Solvent Isotope Effects in the Acidolysis and other Electrophilic Substitution Reactions of Penta-aquaorganochromium(III) Ions in Aqueous Solution

By **Victor Gold** * and **David L. Wood**, King's College London, Strand, London WC2R 2LS

The rates of some reactions of penta-aquaorganochromium(III) ions with electrophilic reagents ($HgMe^+$, Br_2, H_3O^+, and water) have been measured in mixtures of H_2O and D_2O. The first two reagents effect substitution on carbon without the formal involvement of water, and the observed solvent isotope effect is accordingly ascribed to the isotopic change in the five water ligands and, for the reaction with bromine, in the solvation of the incipient bromide ion. With this information an attempt has been made to separate the isotope effects on proton transfer from the isotope effects on the water ligands for aquation reactions involving aqueous hydrogen ion or water as a proton (deuteron) donor. It is shown that the large solvent and product isotope effects observed in these reactions are then readily explained in terms of fractionation factor theory. The analysis leads to transition-state fractionation factors in the range observed for the extensively studied reactions involving a rate-limiting proton transfer to carbon in purely organic substrates.

THE study of the kinetic solvent isotope effect, in general involving the comparison of rate constants for a reaction in deuterium oxide and in ordinary water as solvent, is a widely used technique in the elucidation of organic reaction mechanisms.[1] It has been particularly informative for reactions in which proton transfers are involved (' protolytic processes ') where there is a generally accepted theoretical basis for the explanation of the effects in terms of isotopic fractionation between chemically distinct sites and statistical distribution among chemically equivalent sites for hydrogen attachment. Because the observed changes in rate constants are generally large, ill defined general ' medium effects ' do not play an important role in the explanation of the phenomena.

In addition to the comparison of rate constants in isotopically pure (or nearly pure) solvents, there are two related types of measurement that have provided complementary information, *viz.* product isotope effects and rate measurements in isotopically mixed solvents (H_2O–D_2O mixtures). The methodology and the results of such investigations have been reviewed from different points of view and with varying degrees of sophistication.[2-4]

Kinetic solvent isotope effects have also been measured for many different reactions of transition-metal complexes.[5] There has, however, been a disenchantment with the method and a growing recognition that facile interpretations of solvent isotope effects are often ambiguous or misleading.[1,6] Predominant amongst the underlying difficulties is the ill understood influence of isotopic substitution in ligands, especially in the case of aqua-complexes.[7,8]

It seemed to us that electrophilic substitution reactions of penta-aquaorganochromium(III) complexes $[CrR(OH_2)_5]^{2+}$ (1) [R = $CH_2C_6H_4CN$-*p* (1a), CH_2Cl (1b), CH_3 (1c), $CH(OEt)CH_3$ (1d), $\overline{\mathrm{CHOC_2H_4OC}}\mathrm{H_2}$ (1e), CH_2OH (1f)] would provide a suitable class of reactions through which to extend the methodology of solvent isotope effects, as established and validated in physical organic chemistry, to transition-metal chemistry. The kinetics of many reactions of this type [equation (1) where E–X is H_3O^+, H_2O, Br_2, I_2, IBr, $HgMe^+(aq)$, $Hg_2^{+}(aq)$, *etc.*] have been carefully studied.[9] The products, stoicheiometry, and clean second-order kinetics provide strong evidence that the reactions involve electrophilic substitution on carbon with simultaneous fission of the carbon–chromium bond through which the organic group R is attached to the metal atom. The penta-aquachromium(III) ion, set free as a reactive intermediate, rapidly reacts with solvent (or with an added nucleophile).[10] There is strong evidence that the electrophilic attack occurs exclusively on the carbon atom attached to chromium for the systems under consideration in the present paper although the stereochemistry of the substitution on carbon has not yet been established experimentally.

$$[CrR(OH_2)_5]^{2+} + E\text{–}X \longrightarrow [Cr(OH_2)_5]^{3+} + R\text{–}E + X^- \quad (1)$$

The reaction rates for a given organochromium substrate with a series of electrophiles span a wide range of values, but very similar relative rates are found for each one of a range of different organochromium substrates with the same series of electrophiles,[11-13] suggesting a far-reaching similarity of mechanism throughout. (The rates of reactions with different nucleophiles are related through linear Gibbs-energy relationships with unit slope.)

For the purpose of isotope-effect studies, the reactions fall into two categories: those with non-hydroxylic electrophiles (Br_2, $HgMe^+$, *etc.*) for which the solvent isotope effect cannot be attributed to a protolytic step, and those with the aqueous hydrogen ion, and perhaps also the reaction with water, in which the rate-limiting step involves proton transfer to carbon. The present work reports solvent isotope effect measurements for both types of reaction and attempts a theoretical analysis of the effect in the two cases. The existence of a substantial kinetic solvent isotope effect [in the protonolysis of penta-aquabenzylchromium(III) in aqueous ethanol] was first noted by Kochi and Buchanan.[14] These observations encouraged us to extend such measurements to the better defined entirely aqueous solvent system.

EXPERIMENTAL

Deuterium oxide (99.8%, Aldrich) and tritiated water (5 Ci cm^{-3}; * Radiochemical Centre) were used without prior purification. Singly distilled water was found to be adequately pure (after nitrogen purging) for our purpose. For example, the observed rate constant for acidolysis of penta-aquamethylchromium(III) (1c) was in excellent agreement with the literature value, obtained by measurements in triply distilled water.[15] For the preparation of isotopic mixtures, stock solutions in H_2O and in D_2O were made up, typically containing 0.5 mol dm^{-3} perchloric acid and 0.5 mol dm^{-3} lithium perchlorate. The solutions were mixed by volume, and the atom percentages of the isotopes were calculated from the known densities of isotopic waters, neglecting the volume change on mixing of H_2O and D_2O. To start a reaction, small aliquots of reactants (<0.1 cm^3) were added to the solution (2.8 cm^3) in a cuvette. Rate measurements (Pye–Unicam SP8-100 spectrophotometer) on reactions under pseudo-first-order conditions were generally analysed using a non-linear least-squares technique. Solutions were, as a rule, transferred by syringe, with rigorous exclusion of atmospheric oxygen where appropriate.

To prepare solutions of chromium(II) perchlorate, electrolytic chromium metal (99.9%, B.D.H.) was activated by immersing the lumps in hydrochloric acid (*ca.* 5 mol dm^{-3}) so as to induce vigorous evolution of hydrogen. They were then washed with water and introduced into a nitrogen-purged solution of perchloric acid (typically 3 mol dm^{-3}, 4 cm^3), the acid being in deficit. As the gas evolution slowed down, the solution was warmed (*ca.* 60 °C) until all bubbling ceased. The vessel was continuously flushed with nitrogen. The concentration of chromium(II) was approximately half the initial concentration of perchloric acid.

Three reaction sequences were used for the preparation of organochromium(III) complexes: (*i*) the reaction of an organic bromide with chromium(II) ions (Scheme 1); (*ii*) a

$$\begin{aligned} RBr + Cr^{2+} &\longrightarrow CrBr^{2+} + R^{\cdot} \\ R^{\cdot} + Cr^{2+} &\longrightarrow CrR^{2+} \end{aligned}$$

SCHEME 1

'Fenton reagent' acting on RH (Scheme 2); and (*iii*) a

$$\begin{aligned} Cr^{2+} + H_2O_2 &\longrightarrow Cr^{3+} + OH^- + OH^{\cdot} \\ OH^{\cdot} + RH &\longrightarrow R^{\cdot} + H_2O \\ R^{\cdot} + Cr^{2+} &\longrightarrow CrR^{2+} \end{aligned}$$

SCHEME 2

Fenton reagent acting on a sulphoxide (Scheme 3). In all

$$\begin{aligned} Cr^{2+} + H_2O_2 &\longrightarrow Cr^{3+} + OH^- + OH^{\cdot} \\ OH^{\cdot} + R_2SO &\longrightarrow R^{\cdot} + RSO_2H \\ R^{\cdot} + Cr^{2+} &\longrightarrow CrR^{2+} \end{aligned}$$

SCHEME 3

cases reaction conditions were chosen so as to produce the organochromium ion in a stoicheiometrically complete conversion, as detailed.

