Ultraviolet–Visible Spectrum, and Kinetics of Formation and Decomposition, of Penta-aquahydridochromium(III) and Chromium(I) in Aqueous Perchlorate Solutions: A Pulse-radiolysis Study

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The reaction of hydrogen atoms with Cr^{2+}(aq) has been studied and a specific rate constant of $1{\cdot}5 \times 10^9$ l mol^{-1} s^{-1} determined. The product of this reaction in acid solution is $[Cr(H_2O)_5H]^{2+}$. The absorption spectrum of this complex has been measured and found to be similar to that of complexes containing chromium–carbon bonds. The mechanism of decomposition of $[Cr(H_2O)_5H]^{2+}$ obeys the rate equation $k_{obs} = k_{17} + k_{18}[H_3O^+]$, where $k_{17} \leqslant 1$ s^{-1} and $k_{18} = 1{\cdot}8 \times 10^4$ l mol^{-1} s^{-1} at 22 ± 2 °C. In neutral solutions Cr^+(aq) is formed by reaction of e^-(aq) with Cr^{2+}(aq). The absorption spectrum of Cr^+(aq) and the kinetics of its decomposition are reported and discussed. The implication of these results to the mechanism of dissolution of chromium metal and on the photochemistry of Cr^{2+}(aq) are examined.

RECENT studies have pointed out that aliphatic radicals, $RH^{\bullet}$, which in part are strong reducing agents,[1] oxidize several low-valent transition-metal cations, *e.g.* $[Cr(H_2O)_6]^{2+}$,[2,3] Ti^{III}(aq),[2a,4] $[Fe(H_2O)_6]^{2+}$,[2a,4] and several Co^{II} complexes.[5] The mechanism suggested for these reactions involves formation of complexes containing a metal–carbon σ-bond [equation (1)]. Most of the latter complexes, which might be considered as complexes of $M^{(m+1)+}$ with carbanions, are unstable in aqueous solutions. They hydrolyse as in equation (2). Many of these hydrolysis reactions have been shown to be acid catalysed.[2b,3] A parallel mechanism has been suggested [6-9] for the oxidation of $[Fe(H_2O)_6]^{2+}$ by hydrogen atoms [equations (3) and (4)]. Although the absorption spectrum of the intermediate, $[Fe(H_2O)_6H]^{2+}$, was measured in the near-u.v. region, it was not accurately measured in the u.v. range because of the absorption of $[Fe(H_2O)_6]^{3+}$ formed.[9]

$$[M(H_2O)_n]^{m+} + RH^{\bullet} \longrightarrow [M(H_2O)_{n-1}RH]^{m+} + H_2O \tag{1}$$

$$[M(H_2O)_{n-1}RH]^{m+} + 2H_2O \longrightarrow [M(H_2O)_n]^{(m+1)+} + RH_2 + OH^- \tag{2}$$

$$[Fe(H_2O)_6]^{2+} + H \longrightarrow [Fe(H_2O)_5H]^{2+} + H_2O; \quad k_3 = 2 \times 10^7\ \mathrm{l\ mol^{-1}\ s^{-1}}\ \text{[8]} \tag{3}$$

$$[Fe(H_2O)_5H]^{2+} + H_3O^+ \longrightarrow [Fe(H_2O)_6]^{3+} + H_2; \quad k_4 = 1{\cdot}06 \times 10^4\ \mathrm{l\ mol^{-1}\ s^{-1}}\ \text{[9]} \tag{4}$$

Spectroscopic and chemical properties of a series of $[Cr(H_2O)_5RH]^{2+}$ complexes have been recently studied in detail.[3] It seemed of interest to study the reaction of hydrogen atoms with $[Cr(H_2O)_6]^{2+}$ in the hope of obtaining $[Cr(H_2O)_5H]^{2+}$. Such a study would enable a comparison between the properties of hydride and alkyl radical ligands. Such a comparison is not possible at present for the corresponding $[Fe(H_2O)_5RH]^{2+}$ complexes as the latter have not been isolated. The product of reaction of $[Cr(H_2O)_6]^{2+}$ and H atoms could plausibly be Cr^+(aq) and not $[Cr(H_2O)_5H]^{2+}$. In order to positively identify the product, the properties of Cr^+(aq) formed by reaction (5) were also determined. The results clearly indicate that $[Cr(H_2O)_5H]^{2+}$ is formed, and that its properties are similar in many respects to those of the $[Cr(H_2O)_5RH]^{2+}$ complexes and different from those of Cr^+(aq).

$$[Cr(H_2O)_6]^{2+} + e^-(aq) \longrightarrow Cr^+(aq) \tag{5}$$

EXPERIMENTAL

Materials.—The perchloric acid used was 70% pro-analysis (Merck). All the water used was triple distilled. Chromium(II) perchlorate solutions were prepared by dissolution of Spectrograde chromium metal (Johnson Matthey) in $1{\cdot}0$M-$HClO_4$ under an argon atmosphere.† When solutions at pH > 2 were required, excess of chromium metal was introduced into $0{\cdot}2$M-$HClO_4$. These solutions were diluted when no further dihydrogen evolution was observed. The vessel and technique are described in ref. 3. The solution thus prepared contained 2×10^{-3}—1×10^{-1}M-Cr^{2+}(aq) and less than 5% Cr^{3+}(aq) as determined by e.s.r. measurements.

