Notes

The Acid Strength of Iodine Cyanide

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Measurements of the enthalpy of complex formation of diethylacetamide, diethyl sulphide, and pyridine with iodine cyanide have enabled us to calculate the E_A and C_A parameters of ICN and draw an acceptor-order plot explaining the sequences: $ICl > I_2 > ICN$ towards soft bases and $ICl > ICN > I_2$ towards hard bases.

IN the course of our investigations of complexes of 1-iodoalkynes, IC≡CR, with Lewis bases,[1] we needed to know the position of iodine cyanide, isoelectronic with IC≡CH, in the scale of the acceptor strength of iodinated Lewis acids. The literature values for thermodynamic parameters of ICN complexes with Lewis bases showed that ICN is stronger than iodine towards oxo-bases [2-6] whereas the reverse has been observed towards pyridines [7] and the sulphur base PPh_3S.[6] This reversal cannot be predicted by the hard–soft acid–base theory [8] since both I_2 and ICN are soft acids in the Pearson classification of acids.[8] We therefore turned to the E and C equation, (1), which has proved successful in explaining reversals

$$-\Delta H_{AB} = E_A E_B + C_A C_B \qquad (1)$$

of acceptor or donor strengths.[9] In this equation, ΔH is the enthalpy of complex formation and the acid A and the base B are each characterised by an E value that measures their ability to participate in electrostatic bonding and a C value that measures their ability to participate in covalent bonding. However we could not apply equation (1) to ICN complexes since no reliable enthalpy values exist to date for bases with known E_B and C_B values. We therefore decided to measure the formation enthalpy of ICN complexes and to calculate the E_A and C_A parameters of ICN in order to rationalize its behaviour in the series of iodinated Lewis acids.

RESULTS AND DISCUSSION

Enthalpy Measurements.—Formation enthalpies of ICN complexes with the three bases Et_2S, pyridine, and *NN*-diethylacetamide (dea) were measured in the poorly solvating solvent CCl_4. They were calculated from the temperature dependence of equilibrium constants obtained from i.r. absorbance measurements on the following vibrations: the ν(CO) band of dea at 1 652 cm^{-1} for the ICN–dea complex, the ν(6a) band of pyridine at 603 cm^{-1} for the ICN–pyridine complex, and the ν(CI) band of ICN at 436 cm^{-1} for the ICN–Et_2S complex. The equilibrium constants were calculated at each temperature by the Liptay method.[10] The results are summarized in Table 1.

Calculation of the E_A *and* C_A *Parameters of* ICN.—The E_B and C_B values of dea,† Et_2S, and pyridine are known [9] and their ratio varies in as wide a range as possible from the hard base dea ($C_B/E_B = 2.95$) to the soft base Et_2S

TABLE 1

Thermodynamic properties for complexes of ICN with dea, pyridine, and Et_2S in CCl_4

Complex	θ_c/°C	K/ $dm^3\ mol^{-1}$	$-\Delta H$/ kcal mol^{-1}
ICN–dea	22.2	140 ± 4	6.1 ± 0.2
	32.2	100 ± 3	
	41.9	71 ± 5	
	51.6	56 ± 5	
ICN–pyridine	21.5	85 ± 10	8 ± 0.3
	37.4	44 ± 6	
	51.2	24 ± 3	
ICN–Et_2S	19.5	13 ± 2	5.85 ± 0.3 *
	35.0	7 ± 0.5	
	48.0	5 ± 0.6	

* Obtained by the enthalpy determination procedure of R. S. Drago, R. L. Carlson, and D. A. Wenz, *J. Am. Chem. Soc.*, 1961, **83**, 3572.

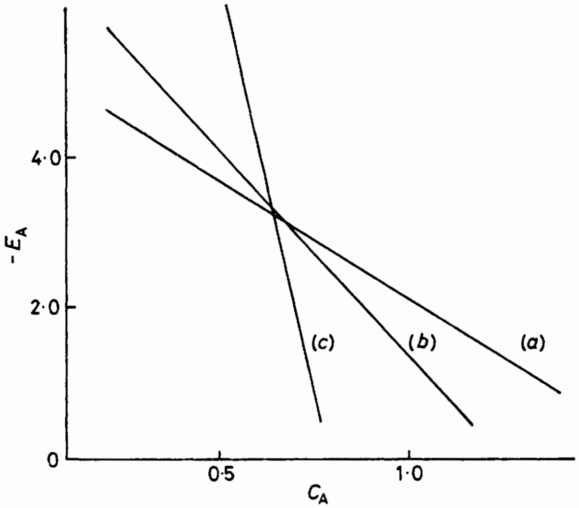

FIGURE 1 Plot of E_A against C_A for ICN with dea (*a*), pyridine (*b*), and Et_2S (*c*)

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† For dea, the values $E_B = 1.16$ and $C_B = 3.61$ were calculated from $\Delta H(I_2) = -4.7$ (unpublished work by the authors) and ΔH(phenol) $= -6.6$ kcal mol^{-1} (D. Neerinck, A. van Audenhaege, and L. Lamberts, *Ann. Chim.* (*Paris*), 1969, **4**, 43).

