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Photochemical Generation and Chemical Reactivity of Hydridopentaaquochromium(III) Ions[1]

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The complex $(H_2O)_5CrH^{2+}$ was prepared by UV flash photolysis of aqueous chromium(II) perchlorate solutions in dilute perchloric acid. This species (λ_{max} = 385 ± 5 nm) has a short lifetime owing to its rapid reaction with H_3O^+ ($k = (1.0 \pm 0.1) \times 10^4$ M^{-1} s^{-1} at 26 °C and μ = 0.20 M) to evolve hydrogen. The rate constant was studied as a function of ionic strength, confirming the 2+ charge, and at μ = 0.20 M as a function of temperature, providing the activation parameters $\Delta H^{\ddagger} = 26.4 \pm 0.9$ kJ mol^{-1}, $\Delta S^{\ddagger} = -79.9 \pm 2.9$ J mol^{-1} K^{-1}. The acidolysis of CrH^{2+} occurs 2×10^6 times more rapidly than that of methylpentaaquochromium(III) ion, $(H_2O)_5CrCH_3^{2+}$. Protonolysis of CrH^{2+} in H_3O^+ as compared to CrD^{2+} in D_3O^+ shows an appreciable kinetic isotope effect (k_H/k_D = 4.8) as does the protonolysis of $CrCH_3^{2+}$ in the same two solvents (k_H/k_D = 6.3). The mechanism in both cases involves O···H bond breaking more so than chromium-hydrogen (or chromium-carbon) cleavage.

Introduction

The hydridopentaaquochromium(III) ion, $(H_2O)_5CrH^{2+}$ (or more simply CrH^{2+}), was first prepared in 1974 with use of the pulse-radiolysis technique.[2] We thought it useful to conduct further investigations of CrH^{2+}, both to develop a synthetic method which would be more widely available outside of specialized installations and to explore further its chemical reactivity. This complex bears some relationship to members of a general family of alkylchromium cations $(H_2O)_5CrR^{2+}$ (R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, etc.) which have been widely investigated[3-5] and might even be regarded as the first member of such a series. Comparisons on such a basis may provide further insight into the chemical reactivity of organochromium complexes.

It occurred to us that a photochemical route to CrH^{2+} should also be possible based on the known UV photochemistry of $Cr^{2+}(aq)$. Considering the high reactivity of CrH^{2+}, it was necessary to use the rapidly responding technique of flash photolysis to explore this possibility and to examine the subsequent reaction of CrH^{2+} with H_3O^+. It has long been known that UV irradiation of aqueous chromium(II) solutions causes evolution of hydrogen gas.[6] The primary event for Cr^{2+}, and for numerous other transition-metal species, is a charge transfer to solvent process in which an electron is ejected from the complex,[7] forming the hydrated electron and the oxidized metal complex. Hydrogen atoms, produced from e_{aq}^- in a well-known secondary reaction[8] with protons, are captured efficiently by $Cr^{2+}(aq)$ (eq 1) to yield the desired inner-sphere hydride complex.[2] We report here on the photochemical preparation of CrH^{2+} and on its reaction (eq 2) with H_3O^+.

$$Cr^{2+}(aq) + H\cdot \rightarrow (H_2O)_5CrH^{2+} \qquad k_1 = 1.5 \times 10^9 \ M^{-1} \ s^{-1} \tag{1}$$

$$(H_2O)_5CrH^{2+} + H_3O^+ \rightarrow Cr(H_2O)_6^{3+} + H_2 \tag{2}$$

Experimental Section

Materials. Solutions of ca. 0.2 M chromium(II) perchlorate were prepared by dissolution of pellets of the pure metal in an insufficient quantity of 5 M perchloric acid under prepurified nitrogen. The Cr(II) content was determined spectrophotometrically (ϵ_{710} 4.85 M^{-1} cm^{-1}) and the residual free perchloric acid by titration after ion exchange. Traces of oxygen were removed from gaseous nitrogen or nitrous oxide by Cr^{2+} scrubbing towers. Solutions of $CrCH_3^{2+}$ were prepared from Cr^{2+} and *tert*-butyl hydroperoxide.[3,4,5d]

