1-Iodoacetylenes. Part 2.[1] Formation Constants of their Complexes with Lewis Bases

Christian Laurence,* Michèle Queignec-Cabanetos, and Bruno Wojtkowiak
Laboratoire de Spectrochimie Moléculaire, U.E.R. de Chimie, Université de Nantes, 44072 Nantes, France

Formation constants of the complexes of 1-iodoacetylenes (1)—(8) with Lewis bases (9)—(15) have been measured in solution by i.r. spectrophotometry. The stoicheiometry of the complexes, the influence of the solvent on the equilibrium position, the existence of linear free energy relationships in the series of iodinated Lewis acids RI, where R = I, Br, Cl, C≡N, and C≡CX, and the relation between i.r. frequency shifts and stability constants are discussed. With any electron donor, 1-iodoacetylenes form less stable complexes than those formed by iodine cyanide. With hard bases, iodocyanoacetylene (8) and ethyl iodopropiolate (7) give complexes which are, respectively, more stable than and as stable as those with iodine; however, iodine complexes with soft bases are more stable. This is rationalized, in terms of empirical acidity scales, by the necessity to correlate the thermodynamic and spectroscopic properties of the RI complexes by a double scale equation.

In Part 1,[1] we showed that 1-iodoacetylenes (1)—(8) form electron donor–acceptor complexes with Lewis bases. In order to characterize the reactivity of these new Lewis acids, we report here equilibrium information concerning their complexes with bases (9)—(15) (the choice of these bases was dictated mostly by experimental constraints, however they cover a wide range of strength and of hardness–softness [2]). We also compare their stability to that of other iodinated Lewis acids RI when R = I, Br, Cl, or CN. In this RI series an important finding is that the order of the strength of the acceptor, as measured by the equilibrium constant, does not remain constant as the common donor species is changed. Consequently, in spite of their structural analogy (an iodine atom as the common electron acceptor site) we cannot characterize the RI acids by a single parameter such as the α-parameter in the Taft–Kamlet scale of acidities[3] or the acceptor number of Mayer and Gutmann.[4] This illustrates the limitations of single parameter acidity scales and offers support for double scale equations such as the *E* and *C* model.[5]

IC≡CX

(1) X = Pr^n
(2) X = $SiEt_3$
(3) X = Ph
(4) X = I

(5) X = CH_2Br
(6) X = p-$NO_2C_6H_4$
(7) X = COOEt
(8) X = CN

(9) Me_2NCN
(10) Et_2NCOMe (DEA)
(11) $(Me_2N)_3PO$ (HMPT)
(12) Ph_3PO

(13) Ph_3AsO
(14) 3-MeC_5H_4N
(15) Ph_3PS

Experimental

Materials and Apparatus.—The preparation of 1-iodoacetylenes has already been described.[1] I_2, IBr, ICl, ICN, the bases (9)—(15), and the solvents are commercial products purified by standard procedures.

Spectroscopic measurements were performed on a Beckman IR 12 spectrophotometer or a Beckman Acta III u.v. spectrophotometer. The temperature of the cells is held constant by circulating temperature-regulated water through their holder, a RIIC WJ-1 water jacket for FH-01 KBr i.r. cells (with pathlengths in the range 0.01—0.2 cm) or a Beckman 198157 rectangular cell holder for 1 cm u.v. silica cells. The temperature is measured by a thermocouple located in the cell.

Stock solutions were made up by weight and diluted with Aspin microburettes having 5 ml capacity with graduations every 0.02 ml. Solutions were prepared and the cells were filled in a dry box protected from the light.

Determination of Equilibrium Constants.—Solvents. The equilibrium $A + D \rightleftarrows AD$ where A is the electron acceptor, D the electron donor, and AD the complex was studied in CCl_4 for the DEA, dimethylcyanamide, and 3-picoline complexes, CS_2 for the Ph_3PS complexes, and benzene for the HMPT, Ph_3PO, and Ph_3AsO complexes. This choice of solvents was dictated by their solubility power and their optical transparency. They are apolar in the sense that their dipole moments equal zero but their influence on the equilibrium position may be quite different and will be discussed below.

Solution non-ideality. The high concentrations (sometimes up to 1M) and the high polarity of the components (up to 5.25 D for the donor Ph_3AsO and 3.83 D for the acceptor $IC{\equiv}CC_6H_4NO_2$) do not appear to justify the assumption $\Gamma_c = 1$ in equation (1) which relates thermodynamic K_a (relative to

$$K_a = a_{AD}/a_Aa_D = K_c\gamma_{AD}/\gamma_A\gamma_D = K_c\Gamma_c \qquad (1)$$

activities) and apparent K_c (relative to molarities) equilibrium constants. However, this assumption is difficult to avoid and will be argued below.

