Drago's e, c and t parameters for some mono- and bivalent metal ions. Lack of correspondence with Pearson's chemical hardness

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Abstract. Drago's e, c and t parameters for a number of chemically important mono- and bivalent metal ions are estimated from the heterolytic bond dissociation energy data of their binary halides, hydrides and methides. An important result is that, for the cationic acids, the c and t parameters are not two independent variables. Attempts to correlate these parameters or any combination of these with Pearson's chemical hardness have been unsuccessful so far.

Keywords. Drago's e-c-t equation; e, c, t parameters; chemical hardness; bond energy equation.

1. Introduction

In the sixties, in an attempt to partition the enthalpy of the interaction between an acid A and a base B into two components – ionic and covalent – Drago and Wayland (Drago and Wayland 1965; Drago 1973) empirically proposed the equation

$$- \Delta H = E_A E_B + C_A C_B, \tag{1}$$

where the parameters E and C are assumed to indicate the tendency of a species to undergo "electrostatic" and "covalent" interactions respectively. Consequently in (1), the first term is intended to specify the ionic, and the second term the covalent part of ΔH. But this equation fails in a situation where $-\Delta H$ exceeds 30 kcal/mol. Such cases arise when the interacting species are ionic. To tackle the interactions which give rise to large enthalpy changes, Marks and Drago (1976) subsequently put forward, again empirically, the relation

$$[D(A^{n+}, nB^-)]/n = [(d_{A^{n+}} - d_{B^-})^2 + o_{A^{n+}} o_{B^-}]^{1/2}. \tag{2}$$

In (2), $D(A^{n+}, nB^-)$ is the energy required in kcal/mol to dissociate an AB_n molecule into the acid A^{n+} and n number of B^- ions (bases), and, d and o are just two parameters. The significance of d and o is not clear. Later, presumably to have a linear equation and some physical meaning, Drago with Kroeger (Kroeger and Drago 1981) suggested another empirical equation,

$$D(A^+, B^-) = e_{A^+} e_{B^-} + c_{A^-} c_{B^-} + t_{A^+} t_{B^-}, \tag{3}$$

where t is associated with the tendency of electron transfer and the significance of the other two parameters is the same as those of E and C respectively. The numerical

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success of Drago's *e-c-t* equation in various situations is now well-known (Huheey 1983). Still, this equation has not been applied so far to most of the chemically important metal ions. This has been attempted by us now. Our main purpose, however, is to examine the correspondence, if any, between the chemical hardness (Pearson 1963, 1966, 1990, *vide infra*) of an ion and its *e*, *c*, *t* parameters.

To accommodate the cationic acids having valency $n > 1$ in Drago's approach, we rewrite (3) as

$$[D(A^{n+}, nB^-)]/n = e_{A^{n+}} e_{B^-} + c_{A^{n+}} c_{B^-} + t_{A^{n+}} t_{B^-}. \tag{4}$$

To work out (4), the experimental values of $D(A^{n+}, nB^-)$ are required. These are not available as such, except for the polyhalides (Hati and Datta 1994a). For molecules other than the polyhalides, the $D(A^{n+}, nB^-)$ values have been estimated from the corresponding homolytic bond dissociation energies, $D(A, nB)$, by a procedure described in Hati and Datta (1994a) with the knowledge of the appropriate ionisation potentials and electron affinities (Pearson 1988). [The sources of the $D(A, nB)$ data used for this purpose are as follows. (a) Monohalides and hydrides: from CRC (1990-1991) except for the hydrides of Co, Ni, Cu, V and Fe which are taken from Armentrout and Georgiadis (1988), (b) Monomethides: from Armentrout and Georgiadis (1988) except for $HgCH_3$ which is taken from Halpern (1982). (c) Polymethides: from Datta and Pearson (1995) except for those of B and Al which are taken from Wilkinson (1982)]. Using the $D(A^{n+}, nB^-)$ values obtained (supplementary material deposited with the editorial office of this journal), we have evaluated the *e*, *c* and *t* parameters of Group IIB and the first-row-transition metals in $+ 1$ and $+ 2$ oxidation states, the doubly positive alkaline earth metals, and Be^+, Ag^+ and Ti^+ (table 1; B^{3+} and Al^{3+} are included for comparison). The procedure adopted is a self-consistent least squares one where the *e*, *c* and *t* values for F^-, Cl^-, Br^-, I^- and H^- reported by Kroeger and Drago (1981) earlier have been kept unchanged but those of CH_3^- have been refined. Convergence is very slow when CH_3^- is included. For the lack of appropriate data we have not been able to consider metal ions having oxidation states > 2 in our study. With the *e*, *c* and *t* parameters given in table 1, the heterolytic dissociation energies of some 148 bonds considered here are reproduced by (4) very satisfactorily [the average error is only 2·0 ($\pm 2·5$) kcal/mol; details in supplementary material]. The conditional standard deviations of the respective *e*, *c* and *t* parameters, calculated by following the methodology of Kroeger and Drago (1981), are also listed in table 1. It is found that for some 44 cations with charge $+ 1$ to $+ 3$ (see table 1), the *c* and *t* parameters are highly correlated,

