The Interaction of Amines with Iron Pentacarbonyl

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Primary and secondary aliphatic amines react with iron pentacarbonyl to form adducts, detected by i.r. spectroscopy in solution. Quantitative studies suggest that all these adducts contain at least two molecules of amine. It is suggested that the amine must be concentrated enough to be in a hydrogen-bonded state in order to form adducts, and that the structure of these substances involves ion-pair or ion-cluster formation.

IT has been reported that iron pentacarbonyl rapidly forms adducts with amines in the liquid phase.[1-3] Dilution with an inert solvent causes reversal of this reaction.[2] Adduct formation occurs simultaneously with the start of substitution reactions which yield $[Fe(CO)_4(am)]$ (am = amine), usually with axial substitution of the trigonal bipyramid, and ionic compounds of the type $[Fe(am)_6]^{2+}[Fe_4(CO)_{13}]^{2-}$. Formation of the latter is favoured by polar solvents,[4] and by the presence of water.[2,3]

Edgell *et al.*[2,3] suggested that formation of adducts is an intermediate step in the substitution reactions and that the adduct is formed by nucleophilic attack by the amine at an axial carbon atom of the metal carbonyl. Substitution is then supposed to ensue by some rather complicated eliminations of carbon monoxide, di-alkylformamide, and carbamates. He later demonstrated that pyrrolidine forms a 2 : 1 adduct with $[Fe(CO)_5]$, which may be isolated in the solid state; the properties of this material suggested an ionic constitution.

Other metal carbonyl systems can add amines, reversibly and irreversibly, but iron pentacarbonyl appears to be the only electrically neutral one to do so. The initial step in the reactions of $[Co_2(CO)_8]$ and $[Mn_2(CO)_{10}]$ with amines may well involve adduct formation. Angelici *et al.*[5-7] have correlated adduct-forming ability with the C–O stretching force constant; carbonyl groups with force constants greater than 16.5 mdyne Å^{-1} † form adducts (carbamoyl complexes) irreversibly whereas those with lower force constants are unreactive. The axial groups of iron pentacarbonyl are borderline and form adducts reversibly.

In this paper we seek to establish more closely which amines form adducts, to determine the formulae of the adducts and to estimate the equilibrium constants for their formation. The system has been studied in various ways, and we report here on the use of the C–O stretching region of the i.r. spectrum to measure the concentration of free $[Fe(CO)_5]$ as a function of amine mole fraction in hexane, and for two cases, in n-heptyl cyanide as an example of a polar solvent.

THEORY

It is assumed that adduct formation occurs in step-wise fashion, *i.e.* equations (1) and (2) *etc.* In the usual way cumulative formation constants β_i are related to the step-wise constants by $\beta_i = \prod_1^i K_j$. The possibility of more than one $[Fe(CO)_5]$ molecule being involved was neglected for solutions which were of the order of millimolar in $[Fe(CO)_5]$ and molar in amine. All formation constants are in terms

$$[Fe(CO)_5] + am \rightleftharpoons Fe(CO)_5{\cdot}am \quad K_1 \tag{1}$$

$$Fe(CO)_5{\cdot}am + am \rightleftharpoons Fe(CO)_5{\cdot}2\,am \quad K_2 \tag{2}$$

of mole fractions. Using standard equations it may be shown that equation (3) holds where C_0 is the added

$$C_0/C = D_0/D = 1 + \sum_i \beta_i x_A{}^i \tag{3}$$

$[Fe(CO)_5]$ concentration, C the free $[Fe(CO)_5]$ concentration, x_A the mole fraction of free amine, and D_0 and D refer to the optical densities of added and free $[Fe(CO)_5]$ respectively.

For a large excess of amine, x_A is approximately equal to the added mole fraction of amine. Under the special condition that only one adduct forms (which appears to be the case in this system), equation (4) holds.

$$\ln[(D_0/D) - 1] = i \ln x_A + \ln \beta_i \tag{4}$$

EXPERIMENTAL

Amines, n-hexane, and n-heptyl cyanide were stored over calcium hydride and distilled in a nitrogen atmosphere before use. Iron pentacarbonyl was used as supplied by Fluka AG. Samples were prepared by mixing measured volumes of amine and the solvent and using the appropriate densities to calculate mole fractions; $[Fe(CO)_5]$ was added to obtain 2.5 millimolar solutions, but the effect of this addition on amine mole fraction was neglected. Infrared spectra were measured using a Perkin-Elmer 225 spectrophotometer and Specac variable path cells with sodium chloride windows. Most measurements were made with a sample thickness of 0.3 mm. The back plate of the cell was thermostatted with a water jacket at 298 K.