Spectrophotometric method. Equilibrium concentrations of A, D, and AD were calculated from absorbance measurements by vibrational and/or electronic spectroscopy when A = I_2, IBr, or ICl and by vibrational spectroscopy when A = ICN or IC≡CX, because ICN and IC≡CX absorb in the medium or far u.v. where the electron donors are generally not transparent. The analytical band corresponds to the visible transition of I_2 and interhalogens or to a vibrator of the electron donor: ν(CO) for DEA, ν(AsO) for Ph_3AsO, ν(PO) for Ph_3PO and HMPT, ν(PS) for Ph_3PS, and ν(6a) for 3-picoline. In some cases the ν(C≡C) vibrator of IC≡CX or the ν(C≡N) vibrator of IC≡CCN was used [in preference to the weak and low ν(CI) band].

Data treatment. Initial concentrations $(A)_0$ and $(D)_0$ and absorbance data were treated by the well known Rose and Drago equation[6] and/or by the Liptay method.[7] These methods avoid the numerical separation of the overlapping bands

Table 1. Equilibrium constants K_c ($dm^3 mol^{-1}$) for complex formation between I_2, ICN, $IC{\equiv}CX$, and bases (9)—(15)

Base	Acid	Solvent	K_c *	t/°C	Analytical band
$Me_2NC{\equiv}N$	$IC{\equiv}CCN$	CCl_4	13 ± 1	22	$\nu(C{\equiv}C)$
Ph_3PS	I_2	CS_2	204 ± 11	20.3	Visible transition
	ICN		31 ± 1.5	21	$\nu(PS)$
	$IC{\equiv}CCN$		13.3 ± 0.7	21	$\nu(PS)$
	$IC{\equiv}CCOOEt$		2.7 ± 0.15	21	$\nu(PS)$
	$IC{\equiv}CI$		2.55 ± 0.15	21	$\nu(PS)$
	$IC{\equiv}CPh$		0.73 ± 0.07	21	$\nu(PS)$
	$IC{\equiv}CPr$		0.45 ± 0.06	21	$\nu(PS)$
3-Picoline	ICN	CCl_4	(70) [a]	27	$\nu(6a)$
	$IC{\equiv}CPh$		1.23 ± 0.05	20	$\nu(6a)$
	$IC{\equiv}CPr$		0.96 ± 0.06	20	$\nu(6a)$
DEA	I_2	CCl_4	7.7 ± 0.6	22	Visible transition
	ICN		140 ± 4	22.2	$\nu(CO)$
	$IC{\equiv}CCN$		50 ± 2.6	22.2	$\nu(CO)$
	$IC{\equiv}CCOOEt$		8 ± 0.8	19.1	$\nu(CO)$
	$IC{\equiv}CPh$		1.6 ± 0.15	22.6	$\nu(CO)$
	$IC{\equiv}CPr$		0.85 ± 0.08	20.3	$\nu(CO)$
Ph_3PO	I_2	C_6H_6	11.8 ± 0.8	21	Visible transition
	ICN		(121) [b]	21	$\nu(PO)$
	$IC{\equiv}CCN$		42 ± 3	21	$\nu(PO)$
	$IC{\equiv}CCOOEt$		10.9 ± 1	21	$\nu(PO)$
	$IC{\equiv}CC_6H_4NO_2$		~7.5	20	$\nu(PO)$
	$IC{\equiv}CI$		9.0 ± 0.4	21	$\nu(PO)$
	$IC{\equiv}CSiEt_3$		2.6 ± 0.3	20	$\nu(PO)$
	$IC{\equiv}CPh$		2.45 ± 0.2	21	$\nu(PO)$
	$IC{\equiv}CPr$		1.55 ± 0.3	21	$\nu(PO)$
HMPT	ICN	C_6H_6	(127) [b]	21	$\nu(PO)$
	$IC{\equiv}CCN$		59 ± 8	22	$\nu(PO)$
	$IC{\equiv}CPh$		6 ± 0.6	21	$\nu(PO)$
	$IC{\equiv}CPr$		4.4 ± 0.3	21	$\nu(PO)$
Ph_3AsO	I_2	C_6H_6	920 ± 60	20.5	Visible transition
	ICN		2 790 ± 520	21	$\nu(AsO)$
	$IC{\equiv}CCN$		1 024 ± 130	21	$\nu(AsO)$
	$IC{\equiv}CCOOEt$		188 ± 17	20.5	$\nu(AsO)$
	$IC{\equiv}CC_6H_4NO_2$		61 ± 7	21	$\nu(AsO)$
	$IC{\equiv}CCH_2Br$		35.5 ± 3	20.5	$\nu(AsO)$
	$IC{\equiv}CI$		98 ± 10	21	$\nu(AsO)$
	$IC{\equiv}CSiEt_3$		12.9 ± 0.9	20	$\nu(AsO)$
	$IC{\equiv}CPh$		14.8 ± 0.5	21	$\nu(AsO)$
	$IC{\equiv}CPr$		5.2 ± 0.3	20.5	$\nu(AsO)$