Procedure.—The pH of chromium(II) perchlorate solutions was determined by immersing an electrode into the solution while bubbling argon through it. The accuracy of the measurements was only $\pm 0{\cdot}05$ pH unit.

The pulse-radiolysis experiments were carried out using $0{\cdot}1$—1 μs, 5 MeV, 200 mA pulses from the linear electron accelerator at the Hebrew University of Jerusalem. The dose per pulse was 1×10^{20}—10×10^{20} eV l^{-1}.‡ The irradiation cell was 4 cm long, and the analysing light travelled three times through the cell. The experimental

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† 1M = 1 mol dm^{-3}.

‡ 1 eV ≈ $1{\cdot}60 \times 10^{-19}$ J; 1 rad = 10^{-2} J kg^{-1}.

[1] J. Lilie, G. Beck, and A. Henglein, *Ber. Bunsengesellschaft Phys. Chem.*, 1971, **75**, 458.

[2] (*a*) H. E. De La-Mare, J. K. Kochi, and F. F. Rust, *J. Amer. Chem. Soc.*, 1963, **85**, 1437; (*b*) W. Schmidt, J. K. Swinehart, and H. Taube, *ibid.*, 1971, **93**, 1117.

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[9] G. G. Jayson, J. P. Keene, D. A. Stirling, and A. J. Swallow, *Trans. Faraday Soc.*, 1969, **65**, 2453.

set-up in Jerusalem and the method used for evaluating the results have been described elsewhere.[10]

Absorption spectra of the intermediates were measured by the pulse-radiolysis technique. The absolute absorption coefficients were determined by comparing the yield of $[Fe(CN)_6]^{3-}$ formed by an identical pulse in an N_2O-saturated solution containing 1×10^{-3}M-$K_4[Fe(CN)_6]$. $G\{[Fe(CN)_6]^{3-}\}$ was taken as 6·1.[11] The kinetics of formation and decomposition of the intermediates were measured at different wavelengths, chosen so that the difference in the molar absorption coefficients between the products and reactants would be maximized. γ-Irradiations were carried out using a ^{60}Co γ source, Noratom Gammacell 3500, with a dose rate of 27 000 rad min^{-1}. The solutions were irradiated in Pyrex bulbs filled under an argon atmosphere. The quantity of the dihydrogen formed on irradiation was determined by a Hewlett–Packard 5750 gas chromatograph using argon as the carrier gas. The accuracy was $\pm 0·002$ cm^3.

E.s.r. measurements were carried out in a *X*-band Varian 4500 spectrometer. All experiments were carried out at room temperature, 22 ± 2 °C.

RESULTS

Acidic Solutions.—Argon-saturated solutions containing 1×10^{-4}—20×10^{-4}M-$[Cr(H_2O)_6]^{2+}$ at $0 < pH < 2$ were irradiated by a short electron pulse from the accelerator. The formation of a short-lived intermediate absorbing in the 250—470 nm range was always observed. The kinetics of formation of this intermediate obeyed a pseudo-first-order rate law, being first order in $[Cr(H_2O)_6{}^{2+}]$ and independent of $[H_3O^+]$ with $k = 1·5 \times 10^9$ l mol^{-1} s^{-1}.

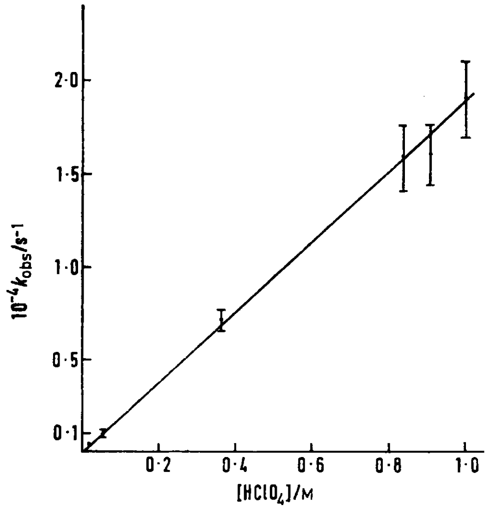

FIGURE 1 pH Dependence of the rate of decomposition of $[Cr(H_2O)_5H]^{2+}$

The absorption of this intermediate decayed by a process obeying a pseudo-first-order rate law, independent of $[Cr(H_2O)_6{}^{2+}]$ or the pulse intensity but proportional to $[H_3O^+]$. The specific rates observed, k_{obs}, fit the relation $k_{obs} = k[H_3O^+]$ where $k = (1·8 \pm 0·2) \times 10^4$ l mol^{-1} s^{-1} (see Figure 1). The absorption spectrum of this intermediate is shown in Figure 2. It is composed of two bands, a weak band at $\lambda_{max.} = 380 \pm 5$ nm ($\varepsilon_{max.}$ 190 ± 20 l mol^{-1} cm^{-1}) and a strong band at $\lambda_{max.} < 260$ nm ($\varepsilon_{max.} > 1\,000$ l mol^{-1} cm^{-1}).

Neutral Solutions.—The specific rate of reaction of $e^-(aq)$ with $[Cr(H_2O)_6]^{2+}$ was measured by following the disappearance of the absorption of $e^-(aq)$ at 600 nm in solutions containing 2×10^{-5}—10×10^{-5}M-$[Cr(H_2O)_6]^{2+}$ at $4·8 \leqslant pH \leqslant 5·1$. Thus a value of $(1·5 \pm 0·5) \times 10^{10}$ l mol^{-1} s^{-1} was determined.