Flash Photolysis and Kinetics. The desired quantities of all solutions other than chromium(II) were placed in a cylindrical 10-cm spectrophotometer cell constructed entirely of quartz, and a rubber septum was wired in place. The contents were extensively deaerated with nitrogen, after which Cr^{2+} was injected through the septum. The cell was brought to the (approximate) desired temperature and then transferred to the flash-photolysis unit for subsequent work. At the conclusion of these determinations, the cell was opened and its temperature determined with a small thermistor probe and a calibrated digital thermometer. The flash itself caused an inappreciable temperature rise (<0.2 °C). Runs conducted away from room temperature were done quickly to minimize any temperature drift.

The flash photolysis[9] itself was conducted with unfiltered UV-visible radiation from fast-extinguishing xenon flash lamps in the Xenon Corp.'s Model 710 system. A typical flash energy was 250 J, although it was varied in some experiments down to 75 J. A storage oscilloscope was used to record the transmittance change accompanying the decay of the transient, which was often monitored at the 380-nm maximum reported[2] for CrH^{2+}. The pseudo-first-order kinetic plots[10] were linear to ≥3 half-lives and were reproducible to within some 3-8% standard deviations.

Results

UV flash photolysis of $\sim 10^{-3}$ M chromium(II) perchlorate solutions in dilute aqueous perchlorate produced a transient readily detected at 380 nm, the reported[2] maximum for the $(H_2O)_5CrH^{2+}$ ion. The transient was formed within the time of the flash, following which it decayed to an absorbance slightly higher than that prior to photolysis. The amplitude of the signal and therefore the concentration of the transient increased linearly with flash energy, 75-250 J. Its spectrum was determined on a point-by-point basis in the wavelength range 320-450 nm. As shown in Figure 1, there is an absorption maximum at 385 ± 5 nm and a minimum at 350 ±

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[1] Based in part on the Ph.D. thesis of D. A. Ryan, Iowa State University, 1981.

[2] Cohen, H.; Meyerstein, D. *J. Chem. Soc., Dalton Trans.* **1974**, 2559.

[3] Schmidt, W.; Swinehart, J. H.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 1117.

[4] Ardon, M.; Woolmington, K.; Parrick, A. *Inorg. Chem.* **1971**, *10*, 2812.

[5] (a) Espenson, J. H.; Williams, D. A. *J. Am. Chem. Soc.* **1974**, *96*, 1008. (b) Chang, J. C.; Espenson, J. H. *J. Chem. Soc., Chem. Commun.* **1974**, 233. (c) Leslie, J. P., II; Espenson, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4839. (d) Hyde, M. R.; Espenson, J. H. *Ibid.* **1976**, *98*, 4463.

[6] Balzani, V.; Carassiti, V. "Photochemistry of Coordination Compounds"; Academic Press: New York, 1970; p 116.

[7] (a) Hartmann, H.; Muller, J.; Kelm, H. *Naturwissenschaften* **1973**, *60*, 256. (b) Raphael, M. W.; Malati, M. A. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1326. (c) Cannon, R. D. *Adv. Inorg. Chem. Radiochem.* **1978**, *21*, 179-225.

[8] Dorfman, L. M.; Taub, I. A. *J. Am. Chem. Soc.* **1963**, *85*, 2370.

[9] Details of the flash-photolysis experiments and of the kinetic data are given in thesis cited.[1]

[10] The transmittance changes were sufficiently small in all these experiments that the kinetic plots could be constructed directly from the voltage scale of the oscilloscope, as ln ($V_t - V_\infty$) vs. time, without conversion to absorbances.

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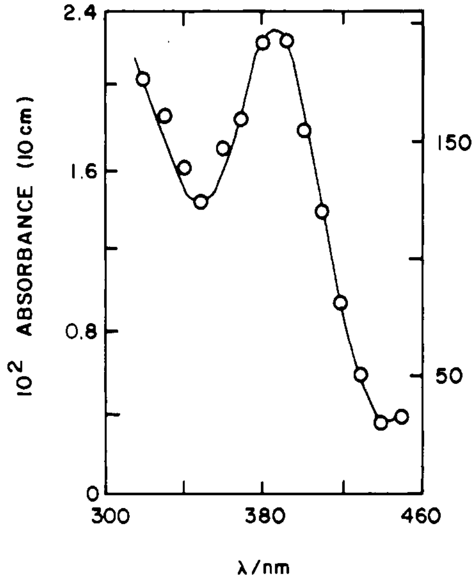

Figure 1. Absorption spectrum of the transient identified as CrH^{2+}. The scale of molar absorptivities is based on the value[2] ϵ_{380} 190 M^{-1} cm^{-1}.