Solutions of penta-aqua(*p*-cyanobenzyl)chromium(III) perchlorate (1a) were prepared according to Scheme 1 by the reaction of chromium(II) perchlorate (10 mmol) with α-bromo-*p*-toluonitrile (2.5 mmol) in aqueous acetone (50% v/v, 40 cm^3) under nitrogen. After 1 h the complex was transferred to a Dowex 50 W-X8 cation-exchange column. The column was washed with aqueous lithium perchlorate (0.1 mol dm^{-3}, 100 cm^3), and the chromium(III) complexes eluted with cold 1 mol dm^{-3} $LiClO_4$ under nitrogen pressure. The green bromo-complex is eluted first, followed by the organochromium complex. The solution of the purified complex was kept under nitrogen at 0 °C and used within 1—2 h of preparation. The kinetics of its reaction with methylmercury(II) ions (introduced as the acetate, Alfa) were followed at 25 °C by spectrophotometric observation at 255 nm of the formation of (*p*-cyanobenzyl)methylmercury(II) as a pseudo-first-order reaction (Table 1).

TABLE 1

Reaction between penta-aqua(*p*-cyanobenzyl)chromium(III) (1a) and methylmercury(II) in H_2O–D_2O mixtures at 25 °C [a]

Atom fraction D (n)	100 $k_{obs.}/s^{-1}$ [b]
0	1.21, 1.22
0.267	1.12
0.405	1.08
0.676	0.954
0.947	0.874, 0.848
1 [c]	0.847

[a] $[Cr(CH_2C_6H_4CN)^{2+}]_0 = 2 \times 10^{-5}$, $[HgMe^+]_0 = 5.2 \times 10^{-4}$, $I = 0.50$ mol dm^{-3} ($[LClO_4] = [LiClO_4] = 0.25$ mol dm^{-3}, L = ^1H or ^2H). [b] Precision of individual rate constants ± 0.02 to ± 0.03. [c] Extrapolated.

The desired second-order rate constant in aqueous solution at an ionic strength $I = 0.5$ mol dm^{-3} $\{[LiClO_4] = [LClO_4] = 0.25$ mol dm^{-3} (L = ^1H or ^2H)$\}$ was found to be 23.8 ± 0.6 dm^3 mol^{-1} s^{-1}, in excellent agreement with Chang and Espenson's [11] value of 23.9 ± 0.4 dm^3 mol^{-1} s^{-1}.

An analogous method of preparation (a modification of Dodd and Johnson's procedure) [16] was used for penta-aqua(chloromethyl)chromium(III) (1b) perchlorate by starting from bromochloromethane. In the chromatography of the solution the column was in this case washed with 0.1 mol dm^{-3} perchloric acid and eluted with a solution containing $HClO_4$ (0.1 mol dm^{-3}) and $LiClO_4$ (0.9 mol dm^{-3}). The position and relative intensities of the u.v. absorption maxima were in excellent agreement with recorded values.[13,17] The reaction of (1b) with bromine was initiated by injecting a solution of the purified complex into a solution of bromine in $HClO_4$. The pseudo-first-order rate of its disappearance was followed spectrophotometrically at 260 nm. Second-order rate constants were calculated by dividing the observed first-order rate constants by the spectrophotometrically determined initial concentration of bromine (measured at 452 nm). The average value in water (1.06 dm^3 mol^{-1} s^{-1}) is in exact agreement with the average result reported by Espenson and Williams.[12] Rate constants in H_2O–D_2O mixtures are given in Table 2.

Penta-aqua(methyl)chromium(III) (1c) in solution was prepared according to Scheme 3 by addition of hydrogen peroxide (deficit, corresponding to a hypothetical concentration of 5×10^{-3} mol dm^{-3}) to a solution of chromium(II)

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* Throughout this paper: 1 Ci = 3.7×10^{10} s^{-1}.

perchlorate (0.05 mol dm^{-3}) and dimethyl sulphoxide[18] (vacuum-distilled off calcium hydride, 0.5 mol dm^{-3}). Its first-order acidolysis upon acidification (0.5 mol dm^{-3} $HClO_4$) of the preparation *in situ* was monitored spectrophotometrically at 390 nm. The calculated second-order rate constant [(5.00 ± 0.06) × 10^{-3} dm^3 mol^{-1} s^{-1}] for a reaction with hydrogen ion in ordinary water at 25 °C in the presence of 0.5 mol dm^{-3} $HClO_4$ and 0.5 mol dm^{-3} $LiClO_4$ was in excellent agreement with Hyde and Espenson's results[15] (4.94 × 10^{-3} dm^3 mol^{-1} s^{-1}) under the same conditions, using the methyl complex obtained by a different method of preparation. Measurements in H_2O–D_2O mixtures at two different ionic strengths are tabulated (Table 3).

TABLE 2

Reaction between penta-aqua(chloromethyl)chromium(III) (1b) and bromine in H_2O–D_2O mixtures at 25 °C [a]

Atom fraction D (n)	$10^3k_{obs.}$/s^{-1} [b]	$10^3[Br_2]_0$/ mol dm^{-3}	k_2/dm^3 mol^{-1} s^{-1} [c]
0	1.88	1.79	1.08
0	1.91	1.85	1.06
0	1.95	1.78	1.12
0.269	1.51	1.79	0.87
0.403	1.43	1.93	0.76
0.538	1.25	1.85	0.69
0.674	1.15	1.82	0.65
0.942	1.08	1.87	0.59
0.942	1.06	1.87	0.58
1 [d]			0.55

[a] $[Cr(CH_2Cl)^{2+}]_0 = 9 \times 10^{-5}$, $I = 1.0$ mol dm^{-3} ($[LClO_4] = [LiClO_4] = 0.50$ mol dm^{-3}, where L = ^1H or ^2H). [b] Precision of individual rate constants *ca.* ± 0.02. [c] $K = k_{obs.}/([Br_2]_0 - 0.5[(Cr(CH_2Cl)^{2+}]_0)$. [d] Extrapolated.

Solutions of penta-aqua(1-ethoxyethyl)chromium(III) (1d) were prepared and purified essentially as described before.[19]

TABLE 3

Acidolysis of penta-aquamethylchromium(III) (1c) in H_2O–D_2O mixtures at 25 °C ($[LClO_4] = 0.5$ mol dm^{-3}; for other concentrations, see text)

$I = 1.0$ mol dm^{-3} [a]		$I = 1.5$ mol dm^{-3} [a]	
n [b]	$10^3k_{obs.}$/s^{-1}	n [b]	$10^3k_{obs.}$/s^{-1}
0	2.50, 2.50 ± 0.04	0	2.81, 2.77 ± 0.04
0.105	2.40 ± 0.10	0.155	2.52 ± 0.07
0.175	2.00 ± 0.07	0.310	2.09 ± 0.06
0.230	2.02 ± 0.06	0.435	1.80 ± 0.06
0.315	1.88 ± 0.06	0.466	1.70 ± 0.06
0.385	1.56 ± 0.06	0.497	1.58 ± 0.06
0.450	1.47 ± 0.05	0.559	1.44 ± 0.06
0.523	1.48 ± 0.07	0.621	1.38 ± 0.06
0.589	1.16 ± 0.07	0.770	0.984 ± 0.06
0.714	1.01 ± 0.06	0.933	0.654, 0.612 ± 0.04
0.798	0.867 ± 0.06	1 [c]	0.465
0.866	0.692 ± 0.05		
0.937	0.537, 0.485 ± 0.04		
1 [c]	0.399		

[a] Maintained by addition of $LiClO_4$. [b] Atom fraction deuterium. [c] Extrapolated.

