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SOLVENT EFFECT ON CARBONYL ^{13}C HYPERFINE SPLITTING OF FREE ANION RADICAL OF 9-FLUORENONE: A MEASURE FOR ANION SOLVATION POWER OF APROTIC SOLVENTS

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The carbonyl ^{13}C splitting of the free anion radical of 9-fluorenone was examined with eight solvents including pyridine to exhibit a large solvent dependence: 3.20 gauss in dimethylsulfoxide to 1.76 gauss in hexamethylphosphoric amide. A linear relationship between Gutmann's acceptor number (AN) and ^{13}C splitting (a_c), as expressed by a_c=0.16 AN + 0.06 (gauss), was found.

ESR studies of anion radicals in solution, produced by alkali metal reduction of aromatic compounds, have been carried out using a number of aprotic solvents which are characterized by strong cation and weak anion solvation. From ESR spectroscopic point of view little attention has been paid for the effect of anion solvation on the spin distribution of anion radicals. Recently, however, when dipolar aprotic solvents (dielectric constant $>$ 15),$^{1)}$ such as hexamethylphosphoric amide (HMPA), dimethylsulfoxide (DMSO), or dimethylformamide (DMF), were used to obtain the ESR spectra of the free anion radicals of nitrobenzene and 9-fluorenone, the solvent dependences of the nitrogen and carbonyl ^{13}C splittings of the free anions were found.$^{2-5)}$ These observations suggest that the interaction of dipolar aprotic solvents with anions containing electron withdrawing groups is enhanced by the accumulation of negative charge on the groups and that the state of solvated free anion is considerably different from that of the unsolvated free anion.

On the basis of the solvent effect of the ^{13}C carbonyl splitting of the free 9-fluorenone anion radical, this communication intends to characterize aprotic solvents with respect to anion solvation power and to estimate the ^{13}C splitting free from the interaction of cation and solvent.

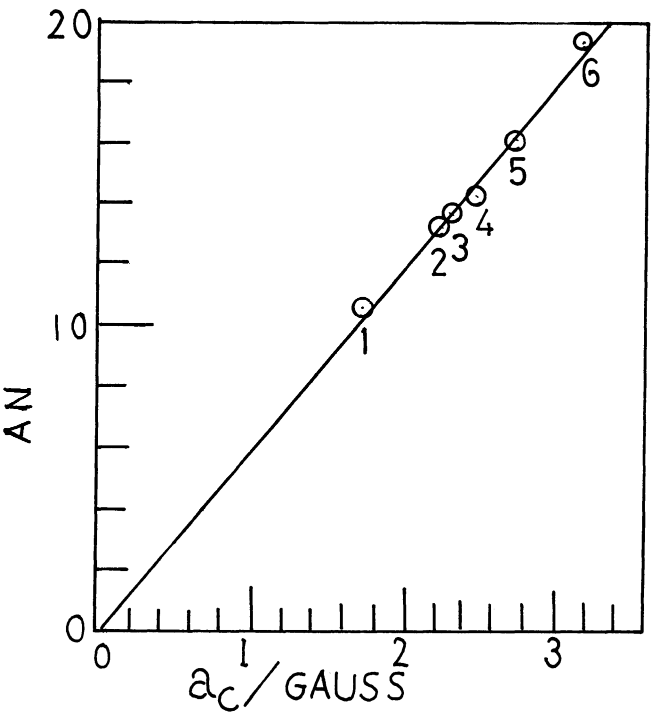
The free fluorenone anion radical is prepared in eight aprotic solvents;[6) pyridine, HMPA, DMF, DMSO, N-methyl-2-pyrolidone (NMP), dimethylacetoamide (DMA), dimethylpropionamide (DMP), and diethylpropionamide (DEP). Except for pyridine (dielectric constant=12.3 at 25°C), these solvents are classified as dipolar aprotic solvents and the ESR spectra consist of that of the free anion alone in concentrations lower than 10^{-3} M. In pyridine, on the other hand, the ESR spectrum shows the equilibrium of the free anion and ion pair down to 10^{-5}M. As listed in Table 1, the ^{13}C splittings obtained exhibit appreciable solvent dependence: 3.20 gauss in DMSO to 1.76 gauss in HMPA. Especially the value in DMSO is comparable to that of the ion pair with a large cation (for example the splitting of the cesium ion pair is 3.80 gauss in tetrahydrofuran at 20°C). This implies that the anion solvation energy of DMSO can not be ignored in comparison with the interaction energy of the ion pair, since it is known that the ^{13}C splitting increases with increasing cationic field acting on the carbonyl oxygen atom.2,3) As seen from a series of DMF, DMA, and DMP, the splitting is reduced with an increase in size of the negative end of solvent dipole. Contrary to the dissociation step of the ion pair, the ^{13}C splitting is not well correlated to dielectric constants of solvents. For example, the solvation of pyridine gives rise to greater perturbation on the spin distribution of the anion than the solvation of HMPA (dielectric constant=28). The temperature dependence of the ^{13}C splitting was also examined. Irrespective of solvent, the splitting is increased with lowering of temperature. For example, the values of the pyridine solution are: 2.42, 2.65, and 2.85 gauss at 20, -10, and -30°C, respectively.

