By contrast, the CD spectrum demonstrates that there are, in fact, a number of optically active transitions in the 195–255-nm region [CD (*c* 0.02, CH_3CN): $[\theta]_{198}$ $-32{,}300°$; $[\theta]_{212}$ $+39{,}200°$; $[\theta]_{226}$ $-168{,}000°$; $[\theta]_{239}$ $+15{,}700°$]. The large negative Cotton effect centered at 226 nm corresponds to the negative Cotton effect which dominates the rotatory dispersion curve. Although the positive Cotton effect at 239 nm does not give rise to extrema in the ORD, it is responsible for the reduction in intensity of the first extremum of the ORD curve. Moreover, the broad band in the 260–290-nm region appears clearly in the CD spectrum as a series of negative Cotton effects which appear to be associated with the fine structure in the uv spectrum.[10]

If the major low-wavelength Cotton effect observed in the ORD and CD spectra is determined by the configuration at the sulfenamide chiral axis rather than the configuration at the asymmetric carbon atom, the Cotton effects in the two diastereomers (*R*,*R*)-**1** and (*R*,*S*)-**1** will be different in sign.[11] If this is the case, and we believe it is likely, the molecular amplitude of the arenesulfonylsulfenamide chromophore must, in actuality, be substantially greater than that observed since there would be considerable cancellation. These rotations may be compared with those of other powerfully rotating chromophores which have been described as "inherently dissymmetric."[12]

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(10) Discussion of the chromophores and transitions involved is deferred to the detailed paper.

(11) If the diastereomers of (*R*,*R*)-**1** exhibit a Cotton effect at 226 nm, then either the epimer at the sulfenamide unit (*R*,*S*)-**1** or the epimer at the asymmetric carbon atom (*S*,*R*)-**1** must show a Cotton effect of inverted sign. We feel that it is at least as likely that a change in the configuration at the sulfenyl unit will reverse the sign since compounds containing only asymmetric carbon atoms as dissymmetric units do not usually exhibit Cotton effects of this magnitude.

(12) P. Crabbé, "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," Holden-Day, San Francisco, Calif., 1965, Chapter 8, and references therein.

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Effect of Pressure on the Kinetics of the Exchange of Oxygen-18 between Hexaaquochromium(III) Ion and Solvent Water. Evidence for an Associative Interchange Mechanism

Sir:

The volume of activation ΔV^* affords a useful criterion of reaction mechanism, since the spatial requirements of the various alternative models can be easily visualized. We have therefore measured the pressure dependence of the rate of reaction 1, since other evidence[1–3] has suggested that aqueous aquochromium(III) species may undergo substitution by an associative interchange mechanism (I_a).[4] Such mechanisms have hitherto been considered rare in octahedral complexes.[5]

$$Cr(H_2O)_6{}^{3+} + H_2{}^{18}O \longrightarrow Cr(H_2O)_5(H_2{}^{18}O)^{3+} + H_2O \quad (1)$$

Aliquots (5.0 ml) of an aqueous solution of hexaaquochromium(III) perchlorate (1.00 *M*) in perchloric acid (1.00 *M*) were diluted to 50.0 ml with 1.5% $H_2{}^{18}O$ (Bio-Rad Laboratories) and thermostated at 45.00 ± 0.05° in a specially constructed Lucite syringe which was pressurized in a steel bomb with hydraulic oil from a hand pump, and from which samples could be withdrawn through a stainless-steel capillary tube fitted with a stainless-steel high-pressure valve.[6] At appropriate intervals, samples of the solution were withdrawn and chilled to 0°, and the hexaaquochromium(III) ion was precipitated as $Cr(H_2O)_6PO_4$.[7] The dried solid was decomposed at ~140° in a vacuum system and the liberated water was condensed onto guanidine hydrochloride for conversion to carbon dioxide.[8] The abundance of $^{12}C^{16}O^{18}O$ relative to $^{13}C^{16}O_2$ was measured using a Hitachi Perkin-Elmer RMU-6D mass spectrometer, taking the mean of ten scans; relative abundances measured in duplicate experiments agreed within 2%. The first-order rate coefficients k for the exchange of *all six* coordinated water molecules were determined at seven different pressures ranging from 1.0 bar to 2.48 kbars. Triplicate measurements at 1.0 bar showed the reproducibility of k to be better than ±3%, regardless of whether reaction 1 had been carried out in the pressure assembly or in a darkened Pyrex vessel, and the mean (4.47×10^{-5} sec^{-1}) agreed satisfactorily with the value obtained by Arrhenius extrapolation of the data of Hunt and Plane[7] (4.2×10^{-5} sec^{-1}).

