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The Interaction of Trifluoroiodomethane with Donor Molecules

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The enthalpies of interaction between trifluoroiodomethane and various electron pair donor molecules D are increased by increasing donicity of D. The plot of the chemical shifts of the ^{19}F NMR spectra of CF_3I at infinite dilution in D vs. donicities of D gives a straight line.

Introduction

Perfluoro organic halides form at low temperatures 1:1 adducts with tertiary amines.[1] Such adducts dissociate reversibly into unchanged starting materials at higher temperatures: for example the trifluoroiodomethane-trimethylamine adduct is formed at–83°C, at this temperature the dissociation pressure being 3.5 Torr. the reversible nature of this interaction suggests an electron pair donor-acceptor reaction involving the N atom of the amine and the iodine atom of the halide.

This interpretation is supported by the results of an infrared study of mixtures of Me_3N and CF_3I in the gas phase at room temperature.[2] The absorption band at 77 cm^{-1} was attributed to N - - - I intermolecular band in CF_3I–NMe_3. There is also evidence for the interaction of CF_3I and 2,4,6–collidine in solution.[3]

We wish now to report a study of the interaction between CF_3I and various electron pair donor molecules.

Experimental Section

Standard vacuum line techniques were used. CF_3I was prepared from CF_3COOAg and iodine.[4] The various donors were purified by standard techniques.[5]

Vapor pressures were measured with a mercury isoteniscope. The donor solvent was weighed and introduced in a small pyrex finger of a mercury isoteniscope (≈ 3 ml volume), the finger was cooled by liquid air and an appropriate amount of CF_3I (5 to 10 mmoles) was condensed into it.

Results

The dissociation pressure of the $D:CF_3I = 2:1$ mixtures were measured at different temperatures below 0°C, so that the vapor pressure of the free donor solvent could be neglected. The reaction

$$2D_{(l)} + ICF_{3(l)} \rightleftarrows D_2ICF_{3(l)};\ \Delta H_1;\ K_1$$

is regarded as algebrical combination of the reactions:

$$CF_3I_{(l)} \rightleftarrows CF_3I_{(g)};\ \Delta H_2;\ K_2$$

and

$$CF_3I_{(g)} + 2D \rightleftarrows D_2ICF_{3(l)};\ \Delta H_3;\ K_3$$

From $1/K_3 = \dfrac{p_{CF_3I} \cdot a^2_{D(l)}}{a_{D_2ICF_3(l)}}$ with a_D and $a_{D_2ICF_3}$ constant and the van't Hoff equation$-\dfrac{d\ln K_3}{dT} = \dfrac{\Delta H_3}{RT^2}$ one obtains $-\dfrac{d\ln p_{FC_3I}}{dT} = \dfrac{\Delta H_3}{RT^2}$.

Straight lines are obtained in the plot of log p_{CF_3I} *vs.* 1/T which are represented by the equations

$$\log p = \frac{A}{T} + B$$

The coefficients A and B are reported in Table I together with the ΔH_1 values for D–CF_3I interactions. The ΔH_1 values are plotted *vs.* the donicity of D in Figure 1.

Table I.

Donor	A	B	ΔH_1
HMPA	2.450	9.05	5.94
Py	1.795	7.60	3.00
DEA	1.710	7.12	2.62
DEF	1.615	6.96	2.17
DMSO	1.485	6.65	1.59
DMA	1.410	6.62	1.22
PDC	1.500	6.21	0.05
DE	985	5.48	–0.70

The position of the ^{19}F NMR resonance signal of CF_3I in the pure liquid state is found at 5.15 ppm relative to CCl_3F as external standard. When CF_3I is dissolved in a solvent, a different ^{19}F chemical shift is observed, which depends both on the nature of D and on the concentration of CF_3I as it is shown in Figure 2 and 3 respectively.