Table I. Rate Constants for the Reaction of CrH^{2+} with H_3O^+ [a]

$[H^+]$/M	k_{obsd}/s^{-1}	$10^{-4}k_{obsd}[H_3O^+]^{-1}$/ M^{-1} s^{-1}
0.010	94.7 ± 4.6	0.95
0.010[b]	95.4 ± 4.4	0.95
0.010[c]	101 ± 7	1.01
0.010[d]	104 ± 2	1.04
0.010[e]	94 ± 6	0.94
0.030	283 ± 7	0.94
0.050	423 ± 63	0.85
0.060	576 ± 49	0.96
0.070	630 ± 46	0.90
0.100	931 ± 58	0.93
0.130	1330 ± 45	1.02
0.150	1365 ± 190	0.91
0.170	2010 ± 90	1.18
0.200	2200 ± 560	1.10
		av = 1.00 ± 0.10

[a] At 26.0 ± 0.5 °C and 0.20 M ionic strength; flash energy = 250 J and λ 380 nm (except as noted). [b] 330 nm. [c] 420 nm. [d] 125 J. [e] 75 J.

5 nm, with the absorbance rising into the UV region. These features agree well with those reported[2] for CrH^{2+} prepared with pulse radiolysis, λ_{max} 380 ± 5 nm (ϵ 190 ± 20 M^{-1} cm^{-1}).

Effect of $[H^+]$. The reaction of CrH^{2+} with H_3O^+ occurs according to eq 2. The kinetics of this reaction were investigated by monitoring the decrease of the absorbance of CrH^{2+} with time. Such determinations were done at varying concentrations of perchloric acid, 0.01–0.20 M, with ionic strength maintained constant at $\mu = 0.20$ M by addition of lithium perchlorate. Most of these determinations were done at 380 nm where the largest absorbance changes were observed. Some experiments were also done at 330 and 420 nm and at lower flash energies, 125 and 75 J. These variations did not affect k_{obsd} within experimental error.

Values of k_{obsd} at the different hydrogen ion concentration in the range 0.01–0.20 M are given in Table I. The value of k_{obsd} increases linearly with $[H^+]$, as shown in Figure 2, which has within experimental error a 0 intercept. (Actually, −57 ± 46 s^{-1}, if the value of the intercept is left to a least-squares adjustment.) The rate law for eq 2 is thus eq 3, and

$$-d[CrH^{2+}]/dt = k_2[CrH^{2+}][H_3O^+] \qquad (3)$$

the average value of k_2, provided the intercept is set to 0

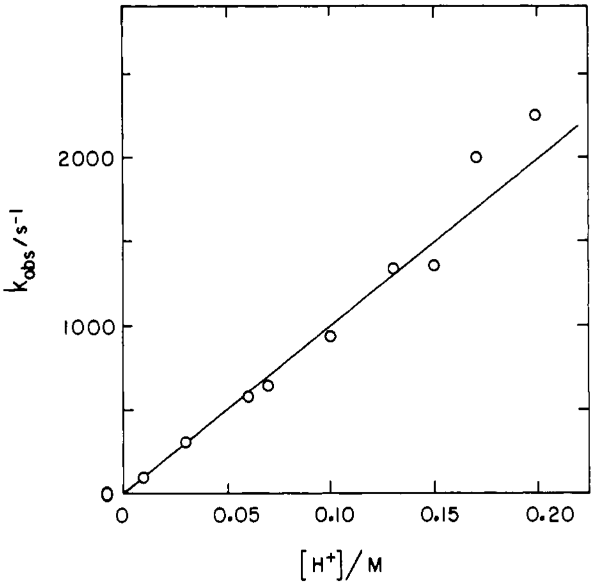

Figure 2. Illustration that values of the pseudo-first-order rate constant for the reaction of CrH^{2+} with H_3O^+ (eq 5) are directly proportional to $[H_3O]^+$ in accord with eq 6.

exactly, is (1.00 ± 0.10) × 10^4 M^{-1} s^{-1} at 26.0 ± 0.5 °C and $\mu = 0.20$ M.

