band is much weaker ($90 < \epsilon_{\text{max}}^2 < 700 \text{ M}^{-1} \text{ cm}^{-1}$), with a maximum in the 390–410-nm range. The second band

Table I. Spectral Data for Chromium-Carbon Compounds, $(\text{H}_2\text{O})_5\text{Cr}^{\text{III}}\text{RH}^{\text{a}}$

Organic solute ^d	:RH ^e	λ^1_{max} , nm	ϵ^1_{max} , $M^{-1} \text{ cm}^{-1}$	λ^2_{max} , nm	ϵ^2_{max} , $M^{-1} \text{ cm}^{-1}$
CH_3OH	: $\text{CH}_2\text{OH}^{f,h}$	282 ^c	2400	392 ^c	570
$\text{CH}_3\text{CH}_2\text{OH}$	$\text{CH}_3\text{CHOH}^{f,i}$	296 ^c	2800	396 ^c	690
$(\text{CH}_3)_2\text{CHOH}$	$(\text{CH}_3)_2\text{COH}^{f,j}$	311 ^c	2500	407 ^c	700
$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$	$\text{CH}_3\text{CH}^i\text{OCH}_2\text{CH}_3^{f,k}$	291 ^c	2200	390 ^c	490
		≤ 300	≥ 1400	390	270
CH_3COOH	: $\text{CH}_2\text{COOH}^{f,h}$	273 ^c	$>960^b$	395 ^c	$>90^b$
$\text{CH}_2(\text{OH})\text{COOH}$: $\text{CH}(\text{OH})\text{COOH}^{f,h}$	300	1650	410	180
$\text{CH}_3\text{CH}(\text{OH})\text{COOH}$	$\text{CH}_3\text{C}(\text{OH})\text{COOH}^{f,k}$	305	1500	385	230
$\text{CH}_3\text{CH}_2\text{COOH}$	$\text{CH}_3\text{CHCOOH}^{f,k}$	283 ^c	2260	395 ^c	160
$\text{CH}_2(\text{COOH})_2$: $\text{CH}(\text{COOH})_2^f$	290 ^c	$>450^b$	400 ^c	$>95^b$
$(\text{CH}_2\text{OH})_2$: $\text{CH}_2\text{CH}(\text{OH})_2^{f,l}$	≤ 270	≥ 2500	395	300
HCONH_2	: CONH_2^g	275	2300	390	210
$\text{HCON}(\text{CH}_3)_2$: $\text{CH}_2\text{N}(\text{CH}_3)\text{C} \begin{matrix} \text{O}^g \\ \parallel \\ \text{H} \end{matrix}$	270	3700	400	300
$(\text{CH}_3)_3\text{COH}$: $\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}^{f,h}$	≤ 270 310 ^c	$>2100^b$ $>530^b$	410 410 ^c	$>170^b$ $>170^b$
$(\text{CH}_3)_3\text{CCOOH}$: $\text{CH}_2\text{C}(\text{CH}_3)_2\text{COOH}^{f,h}$	< 270 256 ^c	$>2200^b$ $>1400^b$	410 393 ^c	$>310^b$ $>300^b$

^a All solutions were saturated with Ar and contained 0.15–1 M organic solute, $(1-15) \times 10^{-4} M \text{Cr}^{\text{III}}_{\text{aq}}^{2+}$, and 0.001–1.5 M HClO_4 . Measurements were made at $22 \pm 2^\circ$. The maximal standard deviation in the molar absorption coefficients is $\pm 15\%$. λ_{max} was determined by the pulse radiolytic technique, with an accuracy ± 10 nm. ^b Lower limit for the molar absorption coefficients which could be greater by a factor of 2 (see Discussion). ^c Determined by measuring with a Cary 17 spectrophotometer; accuracy ± 2 nm. ^d Organic solute used from which the radicals :RH are formed by H abstraction reactions (see Discussion). ^e The identity of the radicals formed by hydrogen abstraction from the organic solutes is known from the literature. References for the identifications are given in the footnotes. ^f The site of H abstraction by OH radicals was calculated from the relative reactivities of the different H atoms in the molecule (ref 8). ^g Reference 9. ^h Only one radical is possible. ⁱ Reference 10. ^j Reference 11. ^k It has been shown that the rate of hydrogen abstraction by H atoms from $\text{CH}_3\text{C}(\text{R}_1)(\text{R}_2)(\text{R}_3)$ is nearly independent of the substitution on the β carbon (see ref 11). This rate is $\leq 3 \times 10^5$ for all methyl groups. The specific rates of hydrogen abstraction from these compounds by H atoms are $> 6 \times 10^6$, indicating abstraction from the α position. ^l See Appendix.

appears in most cases only as a shoulder on the first band (Figure 2), and the measurement of λ_{max} is therefore less accurate.

The absorption spectrum was measured for all the solutes studied by the pulse radiolytic technique. Thus the absorption maxima were determined with an accuracy of ± 10 nm. The large error limit results from (a) the wide entrance 1.7-nm and exit 1.0-nm slits of the Bausch and Lomb monochromator used in order to obtain a high light intensity in the uv range and (b) experimental errors. The optical density was measured in 10- and 5-nm intervals near the maxima. The accuracy in the molar absorption coefficients is $\pm 15\%$; the error limit here is mainly attributed to the uncertainty in the exact yield of the radicals which are the precursors of our products. The yields are relatively accurately known only for dilute solutions.⁷

In order to obtain better spectroscopic data, the absorption spectra of all the products with half-lives longer than 5 min were measured also on a Cary 17 spectrophotometer. For all these solutions very good agreement between the spectra measured by both techniques was found (see for example Figure 2a). The absorption maxima obtained by the Cary 17 have an error limit of ± 2 nm. All the spectroscopic data are summarized in Table I.⁸⁻¹¹ Some typical spectra are shown in Figure 2. For the solutions containing *tert*-butyl alcohol or trimethylacetic acid, the absorption spectra of the products changed with time. Therefore two

sets of spectral data are given for these compounds, one for the relatively short-lived intermediate and one for the long-lived product.

The spectroscopic data obtained for $\text{Cr}^{\text{III}}(\text{H}_2\text{O})_5\text{CH}(\text{CH}_3)\text{OCH}_2\text{CH}_3$ can be compared with those earlier reported.^{1f} The locations of λ^2_{max} are identical in both studies. The agreement for the molar absorption coefficients is poorer. We find $\epsilon^2_{\text{max}} 490 \pm 75 M^{-1} \text{ cm}^{-1}$ as compared with $\epsilon^2_{\text{max}} > 360 M^{-1} \text{ cm}^{-1}$. It is believed that the difference is the result of partial decomposition of the product during the separation on the cation-exchange column.^{1f} All the other spectral data reported are new.

Kinetics of Formation of $\text{Cr}^{\text{III}}(\text{H}_2\text{O})_5\text{RH}$. The specific rates of reaction of the aliphatic radicals with $\text{Cr}(\text{H}_2\text{O})_6^{2+}$, k_5 , were measured by following the formation of the absorption due to chromium-carbon bonds. In all cases pseudo-first-order reactions were observed. At least ten solutions with different $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ concentrations from three different $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ preparations were used for the determination of each rate constant. The results are summarized in Tables II¹²⁻¹⁹ and III. No dependence of the rate constants on H_3O^+ concentration was observed.

(12) H. Zeldes and R. Livingston, *J. Chem. Phys.*, **45**, 1946 (1966).(13) T. Shiga, A. B. Boukhors, and P. Douzou, *J. Phys. Chem.*, **71**, 3559 (1967).(14) K. Eiben and R. W. Fessenden, *J. Phys. Chem.*, **75**, 1186 (1971).(15) A. L. Buley, R. O. C. Norman, and R. J. Pritchett, *J. Chem. Soc. B*, 849 (1966).(16) A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc. A*, 125 (1971).(17) G. P. Laroff and R. W. Fessenden, *J. Chem. Phys.*, **55**, 5000 (1971).(18) R. Livingston and H. Zeldes, *J. Amer. Chem. Soc.*, **88**, 4333 (1966).(19) W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 3119 (1963).

(7) M. Matheson and L. M. Dorfman, "Pulse Radiolysis," Massachusetts Institute of Technology Press, Cambridge, Mass., 1969.