Figure 1 shows that log k is accurately a linear function of the pressure P within the experimental uncertainty, with $|(\partial \Delta V^*/\partial P)_T|$ close to zero and certainly not greater than 2×10^{-4} cm^3 bar^{-1} mol^{-1}, up to 2.5 kbars at least. A least-squares analysis gave $k = (4.49 \pm 0.09) \times 10^{-5}$ sec^{-1} at zero pressure and $\Delta V^* = -9.3 \pm 0.3$ cm^3 mol^{-1}.

Clearly, the transition state of reaction 1 must occupy a markedly smaller volume than the reactants. Since electrostrictive effects will be absent in this reaction, we can conclude that activation by the incoming water molecule is important, *i.e.*, that this water molecule is in the first coordination sphere of the chromium(III) ion in the transition state. Hunt and Taube[9] found $\Delta V^* = +1.2$ cm^3 mol^{-1} for the reaction

$$Co(NH_3)_5{}^{18}OH_2{}^{3+} + H_2O \longrightarrow Co(NH_3)_5OH_2{}^{3+} + H_2{}^{18}O \quad (2)$$

which almost certainly proceeds by a dissociative mechanism,[4] so the volume changes associated with the actual forming or breaking of an aquo-metal bond[10]

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(1) R. J. Baltisberger and E. L. King, *J. Amer. Chem. Soc.*, **86**, 795 (1964).

(2) J. H. Espenson, *Inorg. Chem.*, **8**, 1554 (1969).

(3) L. R. Carey, W. E. Jones, and T. W. Swaddle, *ibid.*, in press.

(4) C. H. Langford, and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965.

(5) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 234 ff.

(6) W. H. Jolley, Ph.D. Thesis, University of Adelaide, 1970.

(7) J. P. Hunt and R. A. Plane, *J. Amer. Chem. Soc.*, **76**, 5960 (1954).

(8) P. D. Boyer, D. J. Graves, C. H. Suelter, and M. E. Dempsey, *Anal. Chem.*, **33**, 1906 (1963).

(9) H. R. Hunt and H. Taube, *J. Amer. Chem. Soc.*, **80**, 2642 (1958).

(10) The volume decrease due to the partial formation of an aquo-metal bond in the transition state of an associative interchange process may be offset by a volume increase due to concomitant stretching of the bond to the ligand being replaced, so that the net contribution of bond

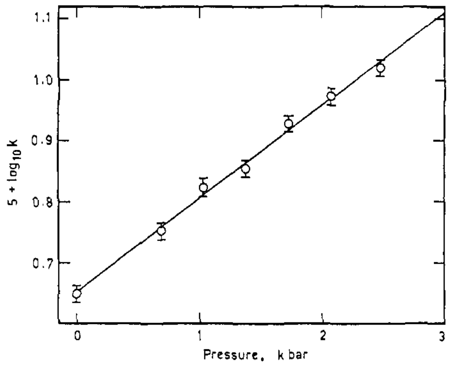

Figure 1. Pressure dependence of the first-order rate coefficient k (sec^{-1}) for the exchange of all six waters of $Cr(H_2O)_6^{3+}$; the error bars represent ±3% uncertainty in k.

are evidently of the order of 1 cm^3 mol^{-1}. The observed ΔV^* for the hexaaquochromium(III) water exchange is therefore about 8 cm^3 mol^{-1} more negative than can be explained on the basis of associative bond forming alone. We suggest that the main contribution to ΔV^* in the chromium(III)–water exchange originates in the vacancy created when the incoming water molecule is transferred to the first coordination sphere; the core complexes $Cr(H_2O)_6^{3+}$ and $Cr(H_2O)_7^{3+}$ can be regarded as being essentially spheres of the same effective radius ($r_{Cr^{3+}} + 2r_{H_2O}$).