Effect of Temperature. Values of k_2 were determined in a similar fashion over a 34° temperature range. The decay of the transient produced by a 250-J flash was monitored at 380 nm. This series of experiments had $[H^+] = 0.010$ M, and the ionic strength was adjusted to 0.20 M by lithium perchlorate as in the earlier determinations. The values of $10^{-4}k_2$ (M^{-1} s^1) are 0.637 ± 0.043 (14.4 °C), 0.616 ± 0.086 (14.7), 0.800 ± 0.048 (20.5), 1.02 ± 0.04 (27.0), 1.50 ± 0.02 (35.5), and 2.17 ± 0.06 (48.1). Analysis of these results using the equation of activated complex theory gives the following activation parameters: $\Delta H_2^{\ddagger} = 26.4 \pm 0.9$ kJ mol^{-1} (6.3 ± 0.2 kcal mol^{-1}) and $\Delta S_2^{\ddagger} = -79.9 \pm 2.9$ J mol^{-1} K^{-1} (−19.1 ± 0.7 cal mol^{-1} K^{-1}).

Effect of Ionic Strength. The variation of k_2 with the ionic strength was also investigated for the purpose of substantiating that the transient is correctly formulated as a dipositive ion. In all but one of these experiments, the hydrogen ion concentration was 0.010 M, and the ionic strength was varied up to 0.20 M by addition of lithium perchlorate; the remaining experiment had $[H^+] = 0.0050$ M and ionic strength 0.0080 M by virtue of the contribution from 10^{-3}M $Cr(ClO_4)_2$. The Brønsted–Debye–Hückel equation expressing the variation of a second-order rate constant with ionic strength is written as eq 4, where A is a known constant (0.509 in water at 25 °C),

$$\log k = \log k^0 + 2z_Az_BA\mu^{1/2}/(1 + \mu^{1/2}) \qquad (4)$$

z_A and z_B represent the charge on each reactant (which are +1 and +2 if eq 2 is the correct elementary reaction). Figure 3 depicts a plot of log *k* vs. the quantity $0.509\mu^{1/2}/(1 + \mu^{1/2})$. Also shown on the graph is a straight line having the "correct" slope of +4.00 ($=2z_Az_B$), assuming eq 4 can properly be applied to the data. The relationship is obeyed at low μ, with systematically greater deviation for values at ionic strength >0.1 M. This linear analysis gives the rate constant extrapolated to 0 ionic strength as $k^0 = 3.2 \times 10^3$ M^{-1} s^{-1}.

A more elaborate analysis[9] of the results can be obtained by including in eq 4 an additional term which is linear in ionic strength.[11] That term, with a variable coefficient, can provide

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(11) (a) Davies, C. W. "Ion Association"; Butterworths: London, 1962. (b) A least-squares treatment of the ionic strength dependence is exemplified by the relation $\log k = \log k^0 - C\mu + 2z_Az_BA\mu^{1/2}/(1 + \mu^{1/2})$.

