J. Am. Chem. Soc. 1981, 103, 2567-2573

1-Iodoacetylenes. 1. Spectroscopic Evidence of Their Complexes with Lewis Bases. A Spectroscopic Scale of Soft Basicity[1]

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Abstract: $IC\equiv CX$ molecules produce distinct changes in the infrared spectra of Lewis bases. In particular, the vibrations $\nu(XO)$ of oxo compounds, $\nu(PS)$ of triphenylphosphine sulfide, $\nu(6a)$ of 3-picoline, and $\nu(NH)$ of *N*-methylaniline are split. Therefore, like iodine cyanide, $IC\equiv CX$ molecules form, in solution, charge-transfer complexes; their strength, deduced from frequency shifts, increases with the electron-withdrawing ability of the X substituent in the order: $IC\equiv CPr < IC\equiv CSiEt_3 < IC\equiv CPh < IC\equiv CI \sim IC\equiv CCH_2Br < IC\equiv CC_6H_4NO_2 < IC\equiv CCOOEt < IC\equiv CCN < ICN$. The decrease in frequency for the C–I stretching vibration of ICN has been reinvestigated and correlated with the formation enthalpy for iodine complexes. By analogy with the empirical $B_{hard} \equiv \Delta\nu_{OH}$ basicity scale based on the $\Delta\nu_{OH}/\Delta H$ correlation in hydrogen-bonded complexes, we have proposed a $B_{soft} \equiv \Delta\nu_{CI}$ scale from this new $\Delta\nu_{CI}/\Delta H_{I_2}$ correlation. $IC\equiv CI$ is shown to give 1:1 and 2:1 complexes in solution and the correlations between $\Delta\nu_{CI}{}^{1:1}(IC\equiv CI)$, $\Delta\nu_{CI}{}^{2:1}(IC\equiv CI)$, $\Delta\nu_{CI}(ICN)$, and ΔH_{I_2} permit the safe use of $\Delta\nu_{CI}{}^{1:1}(IC\equiv CI)$ as a measure of the strength of interaction of iodoacetylenes with Lewis bases. Contrary to $\Delta\nu_{CI}$, $\Delta\nu_{C\equiv C}$ gives no direct information on this strength.

Iodine (I_2) and interhalogens (IBr and ICl) give, with Lewis bases, electron donor–acceptor (EDA) complexes which have been extensively studied in solution or in the solid state.[3] Iodine cyanide (ICN) also forms EDA complexes,[4] which can be qualitatively explained by the pseudo-halogen character of the cyanide ion. Since 1-iodoacetylene ($IC\equiv CH$) and ICN are isoelectronic, we expect that iodoacetylene and, in a wider sense, substituted iodoacetylenes ($IC\equiv CX$) also act as electron acceptors.

This property of 1-iodoacetylenes has been pointed out several times in the literature. A few solid complexes have been isolated between $PhC\equiv CI$ and aniline[5] and morpholine[6] and between $IC\equiv CI$ and dioxane,[7] diethyl ether,[8] triethylamine, dipropylamine, and piperidine.[9] Some structural studies have been undertaken by infrared and/or X-ray spectroscopy on the $IC\equiv CI$–dioxane,[10] $PhC\equiv CI$–morpholine,[11] and $IC\equiv CI$–cyclohexanedione complexes.[12] X-ray,[13] Raman,[14] and infrared[15] spectroscopy have shown that $IC\equiv CCN$ is self-associated in the solid state by charge transfer between the nitrogen and iodine atoms of neighboring molecules. It was claimed that $IC\equiv CI$–dioxane[10] and $PhC\equiv CI$–morpholine[6] complexes do not exist in solution. This is actually wrong. It can only be said that the complex formation is equilibrated in solution, with a low formation constant, and that the concentration conditions in the preceding studies (ref 6 and 10) were not favorable enough to displace the equilibrium toward the complex formation. Indeed, with a concentration of 1-iodo-1-pentyne which was 50 times greater than that of carbonyl, phosphoryl, or sulfuryl bases, Sellier and Wojtkowiak[16] showed, in our laboratory, the existence of the complexes of 1-iodopentyne with these bases in apolar solvents by infrared spectroscopy, and they confirmed a low equilibrium constant value for the iodopentyne–diethylacetamide complex.[17]

Therefore, we see that the Lewis acid character of 1-iodoacetylenes has never been explicitly studied. In particular, 1-iodoacetylene complexes have never been shown to exist in solution (with the exception of the preliminary work on iodopentyne) nor has their strength been compared with that of other iodinated Lewis acids (I_2, IBr, ICl, ICN, . . .). In this paper we show that substituted 1-iodoacetylenes **1**–**8** form EDA complexes with

		$IC\equiv CX$	
X = *n*-Pr	1	CH_2Br	5
$SiEt_3$	2	*p*-$NO_2C_6H_4$	6
Ph	3	COOEt	7
I	4	CN	8

various Lewis bases in apolar solvents. From the changes in the infrared spectra of electron donors we show that these Lewis acids are weaker than ICN and that inside the $IC\equiv CX$ series the Lewis acidity increases with the electron-withdrawing power of the X substituent. Finally, from the changes in the infrared spectra of electron acceptors we confirm that no general basicity scale exists and we propose a "soft basicity scale" (a scale of basicity toward soft Lewis acids). Subsequent papers will treat the thermodynamic properties for the formation of 1-iodoacetylenes complexes with Lewis bases.

Results and Discussion

Perturbations in the Infrared Spectra of Electron Donors. These are summarized in Table I. When we bring 1-iodoacetylenes **1**–**8** and the bases listed in Table I together in apolar solvents, the intensities of the $\nu(XO)$ bands of oxo compounds, of the $\nu(PS)$

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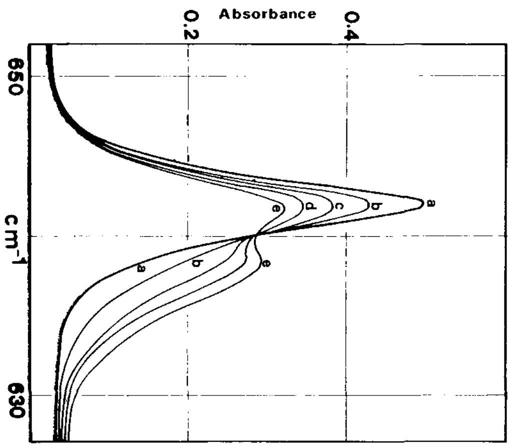

Figure 1. The PS stretching bands of Ph_3PS (0.016 M) and Ph_3PS–ICCPh complex in CS_2 at 21 °C, cell thickness 0.5 mm. The concentrations of ICCPh are (a) 0, (b) 0.233, (c) 0.463, (d) 0.686, and (e) 0.925 M.

