511. *The Ethynyl–Hydrogen Bond. Part I. Association in Ether Solution.*

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Hydrogen-bonded complexes of ethynyl compounds with ether have been studied spectrometrically. Association displaces the ν(CH) and δ(CH) fundamentals of the ethynyl group substantially to lower and higher frequency, respectively. Spectrometric association constants are determined for benzoylacetylene [$K_N(29°) = 2{\cdot}0$] and phenylacetylene [$K_N(29°) = 1{\cdot}1$] in diethyl ether. The heat and entropy of association for phenylacetylene–ether are evaluated from the spectrometric equilibrium constant and existing thermodynamic measurements.[1]

The ethynyl group by virtue of its acidity is expected to form relatively strong hydrogen bonds. This property, first inferred from solubility and thermal measurements,[1,2] was confirmed by early infrared observations of the shift of ν(CH) absorption in solvents of increasing basicity. Much more recently the relative frequency displacement, $\Delta\nu/\nu$, for the ν(CH) band of phenylacetylene in basic solvents has been correlated successfully with (i) its solubility [3] and (ii) the frequency displacements of hydrogen chloride in the same media.[4] As the existing spectral data [3-6] were obtained under low resolutions it seemed worth while to compare the spectra of a series of ethynyl compounds in basic and non-basic solvents at the resolving power obtainable with a grating spectrometer. Association is expected to change the frequency and shape of the two hydrogenic fundamentals, ν(CH) and δ(CH), of the ethynyl group. Such changes, for ether solutions, are described in this paper, and physical evidence is obtained in favour of a hydrogen bond. Studies in other basic solvents will be reported later. The purely spectral evidence is supported by evidence from gas–liquid chromatography, cited in the Experimental section.

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[1] Copley and Holley, *J. Amer. Chem. Soc.*, 1939, **61**, 1599.

[2] Hildebrand and Scott, " Solubility of Non-Electrolytes," Reinhold, New York, 1950, Chap. XV.

[3] Murahashi, Ryntani, and Hatada, *Bull. Chem. Soc. Japan*, 1959, **32**, 1001.

[4] Cook, *J. Amer. Chem. Soc.*, 1958, **80**, 49.

[5] Stanford and Gordy, *J. Amer. Chem. Soc.*, 1941, **63**, 1094.

[6] Shigorin, Shemyakin, and Kolosov, *Isvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1958, 1133.

EXPERIMENTAL

Materials.—The compounds 13—15, 4 and 11, and 12 (see Tables 1—3) were kindly supplied by Mr. A. Baker, Dr. M. C. Whiting, and Mr. P. A. I. Finan respectively. Compounds 1, 2, 8, and 10 were prepared by Dr. M. Krishnamurti by the respective procedures in the literature,[7–10] while nos. 3, 5, 6, 7, and 9 were purified commercial materials. Physical constants were in accord with those given in the literature.

Solvents.—n-Hexane (spectroscopic grade), ether (sodium-dried), and carbon disulphide (" AnalaR ") were used without further purification.

Infrared Measurements.—Spectra were recorded with a Unicam S.P. 100 double-beam spectrophotometer. In the 3300 and 650 cm.$^{-1}$ regions the instrument was operated as a prism-grating spectrophotometer in which the sodium chloride prism was ganged with a 3000 or 1500 line/in. grating respectively. Below 700 cm.$^{-1}$ the instrument was also operated as a potassium bromide prism monochromator. Theoretical slit widths were about 4 cm.$^{-1}$ in each instance. [The observed half-width of an NH_3 vapour line at 3290 cm.$^{-1}$ was 4·0 cm.$^{-1}$, whilst that of the CO_2 line at 667 cm.$^{-1}$ (KBr monochromator) was 4·2 cm.$^{-1}$.] Solutions were studied in 0·05—5 mm. cells at 29° ± 2°. When the solute contained an oxygen function, concentrations were chosen so that self-association was negligible.

The frequency calibration was checked before or after measurements, the precision averaging ±1 cm.$^{-1}$. Peak intensities are given as apparent extinction coefficients ε_a (l. mole^{-1} cm.$^{-1}$), rounded to the nearest 5 units. Band areas B (l. mole^{-1} cm.$^{-2}$) = $(1/cl)\int \ln (I_0/I)\,.\,d\nu$ were found by graphical integration.