[a] J. De Leeuw, M. Van Cauteren, and Th. Zeegers-Huyskens, *Spectrosc. Lett.*, 1974, **7**, 607. [b] Calculated from ref. 20.

Table 2. Equilibrium constants K_c (dm^3 mol^{-1}) for complex formation between I_2, IBr, ICl, ICN, $IC{\equiv}CCN$, and various bases in CCl_4 [a,b]

Base	t/°C	I_2	IBr	ICl	$IC{\equiv}CCN$	ICN
DEA	22	7.7 ± 0.8	169 ± 16	1 461 ± 140	50 ± 5	140 ± 14
Ph_3PO	20	(40.3) [c]	(893) [c]	(3 852) [c]	218 ± 19	(525) [c]
Pyridine	25	(101) [d]	(13 000) [e]	(480 000) [e]		72.5 ± 7
$Me_2NC{\equiv}N$	23	(1.82) [f]	(18.8) [f]	(120) [f]	13.3 ± 1	
Ph_3PS	25	(160) [c]	(1 263) [c]		13.3 ± 1	(46.6) [c]
Propiononitrile	20	(0.43) [g]	(2.3) [g]	(0.7) [g]		

[a] In CS_2 at 21° for Ph_3PS-$IC{\equiv}CCN$. [b] Values in parentheses are literature values. [c] Ref. 20. [d] H. D. Bist and W. B. Person, *J. Phys. Chem.*, 1967, **71**, 2750. [e] A. I. Popov and R. H. Rygg, *J. Am. Chem. Soc.*, 1957, **79**, 4622. [f] E. Aughdahl and P. Klaboe, *Acta Chem. Scand.*, 1965, **19**, 807. [g] W. B. Person, W. C. Golton, and A. I. Popov, *J. Am. Chem. Soc.*, 1963, **85**, 891.

* Errors are 95% confidence limits.

of the complex and of the free species. However the addition of large quantities of A (D) to the donor (acceptor) solution changes the dielectric properties of the medium and bands are shifted by a solvent effect. The above methods are, therefore, no longer valid and a computer resolution of the overlapping bands becomes necessary and was performed by the Jones method.[8]

Initial concentrations $(A)_0$ and $(D)_0$ were chosen to obey the Deranleau criteria [9] as far as permitted by experimental constraints (solubilities, transparency, band shifts, molecular extinction coefficients of the analytical band, *etc.*).

Results

Equilibrium constants K_c relative to molarities are given for I_2, ICN, and $IC{\equiv}CX$ complexes in Table 1 where the solvent, the temperature, and the analytical band are specified. Table 2 summarizes some literature values for I_2, IBr, ICl, and ICN

Table 3. A comparison of equilibrium constants (dm^3 mol^{-1}) obtained from different concentration (mol dm^{-3}) ranges of the donor and of the acceptor, by using various analytical bands