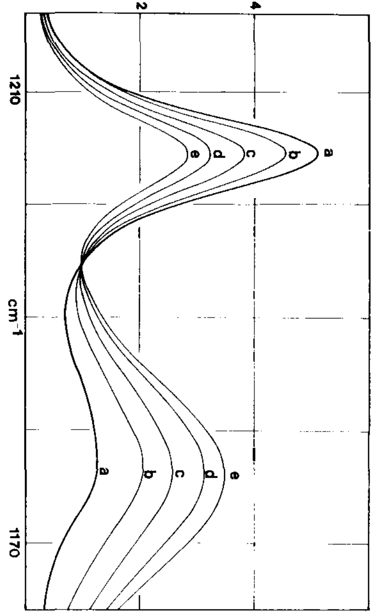

Figure 2. The PO stretching bands of Ph_3PO (0.045 M) and Ph_3PO–ICCCN complex in benzene at 21 °C, cell thickness 0.17 mm. The concentrations of ICCCN are (a) 0, (b) 0.011, (c) 0.022, (d) 0.033, and (e) 0.044 M.

and ν(PSe) bands of triphenylphosphine sulfide and selenide, the ν(6a) band of 3-methylpyridine, and the ν(NH) band of *N*-methylaniline decrease and a new band appears at lower (higher for ν(6a)) frequencies. By analogy with the changes brought about by I_2, IBr, ICl, and/or ICN in the infrared spectra of the same bases,[18] we have assigned this new band to an EDA complex. A study of the concentration and temperature dependences (exemplified in Figures 1 and 2) shows that the complex formation is equilibrated and exothermic. Isosbestic points are always observed with dilute solutions, indicating 1:1 stoichiometry. However, with higher concentrations of 1-iodoacetylenes, a third, more shifted band appears in the ν(AsO) region of triphenylarsine oxide. We have attributed it to a 1:2 EDA complex formed from both lone electron pairs on the donor atoms, as did Grundnes and Dahl[18c] for ICN.

The frequency shifts $\Delta\nu = \nu$(free base) − ν(complex) for the complexes of a reference donor with various Lewis acids were often used to establish a relative order of Lewis acid strength.[19] This attractive procedure was, however, questioned.[20] For the iodinated

Table I. Infrared Frequency Shifts $\Delta\nu = \nu$(free base) − ν(complex) (cm^{-1}) upon Complexation for a Series of Bases and Iodinated Lewis Acids

base	ν free cm^{-1}	solvent	IC≡C-*n*-Pr	IC≡C-$SiEt_3$	IC≡C-Ph	IC≡C-I	IC≡C-CH_2Br	IC≡C-$C_6H_4NO_2$	IC≡C-CO_2Et	IC≡C-CN	ICN	I_2	IBr	ICl
triphenylarsine oxide	ν(ASO) 906	C_6H_6	15	16.5	18.5[c]	20.7	20.3	21.5	23.5[c]	30[c]	35[c]	64	75	76.5
tetramethylene sulfoxide	ν(SO) 1036	CS_2	12	13.7	14	15	15	*b*	17.3	22.4	25.5	37.5	64	70.5
diethylacetamide	ν(CO) 1652	CCl_4	17	18	19	20.5	21	*b*	23.5	29.7	34.5	47	59	64
pyridine *N*-oxide	ν(NO) 1268[a]	CCl_4	15	15.5	16.5	17.5	18	18.4	18	23.5	26	42.5	50.5	53
triphenylphosphine oxide	ν(PO) 1204	C_6H_6	15	16.5	18.5	20.3	*d*	~21.5	25.5	28.5	36	46.5	60	64
triphenylphosphine sulfide	ν(PS) 641.7	CS_2	~3	3.5	3.5	5.4	5	*b*	6	7.5	9.5	17.7	19.5	20
triphenylphosphine selenide	ν(PSe) 566	CS_2			5						8	19.5		
3-methylpyridine	ν(6a) 631	CCl_4	−4.2	−4.5	−5	−5.5	−5.3	*b*	−6.5	−7.5	−10	−11	−15	−17
N-methylaniline	ν(NH) 3435	C_6H_5Cl		50.5		58	59.5	*b*	64.5	76.5	87	100		

[a] The ν(NO) band appears as a doublet in CCl_4 (1275.6, 1265.2), CS_2 (1273.6, 1265.1), and C_6H_6 (1275.5, 1265.3) and as a singlet in MeCN (1252.8). This solvent dependence (ratio of intensities: 0.39, 0.76, 0.13, and 0, respectively) is characteristic of a Fermi resonance. Therefore, the doublet was corrected for Fermi resonance. [b] *p*-Nitrophenyliodoacetylene is not soluble enough. [c] For the 1:2 complex $\Delta\nu$ = 64, 53, 47, and 35 cm^{-1} for ICN, ICCCN, ICCCOOEt, and ICCPh, respectively. [d] A strong absorption of $ICCCH_2Br$ prevents the measurement of ν(PO).

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[18] See, for example: (a) ref 17 (νCO); (b) ref 4c (νPO); (c) J. Grundnes and R. Dahl, *Spectrochim. Acta, Part A*, **26**, 541 (1970) (νAsO); (d) R. Dahl, T. Gramstad, and P. Klaboe, *Acta Chem. Scand.*, **19**, 2248 (1965) (νSO); (e) R. A. Zingaro and R. M. Hedges, *J. Phys. Chem.*, **65**, 1132 (1961) (νPS); (f) J. De Leeuw and Th. Zeegers-Huyskens, *Bull. Soc. Chim. Belg.*, **84**, 861 (1975) (ν6a); (g) T. Kubota, K. Ezumi, M. Yamakawa, and Y. Matsui, *J. Mol. Spectrosc.*, **24**, 378 (1967) (νNO); (h) J. Lauransan and J. Corset, *Ann. Chim.* **4**, 475 (1969) (νNH).

