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THE EFFECTS OF SOLVENTS ON CARBON-13 CHEMICAL SHIFTS OF THE CARBONYL CARBON SYSTEM

Shinichi Ueji*
Institute of Chemistry, College of General Education, Kobe University,
Tsurukabuto, Nada, Kobe 657, Japan
and
Michiko Nakamura
Department of Chemistry, Faculty of Science, Kobe University,
Rokkodai, Nada, Kobe 657, Japan

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Concerning the effects of solvents on carbon-13 chemical shifts of carbonyl carbons, extensive discussions have been done in the literature.[1-3] Surprisingly little work, however, has been reported on the investigation into the correlation between the solvent effects on ^{13}C chemical shifts and on infrared frequency shifts. In the present work the ^{13}C chemical shift changes of the carbonyl carbon system have been studied in a range of solvents having the G-values. The G-value is the solvent constants empirically assingned to solvents by Allerhand and Schleyer[4] in order to explain the behaviour of i.r. frequency shifts. It would be expected to show large changes in both ^{13}C chemical shift and i.r. frequency shift depending upon solvent. This is the reason why the carbonyl carbon system was selected for this study.

Table summarizes the changes in both ^{13}C chemical shift and i.r. frequency shift of the carbonyl carbon system (I) - (III) as a function of solvent. The ^{13}C chemical shifts in Table appear to become greater with an increase in the G-value. In fact the ^{13}C chemical shifts are found to be linearly correlated by the G-value except for acetonitrile (Figure). The success of G-plot means that the ^{13}C chemical shifts show a linear correlation with the i.r.

frequency shifts [(I) $\delta^{13}C = 0.24\Delta\nu - 0.02$, (II) $\delta^{13}C = 0.22\Delta\nu - 0.24$, (III) $\delta^{13}C = 0.55\Delta\nu - 0.57$, from Table] and that the G-value becomes a convenient measure of solvent dependence of ^{13}C chemical shifts. Furthermore, this fact implies that the magnetic anisotropy of solvent molecule can not directly affect the C=O stretching frequency.

Table. The ^{13}C chemical shifts[a)] and i.r. frequency shifts[b)] for carbonyl carbon system as a function of solvent

	G-value	Acetophenone(I)		Cyclohexanone(II)		Acetone(III)[c)]	
Solvents		$\delta^{13}C$	$\Delta\nu$	$\delta^{13}C$	$\Delta\nu$	$\delta^{13}C$	$\Delta\nu$
(1) Hexane	44	0.00	0.0	0.00	0.0		
(2) Cyclohexane	49	0.31	1.2	0.13	1.7		
(3) Diethyl ether	64					0.0	0.0
(4) Carbon tetrachloride	69					0.7	2.0
(5) Toluene	74	1.20	6.1	1.58	7.3		
(6) Benzene	80	1.75	7.2	1.64	10.1	1.2	3.8
(7) Dioxane	86	2.54	8.9	2.61	10.6	2.0	5.9
(8) Methyl iodide	89					2.0	5.9
(9) Acetonitrile	93	3.76	10.2	4.07	17.4	4.1	6.0
(10) Dichloromethane	100	2.97	12.0	3.88	18.2		
(11) Chloroform	106	3.40	14.3	4.19	21.0	4.3	9.0

a) $\delta^{13}C$ (p.p.m.) corresponds to downfield shift from hexane; Reproducibility 0.05 p.p.m. (JNM PS-100 spectrometer); [Solute] ca. 10 mol%.

b) $\Delta\nu$ (cm^{-1}) = ν(hexane) - ν(solvent); Maximum error ± 0.5 cm^{-1}(JASCO DS-402G spectrometer).

c) The ^{13}C chemical shifts taken from Ref. 1; $\delta^{13}C$ and $\Delta\nu$ relative to diethyl ether.

