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OPERATIONISM, MECHANISM, AND HIGH PRESSURE

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A critique of the Langford-Gray operational approach to ligand substitution mechanisms is given. Difficulties arising from the manner in which associative and dissociative interchange (I_a , I_d) processes are defined are examined. Alternative operational criteria based on pressure effects give a clear categorization of solvent exchange reactions which corresponds to the traditional S_N1/S_N2 dichotomy and which correlates well with other evidence regarding the modes of activation of net substitution reactions at the same centres. Conflicts between mechanistic assignments based on ostensibly equivalent but independent operational criteria illustrate fundamental limitations of operationism.

1. Introduction

Most readers of this Journal will undoubtedly associate the name of Percy W. Bridgman primarily with his brilliant pioneering studies in the field of high pressure science¹⁾—work which won him the Nobel Prize. Philosophers of science, however, remember Bridgman chiefly as the originator and leading exponent of *operationism*, a revolutionary system of scientific concept formation which grew out of the crisis in physics that was precipitated by the twin challenges of Einstein's theory of relativity and quantum mechanics.

Coincidentally, both operationism and high-pressure techniques have in recent years been independently applied to the curiously refractory problem of the assignment of mechanism in substitution reactions of octahedral transition-metal complexes in solution. In this article, we examine the usefulness and limitations of operationism in this context, with special reference to the insights gained from experimental work at elevated pressures.

2. The Origins of Operationism

Bridgman's proposals for a new system of concept formation were first set forth in his classic book²⁾ of 1928, in which (p. 3) he noted that the collapse of the Newtonian concepts of absolute time and space as we go to very high velocities and very small distances probably presaged further conceptual difficulties that would arise in dealing with other extreme situations, such as the properties of matter at the enormous pressures of stellar interiors (obviously, a topic with special appeal for him). In order to avoid prejudicing our ability to understand

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our future experiences by the limitations of our present concepts, he proposed that *a scientific concept* [e. g., of length] *be recognized as being synonymous with a corresponding set of operations* [e. g., measurement with a metre stick]. This set would, however, have to be *unique* to avoid ambiguities, although he conceded that rather more general concepts could be retained if several different sets of operations consistently gave identical results. Thus, all scientific knowledge was seen to be *relative*.³⁹ and Bridgman credits Einstein himself with adopting an operationist viewpoint in relativity theory by emphasizing the role of the observer in making observations of "simultaneity".

Bridgman's insistence upon clearly-defined empirical criteria for the definition of concepts will find favour with hard-nosed experimentalists. Certainly, it would seem unscientific to deal in constructs which are not amenable to direct observation or measurement, and furthermore operational methodology simplifies science inasmuch as many gross generalizations or speculations become meaningless by definition and hence redundant. His concern with measurement will strike a sympathetic chord with present-day workers in high pressure science seeking to establish practical pressure scales, especially in the megabar (100 GPa) region.⁴⁰ More generally, Bridgman's underlying conviction, that operationism should make it possible to discover correlations in Nature without assumptions as to the character of those correlations,⁵¹ promises liberation from difficulties created by the constraints of current preconceptions.

3. Limitations of Operationism

While operationism has had a generally beneficial impact, notably in the social sciences, its rigorous application would lead to an ever-expanding proliferation of isolated definitions of what are probably the same concepts and so would run counter to an important aim of Science—the systematization and unification of our understanding of Nature. Any concept that is scientifically truly *useful* will find its application in conjunction with other concepts, i. e., *systematically*. In particular, a scientific term can *not* be synonymous with a single set of operations defining it, since (a) it may also be understood through its systematic role; (b) a single set of operations can define the term only over the limited set of conditions encompassed by the set; (c) other perfectly valid sets may exist; and (d) new scientific knowledge may oblige us to change the operational criteria themselves.⁶¹

Furthermore, Bridgman's proposals lead him to a vehement condemnation of mechanistic explanations of natural phenomena as mere mnemonic devices—he likens the predilection of most physical scientists for such models to original sin!⁷¹ Yet, mechanistic analogies have greatly assisted the progress of science, and their very imperfections can lead to further conceptual developments, just as scientific progress in general may be regarded in terms of the repetitive cycle, paradigm—revolution—new paradigm.⁸¹ Indeed, Bridgman eventually concedes⁹¹ that "the model is a useful and indeed inescapable tool of thought, in that it enables us to think about the unfamiliar in terms of the familiar", and that the role of criticism is to

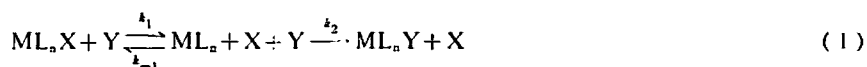
delineate the limitations of a given model.