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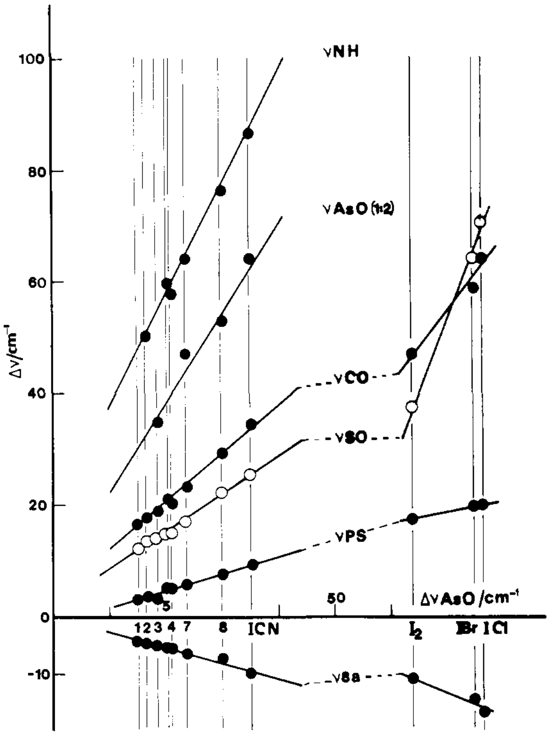

Figure 3. Correlation between the frequency shifts of the ν(NH), ν(AsO), ν(CO), ν(SO), ν(PS), and ν(6a) vibrators for respectively *N*-methylaniline, triphenylarsine oxide, diethylacetamide, tetramethylene sulfoxide, triphenylphosphine sulfide, and 3-methylpyridine, induced by EDA complex formation with added electron acceptors IC≡CX (**1–8**), ICN, I_2, IBr, and ICl.

Lewis acids in this work, we always find the same order of frequency shifts whatever the vibrator considered: ν(CO), ν(PO), ν(SO), ν(NO), ν(AsO), ν(PSe), ν(6a), or ν(NH). This regularity is illustrated in Figure 3 where the frequency shifts for the various vibrators are plotted against the reference frequency shift for the ν(AsO) vibrator. This figure shows moreover that the iodinated Lewis acids series can be divided into two subseries, the first one including I_2, IBr, and ICl and the second one ICN and IC≡CX.

We know from the HSAB principle[21] or from the Drago–Wayland equation[22] that the Lewis acid strength depends on the choice of the reference base. We know also from the mechanics of vibrations that the frequency shift $\Delta\nu$ is not truly proportional, for badly isolated vibrators, to the force constant variation induced by complex formation. Nevertheless, the fact that the same order is observed whatever the softness–hardness character of the donor, varying from the soft selenium and sulfur bases to the hard oxo compounds, and whatever the degree of isolation of the considered vibrator, varying from the pure ν(NH) vibrator to mechanically coupled vibrators, leads us to replace "more shifting than" by "more acidic than" for the symbol < in the sequences: IC≡CPr < IC≡CSiEt$_3$ < IC≡CPh < IC≡CCH$_2$Br ~ IC≡CI < IC≡CC$_6$H$_4$NO$_2$ < IC≡CCOOEt < IC≡CCN < ICN and I_2 < IBr < ICl. This last sequence has been well established for a long time.[3] It has also been well established from thermodynamic measurements that ICN < IBr < ICl.[4f] From the breakdown of the lines between ICN and I_2 in Figure 3 it is not necessarily possible to infer that ICN < I_2 from $\Delta\nu_{\mathrm{ICN}} < \Delta\nu_{\mathrm{I_2}}$.

The first sequence agrees with chemical intuition; the Lewis acid strength increases as the iodine atom becomes more positive due to the electron-attracting properties of the C≡CX (or CN) groups, as shown by dipole moment measurements on iodophenylacetylene and *p*-nitroiodophenylacetylene[23] and by the dual substituent parameter equation[24,25] which is very well obeyed in the IC≡CX series:

$$\Delta\nu(\mathrm{AsO}) = 18.5\sigma_{\mathrm{I}} + 14.2\sigma_{\mathrm{R}} + 17.2 \qquad (1)$$

where the correlation coefficient $R = 0.98$; $n = 8$ points.

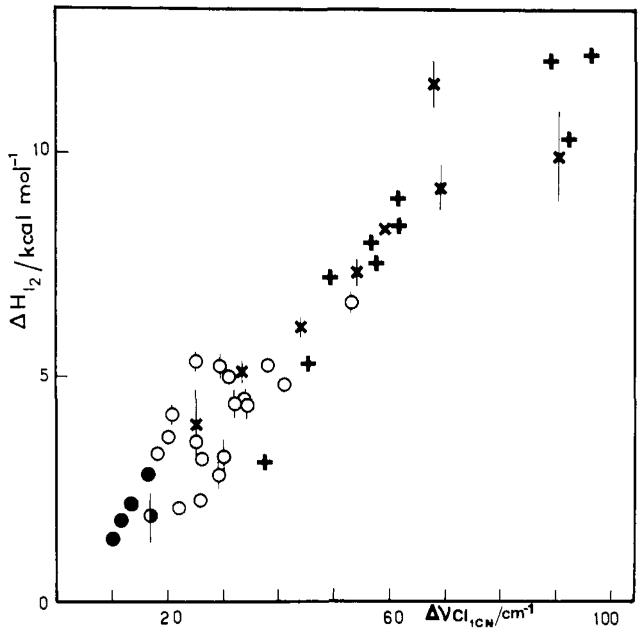

Figure 4. Correlation between formation enthalpy of iodine complexes, and spectral shifts $\Delta\nu_{\mathrm{CI}}$ of iodine cyanogen complexes with various bases: (●) π bases, (○) oxo compounds, (×) sulfur and selenium compounds, (+) nitrogen bases (except acetonitrile, ◑).

Perturbations in the Infrared Spectra of Electron Acceptors. The decrease in the ν(II), ν(IBr), and ν(ICl) frequencies for the XI···D EDA complexes has been studied many times by infrared and Raman spectroscopy.[26] However, the zone of absorption (150–350 cm^{-1}) of iodine and interhalogens is difficult to work in, and difficulties arise from the coupling between ν(IX) and ν(I···D). The frequency shifts $\Delta\nu_{\mathrm{CI}} = \nu$(CI free acid) − ν(CI complex) seem easier to measure for ICN and IC≡CX complexes in the 300–500-cm^{-1} zone, but previous work[4a,d] with ICN has the disadvantage of having dealt with an insufficiently numerous and diverse sample of bases. In particular, no sulfur and selenium bases were studied in spite of their importance in a study of soft iodinated Lewis acids. Moreover no correlation was established between $\Delta\nu_{\mathrm{CI}}$ and the strength of interaction, except for limited correlations between $\Delta\nu_{\mathrm{CI}}$ and the complex formation free enthalpy for sulfoxides,[18d] organophosphoryl compounds,[4c] and pyridines.[27] In this paper, before dealing with IC≡CX molecules, we shall complete previous measurements on ICN.

