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Acid Aquation of Inert Transition Metal Complexes. Correlation of Entropies and Volumes of Activation – Entropy of Activation as a Criterion of Reaction Mechanisms

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The pressure dependence of the rate of a reaction in solution affords its volume of activation ($\Delta V^{\neq}$). This is a measure of the difference between the molal volume of the initial and transition states, and it is generally considered to serve as a particularly pertinent criterion for distinguishing between possible reaction mechanisms. The appeal of assigning mechanisms in this way is, no doubt, largely based on the ease with which results can be (but possible naïvely) "visualised" directly in mechanistic terms. Negative values of $\Delta V^{\neq}$ are anticipated for an associative mechanism, and positive values for a dissociative mechanism.

The interpretation of volumes of activation in terms of mechanism is, however, not necessarily straightforward. Observed values can be considered to be composite parameters consisting of the volume change of the reactant(s) on forming the transition state, and the concomitant change of the volume of solvating molecules. Indeed, the latter may be important, and will be effected by, for example, the charge of the reactant(s) *via* electrostatic attraction with the dipole (permanent or induced) of the solvent molecules. It is not intended to discuss such electrostrictive effects here, but to emphasise that, qualitatively, factors influencing both the sign and magnitude of $\Delta V^{\neq}$ are directly related to the *change in freedom of motion* on going from the solvated initial state to the solvated transition state. It is, therefore, anticipated that for a given class of reactions, under similar conditions, a correlation between $\Delta V^{\neq}$ and the more routinely determined entropy of activation ($\Delta S^{\neq}$) should exist. The pioneering ICI research group classified reactions into three classes according to their collision frequency factors, and the retarding or accelerating effect of applied pressure [1]. Thus a possible interdependence of $\Delta V^{\neq}$ and $\Delta S^{\neq}$ was indicated. However, it was not until some twenty years later (in 1959) that Laidler [2] collected together results for a variety of organic and inorganic reactions, and demonstrated the existence of an approximate correlation between $\Delta V^{\neq}$ and $\Delta S^{\neq}$. A reliable correlation of this type, if only valid within a class of reaction, would be of value since the determination of $\Delta V^{\neq}$ requires additional sophisticated high pressure apparatus that is not necessary for the precise measurement of $\Delta S^{\neq}$.

Recently volumes of activation of a number of inorganic reactions have been determined with the intention of providing a reliable criterion of mechanism. This approach has been increasingly applied to the acid aquation of ligand substitution inert d^3 and d^6 transition metal complexes, and water exchange reactions of related aquo-complexes.

$$[L_5MX]^{n+} \rightarrow [L_5MH_2O]^{(m+n)+} + X^{m-}$$

$X = H_2O^*$, halide ion *etc.*

For reactions in this class that have been the subject of pressure dependence studies, we have collected published rate constants determined over a sufficiently wide temperature range to enable reliable values of $\Delta S^{\neq}$ to be calculated. Whenever possible results were selected that had been obtained under similar conditions to that used in the corresponding high pressure studies. Unfortunately, and rather surprisingly, sufficient reliable rate data are not available for several of the reactions for which $\Delta V^{\neq}$ has been determined. Nonetheless about twenty data sets are available that encompass the experimental range of both $\Delta V^{\neq}$ and $\Delta S^{\neq}$. These are shown in the form of a plot of $\Delta V^{\neq}$ against $\Delta S^{\neq}$ in the Figure. There is a

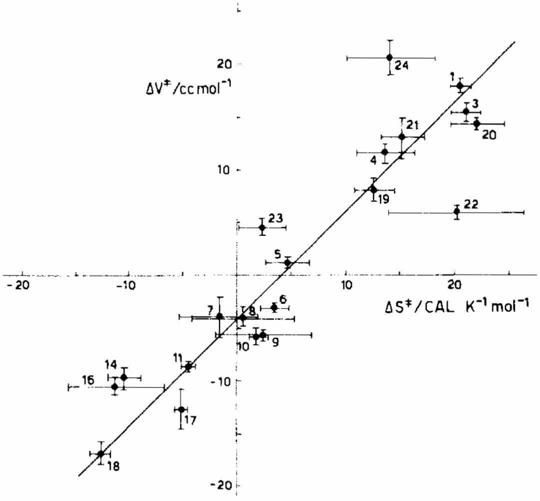

Figure. Plot of volume of activation against entropy of activation for acid aquation and water exchange reactions of low-spin d^3 and d^6 complexes. Indicated errors in $\Delta S^{\neq}$ correspond to 95% confidence limits; errors in $\Delta V^{\neq}$ are twice the standard deviations quoted by the original authors.