Gas–Liquid Chromatography.—Gas–liquid chromatography and solubility [1–3] give similar evidence for hydrogen bonding. The retention time of an ethynyl compound is much increased when hydrogen bonds can be formed with the stationary phase. For example, on Apiezon L (non-basic) at 94° oct-1-ene, oct-1-yne, n-octane, and oct-4-yne are eluted in that order, whereas on " Carbowax 600," which contains $\cdot[CH_2\cdot CH_2\cdot O]_x\cdot$ chains, the order of elution at 20° was n-octane, oct-1-ene, oct-4-yne, and oct-1-yne. The reversal of position for oct-4-yne and oct-1-yne is evidently connected with the ability of the latter to form hydrogen bonds. The data below, kindly supplied by Dr. M. M. Wirth of British Hydrocarbon Chemicals, Grangemouth, are retention volumes, relative to n-pentane, of three ethynyl compounds on different stationary phases. Stronger retention on the oxygen-containing phases " Carbitol " (diethylene glycol monoethyl ether) and tritolyl phosphate is clearly seen: moreover, the implication that 2-methylbut-1-en-3-yne (5, Table 1) forms stronger bonds than but-1-yne is also in line with evidence from the infrared studies.

	B. p.	n-Hexadecane (non-basic) 20° ± 2°	" Carbitol " (basic) 0°	Tritolyl phosphate (basic) 20° ± 2°
But-1-yne	8·6°	0·424	2·43	1·24
Diacetylene	10·3	0·173	>20	6·6
2-Methylbut-1-en-3-yne	35	0·56	10·5	3·68
n-Pentane	36·1	1·0	1·0	1·0

Results

3300 *cm.*$^{-1}$ *Region.*—Spectra were recorded in the liquid (or solid) state and in dilute solution in ether and n-hexane, the last being accepted as the reference spectrum of the unassociated compound. The liquid spectra gave evidence of self-association in all examples studied (Table 2): thus the ν(CH) absorption of ethyl propiolate (12) shifts and broadens considerably as compared with the hexane spectrum, and this is supported by the observed shift in ν(CO). For oct-1-yne (1) the small shift and appreciable broadening probably mark a weak interaction of the ethynyl group with the triple bond of another molecule. A feature of the spectra of benzoylacetylene (11) and *p*-nitrophenylacetylene (10), which were taken in the *solid* state, is that the bands are narrower, for a greater shift, than those of substances reported in the liquid

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[7] Pomeranz, Fookson, Mears, Rothberg, and Howard, *J. Res. Nat. Bur. Stand.*, 1954, **52**, 51

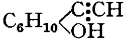
[8] Eglinton and Galbraith, *J.*, 1959, 889.

[9] Manchot, Withers, and Oltrogge, *Annalen*, 1912, **387**, 283.

[10] Cristol and Norris, *J. Amer. Chem. Soc.*, 1954, **76**, 3005.

state. This may indicate that there is a correlation between band width and the mutual orientation of associating molecules, for orientation is expected to be more restricted in the crystal lattice than in the liquid phase.

TABLE 1. 3300 *cm.*$^{-1}$ *region* ν(CH).