ICN. Table II shows that the chosen bases vary within a large range of strength (from benzene to trimethylamine) and of softness (from oxo to selenium compounds). Our aim was to show that the spectroscopic shift $\Delta\nu_{\mathrm{CI}}$ could constitute at least a semiquantitative measurement of the strength of ICN complexes with Lewis bases in the same way that $\Delta\nu_{\mathrm{XH}}$ for proton donors was often adopted as a measure of the strength of hydrogen-bonded complexes.[28] Although the validity of the $\Delta\nu_{\mathrm{XH}}$/hydrogen bond

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Table II. Iodine Complex Formation Enthalpies $-\Delta H_{I_2}$ and Iodine Cyanide Carbon–Iodine Stretching Frequency Shifts $\Delta\nu_{CI}$ with Various Lewis Bases

base	$-\Delta H_{I_2}$[a]	ref	$\Delta\nu_{CI}$[b]	base	$-\Delta H_{I_2}$[a]	ref	$\Delta\nu_{CI}$[b]
benzene	1.32 CCl_4	*c*	10	dimethyl disulfide	5.07 CCl_4	*n*	33.5
toluene	1.8 CCl_4	*d*	11.5	tetramethylurea	5.2 Hept	*j*	29.5
acetonitrile	1.9 CCl_4	*e*	17	diethylacetamide	5.25 Hept	*j*	38
$CHCl_2PO(OEt)_2$	2.04 CCl_4	*f*	22	tetrahydrofuran	5.3 Hept	*i*	25
p-xylene	2.18 CCl_4	*c*	13.5	3-chloropyridine	5.32 Hept	*h*	45.5
trimethyl phosphate	2.22 CCl_4	*f*	26	thioanisol	6.1 CCl_4	*o*	44
diphenyl sulfoxide	2.8 CCl_4	*g*	29	triphenylarsine oxide	6.66 CCl_4	*m*	53
mesitylene	2.86 CCl_4	*c*	16.5	quinoline	7.22 Hept	*h*	50
2-chloropyridine	3.08 Hept	*h*	37.5	triphenylphosphine sulfide	7.3 CCl_4	*m*	54
triethyl phosphate	3.14 CCl_4	*f*	26	pyridine	7.47 Hept	*h*	57.5
methyl phenyl sulfoxide	3.2 CCl_4	*g*	30	2-methylpyridine	7.95 Hept	*h*	56.5
dioxane	3.3 CCl_4	*i*	17	diethyl sulfide	8.3 Hept	*p*	59
$CH_2ClPO(OEt)_2$	3.56 CCl_4	*f*	25	3-methylpyridine	8.33 Hept	*h*	61.5
acetone	3.65 Hept	*j*	18	4-methylpyridine	8.93 Hept	*h*	61.5
ethyl isothiocyanate	3.9 Hept	*k*	25	triphenylphosphine selenide	9.21 CCl_4	*q*	68.5
diethyl ether	4.2 Hept	*i*	20.5	tetramethylthiourea	9.9 Hept	*r*	90
dimethyl sulfoxide	4.4 CCl_4	*l*	32	piperidine	10.3 Hept	*s*	91
tetramethylene sulfoxide	4.4 CCl_4	*l*	34	trioctylphosphine sulfide	11.5 Hept	*t*	67.5
triphenylphosphine oxide	4.5 CCl_4	*m*	34	triethylamine	12 Hept	*u*	88
triethylphosphine oxide	4.77 CCl_4	*f*	41	trimethylamine	12.1 Hept	*s*	96
dimethylformamide	5.0 Hept	*j*	30				

[a] In kcal mol^{-1}. Value followed by the solvent used for measurement. [b] In cm^{-1}. $\Delta\nu_{CI} = \nu$(Cl free acid in CCl_4) $- \nu$(CI complex in benzene, CCl_4, or pure base). Values from this work and from ref 4a, 4d, 18d, 4c, and 27. [c] R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, 77, 2164 (1955). [d] J. A. A. Ketalaar, *J. Phys. Radium*, 15, 197 (1954). [e] W. B. Person, W. C. Golton, and A. I. Popov, *J. Am. Chem. Soc.*, 85, 891 (1963). [f] T. Gramstad and S. I. Snaprud, *Acta Chem. Scand.*, 16, 99 (1962). [g] P. Klaboe, *ibid.*, 18, 999 (1964). [h] V. G. Krishna and B. B. Bhowmik, *J. Am. Chem. Soc.*, 90, 1700 (1968). [i] S. M. Brandon, M. Tamres, and S. Searles, *ibid.*, 82, 2129 (1960). [j] C. Laurence, G. Guiheneuf, and B. Wojtkowiak, *ibid.*, 101, 4793 (1979). [k] E. Plahte, J. Grundnes, and P. Klaboe, *Acta Chem. Scand.*, 19, 1897 (1965). [l] R. S. Drago, B. Wayland, and R. L. Carlson, *J. Am. Chem. Soc.*, 85, 3125 (1963). [m] Reference 4f. [n] B. Nelander and I. Noren, *Acta Chem. Scand.*, 26, 809 (1972). [o] R. J. Niedzielski, R. S. Drago, and R. L. Middaugh, *J. Am. Chem. Soc.*, 86, 1694 (1964). [p] M. Tamres and S. Searles, *J. Phys. Chem.*, 66, 1099 (1962). [q] F. Lux, R. Paetzold, J. Danel, and L. Sobczyk, *J. Chem. Soc., Faraday Trans. 2*, 71, 1610 (1975). [r] R. P. Lang, *J. Phys. Chem.*, 72, 2129 (1968). [s] H. Yada, J. Tanaka, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, 33, 1660 (1960). [t] R. P. Lang, *J. Am. Chem. Soc.*, 93, 5047 (1971). [u] S. Nagakura, *ibid.*, 80, 520 (1958).

formation enthalpy relationship is debated,[28] the $\Delta\nu_{XH}$ shifts have given rise to an empirical solvent basicity scale, the so-called *B* scale,[29] successfully applied to multiparametric approaches to solvent effects.[30] However, since the proton donors used to define *B* are hard electron acceptors, the *B* scale is only a "hard basicity scale". Therefore, if $\Delta\nu_{CI}$ could be correlated to the enthalpy of complex formation for ICN, a rather soft electron acceptor, a "soft basicity scale" could be established from spectral shifts $\Delta\nu_{CI}$. Although we are aware that the softness of I_2 and ICN are different, the availability of relevant literature has obliged us to choose ΔH_{I_2} instead of ΔH_{ICN}.