4. Operationism and Reaction Mechanisms

In view of Bridgman's distaste for mechanical models as being antithetical to operationist philosophy, it is rather ironic that Langford and Gray¹⁰⁾ should have chosen to reclassify ligand substitution processes of inorganic complexes in solution along operational lines. This choice was in response to the difficulty of linking readily-visualized microscopic models of ligand substitution to uniquely identifiable experimental results, especially in the case of complex cations in solution.

Some 50 years ago, Ingold^{11,12)} classified organic nucleophilic substitution reactions (S_N) in a simple bipartite manner according to "the number of molecules undergoing covalency change" in the transition state (S_N1 , unimolecular; S_N2 , bimolecular). He emphasized that, although this dichotomy would often correspond to a distinction between first and second order kinetics, reaction order would *not necessarily* correlate with molecularity, *e. g.*, in solvolysis reactions (because there the nucleophile remains in large and effectively constant excess), in cases where a reagent concentration is buffered, or *where the reactants are not kinetically independent*—that is, where they are preassociated. This latter case is not common in organic substitution reactions, in which the molecule undergoing substitution is usually uncharged, but poses serious problems in substitution reactions of cationic complexes in solution, for which a second coordination sphere comprising solvent molecules and possibly other nucleophiles (notably anions, as ion pairs) is known to exist. Consequently, Basolo and Pearson's¹³⁾ extension of Ingold's S_N1/S_N2 classification to transition metal complexes is difficult to translate into simple kinetic criteria because of the prevalence of this preassociation of reagents ("encounter complexes"¹⁰⁾).

In cases where an intermediate of reduced primary coordination number is involved in the reaction mechanism *and survives long enough to be detectable*, directly or otherwise, one can confidently describe the mechanism as " S_N1 limiting"¹³⁾ or "dissociative (D)"¹⁰⁾; then, for reactions of the type



we have, through the quasi-steady-state assumption,

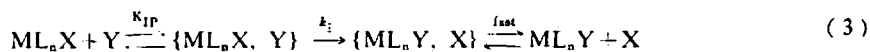
$$-d\ln[ML_nX]/dt = k_1k_2[Y]/(k_{-1}[X] + k_2[Y]) \quad (2)$$

For the case X =solvent, we see that the reaction rate is first order in Y (second order overall) when $k_{-1}[X] \gg k_2[Y]$, but becomes independent of $[Y]$ when this is high enough ($k_{-1}[X] \ll k_2[Y]$). The reactions of aqueous $Co(CN)_5OH_2^{2-}$ with Y^{2-} have been shown by several criteria to exemplify D behaviour^{14,15)}; presumably the intermediate $Co(CN)_5^{2-}$ survives relatively long because its high negative charge will repel anions and the negative

(coordinating) ends of dipolar species such as solvent molecules.

If, as is possible in principle for many transition metal complexes (as distinct from organic substrates) because of the availability of low-lying molecular orbitals derived from the ns, np, and (n-1)d orbitals of the central metal, an intermediate of *expanded* coordination number is involved in the activation process and is sufficiently long-lived to be detectable, we have a "limiting S_N2 "¹³⁾ or "associative (A)"¹⁰⁾ process. Assignment of the A mechanism to thermal substitution reactions of Pt (II), Pd(II) and Au (III) complexes has long been made on kinetic grounds (second-order kinetics with strong dependence of rate on the *nature* of both X and Y but *not* on their charges) as well as steric and stereochemical effects, and the reality of 4-to-5-coordinate equilibria has been established for Pt (II)¹⁶⁾ and Au (III)¹⁷⁾ centres in solution. The possibility that a minor D pathway contributes to substitution rates in aqueous Pt(dien)X⁺ has recently been finally disproven.¹⁸⁾ Thus, we can distinguish D mechanisms from A kinetically—the former reach limiting first-order kinetics at high [Y], while the latter give strict second-order kinetics (unless the intermediate ML_nXY builds up to a substantial fraction of the total complex concentration, but this would be apparent from other chemical evidence).

