

208. *The Relative Stabilities of Halogeno-complexes. Part II.*¹
The Bond-strengths.

By A. J. POË and M. S. VAIDYA.

The few results available for the heats of replacement of one halogen in a complex by another have been used to estimate the relative strengths of the bonds after allowance for hydration effects. Even in those complexes for which the stability order is $\text{Cl} < \text{Br} < \text{I}$ [class (b)] the bond-strengths are in the order $\text{Cl} > \text{Br} > \text{I}$. Although for similar systems the degree of class (b) behaviour can be associated with a narrowing of the bond-strength differences, arguments are presented which suggest that this narrowing cannot be due to d_π -bonding effects accompanied by back-donation. Preliminary calculations, based on an ionic model, indicate that polarisation, caused by increased effective charge on the metal ion, also cannot explain class (b) behaviour and that ionic size may be the major factor in determining the relative bond-strengths in similar systems and thus, indirectly, the degree of class (b) character.

THE empirical division of metal ions into two classes, according to the relative stabilities of their complexes with certain sets of ligands, has been associated with their differing ability to form double bonds by "back-donation" of d -electrons to the ligands.² In particular, metal ions which form halogeno-complexes, the stabilities of which increase from the fluoride to the iodide, are given class (b) status, the iodide being assumed to be most able to attract d -electrons from the metal. Since this inference as to relative bond strengths is made on the basis of equilibrium constants or free energies it is of interest to derive quantitative values for these relative bond strengths.

Estimates of the relative free energies of the bonds in $[\text{HgCl}_4]^{2-}$ and $[\text{HgI}_4]^{2-}$ were made by Grinberg and Nikol'skaya³ who considered the effects of hydration on the reaction $[\text{HgCl}_4]^{2-} + 4\text{I}^- \longrightarrow [\text{HgI}_4]^{2-} + 4\text{Cl}^-$. This calculation can be developed to obtain relative bond strengths by making use of recent data on enthalpies and entropies of formation of halogeno-complexes.^{1,4} Thermodynamic functions for some halogen-interchange reactions have thus been derived and are given in Table I. Since each equilibrium involves interchange of similar ions at a constant ionic strength the functions will be close to the corresponding standard functions. The enthalpy change for the complete interchange of halogen ligands is made up of changes in (a) the hydration enthalpy of the free halide ions, (b) the hydration enthalpy of the complex ion, and (c) the intrinsic enthalpy of the complex

¹ Part I, Poë and Vaidya, *J.*, 1960, 3431.

² Ahrland, Chatt, and Davies, *Quart. Rev.*, 1958, 12, 265.

³ Grinberg and Nikol'skaya, *J. Appl. Chem. (U.S.S.R.)*, 1951, 74, 893.

⁴ Bjerrum, Schwarzenbach, and Sillén, "Stability Constants," Part II, *Chem. Soc. Spec. Publ.* No. 7, 1958, pp. 88—127.

ion which equals minus the change in the bond strengths. By using differences in the hydration enthalpies of the free halide ions derived⁵ from data quoted by Latimer⁶ [*viz.*: $\Delta H^\circ_{\text{hydr.}}(\text{I}^-) - \Delta H^\circ_{\text{hydr.}}(\text{Cl}^-) = 18.55 \text{ kcal./g.-ion}$, and $\Delta H^\circ_{\text{hydr.}}(\text{Br}^-) - \Delta H^\circ_{\text{hydr.}}(\text{Cl}^-) = 8.12 \text{ kcal./g.-ion}$], values are obtained of the relative absolute enthalpies of the hydrated halogeno-complexes. In each of the systems considered the absolute enthalpies