Complex		Analytical band		
		ν(XO) (X = P, C, or As)	ν(C≡C)	ν(C≡N)
IC≡CCN–Ph$_3$PO in C$_6$H$_6$	K_c	42 ± 3	40.4 ± 4	43.5 ± 2.5
	$(A)_0$	1—5 × 10^{-2}	1.2 × 10^{-2}	4—6.5 × 10^{-3}
	$(D)_0$	4.5 × 10^{-2}	8—100 × 10^{-3}	4—60 × 10^{-3}
IC≡CCN–DEA in CCl$_4$	K_c	50 ± 2.6	49 ± 4	55 ± 4
	$(A)_0$	5.5—33 × 10^{-3}	9 × 10^{-3}	6 × 10^{-3}
	$(D)_0$	1.5 × 10^{-2}	9—75 × 10^{-3}	6—55 × 10^{-3}
			Visible transition of I$_2$	
I$_2$–Ph$_3$AsO in C$_6$H$_6$	K_c	984 ± 121	920 ± 60	
	$(A)_0$	1.2—6 × 10^{-3}	5.3—6.3 × 10^{-4}	
	$(D)_0$	1.3—6.4 × 10^{-3}	3—38 × 10^{-4}	
I$_2$–Ph$_3$PO in C$_6$H$_6$	K_c	11.5 ± 1.5	11.8 ± 0.8	
	$(A)_0$	2.5 × 10^{-2}	1 × 10^{-3}	
	$(D)_0$	4.5 × 10^{-2}	8—21 × 10^{-3}	
I$_2$–DEA in CCl$_4$	K_c	8 ± 0.8	7.7 ± 0.6	
	$(A)_0$	1—4 × 10^{-2}	8 × 10^{-4}	
	$(D)_0$	0.8—1.5 × 10^{-2}	0.15—0.85	

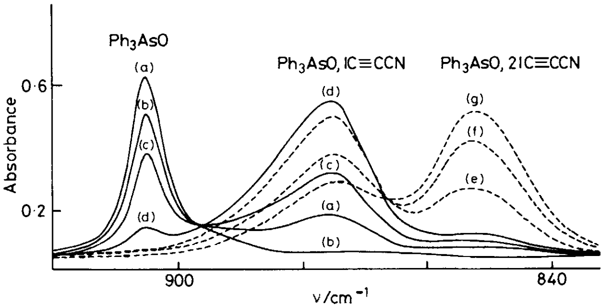

Figure 1. I.r. absorption spectra in the AsO stretching region of Ph$_3$AsO (0.035M) and IC≡CCN in benzene at 21.5 °C; cell thickness 0.027 cm. The concentrations (M) of IC≡CCN are: (a) 0, (b) 0.007, (c) 0.015, (d) 0.037, (e) 0.117, (f) 0.267, and (g) 0.417. A first isosbestic point is observed at 896 cm^{-1} for the equilibrium A + D $\rightleftharpoons$ AD. Then this isosbestic point disappears and a second one appears at 866 cm^{-1} for the equilibrium AD + A $\rightleftharpoons$ A$_2$D

Table 4. Formation constants (dm^3 mol^{-1}) of some RI complexes in CCl$_4$ and in benzene [a]

Solvent	Acceptor	Donor		
		DEA	Ph$_3$PO	Ph$_3$AsO
CCl$_4$	ICN	130 (22)	525 (20) [b]	3 033 (21) [b]
	IC≡CCN	50 (22)	218 (20)	1 308 (21) [b]
	I$_2$	7.7 (22)	40.3 (20) [b]	1 450 (20) [c]
C$_6$H$_6$	ICN	31 (22)	121 (21) [b]	2 790 (21)
	IC≡CCN	12.3 (22)	42 (21)	998 (21.5)
	I$_2$		11.8 (21)	920 (20.5)

[a] This work unless otherwise quoted. Temperature (°C) in parentheses. Errors are in Tables 1 and 2. [b] Calculated from the ΔH and ΔS values of ref. 20. [c] J. Grundnes, P. Klaboe, and E. Plahte, 'Selected Topics in Structural Chemistry,' Universitats Forlaget, Oslo, 1967.

complexes and is completed using the new values found in this study.

In Table 3, the K_c values obtained for the same complex but from various analytical bands are compared. Depending on whether one uses a band of the acceptor or of the donor and depending on the molecular extinction coefficient of the band the $(A)_0$ and $(D)_0$ concentrations vary within a wide range. However, the different numerical values of K_c agree well. In some way this justifies our assumption $K_c \simeq K_a$.

Discussion

Stoicheiometry of the Complexes.—A 1 : 1 stoicheiometry was assumed in order to calculate the K_c values in Tables 1—3. Such an assumption is supported by the existence of an isosbestic point in the spectrum of the mixture of complexed and free species (see Figures 1 and 2 in Part 1 [1]) and the absence of a systematic variation in the ξ_{ik} values of the Liptay absorption matrix.[7]