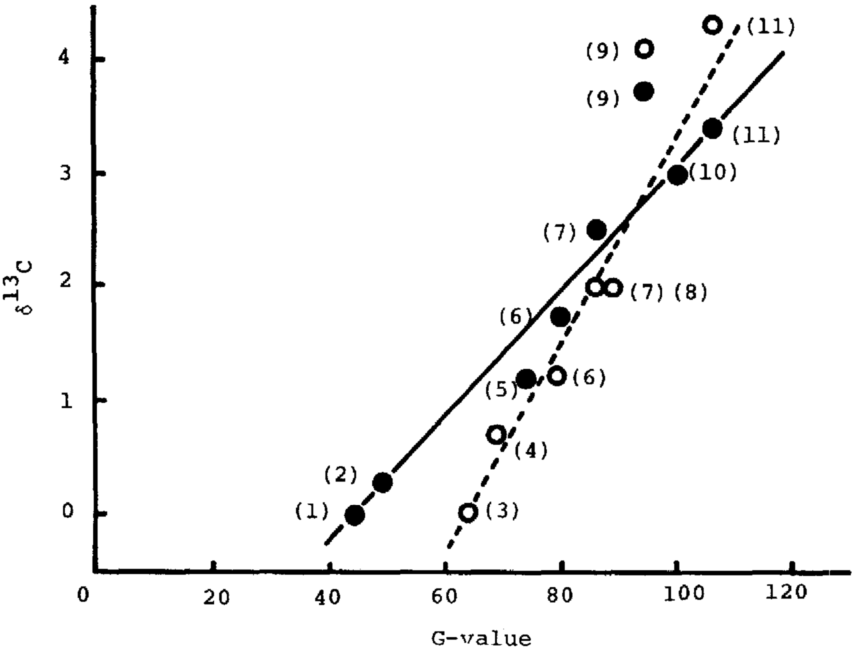


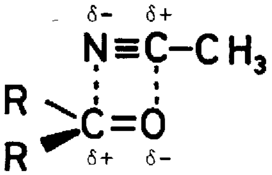
Figure. Correlation between ^{13}C chemical shifts and G-value of the solvents (●, acetophenone; ○, acetone.)

As can be seen in Figure, acetonitrile solvent shows a significant deviation. It is well known that paramagnetic term is the dominate factor in producing most ^{13}C chemical shift changes. However, in cases where the strong solute-solvent interaction such as local association due to H-bonding or dipole-dipole complex is expected, the ^{13}C chemical shifts may be strongly affected by the magnetic anisotropy of solvent molecule. For this reason, the deviation from the G-plot appears to arise from the anisotropy effect of C≡N bond due to local ordering of acetonitrile molecule around the carbonyl group. This possibility can be interpreted by assuming dipolar complex as shown in Scheme. The direction of deviation is consistent with the anisotropy effect of C≡N bond as anticipated from the assumed association model. A similar geometry for dipolar complex was found in the association of polar group such as benzonitrile - dimethyl sulfoxide complex.[5]

Both benzene and toluene molecules also contain strong anisotropy effect, but these solvents show no marked deviation in contrast to acetonitrile solvent. In these aromatic solvents, since the solvation is mainly due to relatively weak association such as dipole-induced dipole[6] or dipole-quadrupole[7] type, one possible explanation is that these solvent molecules remote from the carbonyl group may be disfavourable for the anisotropy effect on ^{13}C chemical shifts.

From the correlation between the G-value and the ^{13}C chemical shifts, it is found that the G-value can explain the charge polarization and variation in bond order included in paramagnetic term, but not a characteristic anisotropy effect in nmr study. The marked deviation from the G-plot, therefore, may be important. It is thus concluded that for the carbonyl carbon system studied here the G-value becomes a convenient measure of the solvent dependence of ^{13}C chemical shifts except for special case.

Scheme



R; Substituent

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References

1) G. E. Maciel and J. J. Natterstad, J. Chem. Phys., 42, 2752 (1965).
2) G. L. Nelson, G. C. Levy and J. P. Neilan, J. Amer. Chem. Soc., 94, 3089 (1972).
3) T. H. Whitesides and J. P. Neilan, J. Amer. Chem. Soc., 97, 908 (1975).
4) A. Allerhand and P. von R. Schleyer, J. Amer. Chem. Soc., 85, 371 (1963).
5) C. D. Ritchie and A. L. Pratt, J. Amer. Chem. Soc., 86, 1571 (1964).
6) W. G. Schneider, J. Phys. Chem., 66, 2653 (1962).
7) K. Nikki, N. Nakahata and N. Nakagawa, Tetrahedron letters, 3811 (1975).