(8) M. Anbar, D. Meyerstein, and P. Neta, *J. Chem. Soc. B*, 742 (1966).(9) E. Hayon, T. Ibatan, N. N. Lichtin, and M. Simic, *J. Amer. Chem. Soc.*, **92**, 3898 (1970).(10) C. Lifshitz and G. Stein, *J. Chem. Soc.*, 3706 (1962).(11) M. Anbar and D. Meyerstein, *J. Phys. Chem.*, **68**, 3184 (1964).

Table II. Specific Rates of Reaction for the Formation and Decomposition of $(\text{H}_2\text{O})_5\text{CrRH}^{2+}$ Compounds^a

RH	$k_s, M^{-1} \text{sec}^{-1}$	$k^1_{\text{h}}, \text{sec}^{-1}$	$k^2_{\text{h}}, M^{-1} \text{sec}^{-1}$	a^{H}_{α} ^d
·CH ₂ OH	1.6×10^8	7×10^{-4} ^b	3.2×10^{-4} ^b	17.6
·CH ₂ CHO ^c	3.5×10^8	$1.8^f, g$	2.2×10^2 ^g	19.0
·CH(OH)CH ₂ OH ^c	1.5×10^8 ^f			15.4
CH ₃ CHOH	7.9×10^7	1.9×10^{-3} ^b	1.2×10^{-3} ^b	15.4
(CH ₃) ₂ COH	5.1×10^7	3.3×10^{-3} ^b	4.7×10^{-3} ^b	
CH ₃ CH(OH)CH ₂ CH ₃	3.4×10^7	$\leq 5 \times 10^{-7}$ ^b	3.8×10^{-5} ^b	13.8
diox ^c	1.0×10^8	$\leq 2 \times 10^{-2}$ ^f	4.8×10^{-1}	17.2
·CH ₂ COOH	2.5×10^8	2.6×10^{-5}	$\leq 1.6 \times 10^{-6}$	21.8
·CH(OH)COOH	1.4×10^8	1.0	≤ 0.1	14.17 ^e
CH ₃ C(OH)COOH	9.2×10^7	4.7×10^2	2.8×10^2	
CH ₃ CHCOOH	1.1×10^8	2.0×10^{-3}	$\leq 3 \times 10^{-4}$	20.18
·CH(COOH) ₂	6.0×10^7	1.8×10^{-4}	5.3×10^{-4}	20.44
·CH ₂ C(CH ₃) ₂ OH	1.0×10^8	1.0×10^2 ^f	1.1×10^3	21.3
		1.4×10^{-4}	3.9×10^{-4}	
·CH ₂ C(CH ₃) ₂ COOH	1.1×10^8	1.8×10^2 ^f	6.0×10^1	
		7.8×10^{-4}	1.8×10^{-4}	

^a All solutions were saturated with argon and contained 0.15–1 *M* organic solute, $(1-15) \times 10^{-4}$ *M* $\text{Cr}_{\text{aq}}^{2+}$, and 0.1–1 *M* HClO_4 . The organic radicals which reacted with the $\text{Cr}_{\text{aq}}^{2+}$ to form the chromium–carbon compounds were generated either by the pulse radiolytic technique or by γ irradiation in a ⁶⁰Co source. Rates of hydrolysis were determined by following the disappearance of the absorption of the chromium–carbon compounds at λ^1_{max} . The organic solutes used are identical with those in Table I. The sources for the identification of the radicals are given in Table I. ^b Values taken from ref 1f. ^c Organic solute is ethylene glycol. For identification of the radical see Appendix. ^d Hyperfine constants for the epr splitting by the α hydrogens; values taken from ref 12–19. ^e Value for the dianion. ^f Values measured at 4.5 > pH > 3.0. ^g The :RH group in the complex is believed to be :CH₂CH(OH)₂; see Appendix.

Table III. Specific Rates of Reaction for the Formation and Decomposition of Chromium–Carbon Bonds with Amides^a

R	$[\text{HClO}_4], M$	$k_s, M^{-1} \text{sec}^{-1}$	$k^{\text{h}}_{\text{obsd}}, \text{sec}^{-1}$
·CONH ₂	3.5×10^{-5} ^b	6.5×10^8	2.5
	0.50		3.9×10^2
	0.84		1.3×10^3
	1.0		2.0×10^3
	1.2		2.4×10^3
·CH ₂ N(CH ₃)CH O	3×10^{-5} ^b	1.1×10^8	$\leq 2 \times 10^{-2}$
	0.11		0.061
	0.20		0.050
	0.66		0.22
	0.83		0.25
	1.2		0.33

^a All solutions were saturated with Ar and contained 1 *M* organic solute and $(1-10) \times 10^{-4}$ *M* $\text{Cr}_{\text{aq}}^{2+}$. Standard deviation is $\pm 10\%$. ^b Saturated with N₂O.

Kinetics of Hydrolysis of $\text{Cr}^{\text{III}}(\text{H}_2\text{O})_5\text{RH}$. The kinetics of the disappearance of the absorption due to the chromium–carbon bonds was always first order. For most of the reactions it was found that the observed rate constant $k^{\text{h}}_{\text{obsd}}$ depends on the H_3O^+ concentration in the manner

$$k^{\text{h}}_{\text{obsd}} = k^1_{\text{h}} + k^2_{\text{h}}[\text{H}_3\text{O}^+]$$

(see for example Figure 3). Therefore, we have measured $k^{\text{h}}_{\text{obsd}}$ at different H_3O^+ concentrations and calculated, from the results, k^1_{h} and k^2_{h} . The results are summarized in Tables II and III.

It should be noted that the disappearance of the absorption caused by the products in solutions containing *tert*-butyl alcohol or trimethylacetic acid indicated two separate steps, each obeying a first-order law. Therefore two sets of data are included in Table II for these compounds.

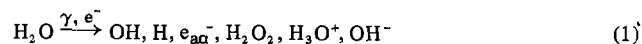
The disappearance of the absorption due to $(\text{H}_2\text{O})_5\text{Cr}^{\text{III}}\text{C}(=\text{O})\text{NH}_2$ and $(\text{H}_2\text{O})_5\text{Cr}^{\text{III}}\text{CH}_2\text{N}(\text{CH}_3)\text{CHO}$ also obeyed a first-order rate law, but another dependence on the H_3O^+ concentration added to the solution was observed. These data are summarized in Table III.

No effect of $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ concentration (which was changed by a factor of more than 5) on $k^{\text{h}}_{\text{obsd}}$ was observed for any of the reactions studied.

Epr Data. Argon-saturated solutions containing 1.0 *M* $\text{CH}_3\text{CO}_2\text{H}$, 1.0 *M* HClO_4 , and approximately 1.0×10^{-3} *M* $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ were irradiated by about 1×10^{20} eV l⁻¹. When the epr spectra of these solutions were measured immediately after the pulse, a small signal due to $\text{Cr}_{\text{aq}}^{3+}$ was observed. However, with time, the intensity of this signal increased considerably. The specific rate of the increase of this signal was identical (within the limited experimental accuracy) with $k^{\text{h}}_{\text{obsd}}$ obtained by the spectrophotometric method, $k^{\text{h}}_{\text{obsd}} = 2.6 \times 10^{-5} \text{sec}^{-1}$.

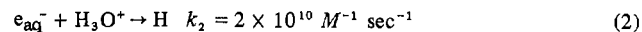
Discussion

The primary processes occurring during radiolysis of water and dilute solutions⁷ may be summarized by



The yields of these primary products in dilute aqueous solutions are known. They are $G_{\text{OH}} = 2.65$, $G_{\text{H}} = 0.60$, $G_{e_{\text{aq}}^-} = 2.65$, $G_{\text{H}_2\text{O}_2} = 0.45$, and $G_{\text{H}_3\text{O}^+} = 0.75$, where “*G* value” is the number of product molecules formed per 100 eV absorbed by the solution. In concentrated solutions, the yield of the radicals produced is often somewhat larger whereas the yield of the “molecular” products is smaller.⁷

In acidic solutions the hydrated electrons react as



Both hydrogen atoms and hydroxyl radicals react with saturated aliphatic solutes⁷ according to



The major site of attack is usually α to a functional group such as hydroxyl, carboxyl, or etheric oxygen.^{8,10-19} The specific rates of reaction of aliphatic solutes with OH radicals exceed $1 \times 10^7 M^{-1} \text{sec}^{-1}$,²⁰ and with H atoms, they are higher than $1 \times 10^5 M^{-1} \text{sec}^{-1}$.²⁰ Therefore under our experimental conditions all primary radicals were transformed into aliphatic radicals by means of reaction 3. Only for the solutions of *tert*-butyl alcohol, trimethylacetic acid, acetic acid, and malonic acid, which react most slowly with H,²⁰