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TABLE. Entropies and Volumes of Activation for Acid Aquation and Water Exchange Reactions of Low-Spin d^3 and d^6 Complexes.

Code[a]	Reactant	$\Delta S^{\neq}_{obs}$ [b] (cal $K^{-1}mol^{-1}$)	$\Delta V^{\neq}_{obs}$ [c] (cm^3 mol^{-1})	$\Delta V^{\neq}_{calc}$ [d] (cm^3 mol^{-1})	$\Delta S^{\neq}_{calc}$ [d] (cal $K^{-1}mol^{-1}$)	Reference
1	$[Fe(NO_2\text{-}phen)_3]^{2+}$	+20.18 ± 0.56	+17.9 ± 0.3	+16.6 ± 2.9		4
3	$[Fe(phen)_3]^{2+}$	+20.82 ± 0.66	+15.4 ± 0.4	+17.2 ± 2.9		4
4	$[Fe(Me_2\text{-}phen)_3]^{2+}$	+13.53 ± 1.42	+11.6 ± 0.6	+9.7 ± 3.0		4
5	$[Co(NH_3)_5H_2O]^{3+}$	+4.65 ± 1.03	+1.2 ± 0.2	+0.4 ± 0.7		5
6	$[Ir(NH_3)_5H_2O]^{3+}$	+3.39 ± 0.60	−3.2 ± 0.1	−0.9 ± 1.2		6
7	$[Co(NH_3)_5NCS]^{3+}$	−1.69 ± 3.7	−4.0 ± 1.0	−6.2 ± 4.6		7
8	$[Rh(NH_3)_5H_2O]^{3+}$	−0.69 ± 2.4	−4.1 ± 0.4	−5.1 ± 3.1		8
9	$[Cr(NH_3)_5H_2O]^{3+}$	+2.21 ± 2.2	−5.8 ± 0.2	−2.1 ± 2.5		9
10	$[Co(NH_3)_5NO_3]^{2+}$	+1.87 ± 0.32	−5.9 ± 0.4	−2.5 ± 0.7		10
11	$[Co(NH_3)_5Br]^{2+}$	−4.43 ± 0.31	−8.7 ± 0.2	−9.0 ± 1.1		11
14	$[Co(NH_3)_5Cl]^{2+}$	−10.5 ± 0.8	−9.9 ± 0.5	−15.3 ± 2.3		12
16	$[Cr(NH_3)_5Cl]^{2+}$	−11.08 ± 2.26	−10.6 ± 0.3	−15.9 ± 4.0		13
17	$[Cr(H_2O)_5NO_3]^{2+}$	−5.10 ± 0.25[c]	−12.7 ± 1.0	−9.7 ± 1.0		14
18	$[Co(NH_3)_5SO_4]^{+}$	−12.53 ± 0.44	−17.0 ± 0.6	−17.4 ± 2.1		15
19	*trans*-$[Coen_2(SeO_3H)H_2O]^{2+}$	+12.7 ± 1.0[c]	+8.0 ± 0.6	+8.8 ± 2.5		16
20[e,g]	*trans*-$[Coen_2(H_2O)_2]^{3+}$	+24.0 ± 1.2[c]	+14.3 ± 0.2	+20.6 ± 3.9		17
21[f,g]	*trans*-$[Coen_2(H_2O)_2]^{3+}$	+15.3 ± 1.0[c]	+13.2 ± 0.7	+11.5 ± 2.8		17
22[h]	*trans*-$[Coen_2(H_2O)_2]^{3+}$	20.1 ± 3.1	+5.9 ± 0.2	+16.5 ± 5.2		18
23[i]	$[Co(en)_2(OH)(H_2O)]^{2+}$	2.30 ± 1.00[c]	+4.6 ± 0.4	−2.0 ± 0.5		19
24[j]	$[Fe(CN)_5(3,5\text{-}Me_2py)]^{2-}$	14.0 ± 2.01[c]	+20.5 ± 0.8	+10.2 ± 3.6		20
2	$[Co(NH_3)_5N_3]^{2+}$		+16.0 ± 0.4		+19.6 ± 2.3	21
15	$[Cr(NH_3)_5Br]^{2+}$		−9.9 ± 0.3		−5.3 ± 1.9	21