TABLE 1. *Thermodynamic data for halogen-replacement reactions.*

	$-\Delta G$ (kcal./ g.-ion)	$-\Delta H$ (kcal./ g.-ion)	ΔS (cal./ deg. mole)	I (M)	ΔH (complex) (kcal./ g.-ion)
^a $[\text{PtCl}_6]^{2-} + 6\text{Br}^- \longrightarrow [\text{PtBr}_6]^{2-} + 6\text{Cl}^-$	2.6	-4	22	0.5	52
^a $[\text{PtCl}_6]^{2-} + 6\text{I}^- \longrightarrow [\text{PtI}_6]^{2-} + 6\text{Cl}^- \dots$	24.6	19	19	0.5	93
^b $[\text{ZnCl}_4]^{2-} + 4\text{Br}^- \longrightarrow [\text{ZnBr}_4]^{2-} + 4\text{Cl}^-$	-1.5	1.2	-9	4.5	31
^b $[\text{ZnCl}_4]^{2-} + 4\text{I}^- \longrightarrow [\text{ZnI}_4]^{2-} + 4\text{Cl}^- \dots$	-3	19.5	-75	4.5	55
^c $[\text{CdCl}_4]^{2-} + 4\text{Br}^- \longrightarrow [\text{CdBr}_4]^{2-} + 4\text{Cl}^-$	2.6	2.6	0	4.5	30
^d $[\text{HgBr}_4]^{2-} + 4\text{I}^- \longrightarrow [\text{HgI}_4]^{2-} + 4\text{Br}^-$	9.7	17	-24	0	25
$[\text{HgCl}_4]^{2-} + 4\text{I}^- \longrightarrow [\text{HgI}_4]^{2-} + 4\text{Cl}^- \dots$	—	25 ^e	-30	(corr.) 0.5 ^e	49

^a Poë and Vaidya, ref. 1. ^b Shchukarev, Lilich, and Latysheva, *Zhur. neorg. Khim.*, 1956, **1**, 225 (ΔS_3 for the formation of $[\text{ZnCl}_2]^-$ is taken as +46 cal./deg. mole, *i.e.*, as calculated from $\Delta S_3 = (\Delta H_3 - \Delta G_3)/T$, and not +63.1 cal./deg. mole as quoted in ref. 4). ^c Shchukarev, Lilich, and Latysheva, *Uchenye Zapiski Leningrad Univ. Ser. khim. Nauk*, 1957, No. 15, 211. ^d Williams, *J. Phys. Chem.*, 1954, **58**, 121. ^e Van Eck, ref. 9(b), p. 98. Yatsimirskii and Astasheva, *Zhur. fiz. Khim.*, 1952, **26**, 239 (I variable).

of the hydrated complex ions increase from the chloride to the iodide. In order to estimate how much, if any, of this increase is due to differing bond strengths, and how much is due to the smaller hydration of the larger ion, the relative enthalpies of hydration of the complex ions must be estimated.

The Free Energies, and Enthalpies, of Hydration of the Complex Ions.—The free energies of hydration of large, weakly polarising, ions can be estimated by using the Born equation⁷ which, for water at 25°, is: $\Delta G_{\text{hydr.}} = -162 z^2/r \text{ kcal./g.-ion}$,⁸ where r is the effective radius (in Å) of the ion in solution, and z is its valency. The effective radius is usually taken to be larger than the crystallographic radius by an amount which has been estimated in various ways in an attempt to obtain good agreement with measured values.^{8,9} We have taken r to be equal to the metal-ligand bond length plus the van der Waals radius of the ligand, which gives an upper limit to the free-energy difference in so far as variation with radius is concerned. As an illustration of the procedure, the hexahalogenoplatinates will be considered in detail.

The Pt(IV)–Cl and Pt(IV)–Br bond lengths¹⁰ are both close to the sums of the respective covalent radii, and an estimate of 2.54 Å can therefore be made for the Pt(IV)–I bond length. The radii of the chloro-, bromo-, and iodo-platinates are therefore taken as 4.13, 4.39, and 4.79 Å, respectively, and the hydration free energies of the hexbromo- and hexaiodo-platinate ions are then calculated to be larger (*i.e.*, less negative) than that of the hexachloroplatinate ion by 9 and 22 kcal./g.-ion, respectively.

For hypothetical, simple ions of the same charge and size as these complex ions, the entropy differences caused by differing hydration could be estimated¹¹ from the Born equation, or from empirical relations such as that suggested by Powell and Latimer.¹² Neither of these methods predicts entropy differences of more than a few units whereas

⁵ Benjamin and Gold, *Trans. Faraday Soc.*, 1954, **50**, 797.

⁶ Latimer, "Oxidation Potentials," Prentice-Hall, New York, 2nd edn., 1952.

⁷ Born, *Z. Physik*, 1920, **1**, 45.