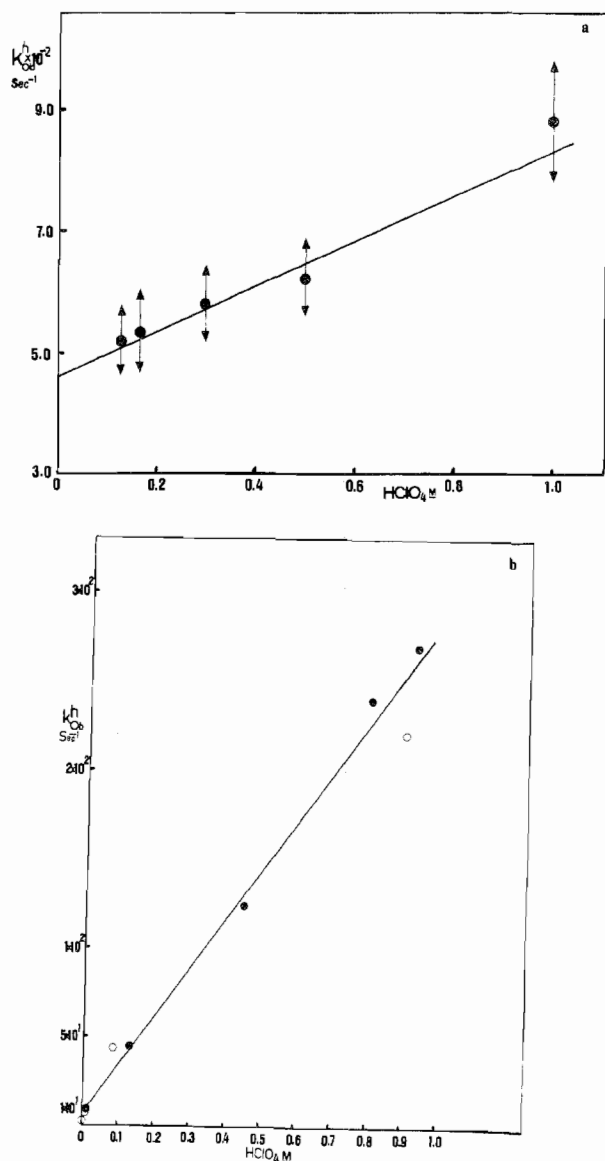


Figure 3. pH dependence of the rate of decomposition of chromium-carbon compounds: (a) $(\text{H}_2\text{O})_5\text{CrC}(\text{OH})(\text{CH}_3)\text{COOH}^{2+}$; (b) $(\text{H}_2\text{O})_5\text{CrCH}_2\text{CH}(\text{OH})_2$. The full dots represent conditions where $\cdot\text{CH}_2\text{CHO}$ reacted with $\text{Cr}_{\text{aq}}^{2+}$, whereas the open circles represent conditions where $\cdot\text{CH}(\text{OH})\text{CH}_2\text{OH}$ reacted with $\text{Cr}_{\text{aq}}^{2+}$.

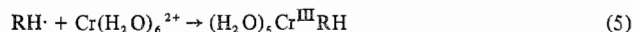
did a major part of the latter disappear through²¹



and not by means of reaction 3. If this is the case, the reported molar absorption coefficients in the presence of these solutes should be considered lower limits. (The correct values might be larger by a factor of 2.) We could not check this point by a further increase in the concentration of the organic solute because an increase might affect the primary radical yields.

The structure of the organic radicals formed by reaction 3 is known, mainly from epr measurements.^{8,10-19} The disappearance reactions of these radicals in the absence of $\text{Cr}_{\text{aq}}^{2+}$ were found to obey second-order kinetics with specific rates approaching the diffusion-controlled limit. The products of these dimerization or disproportionation reactions do not absorb in the spectral range studied (or they have too small

molar absorption coefficients to be observed by the technique used, e.g., $(\text{CH}_3)_2\text{CO}$). The $\text{Cr}_{\text{aq}}^{2+}$ concentrations were chosen so that more than 95% of the radicals formed react as



and not by dimerization or disproportionation



The products of reaction 5 were identified as chromium complexes containing a σ carbon-to-metal bond by the following criteria. (a) All the products have similar absorption spectra composed of two bands. The band with the maximum at 390–410 nm is typical for chromium-carbon σ bonds^{1f} (a third very weak band around 550–600 nm^{1f} was observed for the relatively stable products by long irradiation in the γ source). (b) The specific rates of decomposition of most products are many orders of magnitude greater than those for common ligand-exchange reactions of $\text{Cr}(\text{III})$.²²

Absorption Spectra due to Chromium-Carbon Bonds.

All the products studied which contain a chromium-carbon bond have an absorption spectrum consisting of three bands within the spectral range studied. The data gathered in this study concern only the two bands in the near-uv region because the band in the visible region is too weak to be studied effectively by the pulse radiolytic technique.

The two bands (Table I) are due to different types of transitions. This conclusion is drawn from the effect of the nature of $-\text{RH}$ on the location of the absorption maxima of $(\text{H}_2\text{O})_5\text{CrRH}^{2+}$. Thus λ_{max}^1 is strongly affected by the nature of $-\text{RH}$: $256 \text{ nm} < \lambda_{\text{max}}^1 < 310 \text{ nm}$ for the compounds studied or $\lambda_{\text{max}}^1 = 102 \pm 10 \text{ kcal/mol}$. On the other hand we have $390 \text{ nm} < \lambda_{\text{max}}^2 < 410 \text{ nm}$ or $\lambda_{\text{max}}^2 = 71.4 \pm 1.8 \text{ kcal/mol}$ for the same compounds.

The uv absorption bands of $(\text{H}_2\text{O})_5\text{CrCH}_2\text{C}_6\text{H}_5^{2+}$ and of substituted benzylchromium complexes have been attributed to charge-transfer transitions from the ligand to the chromium.^{1b} The large effect of the nature of $-\text{RH}$ on λ_{max}^1 suggests that this band results from a charge-transfer transition. This assignment is in agreement with the relatively high molar absorption coefficients for this band. This assignment is also in accord with the observation that both electron-withdrawing groups (e.g., Cl ,²³ Br ,²³ I ,²³ CO_2H) and electron-donating groups, e.g., CH_3 , cause a red shift of λ_{max}^1 . Thus for all the compounds studied $\lambda_{\text{max}}^1 > \lambda_{\text{max}}^1(\text{Cr}(\text{H}_2\text{O})_5\text{CH}_3^{2+})$.²⁴ It is reasonable that the optical electronegativity of all the CH_2R groups will be lower than that of CH_3 . Thus λ_{max}^1 increases, as expected, along the following series: (1) CH_3 , CH_2Cl , CHCl_2 , CH_2Br , CHBr_2 , and CH_2I ;²³ (2) CH_2OH , $\text{CHOH}(\text{CH}_3)$, and $\text{COH}(\text{CH}_3)_2$; (3) $\text{CH}_2\text{CO}_2\text{H}$ and $\text{CHCH}_3(\text{CO}_2\text{H})$; (4) $\text{CH}_2\text{CO}_2\text{H}$ and $\text{CH}(\text{CO}_2\text{H})_2$; (5) $\text{CH}_2\text{CO}_2\text{H}$, CH_2OH , $\text{CHOH}(\text{CO}_2\text{H})$, and $\text{COHCH}_3(\text{CO}_2\text{H})$. It is suggested that the bands around 360 nm for the substituted benzyl complexes^{1b} and around 320 nm for the substituted pyridinomethyl complexes^{1d} occur because of charge-transfer transitions. The optical electronegativities of these ligands are expected to be lower than those of the saturated aliphatic ligands.

It is of interest to note that λ_{max}^1 for all the alkyl compounds studied is similar to λ_{max}^1 for $\text{Cr}(\text{NH}_3)_5\text{r}^{2+}$,²⁵ 290

(22) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," Wiley, New York, N. Y., 1967.

(23) D. Dodd and M. D. Johnson, *J. Chem. Soc. A*, 34 (1968).

(24) M. Ardon, K. Woolmington, and A. Pernick, *Inorg. Chem.*, 10, 2812 (1971).

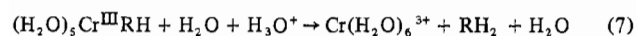
(25) M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, 266, 4 (1951).