When large amounts of the 1-iodoacetylenes are added to a solution of Ph$_3$AsO in benzene, A$_2$D complexes are formed from both electron pairs on the oxygen atom.[1] However, with the correct choice of the $(A)_0/(D)_0$ ratio, the equilibrium A + D $\rightleftharpoons$ AD can be observed almost exclusively followed by the equilibrium AD + A $\rightleftharpoons$ A$_2$D. This is illustrated in Figure 1 for the Ph$_3$AsO–IC≡CCN and Ph$_3$AsO–(IC≡CCN)$_2$ complexes. Thus it is easy to calculate for K_c (2 : 1) 3.9 ± 0.3 dm^3 mol^{-1} at 22 °C for this complex, as Grundnes and Dahl [10] did for ICN. With weaker acceptors, such as iodophenylacetylene,' the overlapping of the three ν(AsO) bands corresponding to D, AD, and A$_2$D requires a numerical separation of bands and less straightforward calculations [11] lead to K_c(2 : 1) 0.6 ± 0.2 dm^3 mol^{-1}. As expected, the K_c(2 : 1) order for the (ICN)$_2$–, (IC≡CCN)$_2$–, and (IC≡CPh)$_2$–Ph$_3$AsO complexes is consistent with the K_c(1 : 1) order in Table 1.

AD$_2$ complexes are observed with di-iodoacetylene in the presence of large amounts of electron donors.[1] In Table 1 the equilibrium constants for the Ph$_3$PS–, Ph$_3$PO–, and Ph$_3$AsO–IC≡CI complexes have been calculated under the experimental conditions $(D)_0/(A)_0 \leqslant 1$, for which the absence of the ν_a(CI) band characteristic of AD$_2$ complexes was previously checked. In fact for a much stronger electron donor, triethylamine, the AD$_2$ complex does not appear before reaching a $(D)_0/(A)_0$ ratio $\geqslant 2$.

Solvent Effects on Equilibrium Constants.—As illustrated in Table 4 for the complexes of I$_2$, ICN, and IC≡CCN with Ph$_3$PO, Ph$_3$AsO, and DEA, the equilibrium constants are

Table 5. Apparent formation constant ($dm^3\ mol^{-1}$) for the complex of IC≡CCN with DEA in benzene–CCl_4 mixtures at 22 °C

% v/v C_6H_6	$(S)_0$ [a]	K_{app}
0	0	50 ± 2.6
10	1.12	40.9 ± 2
50	5.61	22.4 ± 2
70	7.86	18.3 ± 2
90	10.10	13.2 ± 1
100	11.22	12.3 ± 1.1

[a] Concentration ($mol\ dm^{-3}$) of benzene in CCl_4.

strongly dependent on the solvent, which varies from CCl_4 to benzene. Two extreme views seek to interpret these solvent effects either purely in terms of non-specific interactions or purely in terms of specific interactions between the complex, or its components, and the solvent.[12,13]

Change in the equilibrium constant by non-specific solvent effects seems well correlated by the Hildebrand solubility parameter δ_S, as shown by Huong *et al.*[14] for the iodine–pyridine complex. This parameter predicts $K_c(CCl_4) > K_c(C_6H_6) > K_c(CS_2)$.

However, a specific interaction between the solvent S and the components A, D, and/or AD (for example $A + S \rightleftharpoons AS$ if S is an electron donor) can compete with the interaction $A + D \rightleftharpoons AD$. One then measures an apparent constant inferior to the true constant. This could be the case for the interaction of CCl_4 with 3-picoline [15] or of CS_2 with I_2 [16] and, most certainly and most importantly, for the interaction of A with benzene, the electron donor ability of which is well documented, in particular towards I_2 [17] and ICN.[18] It seems evident that the lowering of K_c when going from CCl_4 to benzene in Table 4 originates mainly from the interaction of I_2, ICN, and IC≡CCN with the π cloud of benzene.

It can be shown that equation (2) applies where K_{app} is the measured apparent constant, K_c is the constant for the

$$K_{app}^{-1} = K_c^{-1}\,[1 + K_s(S)_0] \qquad (2)$$

equilibrium $A + D \rightleftharpoons AD$, K_s is the constant for the equilibrium $A + S \rightleftharpoons AS$, and $(S)_0$ is the initial concentration of the ' active ' solvent (by contrast with the ' inert ' solvent in which A, D, AD, S, and AS are dissolved). A thorough study of the influence of the interaction of IC≡CCN with benzene on the formation constant of the complex DEA–IC≡CCN has been performed with mixtures of benzene and CCl_4. Table 5 shows that K_{app} decreases regularly when the percentage of benzene in CCl_4 increases from 0 to 100. A plot of K_{app}^{-1} *versus* $(S)_0$ is linear up to $(S)_0$ 8 mol dm^{-3} and gives K_s 0.22 $dm^3\ mol^{-1}$ from the slope. This value for the association constant of IC≡CCN with benzene in CCl_4 at 22 °C is quite consistent with the 0.15 $dm^3\ mol^{-1}$ value found for the interaction of I_2 with benzene in CCl_4 at 25 °C.[17]

This discussion shows that values referring to different solvents in Table 1 cannot be directly compared, unless they are previously corrected for specific interactions by formula such as equation (2) or for non-specific interactions by formula such as $\log K_c = a\delta_s + b$.[14] The following discussion is therefore restricted to a comparison of equilibrium constants for the complexes of RI acids towards a common base in a common solvent.