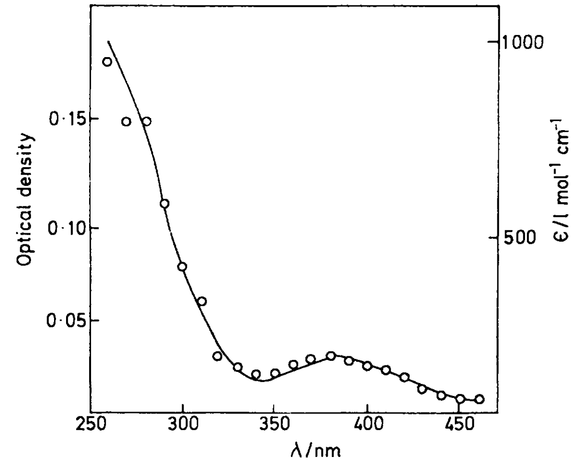

FIGURE 2 Absorption spectrum of $[Cr(H_2O)_5H]^{2+}$: (—), obtained from argon-saturated solutions containing 1M-$HClO_4$ and $1·4 \times 10^{-3}$M-Cr^{2+}(aq); (○), obtained from argon-saturated solutions at pH 3·85 containing $4·4 \times 10^{-3}$M-Cr^{2+}(aq), normalized to (—) at 300 nm (see text)

The absorption of the intermediates formed by the pulse in argon-saturated solutions in the pH range 2·0—5·0 decayed by two well separated processes (see for example the inset in Figure 3). The relative contributions of these processes depended linearily on the $[H_3O^+] : [Cr^{2+}(aq)]$ ratio (Figure 4). Optical densities observed 2 µs after the pulse, as well as the contribution of the short-lived intermediate, (I), are plotted against wavelength in Figure 3. The spectrum of the long-lived intermediate, (II), is shown in Figure 2. Absolute absorption coefficients were normalized in this case so that they would fit the spectrum of the intermediate formed in the acidic solutions at 300 nm. The calculation of absolute absorption coefficients of the different intermediates depended on their yields. Experimentally, only $G \times \varepsilon$ for any intermediate can be determined. Thus for a solution containing $4·4 \times 10^{-4}$M-Cr^{2+}(aq) at pH 3·85, $G\varepsilon = 530 \pm 50$ and 240 ± 25 l mol^{-1} cm^{-1} at 350 nm for (I) and (II) respectively.

The kinetics of disappearance of (I) indicated a first-order process (see Figure 5) with a small contribution by a second-order process. Thus the specific rates observed were nearly independent of wavelength, but depended slightly on the pulse intensity (see Figure 5 and Table 1). The specific rate of this reaction was independent of $[Cr(H_2O)_6{}^{2+}]$ and pH (Table 1). The kinetics of disappearance of (II) obeyed a pseudo-first-order rate law with a

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[10] (*a*) D. Meyerstein and W. A. Mulac, *J. Phys. Chem.*, 1968, **72**, 784; (*b*) Internal Report of the Accelerator Lab., Hebrew University, Jerusalem; (*c*) H. Cohen and D. Meyerstein, *J. Amer. Chem. Soc.*, 1971, **93**, 4179.

[11] G. E. Adams, J. W. Boag, and B. D. Michael, *Trans. Faraday Soc.*, 1965, **61**, 492.

first-order dependence on $[H_3O^+]$. As the spectrum of (II) fitted that of the intermediate formed in acidic solutions (see Figure 2), we checked whether the kinetics fitted the same rate law. At pH 4·15, $k_{obs} = 2{\cdot}15\ s^{-1}$. From the relation $k_{obs} = 1{\cdot}8 \times 10^4[H_3O^+]$ obtained in acidic solutions, we calculate, for this pH, $k_{obs} = 1{\cdot}4\ s^{-1}$, which is in fair agreement with the experimental value. Therefore if (II) observed in neutral solutions is identical with the intermediate observed in acidic solutions (an assumption which is justified in the Discussion section), then its rate of decomposition is given by $k_{obs} = k_{17} + k_{18}[H_3O^+]$, where $k_{17} < 1{\cdot}0\ s^{-1}$ and $k_{18} = 1{\cdot}8 \times 10^4\ l\ mol^{-1}\ s^{-1}$.