The regression of $-\Delta H_{I_2}$ into $\Delta\nu_{CI}$ was forced to pass through the origin as physically expected and is illustrated in Figure 4. The result (eq 2) is found to be rather good, in spite of the fact

$$-\Delta H_{I_2} = 0.132(\pm 0.003)\Delta\nu_{CI} \qquad (2)$$

$R = 0.95$; $n = 41$; standard deviation of the estimate $s = 0.96$ kcal mol^{-1}

that $\Delta\nu_{CI}$ was measured for slightly different physical states of the complex (pure base or ternary solution in CCl_4 or benzene) that $-\Delta H_{I_2}$ was used instead of ΔH_{ICN} and taken from various publications and measured also in slightly different mediums (CCl_4 or heptane). The success of this spectral shift–enthalpy correlation enables us now to use $\Delta\nu_{CI}$ as a (soft) basicity scale.

The comparison between $\Delta\nu_{CI}$(ICN) $\equiv B_{soft}$ and $\Delta\nu_{OH}$(phenol) $\equiv B_{hard}$ was made for 68 bases collected in Table III and is illustrated in Figure 5. As expected and as shown by the overall correlation coefficient ($R = 0.79$), B_{hard} and B_{soft} do not correlate. On the contrary, the necessity to distinguish oxygen, nitrogen, π, and sulfur bases is clearly apparent from Figure 5 (ortho-substituted pyridines stand outside the cloud of nitrogen bases because of the different steric requirement of hydrogen and iodine). These findings are at variance with a single basicity scale, the *B* scale, or the donor number scale,[31] for all kinds of bases toward all kinds

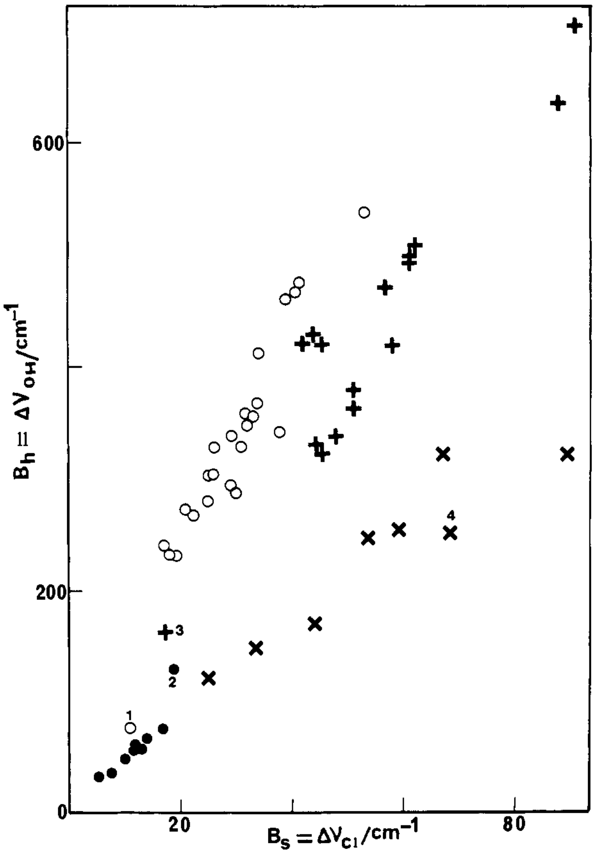

Figure 5. Plot of hard vs. soft basicity scale: (○) oxo compounds (with nitrobenzene, 1), (×) sulfur compounds (with Ph_3PSe, 4), (●) π bases (with 2-heptyne, 2), (+) nitrogen bases (with acetonitrile, 3).

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(29) C. Reichardt, "Solvent Effects in Organic Chemistry", Verlag Chemie, New York, 1979, p 248.

(30) I. A. Koppel and V. A. Palm, "Advances in Linear Free Energy Relationships", N. B. Shapman and J. Shorter, Eds., Plenum Press, London, 1972, p 203.

Table III. Phenol Hydroxyl Frequency Shifts $\Delta\nu_{OH}$ by Hydrogen Bonding and ICN Carbon–Iodine Frequency Shifts $\Delta\nu_{CI}$ by EDA Complexation with Various Bases (cm^{-1})

	$\Delta\nu_{OH}$[a]	$\Delta\nu_{CI}$[b]
CCl_4	0	0
$CHCl_3$	15[c]	1
CH_2Cl_2	29[c]	2
π Bases		
chlorobenzene	33[d]	5.5
bromobenzene	37[d]	7.5
benzene	48	10
anisole	57	12.5
toluene	58[d]	11.5
tert-butylbenzene	60[d]	11.5
p-xylene	66	13.5
o-xylene	68[d]	13.5
m-xylene	69[d]	13.5
mesitylene	76	16.5
2-heptyne	132	18.5
Oxo Compounds		
nitrobenzene	77	11
cyclohexanone	235[e]	19
acetone	236[f]	18
dioxane	242	17
diethyl ether	273[g]	20.5
tetrahydrofuran	283[h]	25
dimethylformamide	289[f]	30
tetramethylurea	340[f]	29.5
diethylacetamide	345[f]	38
$CHCl_2PO(OEt)_2$	270[i]	22
$CH_2ClPO(OEt)_2$	305[i]	25
trimethyl phosphate	305[i]	26
triethyl phosphate	330[i]	26
triphenylphosphine oxide	415[i]	34
trimethylphosphine oxide	464[i]	39
triethylphosphine oxide	468[i]	41
trioctylphosphine oxide	478	41.5
diphenyl sulfoxide	294[j]	29
dibenzyl sulfoxide	330[j]	31
dimethyl sulfoxide	350[j]	32
diethyl sulfoxide	360[j]	33
Me_2NSOMe	360[k]	32
tetramethylene sulfoxide	370[j]	34
triphenylarsine oxide	540	53
Sulfur and Selenium Bases		
ethyl isothiocyanate	123	25
dimethyl disulfide	150	33.5
thioanisol	170[l]	44
triphenylphosphine sulfide	250	54
triphenylphosphine selenide	252	68.5
diethyl sulfide	256[m]	59
tetramethylthiourea	324	90
trioctylphosphine sulfide	326	67.5
Nitrogen Bases		
acetonitrile	166	17
p-chloroaniline	326[n]	45
p-bromoaniline	331[n]	44.5
aniline	341[n]	48
p-toluidine	366[n]	51
p-anisidine	381[n]	51
N,N-dimethylaniline	422[o]	58
2-chloropyridine	338	37.5
3-chloropyridine	425	45.5
3-bromopyridine	425	42
3-iodopyridine	431	44
2,2'-bipyridine	454	40
pyridine	473	57.5
3-methylpyridine	497	61.5
quinoline	498	50
4-picoline	500	61.5
4-ethylpyridine	510	62
2,6-dimethylpyridine	536	51.5
2,4-dimethylpyridine	538	55
2,4,6-trimethylpyridine	546	52
triethylamine	627[p]	88
piperidine	706[o]	91