The rate of acidolysis in H_2O–D_2O mixtures was followed as for the methyl complex (Table 4). The calculated second-order rate constant in H_2O (3.1 × 10^{-5} dm^3 mol^{-1} s^{-1}) at 25 °C was in only fair agreement with the previously reported value [(3.8 ± 0.2) × 10^{-5} dm^3 mol^{-1} s^{-1}].[19] The concentration of a solution of the complex was determined by measurement of the spectrum of the chromate solution (ε = 4 340 dm^3 mol^{-1} cm^{-1} at $\lambda_{max.}$ 372 nm) produced on oxidation with alkaline hydrogen peroxide. With this information, the molar absorption coefficients of the chromium(III) complex were determined ($\varepsilon_{max.}$ = 440 ± 40 dm^3 mol^{-1} cm^{-1} at 390 nm, compared with literature values of 490 and 360 dm^3 mol^{-1} cm^{-1}, and 2 300 ± 300 dm^3 mol^{-1} cm^{-1} at 285 nm, compared with a literature value of 2 200 dm^3 mol^{-1} cm^{-1} at 291 nm).[19,20]

For the determination of the tritium isotope effect, purified (1d) [in known concentration, (1.8 ± 0.2) × 10^{-3} mol dm^{-3}] was added to an acidic solution (1 mol dm^{-3} $HClO_4$) of tritiated water (22 cm^3) in a septum-closed vessel under nitrogen also containing diethyl ether (25 cm^3) as carrier (two-phase system). After 24 h (94% reaction) carrier diethyl ether was salted out by addition of solid sodium hydroxide, and separated. It was washed with successive portions (20 × 3 cm^3) of ice-cold saturated potassium carbonate solution, and dried successively over NaOH and CaH_2. Its tritium content was determined by liquid scintillation counting (Hewlett–Packard model 2 420, using 2,5-diphenyloxazole–1,4-bis(5-phenyloxazol-2-yl)benzene–toluene scintillator solution),* following purification by gas chromatography (modified Hewlett–Packard F & M model 770, with a 1.8 m × 1.3 cm Carbowax 20 M column, 20% on 80—120 mesh Celite). The yield of tritiated diethyl ether, based on the amount of complex decomposed, was 5.3 ± 0.7% of the value expected in the absence of an isotope effect. The efficiency of the removal of tritiated water by the purification procedure used was checked by a blank experiment with omission of the complex. The residual activity of the diethyl ether was 0.5—2% of the value found in the presence of complex, and indistinguishable from the background activity. Similar tritium product isotope effect experiments on unpurified complex (*i.e.* on the complex in solution as prepared) gave a yield of tritiated diethyl ether of 3.4 ± 0.3%, based on the amount of hydrogen peroxide used in the preparation on the assumption of Scheme 2. The discrepancy gives an approximate indication of the efficiency of the reaction forming the complex. However, the yield as determined by the absorbance at 391 nm of solutions of the complex formed *in situ* was approximately constant for concentrations of diethyl ether in the range 0.12—0.48 mol dm^{-3}, whereas it fell off at lower concentrations. This suggests

TABLE 4

Acidolysis of penta-aqua(1-ethoxyethyl)chromium(III) (1d) in H_2O–D_2O mixtures [a]

Atom fraction D (n)	$10^5k_{obs.}$/s^{-1} [b]
0	1.61, 1.53, 1.51
0.105	1.56
0.210	1.43
0.315	1.26
0.420	1.08
0.502	0.963
0.589	0.860
0.728	0.725
0.831	0.631, 0.695
0.937	0.554, 0.422

[a] $[LClO_4] = 0.5$ mol dm^{-3}; $I = 1.0$ mol dm^{-3}, maintained with $LiClO_4$; solution of complex prepared *in situ* from $(C_2H_5)_2O$ (0.5 mol dm^{-3}), Cr^{2+} (0.05 mol dm^{-3}), H_2O_2 (5 × 10^{-3} mol dm^{-3}). [b] Precision *ca.* ±0.04.

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* PPO–POPOP–toluene.

that the reaction (although not necessarily the formation of the required complex) was essentially quantitative.

Because of the high reactivity of the penta-aqua(dioxanyl)chromium(III) ion (1e), a corresponding study of the product isotope effect in the acidolysis of (1e) had to be performed on unpurified complex *in situ*. Hydrogen peroxide (0.45 mmol) was added to a solution containing chromium(II) perchlorate (0.05 mol dm^{-3}), dioxan (0.53 mol dm^{-3}), and $HClO_4$ (0.05 mol dm^{-3}). After 20—30 min, carrier dioxan (20 cm^3) and then sodium hydroxide (5 g) were added. The solution was saturated by addition of anhydrous potassium carbonate, and the dioxan layer was filtered off, using Whatman 1PS phase-separating filter paper, and dried (K_2CO_3). It was then washed with saturated potassium carbonate solution (20 × 3 cm^3) and dried (K_2CO_3 followed by CaH_2). The sample was purified by two passages through the g.l.c. (gas–liquid chromatography) column (as for the corresponding experiment with diethyl ether), and the activity was assayed after each passage. It was found not to have decreased after the first passage. The yield of tritiated dioxan, based on the amount of hydrogen peroxide used, was 4.0%. A blank experiment again established the efficiency of the separation of tritiated water.

TABLE 5

Aquation of penta-aqua(hydroxymethyl)chromium(III) (1f) in H_2O–D_2O mixtures at 25 °C [a]

$[LClO_4]$ = 0.100 mol dm^{-3}		0.298 mol dm^{-3}		0.475 mol dm^{-3}		0.710 mol dm^{-3}	
n [b]	$10^4k_{obs.}$/s^{-1} [c]	n	$10^4k_{obs.}$/s^{-1}	n	$10^4k_{obs.}$/s^{-1}	n	$10^4k_{obs.}$/s^{-1}
0	7.13	0	7.93	0	8.82	0	9.67
0.197	5.44	0.204	5.78	0.202	6.45	0.200	7.08
0.395	3.97	0.409	4.16	0.405	4.59	0.400	5.00
0.527	3.01	0.546	3.24	0.541	3.59	0.534	3.97
0.727	2.01	0.753	2.08	0.746	2.34	0.736	2.37
0.928	1.12	0.961	1.12	0.952	1.14	0.939	1.19

[a] I = 1.0 mol dm^{-3} (maintained by addition of $LiClO_4$; $[Cr(CH_2OH)^{2+}]_0 = 2 \times 10^{-3}$ mol dm^{-3} (based on amount of hydrogen peroxide added, according to Scheme 2); [MeOH] = 0.2 mol dm^{-3}; $[Cr^{2+}]$ = 0.018 mol dm^{-3}. [b] Atom fraction of deuterium. [c] Precision *ca.* ±0.10.