($C_B/E_B = 21.8$). Hence the slopes of the lines $-E_A = (C_A C_B/E_B) + (\Delta H/E_B)$ differ sufficiently for the three simultaneous equations (1) to be solved graphically in a plot of $-E_A$ against C_A as illustrated in Figure 1. The mean of the three intersections leads to $E_A = 3.27$ and $C_A = 0.65$. Compared to iodine, for which the E_A and C_A parameters were arbitrarily set at 1.00 each, the increase of E_A agrees with the greater dipole moment of ICN ($\mu = 3.76$ D * in benzene) and the decrease of C_A is in line with the electron affinity of ICN, estimated to be *ca.* 0.8 eV less than for iodine.[5]

The Acceptor Order of I_2, ICN, *and* ICl †.—The acceptor strength of these acids can easily be discussed from the acceptor-order plot of Cramer and Bopp[11] where one plots $-\Delta H/(C_B + E_B)$ against $R_B = (C_B - E_B)/(C_B + E_B)$ according to equation (2), a rearrangement of (1).

$$-\Delta H/(C_B + E_B) = (C_A + E_A)/2 + R_B[(C_A - E_A)]/2 \quad (2)$$

In Figure 2, the quantity $-\Delta H/(C_B + E_B)$ on the vertical axis can be viewed as an inherent acceptor strength normalized for the interaction with various bases, while the quantity R_B on the horizontal axis, ranging from +1 ($E_B = 0$) to −1 ($C_B = 0$), indicates the relative importance of the covalent or electrostatic nature of the base.[9] A line has been constructed for each acid in the plot. The crossing of the I_2 and ICN lines means that their acceptor order reverses in passing from covalent bases to electrostatic bases. The intersection occurs near the R_B value of pyridine, a borderline base in the Pearson classification.[8] On the contrary, the ICl line is above and does not cross ICN. Therefore the acid ICl will always be stronger than ICN.

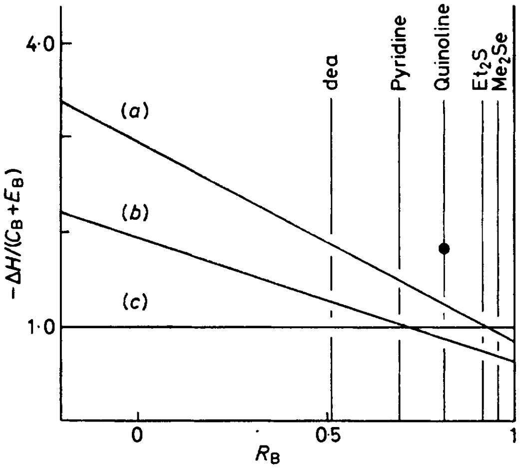

FIGURE 2 The acceptor-order plot of ICl (*a*), ICN (*b*), and I_2 (*c*). The point for the quinoline–ICl complex [$-\Delta H/(E_B + C_B) = 1.82$ and $R_B = 0.81$] lies above the ICl line

The comparison between ICl and I_2 is less straightforward. By drawing the ICl line from $E_A = 5.10$ and $C_A = 0.83$, we see that it crosses the I_2 line near $R_B = 0.93$, a value characterising very soft bases, and we can therefore predict that I_2 must be stronger than ICl towards such soft bases such as Me_2Se. However the recent enthalpy results of Biselx *et al.*[12] for the complexes of quinoline with I_2 and ICl cast doubt on this crossing since quinoline ‡ lies far above the ICl line. Most probably the E_A and C_A values of ICl calculated mainly from hard bases need to be recalculated from borderline (such as quinoline) and soft bases. At the present time we can conclude from experimental data available to date that ICl is a stronger electron acceptor than I_2.

This discussion illustrates the importance of the strength of interaction (the magnitude of the E and C numbers) as the cause for not obtaining a reversal in acceptor order: although ICN and ICl have similar C_A/E_A ratios (0.20 and 0.16), the first reverses with I_2 but not the second because of the magnitude of its E_A and C_A numbers.

EXPERIMENTAL

The compounds carbon tetrachloride, iodine cyanide, pyridine, diethyl sulphide, and *NN*-diethylacetamide were commercial products purified by standard procedures. Infrared spectra were recorded on a Beckman IR 12 spectrophotometer. Cell pathlengths, ranges of donor and acceptor concentrations, and absorbance changes are summarized in Table 2. Solutions were stable during the measurements except for pyridine–iodine cyanide which gradually became yellow so these were prepared (in a dry-box) just before each measurement. The temperature of the solutions was measured with a thermocouple immersed in the cells.

TABLE 2

Experimental conditions for equilibrium constant determinations

Complex	Cell pathlength/ cm	Range of concentrations (mol dm^{-3}) Acceptor	Donor	Absorbance changes
ICN–dea	0.05	3—13 × 10^{-3}	3.5—15 × 10^{-3}	0.05—0.15
	0.1			0.06—0.2
ICN–pyridine	0.06	5—20 × 10^{-2}	0.13—0.3	0.06—0.35
ICN–Et_2S	0.06	4—24 × 10^{-2}	0.2—1	0.12—0.62

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* Throughout this Note: 1 D ≈ 3.336 × 10^{-30} C m; 1 eV ≈ 1.60 × 10^{-19} J; 1 cal = 4.184 J.

† The compound IBr is not included in this discussion because its E_A and C_A values are only tentative.

‡ For quinoline, values of $E_B = 0.78$ and $C_B = 7.52$ are calculated from $\Delta H(I_2) = -8.3$ (ref. 12) and ΔH(phenol) = −6.7 kcal mol^{-1} (D. Neerinck and L. Lamberts, *Bull. Soc. Chim. Belg.*, 1966, **75**, 484).

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