[a] $\Delta\nu_{OH} = \nu_{OH}$(free phenol in CCl_4) − ν_{OH}(complex in CCl_4). Values from this work unless otherwise quoted. No correction was made for the base concentration dependence of ν_{OH} complex. [b] Same meaning and same origin as in Table II. [c] Pure solvent: J. Lascombe, Thesis, Bordeaux, 1960. [d] E. Osawa, T. Kato, and Z. I. Yoshida, *J. Org. Chem.*, 32, 2803 (1967). [e] L. J. Bellamy and R. J. Pace, *Spectrochim. Acta, Part A*, 27, 705 (1971). [f] C. Laurence, G. Guihéneuf, and B. Wojtkowiak, *J. Am. Chem. Soc.*, 101, 4793 (1979). [g] A. Allerhand and P. v. R. Schleyer, *ibid.*, 85, 371 (1963). [h] T. Gramstad, *Spectrochim. Acta*, 19, 497 (1963). [i] T. Gramstad, *Acta Chem. Scand.*, 15, 1337 (1961). [j] T. Gramstad, *Spectrochim. Acta*, 19, 829 (1963). [k] H. Mollendal, J. Grundnes, and P. Klaboe, *ibid.*, 24, 1669 (1968). [l] Footnote *o* of Table II. [m] G. C. Vogel and R. S. Drago, *J. Am. Chem. Soc.*, 92, 5347 (1970). [n] A. M. Dierckx, P. Huyskens, and Th. Zeegers-Huyskens, *J. Chim. Phys.*, 62, 336 (1965). [o] I. A. Koppel and A. I. Paju, *Org. React.*, 11, 121 (1974). [p] Calculated in this work from correlations between $\Delta\nu_{OH}$ and $\Delta\nu_{OD}$ [H. Fritzche, *Ber. Bunsenges. Phys. Chem.*, 68, 459 (1964)], $\Delta\nu_{OH}$ and $\Delta\nu_{NH}$(pyrrole) [M. S. Nozari and R. S. Drago, *J. Am. Chem. Soc.*, 92, 7086 (1970)], and $\Delta\nu_{OH}$ and $\Delta\nu_{OH}$(trifluoroethanol) [K. F. Purcell and S. T. Wilson, *J. Mol. Spectrosc.*, 24, 468 (1967)].

of acids but agree qualitatively with the HSAB principle[21] and the Drago–Wayland equation.[22]

$IC{\equiv}CI$. The success of the $\Delta H_{I_2}/\Delta\nu_{CI}(ICN)$ correlation prompted us to study the ν(CI) vibration of 1-iodoacetylenes in the same way. The antisymmetric carbon–iodine stretching vibration of diiodoacetylene absorbs weakly ($\epsilon \simeq 30$ L mol^{-1} cm^{-1}) at 721 cm^{-1} in CS_2.[32] When we add about 0.2 mol of base to a 0.05 M CS_2 solution of $IC{\equiv}CI$, a new band appears at lower frequencies which is assigned to ν_{as}(CI) in the 1:1 complex. When new quantities of base are added, a third, more shifted band appears. It is assigned to ν_{as}(CI) in the 2:1 complex $D\cdots IC{\equiv}CI\cdots D$. As for ICN,[4a,d] a strong enhancement of intensity is observed. This is illustrated in Figure 6 for the $IC{\equiv}CI$–triethylamine complex.

Table IV summarizes $\nu_{as}{}^{1:1}$(CI) and $\nu_{as}{}^{2:1}$(CI) for $IC{\equiv}CI$ complexes in CS_2 solution. The frequency shifts due to complex formation, $\Delta\nu_{as}$(CI), range from 4.5 with mesitylene to 31.5 cm^{-1} with triethylamine for the 1.1 complex and extends to 52.5 cm^{-1} for the 2:1 complex. $\Delta\nu_{as}{}^{1:1}{}_{(CI)}$ parallels well $\Delta\nu_{as}{}^{2:1}{}_{(CI)}$ (eq 3) and both parallel $\Delta\nu_{CI}(ICN)$ (eq 4 and 5) and therefore ΔH_{I_2} (eq 6).

$$\Delta\nu_{as}{}^{2:1}{}_{CI} = 1.77(\pm0.03)\Delta\nu_{as}{}^{1:1}{}_{CI} \qquad (3)$$

$$R = 0.98;\ n = 19$$

$$\Delta\nu_{as}{}^{1:1}{}_{CI} = 0.351(\pm\ 0.009)\Delta\nu_{CI}(ICN) \qquad (4)$$

$$R = 0.96;\ n = 26$$

$$\Delta\nu_{as}{}^{2:1}{}_{CI} = 0.62(\pm0.02)\Delta\nu_{CI}(ICN) \qquad (5)$$

$$R = 0.95;\ n = 18$$

$$-\Delta H_{I_2} = 0.31(\pm0.03)\Delta\nu_{as}{}^{1:1}{}_{CI} + 1.7(\pm0.5) \qquad (6)$$

$$R = 0.92;\ n = 20$$

These correlations show that the frequency shift of the antisymmetric carbon–iodine stretching vibration of diiodoacetylene