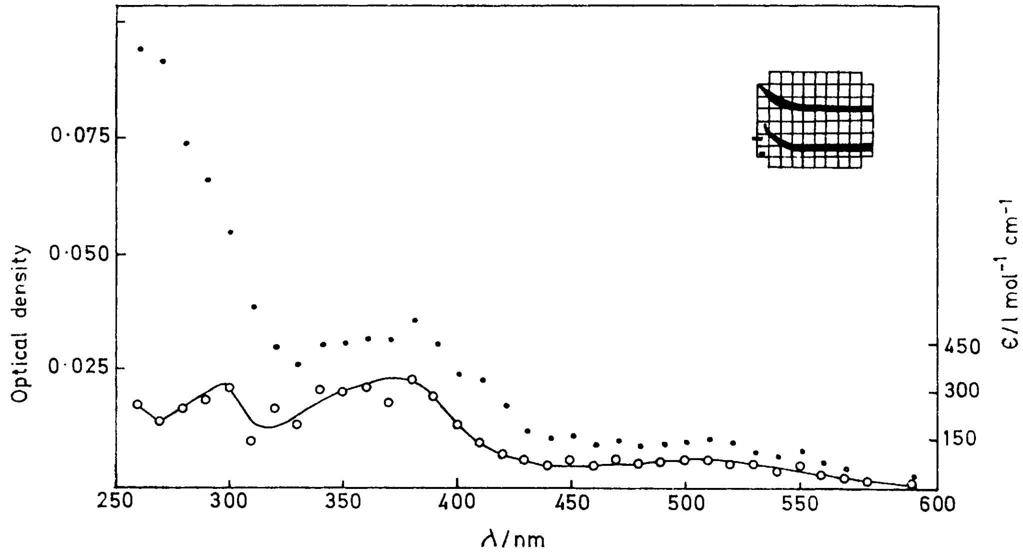

Figure 3 Absorption spectrum of the intermediates formed by irradiating argon-saturated solutions at pH 3·85 containing $4{\cdot}4 \times 10^{-3}$M-Cr^{2+}(aq): (●), formed immediately after the pulse; (○), absorption due to Cr^+(aq) (see text). The inset shows a typical oscillogram in neutral solutions. The abscissae of the upper trace is 200 μs division⁻¹ and of the lower trace 50 ms division⁻¹. For both traces the ordinate is 0·02 V division⁻¹ and $I_0 = 0{\cdot}800$ V

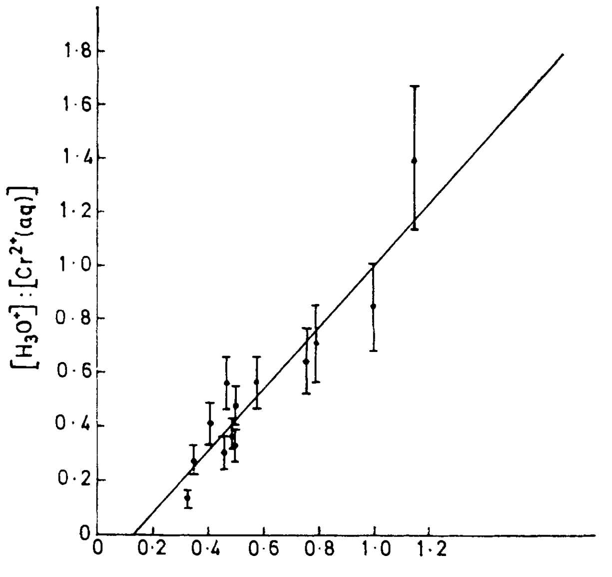

Figure 4 Dependence of the ratio $[H_3O^+] : [Cr^{2+}(aq)]$ on the Gε ratio for $[Cr(H_2O)_5H]^{2+}$ and Cr^+(aq) at 350 nm

Dihydrogen Yields.—The yield of dihydrogen, $G(H_2)$, formed on γ irradiation of samples containing $[Cr(H_2O)_6]^{2+}$ at different pH values, was measured. The results are summarized in Table 2.

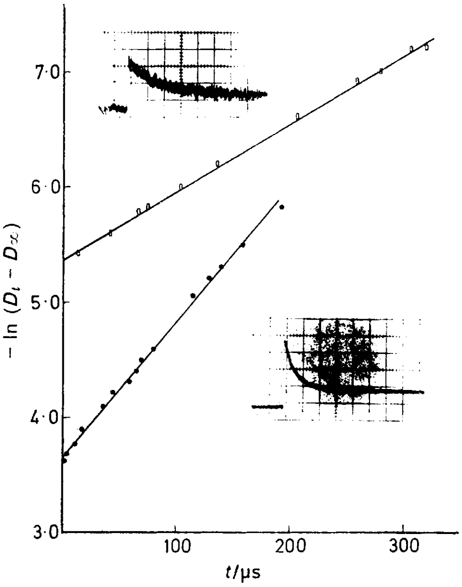

Figure 5 First-order plot for the decay of Cr^+(aq): (○), $\Delta(D_0) = 0{\cdot}0056$; (●), $\Delta(D_0) = 0{\cdot}0400$ measured at 350 nm

DISCUSSION

The radiolysis of water may be described by equation (6). The yields of the primary products in dilute

$$H_2O \xrightarrow{\gamma,e^-} OH,\ H,\ e^-(aq),\ H_2O_2,\ H_3O^+,\ \text{and } OH^- \quad (6)$$

aqueous solutions are $G(\mathrm{OH}) = 2{\cdot}65$, $G(\mathrm{H}) = 0{\cdot}60$, $G[\mathrm{e^-(aq)}] = 2{\cdot}65$, $G(\mathrm{H_2}) = 0{\cdot}45$, and $G(\mathrm{H_2O_2}) = 0{\cdot}75$,[12] where G is the number of product molecules formed per 100 eV absorbed by the solution. In acidic solutions the hydrated electrons react as in equation (7). Therefore in dilute acidic solutions containing $[\mathrm{Cr(H_2O)_6}]^{2+}$