Linear Free Energy Relationships.—The K_c values of Tables 1 and 2 lead to the following thermodynamic order of acidity. Whatever the reference base, we observed (> = more acidic than): ICN > IC≡CCN > IC≡CCOOEt > IC≡CI * > IC≡$CC_6H_4NO_2$ > IC≡CCH_2Br > IC≡$CSiEt_3$ ~ IC≡CPh > IC≡CPr and ICl > IBr > I_2. Depending on the reference base, the harder the base the more the sub-series I_2, IBr, ICl interpenetrates the sub-series ICN, IC≡CX, leading to the two extreme sequences in Figure 2.

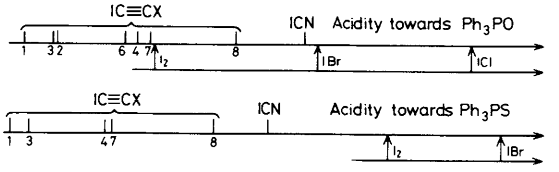

Figure 2. Stability orders of RI complexes with a soft sulphur base (Ph_3PS) and with a hard oxo base (Ph_3PO). Data from Table 1

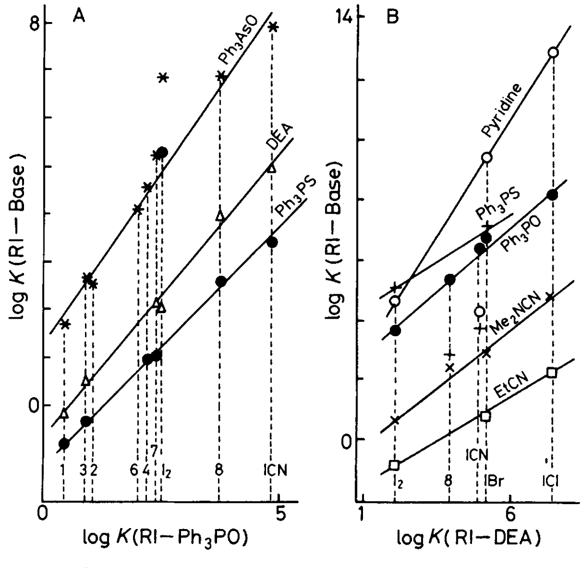

Figure 3. Linear free energy for the complex formation between RI acids and Lewis bases. (A) Data from Table 1. Sub-series ICN and IC≡CX. I_2 is outside the lines. (B) Data from Table 2. Sub-series I_2, IBr, and ICl. ICN and IC≡CCN are outside the lines

In each sub-series the interactions with any base is quantitatively expressed by an l.f.e.r.: the free enthalpy of formation of the complexes of the acids RI with any base B_i, $\Delta G_i(RI\text{-}B_i)$, is linearly related to $\Delta G_0(RI\text{-}B_0)$ for the complexes with a reference base B_0, as illustrated (with log *K* instead Δ*G*) in Figure 3A for IC≡CX and ICN and in Figure 3B for I_2, IBr, and ICl. We see in Figure 3 that the two sub-series obey the same l.f.e.r. only if B_i and B_0 have the same hardness–softness (for example B_i, B_0 = Ph_3PO, DEA). In the opposite case (for example B_i, B_0 = Ph_3PS, Ph_3PO in Figure 3A and pyridine, DEA or Ph_3PS, DEA in Figure 3B), I_2 lies out of the line of the sub-series ICN and IC≡CX in Figure 3A and ICN and IC≡CCN lie out of the I_2, IBr, and ICl line in Figure 3B.