[a] As used in Figure. [b] Errors are standard deviations corrected for the number of degrees of freedom such that doubling them produces 95% confidence limits. [c] Values and error limits as given by original authors. [d] Calculated using equation 1. [e] At 0.05 mol l^{-1} $HClO_4$. [f] At 1.0 mol l^{-1} $HClO_4$. [g] Isomerization to *cis*-complex. [h] Water exchange. [i] Interchange reaction with $C_2O_4^{2-}$. [j] Reaction with CN^-.

fairly good correlation between $\Delta V^{\neq}$ and $\Delta S^{\neq}$, and graphical analysis of these data affords the relationship:

$$\Delta V^{\neq} = (1.04 \pm 0.10)\Delta S^{\neq} - (4.4 \pm 0.3)\ \mathrm{cm^3\ mol^{-1}} \tag{1}$$

It is notable that included in the correlation are reactions involving charged and neutral leaving groups, with examples from both associative and dissociative mechanistic classes. The correlation therefore holds across the range of mechanism. It is also noteworthy that this graph does not pass through the origin, so that the significance of $\Delta S^{\neq} = 0$ is not the same as that of the easily visualisable $\Delta V^{\neq} = 0$. The slope of this plot is close to unity but this, in itself, is not significant since in different units (*e.g.* SI) it would be totally different. This correlation does, however, vindicate the suggestion that factors influencing the value of $\Delta V^{\neq}$ for a given reaction are the same as those determining $\Delta S^{\neq}$ under the same conditions. Within this class of reaction there could be several causes for deviations from that predicted by the correlation, for instance the use of different experimental conditions (*e.g.* ionic strength, pH), as well as unreliable data. If $\Delta S^{\neq}$ is not temperature independent (*e.g.* conditions change with temperature, or $\Delta Cp^{\neq} = 0$ as appears to be the case for some of the reactions considered [3]) it is highly desirable that the mid-point of the temperature range over which $\Delta S^{\neq}$ is determined corresponds to the temperature at which $\Delta V^{\neq}$ is obtained. Moreover, in a number of instances $\Delta V^{\neq}$ is pressure dependent, and correcting or not correcting doubtfully curved logk/P plots can have a considerable effect on reported values of $\Delta V^{\neq}$.

Given reliable values of $\Delta S^{\neq}$, this correlation enables reasonable estimates of $\Delta V^{\neq}$ to be calculated for other reactions in this class. This approach is illustrated in the Table which contains observed and calculated values of $\Delta V^{\neq}$. Given reliable values of $\Delta S^{\neq}$, the corresponding calculated values of $\Delta V^{\neq}$ are meaningfully close to the observed value, implying that here $\Delta S^{\neq}$ is as useful a criterion of mechanism as is $\Delta V^{\neq}$. This conclusion provides further justification for the routine determination of fairly precise activation parameters [22]. Moreover, the Table also contains predicted values of $\Delta S^{\neq}$ calculated by means of equation (1) for reactions for which $\Delta V^{\neq}$ has been determined, but accurate rate constants over a range of temperatures are not available. It will be of interest to compare these with values determined directly from rate constants obtained under similar conditions in the pressure dependence experiments.

References and Notes

1 M. W. Perrin, *Trans. Faraday Soc., 34,* 144 (1938).

2 D. T. Y. Chen and K. J. Laidler, *Canad. J. Chem., 37,* 599 (1959); see also: "Physico-Chemical Effects of Pressure", by S. D. Hamann, Butterworths, 1957.

3 *E.g.* A. M. Newton and T. W. Swaddle, *J. Phys. Chem., 79,* 795 (1975).

4 J.-M. Lucie, D. R. Stranks and J. Burgess, *J. Chem. Soc. Dalton,* 245 (1975); J. Burgess and R. H. Prince, *J. Chem. Soc.,* 5752 (1963); J. Burgess, *Ph.D. Thesis,* Cambridge University, 1963.