(21) H. Cohen and D. Meyerstein, *J. Chem. Soc., Dalton Trans.*, in press.

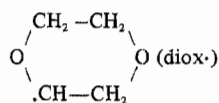
nm, and to λ_{\max}^1 expected for $\text{Cr}(\text{H}_2\text{O})_5\text{I}^{2+}$. The uv spectrum of the latter compound features a shoulder at 306 nm with ϵ 2115 $M^{-1} \text{cm}^{-1}$ and a peak at 260 nm with ϵ 5740 $M^{-1} \text{cm}^{-1}$.²⁶ Furthermore λ_{\max}^1 for bis(ethylenediamine)-chromium alkyl compounds in ethanol is also around 300 nm.²⁷ Thus the spectra suggest that the optical electro-negativities for most of the alkyl derivatives studied are somewhat larger than those of I^- . The latter conclusion is in agreement with other observations.²⁸

The location of the peak of the second band, λ_{\max}^2 , is only slightly affected by the nature of -RH, and the molar absorption coefficients of most of the compounds studied are relatively low. (The coefficients caused by the second band are considerably smaller than those observed because of the partial overlap with the intense uv band, Figure 2.) We assign this band to a d-d transition. The intensity of this band is much higher than those of most d-d transitions. This observation might be explained by the relatively large covalent nature of the chromium-carbon bond or by the interaction between the d-d transition and the charge-transfer state. The corresponding transition is not observed for the benzylchromium^{1b} and pyridinomethylchromium complexes.^{1d} This could be explained by the large red shift of the charge-transfer band which thus overlaps the weaker d-d bands.

Specific Rates of Reaction of Aliphatic Radicals with $\text{Cr}(\text{H}_2\text{O})_6^{2+}$. The reactions of the aliphatic radicals with $\text{Cr}(\text{H}_2\text{O})_6^{2+}$, reaction 5, might be considered formally as a redox process. In these reactions the organic radical oxidizes the metal cation. This is evident because reaction 5 is followed by the hydrolysis reaction



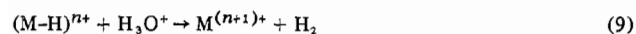
Thus many of the radicals which are known to be strong reducing agents,²⁹ e.g., $\cdot\text{CHOHCH}_2\text{OH}$, $\cdot\text{CH}_2\text{OH}$, CH_3CHOH , $(\text{CH}_3)_2\text{COH}$, $\cdot\text{CH}(\text{OH})\text{CO}_2\text{H}$, $\text{CH}_3\dot{\text{C}}(\text{OH})\text{CO}_2\text{H}$, $\text{CH}_3\dot{\text{C}}\text{HOCH}_2\text{CH}_3$, and



react as oxidizing agents in reaction 5. The polarographic half-wave potentials for the reduction of several of these radicals have been reported.^{29a} From the latter it would seem that none of the radicals should be capable of oxidizing $\text{Cr}(\text{H}_2\text{O})_6^{2+}$. It must therefore be concluded that the measured polarographic half-wave potentials stem from large overpotentials. The mechanism of oxidation of transition metal complexes by aliphatic radicals seems to be similar in its nature to the oxidation of several cations by hydrogen atoms



which is followed by



The latter reaction has been reported for $\text{Fe}(\text{H}_2\text{O})_6^{2+}$,³⁰ $\text{Ti}_{\text{aq}}^{3+}$,³¹ and $\text{Cr}(\text{H}_2\text{O})_6^{2+}$.²¹

(26) T. W. Swaddle and E. L. King, *Inorg. Chem.*, **4**, 532 (1965).

(27) J. K. Kochi and J. W. Powers, *J. Amer. Chem. Soc.*, **92**, 137 (1970).

(28) C. K. Jorgensen, *Progr. Inorg. Chem.*, **12**, 101 (1970).

(29) (a) J. Lilie, G. Beck, and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **75**, 458 (1971); (b) H. Cohen and D. Meyerstein, *J. Amer. Chem. Soc.*, **94**, 6944 (1972).

The oxidation of transition metal complexes by aliphatic radicals has been demonstrated for a series of aquo ions. The order of reactivity has been shown to follow the redox properties of these cations: $\text{Cr}_{\text{aq}}^{2+} > \text{Ti}_{\text{aq}}^{3+} > \text{Fe}_{\text{aq}}^{2+}$.¹¹ Furthermore similar reactions were demonstrated for $\text{Co}(\text{CN})_5^{3-}$ ^{1h} and for a series of other cobalt complexes used as models for vitamin B₁₂.^{1g} However the effect of the detailed structure of the radicals on the specific rates of these reactions has not been studied. Three major factors might influence these specific reaction rates with a given cation. (a) Steric hindrance by groups bound to the reacting carbon atom might lower the specific rates of reaction. (b) Reaction 5 might be considered a combination of two radicals to form a σ bond. Its specific rate of reaction is therefore expected to vary directly with the probability that the unpaired electron will be located on the reacting carbon. (c) Because the σ bond that is formed contains an e_g electron of the chromium atom, the location of the unpaired electron in a non-bonding p orbital rather than in a resonance-stabilized π system would favor reaction because of symmetry considerations.

We shall now analyze the contribution of each of these factors to the measured specific rates of reaction, Tables II and III. Such an analysis seems justified because the specific rates of reactions, although high, are not diffusion controlled. Therefore structural effects on the reaction rates are expected to be significant, though rather small.

The results indicate that steric factors have only a minor effect if any, on the specific rates of reaction of these organic radicals with $\text{Cr}(\text{H}_2\text{O})_6^{2+}$. Thus it is found that $k_{\text{CHOHCH}_2\text{OH}} \sim k_{\text{CH}_2\text{OH}}$, $k_{\text{diox}\cdot} > k_{\text{CH}_3\text{CHOCH}_2\text{CH}_3}$, and $k_{\text{CH}_3\dot{\text{C}}(\text{OH})\text{CO}_2\text{H}} > k_{\text{CH}_3\dot{\text{C}}\text{HOH}}$ whereas steric factors would require the reverse order of reactivities for these examples. However, because it is difficult to envisage factors involving electronic configurations (see below) which will cause $k_{\text{CH}_2\text{CO}_2\text{H}} > k_{\text{CH}_2\text{OH}}$ and $k_{\text{CH}_3\dot{\text{C}}(\text{OH})(\text{CH}_3)_2} > k_{\text{CH}_3\dot{\text{C}}(\text{CO}_2\text{H})(\text{CH}_3)_2}$, it is possible that steric hindrance affects the latter specific rates of reaction.

The results clearly point out that substitution of an α hydrogen by the electron-donating methyl group decreases the specific rates of reaction, k_5 , whereas substitution by the electron-withdrawing group, CH_2OR , increases these rates. Thus the order of reactivities is as follows: (1) $\cdot\text{CH}_2\text{OH} > \cdot\text{CH}(\text{CH}_3)\text{OH} > \cdot\text{C}(\text{CH}_3)_2\text{OH}$, (2) $\cdot\text{CH}_2\text{CO}_2\text{H} > \cdot\text{CH}(\text{CH}_3)\text{CO}_2\text{H}$, (3) $\cdot\text{CH}(\text{OH})\text{CO}_2\text{H} > \cdot\text{C}(\text{CH}_3)(\text{OH})\text{CO}_2\text{H}$, and (4) $\text{diox}\cdot > \text{CH}_3\dot{\text{C}}\text{HOCH}_2\text{CH}_3$. It has been suggested³² that electron-donating groups decrease the probability that the unpaired electron is located on the reacting carbon atom by increasing the spin density on the α -hydroxyl or carbonyl groups. Electron-withdrawing groups are expected to induce the opposite effect. The present data are therefore in agreement with our earlier conclusions,² based on only a few rate constants, that a major factor influencing the specific rates of reaction of $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ with aliphatic radicals is the probability of locating the unpaired electron on the reacting carbon atom. However the suggested simple correlation of the specific rates of reaction with the value of the hyperfine constants for the epr splitting by the α hydrogens, a^{H}_{α} , does

(30) (a) G. Czapski, J. Jortner, and G. Stein, *J. Phys. Chem.*, **65**, 960 (1961); (b) H. A. Schwarz, *ibid.*, **67**, 2827 (1963); (c) G. G. Jayson, J. P. Keene, D. A. Stirling, and A. J. Swallow, *Trans. Faraday Soc.*, **2453** (1969).