$$c = -0·287 + 0·588t, \tag{5}$$

(correlation coefficient $= 0·998$). Consequently, at least for cations, *c* and *t* are not independent variables. This is an important new observation which casts doubts on the proposed significance of these two parameters.

In 1963, Pearson introduced a concept called "hardness' to classify various Lewis acids and bases into three broad categories: hard, soft and borderline (Pearson 1963, 1966, 1990). But the idea of hardness remained qualitative for a very long time. Only in 1983, Pearson together with Parr gave a working formula for the hardness η of a chemical species in terms of its ionisation potential I and electron affinity A as $\eta = (I - A)/2$; the hardness of a chemical species increases as η increases (Parr and Pearson 1983). However, this definition has some problems. It gives the global hardness

Table 1. The e, c and t parameters for some ionic acids and bases[a]

Acid/base	N	e	c	t
H^+	46[b]	8·654(40·114)	8·554(8·495)	15·040(0·552)
Li^+	12[b]	23·066(0·753)	0·968(1·278)	1·715(1·182)
Na^+	9[b]	21·798(0·870)	0·546(0·280)	1·030(4·507)
K^+	13[b]	21·378(2·177)	0·148(0·406)	0·300(0·714)
Be^+	4	35·608(1·094)	1·476(1·635)	2·562(0·479)
Sr^+	6[b]	22·494(0·482)	1·023(0·534)	1·742(1·595)
Ti^+	4	83·713(0·570)	− 8·239(0·719)	− 12·074(0·290)
V^+	4	15·734(0·296)	3·276(0·443)	5·574(0·130)
Cr^+	6	− 0·1(0·8)	4·9(0·6)	8·6(1·8)
Mn^+	5	0·627(0·227)	5·166(0·268)	9·049(0·363)
Fe^+	4	12·2(0·9)	3·0(1·3)	5·4(0·3)
Co^+	6	− 0·5(0·3)	5·7(0·4)	9·9(0·2)
Ni^+	6	3·3(0·9)	5·0(0·8)	8·8(0·8)
Cu^+	7[b]	23·621(23·075)	1·653(0·828)	3·096(0·802)
Zn^+	6	8·3(1·4)	4·4(0·8)	7·7(5·0)
Cd^+	5	8·645(0·674)	3·981(0·735)	6·978(1·070)
Hg^+	5	14·9(1·1)	3·2(1·2)	5·8(0·2)
Ag^+	5	− 5·387(0·613)	5·899(0·667)	10·343(0·973)
Tl^+	5	13·790(0·162)	2·285(0·215)	4·022(0·064)
CH_3^+	18[b]	20·326(12·700)	3·592(5·985)	6·627(0·728)
$C_2H_5^+$	12[b]	26·500(0·172)	1·547(0·096)	3·106(0·252)
$i\text{-}C_3H_7^+$	11[b]	28·080(0·643)	0·744(0·476)	1·697(0·689)
Bi^+	7[b]	25·846(5·920)	0·700(0·622)	1·513(0·412)
Pb^+	6[b]	24·133(0·223)	0·836(0·337)	1·659(0·335)
$C_5H_5Ni^+$	9[b]	1·977(3·201)	2·285(2·335)	3·890(0·117)
Be^{2+}	4	25·874(0·106)	6·216(0·127)	11·062(0·051)
Mg^{2+}	4	14·827(0·117)	5·918(0·147)	10·287(0·590)
Ca^{2+}	4	0·996(0·096)	6·899(0·123)	11·660(0·050)
Sr^{2+}	4	35·184(0·168)	0·622(0·211)	2·104(0·086)
Ti^{2+}	4	28·752(0·026)	2·981(0·033)	6·255(0·013)
V^{2+}	4	25·606(0·054)	3·710(0·069)	7·637(0·028)
Cr^{2+}	4	13·832(0·566)	5·905(0·715)	10·796(0·287)
Mn^{2+}	4	19·928(0·221)	4·702(0·279)	9·091(0·112)
Fe^{2+}	4	9·326(0·339)	6·946(0·427)	12·547(0·173)
Co^{2+}	4	11·944(0·290)	6·680(0·336)	12·185(0·147)
Ni^{2+}	4	5·393(0·352)	8·017(0·445)	14·331(0·180)
Cu^{2+}	4	2·538(0·615)	8·646(0·775)	15·609(0·313)
Zn^{2+}	5	− 10·6(0·7)	10·7(0·7)	18·9(0·2)
Cd^{2+}	5	− 11·1(0·6)	9·9(0·5)	17·7(0·2)
Hg^{2+}	5	12·1[c]	10·7(0·6)	19·3(0·2)
Sn^{2+}	4	20·409(0·243)	4·260(0·307)	8·110(0·124)
Pb^{2+}	4	0·829(0·145)	7·260(0·183)	12·737(0·074)
B^{3+}	5	− 25·8(0·8)	21·3(0·9)	36·6(0·6)
Al^{3+}	5	− 18·2(0·6)	15·8(0·5)	27·1(0·4)
F^-	16[b]	6·154(0·148)	34·768(3·859)	1·108(39·841)