		n-Hexane solution			Ether solution						Fraction
					Free		Associated				associated
No.	Compound	ν	(ε$_a$)	Δν$_{½}$ [a]	ν	(ε$_a$)	ν	(ε$_a$)	Δν$_{½}$ [a]	10^{2}Δν/ν [b]	in ether
1	$CH_3{\cdot}[CH_2]_5{\cdot}C{\vdots}CH$	3319	(180)	6·5	3317	(50)	3267	(35)	36	$1{\cdot}5_0$	0·3
2	$HC{\vdots}C{\cdot}[CH_2]_{10}{\cdot}C{\vdots}CH$	3319	(200) [a]	6·5	3317	(65) [a]	3267	(45) [a]	*e*	$1{\cdot}5_1$	0·3
3	 $C_6H_{10}\langle{}^{C{\vdots}CH}_{OH}$	3315	(230)	7·5	3313	(<80)	3257	(60)	*e*	$1{\cdot}6_9$	—
4	$\Delta^1\text{-}C_6H_9{\cdot}C{\vdots}CH$	3319	(130)	6·5	3317	(70)	3260	(55)	*e*	$1{\cdot}7_2$	—
5	$CH_2{:}CHMe{\cdot}C{\vdots}CH$	3313	(125)	18	3314	(50)	3253	(65)	*e*	$1{\cdot}8_6$	0·6
6	$Br{\cdot}CH_2{\cdot}C{\vdots}CH$	3316	(175)	11	3315	(45)	3250	(60)	*e*	$1{\cdot}9_6$	0·6
7	$Cl{\cdot}CH_2{\cdot}C{\vdots}CH$	3318	(115)	8·5	3317	(46)	3250	(65)	*e*	$2{\cdot}1_1$	0·6
8	*p*-$MeO{\cdot}C_6H_4{\cdot}C{\vdots}CH$	3323	(175)	9·5	3322	(65)	3252	(65)	*e*	2·1	—
9	$Ph{\cdot}C{\vdots}CH$	3323	(125)	22	3320	(55)	3250	(75)	*e*	2·1	0·6 ($0{\cdot}5_5$ [c])
10	*p*-$NO_2{\cdot}C_6H_4{\cdot}C{\vdots}CH$	3319	*d*	9	3316	(40)	3232	(85)	56	$2{\cdot}5_3$	—
11	$Ph{\cdot}CO{\cdot}C{\vdots}CH$	3306	(250)	9	3304	(30)	3219	(70)	70	$2{\cdot}5_7$	0·7 ($0{\cdot}6_7$ [c])
12	$EtO_2C{\cdot}C{\vdots}CH$	3310	(160)	7·5	3309	(25)	3220	(75)	69	$2{\cdot}6_8$	0·7

[a] ε$_a$/2. [b] $\Delta\nu = \nu_{\text{hexane}} - \nu_{\text{ether}}$. [c] From eqn. (2). [d] Sparingly soluble. [e] Width (approx. 40—50 cm.$^{-1}$) cannot be given accurately owing to fusion with " free " ν(CH) peak. [f] Includes some absorption from bonded -OH.

TABLE 2. *Spectral changes in liquid and solid state.*

		ν(CH) in hexane		ν(CH) in liquid state		
No.	Compound	cm.$^{-1}$	Δν$_{½}$ [a]	cm.$^{-1}$	Δν$_{½}$ [a]	Association
1	$CH_3{\cdot}[CH_2]_5{\cdot}C{\vdots}CH$	3319	6·5	3316	28	Weak self-association
13	$EtO{\cdot}C{\vdots}CH$	3339	12	3315	43	$\vdots C\text{–}H\cdots O<$
14 *	$Tp{\cdot}O{\cdot}CH_2{\cdot}C{\vdots}CH$	3319	6	3293	60	$\vdots C\text{–}H\cdots O<$
11	$Ph{\cdot}CO{\cdot}C{\vdots}CH$	3306	9	3233 [a]	26	$\vdots CH\cdots OC<$
12	$EtO_2C{\cdot}C{\vdots}CH$	3310	7·5	3277	70	$\vdots CH\cdots O{:}C<$
10	*p*-$NO_2{\cdot}C_6H_4{\cdot}C{\vdots}CH$	3319	9	3253 [a]	~20	$\vdots CH\cdots O_2N\text{–}$
15	$Et_2N{\cdot}CHMe{\cdot}C{\vdots}CH$	3316	6	3311 3222*w*	30 ~160	Self-association $\vdots CH\cdots N{\leqq}$
		ν(C:O) in hexane		ν(C:O) in liquid state		
11	$Ph{\cdot}CO{\cdot}C{\vdots}CH$	1668	6	1643 [a]	22	$>C{:}O\cdots H\text{–}C\vdots$
12	$EtO_2C{\cdot}C{\vdots}CH$	1729	9	1719	~25	$>C{:}O\cdots H\text{–}C\vdots$