(31) D. Behar, A. Samuni, and R. W. Fessenden, submitted for publication in *J. Phys. Chem.* (We thank Dr. A. Samuni for communicating his results prior to publication.)

(32) (a) D. Asmus, A. Henglein, A. Wigger, and G. Beck, *Ber. Bunsenges. Phys. Chem.*, **70**, 756 (1966); (b) M. Simic, P. Neta, and E. Hayon, *J. Phys. Chem.*, **73**, 3794 (1969); **73**, 4214 (1969).

not hold for the present data. (Thus the latter splittings for $\cdot\text{CH}_2\text{CO}_2\text{H}$ and $\cdot\text{CH}(\text{CO}_2\text{H})_2$ are 21.8 and 20.44 G, respectively; these values are considerably higher than those observed for all the alcohol and ether radicals, Table II.) This observation is not too astonishing because it is well known that the electron spin densities on the α carbon are not linearly correlated to the α -hydrogen splittings. Therefore the only correlations that can be expected between the epr splittings and the measured specific rate constants are those within a given group of very similar radicals, e.g., α -alcohol, α -ether, and α -carboxyl radicals. These expectations are in agreement with the experimental results (Table II).

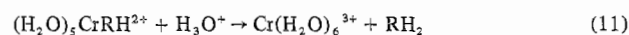
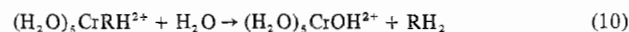
The results are inconclusive with respect to the effect of α -carboxyl and α -hydroxyl groups on the reactivity of aliphatic radicals toward $\text{Cr}(\text{H}_2\text{O})_6^{2+}$. This question could be answered by measuring the rate of reaction of methyl radicals with $\text{Cr}(\text{H}_2\text{O})_6^{2+}$. The solubility of methane is too low for measuring this rate under our experimental conditions. We hoped that the specific rates of $\cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$ and $\cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{CO}_2\text{H}$ would be similar to those of methyl radicals. The observed rates are lower than those for $\cdot\text{CH}_2\text{CO}_2\text{H}$ and $\cdot\text{CH}_2\text{OH}$, the reverse of the order expected from the probabilities of location of the unpaired electron on the carbon atom. This observation might be explained, as stated above, by steric factors.

The correlation between the probability of the unpaired electron being located on the reacting carbon atom and the specific rate of reaction of the radical could be explained by arguing that (a) the reactivity of the radicals is correlated to the spin density on the carbon atom or (b) a lower spin density on the carbon atom indicates a larger π character of the orbital in which the unpaired electron is located^{29b} thus decreasing the reactivity toward $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ (where the reacting electron is in an e_g orbital) because of poor overlap. Due to the expected parallelism between these effects it is impossible to study their relative importance by measuring the specific rates of reaction of a series of radicals with a given metal cation. Similar reactions with $\text{Ti}_{\text{aq}}^{3+}$ and $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ have been reported recently.³¹ Because of the low reactivities of these cations toward aliphatic radicals, the pulse radiolytic technique is not applicable for measuring the absolute rates of these reactions. However it was shown that $k_{\text{CH}(\text{CO}_2\text{H})_2 + \text{Ti}_{\text{aq}}^{3+}} > k_{\text{CH}_2\text{CO}_2\text{H} + \text{Ti}_{\text{aq}}^{3+}}$ and the results also indicate that $k_{\text{CH}_2\text{CO}_2\text{H} + \text{Fe}(\text{H}_2\text{O})_6^{2+}} > k_{\text{CH}(\text{CO}_2\text{H})_2 + \text{Fe}(\text{H}_2\text{O})_6^{2+}}$.³¹ Thus it seems that this pair of radicals has the same order of reactivities toward $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ and $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ and the opposite order toward $\text{Ti}_{\text{aq}}^{3+}$. The electronic configurations of these three cations are $t_{2g}^3 e_g^1$, $t_{2g}^4 e_g^2$, and t_{2g}^1 , respectively. It is reasonable to assume that an e_g electron participates in the reactions with $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ and $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ whereas a t_{2g} electron participates in the reactions with $\text{Ti}_{\text{aq}}^{3+}$. Therefore, though the experimental data are limited, it is tempting to argue that the symmetry character of the orbital in which the unpaired electron is located affects the rates of oxidation of transition metal cations by aliphatic radicals. Thus we speculate that for a series of similar radicals the reactivity toward cations with a reactive e_g electron is expected to decrease with an increase in the π character of the orbital in which the unpaired electron is located. The opposite order is expected toward cations with a reactive t_{2g} electron. The measurement of the specific rates of reaction of a series of radicals with other transition metal complexes should clarify this point.

Mechanism of Hydrolysis of the Chromium-Carbon Bonds.

In principle there exist three basic mechanisms for the cleavage of chromium-carbon bonds: (a) a homolytic process

yielding a Cr(II) derivative, (b) a heterolytic process leaving the metal in the formal Cr(III) oxidation state, and (c) a heterolytic process leaving the metal in the formal Cr(I) oxidation state. The last mechanism has been suggested for the cleavage of some cobalt-carbon bonds.³³ However this mechanism seems highly unlikely for aquochromium cations and has not been observed for any of the chromium-carbon compounds so far studied. The homolytic mechanism has been reported for the aquation of the pentaquopyridino-methylchromium complex in acidic solutions.^{1e,3} The reported mechanism of aquation of all other chromium-carbon compounds is the heterolytic process^{1c,f}



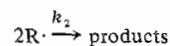
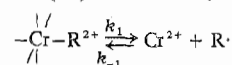
The distinction between the homolytic and heterolytic mechanisms is based on two types of experimental data. (a) A homolytic mechanism requires a rate law which is second order in the chromium-carbon compound and minus second order in $\text{Cr}(\text{H}_2\text{O})_6^{2+}$.³⁴ On the other hand a heterolytic mechanism requires a rate law which is first order in the chromium-carbon compound and independent of the $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ concentration. All the compounds described in the present study obeyed a rate law of the latter kind. (b) The products of a homolytic decomposition process are expected to contain dimers of the organic radical, HRRH, whereas in the heterolytic process the only organic products expected are the reduced organic radicals RH_2 . In the present study we did not analyze the products because of the very low concentrations obtained by the radiolytic techniques.³⁵ However it has been shown for $\text{CrCH}_2\text{OH}^{2+}$ and CrCH_3^{2+} ,^{1f,24} that the only products are CH_3OH and CH_4 , respectively. (It is known that both $\cdot\text{CH}_2\text{OH}$ and $\cdot\text{CH}_3$ radicals, as well as most other radicals studied, disappear *via* a dimerization reaction.) There is no reason to assume that the aquation of the other compounds studied proceeds by a different mechanism. Therefore because the rate laws observed indicate a heterolytic process, we conclude that that is the mechanism of aquation of the CrRH^{2+} compounds studied in acidic solutions.

It should be pointed out that no correlation is found between the specific rates of reactions of the radicals with $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ and the specific rates of hydrolysis of the products. Thus, for example, the specific rates of reaction of $\cdot\text{CH}_2\text{OH}$ and $\cdot\text{CH}(\text{OH})\text{CO}_2\text{H}$ with $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ are identical within the error limit, whereas the specific rates of hydrolysis of the corresponding complexes differ by more than three orders of magnitude.

When we compare the simplest ligands studied, it is seen

(33) G. Costa, *J. Pure Appl. Chem.*, **30**, 335 (1972).

(34) For a homolytic mechanism

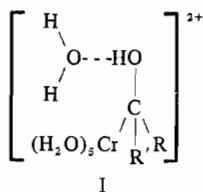


under the experimental conditions, where $k_{-1}[\text{Cr}^{2+}] \gg k_2[\text{R}\cdot]$, the observed rate law should be

$$\frac{-d[\text{CrR}^{2+}]}{dt} = 2 \frac{k_2 k_1^2}{k_{-1}^2} \frac{[\text{CrR}^{2+}]^2}{[\text{Cr}^{2+}]^2}$$

(35) In order to eliminate the possibility of reaction of free radicals with the chromium-carbon compounds the concentration of the latter has to be maintained below 5% of the initial $\text{Cr}_{\text{aq}}^{2+}$ and organic solute concentrations.