RESULTS

Figure 1 shows the spectra of $[Fe(CO)_5]$ in hexane, pyridine, and cyclohexylamine; the last case is one in which the $[Fe(CO)_5]$ is completely converted to adduct. In pyridine no adduct is formed but the $[Fe(CO)_5]$ bands are broadened and shifted relative to those in the hexane solution. In liquids where adduct is partially formed the free $[Fe(CO)_5]$ bands appear similar to those in pyridine. The spectrum in n-heptyl cyanide is very similar to that in pyridine.

The spectra in various pure amines are summarised in Table 1. Bands due to adduct and the substituted product

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† Throughout this paper: 1 dyne = 10^{-5} N; 1 cal = 4.184 J.

TABLE 1

Carbonyl stretching frequencies (cm^{-1}) for adducts and substituted compounds

Amine	Approx % conversion to adduct	Adduct absorptions			Substituted product $[Fe(CO)_4(am)]$ absorptions		
		A_1(w)	A_1(m)	E(s)	A_1(w)	A_1(m)	E(s)
Ethylamine	100	2 010	1 925	1 920 to 1 870	2 042	1 945	1 927
n-Butylamine	100	2 015	1 918	1 907 to 1 882	2 039	1 945	1 925
s-Butylamine	100	2 016	1 925	1 895	2 041	1 948	1 925
t-Butylamine	50	2 021	1 930	1 900 1 890	2 042	1 952	1 926
Cyclohexylamine	100	2 012	1 928	1 890	2 039	1 945	1 924
Pyrrolidine	100	2 014	1 925	1 890	2 040	1 945	1 925
Piperidine	50	2 014	1 921	1 899 1 885	2 042	1 950	1 921
Diethylamine	0	No adduct formed			2 044	1 952	1 926
Di(n-butyl)amine	0	No adduct formed			2 043	1 956	1 928
Pyridine	0	No reaction observed under these conditions					

$[Fe(CO)_4(am)]$ are shown where appropriate. The following amines were tested and found to be unreactive under ambient conditions: aniline, *N*-methylaniline, pyridine, 2-aminopyridine, diphenylamine, trimethylamine, and quinuclidine. Di(cyclohexyl)amine yielded a trace of substitution but no adduct. It is apparent that only primary and secondary aliphatic amines form adducts or give substitution under ambient conditions. Steric effects are apparent and are more stringent as regards adduct formation. For example, diethylamine gives slow substitution but does not form any adduct.