5 H. R. Hunt and H. Taube, *J. Am. Chem. Soc., 80,* 2642 (1959); A. C. Rutenberg and H. Taube, *J. Chem. Phys., 20,* 825 (1952); H. R. Hunt and H. Taube, *J. Am. Chem. Soc., 80,* 2642 (1958).

6 S. B. Tong and T. W. Swaddle, *Inorg. Chem., 13,* 1538 (1974); E. Borghi and F. Monacelli, *Inorg. Chim. Acta, 5,* 211 (1971).

7 (a) W. E. Jones, L. R. Corey and T. W. Swaddle, *Canad. J. Chem., 17,* 2739 (1972); (b) D. L. Gay and G. C. Laylor, J. Chem. Soc., 1179 (1966).

8 (a) T. W. Swaddle and D. R. Stranks, *J. Am. Chem. Soc., 94,* 8357 (1972); (b) Monacelli and E. Viel, *Inorg. Chim. Acta, 1,* 467 (1967).

9 See ref. 8(a), N. V. Duffy and J. E. Earley, *J. Am. Chem. Soc., 89,* 272 (1967).

10 See ref. 7(a); W. E. Jones, R. B. Jordan and T. W. Swaddle, *Inorg. Chem., 8,* 2504 (1969).

11 See ref. 7(a) and ref. 3.

12 See ref. 7(a), and S. C. Chan, *J. Chem. Soc. A,* 291 (1967).

13 (a) G. Guastalla and T. W. Swaddle, *Canad. J. Chem., 51,* 821 (1973); (b) see ref. 9(a); A. E. Ogard and H. Taube, *J. Am. Chem. Soc., 80,* 1084 (1958); A. Rogers and P. J. Staples, *J. Chem. Soc.,* 6834 (1965).

14 L. R. Corey, W. E. Jones and T. W. Swaddle, *Inorg. Chem., 10,* 1566 (1971); T. W. Swaddle, *J. Am. Chem. Soc., 89,* 4338 (1967); M. Ardon and N. Sutin, *Inorg. Chem., 6,* 2268 (1967).

15 See ref. 7(a) and ref. 3 (*N.B.* sign error in this paper).

16 Data of N. Vanderhoek and D. R. Stranks, cited in: D. R. Stranks, *Pure and Applied Chem., 38,* 303 (1974).

17 D. R. Stranks and N. Vanderhoek, *inorg. Chem., 15,* 2639 (1976).

18 S. B. Tong, H. R. Krouse and T. W. Swaddle, *Inorg. Chem., 15,* 2643 (1976); W. Kruse and H. Taube, *J. Am. Chem. Soc., 83,* 1280 (1961).

19 D. R. Stranks and N. Vanderhoek, *Inorg. Chem., 15,* 2645 (1976).

20 J. Burgess, personal communication, 1977.

21 See refs. 7(a) and 13(a). The observed $\Delta V^{\neq}$ of -9.2 ± 0.2 cm^3 mol^{-1} for $[Cr(NH_3)_5I]^{2+}$ (ref. 13(a)) leads to a calculated value for $\Delta S^{\neq} = -4.6 \pm 0.8$ cal K^{-1} mol^{-1}. Values of -0.2 ± 0.9 and $+16.4 \pm 1.0$ cal K^{-1} mol^{-1} have been reported: T. W. Swaddle and E. L. King, *Inorg. Chem., 4,* 532 (1965); J. H. Espenson, *ibid., 3,* 968 (1964). It appears that these differences are due to accidental photo-catalysis.

22 Rate constants at two or more temperatures are usually available for reactions of the type considered here. Although not difficult to obtain, sufficient precise data over a suitable temperature range to reduce errors in $\Delta S^{\neq}$ to ~ ± 1 cal K^{-1} mol^{-1} are seldom obtained. An important limiting factor here is the high correlation of errors in $\Delta S^{\neq}$ with those in $\Delta V^{\neq}$, see: R. R. Krug, W. G. Hunter and R. A. Greiger, *J. Phys. Chem., 80,* 2335 (1976) and p. 2341.