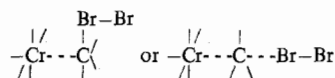
that the specific rates of hydrolysis decrease along the series $:\text{CH}_2\text{OH} > :\text{CH}_3^{1f} > :\text{CH}_2\text{CO}_2\text{H} > :\text{CH}(\text{CH}_3)\text{OCH}_2\text{CH}_3$. The relatively high reactivity of the $:\text{CH}_2\text{OH}$ complex has been attributed to the hydroxyl group, which enables through hydrogen bonding the formation of the activated complex I.^{1f} The low reactivity of the diethyl ether ligand has been



attributed to the lack of a hydroxyl group and to steric factors.^{1f} The low reactivity of the $:\text{CH}_2\text{CO}_2\text{H}$ ligand seems to be ascribed with its electron-withdrawing properties and the larger distance between its oxygen atoms and the reactive chromium-carbon bond; thus, a water molecule bound by hydrogen bonds to the carboxylic group is too far from the metal-carbon bond. The stabilizing effect of electron-withdrawing groups is in agreement with the relative stability of $(\text{H}_2\text{O})_5\text{CrCH}_2\text{X}^{2+}$ and $(\text{H}_2\text{O})_5\text{CrCHX}_2^{2+}$, where X is a halogen atom.²³ It has also been shown that when methyl, an electron-donating group, is the substituent, the rate of hydrolysis increases.^{1f} This finding, which is in accord with our results, can be seen by comparing the couples $:\text{CH}(\text{CH}_3)\text{CO}_2\text{H}$, $:\text{CH}_2\text{CO}_2\text{H}$ and $:\text{CH}(\text{OH})\text{CO}_2\text{H}$, $:\text{C}(\text{CH}_3)(\text{OH})\text{CO}_2\text{H}$. These effects of electron-withdrawing and electron-donating groups are consistent with the suggestion^{1f} that the mechanism of aquation requires a proton to be associated with the bound carbon prior to the dissociation to the carbon-metal bond.³⁶

However it is evident from the results that other factors have large effects on the rate of hydrolysis. Thus a CH_2OR group is an electron-withdrawing substituent, but it causes an enormous enhancement of the rates of aquation. (Compare $:\text{CH}(\text{CH}_3)\text{OCH}_2\text{CH}_3^{1f}$ with diox.). Similar high rates of hydrolysis are observed for the derivatives of α -hydroxy acids and of $:\text{CH}_2\text{CH}(\text{OH})_2$. Thus the rates of aquation of the complexes of $:\text{CH}(\text{OH})\text{CO}_2\text{H}$ and $:\text{C}(\text{CH}_3)(\text{OH})\text{CO}_2\text{H}$ are much higher than those of $:\text{CH}_2\text{OH}$, $:\text{CH}_2\text{CO}_2\text{H}$ and $:\text{CH}(\text{CH}_3)\text{OH}$, $:\text{CH}(\text{CH}_3)\text{CO}_2\text{H}$, respectively. It is suggested that the specific rates of aquation of the ligands with two functional groups containing oxygen atoms (e.g., OH, CO_2H , or OR) result from hydration of the ligand in the transition state. For all these ligands the distance between the oxygen atoms in the two groups is such that it could stabilize an H_2O or H_3O^+ group bound to both groups by hydrogen bonds. It is therefore of interest to note that both the H_3O^+ -dependent and H_3O^+ -independent rate constants are enhanced for these complexes. For $:\text{CH}(\text{CO}_2\text{H})_2$ as a

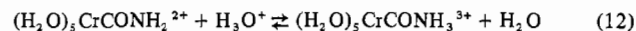
(36) After this paper had been submitted for publication, J. H. Espenson and D. A. Williams, *J. Amer. Chem. Soc.*, **94**, 1008 (1974), reported that the products of the cleavage reaction of alkylchromium cations with bromine are $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ and alkyl bromides. They interpreted these results in terms of an SE_2 mechanism with an open transition state



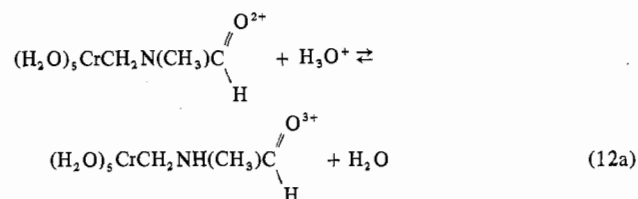
It is plausible that the hydrolysis reactions reported in the present study proceed via a similar mechanism. The effects of electron-donating or -withdrawing substituents on the carbon atom, as well as of hydration of the ligand for this mechanism, are expected to be similar to those discussed in the text.

ligand where the oxygen-oxygen distance is larger, no such enhancement of the specific rates of aquation is observed. It has been suggested that the low rates of aquation of the diethyl ether derivative stem from steric factors and its hydrophobic character.^{1f} The high rate for the dioxane derivative suggests that the steric effects are less significant than those caused by the hydration of the ligand.

The high rates of aquation of the complexes of $:\text{C}(=\text{O})\text{NH}_2$ and $:\text{CH}_2\text{N}(\text{CH}_3)\text{C}(=\text{O})\text{H}$ might be explained both by strong hydration and by the electron-donating properties of the adjacent nitrogen atom. The complicated dependence of the rates on the $[\text{H}_3\text{O}^+]$ added (Table III) is believed to be due to the equilibrium

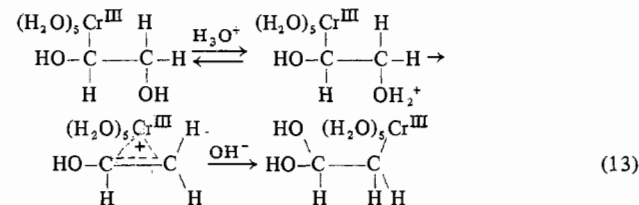


and



In conclusion, it seems that of the several factors influencing the specific rates of aquation of the $\text{Cr}(\text{H}_2\text{O})_5\text{RH}^{2+}$ complexes, a major factor is apparently the degree of hydration of the ligand. In this respect the hydrogen bonding of H_3O^+ to the ligand is included in the term "hydration." A second important factor seems to be the nature of substituents on the carbon atom bound to the chromium. For ligands with similar hydration, electron-withdrawing substituents decrease the specific rates of aquation and electron-donating substituents enhance them. Finally steric factors could have some effect on the specific rates, but these effects seem to be minor, relative to the other factors.

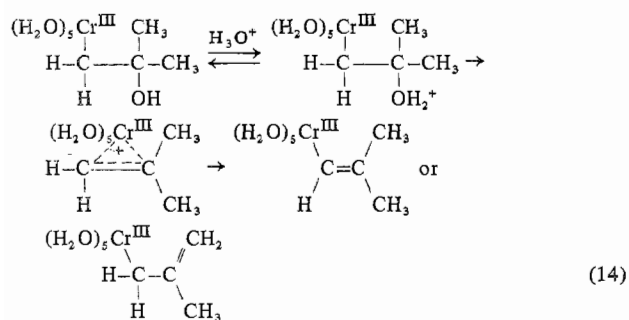
Rearrangements in the Chromium-Carbon Compounds. For the complex $(\text{H}_2\text{O})_5\text{CrCH}_2\text{C}(\text{CH}_3)_2\text{OH}^{2+}$ two separate first-order processes were observed after the formation of the complex. In this complex an OH group exists in a β position to the chromium carbon bond. It is known that chromium catalyzes an HX elimination reaction when X is a good leaving group, e.g., Br^- .³⁷ The hydroxyl group is also such a group and the observation that $(\text{H}_2\text{O})_5\text{CrCH}(\text{OH})\text{CH}_2\text{OH}$ is transformed into $(\text{H}_2\text{O})_5\text{CrCH}_2\text{CH}(\text{OH})_2$ with $k \geq 5 \times 10^5 \text{ sec}^{-1}$ at $\text{pH} < 4.0$ (appendix) is in accord with the mechanism



This mechanism has been proposed for the parallel reaction with a vitamin B₁₂ Co(III) analog.³⁸ It is suggested that the first reaction observed for the $(\text{H}_2\text{O})_5\text{CrCH}_2\text{C}(\text{OH})(\text{CH}_3)_2^{2+}$ complex is shown in eq 14.

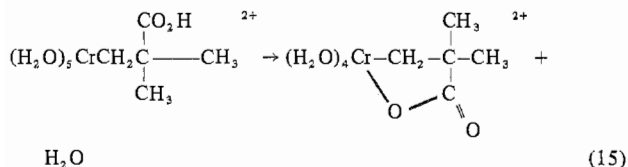
(37) (a) D. M. Singleton and J. K. Kochi, *J. Amer. Chem. Soc.*, **89**, 6547 (1967); (b) J. K. Kochi and D. M. Singleton, *ibid.*, **90**, 1582 (1968).