In cases where the species ML_n or ML_nXY are *transient* (*i.e.*, short-lived on the time-scale of relaxation of the second coordination sphere¹⁹⁾), however, the pre-equilibrium governing the formation of the encounter complex obscures the kinetic order criterion of molecularity.



For large excesses of Y, the rate expression becomes

$$-d\ln[ML_nX]/dt = k_i K_{IP} [Y] / (1 + K_{IP} [Y]) \quad (4)$$

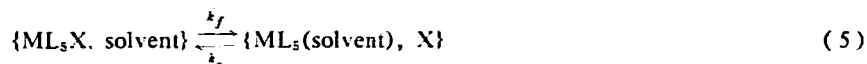
which is second-order overall at low [Y] but first order at high [Y], regardless of whether bond-making by Y is involved in the activation process or not, *i.e.*, of whether the mechanism is S_N2 or S_N1 . (For X=solvent, behaviour according to Eq. 4 is not distinguishable from that according to Eq. 2, but there should be other evidence for *either* encounter-complex formation or the involvement of a long-lived ML_n to provide the distinction.) Langford and Gray¹⁰⁾ therefore proposed that all reactions of this type be classed as *interchange* (I), so emphasizing the role of the encounter complex (and, incidentally, avoiding reference to Y as a nucleophile, since the possibility of "back-bonding" from M to Y obscures the concept of the attacking reagent as an electron donor). The essential feature of I processes, then, is that no intermediates of expanded or reduced coordination number are kinetically detectable, although it should be possible in appropriate cases (ion pair formation, *etc.*) to demonstrate the involvement of an encounter complex. The Langford-Gray classification, then, is basically operationist.

Thus, the classic S_N1/S_N2 distinction is lost. Nevertheless, one would still expect to find some indication of whether the mode of activation within the encounter complex is associative (a) or dissociative (d) (corresponding to the old S_N2 and S_N1 classes) through some manifestation

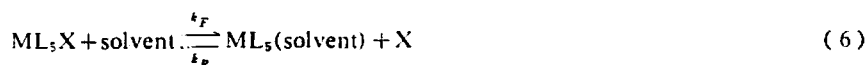
of the "nucleophilicity", or lack thereof, of Y. Langford and Gray¹⁰ therefore propose that we simply distinguish *operationally* between two classes of behaviour within the I category: if the reaction rate is "approximately as sensitive (or more sensitive) to variation of the entering group as to variation of the leaving group", the reaction will be classed as I_e , whereas if it is much more sensitive to the nature of the leaving group, it is I_d . True to operationist principles, this amounts to a simple classification scheme which is based directly upon observation rather than upon modelling of the billiard-ball variety, and which should therefore be, in principle, applicable without prejudicing our ability to adapt our ideas to accommodate new findings.

5. Critique of the Langford-Gray Operational Approach

The application of the definitions of the I_e and I_d classifications as given above is complicated somewhat by the fact that direct substitution of X by Y in ML_nX in I mechanisms is not often observed: usually, solvolysis precedes further substitution.^{10,13,19} One must also decide how to gauge "sensitivity" to the nature of X and Y. It is therefore convenient to recast the problem in a semi-quantitative form by comparing the free energies of activation for the forward and reverse reactions (5).



For d activation, k_r will be essentially the same for all X, and so the free energy relationship (FER) of $\ln k_f$ to $\ln q$ ($q = k_f/k_r$) will be linear with slope $\alpha = 1.0$. For a activation however, k_r will be sensitive to the nature of X, and we have shown elsewhere¹⁹ that the FER will then be a *curve*, with tangent $\alpha \sim 0.5$ when ΔG^\ddagger for the reaction ~ 0 but approaching 1.0 as we go to situations where the right hand side of Eq. (5) is strongly favoured. (In response to comments by Ferrer and Sykes,²⁰ it may be noted that the most recent experimental^{21a}, and theoretical^{21b}, results confirm that the general FER for ligand interchange is indeed a curve. Our arguments¹⁹ however, apply strictly only to interchange processes: thus, it is quite possible to find $\alpha = 1.0$ for some A reactions of Pt(II)²² and Pd(II)²³, in which the intermediate of expanded coordination number is presumably a distinct, long-lived entity.) For reactions in water at least, the formation constants for $\{ML_5OH_2, X\}$ will be essentially the same for a series of given M, L, and charge type, so that k_f and k_r can be replaced by the overall rates k_F and k_R (with $Q = k_F/k_R$).