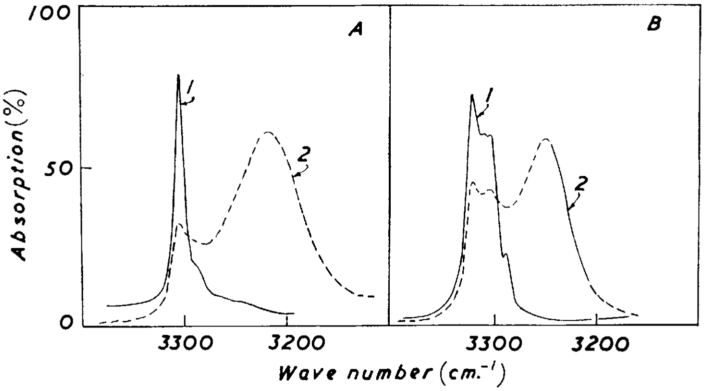
[a] Solid state spectrum (Nujol); the main ν(CH) band is accompanied by a weak but broad " tail " on the low-frequency side. *w* = Weak. * Tp = Tetrahydropyranyl.

Table 1 summarises measurements near 3300 cm.$^{-1}$ in n-hexane and in ether. The general spectral characteristics in this region are the same for all compounds studied: (i) the hydrogen bond complex in ether gives a broad band displaced 50—90 cm.$^{-1}$ to lower frequency from the " free " ethynyl absorption, (ii) association is incomplete, so that ether solutions show both " free " and " associated " ν(CH) peaks, and (iii) the " free " ν(CH) band has a slightly lower frequency and appreciably greater half-width in ether than in n-hexane. The " free " ν(CH) bands were symmetrical for n-hexane solutions, except for weak absorption (presumed to be a combination tone intensified by Fermi resonance) present on the low-frequency wing in all examples studied. Fermi resonance was strong in the spectra of the aryl-acetylenes (see below). Fig. 1 shows the shape of the ν(CH) band of phenylacetylene (9) and benzoylacetylene (11) in n-hexane and in ether. Previous workers [3–5] have not remarked the presence of the " free " ν(CH) peak in ether and similar solvents, though it is visible under the resolution of a sodium chloride monochromator.

To confirm the nature of the complex, phenylacetylene absorption was recorded for ether solutions at concentrations ranging from 0·5 to 0·01M, the number of molecules in the path being kept constant; no change in intensity was observed and so the complex must involve one molecule of phenylacetylene only. Similar results were obtained with benzoylacetylene (11). Although it was not possible to establish the molecularity of the complex with respect to ether, yet it is natural to assume that bonding leads to binary (1 : 1) association. At all events, 2 : 1 complexes [*e.g.*, $(Ph{\cdot}C_2H)_2,OEt_2$] are not produced.

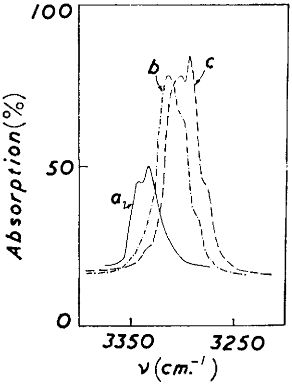
The final column of Table 1 gives for some molecules an estimate of the degree of association in ether, obtained from the ratio of areas of the free ν(CH) absorption in n-hexane and ether. Although the areas in ether are uncertain to the extent that the " free " and association ν(CH) peaks are fused (Fig. 1*A* shows an example), the relative values have significance. Thus there is a fairly good correlation between the displacements, $10^2\Delta\nu/\nu$, and the proportion of hydrogen-bonded complex, and the arrangement in ascending order of " acidity " is broadly that expected from the electronic properties of the group attached to –C⋮CH. Consequently, a rough parallel can be seen between the apparent acidity of ethynyl compounds as deduced from the infrared measurements and their reactivity in chemical processes initiated by removal of the ethynyl proton (*e.g.*, ethynylation of benzophenone [11] and oxidative coupling; [8] Grignard exchange, however, appears not to fall in this class [12]). The " free " ν(CH) frequency tends to fall with increasing apparent acidity of the ethynyl group: an exact parallelism is not observed, perhaps because Fermi resonance influences the precise value of ν(CH). With phenylacetylene, for instance, the components of Fermi resonance appear with different emphasis in hexane solution (Fig. 1*B*), the vapour state, and carbon tetrachloride or carbon disulphide solutions (Fig. 2).