(38) R. B. Silverman and D. Dolphin, *J. Amer. Chem. Soc.*, **95**, 1686 (1973).



This mechanism is in accord with the strong H_3O^+ catalysis observed. We cannot prove which of the two products is formed though we prefer the vinylic product because the uv absorption peak is shifted to the red (λ_{max}^1 310 nm), which indicates a low optical electronegativity and a parallel mechanism with the ethylene glycol compound. The product must contain a chromium-carbon bond because the absorption spectrum around 400 nm is not affected by this reaction. It is reasonable to assume that similar products are formed also in all other chromium-catalyzed trans β eliminations.^{37,39}

The mechanism of decomposition of the $(\text{H}_2\text{O})_5\text{CrCH}_2\text{-(CO}_2\text{H)(CH}_3)_2$ involves also two consecutive reactions (Table II). However the spectrum of the product of the first reaction in this case is similar to that of the $\cdot\text{CH}_3$ complex.²⁴ Furthermore the rate of this reaction is independent of $[\text{H}_3\text{O}^+]$, and decarboxylation is not expected because CO_2H is not a good leaving group and because the product of such a reaction has to be identical with that of the latter case. One plausible reaction causing the observed optical change might be

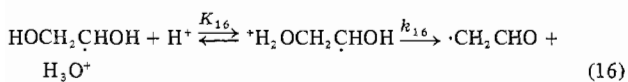


It is clear that other similar reactions must be discovered before the latter mechanism can be proved or disproved.

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Appendix

The radical $\cdot\text{CH(OH)CH}_2\text{OH}$ is known to lose a water molecule *via* an acid-catalyzed process⁴⁰



(39) After this paper had been submitted for publication K. M. Bansal, A. Henglein, E. Janata, and R. M. Sellers, *Ber. Bunsenges. Phys. Chem.*, **77**, 1139 (1973), reported that the reduction of $\cdot\text{CH}_2\text{C(CH}_3)_2\text{OH}$ radicals by polarography or by Ni^+ produces $\text{CH}_2=\text{C(CH}_3)_2$. It has been pointed out that this process is acid catalyzed. These findings corroborate the proposed reaction mechanism.

(40) (a) C. E. Burchill and K. M. Perron, *Can. J. Chem.*, **49**, 2382 (1971); (b) K. M. Bansal, M. Gratzel, A. Henglein, and E. Janata, *J. Phys. Chem.*, **77**, 16 (1973).

Table IV. Specific Rates of Reaction of Radicals Produced from Ethylene Glycol with $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ ^a

$[\text{H}_3\text{O}^+], M$	$10^{-8}k_{16} \cdot \text{RH} + \text{Cr}(\text{H}_2\text{O})_6^{2+}, M^{-1} \text{sec}^{-1}$
1.1×10^{-4} ^b	1.5
6.5×10^{-3}	2.4
6.5×10^{-2}	3.1
0.45	3.5
1.0	3.5

^a All solutions were saturated with Ar and contained 0.1–1 *M* ethylene glycol, $(1.0\text{--}1.5) \times 10^{-3}$ *M* $\text{Cr}_{\text{aq}}^{2+}$, and 10^{-4} –1 *M* HClO_4 . Measurements were made at $22 \pm 2^\circ$. Standard deviation is $\pm 15\%$.

^b Saturated with N_2O .

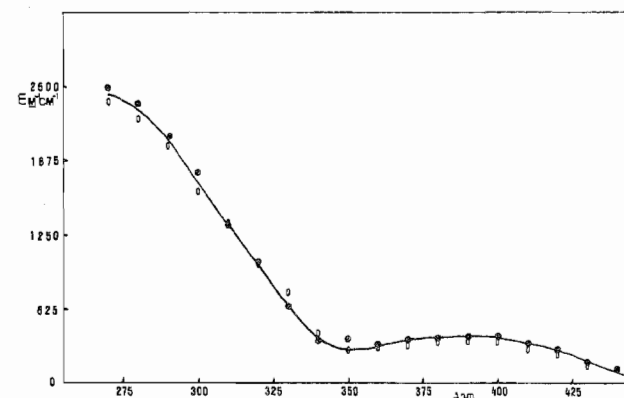
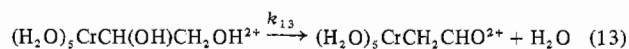


Figure 4. Absorption spectra of the chromium-carbon compounds formed in the presence of ethylene glycol under different conditions: ●, conditions where the reacting radical is $\cdot\text{CH(OH)CH}_2\text{OH}$; ○, conditions where the reacting radical is $\cdot\text{CH}_2\text{CHO}$.

where $K_{16} = 1.8 \times 10^{-1} M^{-1}$ and $k_{16} = 8.6 \times 10^5 \text{ sec}^{-1}$.^{40b} One expects therefore that in solutions containing low $\text{Cr}_{\text{aq}}^{2+}$ concentrations and high acid concentrations the observed chromium-carbon compound would be $(\text{H}_2\text{O})_5\text{CrCH}_2\text{CHO}$, whereas in neutral solutions or acidic solutions with high $\text{Cr}_{\text{aq}}^{2+}$ concentrations $(\text{H}_2\text{O})_5\text{CrCH(OH)CH}_2\text{OH}$ should be formed. Indeed it was found that the specific rate of reaction of the radical with $\text{Cr}_{\text{aq}}^{2+}$ depends on the pH (Table IV), thus indicating that two different radicals react with $\text{Cr}_{\text{aq}}^{2+}$ under these conditions. However the absorption spectra of the chromium-carbon compounds formed under both conditions are identical (Figure 4). Furthermore the rate law for the hydrolysis reaction is independent of the reacting radical with $k_{16}^1 = 1.8 \text{ sec}^{-1}$ and $k_{16}^2 = 2.2 \times 10^2 M^{-1} \text{ sec}^{-1}$. This is demonstrated Figure 3b, with the full dots representing conditions where $\cdot\text{CH}_2\text{CHO}$ reacted with $\text{Cr}_{\text{aq}}^{2+}$ and the circles representing conditions where $\cdot\text{CH(OH)CH}_2\text{OH}$ reacted with $\text{Cr}_{\text{aq}}^{2+}$. (The nature of the reacting species was determined from $[\text{H}_3\text{O}^+]$, $[\text{Cr}_{\text{aq}}^{2+}]$, the measured rates of reaction of $\cdot\text{CH(OH)CH}_2\text{OH}$ with $\text{Cr}_{\text{aq}}^{2+}$, K_{16} , and k_{16} .) We must conclude that the same chromium-carbon compound is obtained under all conditions and therefore that the reaction



has a specific rate of $k_{13} > 5 \times 10^5 \text{ sec}^{-1}$ even at $\text{pH} < 4.0$ (otherwise we should have observed the transition between the two compounds). As $\text{Cr}(\text{H}_2\text{O})_5^{3+}$ is a strong electrophile, it is reasonable to assume that $(\text{H}_2\text{O})_5\text{CrCH}_2\text{CHO}^{2+}$ exists in aqueous solutions in the form of $(\text{H}_2\text{O})_5\text{CrCH}_2\text{CH(OH)}_2^{2+}$.