TABLE 6

Aquation of penta-aqua(hydroxymethyl)chromium(III) (1f): interpolated rate constants at rounded values of n (data from Table 5)

	$10^4k_{obs.}$/s^{-1} [a]				10^4k_1/s^{-1}	10^4k_2 [b]/dm^3 mol^{-1} s^{-1}
n	0.100 [c]	0.298 [c]	0.475 [c]	0.710 [c]		
0.00	7.14	7.92	8.83	9.67	6.70	4.2
0.20	5.14	5.84	6.45	7.11	5.15	2.7
0.40	3.90	4.21	4.64	5.04	3.70	1.9
0.53	3.05	3.34	3.68	3.92	2.85	1.6
0.74	1.90	2.16	2.36	2.39	1.80	1.1
0.94	1.08	1.12	1.14	1.19	1.05	0.3
1.00					0.80 [d]	

[a] Precision *ca.* ±0.10. [b] Precision *ca.* ±0.20. [c] $[LClO_4]$ in mol dm^{-3}. [d] Extrapolated value.

Penta-aqua(hydroxymethyl)chromium(III) (1f) for kinetic experiments was prepared *in situ* by the procedure described above for (1e). The occurrence of a pH-independent reaction precluded chromatographic purification. Spectrophotometry at 392 nm was used to monitor the aquation at different concentrations of $HClO_4$ in H_2O–D_2O mixtures (atom fraction of deuterium n). The values of the rate constants k_1 and k_2 [defined below in equation (22)] in light water [$k_1 = (6.70 \pm 0.10) \times 10^{-4}$ s^{-1}, $k_2 = (4.2 \pm 0.2) \times 10^{-4}$ dm^3 mol^{-1} s^{-1}] are in reasonable agreement with previous determinations at essentially the same ionic strength, I = 1.0 mol dm^{-3} ($k_1 = 7.0 \times 10^{-4}$ and 6.6×10^{-4} s^{-1}, $k_2 = 3.2 \times 10^{-4}$ and 4.65×10^{-4} dm^3 mol^{-1} s^{-1}).[15,19] Observed pseudo-first-order rate constants are given in Table 5. A polynomial fitted to the data was used to obtain sets of values of $k_{obs.}$ at different acid concentrations for the same small number of values of n (Table 6). Values of k_1 and k_2 were derived from each one of the rows of results in Table 6 by linear regression of $k_{obs.}$ upon $[L_3O^+]$. These rate constants are given in the final two columns of the Table.

The estimated uncertainty in the isotopic composition of solutions was *ca.* ±2% of the value of n.

RESULTS AND DISCUSSION

Table 7 summarises results for the different reactions studied. The first two rows relate to reactions not involving proton transfer (type A), whereas the other reactions do (type B). Reactions of type (B) show much larger solvent isotope effects than do those of type (A).

According to the theory of solvent isotope effects, the isotopic rate ratio k_n/k_{H_2O} is given by equation (2) where

$$k_n/k_{H_2O} = \prod^{i}(1 - n + n\phi_i^{\ddagger})/\prod^{j}(1 - n + n\phi_j) \quad (2)$$

k_n is the rate constant in an isotopically mixed solvent characterised by an atom fraction of deuterium n, and the products are taken over the i sites containing exchangeable hydrogen in the transition state or over the j corresponding sites in the reactants respectively. The fractionation factors ϕ are defined in terms of the isotopic abundance at a specified site in a solute relative to that in the solvent, *i.e.* equation (3). The limiting

$$\phi = \frac{(D/H)_{solute}}{(D/H)_{solvent}} \quad (3)$$

case $n \longrightarrow 1$ corresponds to solutions in D_2O, and the rate ratio for the isotopically pure solvents is accordingly given by equation (4).

$$k_{D_2O}/k_{H_2O} = \prod^{i}\phi_i^{\ddagger}/\prod^{j}\phi_j \quad (4)$$

The assumptions involved in the derivation of equations (2) and (4) have been reviewed,[2] but two points should be noted. First, it has been assumed that the equilibrium constants for the isotopic disproportionations of types (5) and (6) are governed by symmetry numbers

$$H_2O + D_2O \rightleftharpoons 2HOD \quad (5)$$

$$2H_3O^+ + D_3O^+ \rightleftharpoons 3H_2DO^+ \quad (6)$$

alone. This approximation and its consequences have been discussed.[2,4,21,22] For measurements of high precision an alternative treatment incorporating a first-order correction has been proposed and used:[4,22] this elaboration would be unjustified for our purpose. Secondly, the treatment assumes that the Gibbs-energy change associated with the transfer of a species between isotopically different solvents is entirely expressible in terms of fractionation factors. Equations (2) and (4) are therefore taken to include sites concerned with solvation effects, for which the fractionation factors differ only slightly from unity but which, because of their large number, are nevertheless of consequence.[23] If there are s equivalent sites of this type, they will give rise to a factor of form (7) in equation (2) where y_n can

$$y_n = (1 - n + n\phi_s)^s \qquad (7)$$

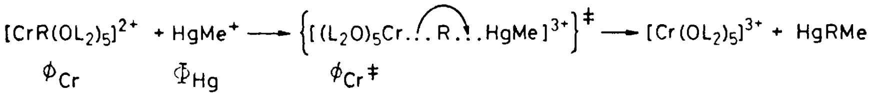
be thought of as a transfer activity coefficient (or a factor of a transfer activity coefficient if there are several sets of such sites). Since ϕ_s has a value close to unity, equation (7) is satisfactorily approximated by equation (8) where Y_s is the transfer activity coefficient

$$y_n = \phi_s{}^{sn} = Y_s{}^n \qquad (8)$$

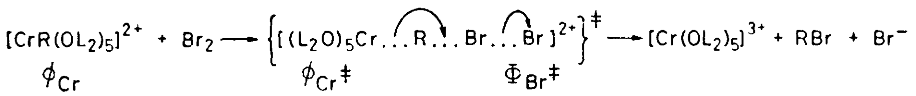
for transfer from H_2O to D_2O attributable to fractionation of the s sites. To emphasise that the transfer activity coefficient is explicable in terms of fractionation, the notation Φ [equation (9)] has been proposed[4] and will be used in the following.

$$\Phi_s = Y_s = \phi_s{}^s \qquad (9)$$

For reactions of type (A) a solvent isotope effect is, on the basis of this theory, attributable only to sites concerned with solvation or aquation of reactants. The corresponding fractionation factors in reactants and transition states for reactions (1A) and (2A) are designated by the symbols given in equations (10) and (11) respectively. (The symbol L designates a hydrogen atom in isotopic exchange equilibrium with the solvents.) The fractionation factors at other sites are assumed to be indistinguishable from unity or else to be unchanged on going from reactants to transition state. The stereochemical arrangement about mercury in the transition state of (10), remembering that in all known cases bimolecular electrophilic substitution on mercury occurs with retention of configuration,[24] renders it improbable that there can be significant solvation of mercury at that stage. The incipient bromide ion in the transition state of (11) is expected to be solvated less than an ordinary bromide ion, and to be associated with a value of Φ between that of the bromide ion and unity ($\Phi_{Br}{}^{\ddagger} = \Phi_{Br}{}^{\beta}$, with $0 < \beta < 1$).



$$\underset{\phi_{Cr}}{[CrR(OL_2)_5]^{2+}} + \underset{\Phi_{Hg}}{HgMe^+} \longrightarrow \left\{\underset{\phi_{Cr}{}^{\ddagger}}{[(L_2O)_5Cr\ldots R\ldots HgMe]^{3+}}\right\}^{\ddagger} \longrightarrow [Cr(OL_2)_5]^{3+} + HgRMe \qquad (10)$$



$$\underset{\phi_{Cr}}{[CrR(OL_2)_5]^{2+}} + Br_2 \longrightarrow \left\{[(L_2O)_5\underset{\phi_{Cr}{}^{\ddagger}}{Cr\ldots R}\ldots Br\ldots \underset{\Phi_{Br}{}^{\ddagger}}{Br}]^{2+}\right\}^{\ddagger} \longrightarrow [Cr(OL_2)_5]^{3+} + RBr + Br^- \qquad (11)$$

Applying equations (2), (7), (8), and (9) to the reactants and transition states in equations (10) and (11), we obtain equations (12) and (13) respectively.