⁸ Laidler and Pegis, *Proc. Roy. Soc.*, 1957, *A*, **241**, 80.

⁹ (a) Latimer, Pitzer, and Slansky, *J. Chem. Phys.*, 1939, **7**, 108; (b) Van Eck, "Hydration and Complex Formation of Ions in Solution," Thesis, Leiden University, 1958.

¹⁰ Sutton *et al.*, "Interatomic Distances," *Chem. Soc. Spec. Publ.* No. 11, 1958.

¹¹ Cf., *e.g.*, ref. 8.

¹² Powell and Latimer, *J. Chem. Phys.*, 1951, **19**, 1139.

equilibria studies show that the partial molal entropies of the aqueous bromo- and iodo-platinate ions are larger by 60 and 97 cal./deg. mole, respectively,¹³ than that of the chloro-platinate. (These differences are much larger than the 4 and 10 cal./deg. mole predicted on the basis of Cobble's empirical relation¹³ between the partial molal entropies of complex ions.) Although part of the large entropy differences may be caused by different "structure-breaking" effects of these large, weakly polarising anions,¹⁴ a large part must be due to different intrinsic entropies. Latimer (ref. 6, p. 364) has given a method for calculating intrinsic entropies of complex ions and by using his data the intrinsic entropies of the bromo- and iodo-platinate ions are estimated to exceed that of the chloro-platinate by 17 and 33 cal./deg. mole respectively. The estimated differences in the standard entropies of the aqueous complex ions, obtained by adding the solvation and the intrinsic-entropy estimates, are therefore smaller than the total entropy differences observed, and the use of such estimates in a calculation of the enthalpy changes from equilibrium-constant measurements at a single temperature would have led to large errors. *E.g.*, the complete replacement of chloride, in the chloro-platinate, by bromide would have been predicted to be exothermic by about 9 kcal./mole whereas it is, in fact, slightly endothermic (Table 1). Which of the contributions to the estimated entropy differences is likely to be more in error is not certain, but the non-spherical nature of the ions and the differing charge distributions within them will make hydration-entropy estimates very approximate. The hydration-entropy differences between the bromo- and the iodo-platinate ion and the chloro-platinate ion can therefore be taken as 22 ± 22 and 32 ± 32 cal./deg. mole, respectively, thereby allowing for the errors' arising entirely either from the hydration or from the intrinsic-entropy estimates, the former being more probable.

If the free-energy and the entropy estimates are combined, the hydration enthalpy of the bromo- and iodo-platinates are found to be larger than that of the chloro-platinate by 16 ± 7 and 32 ± 10 kcal./g.-ion, respectively, where the uncertainties are those arising from the entropy estimates. The intrinsic enthalpy of the iodo-platinate is, therefore, about 60 kcal./g.-ion larger than that of the chloro-platinate, and the average strength of the individual Pt-I bond is about 10 kcal./mole *less* than that of the Pt-Cl bond. The Pt-Br bond is calculated, in a similar way, to be about 6 kcal./mole weaker than the Pt-Cl bond. Apart from the effect of relatively small errors in the measured quantities, the uncertainties in the relative bond strengths are made up of uncertainties in the differences between the hydration enthalpies of the free halides and one-sixth of any uncertainty in the differences between the hydration enthalpies of the complex ions. Recent values of the differences for the free halides range from 16 to 24 kcal./g.-ion for the chloride-iodide difference, and from 7 to 11 kcal./g.-ion for the chloride-bromide difference.¹⁵ (The lower values were obtained by combining free energy values, given in ref. 15*a*, with hydration entropy values derived from data in ref. 6.) The estimates of the hydration entropies of the complex ions lead to uncertainties of 1—1.5 kcal./mole in the relative bond strengths, but the uncertainties in the corresponding differences in the hydration free energies are difficult to estimate. However, calculations of the hydration free energies, based on the Born equation, are found to be more reliable than those of the entropies.⁸ This would be expected on general grounds since any errors in the entropies and enthalpies caused by crudities in the model would tend to cancel each other, so that the free energy is less in error. The Born equation estimates only the electrostatic free energy, but the non-electrostatic contribution is small^{8,16} and can be neglected when calculating differences.

The values for the relative bond strengths are therefore only approximate but, even if

¹³ Cobble, *J. Chem. Phys.*, 1953, **21**, 1451.