$$\mathrm{e^-(aq) + H_3O^+ \longrightarrow H;} \quad k_7 = 2{\cdot}3 \times 10^{10}\ \mathrm{l\ mol^{-1}\ s^{-1}}\ {}^{12} \qquad (7)$$

reactions (8)—(10) may occur. The specific rates of

$$[\mathrm{Cr(H_2O)_6}]^{2+} + \mathrm{OH} \longrightarrow [\mathrm{Cr(H_2O)_6}]^{3+} + \mathrm{OH^-}; \quad k_8 = 1{\cdot}2 \times 10^{10}\ \mathrm{l\ mol^{-1}\ s^{-1}}\ {}^{13} \qquad (8)$$

$$[\mathrm{Cr(H_2O)_6}]^{2+} + \mathrm{H} \longrightarrow \text{Intermediate} \qquad (9)$$

$$[\mathrm{Cr(H_2O)_6}]^{2+} + \mathrm{H_2O_2} \longrightarrow [\mathrm{Cr(H_2O)_6}]^{3+} + \mathrm{OH}; \quad k_{10} = 2{\cdot}7 \times 10^{4}\ \mathrm{l\ mol^{-1}\ s^{-1}}\ {}^{13} \qquad (10)$$

reactions (8) and (10) are clearly different from the specific rate of formation of the intermediate observed in acidic solutions, $k = 1{\cdot}5 \times 10^9\ \mathrm{l\ mol^{-1}\ s^{-1}}$. Furthermore, its absorption spectrum (Figure 2) does not resemble the known absorption spectrum of $[\mathrm{Cr(H_2O)_6}]^{3+}$. It seems, therefore, reasonable to suggest that the precursors of the observed intermediate are the hydrogen atoms. This suggestion is corroborated by the following observations. (a) The observed yield of dihydrogen in acidic solutions equals within experimental error $G(\mathrm{H}) + G(\mathrm{H_2}) = 3{\cdot}6 + 0{\cdot}45 = 4{\cdot}05$ (see Table 2). This observation indicates that hydrogen atoms react with $[\mathrm{Cr(H_2O)_6}]^{2+}$ *via* a mechanism yielding one $\mathrm{H_2}$ molecule per H atom. No other source of $\mathrm{H_2}$ in this system can be envisaged. (b) The absorption spectrum of the intermediate, and the pH dependence of its lifetime, are in agreement with the expected properties of $[\mathrm{Cr(H_2O)_5H}]^{2+}$ (see below).

TABLE 1

Specific rates of decomposition of $\mathrm{Cr^+(aq)}$ [a]

$[\mathrm{Cr^{2+}(aq)}]$/M	pH	$\Delta(D_0)$	$10^{-4}k_{\mathrm{obs}}/\mathrm{s^{-1}}$
$8{\cdot}7 \times 10^{-4}$	3·8	0·00320	1·3
$1{\cdot}9 \times 10^{-3}$	3·4	0·0400	1·3
$1{\cdot}9 \times 10^{-3}$	3·4	0·0056	0·58
$4{\cdot}2 \times 10^{-4}$	4·3	0·0200	0·83
$1{\cdot}2 \times 10^{-3}$	4·3	0·0325	0·93
$1{\cdot}2 \times 10^{-3}$	3·0	0·0095	0·74
$2{\cdot}1 \times 10^{-3}$	4·2	0·0384	1·0
$1{\cdot}3 \times 10^{-2}$	3·4	0·0416	1·0
$4{\cdot}4 \times 10^{-4}$	3·8	0·0202 [b]	1·4 [b]
$4{\cdot}4 \times 10^{-4}$	3·8	0·0063 [c]	1·3 [c]
$4{\cdot}4 \times 10^{-4}$	3·8	0·0046 [d]	1·0 [d]

[a] Argon-saturated solutions containing chromium(II) ions at 22 ± 2 °C. The maximum standard deviation was ±15%. All kinetic runs were followed at 350 nm. [b] Same pulse used as in (*c*) and (*d*). [c] Followed at 500 nm. [d] Followed at 440 nm.

TABLE 2

Yield of dihydrogen in acid and neutral solutions in the presence of chromium(II) ions *

pH	$[\mathrm{Cr^{2+}(aq)}]$/M	$G(\mathrm{H_2})$
0	$1{\cdot}9 \times 10^{-2}$	3·8
1·9	$1{\cdot}1 \times 10^{-1}$	3·8
2·9	$5{\cdot}8 \times 10^{-3}$	3·4
3·4	$4{\cdot}8 \times 10^{-3}$	2·9

* Argon-saturated solutions containing chromium(II) ions were irradiated using a $\mathrm{Co^{60}}$ γ source. The standard deviation of the measurements was ±10%. As a reference, the same bulbs containing 1×10^{-3}M-KBr were irradiated, assuming $G(\mathrm{H_2}) = 0{\cdot}40$.