FIG. 1.



(*A*) Ph·CO·C⋮CH, (1) 0·05M *in n-hexane* (0·5 mm.); (2) 0·1M *in ether* (0·5 mm.). (*B*) Ph·C⋮CH, (1) 0·1M *in n-hexane* (0·5 mm.); (2) 0·1M *in ether* (0·5 mm.).

FIG. 2.



Ph·C⋮CH *as* (*a*) *vapour*, (*b*) 0·1M-*soln. in* CCl$_4$ (0·5 mm.), *and* (*c*) 0·5M-*soln. in* CS$_2$ (0·1 mm.).

640 *cm.*$^{-1}$ *Region.*—Fig. 3 shows the effect of hydrogen bonding on the bending fundamentals of five selected compounds. The complex is marked by a very broad band displaced somewhat to higher frequency from the " free " δ(CH) peak. Oct-1-yne shows a net increase in integrated absorption from n-hexane ($B = 0{\cdot}74 \times 10^4$) to ether ($B = 1{\cdot}1 \times 10^4$) and hence, the degree of association in ether being taken as 30% (Table 1), the complex absorbs with 2 or 3 times the intensity of the free molecule in this region. In other examples, overlapping absorption precluded a satisfactory evaluation of areas. Spectra in carbon disulphide and n-hexane were essentially the same in the two cases studied.

When several bands were present in the 600—700 cm.$^{-1}$ region the assignment of the δ(CH) fundamental was made as follows. (i) It is well known that the overtone 2δ(CH) is comparatively strong; in the *liquid state* this overtone is marked by a characteristically broad band whose identification enabled the fundamental to be picked out. (ii) δ(CH) character could be taken as absent for a band having the same intensity in ether as in an inactive solvent. Phenylacetylene, for instance, absorbs in carbon disulphide at 690, 648, and 611 cm.$^{-1}$ (Table 3). In the overtone region broad bands were observed at 1284 and 1220 cm.$^{-1}$, indicating that the 648 and 611 cm.$^{-1}$ peaks were connected with the C–H deformation: this was supported by the fact that their intensity (ε_a) fell to less than one-half in ether, whereas the intensity at 690 cm.$^{-1}$ was unchanged (Table 3). In this example interaction with other group vibrations appears to split the δ(CH) fundamental (doubly degenerate in an axially symmetric molecule) into two components. Ethyl propiolate (12) also yields a double band (687 and 650 cm.$^{-1}$) though in

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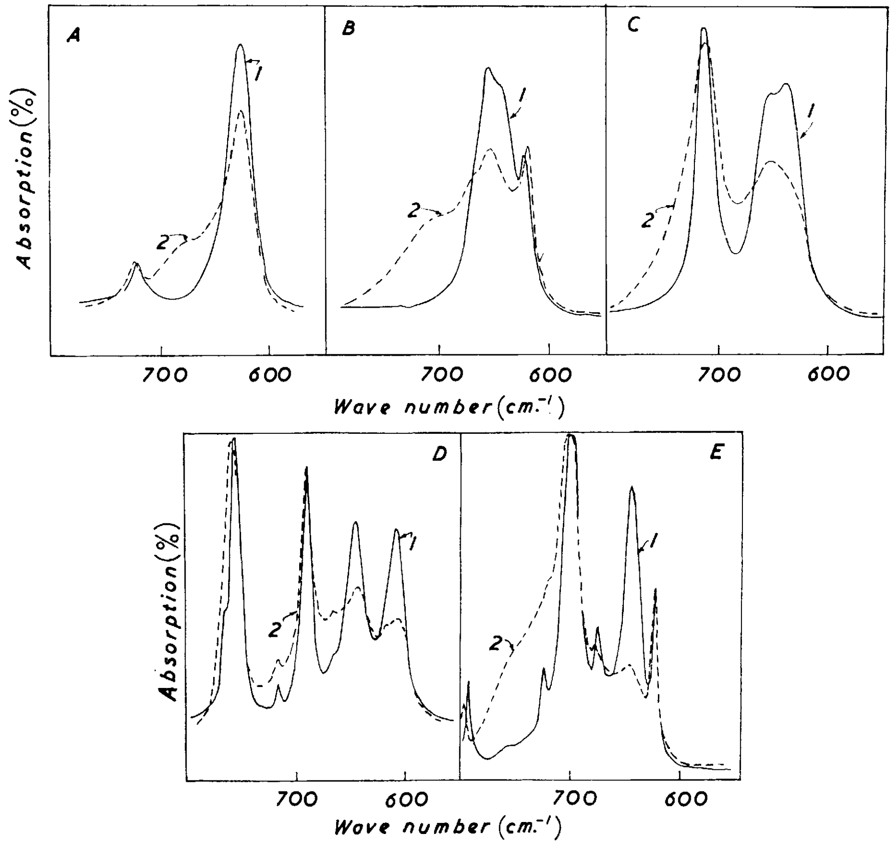
[11] Chodkiewicz, *Ann. Chim.* (*France*), 1957, 819.