¹⁴ Frank and Evans, *J. Chem. Phys.*, 1945, **13**, 507.

¹⁵ (a) Randles, *Trans. Faraday Soc.*, 1956, **52**, 1573; (b) Brewer, Bromley, Gilles, and Lofgren, "Chemistry and Metallurgy of Miscellaneous Materials," McGraw-Hill Book Co., New York, 1950.

¹⁶ Latimer, *J. Chem. Phys.*, 1955, **23**, 90.

all the uncertainties were combined in the same sense, the order of bond strengths would not be reversed. Comparison of values for similar systems should be more accurate since the uncertainties in the hydration of the free halides, for example, will have the same effect in each system. Older enthalpy data for the halogenoplatinates⁶ can be used in a similar

TABLE 2. *Relative strengths of the M-Hal bonds in some halogeno-complexes.*

Complex	[PtHal ₄] ²⁻	[ZnHal ₄] ²⁻	[CdHal ₄] ²⁻	[HgHal ₄] ²⁻
Bond-strength difference { M-Cl — M-Br	6	4	4.5	4
{ M-Cl — M-I	10	9	—	7

way. The calculated strengths of the bonds again decrease from chloride to iodide but not quite so sharply.

Similar calculations have been made for the other systems given in Table 1 and the bond-strength differences are shown in Table 2. Values for the bond-lengths were obtained either from ref. 10 or by summing the covalent radii.

Although the zinc and mercury complexes were studied at very different ionic strengths a rough calculation of the relative strengths of the bonds in corresponding complexes can be made by using enthalpy changes for the reaction: $[\text{ZnHal}_4]^{2-} + \text{Hg}^{2+} \longrightarrow [\text{HgHal}_4]^{2-} + \text{Zn}^{2+}$, derived from data in ref. 4. When Hal = Cl, $\Delta H = -15$ kcal./g.-ion and when Hal = I, $\Delta H = -25$ kcal./g.-ion. Since the hydration enthalpy of Zn^{2+} is 44 kcal./g.-ion less⁶ than that of Hg^{2+} the Zn-Cl bond can be shown to be slightly stronger than the Hg-Cl bond and the Zn-I and Hg-I bonds are of about the same strength.

Discussion.—Some of the estimates of relative bond strengths are supported by values of force constants derived from Raman spectra.¹⁷ Those for the symmetrical stretching vibrations in the $[\text{HgHal}_4]^{2-}$ and $[\text{ZnHal}_4]^{2-}$ ions decrease from the chloro- to the iodo-complexes and that for $[\text{CdI}_4]^{2-}$ is less than that for $[\text{CdBr}_4]^{2-}$. The Hg-Cl force constant is less than that for Zn-Cl, and the Hg-I and Zn-I force constants are equal.

The examples considered above include some which involve metals of pronounced class (b) character and provide confirmation of Basolo and Pearson's conclusion¹⁸ (based on dissociation energies of metal halides) that in all halogeno-complexes the bond strengths are in the order M-Cl > M-Br > M-I, irrespective of the order of stability constants.

Ahrland, Chatt, and Davies² have emphasised that any inferences as to class (a) or class (b) character must be made on the basis of heats rather than free energies. If this is applied to the $[\text{ZnHal}_4]^{2-}$ complexes it is found that zinc is a class (b) metal, in contrast to its previous classification.² The relative instability of $[\text{ZnI}_4]^{2-}$ arises because the favourable heat of formation is overcome by an unusually large and unfavourable entropy of formation.⁴ Other cases of such a reversal are apparent from data in ref. 4, e.g., ΔH for the reaction, $[\text{FeCl}]^{2+} + \text{Br}^- \longrightarrow [\text{FeBr}]^{2+} + \text{Cl}^-$, is -2.4 kcal./g.-ion, whereas ΔG is $+1.2$ kcal./g.-ion.