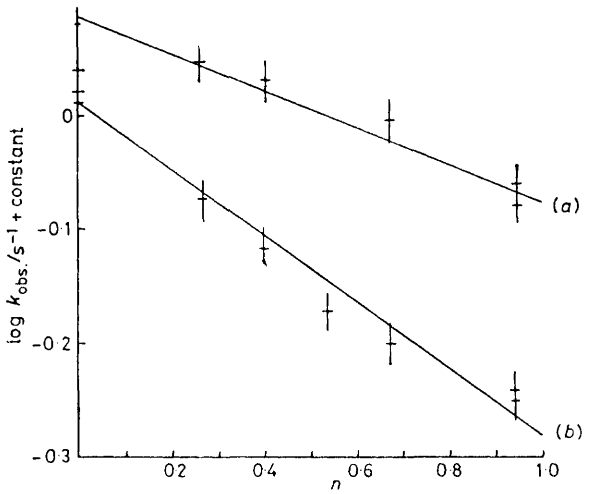


FIGURE 1 Solvent isotope effect for reactions of organochromium(III) compounds with methylmercury(II) and with bromine. (*a*) $[Cr(CH_2C_6H_4CN\text{-}p)(OL_2)_5]^{2+}$ (1a) with methylmercury(II); (*b*) $[Cr(CH_2Cl)(OL_2)_5]^{2+}$ (1b) with bromine

$$k_n/k_{H_2O} = (1 - n + n\phi_{Cr}{}^{\ddagger})^{10}/(1 - n + n\phi_{Cr})^{10}\,\Phi_{Hg}{}^{n} \qquad (12)$$

$$k_n/k_{H_2O} = (1 - n + n\phi_{Cr}{}^{\ddagger})^{10}\,\Phi_{Br}{}^{\beta n}/(1 - n + n\phi_{Cr})^{10} \qquad (13)$$

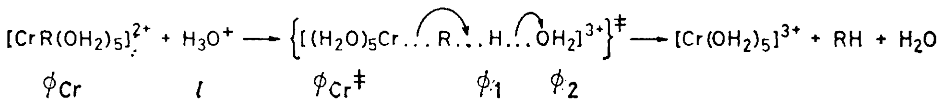
Using the approximation of equation (8), for the ten hydrogen sites of water ligands attached to chromium, *i.e.* $\Phi_{Cr} = \phi_{Cr}{}^{10}$, $\Phi_{Cr}{}^{\ddagger} = (\phi_{Cr}{}^{\ddagger})^{10}$ and writing equation (14) equations (12) and (13) reduce to (15) and (16)

$$\Phi_{\Delta} = \Phi_{Cr}{}^{\ddagger}/\Phi_{Cr} \qquad (14)$$

$$k_n/k_{H_2O} = (\Phi_{\Delta}/\Phi_{Hg})^n \qquad (15)$$

$$k_n/k_{H_2O} = (\Phi_{\Delta}\Phi_{Br}{}^{\beta})^n \qquad (16)$$

respectively. The implied linear relationship between log k_n and n (Figure 1) is satisfied by the data within the limits of experimental precision ($\pm 5\%$) and leads to extrapolated rate ratios of 0.69 and 0.51 for the substitutions by methylmercury and bromine respectively.



$$[CrR(OH_2)_5]^{2+} + H_3O^+ \longrightarrow \{[(H_2O)_5Cr\cdots R\cdots H\cdots OH_2]^{3+}\}^{\ddagger} \longrightarrow [Cr(OH_2)_5]^{3+} + RH + H_2O \qquad \phi_{Cr} \quad l \quad \phi_{Cr^{\ddagger}} \quad \phi_1 \quad \phi_2 \tag{17}$$

No experimental values for the transfer activity coefficient for $HgMe^+$ are available. Measurements for the related cations cadmium [25] (0.94) and silver [26] (0.85) suggest that the value for $HgMe^+$ is likely to lie in the range 0.90 ± 0.05. Accordingly, it is possible to estimate the value of Φ_Δ in this reaction to be $0.69 \times 0.90 = 0.62 \pm 0.03$.

The far-reaching parallelism between substituent effects and relative reactivities towards different electrophiles throughout the many studied examples of electrophilic substitution reactions in organochromium(III) compounds [11-13] implies that Φ_Δ is likely to have a similar value for the different reactions and penta-aquaorganochromium(III) salts examined in the present investigation. Applying this hypothesis to the substitution by bromine, we deduce from equation (16) a value of $0.51/0.62 = 0.82$ for $\Phi_{Br}{}^{\beta}$. The experimentally determined value [27] of Φ_{Br} is 0.62, whence it follows that the exponent β has the value of 0.42. The interpretation thus requires the solvation shell of the incipient bromide ion to have acquired *ca.* 40% of the characteristics of a fully developed bromide ion.

The inference that Φ_Δ is less than unity is reasonable. It is in the same direction as the change in ϕ as water is attached to a proton. All reactions exemplified by equation (1) involve an increase in the net positive charge of the chromium ion, with some progress in that charge redistribution in the transition state. The change in the fractionation factor per position (*i.e.* the effect on the ratio $\phi_{Cr^{\ddagger}}/\phi_{Cr}$) is quite small, $0.62^{1/10} = 0.953$. This value may be compared with the fractionation factor of 0.69 per position that attends the co-ordination of water to a proton.

In reactions of type (B) listed in Table 7, typically the acidolysis of penta-aquaorganochromium(III) complexes by hydrogen ions, three additional fractionation factors, as indicated in equation (17), must be taken into account. Of these, l, the fractionation factor of the sites in the aqueous oxonium ion, has the value 0.69. There are two fractionation factors for the transition state: ϕ_1 relates to the ' proton in transit ', and ϕ_2 to the incipient water molecule set free as a consequence of proton transfer from the oxonium ion. Applied to equation (17), equations (2) and (4) [making use of the substitutions summarised in equations (7)—(9) and (14)] take the form of equations (18) and (19).

TABLE 7

Kinetic isotope effect measurements for electrophilic substitution in $[CrR(OH_2)_5]^{2+}$

No. and type	Substrate	Electrophile	k_{H_2O}/k_{D_2O}	ϕ_1 [a]
(1A)	(1a)	$HgMe^+$	1.4	
(2A)	(1b)	Br_2	2.1	
(3B)	(1c)	H_3O^+	6.1	
(4B)	(1d)	H_3O^+	$\geqslant 6$	0.13
(5B)	(1e)	H_3O^+		0.11 [b]
(6B)	(1f)	H_3O^+	*ca.* 6	
(7B)	(1f)	H_2O	8.4	

[a] Fractionation factor of ' proton-in-transit,' derived from product isotope effect. [b] This is a minimum value, based on the yield of tritiated product from the complex formed *in situ*, without allowance for side reactions.

$$k_n/k_{H_2O} = (\Phi_\Delta)^n(1 - n + n\phi_1)(1 - n + n\phi_2)^2/(1 - n + nl)^3 \tag{18}$$

$$k_{D_2O}/k_{H_2O} = \Phi_\Delta\phi_1\phi_2{}^2/l^3 \tag{19}$$

With the assumption that Φ_Δ has the same value (0.62) as for reactions of type (A), it is possible to derive the product $\phi_1\phi_2{}^2$ from the rate ratio k_{D_2O}/k_{H_2O}, *viz.* equation (20). In principle, two approaches are possible

$$\phi_1\phi_2{}^2 = (l^3/\Phi_\Delta)(k_{D_2O}/k_{H_2O}) \tag{20}$$

to evaluate the individual fractionation factors ϕ_1 and ϕ_2. First, measurement of k_n/k_{H_2O} for at least one additional value of n and use of equation (18) provides the required one or more independent equations. Alternatively, a direct measure of ϕ_1 may be obtained by determination of the isotopic abundance in the reaction product RH. Each of these approaches has its advantages and disadvantages, and both have been used in the present study.