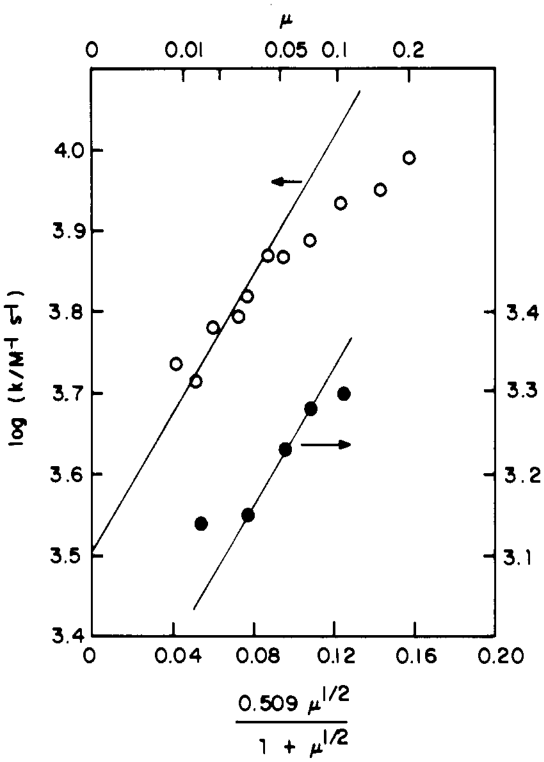

Figure 3. Illustration of the ionic strength dependence of the rate constants for reactions of CrH^{2+} + H_3O^+ (eq 5, open circles) and CrD^{2+} + D_3O^+ (eq 8, filled circles). The lines are drawn to have the theoretical values of the slopes ($=2z_Az_B$) according to the Brønsted-Debye-Hückel equation.

a correlation of the results over the entire ionic strength range, although the additional parameterization makes this approach unwarranted for the present system considering the accuracy of the rate constants and the goal of the determination, which was to confirm the 2+ charge on CrH^{2+}.

Effect of Deuterium Substitution. The fully deuterated analogue, $(D_2O)_5CrD^{2+}$, was prepared by identical methods in D_2O solutions in which the mole fraction of deuterium was >0.98. A transient similar to CrH^{2+} was observed, characterized by a slower reaction with D_3O^+ (eq 5) than that shown

$$(D_2O)_5CrD^{2+} + D_3O^+ \rightarrow Cr(D_2O)_6^{3+} + D_2 \quad (5)$$

in eq 2. Kinetic studies were conducted without addition of lithium perchlorate, the ionic strength being governed by the perchloric acid concentration, and thus varied from experiment to experiment. Since it has been well established that the rate of reaction 2 is directly proportional to hydrogen ion concentration, the same may safely be assumed for eq 5. Values of log k_5 are shown vs. the ionic strength function in Figure 3, once again with the straight line drawn to have a slope equal to the theoretical value of $2z_Az_B$ (=4.00) at low ionic strength. The limiting value of k_5^0 at 0 ionic strength is 6.7 × 10^2 M^{-1} s^{-1}, a factor of 4.8 ± 1.2 lower than the corresponding value of k_2^0 for CrH^{2+}.

This series of experiments was necessarily limited to runs in which there was further deuterium substitution than that merely represented by the change from CrH^{2+} to CrD^{2+}. The five coordinated water molecules were also changed from H_2O to D_2O, as was the bulk solvent. In an effort to allow for this effect, we carried out measurements on the corresponding protonolysis of the methylchromium(III) ion both in H_2O (eq 6) and in D_2O (eq 7). In both instances the complex was prepared[3] by reaction of $(CH_3)_3COOH$ with $Cr^{2+}(aq)$ in the desired solvent.

$$(H_2O)_5CrCH_3^{2+} + H_3O^+ \rightarrow Cr(H_2O)_6^{3+} + CH_4 \quad (6)$$

$$(D_2O)_5CrCH_3^{2+} + D_3O^+ \rightarrow Cr(D_2O)_6^{3+} + DCH_3 \quad (7)$$

The determinations of the rate constants for eq 6 and 7 were carried out at 24.8 °C and μ = 0.10 M, giving k_6 = (6.2 ± 0.2) × 10^{-3} M^{-1} s^{-1} and k_7 = (9.9 ± 0.1) × 10^{-4} M^{-1} s^{-1}. The latter was determined in solutions containing >0.98 mole fraction of deuterium. Thus the protonolysis rate of methylchromium ion also shows a substantial isotope effect, k_6/k_7 = 6.3 ± 0.2.