Registry No. $\cdot\text{CH}_2\text{OH}$, 2597-43-5; $\cdot\text{CH}_2\text{CHO}$, 4400-01-5; $\cdot\text{CH(OH)CH}_2\text{OH}$, 3250-66-6; $\cdot\text{CH(OH)CH}_3$, 2348-46-1; $\cdot\text{C(CH}_3)_2\text{OH}$,

5131-95-3; $\cdot\text{CH}(\text{CH}_3)\text{OCH}_2\text{CH}_3$, 2229-06-3; $\cdot\text{diox}$, 4598-47-4; $\cdot\text{CH}_2\text{-CO}_2\text{H}$, 2887-46-9; $\cdot\text{CH}(\text{OH})\text{CO}_2\text{H}$, 3293-65-0; $\cdot\text{C}(\text{CH}_3)(\text{OH})\text{CO}_2\text{H}$, 15552-92-8; $\cdot\text{CH}(\text{CH}_3)\text{CO}_2\text{H}$, 15671-30-4; $\cdot\text{CH}(\text{CO}_2\text{H})_2$, 3247-02-7; $\cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$, 5723-74-0; $\cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{CO}_2\text{H}$, 26299-74-1; $\cdot\text{C}(\text{O})\text{NH}_2$, 2858-51-7; $\cdot\text{CH}_2\text{N}(\text{CH}_3)\text{CHO}$, 17526-06-6; $\text{Cr}(\text{H}_2\text{O})_6^{2+}$, 20574-26-9; $(\text{H}_2\text{O})_5\text{CrCH}_2\text{OH}^{2+}$, 32108-95-5; $(\text{H}_2\text{O})_5\text{CrCH}(\text{OH})\text{-CH}_3^{2+}$, 32108-94-4; $(\text{H}_2\text{O})_5\text{CrC}(\text{CH}_3)_2\text{OH}^{2+}$, 32108-93-3; $(\text{H}_2\text{O})_5\text{-}$

$\text{CrCH}(\text{CH}_3)\text{OCH}_2\text{CH}_3^{2+}$, 32108-97-7; $(\text{H}_2\text{O})_5\text{Cr}(\text{diox})^{2+}$, 51965-43-6; $(\text{H}_2\text{O})_5\text{CrCH}_2\text{CO}_2\text{H}^{2+}$, 52032-35-6; $(\text{H}_2\text{O})_5\text{CrCH}(\text{OH})\text{CO}_2\text{H}^{2+}$, 52109-46-3; $(\text{H}_2\text{O})_5\text{CrC}(\text{CH}_3)(\text{OH})\text{CO}_2\text{H}^{2+}$, 51965-44-7; $(\text{H}_2\text{O})_5\text{CrCH}(\text{CH}_3)\text{-CO}_2\text{H}^{2+}$, 51965-45-8; $(\text{H}_2\text{O})_5\text{CrCH}(\text{CO}_2\text{H})_2^{2+}$, 51965-46-9; $(\text{H}_2\text{O})_5\text{-CrCH}_2\text{CH}(\text{OH})_2^{2+}$, 51965-47-0; $(\text{H}_2\text{O})_5\text{CrC}(\text{O})\text{NH}_2^{2+}$, 51965-48-1; $(\text{H}_2\text{O})_5\text{CrCH}_2\text{N}(\text{CH}_3)\text{CHO}^{2+}$, 51965-49-2; $(\text{H}_2\text{O})_5\text{CrCH}_2\text{C}(\text{CH}_3)_2\text{-OH}^{2+}$, 51965-50-5; $(\text{H}_2\text{O})_5\text{CrCH}_2\text{C}(\text{CH}_3)_2\text{CO}_2\text{H}^{2+}$, 51965-51-6.

Contribution from the Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

Electrochemical Reduction of Chromium(III) Complexes in the Presence of Nitrite Ion. Preparation of Nitrosyl Complexes¹

JOHN G. MASON*² and JAMES M. VANDER MEER

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The electrochemical reduction of the ethylenediaminetetraacetatochromate(III), 1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetatochromate(III), and hexacyanochromate(III) ions in the presence of nitrite ion have been studied by polarography and controlled-potential electrolysis. In each case, a chromium-nitrosyl complex was formed which was identified by direct synthesis. An interpretation of the unusual current-time behavior observed during the cpe is given and a mechanism of formation of the nitrosyls during electrolysis is proposed.

Introduction

Polarographic reduction of a reducible species in the presence of an electroinactive oxidant produces an increase in the observed limiting current provided the oxidant is kinetically capable of reacting with the reduced form at a sufficiently rapid rate. The experimental evaluation of such "catalytic" waves can lead to the extraction of reaction orders and rate constants in favorable cases.³ This investigation was initiated to study the catalytic behavior produced by NO_2^- ions on the polarography of Cr(III) complexes as a convenient method of studying the oxidation of Cr(II) complexes.

Chromium(II) and chromium(III) complexes as reducing agents have been the subject of numerous kinetic, mechanistic, and stoichiometric investigations. Typical studies are those involving the reduction of coordination compounds⁴ and organic compounds.⁵ The reactions of Cr(II) and its complexes with oxy anions such as nitrate or nitrite have been less thoroughly studied but some results have been reported. Lingane and Pecsok⁶ have reported a method for the determination of NO_3^- by Cr(II) which is most effective with titanium salts as catalysts. The terminal reduction product is NH_3 . Ardon and Herman⁷ have reported the preparation of CrNO^{2+} by reduction of NO_3^- and NO with Cr(II). Armor and Buchbinder⁸ have studied the reaction between Cr(II) and nitric oxide in detail. Several polarographic investigations of the catalytic behavior of nitrate ion on the reduction waves of Cr(III) complexes have been reported and analytical methods have been developed utilizing

chromium(III) complexes of ethylenediaminetetraacetic acid,⁹ glycine,¹⁰ and other amino acids.¹¹ Very little work was found in which nitrite had been studied.

Preliminary investigation of the effect of NO_2^- on the polarographic reductions of a series of chromium(III) complexes showed that the catalytic wave enhancement of the reduction wave of the chromium(III) complex with ethylenediaminetetraacetic acid was significantly larger than the effect reported for nitrate. This work was then formulated to study the effect of NO_2^- on the ethylenediaminetetraacetatochromate(III) ion *via* polarography and controlled-potential electrolysis and expanded to include the complexes *trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetatochromate(III) (CrCyDTA) and hexacyanochromate(III) ion.

Experimental Section

Reagents. Hydrogen ethylenediaminetetraacetatoaquochromate(III), $[\text{CrH}(\text{EDTA})\text{H}_2\text{O}]$, was prepared according to the method of Hamm.¹² The pure product was identified by comparison with the reported visible spectrum¹³ and polarographic data.⁹ 1,2-Diaminocyclohexanetetraacetatoaquochromate(III) ion, Cr(CyDTA)⁻, was prepared in aqueous solution by heating a mixture of $\text{Cr}(\text{ClO}_4)_3$ and CyDTA. The slight excess of Cr(III) was removed by ion exchange with a sodium counterion. The visible spectrum of the final product agreed well with the reported spectrum.¹⁴ Pentaquonitrosylchromium(I) ion, $\text{Cr}(\text{NO})(\text{H}_2\text{O})_5^{2+}$, was prepared in solution by the nitrite reoxidation of electrochemically reduced chromium(III) perchlorate. The reddish brown product was separated on an Amberlite 1R-120, 20-50 mesh, cation-exchange resin in the acid form. The product was eluted with 0.75 M HClO_4 and its visible spectrum was identical with the literature spectrum.⁷ The *in situ* preparation of Cr(NO)EDTA and Cr(NO)CyDTA was accomplished by mixing of CrNO^{2+} with the appropriate ligand followed by neutralization with Na_2CO_3 . The reaction was complete in several minutes at room temperature when EDTA was the ligand but much slower with Cy-

(1) Taken in part from the Ph.D dissertation of J. M. V., 1973.
 (2) To whom correspondence should be addressed.
 (3) R. L. Birke and W. F. Marzluff, Jr., *J. Amer. Chem. Soc.*, **91**, 3481 (1969).
 (4) R. G. Linck, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci.: Inorg. Chem., Ser. One*, **9**, 303 (1972).
 (5) For example, J. K. Kochi, and J. W. Powers, *J. Amer. Chem. Soc.*, **92**, 137 (1970).
 (6) J. J. Lingane and R. L. Pecsok, *Anal. Chem.*, **21**, 622 (1949).
 (7) M. Ardon and J. I. Herman, *J. Chem. Soc. A*, 507 (1962).
 (8) J. N. Armor and M. Buchbinder, *Inorg. Chem.*, **12**, 1086 (1973).

(9) N. Tanaka and T. Ito, *Bull. Chem. Soc. Jap.*, **39**, 1043 (1966).
 (10) R. E. Hamm and C. D. Withrow, *Anal. Chem.*, **27**, 1913 (1955).
 (11) H. Hamaguchi, J. Hashimoto, and N. Fukushi, *Nippon Kagaku Zasshi*, **79**, 1482 (1958); *Chem. Abstr.*, **53**, 7362 (1959).
 (12) R. E. Hamm, *J. Amer. Chem. Soc.*, **75**, 5670 (1953).
 (13) C. Furlani, G. Morpurgo, and G. Sartaro, *Z. Anorg. Allg. Chem.*, **303**, 1 (1960).
 (14) A. R. Selmer-Olson, *Anal. Chim. Acta*, **26**, 482 (1962).