[12] Wotiz, Hollingsworth, and Dessy, *J. Org. Chem.*, 1955, **20**, 1546.

FIG. 3.



(*A*) $C_6H_{13}\cdot C{\vdots}CH$, (*B*) $Br\cdot CH_2\cdot C{\vdots}CH$, (*C*) $Cl\cdot CH_2\cdot C{\vdots}CH$, (*D*) $Ph\cdot C{\vdots}CH$, *and* (*E*) $Ph\cdot CO\cdot C{\vdots}CH$ *in* CS_2 (1) *and ether* (2). *Solutions ca.* 1M *in* 0·05 mm. *cell.*

TABLE 3. 550—800 *cm.*$^{-1}$ *region.*

		CS_2 solution [a]			Ether solution [b]		Association band	Other
No.	Compound	cm.$^{-1}$	(ε_a)	$\Delta\nu_{\frac{1}{2}}$ [a]	cm.$^{-1}$	(ε_a)		assignments *
1	$CH_3\cdot[CH_2]_5\cdot C{\vdots}CH$	**629**	(180)	17	**629**	(85)	*ca.* 670	
		724	(10)	12	726	(10)		$\rho(CH_2)$
5	$Br\cdot CH_2\cdot C{\vdots}CH$	622	(60)		619	(65)		ν(C–Br)
		655	(130)	33	**652**	(60)	*ca.* 700	
6	$Cl\cdot CH_2\cdot C{\vdots}CH$	**642** **654**	(95)	33	**653**	(40)	650—750	
		712	(~200)	10	711	(~160)		ν(C–Cl)
9	$Ph\cdot C{\vdots}CH$	**611**	(115)	17	**611**	(40)	650—750	
		648	(120)	15	**646**	(60)		
		690	(160)	5	692	(160)		ω(CH) arom.
		756	(>350)	5	758	(>350)		
11	$Ph\cdot CO\cdot C{\vdots}CH$	626	(50)	4	626	(35)		
		646	(160)	11	**645**	(15)	680—800 (max. *ca.* 725)	
		677	(weak)		678	(weak)		
		701	(>350)		703	(>350)		ω(CH) arom.
		792	(weak)	4	795	(weak)		
12	$EtO_2C\cdot C{\vdots}CH$	600	(weak)	15	600	(weak)		
		650	(85)	16	**650**	(20)	700—800	
		687	(60)	20	**690**	(25)		
		753	(180)	7	756	(160)		

[a, b] 0·5 and 0·05 mm. cells, respectively. δ(CH) fundamentals are given in heavy type.
* ν = stretching, δ = deformation, ρ = rocking, ω = wagging.

other instances the degeneracy is unresolved (for propargyl chloride, partly resolved) presumably because the molecules lack a vibration of the right frequency to interact with the C–H deformation.