Recently Gutmann proposed Acceptor Number (AN) to classify the anion solvation power of solvents on the basis of solvent dependence of the ^{31}P NMR chemical shift of triethylphosphate: The greater AN of solvent corresponds to the stronger anion solvation power.7-9) When AN of a solvent is correlated to the ^{13}C splitting in the solvent, there is a good linear relationship between AN and the ^{13}C splitting (a_c), as shown in Fig. 1. According to the least square method, a_c is explained by Eq. (1)

$$a_c = 0.16\ \mathrm{AN} + 0.06 \quad \text{(gauss)} \qquad (1)$$

where 0.06 gauss corresponds to the ^{13}C splitting in the hexane solution (AN of hexane is defined as zero). Since hexane is a very inert solvent, the splitting of the unsolvated anion will be comparable to that in the haxane solution, being close to zero gauss. Using Eq. (1) the AN of DMP and DEP which have not yet apperaed in the literature can be estimated as listed in Table 1. Thus, the ^{13}C splitting of the free

Fig. 1. Linear relation between acceptor number (AN) and ^{13}C splitting (a_c).



Solvent: 1: HMPA, 2: NMP, 3: DMA, 4: pyridine, 5: DMF, 6: DMSO.

Table 1. Solvent dependence of ^{13}C splitting (a_c).

solvent	a_c(gauss)	acceptor number[a) (AN)
HMPA	1.76[b)	19.3
DEP	2.04	(12.4)
DMP	2.13	(12.9)
NMP	2.24	13.3
DMA	2.30	13.6
pyridine	2.47	14.2
DMF	2.75[c)	16.0
DMSO	3.20	19.3

a): Reference 8).
b): Reference 3).
c): Reference 2).
HMPA: hexamethylphosphoric amide.
DEP: N,N-diethylpropionamide.
DMP: N,N-dimethylpropionamide.
NMP: N-methyl-2-pyrolidone.
DMA: N,N-dimethylacetoamide.
DMF: N,N-dimethylformamide.
DMSO: dimethylsulfoxide.
AN in parentheses is estimated by using Eq. (1).

anion in a solvent can be used as a measure of its anion solvation power. The possible explanation for the existence of the good correlation between AN and the ^{13}C splitting is as follows. Approaching of the positive part of solvent dipole to the oxygen atom of the carbonyl or PO group can inductively reduce the electron density around the carbon or phosphorous nucleus respectively. This reduction leads to the increase of the ^{13}C splitting or the lower field shift of ^{31}P NMR which is related to the increase of AN by Gutmann. Thus, the same mechanism would be responsible for the increase of both AN and ^{13}C splitting. According to the above consideration, the interaction between anion and solvent molecules is rather specific, and when the ion pair is formed the cation excludes most of solvent molecules from the vicinity of the oxygen atom; consequently the interaction of the anion with solvent molecules is greatly reduced. It should be noted that the change of the ^{13}C splitting on forming the ion pair consists of an positive increment arising from the interaction of the anion with the cation and a negative increment from the reduction of anion solvation. As far as the fluorenone anion concerned, the latter increment can not be negligible and the actual increase of the ^{13}C splitting due to the formation of the ion pair is considerably larger than the apparent one.

References and notes

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6) The anion radical was prepared as follows: In general the fluorenone anion radical was produced with alkali metal reduction (Na or K) in tetrahydrofuran (THF). After evaporation of THF, the solvent under study was added. Except for DMSO, pyridine, and DMF, the direct contact of fluorenone with alkali metal in these solvents could also produce the desired anion radical. All operation was carried out under high vacuum. The fluorenone anions in these solvents were stable for longer than one month to allow ESR measurement.

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