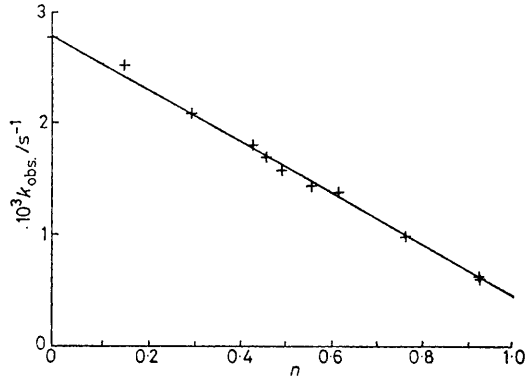


FIGURE 2 Solvent isotope effect for reaction of $[CrMe(OL_2)_5]^{2+}$ (1c) with aqueous lyonium ions (*i.e.* H_3O^+, H_2DO^+, HD_2O^+, D_3O^+). Crosses are experimental points (error bars) at $I = 1.5$ mol dm^{-3}; curve is calculated from equation (18) with $\Phi_\Delta = 0.62$, $\phi_1 = 0.16$, $\phi_2 = 0.74$, and $k_{H_2O} = 2.79 \times 10^{-3}$ s^{-1}

A non-linear least-squares fit to equation (18) of the rate measurements in H_2O–D_2O mixtures for (1c) [reaction (3B) of Table 7] leads to the values: $\phi_1 = 0.16 \pm 0.03$; $\phi_2 = 0.74 \pm 0.03$ at $I = 1.5$ mol dm^{-3}

and 0.72 ± 0.03 at $I = 1.0$ mol dm^{-3}. The fit is shown in Figure 2. The experimental rate constants show a linear dependence on n, and it must be emphasised that this is due to an accidental compensation. In related proton-transfer reactions (such as to olefinic carbon atoms) the corresponding curves are concave to the n axis.[28] It is the presence in equation (18) of the factor $(\Phi_\Delta)^n$, which by itself shows the opposite curvature, that results in the observed, but fortuitous, linear dependence of k_n upon n. The quality of the fit is not sensitive to the precise value taken for Φ_Δ, although this affects the deduced value of ϕ_2.

For the reaction of (1d) with hydrogen ion the product isotope effect was determined using tritium in tracer quantity. (The relationship between rate and product isotope effects is explicitly given in earlier papers.)[2,28,29] The tritium incorporation into the diethyl ether formed was $5.3 \pm 0.7\%$ of the amount expected in the absence of an isotope effect. Accordingly, the value of the fractionation for the proton in transit, using the tritium isotope, is 0.053. Using the Swain–Schaad relation[30] to calculate the corresponding fractionation factor for deuterium, we obtain $\phi_1 = (0.053 \pm 0.007)^{1/1.443} = 0.13 \pm 0.02$. A similarly small value ϕ_1 *ca.* 0.10 is found in corresponding experiments with the 1,4-dioxanyl complex, but is probably a slight underestimate because the yield of tritiated product was in this instance based on the concentration of the reactants from which the organochromium complex was formed, and not on the concentration of pure complex. Consequently, the occurrence of side reactions also contributes to the lowness of the yield. For this reason, the correct value of ϕ_1 for (1e) is estimated to be *ca.* 0.12—0.13.

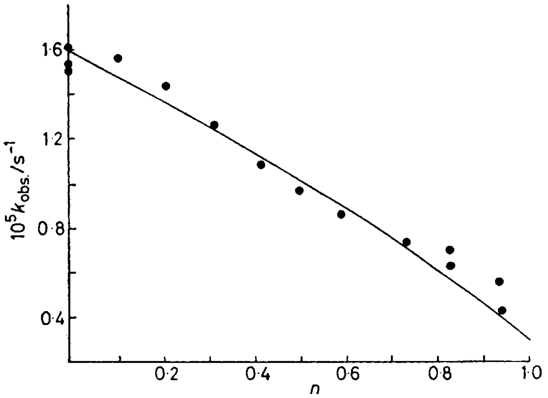


FIGURE 3 Solvent isotope effect for reaction of $[Cr\{CH(OEt)CH_3\}(OL_2)_5]^{2+}$ (1d) with aqueous lyonium ions. Experimental points and theoretical curve calculated from equation (18) with $\Phi_\Delta = 0.62$, $\phi_1 = 0.13$, $\phi_2 = 0.856$, and $k_{H_2O} = 1.60 \times 10^{-5}$ s^{-1}

Rate measurements with (1d) were not very reproducible. Figure 3 shows the experimental points, together with a curve calculated for equation (18) using the value of Φ_Δ determined for other substrates and the value of ϕ_1 deduced from the tritium product study. The calculated curve is not the ' best ' one that could be drawn through the experimental data but, in view of the scatter, is compatible with them. The extrapolated rate ratio k_{H_2O}/k_{D_2O} is 6.0, corresponding to $\phi_2 = 0.824$.

The low value of ϕ_1 indicated for both (1c) and (1d) confirms that the reactions involve rate-limiting proton transfers. The fractionation factors ϕ_2 may be related to α, the degree to which the non-transferred part of the H_3O^+ grouping has been converted into H_2O, by equation (21).[31] When measurements of reaction rates in

$$\phi_2 = l^{1-\alpha} \qquad (21)$$

H_2O–D_2O mixtures are of good accuracy (and the analysis uncomplicated by uncertainties in the assumption that Φ_Δ has *exactly* the same value for all reactions) the value of α deduced has been found to be similar to (although not necessarily identical with) that of the Brønsted exponent for general acid catalysis.[28,32] Values of α can similarly be deduced for our examples. Significantly, these values are in the required range $0 < \alpha < 1$ but their error limits are wide. The result $\phi_2 = 0.73 \pm 0.04$ deduced for (1c) corresponds to $\alpha = 0.15 \pm 0.15$, and the value $\phi_2 = 0.824$, found for (1d), leads to $\alpha = 0.48$ with even wider error limits. However, the fact that the α values seem to lie well below unity suggests the likelihood that the acidolytic breakdown of the organochromium(III) complexes (1) is subject to general acid catalysis. There are some indications in the literature that this may be so.[14] The possibility has not so far been properly investigated and, in the light of our conclusions, would merit further study. (The inclusion of a factor to allow for departures from the rule of the geometric mean for isotopically mixed hydrogen ions and for HOD[4,22] does not affect the quality of the fit obtained but changes the derived value of α.)

The analysis of the measurements for reactions (3B)—(5B) can be regarded as very satisfactory since the data not only show the theoretically expected functional dependence of k_n upon n but also lead to values of fractionation factors similar to those found for purely organic reactions involving a rate-limiting proton transfer to carbon.