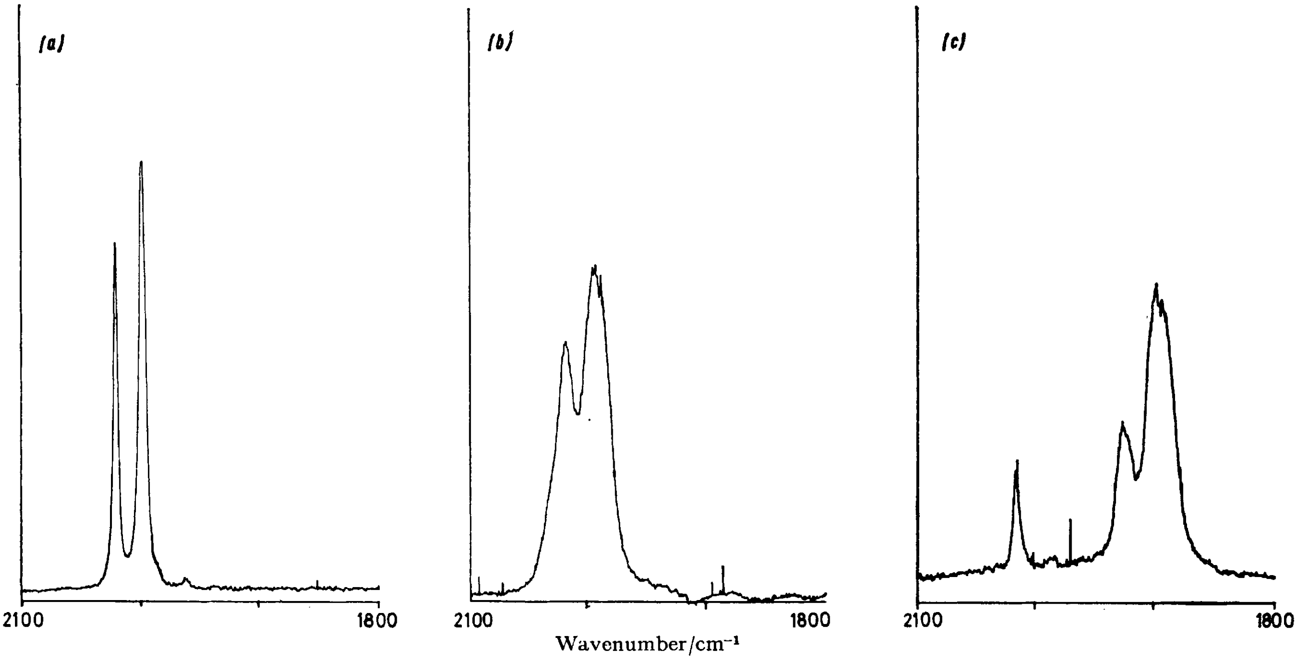

FIGURE 1 Infrared spectra of $[Fe(CO)_5]$ (optical density 0—1): (*a*) solvent = n-hexane, concentration = 2.5×10^{-3} mol dm^{-3}, sample thickness = 0.21 mm; (*b*) pyridine, 2.2×10^{-2} mol dm^{-3}, 0.13 mm; (*c*) cyclohexylamine, 2.2×10^{-2} mol dm^{-3}, 0.13 mm

The variation of optical density of the two $[Fe(CO)_5]$ bands with amine mole fraction is shown in Tables 2 and 3 for pyridine and cyclohexylamine respectively; other cases are similar,* Table 4 gives a summary.

In equations (3) and (4) the quantity D_0 refers to the optical density of added $[Fe(CO)_5]$ in the solvent mixture concerned. It is apparent from the results for pyridine and diethylamine, which do not form adducts, that D_0 is itself a function of x_A; it is therefore not possible to measure D_0 for an amine which forms adducts. However the D_0 values for pyridine and diethylamine correlate very well and it was therefore assumed that D_0 would behave in the same way for other amine–hexane mixtures; thus D_0 values were taken from the pyridine–hexane system. Figures 2 and 3 show the variation of D_0/D with x_A for the E' band (*ca.* 2 000 cm^{-1}) of $[Fe(CO)_5]$ in cyclohexylamine and the corresponding $\log_e$ plot [equation (4)]. The errors in the logarithms tend to infinity when x_A is small and only points for $x_A > 0.11$ are included; below this value D_0/D was not significantly greater than one and it was not possible to detect adduct peaks in the spectra, even at an enhanced $[Fe(CO)_5]$ concentration of 25 millimolar. Similar behaviour was found in all cases where adduct formed at high amine concentration. For t-butylamine–hexane no adduct was detectable for $x_A < 0.8$ and the conversion was not complete even in the pure amine.

In other cases it was found that free $[Fe(CO)_5]$ was undetectable at $x_A > 0.5$.

Piperidine behaves anomalously under these conditions although a solid 3 : 1 adduct may be isolated. For the

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* Data for the other systems are available on request.

range $0 < x_A < 0.4$ the spectra are very similar to those of cyclohexylamine and n-butylamine, but at $x_A = 0.41$ D_0/D shows a sharp maximum, indicating a maximum in adduct formation. Although no definite explanation of this phenomenon is available, it is possibly due to a change in the piperidine–hexane system such as specific association or micelle formation which reduces the availability of the amine for adduct formation with $[Fe(CO)_5]$. It is also possible that there is an anomaly in D_0.