Thus, the FERs reported in the literature are generally cast in terms of $\ln k_F$ and $\ln Q$. Now, according to the strict operational definitions Langford and Gray, the I_e label will apply when α is 1.0 or close to it, but the I_d category would apply only when the sensitivity of rates to the natures of entering and leaving groups is *about equal*, which corresponds

to $\alpha \sim 0.5$. For $M = \text{Co(III)}$ with $L = \text{NH}_3$ in water, $\alpha = 1.0$,^{19,19)} and an I_a mechanism is operationally appropriate. For $M = \text{Cr(III)}$ with $L = \text{H}_2\text{O}$ in water, the FER appears linear with $\alpha = 0.56$, and the I_a label is operationally correct¹⁹⁾.

For $M = \text{Cr(III)}$ with $L = \text{NH}_3$ in water, however, it seemed until recently that $\alpha = 0.9 \pm 0.1$, and Sykes *et. al.*²⁴⁻²⁶⁾ followed operational criteria in assigning an I_a mechanism in spite of evidence from pressure effects (see below)¹⁹⁾ that aqua exchange ($X = \text{solvent} = \text{H}_2\text{O}$) is *associatively* activated. These assignments are inconsistent: if d activation provides the main reaction pathway for the substitution of $\text{Cr}(\text{NH}_3)_5\text{OH}_2^{3+}$ by $X = \text{NCS}^-$, HC_2O_4^- , $\text{C}_2\text{O}_4^{2-}$, and $^-\text{NH}_3\text{CH}_2\text{CO}_2^-$, it must be available for aqua exchange too, since k_r (Eq. 5) for these anions²⁴⁻²⁶⁾ amounts to 40 to 100% of the rate of water exchange and this cannot be explained away in terms of ion-pairing effects.^{19,27)} Furthermore, steric effects^{19,28)} on the rates of aquation of $\text{M}(\text{NH}_3)_5\text{Cl}^{2+}$ through N-methylation are *opposite* for $M = \text{Co(III)}$ (20-fold acceleration) and Cr(III) (33-fold retardation), in accordance with dissociative activation in the Co(III) series but associative in the Cr(III) amines. Finally, pressure effects on the aquation rates of $\text{Cr}(\text{NH}_3)_5\text{X}^{(3-\nu)+}$ relative to the Co(III) analogues show qualitative differences consistent with a and d activation respectively (see below).

Recently, Ferrer and Sykes²⁹⁾ have extended the range of rate data on the $\text{Cr}(\text{NH}_3)_5\text{OH}_2^{3+}/\text{X}^{n-}$ series, giving $\alpha = 0.7-0.9$, and acknowledge that this is indicative of some significant associative contribution. They correctly remark that the inconsistency in mechanistic assignment in this case arose because of the way in which the I_a category is defined, but I feel that the problem goes beyond mere semantics. We have here an instance where there is good evidence for associative activation, yet the Langford-Gray *operational* approach would oblige us to use a d label. While this may serve some taxonomic purpose, there are at least two objections: (a) it prevents us from making a useful generalization, *viz.*, that simple substitution in Cr(III) cations is associatively activated (though the degree of "push" given to outgoing X in CrL_5X by incoming Y will obviously vary widely with X, Y, and also L); and (b) any theoretical treatment of electronic influences on reactivity in metal complexes inevitably requires knowledge of whether the primary coordination number increases or decreases on going to the transition state.