Two plausible intermediates might be formed by the reaction of hydrogen atoms with $[\mathrm{Cr(H_2O)_6}]^{2+}$ [equations (11) and (12)]. If reaction (12) is appropriate, the

$$[\mathrm{Cr(H_2O)_6}]^{2+} + \mathrm{H} \longrightarrow [\mathrm{Cr(H_2O)_5H}]^{2+} \qquad (11)$$

$$[\mathrm{Cr(H_2O)_6}]^{2+} + \mathrm{H} \longrightarrow \mathrm{Cr^+(aq)} + \mathrm{H^+} \qquad (12)$$

intermediate formed should be identical with that formed in the reaction of $\mathrm{e^-(aq)}$ with $[\mathrm{Cr(H_2O)_6}]^{2+}$ [reaction (5)]. However, the absorption spectra of the intermediates formed in neutral solutions (Figure 3) differ from that formed in acidic solutions. In neutral solutions two intermediates are formed, a relatively short-lived intermediate, (I), $k \simeq 1 \times 10^4\ \mathrm{s^{-1}}$ (for decay at pH 4·15), and a relatively long-lived one, (II), $k \simeq 2{\cdot}2\ \mathrm{s^{-1}}$. The absorption spectrum of (II) is identical with that of the intermediate formed in acidic solutions. Furthermore, the rate law for decay of (II) in neutral solutions agrees, within experimental error, with that observed for the intermediate in acidic solutions. It is therefore concluded that these intermediates are identical. These results suggest that (I) in neutral solutions is $\mathrm{Cr^+(aq)}$ whereas (II) is $[\mathrm{Cr(H_2O)_5H}]^{2+}$. The mechanism of formation of these intermediates is represented by reactions (5), (7), and (11). The possibility that $[\mathrm{Cr(H_2O)_5H}]^{2+}$ is formed *via* equation (13)

$$\mathrm{Cr^+(aq) + H_2O} \longrightarrow [\mathrm{Cr(H_2O)_5H}]^{2+} + \mathrm{OH^-} \qquad (13)$$

can be ruled out as even at 260 nm the optical density decreases, $k_{\mathrm{obs}} = 1{\cdot}3 \times 10^4\ \mathrm{s^{-1}}$, though at this wavelength $\varepsilon\{[\mathrm{Cr(H_2O)_5H}]^{2+}\} > \varepsilon[\mathrm{Cr^+(aq)}]$.

According to the suggested mechanism the yields (14) and (15) of $\mathrm{Cr^+(aq)}$ and $[\mathrm{Cr(H_2O)_5H}]^{2+}$ are expected.

$$G[\mathrm{Cr^+(aq)}] = \frac{G[\mathrm{e^-(aq)}]k_5[\mathrm{Cr(H_2O)_6}^{2+}]}{k_5[\mathrm{Cr(H_2O)_6}^{2+}] + k_7[\mathrm{H_3O^+}]} \qquad (14)$$

$$G\{[\mathrm{Cr(H_2O)_5H}]^{2+}\} = G(\mathrm{H}) + \frac{G[\mathrm{e^-(aq)}]k_7[\mathrm{H_3O^+}]}{k_5[\mathrm{Cr(H_2O)_6}^{2+}] + k_7[\mathrm{H_3O^+}]} \qquad (15)$$

Thus one obtains equation (16). The results plotted in

$$\frac{G\{[\mathrm{Cr(H_2O)_5H}]^{2+}\}}{G[\mathrm{Cr^+(aq)}]} = \frac{G(\mathrm{H})}{G[\mathrm{e^-(aq)}]} + \left\{1 + \frac{G(\mathrm{H})}{G[\mathrm{e^-(aq)}]}\right\} \frac{k_7[\mathrm{H_3O^+}]}{k_5[\mathrm{Cr(H_2O)_6}^{2+}]} \qquad (16)$$

Figure 4 indicate that a linear correlation between $[\mathrm{Cr(H_2O)_5H^{2+}}]/[\mathrm{Cr^+(aq)}]$ and $[\mathrm{H_3O^+}]/[\mathrm{Cr(H_2O)_6}^{2+}]$ exists indeed, within experimental error. (The large deviations

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[12] M. Matheson and L. M. Dorfman, ' Pulse Radiolysis,' M.I.T. Press, 1969.

[13] A. Samuni, D. Meisel, and G. Czapski, *J.C.S. Dalton*, 1972, 1275.

are due mainly to uncertainties in [H_3O^+] as the pH measurements had an error limit of $\pm 0{\cdot}05$.) For the solution used to measure the molar absorption coefficients, pH 3·85 and $[Cr(H_2O)_6{}^{2+}] = 4{\cdot}4 \times 10^{-4}$M, we calculate $G[Cr^+(aq)] = 1{\cdot}76 \pm 0{\cdot}10$ and $G\{[Cr(H_2O)_5H]^{2+}\} = 1{\cdot}44 \pm 0{\cdot}10$. Therefore we obtain $\varepsilon = 300 \pm 60$ and 165 ± 40 l mol^{-1} cm^{-1} respectively for $Cr^+(aq)$ and $[Cr(H_2O)_5H]^{2+}$ at 350 nm. The latter value is in fair agreement with a value of 135 ± 15 l mol^{-1} cm^{-1} determined in acidic solutions. Furthermore, from these absorption coefficients and the intercept and gradient of the plot in Figure 4, we calculate $G(H)/G[e^-(aq)] = 0{\cdot}23 \pm 0{\cdot}02$ and $k_7/k_5 = 1{\cdot}57 \pm 0{\cdot}15$ as compared with the independently measured values of $G(H)/G[e^-(aq)] = 0{\cdot}23$ and $k_7/k_5 = 1{\cdot}6 \pm 0{\cdot}15$. The results thus support the suggestion that the mechanism of formation of the two intermediates in neutral solutions is given by reactions (5), (7), and (11).