TABLE 2

Variation of optical density with mole fraction of amine for the pyridine–iron pentacarbonyl system

Mole fraction of pyridine (x_A)	Optical density of iron pentacarbonyl	
	D_0(2 022)	D_0(2 000)
0.0000	0.749	1.062
0.0131	0.640	0.908
0.0261	0.626	0.862
0.0389	0.613	0.850
0.0516	0.600	0.827
0.0642	0.575	0.805
0.0766	0.550	0.776
0.0889	0.538	0.758
0.1011	0.516	0.729
0.1132	0.502	0.705
0.1252	0.485	0.690
0.1488	0.463	0.658
0.1719	0.434	0.608
0.1940	0.423	0.588
0.2169	0.390	0.571
0.2388	0.375	0.560
0.2918	0.358	0.490
0.3424	0.344	0.465
0.3908	0.318	0.420
0.4372	0.315	0.428
0.4817	0.300	0.378
0.5243	0.290	0.366
0.6025	0.268	0.341
0.6769	0.254	0.329
0.8103	0.276	0.348

Solvent = hexane $[Fe(CO)_5]$ (mmol dm^{-3}) = 2.5, sample thickness (mm) = 0.30.

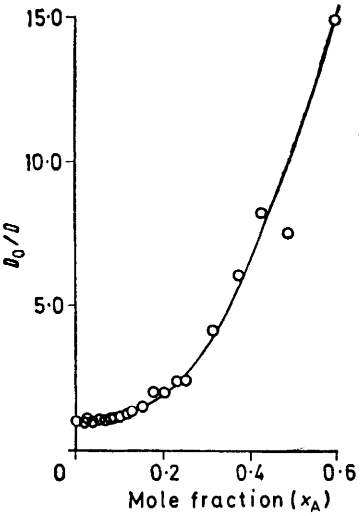


FIGURE 2 Plot of D_0/D against x_A for the E' band of $[Fe(CO)_5]$ at 2 000 cm^{-1} in hexane–cyclohexylamine mixtures

A further difficulty with piperidine is the relatively rapid substitution reaction shown by the appearance of peaks due to $[Fe(CO)_4(am)]$. In high mole fractions this reaction was too fast to allow quantitative monitoring of the adduct equilibria.

The adduct band at 2 015—2 024 cm^{-1} overlaps with the A_2'' band of $[Fe(CO)_5]$ at 2 020 cm^{-1}, but is of much smaller extinction coefficient than the $[Fe(CO)_5]$ band in hexane. Where conversion to adduct is large, therefore, it would be expected that the D values would be affected. For this reason the results from the E' band at 2 000 cm^{-1} are probably more realistic. However, in all cases where adduct peaks were directly detectable, the variation of D_0/D with x_A followed a similar pattern for both bands. Log$_e$ plots were made for points where D_0/D was significantly greater than one, and were found in all cases to give reasonably straight lines with slopes between two and three (except for t-butylamine). In heptyl cyanide the 2 015 cm^{-1} band intensities are more nearly comparable and only 2 000 cm^{-1} band results are reported.

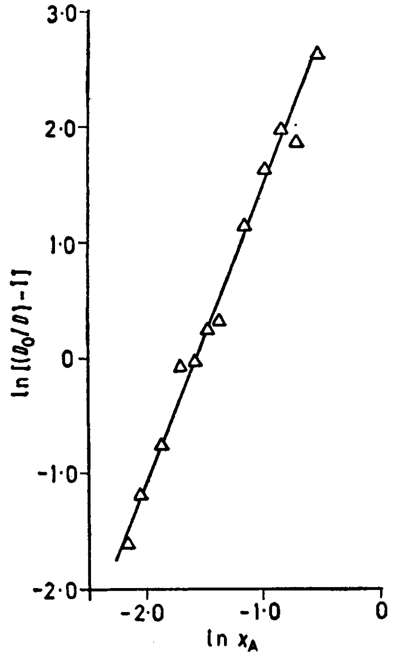


FIGURE 3 Plot of ln[(D_0/D) − 1] against ln x_A, data as in Figure 2

DISCUSSION

It is clear from the spectra in pure amines that only primary and secondary aliphatic amines can form adducts with $[Fe(CO)_5]$, and that this activity is constrained by steric hindrance from substituents. In order to determine whether steric effects were the real reason for the inactivity of tertiary amines some experiments were carried out with quinuclidine, thereby minimising steric hindrance. No adduct peaks were detected in saturated solutions in hexane and it was found that the vapour pressure of the $[Fe(CO)_5]$–quinuclidine binary system [8] behaved almost ideally. It was therefore concluded that tertiary amines cannot form adducts with $[Fe(CO)_5]$, even when steric hindrance is minimised.