At the root of the problem is the inherent requirement of operationism that a definition shall be cast in terms of a *unique* set of operations. As we shall see, pressure effects could be used to set up another set of criteria to distinguish a from d behaviour, but would lead to some assignments opposite to those according to the criteria of Langford and Gray. A current controversy²⁹⁻³¹⁾ over the mechanism of substitution on manganese(II) in solution is a case in point: pressure effects on the rates of solvent exchange in methanol³²⁾ and water^{33,34)} give markedly negative volumes of activation ΔV_{\ddagger}^* which indicate associative activation, yet net substitution rates for Mn(II) complexes show no marked dependence on the nature of the incoming ligand and hence an I_a label would have to be assigned operationally.²⁹⁾ In fact, there are good reasons to believe that Mn(II) substitutions are indeed a-activated^{31,34)}; the

apparent lack of discrimination in reaction rates may reflect the limited scope and precision of the available data,³⁰ but in any case a narrow range of nucleophilicities is expected for the "hard-hard" interactions typical of aqueous Mn(II) chemistry.^{19,31,34}

There are, then, both experimental and theoretical reasons to indicate that assignments of I_d mechanism on the purely operational criteria proposed by Langford and Gray¹⁰ may not always correspond to actual dissociative activation; the fault lies ultimately with operationism *per se*.

6. The Role of High Pressure Kinetic Studies: Solvent Exchange Reactions

According to transition state theory, the effect of pressure P on the rate coefficient k of a chemical reaction is governed by Eq. (7), in which the volume of activation, ΔV^\ddagger , represents the difference in molar volume between the transition and initial states and may itself be pressure-dependent.

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\Delta V^\ddagger / RT \quad (7)$$

The interpretation of ΔV^\ddagger data is the subject of a companion article in this issue of *Rev. Phys. Chem. Japan* by van Eldik and Kelm. We shall consider here only some representative cases in which pressure studies have provided special insights into the problem of ligand substitution mechanisms.

Firstly, as a matter of empirical observation, ΔV^\ddagger for ligand substitution in complex ions in polar solvents is independent of pressure within the experimental accuracy for cases in which significant solvational change or the involvement of long-lived intermediates are not likely to occur *en route* to the transition state. In particular, the exchange of solvent on metal cations, as studied by isotopic labelling methods or by NMR line broadening (T_2) measurements, shows a linear dependence of $\ln k$ on P .

Solvent exchange is important for the understanding of substitution reactions because it is the simplest example of such processes and also because it goes on in competition with net chemical reactions. Insights into the mechanisms of solvent exchange processes are very hard to obtain by conventional means because of the symmetrical nature of these "non-reactions" (and the fact that free solvent is present in large and constant excess), but by the same token the interpretation of the constant ΔV^\ddagger data is simplified. As argued elsewhere,^{19,31} a positive value of ΔV^\ddagger is strong evidence for d activation, and a negative one for a. This represents an application of the "pressure-coordination rule" of Gutmann and Mayer,³⁵ according to which an increase in pressure will favour processes involving an increase in coordination number (such as a-activated solvent exchange) and suppress those which involve a decrease in coordination number (d solvent exchange). Langford²⁹ correctly points out that the magnitude of $|\Delta V^\ddagger|$ will be diminished by contraction of the non-reacting metal-ligand bond distances in d activation, and, conversely, by lengthening in a, but this effect will be

insufficient to reverse the *sign* of ΔV_{\ddagger}^* ,^{30,31)} which can therefore serve as a kind of "litmus paper of mechanism", in the absence of special complicating effects.

Thus, a determined operationist could classify solvent exchange reactions according to whether they are accelerated by pressure (let us call these "PA") or pressure-decelerated ("PD"). Such operational distinctions would be clear-cut in almost every case, since essentially all the ΔV_{\ddagger}^* values reported to date differ from zero by more than the experimental error (which is typically $\pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$); this contrasts with the extensive "grey area" between the operationally-defined I_a and I_d mechanisms. The above discussion relates PD behaviour with d activation, and PA with a, but of course the *raison d'être* of operational definitions is that they are independent of such mechanical models as "activation", which may be found wanting in the future. Interestingly, this PD/PA dichotomy takes us right back to the simple Ingoldian division between S_N1 and S_N2 : the divisions between I_d and D, and between I_a and A, are rendered unnecessary in this context, although one may wish to distinguish between cases in which the pressure effect is small and ones in which it approaches an upper limit ("PD lim.", "PA lim.").