2100 *cm.*$^{-1}$ *Region.*—At the relatively low resolving power available (sodium chloride prism, 1500 lines/in. grating blazed for 900 cm.$^{-1}$) no significant differences were evident when the ν(C⋮C) fundamentals were examined for n-hexane and then for ether solutions. The compounds (in hexane) had ν(C⋮C) at (1) 2117, (2) 2117, (3)2110, (4) 2095, (5) 2103, (6) 2126, (7) 2131, (8) 2109, (9) 2110, (10) 2113, (11) 2097, and (12) 2120 cm.$^{-1}$. *Apparent* extinction coefficients averaged 10—20 l. mole^{-1} cm.$^{-1}$, except for compounds (11) and (12), which absorbed strongly (*ca.* 150 units) owing to conjugation of the triple bond with the carbonyl grouping.

Discussion

We assume that in a system containing an ethynyl compound (A) and diethyl ether (B) there are three species A, AB, and B in mutual equilibrium, and that their solutions in an inert solvent S form an ideal mixture. In spectrophotometry, A + B + S is always dilute with respect to A (in practice, the stoicheiometric mole-fraction x_A is $<0{\cdot}01$), thus $x_B + x_S \approx 1$. Under these conditions the equilibrium constant in terms of mole-fractions can be written

$$K_N = m_{AB}/m_A x_B \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

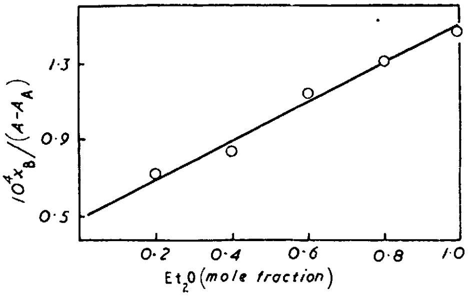


FIG. 4. *Equilibrium in the system* Ph·CO·C⋮CH + Et$_2$O.

in which m_{AB} and m_A are the *actual* molarities of AB and A, and x_B is the stoicheiometric mole-fraction of B. A and AB give partly superposed absorption in the infrared region (Fig. 1), and moreover AB is formed incompletely even in pure ether so that its absorption intensity is not known. However, from considerations of Beer's law [13] we have

$$x_B/(A - A_A) = x_B/(A_{AB} - A_A) + 1/K_N(A_{AB} - A_A) \quad . \ . \ . \quad (2)$$

as the equation connecting the true integrated absorption intensity A of a mixture containing both A and AB with the ether mole-fraction x_B. Here A_A and A_{AB} represent the absorption intensity of A and AB, the former being measurable in solution in the pure inert solvent S. Equation (2) can be used to determine K_N and A_{AB} from the slope and intercept formed by plotting the left-hand side against the corresponding value of x_B. Such a plot is given in Fig. 4 for the 3100—3400 cm.$^{-1}$ absorption bands of benzoylacetylene in mixtures of ether and carbon tetrachloride. The points show scatter but no trend which might invalidate the assumption of thermodynamic ideality. The method of least squares gives

$$K_N(29°) = 2{\cdot}0 \pm 0{\cdot}2 \quad . \ . \ . \ . \ . \ . \ . \ . \quad (3)$$

and

$$A_{AB} = 1{\cdot}7 \times 10^4 \text{ l. mole}^{-1} \text{ cm.}^{-2} \quad . \ . \ . \ . \ . \ . \quad (4)$$

Since $A_A = 0{\cdot}72 \times 10^{-4}$, it follows that the benzoylacetylene–ether complex absorbs with about 2·4 times the intensity of the free molecule. The degree of association $m_{AB}/(m_A +$

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[13] Brand and Sneddon, *Trans. Faraday Soc.*, 1957, **53**, 894.

m_{AB}) of a dilute solution of the acetylene in pure ether is 0·67 ± 0·03. This result gives assurance that the rough estimates of association in Table 1, col. 8, are not seriously wrong.

The values in (3) and (4) may be in error for either of two reasons. (i) A_A and A_{AB} are supposed to be unchanged in ether, carbon tetrachloride, and their mixtures. (This assumption is always implied in the spectrometric method.) (ii) Apparent integrated absorption intensities B have actually been used in Fig. 3 in place of the true integrated intensities A appearing in eqn. (2). The error is negligible for AB, owing to the width of its absorption band, but significant for A, where Ramsay's slit corrections [14] suggest that B_A may be in deficit by 5%. As the slit corrections cannot be applied to superposed absorption of A and AB, they have been omitted throughout.