Absorption Spectrum of $[Cr(H_2O)_5H]^{2+}$.—The measured absorption spectrum of $[Cr(H_2O)_5H]^{2+}$ is very similar to those of $[Cr(H_2O)_5RH]^{2+}$ complexes[2b,3] (RH = aliphatic residue). It is therefore reasonable to assume that the absorption bands are due to the same electronic transitions. We suggest that the band at 380 nm is due to a *d–d* transition, and the u.v. band is due to a ligand-to-metal charge-transfer transition. The observation of $\lambda_{max.} \leqslant 260$ nm for the latter transition indicates that the optical electronegativity of the hydride is larger than those of iodide and of most of the aliphatic derivatives. The latter conclusion is in agreement with other observations.[14]

Kinetics of Formation of $[Cr(H_2O)_5H]^{2+}$.—The specific rate of reaction of H atoms with $[Cr(H_2O)_6]^{2+}$, $k = 1{\cdot}5 \times 10^9$ l mol^{-1} s^{-1}, can be compared with corresponding rates of reaction of H atoms with $Fe^{2+}(aq)$ and $Ti^{3+}(aq)$ which are 2×10^7 and $4{\cdot}2 \times 10^7$ l mol^{-1} s^{-1} respectively.[15] The same order of reactivities was reported for the oxidation of these cations by aliphatic radicals,[2a] and has been attributed to the redox properties of the cations. However, another factor might influence these specific rates. This reaction requires formation of a chemical bond between the attacking hydrogen atom and the cation. The upper limit for the rate of such a reaction should be the specific rate of ligand exchange in the inner solvation shell of the cations. However, the reported rates for water exchange in the inner solvation shell of Ti^{III} and $Fe^{2+}(aq)$ are 1×10^4 (ref. 16) and 3×10^6 s^{-1} respectively.[17] These results clearly indicate that the reaction of hydrogen atoms with these cations proceeds *via* seven-co-ordinate intermediates. {The mechanism of reduction of $[Co(NH_3)_6]^{3+}$ and $[Ru(NH_3)_6]^{3+}$ by hydrogen atoms might also involve penetration of the hydrogen atom into the inner co-ordination sphere.[18]} On the other hand, for $[Cr(H_2O)_6]^{2+}$ with the Jahn–Teller distortion which causes the very high ligand-exchange rate,[17] no seven-co-ordinate intermediate has to be postulated. This might explain the very high specific rate of reaction (11).

Kinetics of Decomposition of $[Cr(H_2O)_5H]^{2+}$.—The mechanism of decomposition of $[Cr(H_2O)_5H]^{2+}$ is as in equations (17) and (18). It is of interest to compare

$$[Cr(H_2O)_5H]^{2+} + H_2O \longrightarrow [Cr(H_2O)_5OH]^{2+} + H_2; \quad k_{17} < 1\ s^{-1} \qquad (17)$$

$$[Cr(H_2O)_5H]^{2+} + H_3O^+ \longrightarrow [Cr(H_2O)_6]^{3+} + H_2; \quad k_{18} = 1{\cdot}8 \times 10^4\ l\ mol^{-1}\ s^{-1} \qquad (18)$$

k_{18} with the specific rates of the corresponding reactions (19), where RH is an aliphatic derivative. The rates of

$$[Cr(H_2O)_5RH]^{2+} + H_3O^+ \longrightarrow [Cr(H_2O)_6]^{3+} + RH_2 \qquad (19)$$

reaction (19) for 13 different aliphatic residues have been reported.[3] These rates are all smaller than k_{18} ranging from $<1{\cdot}6 \times 10^{-6}$ (RH = $CH_2{\cdot}CO_2H$) to $2{\cdot}2 \times 10^2$ l mol^{-1} s^{-1} [$CH_2{\cdot}CH(OH)_2$]. On the other hand, k_{17} is within the range of the specific rates of the corresponding reactions (20). These rates range from

$$[Cr(H_2O)_5RH]^{2+} + H_2O \longrightarrow [Cr(H_2O)_5OH]^{2+} + RH_2 \qquad (20)$$

5×10^{-7} (RH = $MeCH{\cdot}O{\cdot}Et$) to $4{\cdot}7 \times 10^2$ s^{-1} [$MeC(OH){\cdot}CO_2H$]. The results thus indicate that the nature of the chromium–hydride bond in aqueous solutions does not differ significantly from that of the chromium–carbon bond in the complexes studied. It is of interest to note that k_{18} is nearly identical with the specific rate of the corresponding reaction of $[Fe(H_2O)_5H]^{2+}$, where $k_4 = 1{\cdot}06 \times 10^4$ l mol^{-1} s^{-1}.[9] These relatively low rate constants indicate that the metal–hydride bonds in these complexes are more covalent than ionic.