(Continued)

Table 1. *(Continued)*

Acid/ base	N	e	c	t
Cl$^-$	19[b]	5·111(0·317)	2·730(49·435)	17·508(53·371)
Br$^-$	16[b]	4·897(0·189)	4·863(63·044)	15·670(10·132)
I$^-$	16[b]	4·517(0·111)	$-2·502(56·694)$	19·608(15·662)
H$^-$	14[b]	5·334(0·052)	$-267·005$[c]	175·307(5·105)
CH$_3^-$	16	7·3(6·1)	$-37·6(3·4)$	44·5(1·7)

[a]N is the number of bond energy data used to optimise e, c and t parameters· For the meanings of the other symbols, see text· Conditional standard deviations are in parentheses;
[b]from Kroeger and Drago (1981);
[c]this parameter was not allowed to vary

of a chemical species, while in order to understand its reactivity, one actually needs to know its hardness at the binding site(s) which is a local property. Moreover, it is not applicable experimentally to most of the monovalent anions since in these cases the relevant A values are not accessible in practice (Pearson 1988; Hati and Datta 1996a). We have been trying for quite some time to develop suitable measures for the hardness of an ion in a molecule. So far, our approaches have been based on bond energies (Datta and Singh 1991; Datta 1992; Hati and Datta 1994a) and static electric dipole polarisabilities (Hati and Datta 1994b; Hati and Datta 1996b; Hati *et al* 1996). Here we now explore the possibility of using the e, c and t parameters for this purpose.

In 1972, when no quantitative definition of hardness was available, Drago and Pearson independently felt that C/E could be used as a sort of index of hardness; qualitatively hardness has been proposed to decrease as E/C decreases (Drago and Kabler 1972; Pearson 1972; Drago 1973). However, our results have been very disappointing. On seeking a correspondence between e, c, t and hardness, we have found that none of these parameters nor any combination of these [e.g. e/c, $e/(c + t)$ or $e/(c - t)$] can be regarded as even a very rough measure of Pearson's chemical hardness.

Supplementary material: Table 1 containing the known average heterolytic dissociation energies of some 148 bonds and those calculated from (4).

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