There is difficulty, however, in determining what these limits should be. Empirically, Table 1 shows that $|\Delta V_{\ddagger}^*|$ ranges up to $9 \pm 2 \text{ cm}^3 \text{ mol}^{-1}$ for a variety of solvents and complexes, despite a wide range in molar volumes V_S^0 of the solvents. There is no obvious correlation of $|\Delta V_{\ddagger}^*|$ with V_S^0 , and in no case does $|\Delta V_{\ddagger}^*|$ approach V_S^0 even remotely. Further to this, we note that $\text{Co}(\text{CN})_5\text{OH}_2^{2-}$ (for which aqua exchange rate data are not available, but which provides the classic example of a D or S_N1 lim mechanism^{14,15)}) gives ΔV_{\ddagger}^* close to $+9 \text{ cm}^3 \text{ mol}^{-1}$ for reactions with each of Br^- , I^- , and NCS^- ³⁶⁾ in water, confirming that the extreme value of $|\Delta V_{\ddagger}^*|$ for aqueous systems is about $9 \text{ cm}^3 \text{ mol}^{-1}$. The often-cited postulate³⁷⁾ that the molar volumes of species ML_n and ML_{n-1} are equal in solution is therefore clearly erroneous, as this would predict that $|\Delta V_{\ddagger}^*|$ should be close to V_S^0 for D or A mechanisms.

More realistically, we can regard a coordinated solvent molecule as being in a close-packed state, i. e., as having lost the free volume which characterizes its liquid state. For the water molecule, which can be regarded as a sphere of radius 138 pm, a cubic closepacked array would have a molar volume of $9.0 \text{ cm}^3 \text{ mol}^{-1}$, so that the volume change on coordinating a water molecule would be $(18-9) = 9 \text{ cm}^3 \text{ mol}^{-1}$, which corresponds well to the upper limits of $|\Delta V_{\ddagger}^*|$ for water exchange (Table 1).³¹⁾ The model is reasonable: the octahedral interstices in the close-packed water would accommodate a typical M^{3+} ion almost exactly, and interestingly Liebermann's two-structure model for water⁴⁷⁾ gives a volume difference of $9.7 \text{ cm}^3 \text{ mol}^{-1}$ between hypothetical close-packed and loosely-packed structures. The cubic close-packing model represents dissociative activation more realistically than associative, for octahedral complexes, since it is properly limited to a maximum coordination number of 6: a value of ΔV_{\ddagger}^* somewhat less negative than $-9 \text{ cm}^3 \text{ mol}^{-1}$ might therefore be anticipated for associatively activated aqua exchange (cf. $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, $\text{Mn}(\text{H}_2\text{O})_6^{2+}$, etc.). If this is so, the value of -9.3 for $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ is somewhat anomalous and may reflect spin-pairing of the $3d^3$ electrons

Table 1. Volumes of activation JV_{\ddagger}^* and solvent molar volumes V_s° for solvent exchange reactions of $ML_n(\text{solvent})^{m+}$

Solvent	$V_s^\circ/\text{cm}^3\text{mol}^{-1}$, 293K	ML_n^{m+}	JV_{\ddagger}^* $\text{cm}^3\text{mol}^{-1}$	Ref.
H ₂ O	18.0	Cr(H ₂ O) ₆ ³⁺	-9.3	19
		Cr(NH ₃) ₆ ³⁺	-5.8	19
		Fe(H ₂ O) ₆ ³⁺	-5.6	38
		Co(NH ₃) ₆ ³⁺	+1.2	39
		<i>trans</i> -Co(en) ₂ OH ₂ ²⁺	+5.8	40
		Rh(NH ₃) ₆ ³⁺	-4.1	19
		Ir(NH ₃) ₆ ³⁺	-3.2	19
		Mn(H ₂ O) ₆ ²⁺	-5.4	34
		Fe(H ₂ O) ₆ ²⁺	+3.8	34
		Co(H ₂ O) ₆ ²⁺	+6.1	34
		Ni(H ₂ O) ₆ ²⁺	+7.2	34
CH ₃ OH	40.5	Mn(CH ₃ OH) ₆ ²⁺	-5.0	32
		Fe(CH ₃ OH) ₆ ²⁺	+0.4	32
		Co(CH ₃ OH) ₆ ²⁺	+8.9	32
		Ni(CH ₃ OH) ₆ ²⁺	+11.4	32
CH ₃ CN	52.3	Co(CH ₃ CN) ₆ ²⁺	+6.3	41
		Ni(CH ₃ CN) ₆ ²⁺	+7.3	41
		Ni(CH ₃ CN) ₆ ²⁺	+9.6	42
(CH ₃) ₂ SO	70.9	Cr(DMSO) ₆ ³⁺	-11.	43
(DMSO)		Co(NH ₃) ₆ ³⁺	+10.	44
HCON(CH ₃) ₂	77.0	Cr(DMF) ₆ ³⁺	-6.3	45
(DMF)		Co(NH ₃) ₆ ³⁺	+3.2	46
		Rh(NH ₃) ₆ ³⁺	-1.4	46
		Co(DMF) ₆ ²⁺	+6.7	42
		Co(DMF) ₆ ²⁺	+9.1	42
		Ni(DMF) ₆ ²⁺	+9.1	42