Effect of Nitrous Oxide. The intensity of the transient was greatly reduced when the solution was saturated with nitrous oxide instead of nitrogen. For example, a solution of 10^{-3} M chromium(II) in 10^{-3} M $HClO_4$ produced a transient absorbance change at 380 nm of 0.0044 (10-cm optical path) under nitrous oxide, compared to 0.02 under nitrogen. This amounts to a 78% reduction. The primary photochemical event is believed to be electron ejection from $Cr^{2+}(aq)$ to solvent. Nitrous oxide is an efficient scavenger for the hydrated electron, resulting in a diminished yield of hydrogen atoms from eq 3 by virture of competition with eq 8.

$$e_{aq}^- + N_2O \xrightarrow{H^+} N_2 + HO\cdot \qquad k_8 = 8.7 \times 10^9\ M^{-1}\ s^{-1} \quad (8)$$

The expected reduction in yield of H·, and thus of CrH^{2+}, can be calculated from these equations, although allowance must be made for a further route[2] for consumption of e_{aq}^-

$$e_{aq}^- + Cr^{2+}(aq) \rightarrow Cr^+(aq) \qquad k_9 = 1.4 \times 10^{10}\ M^{-1}\ s^{-1} \quad (9)$$

Consequently at $[H^+]$ = 10^{-3} M and with saturated (0.025 M) N_2O, the yield of CrH^{2+} is calculated to be 85% less (and observed to be 77% less) than that in the absence of N_2O. The calculated value is based on the further assumption that, in both instances, all of the H atoms are converted to CrH^{2+} by efficient reaction with Cr^{2+} in eq 1.

The efficiency of trapping e_{aq}^- by N_2O is, of course, expected to be less at higher $[H^+]$, where the reaction of e_{aq}^- with H_3O^+ is necessarily more important. In keeping with this, N_2O saturation at higher $[H^+]$ would cause less of a decrease in yield of CrH^{2+} than it did in these experiments at 10^{-3} M H^+.

Effect of Methanol. Photolysis of chromium(II) perchlorate in 0.1 M perchloric acid to which methanol (5 M) had been added gave rise to a relatively stable spectrum characteristic of an organochromium ion rather than a rapidly decaying transient. The species formed had a spectrum (λ_{max} 390 nm, 280, sh) and a lifetime toward protonolysis (k = (8.9 ± 0.2) × 10^{-4} s^{-1} at 25 °C, $[H^+]$ = μ = 0.1 M) consistent with that known for $(H_2O)_5CrCH_2OH^{2+}$ (λ_{max} 392 and 280 nm; for $CrCH_2OH^{2+} + H_2O, H_3O^+ \rightarrow Cr^{III} + CH_3OH$, k = 7.1 × 10^{-4} s^{-1} at 25 °C, $[H^+]$ = 0.1 M, μ = 1.0 M).[14] Formation of $CrCH_2OH^{2+}$ is consistent with the chemistry expected because the $\cdot CH_2OH$ radical, formed by the reaction of hydrogen atoms with methanol (eq 10), is efficiently captured by $Cr^{2+}(aq)$ (eq 11).

$$H\cdot + CH_3OH \rightarrow H_2 + \cdot CH_2OH \qquad k_{10} = 2 \times 10^6\ M^{-1}\ s^{-1}\ {}^{13} \quad (10)$$

$$Cr^{2+}(aq) + \cdot CH_2OH \rightarrow CrCH_2OH^{2+} \qquad k_{11} = 1.6 \times 10^8\ M^{-1}\ s^{-1}\ {}^{14} \quad (11)$$

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(12) The rate of eq 2 was previously[2] studied from 0.01 to 1.0 M $HClO_4$. The ionic strength was not maintained constant.

(13) Anbar, M.; Ross, F.; Ross, A. B. *Natl. Stand. Ref. Data Ser. U.S., Natl. Bur. Stand.*) **1975**, *NSRDS-NBS 51*, 36.

(14) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1974**, *13*, 2434.