However, for halogeno-complexes, if an estimate of relative bond strengths is to be made from equilibria data, not only must the relative heats of formation be considered but quantitative allowance must also be made for solvation effects, as has been done above. The overall heat of replacement of chloride, in a complex, by iodide is determined by the relative magnitude of the opposing effects of solvation and bond strengths. In aqueous solution the bond-strength effect usually just overcomes the preferential hydration of the smaller halide ion and the chloro-complex is stronger than the iodo-complex, but when the bonding in the iodo-complex becomes relatively less weak, hydration effects become dominant, and the iodo-complex becomes the stronger. The effect of hydration of the complex ions (which favours the smaller chloro-complex) will, of course, be greater the larger the ion charge and for negatively charged halogeno-complexes the lower the oxidation state of the metal the less will solvation favour the iodo-complex. This effect might be

¹⁷ Woodward, *Trans. Faraday Soc.*, 1954, **50**, 1275.

¹⁸ Basolo and Pearson, "Mechanisms of Inorganic Reactions," Wiley and Sons, New York, 1958, pp. 179—180.

large enough to result in different stability orders for $[\text{MHal}_6]^{2-}$ and $[\text{MHal}_6]^{3-}$ and is to be contrasted with the prediction² that lower oxidation states of transition metals will show more class (b) character because of easier back-donation. The point at which the solvation-bond-strength balance changes is clearly solvent-dependent, and the borderline between classes (a) and (b) will only fortuitously be the same when defined by stabilities of halogeno-complexes, as when defined by the stabilities of complexes involving the weakly solvated uncharged ligand molecules which contain elements from groups 5 and 6. However, other things being equal, the greater the class (b) character the less will the difference between the M-I and M-Cl bond strength be, but this does not mean that the *absolute* strengths of the M-Hal bonds are greater—the reverse may well be true. Thus the greater class (b) character of Hg(II) than of Zn(II) arises partly because the Hg-Cl bond is weaker than the Zn-Cl bond while the Hg-I and the Zn-I bond are of the same strength. The much greater stability of the Hg(II) complexes is due to the relatively low heat of hydration of the Hg^{2+} ion. Although the larger size of the Hg^{2+} ion accounts for the weakness of the more ionic bonds in the hydrates, the bonding in the halogeno-complexes is more covalent owing to the larger polarisability of the halides. The covalent bonding is stronger with mercury than with zinc because of the larger ionisation potential for mercury and this just compensates for the weaker ionic bonding.

The increasing relative stability of iodo-complexes with increasing class (b) character has been assumed to be due to increasing covalency, and an increase in the relative strength of the M-I bond, caused either by d_π -bonding involving electron-withdrawal from the metal² or by increasing polarisation involving movement of electrons towards the metal.¹⁹ Thus the stabilities of the $[\text{AgHal}]$ complexes increase much more rapidly from the chloride to the iodide than do those of the $[\text{CdHal}]^+$ complexes, and this has been taken to reflect the greater ease of withdrawing d -electrons from the, formally, singly charged Ag(I) species than from the doubly charged Cd(II).²⁰ However, as was shown above, the larger the charge on the complex ion the more unfavourable to the iodo-complex are the solvation effects. Application of the Born equation suggests that this factor would make the increase in stability from $[\text{CdCl}]^+$ to $[\text{CdI}]^+$ about 4–5 kcal./g.-ion less than that from $[\text{AgCl}]$ to $[\text{AgI}]$. The decrease in bond strength is also likely to be larger for the cadmium than for the silver complexes. This is because, first, the absolute strengths of the Ag-Hal bonds are about one-half of those of the corresponding Cd-Hal bonds. This can be confirmed by a calculation involving tabulated heats of hydration of the metal and halogen ions, estimates of the heats of hydration of the aquo- and complex ions by means of the Born equation, data for the heats of formation of the complex ions,⁴ and the heat of vaporisation of water. In this way the strength of the Ag-Cl bond is found to be about 130 kcal./mole and that of the Cd-Cl bond is about 240 kcal./mole. Since the absolute bond strengths are smaller in the Ag(I) complexes, the (M-Cl)-(M-I) bond-strength differences are also likely to be smaller by a similar factor. This intuitive expectation is supported by preliminary calculations²¹ of relative bond strengths, in which Garrick's treatment,²² based on an ionic model, was used. Comparison with the zinc and the mercury complexes suggests that the difference in strength between the Cd-Cl and Cd-I bonds is about 8–10 kcal./mole and the (Ag-Cl)-(Ag-I) difference will therefore be about 4–5 kcal./mole. The size of the two main factors opposing the replacement of chloride by iodide is therefore 8–10 kcal./mole larger in the cadmium complexes, and the relative values of the stability constants can therefore be satisfactorily explained without the need for postulating different d_π -bonding effects.