† May be taken as temperature independent

in the activation process, as suggested by Spees *et. al.*⁴⁸⁾, resulting in an unusually highly collapsed seven-coordinate transition state.

Naive calculations based on close-packing would not be very appropriate for the other, markedly non-spherical, solvent molecules listed in Table 1. Since liquid water has an anomalously open structure because of extensive hydrogen-bonding, however, the volume loss for the aprotic solvents DMF, DMSO, and CH₃CN on coordination can be expected to be a much smaller fraction of V_s° than is the case for water, while the partially H-bonded solvent methanol should be intermediate between water and the aprotic solvents. Indeed, taking as an example Ni(solvent)₆²⁺, we obtain from Table 1 $JV_{\ddagger}^*/V_s^\circ = 0.40, 0.28, 0.12$, and 0.14 for the solvents H₂O, CH₃OH, DMF and CH₃CN respectively.

7. Solvent Exchange Reactions in Relation to Other Ligand Substitution Processes

We have seen that pressure effects on the solvent exchange kinetics of $ML_5(\text{solvent})^{m+}$ place $ML_5^{m+} = Co(NH_3)_5^{3+}$, *trans*- $Co(en)_2OH_2^{3+}$, $Fe(\text{solvent})_5^{2+}$, $Co(\text{solvent})_5^{2+}$, and $Ni(\text{solvent})_5^{2+}$ operationally in the PD class, and that this can be interpreted to mean that these exchange reactions are dissociatively activated. This observation is arguably not especially significant *per se*; what is important is that, with the exception of the iron(II) species (for which the data are too limited), the other conventional criteria of mechanism (*e.g.*, lack of display of range of nucleophilicities of incoming ligands) are consistent with the general occurrence of dissociative activation^{13,19,49} in simple ligand substitution reactions of these species $ML_5(\text{solvent})^{m+}$. Similarly, where $ML_5(\text{solvent})^{m+}$ falls in the PA category for solvent exchange, for which associative activation can then be inferred, we find that other mechanistic evidence is consistent with associative activation for net substitution reactions (Eq. 6) of $ML_5(\text{solvent})^{m+}$ in general.^{19,46,49,50} This is well-documented for $Cr(\text{solvent})_6^{3+}$,^{19,27} while for $Cr(NH_3)_5OH_2^{3+}$ the effect of pressure on the solvent exchange reaction was instrumental in bringing about reconsideration of the earlier assignment of dissociative activation, as noted above.

Similarly, difficulties arising from inconsistencies in experimental conditions between different investigators, from the "proton ambiguity", *etc.*, have tended to obscure the fact that the relative rates of reactions of $Fe(H_2O)_6^{3+}$ with X^- provide good evidence for associative activation at the iron(III) centre^{19,50}: the author's recent high-pressure measurements in Prof. A. E. Merbach's laboratory show that the $Fe(H_2O)_6^{3+}$ aqua exchange is firmly in the PA category and so a activation is confirmed (the species $Fe(H_2O)_5OH_2^{2+}$, however, is PD, just as expected for conjugate bases of complexes^{13,19,38}). The kinetic evidence relating to the mode of activation of $Mn(\text{solvent})_6^{2+}$ is ambiguous, as noted above, but the PA categorization is very clear. Information on $(NH_3)_5Rh(\text{solvent})^{3+}$ is somewhat less decisive: there is good evidence, apart from the PA behaviour, that its activation is indeed associative,^{28,46} but not strongly so. Here again, it may be that the pressure effect on the solvent exchange process gives the clearest mechanistic clue.