As well as steric hindrance, delocalisation of the nitrogen lone pairs in aromatic amines prevents adduct formation, as for example with aniline and N-methylaniline. 2-Aminopyridine also gave no evidence for adduct formation although here one might expect that the cyclic tertiary nitrogen could supply the necessary lone pairs whilst the 2-amino-group supplied the primary hydrogen.

The spectroscopic changes in the range of low amine mole fractions are particularly significant. As x_A is increased the peak intensity of the $[Fe(CO)_5]$ bands decreases but, for small x_A, there is no corresponding appearance of adduct peaks, even in solutions as strong as 25 mmol dm^{-3} $[Fe(CO)_5]$. The initial decrease of peak intensity follows the pattern for pyridine fairly closely and is therefore assigned to be a band broadening effect associated with the polarity of the amine. This decrease is very largely corrected by using D_0 values from the pyridine system for the calculation of D_0/D. The compensated values of D_0/D do not change significantly from one until x_A *ca.* 0.1 or more; at this stage D_0/D starts to increase and adduct peaks become detectable. It is believed that this behaviour can be explained only if the system forms 1 : 2 and higher adducts, but that 1 : 1 adducts have no experimentally significant existence. The presence of 1 ; 1 adducts would place a linear term in equation (3) and D_0/D would show a positive slope at $x_A = 0$, which is not detectable; the ln $[(D_0/D) - 1]$ plots would also show a slope of one for small x_A, increasing on curves to higher limiting values, also not observed. Furthermore 1 : 1 adducts might be expected to show absorption spectra different from higher adducts but no peaks were observed in any system which could be assigned in this way. The non-existence of 1 : 1 adducts is consistent with the inability of tertiary amines to form adducts; if the nitrogen lone pair alone were required it would be expected that

TABLE 3

Variation of optical density with mole fraction of amine for the cyclohexylamine–iron pentacarbonyl system

Mole fraction cyclohexylamine (x_A)	ln x_A	D (2 022)	D_0/D (2 022)	ln$[(D_0/D) - 1]$	D (2 000)	D_0/D (2 000)	ln$[(D_0/D) - 1]$
0.0000	$-\infty$	0.749	1.00	$-\infty$	1.062	1.00	$-\infty$
0.0130	-4.342	0.670	0.96	$-\infty$	0.947	0.96	$-\infty$
0.0260	-3.650	0.620	1.01	-4.61	0.832	1.04	-3.22
0.0390	-3.244	0.616	1.00	$-\infty$	0.840	1.01	-4.61
0.0519	-3.96	0.592	1.01	-4.61	0.810	1.02	-3.91
0.0648	-2.74	0.568	1.01	-4.61	0.792	1.02	-3.91
0.0776	-2.56	0.560	0.98	$-\infty$	0.741	1.05	-3.00
0.0904	-2.40	0.554	0.96	$-\infty$	0.715	1.06	-2.81
0.1031	-2.27	0.527	0.98	$-\infty$	0.680	1.07	-2.66
0.1158	-2.16	0.466	1.07	-2.66	0.592	1.20	-1.61
0.1285	-2.05	0.422	1.15	-1.90	0.530	1.30	-1.20
0.1537	-1.87	0.350	1.31	-1.17	0.441	1.47	-0.76
0.1787	-1.72	0.271	1.60	-0.51	0.321	1.92	-0.08
0.2036	-1.59	0.240	1.71	-0.34	0.300	1.95	-0.05
0.2284	-1.48	0.215	1.83	-0.19	0.245	2.27	0.24
0.2529	-1.38	0.170	2.22	0.20	0.225	2.35	0.30
0.3137	-1.16	0.103	3.36	0.86	0.116	4.10	1.13
0.3735	-0.99	0.060	5.38	1.48	0.072	6.00	1.61
0.4324	-0.84				0.049	8.16	1.97
0.4904	-0.71				0.050	7.44	1.86
0.6038	-0.51				0.023	14.78	2.62

Solvent = hexane, $[Fe(CO)_5]$ (mmol dm^{-3}) = 2.5, sample thickness (mm) = 0.30.