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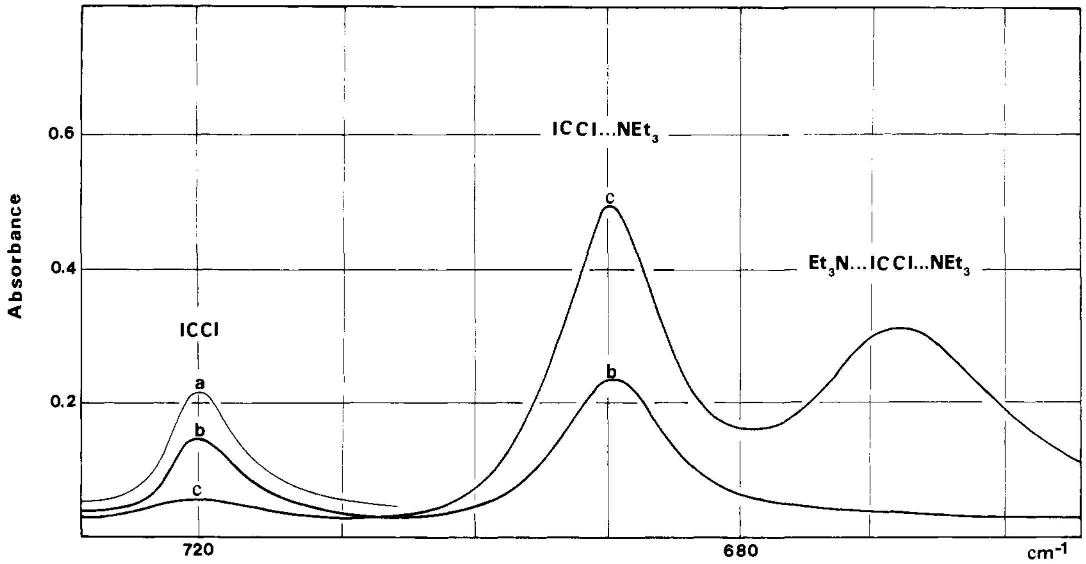

Figure 6. The asymmetric CI stretching vibration of diiodoacetylene (~0.06 M), ICCI–NEt$_3$, and ICCI–2NEt$_3$ in CS$_2$, cell thickness 1 mm. The concentrations of triethylamine are (a) 0, (b) ~0.1, and (c) ~1 M.

Table IV. Frequency Shifts (cm^{-1}) of the ν_{as}(CI) Band for IC≡CI 1:1 and 2:1 Complexes with Various Bases in CS$_2$ Solution

	$\nu_{as}^{1:1}$(CI)	$\Delta\nu_{CI}^{1:1}$	$\nu_{as}^{2:1}$(CI)	$\Delta\nu_{CI}^{2:1}$
(carbon disulfide)	(721)	0	(721)	0
mesitylene	716.5	4.5		
2-heptyne	715	6		
diethyl ether	714.5	6.5	709	12
ethyl isothiocyanate	714.5	6.5		
dioxane	714	7	709	12
acetone	714	7	708.5	12.5
dimethyl disulfide	713.5	7.5	*a*	
cyclohexanone	713	8	*a*	
tetrahydrofuran	712	9	705	16
tetramethylurea	709	12	701.5	19.5
2,2'-bipyridine	709	12	700	21
dimethylformamide	708.5	12.5	700	21
diethylacetamide	708.5	12.5	698	23
triphenylphosphine oxide	706.5	14.5	*a*	
trioctylphosphine oxide	703.5	17.5	691	30
triphenylphosphine sulfide	703.5	17.5	*a*	
2,6-dimethylpyridine	703	18	682.5	38.5
diethyl sulfide	702.5	18.5	691	30
quinoline	700.5	20.5	685.5	35.5
3-methylpyridine	700	21	683.5	37.5
2,4-dimethylpyridine	699	22	682	39
4-methylpyridine	699	22	676	45
trioctylphosphine sulfide	698.5	22.5	680	41
triphenylarsine oxide	698	23	*a*	
tetramethylthiourea	693	28	675	46
triethylamine	689.5	31.5	668.5	52.5

[a] The base absorbs too strongly at the high concentrations necessary to form 2:1 complexes.

Table V. Frequency Shifts (cm^{-1}) of ν(CI), ν(C≡C), ν(C≡N), and δ(CC≡C) Bands for IC≡CCN Complexes with Various Bases

base	$\Delta\nu_{CI}$[a]	$\Delta\nu_{C≡C}$[b]	$\Delta\nu_{C≡N}$[c]	$\Delta\delta_{CC≡C}$[d]
diethyl ether	4.2	5.5	4	−7.2
dimethylcyanamide	6	8.5		−12.2
diethylacetamide	11	11	7.6	−15.2
triphenylphosphine oxide	12	13.5	10.5	−18.2
tetramethylene sulfoxide	13	12	8	−14.7
pyridine *N*-oxide	16	12.5	8	−16.8
triphenylphosphine sulfide	16.5	13	8.3	−7.7
diethyl sulfide	19.5	10	6	−6.7
triphenylarsine oxide	≈21[e]	17.7	12.5	−21
3-methylpyridine	23.8	14.4	8	−16

[a] In benzene; ν(free IC≡CCN) = 355.5 cm^{-1}. [b] In CCl$_4$; ν(free IC≡CCN) = 2120 cm^{-1}. [c] In CCl$_4$; ν(free IC≡CCN) = 2263 cm^{-1}. [d] In benzene; δ(free IC≡CCN) = 300 cm^{-1}. [e] Approximate value due to overlapping of ν(CI) and δ(CC≡C) in the complex.

constitutes a semiquantitative relative measurement of the strength of interaction of IC≡CI with Lewis bases.

A concluding remark comes from the ν_{as}(CI) shift for IC≡CI in 2-heptyne. It is well known that 1-alkynes are self-associated in concentrated solution by hydrogen bonding on the triple bond. Since the 2-heptyne complexes with diiodoacetylene, we expect 1-iodoacetylenes to be self-associated in the liquid or solid states by charge transfer from iodine of one molecule to the triple bond of another molecule (when no other more basic site than the triple bond is available).

IC≡CCN. A more detailed study of the perturbation of the vibrational spectra of 1-iodoacetylenes by complex formation has been performed on the linear molecule IC≡CCN. The results are reported in Table V and illustrated in Figure 7 for the Ph$_3$PO–IC≡CCN complex. The weak ν(CI) band ($\epsilon \simeq 4$ L mol^{-1} cm^{-1}) at 356 cm^{-1} in benzene[14,15] is shifted toward low wavenumbers and made more intense ($\epsilon \simeq 8$) by complex formation. The stronger the electron donor, the greater the frequency shifts are. They are well correlated with $\Delta\nu_{CI}$(ICN) (both in benzene, eq 7). Other stretching vibrations are also shifted to low wavenumbers and deformation vibrations to high wavenumbers (Figure 7, Table V) by complex formation, but the shifts are not correlated to the strength of the complex; for example, the correlation coefficient between $\Delta\nu_{C≡C}$ and $\Delta\nu_{CI}$ is only 0.78 ($n = 10$). On the other hand, the nitrile triple bond shift is correlated to the acetylenic triple bond shift (eq 8). Finally, we note that $\Delta\nu_{CN}$ is of the same order of magnitude in ICN and IC≡CCN complexes.