The yield of $CrCH_2OH^{2+}$ after a single flash was roughly 1.5×10^{-5} M; consideration of the competition between eq 1 and 10 the initial yield of H· in a 250-J flash is ca. $(1.8 \pm 0.1) \times 10^{-5}$ M. This value, applied to the absorbance change detected in the absence of methanol, gives a value for the molar absorptivity of CrH^{2+}, ϵ_{380} $(1.3 \pm 0.3) \times 10^2$ M^{-1} cm^{-1}, which is in adequate agreement with the value $(1.9 \pm 0.2) \times 10^2$ M^{-1} cm^{-1} found with use of pulse radiolysis.[2]

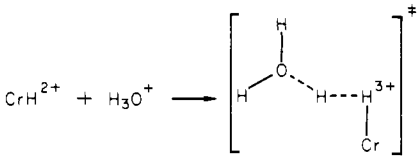
If several successive flashes at ca. 10-s intervals were done, there was produced a second slowly decaying species which was decomposed prior to protonolysis of $CrCH_2OH^{2+}$ which appeared to be formed in about the expected yield. It seems likely that secondary photolysis of $CrCH_2OH^{2+}$ had occurred, however, considering its strong UV absorption and the absence of this complication during single-shot experiments. The nature of the new species was not established. The results cited above were based on single-shot photolysis.

Interpretation and Discussion

Numerous instances in which thermal reactions as well as pulse radiolysis can be used to produce hydrido complexes of hydrated metal cations have been noted in the literature, including CuH^+,[15] AgH^+ and AgH,[16] FeH^{2+},[17] and TiH^{3+}.[18] In the cases of complexes formed by combination of the hydrogen atom, its reaction with the hydrated metal ion (invariably a strong reducing agent such as Cr^{2+}, Fe^{2+}, or Ti^{3+}) results in one-electron oxidation of the latter. The dual oxidizing and reducing nature of H· is now well recognized.[19,20] In those instances in which a hydrido complex is formed, it proved to be a reactive, transient entity.

Indirect evidence that UV photolysis of $Cr^{2+}(aq)$ (λ 270 nm, $\epsilon \sim 15$ M^{-1} cm^{-1}) was accompanied by ejection of e_{aq}^- was provided by trapping experiments based on addition of nitrous oxide;[7a] $N_2(g)$ was one of the products (eq 11), and the ratio of N_2 to H_2 as a function of $[N_2O]$ gave further substantiation. The evidence we offer that the photochemical transient observed during the course of this work is, indeed, the hydridochromium(III) ion is the following. (1) Its spectrum matches that attributed to CrH^{2+} prepared with pulse-radiolysis methods wherein the basic radiation chemistry is different from the UV photochemistry. (2) The yield of CrH^{2+} could be diminished in a predictable manner upon addition of N_2O, consistent with the photochemical and thermal reactions believed to be responsible for its generation. (3) The reaction of our CrH^{2+} with H_3O^+ occurred with the same rate law as found[2] for the radiolytically produced species. (4) The rate constant for eq 2 ($(1.0 \pm 0.1) \times 10^4$ M^{-1} s^{-1} at 26 °C and $\mu = 0.2$ M) can be considered to be in adequate agreement with previous results[2] considering the conditions employed ($(1.8 \pm 0.2) \times 10^4$ M^{-1} s^{-1} at 22.2 °C and variable ionic strength[12]). (5) Addition of methanol prior to photolysis yielded $CrCH_2OH^{2+}$ rather than CrH^{2+}. (6) The ionic strength dependence is consistent with that expected for the reaction with H_3O^+ of a species having a 2+ ionic charge.

Experiments comparing CrD^{2+} and CrH^{2+} were necessarily limited to those in which the bulk solvent and the coordinated solvent molecules were concurrently substituted as well. Although this experiment gave a substantial isotope effect ($k_H/k_D = 4.8 \pm 1.2$), a "calibration" experiment based on $CrCH_3^{2+}$ showed an effect every bit as large (6.3 ± 0.2). The former is assumed to be the product of two factors, one reflecting the effect of the solvent change, the other the change in the hydrogen–chromium bond itself. If the first of these factors is approximated by the value found for $CrCH_3^{2+}$, the latter is within experimental error of unity (0.76 ± 0.23). This result suggests that metal–hydrogen bond dissociation is not the key factor in the mechanism. Rather, the cleavage of an O–H bond is important. Such a process (eq 12) is reasonable