These findings are at variance with the Gutmann equation [4] $\Delta H = DN.AN/100$, where the enthalpy of a donor–acceptor interaction is expressed as the product of a single donor number DN by a single acceptor number AN. Starting from the isoequilibrium relationship (3), found valid for complex formation between I_2, IBr, ICl, ICN, IC≡CX, and bases,[19] where β is the isoequilibrium temperature and ΔH_0 and ΔG_0

$$\Delta G = \frac{\beta - T}{\beta}(\Delta H - \Delta H_0) + \Delta G_0 \qquad (3)$$

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* When K_c is divided by the statistical factor of 2, IC≡CI stands between IC≡$CC_6H_4NO_2$ and IC≡CCH_2Br.

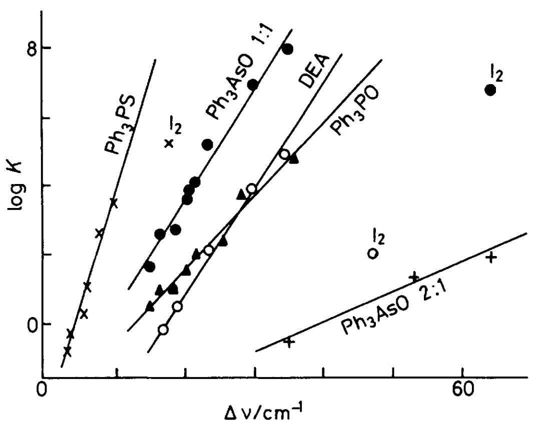

Figure 4. Correlation between log K (from Table 1) and $\Delta\nu$ (from ref. 1)

refer to a reference donor–acceptor complex, we obtain (4) by setting $(\mathrm{DN})' = (\beta - T)\mathrm{DN}/100\beta$ and $W = \Delta G_0 - \Delta H_0(\beta - T)/\beta$ This equation (4) predicts a common l.f.e.r. for all

$$\Delta G = (\mathrm{DN})'.\mathrm{AN} + W \qquad (4)$$

RI acids (that is without separating them into two sub-series) whatever the pair B_0, B_i of bases, which is obviously inconsistent with Figure 3. On the contrary, the E and C equation[5] (5)

$$-\Delta H = E_A E_B + C_A C_B \qquad (5)$$

(where ΔH is the enthalpy of formation of the complex between acid A and base B, A refers to acid and B to base, and E and C are empirical parameters related to the tendency to undergo, respectively, electrostatic and covalent bonding) explains why distinct l.f.e.r.s are observed for the two sub-series of RI acids with some pairs of bases. By combining (3) and (5) we obtain (6) by setting $E'_B = E_B(\beta - T)/\beta$ and $C'_B = C_B(\beta - T)/\beta$ (with $C'_B/E'_B = C_B/E_B$). Simple algebra shows that a series of acids will obey the l.f.e.r. (7) whatever the pair B_0, B_i if

$$-\Delta G = E_A E_B' + C_A C_B' - W \qquad (6)$$

$$\Delta G_i(\mathrm{RI{-}B}_i) = a_i\,\Delta G_0(\mathrm{RI{-}B}_0) + b_i \qquad (7)$$

relation (8) between the parameters E_A and C_A and the parameters E_{A0} and C_{A0} of a reference acid is obeyed. That the

$$(C_A - C_{A0})/(E_A - E_{A0}) = \text{constant} \qquad (8)$$

l.f.e.r. followed by ICN and IC≡CX are distinguishable from the l.f.e.r. followed by I_2, IBr, and ICl is explained by the difference of the ratio (8) for the two sub-series. However, whatever the ratio (8), the two sub-series come together for a given pair B_i, B_0 if $C_{B_i}/E_{B_i} = C_{B_0}/E_{B_0}$. It is evident that such a relationship can be approximately obeyed by two hard (electrostatic) bases, such as Ph_3PO and DEA, and not by a hard base and a soft (covalent) base, such as Ph_3PO and Ph_3PS.*

Frequency Shifts–Free Enthalpy Relationship.—The spectroscopic order of acidity previously found[1] from the shifts induced in the base vibrator upon complex formation is consistent with the thermodynamic order discussed above, provided that one sets apart the two sub-series. Figure 4 illustrates the correlation between log K and $\Delta\nu$ for the ν(CO) (DEA), ν(PO)(Ph_3PO), ν(AsO)(Ph_3AsO), and ν(PS)(Ph_3PS) vibrators in the ICN, IC≡CX sub-series. I_2 stands outside the lines. If ΔH[19] takes the place of log K, for the complex formation between RI and DEA, the same relationship with $\Delta\nu$(CO) and the same distinction between the sub-series is observed in Figure 5.