$$\Delta\nu_{CI}(\text{IC}{\equiv}\text{CCN}) = 0.43(\pm 0.02)\Delta\nu_{CI}(\text{ICN}) \qquad (7)$$

$$R = 0.96;\ n = 7$$

$$\Delta\nu_{C{\equiv}C}(\text{IC}{\equiv}\text{CCN}) = 1.49(\pm 0.05)\Delta\nu_{C{\equiv}N} \qquad (8)$$

$$R = 0.93;\ n = 9$$

Experimental Section

Materials. Solvents and electron donors are commercial products purified by standard procedures. The 1-iodoacetylenes are prepared by iodination of the respective acetylenes using two different methods. In the first one, the 1-alkynes are treated with a potassium iodide/iodine solution under alkaline conditions as described for iodocyanoacetylene by Kloster-Jensen[33] (diiodoacetylene was prepared according to Biltz and

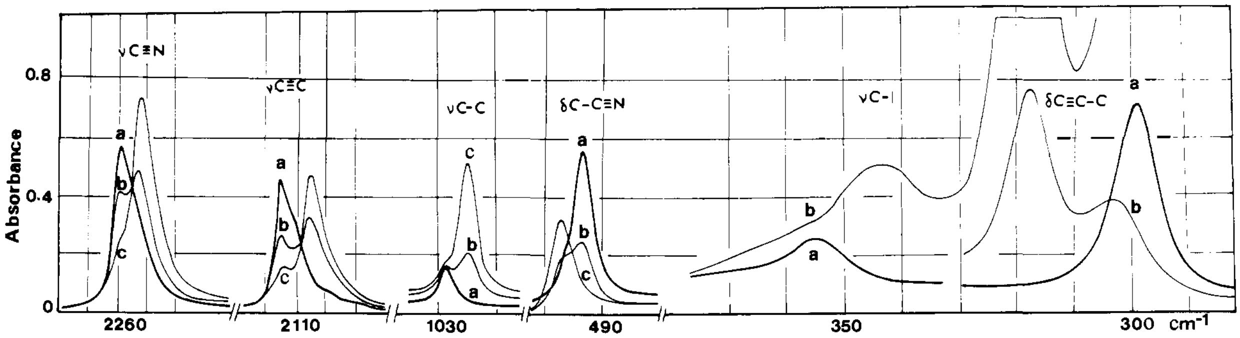

Figure 7. Frequency shifts in the vibrational spectrum of iodocyanoacetylene induced by complex formation with triphenylphosphine oxide (with Et_2S for ν(C–C)) in benzene (in CS_2 for ν(C–C)). Cell thickness and concentrations: ν(CN) 1.5 mm, IC≡CCN 0.006 M, Ph_3PO (a) 0, (b) 0.011, (c) 0.036 M; ν(C≡C) 6 mm, IC≡CCN 0.012 M, Ph_3PO (a) 0, (b) 0.02, (c) 0.06 M; ν(C-C) 1 mm, IC≡CCN 0.11 M, Et_2S (a) 0, (b) 0.2, (c) 1 M; δ(CCN) 0.5 mm, IC≡CCN 0.15 M, Ph_3PO (a) 0, (b) 0.04, (c) 0.27 M; ν(CI) 1 mm, IC≡CCN 0.4 M, Ph_3PO (a) 0, (b) 0.36 M; and δ(C≡CC) 1 mm, IC≡CCN 0.13 M, Ph_3PO (a) 0, (b) 0.14 M.

Küppers).[34] In the second method, the 1-alkynes react with mercury acetate and iodine as described for iodotrimethylethinylsilane by Shostakovskii et al.[35] The second method can be carried out on a larger scale with better yields and was generally preferred. 1-Iodoacetylenes are purified by vacuum distillation on a spinning-band column for IC≡CPr (bp 53 °C (22 mm)), IC≡CPh (bp, 90–91 °C (2 mm)), $IC{\equiv}CCH_2Br$ (bp 62–63 °C (3–5 mm)), and $IC{\equiv}CSiEt_3$ (bp 60 °C (2 mm)) or by recrystallization in cyclohexane for $IC{\equiv}CC_6H_4NO_2$ (mp 182 °C), IC≡CCN (mp 152 °C), IC≡CCOOEt (mp 74.5 °C) or in pentane for IC≡CI (mp 78 °C). When purified and if not immediately used they are protected from light and stored in the cold. Most of the starting 1-alkynes are commercial products with the exception of triethylethinylsilane prepared from HC≡CMgBr and Et_3SiBr as described by Shchukovskaya and Petrov,[36] cyanoacetylene prepared from propiolic acid as described by Miller and Lemmon,[37] and *p*-nitrophenylacetylene prepared from *trans*-*p*-nitrocinnamic acid by the method of Cristol et al.[38]

Infrared spectra were recorded on a Beckman IR12 spectrophotometer with KBr cells in the 4000–400-cm⁻¹ region and CsI cells in the 250–400-cm⁻¹ region. Overlapping free and complex bands were mathematically separated using the program of Jones et al.[39]

Solutions were prepared and the cells were filled in a dry box. They were carefully protected from light. Reactions occur between 1-iodoacetylenes and some bases, for example, between *N*-methylaniline and IC≡CCN or IC≡CPh or between Ph_3PSe and IC≡CPh, but the reaction is slow enough so that spectra could be recorded. Some difficulties were also encountered with the complex solubility in apolar solvents.

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The Role of Collision Complexes in the Reaction of Silyl Ions with Ethylene[1]

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Abstract: The reaction of SiH_3^+ ions with C_2H_4 was studied at laboratory energies in the range of 2.5–4.7 eV and pressures of 0.25–5 mtorr, using a tandem mass spectrometric technique. In agreement with earlier work, it was found that long-lived collision complexes play a major role in the reaction. However, at the reactant-ion energies and target gas pressures studied, the traditional mechanism of collisional stabilization plays no role; the route to detectable (i.e., long-lived) complexes involves a moderation of the kinetic energy of the reactant ions via complex formation and dissociation back to reactants.

Persistent collision complexes have long been cited as intermediates in chemical reactions and in recent years have received considerable emphasis in studies of ion–molecule reactions. Indirect evidence from beam studies in the form of velocity and angular distributions of product ion intensities[2-11] is strongly supportive of the existence of long-lived collision complexes. However, by far the strongest demonstration for the existence of a persistent collision complex is the actual registration at the detector of the 1:1 adduct of reactants under conditions such that

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