Mechanism of Decomposition of $Cr^+(aq)$.—The kinetics of decay of $Cr^+(aq)$ indicate a first-order process (see Figure 5). However, the specific rate of this process seems to depend slightly on the dose of the pulse (see Figure 5 and Table 2). Thus a factor of 6·2 in the dose affects the observed rate by a factor of 2·1. The observed rate is independent of the concentrations of $[Cr(H_2O)_6]^{2+}$, H_3O^+, $ClO_4{}^-$, and $[Cr(H_2O)_6]^{3+}$. {The latter is always present as 1—5% of the $[Cr(H_2O)_6]^{2+}$ concentration.} Therefore reactions (21)—(24) can be

$$Cr^+(aq) + H_3O^+ \longrightarrow \text{Products} \qquad (21)$$

$$Cr^+(aq) + Cr^{2+}(aq) \longrightarrow \text{Products} \qquad (22)$$

$$Cr^+(aq) + ClO_4{}^- \longrightarrow \text{Products} \qquad (23)$$

$$Cr^+(aq) + Cr^{3+}(aq) \longrightarrow 2Cr^{2+}(aq) \qquad (24)$$

ruled out as major processes contributing to the decay of $Cr^+(aq)$. The disproportionation reaction (25) is also

$$2Cr^+(aq) \longrightarrow Cr^0 + Cr^{2+}(aq) \qquad (25)$$

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not the major process by which $Cr^+(aq)$ decomposes because of the following reasons. (*a*) Reaction (25) is a second-order process. (*b*) The maximal yield of dihydrogen in solutions containing a high ratio of $[Cr^{2+}(aq)] : [H_3O^+]$ would be $G(H_2) = G(H_2) + G(H) + \frac{1}{2}G[e^-(aq)] = 2{\cdot}4$, which is considerably lower than the observed yield. [$G(H_2)$ was calculated assuming that all the Cr^0 formed will dissolve producing $Cr^{2+}(aq) + H_2$.] In order to explain the observed yield of $G(H_2) = 2{\cdot}95$, one would have to assume that over a third of $e^-(aq)$ reacts with H_3O^+ and not with $Cr^{2+}(aq)$ ion in a solution containing $[Cr^{2+}(aq)] = 4{\cdot}8 \times 10^{-3}$ and $[H_3O^+] = 4{\cdot}0 \times 10^{-4}$M which contradicts the observed specific rates of reaction.

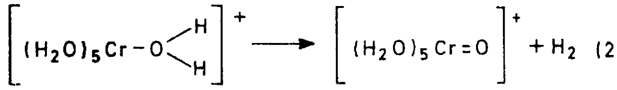
The results therefore indicate that the major process contributing to the disappearance of $Cr^+(aq)$ is (26).

$$Cr^+(aq) + H_2O \longrightarrow Cr^{3+}(aq) + H_2 \qquad (26)$$

This process is expected to obey a first-order rate law and $G(H_2)$ should be independent of pH. The slight second-order contribution and decrease in $G(H_2)$ may be explained by the reaction (27) if k_{27} is larger than

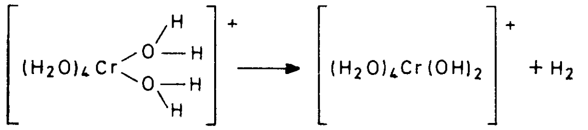
$$Cr^+(aq) + H_2O_2 \longrightarrow Cr^{2+}(aq) + OH + OH^- \qquad (27)$$

k_{10} by a factor of 10^5 at least. The latter suggestion is not unreasonable. It is concluded that the most probable mechanism for the decomposition of $Cr^+(aq)$ under the conditions of this study involves reaction (26) with a small contribution from reaction (27) and perhaps (25). The specific rate of reaction (26) is therefore $k \leqslant 5 \times 10^3\ s^{-1}$. This rate is considerably higher than k_{17}. The reason for this difference may be that the mechanism of reaction (26) does not require cleavage of a chromium–ligand bond, and might be described by (28)



$$[(H_2O)_5Cr{-}OH_2]^+ \longrightarrow [(H_2O)_5Cr{=}O]^+ + H_2 \qquad (28)$$

or (29). Such a mechanism can be suggested only for cations which are able to undergo a two-electron



$$[(H_2O)_4Cr(OH_2)_2]^+ \longrightarrow [(H_2O)_4Cr(OH)_2]^+ + H_2 \qquad (29)$$

oxidation process. It is evident that the mechanism of decomposition of $Zn^+(aq)$, $Cd^+(aq)$, and $Ni^+(aq)$ proceeds *via* second-order disproportionation reactions.[10a,19] Finally if reaction (26) describes the mechanism of decomposition of $Cr^+(aq)$, it has to be concluded that acid dissolution of chromium metal does not involve formation of $Cr^+(aq)$ as an intermediate. Otherwise $Cr^{3+}(aq)$ and not $Cr^{2+}(aq)$ would be formed in this reaction. The small percentage of $Cr^{3+}(aq)$ always produced on dissolution of the metal might be formed *via* $Cr^+(aq)$.

Recently, photochemically induced oxidation of $Cr^{2+}(aq)$ has been reported,[20] and the formation of $e^-(aq)$ as an intermediate has been suggested. However, reactions (11), (18), and (26) were not considered in the suggested mechanism. We feel that the photochemical results are better explained when these reactions are added to the suggested mechanism. However, we cannot quantitatively explain the reported results even with the added information concerning these reactions. Further photochemical studies seem to be required to elucidate the full mechanism.*

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* *Note added at proof:* After submission of this paper, it was pointed out that the absorption spectrum of $Cr^+(aq)$ differs from that expected for a d^5 ion. We have no explanation for this discrepancy.

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