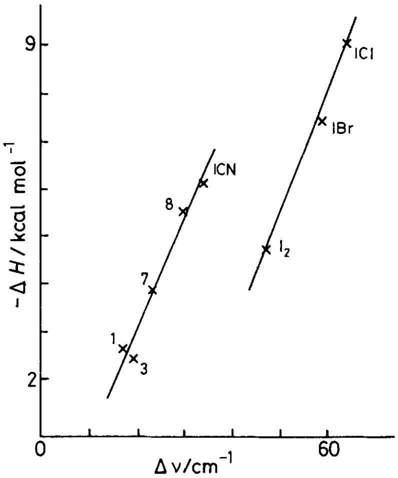

Figure 5. Correlation between ΔH (from ref. 19) and $\Delta\nu$ (from ref. 1) for complex formation between RI acids and DEA in CCl_4

We notice in Figures 4 and 5 that iodine always gives greater frequency shifts than ICN or IC≡CX even if its corresponding equilibrium constants or enthalpies are less. The vibrator ν(CI) of ICN behaves similarly: for example, $\Delta\nu$(CI) is greater with Ph_3PS than with Ph_3PO[1] but ΔH(Ph_3PO–ICN) is greater than ΔH(Ph_3PS–ICN).[20] Most probably the force constant variation induced by complex formation is more sensitive than the formation enthalpy to the covalent part of the interaction, and therefore is greater for the complexes of I_2, a more covalent acid than ICN[21] or IC≡CX,[22] and for the complexes of Ph_3PS, a more covalent base than Ph_3PO.* In other words the C/E ratios of the E and C equation applied to frequency shifts[5] are greater than the C/E ratios of the E and C equation applied to enthalpies, and this is the origin of the inversions.

References

1 Part 1, C. Laurence, M. Queignec-Cabanetos, T. Dziembowska, R. Queignec, and B. Wojtkowiak, *J. Am. Chem. Soc.*, 1981, **103**, 2567.
2 R. G. Pearson, ' Hard and Soft Acids and Bases,' Dowden, Hutchinson and Ross, Stroudsburg, 1973.
3 R. W. Taft and M. J. Kamlet, *J. Am. Chem. Soc.*, 1976, **98**, 2886.
4 V. Gutmann, ' The Donor-Acceptor Approach to Molecular Interactions,' Plenum Press, New York, 1978.
5 R. S. Drago, *Co-ord. Chem. Rev.*, 1980, **33**, 251.
6 N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, 1959, **81**, 6138.
7 W. Liptay, *Elektrochem.*, 1961, **65**, 375.
8 R. N. Jones, N.R.C. Bulletins, 1968—1969, Nos. 11—13.
9 D. A. Deranleau, *J. Am. Chem. Soc.*, 1969, **91**, 4044.
10 J. Grundnes and R. Dahl, *Spectrochim. Acta, Part A*, 1970, **26**, 541.
11 M. Queignec-Cabanetos, Thesis, University of Nantes, 1982.
12 K. M. C. Davis, in ' Molecular Association,' ed. R. Foster, Academic Press, London, 1975, vol. 1, ch. 3.

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* Tentative calculations indicate, as expected, $(C_B/E_B)_{Ph_3PS} \gg (C_B/E_B)_{Ph_3PO}$.

13 S. D. Christian and E. H. Lane, in ' Solutions and Solubilities,' ed. M. R. J. Dack, in ' Techniques of Chemistry,' ed. A. Weissberger, Wiley, New York, 1975, vol. 8, ch. 6.
14 P. V. Huong, N. Platzer, and M. L. Josien, *J. Am. Chem. Soc.*, 1969, **91**, 3669.
15 The interaction of amines with CCl_4 is well known. See, for example K. M. C. Davis and M. F. Farmer, *J. Chem. Soc. B*, 1967, 28.
16 V. Lorenzelli, *C.R. Acad. Sci.*, 1964, **258**, 5386.
17 R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, 1955, **77**, 2164.
18 D. A. Bahnick and W. B. Person, *J. Chem. Phys.*, 1968, **48**, 5637.
19 M. Queignec-Cabanetos and C. Laurence, *J. Chim. Phys.*, in the press.
20 H. P. Sieper and R. Paetzold, *Z. Phys. Chem.* (*Liepzig*), 1974, **255**, 1125.
21 C. Laurence and M. Queignec-Cabanetos, *J. Chem. Soc., Dalton Trans.*, 1981, 2144.
22 R. Queignec and M. Queignec-Cabanetos, *J. Chromatogr.*, 1981‘ **209**, 345.

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