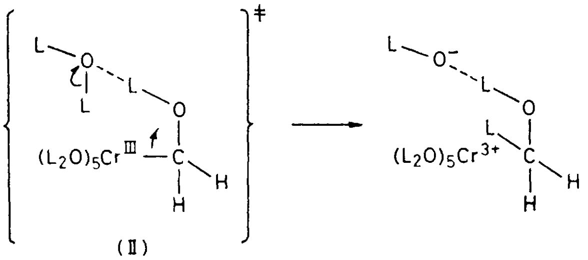
Reactions (3B)—(5B) all follow clean second-order kinetics, in the sense that any pH-independent contribution is negligible. This is not true for substrate (1f), the kinetics of aquation of which are expressible in the form[19] of equation (22). Both k_1 and k_2 are subject to

$$k_{obs.} = k_1 + k_2[H_3O^+] \qquad (22)$$

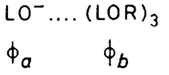
large solvent isotope effects (Table 6) but, because the acid-catalysis term is small relative to the pH-independent term, the values of k_2, especially at high values of n, are subject to greater uncertainty than those of k_1. In particular, the extrapolation to obtain the value of k_2 for D_2O solution [and hence $(k_2)_{H_2O}/(k_2)_{D_2O}$] from our data would be unreliable. All that can be said reasonably confidently is that the ratio has a value $\geqslant 6$.

The presence of a sizeable pH-independent term appears to be confined to organochromium(III) complexes (I) containing alcoholic hydroxyl substituents. In view of the unusually large solvent isotope effect in the case examined here, it seemed of interest to analyse it in terms of the theory given above.

The occurrence of the pH-independent path has been associated with the possibility of hydrogen bonding in the transition state between the organic hydroxyl group and the oxygen atom of the water molecule that acts as proton donor in the substitution reaction, as in formula (II). Alternatively it could be envisaged that this path involves intramolecular proton transfer from a ligand water. This second model of the reaction would not readily explain why the pH-independent term is absent from the rate equation unless the organic ligand contains a hydroxyl group. It has accordingly been ruled out from more detailed consideration. Formula (II) may, however, be an over-simplification. If it is assumed that the hydroxide ion produced must acquire three hydrogen bonds to its oxygen atom,[33] as in formula (III), then the corresponding transition state, (IV), would contain a five-co-ordinate oxygen atom. Such an awkward arrangement around oxygen is unknown. It could be avoided either by assuming that the hydroxide ion is formed in a partially desolvated form or, perhaps more plausibly, that the co-operation of an additional water molecule is involved, as in a transition state (V). The hydrogen atoms that undergo a significant change on going from reactants to transition state for both models are numbered 1—5 in the formulae, and Table 8 sets out the chemical environment and associated fractionation factors for these positions. In each case the corresponding positions in the reactants are hydroxylic (water or hydroxymethyl), for both of which the fractionation factor is taken to be unity. For positions involved only in secondary isotope effects we may assume the fractionation factor to have a value intermediate between that for water (unity) and the final value. For example, position 2 changes from a water site to an *a* site of the aqueous hydroxide ion (III). Taking the fractional degree of this progress to be α $(0 < \alpha < 1)$, we write $\phi_2 = \phi_a^{\alpha}$. The fractionation factor for the *b* sites of the hydroxide ion (III) is assumed to be the same whether the hydrogen-bonding hydroxyl groups belong to a water molecule or to a hydroxymethyl group.

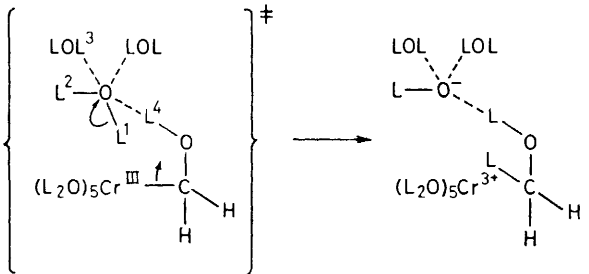


(II)

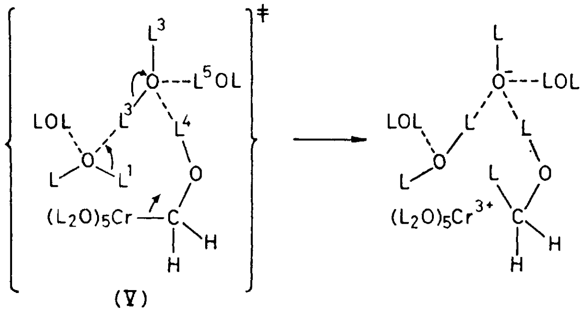


$$\underset{\phi_a}{LO^-} \cdots\cdots \underset{\phi_b}{(LOR)_3}$$

(III)



(IV)



(V)

TABLE 8

Hydrogen positions and fractionation factors in transition states (IV) and (V)

Hydrogen atom	Position and fractionation factors in transition state	
	(IV)	(V)
1	In transit to carbon: ϕ_1	As for (IV): ϕ_1
2	Intermediate between water and position *a* of hydroxide ion: ϕ_a^{α}	As for (IV): ϕ_a^{α}
3	Intermediate between water and position *b* of hydroxide ion: ϕ_b^{α} (2 ×)	As for (IV): ϕ_b^{α} (1 ×)
4	Intermediate between hydroxyl ($-CH_2OH$) and position *b* of hydroxide ion: ϕ_b^{α}	As for (IV): ϕ_b^{α}
5		In transit to position *b* of hydroxide ion

Substituting these fractionation factors for transition state (IV) in equations (2) and (4), and inserting the factor Φ_{Δ} as before, we obtain the expressions (23) and (24).

$$k_n/k_{H_2O} = (\Phi_{\Delta})^n(1 - n + n\phi_1)(1 - n + n\phi_a^{\alpha})(1 - n + n\phi_b^{\alpha})^3 \quad (23)$$

$$k_{D_2O}/k_{H_2O} = \Phi_{\Delta}\phi_1\phi_a^{\alpha}\phi_b^{3\alpha} \quad (24)$$

With the values $\phi_a = 1.2$, $\phi_b = 0.7$, $\Phi_{\Delta} = 0.62$ (as before) we find that the parameters $\phi_1 = 0.22$ and $\alpha = 0.15 \pm 0.09$ satisfy the experimental value of the (slightly extrapolated) rate ratio $k_{H_2O}/k_{D_2O} = 8.4$ as well as the shape of the entire curve of k_n *vs.* n (Figure 4) according to equation (23).

The information in Table 8 shows that almost the same equations follow if we adopt the model of transition state (V). The only difference is that one of the factors ϕ_b^{α} has been replaced by the fractionation factor for position 5 corresponding to a proton in transit from ordinary water to a hydrogen-bonding position b.

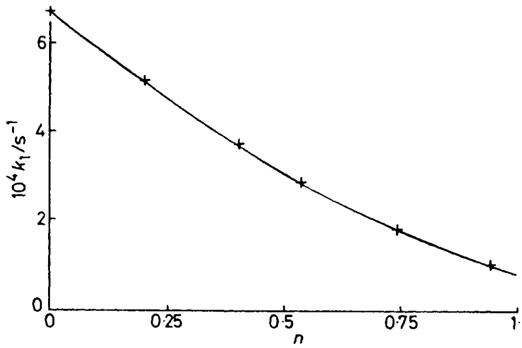
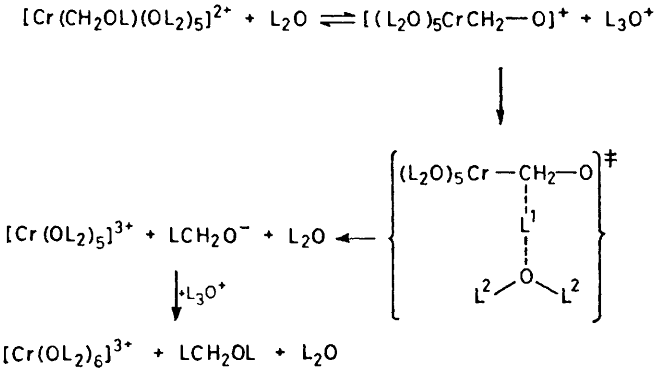


FIGURE 4 Solvent isotope effect for reactions of $[Cr(CH_2OL)(OL_2)_5]^{2+}$ (1f) with water. Experimental points (error bars) and theoretical curve calculated from equation (23) with $\Phi_\Delta = 0.62$, $\phi_a = 1.2$, $\phi_b = 0.7$, $\phi_1 = 0.22$, and $\alpha = 0.15 \pm 0.09$

However, it has also been shown that isotope effects on proton transfers between electronegative centres are satisfactorily reproduced on the assumption that they can be treated as if they were secondary isotope effects.[3,34] In the present instance this leads to the result that $\phi_5 = \phi_b^{\alpha}$, and the overall conclusion that the two models of the transition state are indistinguishable on the basis of kinetic solvent isotope effects.