TABLE 4. *Equilibrium constants and thermodynamic parameters.**

System	Ph·CO·C⋮CH + Et_2O Sp	Ph·C⋮CH + Et_2O Sp	$CDCl_3$ + Et_2O Sp[15]	$CHCl_3$ + dioxan (1 : 1 complex) Th[18]	$CHCl_3$ + Me_2CO Sp[17]	$CHCl_3$ + Me_2CO Th[19]
Temp.	29	29	22	50	28	25
K_N	2·0	1·1	7·6	1·11	1·8	0·8
ΔH (cal. mole^{-1})		−1400		−2000	−2500	−2700
ΔS (cal. mole^{-1} deg.$^{-1}$)		−4·5		−6·0	−7·1	−9·5

* Sp, spectrometric, Th, thermodynamic measurements.

Similar results for phenylacetylene + ether in carbon tetrachloride gave $K_N(29°) = 1·1 \pm 0·3$ (Table 4). This system is of interest because the molar heat of mixing, $\Delta_m H$, has been measured [1] and thus the heat, ΔH, of the chemical reaction A + B = AB can be calculated. For the binary mixture A + B, when B is not necessarily in great excess over A, K_N can be written

$$K_N = n_{AB}(1 - n_{AB})/(x_B - n_{AB})(1 - x_B - n_{AB}) \quad . \quad . \quad . \quad . \quad (5)$$

where n_{AB} is the *actual* number of moles of AB per mole of the stoicheiometric mixture A + B. ΔH is then given by $\Delta H = \Delta_m H/n_{AB}$. In the tabulation below, $\Delta_m H$ (at 3°) is taken from Copley and Holley's diagram,[1] and the spectrometric K_N (and its implied temperature coefficient) is used to calculate n_{AB} and hence ΔH. The mean value obtained is $\Delta H = -1400 \pm 300$, where the uncertainty encompasses that in K_N as well as in the spread of values resulting from the individual $\Delta_m H$.

Heat of reaction: phenylacetylene + ether.

x_B	0·720	0·703	0·689	0·511	0·504	0·502	0·438	0·304	0·222
$\Delta_m H$	182	186	195	270	281	268	266	198	143
ΔH	1330	1310	1330	1520	1580	1500	1530	1370	1260

As the halogenoforms are known [15-17,19] to form C–H···O hydrogen bonds it is of interest to establish how, for instance, chloroform and phenylacetylene compare in this respect. Some recent examples are in Table 4. ΔH and ΔS for chloroform + dioxan [18] and chloroform + acetone [19] are from thermodynamic measurements, supported in the second example by spectrometric nuclear magnetic resonance data.[17] The heat evolved in formation of the Cl_3C–H···O bond (chloroform–dioxan) is somewhat greater than for C⋮C–H···O (phenylacetylene–ether) on the basis of the information available. It is curious that $\Delta\nu/\nu$ for phenylacetylene (Table 1) is much greater than for chloroform [15,16] and even greater, in relation to ΔH, than the corresponding $\Delta\nu/\nu$ for phenol and alcohols.[20]

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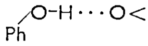
[19] Saroléa-Mathot, *Trans. Faraday Soc.*, 1953, **49**, 8.
[20] Nagakura, *J. Amer. Chem. Soc.*, 1954, **76**, 3071.

Evidently, $\Delta\nu/\nu$ is a comparative measure of hydrogen-bond strength only for molecules of the same type. It is also noteworthy that the decrease in entropy in the system phenylacetylene + ether is relatively small. Complexes of phenol[20] with various oxygen bases have values of ΔS in the range —7 to —9 in the units taken in Table 4 (ideal unit mole-fraction). One factor may be that internal rotation about the $-C{\vdots}C-H\cdots O$ axis (I) is less hindered by surrounding solvent molecules than the corresponding motion of the angular phenol complexes (II).

(I) $Ph-C{\vdots}C-H\cdots O<$


(II)

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