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(1) N.F. Cheetham and A.D.E. Pullin, *Chem. Comm.*, 418 (1965).
(2) N.F. Cheetham and A.D.E. Pullin, *Chem. Comm.*, 233 (1967).
(3) A.N. Larsen and A.L. Allred, *J. Phys. Chem.*, *69*, 2400 (1965).
(4) R.N. Haszeldine, *J. Chem. Soc.*, 584 (1951).
(5) V. Gutmann, Coordination Chemistry in Non-Aqueous Solutions Springer-Verlag, Wien, New York (1968).

Conclusions

Quantitative calorimetric measurements of the interactions between D and CF_3I were not attempted because of the difficulties of handling the very volatile trifluoroiodomethane. The ΔH_1 values for the interactions were obtained from vapor pressure data, as reported in the preceeding section. With weak donor molecules no substantial interactions occur. The plots of ΔH_1 *vs.* the donicity of the donor solvent[5,6] show that with stronger donors the ΔH_1-values rise sharply with increasing donicity of D and for DMA, DMSO, DEF, DEA, Py, and HMPA the relationship between ΔH_1 and DN is such that nearly a straight line is obtained (Figure 1).

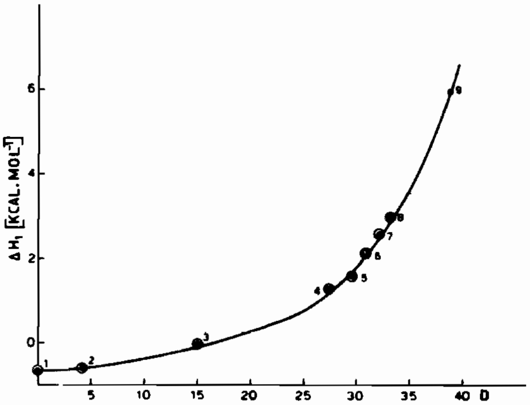

Figure 1. ΔH values *vs.* the donicity of D: 1,2-Dichloroethane (1), Nitrobenzene (2), Propanediol-1,2-carbonate (3), N,N-Dimethylacetamide (4), Dimethyl sulphoxide (5), N,N-Diethylformamide (6), N,N-Diethylacetamide (7), Pyridine (8), Hexamethylphosphoramide (9).

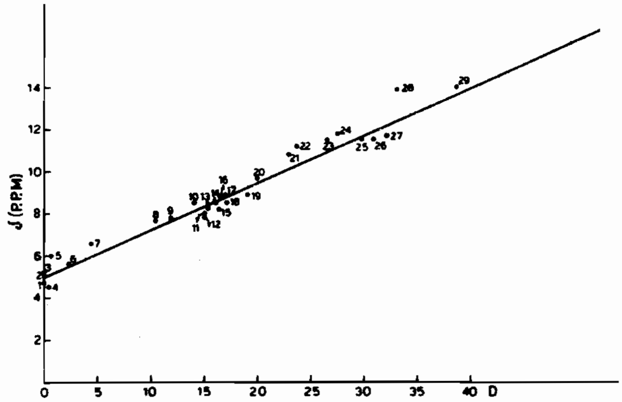

Figure 2. ^{19}F-NMR chemical shifts at infinite dilution of CF_3I in the donor solvent D *vs.* donicity of D=

1 pure CF_3I
2 1,2 Diechloethane
3 Sulphpryl chloride
4 Thionyl chloride
5 Acetyl chloride
6 Benzoyl chloride
7 Nitrobenzene
8 Acetic Anhydride
9 Benzonitrile
10 Acetonitrile
11 Propanediol-1,2-carbonate
12 Benzyl cyanide
13 iso-Butyronitrile
14 Propionitrile
15 Ethylene carbonate
16 Methylacetate
17 Acetone
18 Ethylacetate
19 Diethylether
20 Tetrahydrofurane
21 Trimethyl phosphate
22 Tributhyl phosphate
23 Dimethylformamide
24 N,N-Dimethylacetamide
25 Dimethyl sulpoxide
26 N,N-Dietylformamide
27 N,N-Dietylacetamide
28 Pyridine
29 Hexamethylphosphoramide

The stronger interaction of CF_3I with D of increasing donicity is also demonstrated by the evaluation of the NMR data. At very diluited solution of CF_3I in a donor solvent two effects appear to contribute to the actual chemical shift, namely

(a) the change in bulk diamagnetic susceptibility of the solvent,

(b) the extent of interaction between D and CF_3I.