Pressure effects on net ligand replacement reactions such as Eq. 6 are more difficult to interpret than for solvent exchange because of solvational changes, which can be the predominant component of ΔV^\ddagger ,^{19,37,51} as well as the contributions of net chemical change to volume properties. On the other hand, significant solvational change is usually heralded by a marked pressure dependence of ΔV^\ddagger , and this can be put to use to learn about the contribution of solvation to reactivity, *e.g.*, to estimate the change in the number of solvating molecules during the activation process.¹⁹ Even without a detailed breakdown of ΔV^\ddagger into its components, however, some clues to mechanism can be noted; for example, for the aquation of aqueous $M(NH_3)_5OH_2^{3+}$ (obtained either directly or by subtracting the volume of reaction from ΔV^\ddagger for the aquation of $M(NH_3)_5X$ at zero pressure), we find $\Delta V^\ddagger \sim +1$ to $+2 \text{ cm}^3\text{mol}^{-1}$ for $M = Co^{3+}$ for a variety of mononegative X^- , for SO_4^{2-} , and for aqua-exchange, confirming that

Co-OH₂ bond breaking is the common activating process (and, incidentally, that the ion-pairing contribution to the kinetics must be less important than usually believed, as Palmer, van Eldik and Kelm⁵²⁾ have maintained: desolvation during ion-pairing must be negligible in this *dynamic* process).

By contrast, ΔV^\ddagger for the corresponding reactions of $\text{Cr}(\text{NH}_3)_5\text{OH}_2^{3+}$ are all negative and variable (~ -2 to $-6 \text{ cm}^3\text{mol}^{-1}$), indicating associative activation. For chloride anation of $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{3+}$, ΔV^\ddagger is a striking $-20 \text{ cm}^3\text{mol}^{-1}$,⁵³⁾ indicating an extreme example of associative activation. Unfortunately, ΔV^\ddagger for the analogous reaction of $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ is reported to be $+3 \text{ cm}^3\text{mol}^{-1}$,⁵²⁾ but this may not be definitive, since some desolvation of the attacking anion (and hence a positive contribution to ΔV^\ddagger) must occur in associative activation: thus, controversy over the mode of activation of Rh(III) complexes is likely to continue. In general, however, high pressure studies on ligand replacement kinetics lend support to mechanistic assignments made on conventional grounds, and these in turn show a clear correlation with the PA/PD classification described above.

8. Conclusions

Ligand substitution kinetics have provided a testing-ground for Bridgman's operational approach to concept formation. Langford and Gray's D/I_a/I_s/A system of operational classification of kinetic behaviour encounters difficulties because the strict definition of the I_s category leaves a grey area between it and I_a. Furthermore, Bridgman's insistence that operational definitions be unique and made without possibly prejudicial reference to mechanistic models is seen to be self-defeating in this context: operationism places in the I_s category some reactions which, by alternative but equally valid operational definitions based on pressure effects, belong in the equivalent of the I_a class. The effect of pressure on solvent exchange reactions, on the other hand, leads to a sharply-defined operational criterion (pressure-decelerated *versus* pressure-accelerated) which is readily linked to the classic Ingoldian S_N1/S_N2 dichotomy.

Perhaps the most useful aspect of studies of pressure effects on solvent exchange kinetics is that a clear correlation of trends in ΔV^\ddagger with the *d*-electron configuration of the central metal ion is discernable. This has been commented upon at length elsewhere,^{31,32)} and may indicate new avenues of approach to the question of ligand field effects on reactivity in transition metal complexes. Be this as it may, high pressure kinetic studies continue to provide a perspective on ligand substitution dynamics which is different from, and independent of, more conventional approaches: the results are generally gratifyingly supportive of conclusions based on other evidence, but a few disparities serve to point out weaknesses in our conceptual approach.

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