TABLE 4

Summary of parameters from $\log_e$ plots

Amine solvent (wavenumber/cm^{-1})	ln β	α_β, error in intercept	$\Delta G^\ominus$/ kcal mol^{-1}	i	α_i, error in slope
n-Butylamine–hexane					
(2 022)	2.14	0.10	2.9	2.67	0.14
(2 000)	1.97	0.09	2.7	2.27	0.21
s-Butylamine–hexane					
(2 022)	1.79	0.12	2.5	2.64	0.17
(2 000)	1.62	0.25	2.2	2.25	0.33
t-Butylamine–hexane					
(2 022)	-0.10	0.07	-0.13	8.36	1.11
(2 000)	-0.02	0.12	-0.05	8.88	1.88
t-Butylamine–heptyl cyanide					
(2 000)	0.46	0.06	0.70	1.70	0.12
Cyclohexylamine–hexane					
(2 022)	1.82	0.11	2.5	2.86	0.17
(2 000)	1.70	0.06	2.3	2.48	0.10
Cyclohexylamine–heptyl cyanide					
(2 000)	2.74	0.24	3.8	3.58	0.37
Piperidine–hexane					
(2 022)	2.04	0.14	2.8	3.20	0.20
(2 000)	1.69	0.09	2.3	2.57	0.14

any type of reasonably basic amine could form 1 : 1 adducts. It is therefore essential that there is a co-operative effect between the nitrogen lone pairs and the *N*-hydrogen atom of a second molecule.

Three possibilities present themselves for the mode of bonding: (i) hydrogen bonding, (ii) nitrogen–carbon bonding, (iii) nitrogen–iron bonding. It is difficult to believe that hydrogen bonding alone could be responsible for the observations; the less basic amines such as aniline might be expected to show the greater ability to hydrogen bond to the carbonyl oxygen atoms and it is not possible to understand why 1 : 1 adducts should not form. The latter argument would also apply to the other possible modes of bonding if they were taken in isolation. It is therefore suggested that hydrogen bonding must be considered only in conjunction with other bonding.

Nitrogen–iron bonding would produce an octahedral complex of approximately C_{4v} symmetry (sufficiently distorted from O_h so as not to become paramagnetic); this structure can be compared with complexes of the type $[Cr(CO)_5(am)]$ [9-11] which give C–O stretching frequency patterns in the i.r. (hexane solution) at 2 067 cm^{-1} (weak, A_1), 1 937 cm^{-1} (strong, E), and 1 917 cm^{-1} (medium, A_1). In more polar solvents the lower two frequencies decrease by *ca.* 35 cm^{-1}. The average of these frequencies is noticeably higher than that of the iron adducts (Table 1) even allowing for the more polar environment in which the adducts form. This might suggest a greater transfer of negative charge into the carbonyl groups of the iron compounds. There is a difference of intensity pattern in the three bands of the two systems, but of greater significance is the greater range over which the frequencies of the chromium compounds are spread. This is taken to indicate that the number of coupled carbonyl groups in the chromium complexes is greater and hence that the iron adducts are in fact not pentacarbonyls but tetracarbonyls as suggested previously. Iron–nitrogen bonding thus seems to be unlikely, in agreement with Edgell's conclusion for pyrrolidine.

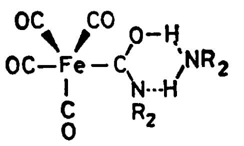
The C–O stretching frequency patterns of the adducts are in fact consistent with the complex type $[Fe(CO)_4L]$, with a ligand L in the axial position of a trigonal bipyramid. They are indeed similar in shape to those of the substituted compounds $[Fe(CO)_4(am)]$ which are produced more slowly in the same solutions. These latter spectra are assigned as shown in the Table. The possible C_{2v} structure (equatorial substitution) would yield four bands with the central two close together or co-incident. In the latter event the central band of the three would be the most intense. The adduct frequencies are generally *ca.* 30 cm^{-1} lower than those of the substituted compounds, showing that the ligand involved is a very strong electron donor or that the complex is anionic. The strong low-frequency band is broad and sometimes split into two components, indicating the assignment to the E mode showing the splitting effects of a bulky and asymmetric ligand.