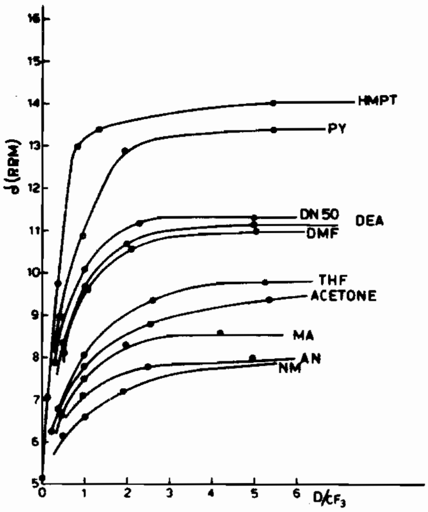

Figure 3. ^{19}F-NMR chemical shifts of the system D-ICF_3 referred to CCl_3F as external reference at different molar ratios D-CF_3I.

The magnitude of the shifts observed when CF_3I is dissolved in a donor solvent D cannot be accounted for by considering only the bulk susceptibility difference between CF_3I and D. This shift calculated according to[7]

$$\frac{2}{3}\pi(\chi_{CF_3I}-\chi_D)$$

is found smaller than ± 1 ppm in this particular case.

The correlation between ^{19}F chemical shifts and the electronegativities of the atoms or groups to which fluorine is bonded[8] leads to a shift of the ^{19}F resonance signal at higher field, when F is attached to less electronegative atoms or groups. Thus an increase in electron density at the fluorine atoms produces a shift towards higher field.[8]

The coordination of D at the iodine atom of CF_3I is expected to lead to an increase in electron density at the fluorine atoms:

$$D+I{-}CF_3 \rightarrow D{\rightarrow}IC{-}F_3$$

and this is in accordance with the observed shifts of the ^{19}F resonance signal to higher field.

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It may further be expected that a relationship exists between the ^{19}F chemical shift of CF_3I and the donicity of D. Figure 2 reveals that there is a linear relationship between the donicity of D and the chemical shift.

Figure 3 shows that for a molar ratio $D:CF_3I = 2:1$ the chemical shift has reached a value, approaching that at infinite dilution provided that D is a strong donor possibly due to the interaction:

$$2D + ICF_3 \rightleftarrows D_2ICF_3$$

With a solvent of low donicity a higher $D:CF_3I$ ratio is required to obtain the final value for the chemical shift, since $D_2 . CF_3I$ adducts are appreciably dissociated into D and CF_3I.

The results are unequivocal proof that in this particular system the formation of the charge transfer complex is a function of the donor properties of D as expected by the donicity and not, as has previously been assumed by the ionization potential of the donor molecule.[9] It may be expected that the relationship will be valid for the formation of other charge-transfer complexes of the $n-\sigma$-type, where no change in the oxidation numbers of the atoms in the species of the system are involved.[10,11]

For strong $D-ICF_3$ interaction, ionization is expected to occur. In the systems under investigation no ionization was however observed as long as no light was admitted. Only in the presence of light the $D-CF_3I$ systems in nitrobenzene gave conducting solutions for D = DMSO, Py, or HMPA and the conductivities were found to increase with time. Electrolysis of these conductive solutions gave iodine at the cathode, indicating the presence of iodine in the +1 oxidation state in solution. The nature of the ionic species in the solutions has not been established.

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