Leden and Chatt have shown²³ that the replacement of the water molecule in *trans*- $[\text{C}_2\text{H}_4\text{PtCl}_2, \text{H}_2\text{O}]$ is much easier by iodide than by chloride, and that the Pt(II) is therefore

¹⁹ Williams, *Proc. Chem. Soc.*, 1960, 20.

²⁰ Ahrland, Chatt, Davies, and Williams, *J.*, 1958, 1403.

²¹ Poë, unpublished work.

²² Garrick, *Trans. Faraday Soc.*, 1932, **14**, 914.

²³ Ledén and Chatt, *J.*, 1955, 2936.

acting as a strongly class (*b*) ion. However, it is generally accepted that the bond between the ethylene molecule and the platinum involves a large amount of π -bonding by back-donation of electrons from *d*- or *dp*-hybrid orbitals. This should drastically reduce any tendency to back-donation to atoms in the position *trans* to the ethylene, and the halogeno-complexes should therefore exhibit class (*a*), or weak class (*b*), behaviour if π -bonding is the decisive factor. A similar competition for *d*-electrons by ligands has been used to explain the greater stability of *cis*- than of *trans*-[Pt(PEt₃)₂Cl₂],²⁴ and the *cis*-dihalogeno-complexes of this type should also show class (*a*) character if *d_π*-bonding is important. π -Bonding by back-donation does not, therefore, appear to play a significant part in determining the degree of class (*b*) character of halogeno-complexes.

The alternative explanation, whereby class (*b*) character is caused by the high polarising power of the metal ions associated with high ionisation potentials, can be tested by the calculations²¹ based on the ionic model. These show that the difference in strength between the M-Cl and M-I bonds (*a*) decreases sharply with increase in the metal ion radius, † (*b*) increases with z^* , the effective charge on the metal ion, and (*c*) decreases with a decrease in the (M-Cl)-(M-I) bond-length difference such as would occur when the M-I bond becomes relatively more covalent. Thus, for tetrahedral [MHal₄]²⁻ complexes, an increase in the metal ion radius from 0.8 to 1.2 Å decreases the difference by about 3 kcal./mole. When the metal ion radius is 1 Å, an increase of z^* from 2 to 2.4 increases the difference by about 3.5 kcal./mole and a decrease in the bond-length difference of 0.05 Å decreases the bond-strength difference by about 2.5 kcal./mole. These changes are large enough to account completely for reversals of stability orders. Since covalent halides also show a lessening of the (X-Cl)-(X-I) bond-strength difference as X increases in size²⁵ the contribution of covalency to the bonding is unlikely to modify the position appreciably.

Thus an increase in the effective charge, and polarising power, of the metal ion tends, first, to increase the difference in the bond strengths and therefore to *decrease* the class (*b*) character. This is because of the sharp increase in the absolute strengths of the bonds. This is offset by any narrowing of the bond-length difference which might occur simultaneously, and the calculated resultant of these conflicting effects probably does not have much exact significance although the effects will tend to cancel. Thus it seems likely that, in many halogeno-complexes, the size of the metal ion plays the decisive part in determining the relative bond strengths and thus, indirectly, the stability order, larger ions showing more class (*b*) character than smaller ones. The case of the Tl(I) and Tl(III) halides² is not necessarily in conflict with this conclusion since excitation of the inert pair into an *sp*-hybrid may occur to different extents with different halides. These calculations also suggest that there may be cases in which, although halogeno-complexes are too weak to be formed in aqueous solution, they would—if they were formed—have the class (*b*) stability order.

INORGANIC CHEMISTRY RESEARCH LABORATORIES,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W.7.

[Received, July 29th, 1960.]

† Although differing Hal-Hal repulsion contributes towards this decrease, the main factor is the decrease in the (negative) gradient of the plot of bond strength against bond length as the bond length increases, a factor which operates even when only one ligand is present.

²⁴ Chatt and Wilkins, *J.*, 1952, 273.

²⁵ Cottrell, "The Strengths of Chemical Bonds," Academic Press, New York, 2nd edn., 1958.