The results in Table 4 show that the adduct stoicheiometry is 1 : 2 or 1 : 3 with the exception of t-butylamine, the actual stoicheiometry is dependent upon both the choice of amine and the nature of the solvent. The uncertainty in the actual number arises from the assumption that the band-broadening effect for all the amines studied is the same as that observed for pyridine. Together with the assignment of the i.r. spectra, this suggests strongly that the carbamoyl type of arrangement is formed in a manner similar to that of cationic carbonyls, *e.g.* equations (5) and (6). A related kinetic

$$[Mn(CO)_5(NH_2Me)]^+ + 2\,RNH_2 \longrightarrow RNH_3^+ + [Mn(CO)_4(NH_2Me)(OCNHR)] \tag{5}$$

$$[Fe(CO)_5] + 2\,RNH_2 \rightleftharpoons RNH_3^+ + [Fe(CO)_4(OCNHR)]^- \tag{6}$$

result is that of amine attack on the thiocarbonyl $[W(CO)_5(CS)]$, which is second order in amine concentration, and is thought to involve amine molecules which are hydrogen bonded to each other rather than a termolecular reaction.[12] In the case of a similar formation of the iron carbonyl adducts, two ions would be formed and in a medium of low dielectric constant would be expected to remain together as an ion pair. A slightly different possibility occurs to us, that of a hydrogen-bonded ring system (see below). This is an effectively structured form of ion pair and would be consistent with the rapid dissociation of the adducts on dilution with hexane and with the fact that the amine must be concentrated to form adduct. The free energies shown in Table 4 are doubtless subject to considerable error, but nonetheless it is noteworthy that the formation of adduct is exothermic; 3 cm^3 of $[Fe(CO)_5]$ and of n-butylamine give a temperature rise of some 60 °C on mixing. Thus it is to be anticipated that adduct formation is accompanied by a large decrease of entropy, which would be more likely for a single condensed species than for separated ions.



The large number of amine molecules apparently involved in the adducts with t-butylamine is difficult to interpret. The fact that adduct does not form in mixtures much less than 80% amine confirms that intermolecular hydrogen bonding of the amine is a condition for adduct formation. The effective basicity of the amine is increased by hydrogen bonding, perhaps in a way similar to the enhanced acidity of hydrogen fluoride on hydrogen-bond formation. t-Butylamine is a sterically hindered molecule and no doubt only forms hydrogen bonds, and hence $[Fe(CO)_5]$ adducts, when it is concentrated, but the large *number* of molecules necessary to stabilise the iron carbonyl adduct is probably sufficient to make up a complete solvation shell. In this case then, it is not sufficient to form an ion pair or ring, but the whole system must be solvated by amine as well for stability to be achieved. This idea is confirmed by the need for only two t-butylamine molecules when the more polar heptyl cyanide is the background solvent.

With regard to the mechanism proposed by Edgell for the substitution process using adducts as an intermediate, we would suggest that this is possible only in the presence of water. Under anhydrous conditions substitution, to produce [Fe(CO)$_4$(am)], proceeds in cases where no adduct is detectable [*e.g.* diethylamine and di(cyclohexyl)amine]. Where adduct is formed the rate of substitution does not increase rapidly with increasing amine concentration except in the case of piperidine. With this amine the substitution reaction

$$[\mathrm{Fe(CO)_5(am)_2}] \rightleftharpoons [\mathrm{Fe(CO)_5}] + 2\mathrm{am} \longrightarrow [\mathrm{Fe(CO)_4(am)}] + \mathrm{am} + \mathrm{CO} \quad (7)$$

becomes rapid when the adduct formation is past the anomalous maximum. These facts suggest that the adduct is a stable side-product and that the substitution reaction proceeds from adduct with free [Fe(CO)$_5$] as an intermediate, *i.e.* equation (7).

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