The high degree of linearity of Figure 1 is unusual and merits comment. Hunt and Taube[9] point out that, because the compressibility of bulk water is large (8.0×10^{-4} cm^3 bar^{-1} mol^{-1} at 45° and 1 bar) compared with that of the first coordination sphere of a tripositive cationic complex, ΔV^* should be strongly pressure dependent for a water exchange process which involves equilibrium between solvent water and coordinated water, such as the associative (A) mechanism

$$H_2O + [\{Cr(H_2O)_6\}(H_2O)_x]^{3+} \overset{\text{fast}}{\rightleftharpoons} [\{Cr(H_2O)_6\}(H_2O)_{x+1}]^{3+} \quad (3)$$

$$[\{Cr(H_2O)_6\}(H_2O)_{x+1}]^{3+} \overset{\text{slow}}{\rightleftharpoons} [\{Cr(H_2O)_7\}(H_2O)_x]^{3+} \quad (4)$$

Here, the lifetime of the seven-coordinate complex is long relative to the time for exchange of the x labile waters of the presumed second coordination sphere (solvation sheath) with bulk solvent and, because this complex is more compacted and therefore even less compressible than $[\{Cr(H_2O)_6\}(H_2O)_x]^{3+}$, $(\partial\Delta V^*/\partial P)_T$ would be slightly greater than $+8.0 \times 10^{-4}$ cm^3 bar^{-1} mol^{-1}. The observation that $|(\partial\Delta V^*/\partial P)_T| < 2.0 \times 10^{-4}$ cm^3 bar^{-1} mol^{-1} is therefore difficult to reconcile with an A mechanism, but is consistent with an associative interchange (I_a) mechanism in which only the relatively incompressible solvated aquo complexes, and *not* bulk water, are directly involved in the activation process.

$$[\{Cr(H_2O)_6\}(H_2O)_x]^{3+} \longrightarrow [\{Cr(H_2O)_7\}(H_2O)_{x-1}]^{3+*} \quad (5)$$

The lifetime of seven-coordination in (5) is short even relative to the time for exchange of the labile $(H_2O)_x$ with bulk solvent, and $[\{Cr(H_2O)_7\}(H_2O)_{x-1}]^{3+}$ may exist only momentarily as the transition state. In this I_a model, the major contributor to ΔV^* is presumably the collapse of part of the solvation sheath when one of its x water molecules is transferred to the first coordination sphere.

The present data, combined with those of Hunt and Plane[7] for similar concentrations but lower temperatures, give $\Delta H^* = 26.2 \pm 0.3$ kcal mol^{-1} and, for the exchange of *one* of the six coordinated water molecules by a *first-order* process (*i.e.*, ignoring the concentration of bulk water), $k'(25.0°) = 4.3 \times 10^{-7}$ sec^{-1} and $\Delta S^* = +0.3 \pm 1.0$ cal deg^{-1} mol^{-1}, at atmospheric pressure. This near-zero value of ΔS^* is consistent with the above view of the reaction mechanism as involving only modest relocations of water molecules within an independent $[\{Cr(H_2O)_6\}(H_2O)_x]^{3+}$ entity; the transition state $[\{Cr(H_2O)_7\}(H_2O)_{x-1}]^{3+}$ need not be significantly more or less ordered than the initial state.

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making and breaking to ΔV^* could be zero or even positive. Thus, in the absence of electrostriction effects, a small, positive ΔV^* in a reaction such as (2) is not necessarily indicative of a dissociative mechanism, but a negative ΔV^* is strong evidence for an associative process.

(11) On leave with the University of Adelaide until Aug 1971.

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Reaction of Ammonia Gas with Crystalline Benzoic and Related Acids

Sir:

Although there have been scattered reports of reactions believed to have occurred between a molecular crystalline solid and a gas[1] there appears to have been no detailed study of such a reaction. We have now found that benzoic acid and a number of related carboxylic acids react, either as powders or as single crystals, with ammonia gas at 1 atm to give 1:1 ammonium salts. In each case, the product "crystal" is opaque but retains approximately the external shape of the crystal from which it was formed and in general has greater mechanical strength (resistance to crumbling) than the original crystal. Microanalysis of the product without any purification whatever gives carbon, hydrogen, and nitrogen values within 0.3% of the theoretical for the 1:1 salt. This gas–solid reaction is undoubtedly the method of choice for the preparation of many 1:1 ammonium salts.

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