On the other hand, the solvent isotope effect clearly distinguishes these models (and the underlying assumption of the hydrogen-bonding involvement of the hydroxymethyl group) for the pH-independent reaction path from a simpler alternative [equation (25)]. This third



(25)

model assumes a pre-equilibrium proton loss from the hydroxyl group, the intermediate being present in low concentration.

Considering the transition state, fractionation factor theory now predicts the isotopic rate ratio to be given by equation (26) where the final factor follows from the

$$k_{D_2O}/k_{H_2O} = \Phi_\Delta \phi_1 \phi_2^2 \phi_b^3 \qquad (26)$$

assumption that the basic $-CH_2O^-$ grouping will be hydrogen-bonded to three water molecules. With the values $k_{H_2O}/k_{D_2O} = 8.4$, $\Phi_\Delta = 0.62$, $\phi_b = 0.70$ we can evaluate the product $\phi_1\phi_2^2$ as 0.56. Since ϕ_2 $(= l^{1-\alpha})$ must lie in the range 0.69—1, it then follows that ϕ_1 would have to have a value between 0.56 and 1.1. The fractionation factors for a number of proton-transfer reactions from the aqueous hydrogen ion to carbon have been determined (both previously[30] and in the present work), and they are invariably much smaller (0.13—0.26). The calculated value 0.56 is well outside this range and hence it is concluded that the underlying mechanism of equation (25) is not tenable.

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REFERENCES

[1] See, P. M. Laughton and R. E. Robertson, in 'Solute–Solvent Interactions,' eds. J. F. Coetzee and C. D. Ritchie, Marcel Dekker, New York, 1969, ch. 6.

[2] V. Gold, *Adv. Phys. Org. Chem.*, 1969, **7**, 259.

[3] R. L. Schowen, *Prog. Phys. Org. Chem.*, 1972, **9**, 275.

[4] W. J. Albery, in 'Proton-Transfer Reactions,' eds. E. F. Caldin and V. Gold, Chapman and Hall, London, 1975, ch. 9.

[5] See, for example, J. Hudis and R. W. Dodson, *J. Am. Chem. Soc.*, 1956, **78**, 911; R. K. Knight and R. N. Sylva, *J. Inorg. Nucl. Chem.*, 1975, **37**, 779; S. Fukushima and W. L. Reynolds, *Talanta*, 1964, **11**, 283; G. G. Jayson, B. J. Parsons, and A. J. Swallow, *J. Chem. Soc., Faraday Trans. I*, 1972, 2053; M. M. Itzkowitz and F. R. Nordmeyer, *Inorg. Chem.*, 1975, **14**, 2125; M. Parris and W. J. Wallis, *ibid.*, 1964, **3**, 133; R. G. Pearson, N. C. Stellwagen, and F. Basolo, *J. Am. Chem. Soc.*, 1960, **82**, 1077; C. K. Poon, *Inorg. Chim. Acta Rev.*, 1970, 123; J. Reuben and D. Fiat, *J. Am. Chem. Soc.*, 1969, **91**, 4652.

[6] H. Taube, 'Electron Transfer Reactions of Complex Ions,' Academic Press, London, 1970, p. 37; M. J. Weaver and S. M. Nettles, *Inorg. Chem.*, 1980, **19**, 1641.

[7] J. Bigeleisen, *J. Chem. Phys.*, 1960, **32**, 1583.

[8] N. Sutin, J. K. Rowley, and R. W. Dodson, *J. Phys. Chem.*, 1961, **65**, 1248.

[9] For a review, see M. D. Johnson, *Acc. Chem. Res.*, 1978, **11**, 57.

[10] R. G. Coombes and M. D. Johnson, *J. Chem. Soc. A*, 1966, 1905.

[11] J. C. Chang and J. H. Espenson, *J. Chem. Soc., Chem. Commun.*, 1974, 233.

[12] J. H. Espenson and D. A. Williams, *J. Am. Chem. Soc.*, 1974, **96**, 1008.

[13] J. P. Leslie and J. H. Espenson, *J. Am. Chem. Soc.*, 1976, **98**, 4839.

[14] J. K. Kochi and D. Buchanan, *J. Am. Chem. Soc.*, 1965, **87**, 853.

[15] M. R. Hyde and J. H. Espenson, *J. Am. Chem. Soc.*, 1976, **98**, 4463.

[16] D. Dodd and M. D. Johnson, *J. Chem. Soc. A*, 1968, 34.

[17] J. I. Byington, R. D. Peters, and L. O. Spreer, *Inorg. Chem.*, 1979, **18**, 3324.

[18] V. Gold and D. L. Wood, *J. Chem. Soc., Dalton Trans.*, following paper.

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

[20] H. Cohen and D. Meyerstein, *Inorg. Chem.*, 1974, **13**, 2434.

[21] V. Gold, *Trans. Faraday Soc.*, 1968, **64**, 2770.

[22] W. J. Albery and M. H. Davies, *Trans. Faraday Soc.*, 1969, **65**, 1059.

[23] V. Gold, *Trans. Faraday Soc.*, 1968, **64**, 2143.

[24] L. H. Gale, J. Landgiebe, and F. R. Jensen, *Chem. Ind. (London)*, 1960, 118; R. E. Dessy, Y. K. Lee, and J.-Y. Kim, *J. Am. Chem. Soc.*, 1961, **83**, 1163; R. E. Dessy, G. F. Reynolds, and J.-Y. Kim, *ibid.*, 1959, **81**, 2683; S. Winstein and T. G. Traylor, *ibid.*, 1956, **78**, 2597.

[25] P. Salomaa and V. Aalto, *Acta Chem. Scand.*, 1966, **20**, 2035.

[26] R. W. Ramette and E. A. Dratz, *J. Phys. Chem.*, 1963, **67**, 940.

[27] P. Salomaa, *Acta Chem. Scand.*, 1971, **25**, 367.

[28] See, for example, V. Gold and M. A. Kessick, *J. Chem. Soc.*, 1965, 6718; V. Gold and D. C. A. Waterman, *J. Chem. Soc. B*, 1968, 839.

[29] V. Gold and M. A. Kessick, *Proc. Chem. Soc.*, 1964, 295.

[30] C. G. Swain, E. C. Stivers, J. F. Reuwer, and L. J. Schaad, *J. Am. Chem. Soc.*, 1958, **80**, 5885.

[31] A. J. Kresge, *Pure Appl. Chem.*, 1964, **8**, 243.

[32] J. M. Williams and M. M. Kreevoy, *Adv. Phys. Org. Chem.*, 1968, **6**, 63.

[33] V. Gold and S. Grist, *J. Chem. Soc., Perkin Trans. 2*, 1972, 89.

[34] C. G. Swain, D. A. Kuhn, and R. L. Schowen, *J. Am. Chem. Soc.*, 1965, **87**, 1553.