(12)

in that it avoids formation of an incipient free hydride anion, a species which is an enormously basic entity in these circumstances. It should also be noted that earlier workers,[3] who also found an appreciable deuterium solvent isotope effect on the protonolysis of $CrCH_3^{2+}$, concluded that a mechanism similar to that shown in eq 12 applied. That CrH^{2+} shows an inappreciable isotope effect, after allowance for the solvent effect, is not altogether unexpected. Small effects are common for other protonolysis reactions of hydrides[21] and are found experimentally[22] and theoretically[23] for hydride transfers such as the hydrolysis of the boron–hydrogen bond in pyridinedialkylboranes.[22a]

It is interesting to examine whether CrH^{2+} might possibly have a chemical relationship to members of the family of alkylpentaaquochromium(III) ions. If CrH^{2+} is to be regarded as the simplest member of that series $(H_2O)_5CrR^{2+}$, then it is by far the most reactive toward acidolysis. The reactivity toward H_3O^+ of CrH^{2+} compared to $CrCH_3^{2+}$ under similar circumstances is $k_2/k_6 = 2 \times 10^6$. This very large enhancement in reactivity is not unreasonable, however, considering how very sensitive to steric factors are the electrophilic substitution reactions of CrR^{2+} with H_3O^+,[5d] Hg^{2+},[5c] Br_2, and I_2,[5a] and of $RCo(dmgH)_2H_2O$ with Hg^{2+}.[24]

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Registry No. $(H_2O)_5CrH^{2+}$, 79329-65-0; H_3O^+, 13968-08-6; deuterium, 7782-39-0.

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(15) (a) Peters, E.; Halpern, J. *Can. J. Chem.* **1955**, *33*, 356; *J. Phys. Chem.* **1955**, *59*, 793. (b) Halpern, J.; Macgregor, E. R.; Peters, E. *J. Phys. Chem.* **1956**, *60*, 1455.

(16) Webster, A. H.; Halpern, J. *J. Phys. Chem.* **1957**, *61*, 1239.

(17) (a) Halpern, J.; Czapski, G.; Jortner, J.; Stein, G. *Nature* (*London*) **1960**, *186*, 629. (b) Czapski, G.; Jortner, J.; Stein, G. *J. Phys. Chem.* **1961**, *65*, 910. (c) Jayson, G. G.; Keene, J. P.; Stirling, D. A.; Swallow, A. J. *Trans. Faraday Soc.* **1969**, *65*, 2453. (d) Nenadović, M. T. Mićić, O. I.; Muk, A. *J. Chem. Soc., Dalton Trans* **1980**, 586.

(18) (a) Behar, D.; Samuni, A. *Chem. Phys. Lett.* **1973**, *22*, 105. (b) Behar, D.; Samuni, A.; Fessenden, R. W. *J. Phys. Chem.* **1973**, *77*, 2055. (c) Mićić, O. I.; Nenadović, M. T. *J. Chem. Soc., Dalton Trans.* **1979**, 2011.

(19) (a) Lyhourezos, P. A. P.; Kanellopoulos, A.; Katakis, D. *J. Phys. Chem.* **1968**, *72*, 2330. (b) Mazumdar, A. S. G.; Srinivasan, B.; Natarajan, P. *Int. J. Radiat. Phys. Chem.* **1973**, *5*, 51. (c) Freiberg, M.; Meyerstein, D. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 622.

(20) (a) Baxendale, J. H.; Rodgers, M. A. J. *Chem. Soc. Rev.* **1978**, *7*, 235. (b) Buxton, G. V.; Sellers, R. M. *Coord. Chem. Rev.* **1977**, *22*, 195.

(21) Saunders, W. J., Jr. *Techn. Chem.* **1974**, *6*.

(22) (a) Hawthorne, M. F.; Lewis, E. S. *J. Am. Chem. Soc.* **1958**, *80*, 4296. (b) Kaplan, L.; Wilzback, K. E. *Ibid.* **1955**, *77*, 1297. (c) Bartlett, P. D.; McCollum, J. D. *Ibid.* **1956**, *78*, 1441.

(23) More O'Farrall, R. A. *J. Chem. Soc. B* **1970**, 785.

(24) (a) Adin, A.; Espenson, J. H. *J. Chem. Soc. D* **1971**, 653. (b) Fritz, H. L.; Espenson, J. H.; Williams, D. A.; Molander, G. A. *J. Am. Chem. Soc.* **1974**, *96*, 2378.