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Solvent effects on infrared spectra of 2-methyl-4, 5-dimethoxy-3-oxo-2H-pyridizine: Part 1. Single solvent systems

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Abstract: Infrared spectroscopy studies of 2-methyl-4, 5-dimethoxy-3-oxo-2H-pyridizine (MDOP) in 12 pure organic solvents were undertaken to investigate the solvent-solute interactions. The frequencies of the carbonyl ($C=O$) of MDOP were correlated with solvent properties such as solvent acceptor number (AN) and the linear solvation energy relationships (LSER). These frequencies showed a good correlation with the solvent acceptor number (AN) and the LSER.

Key words: Infrared spectroscopy, Solvent effects, Correlation analysis, Solvent-solute interaction
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INTRODUCTION

Solvent effects play an important role in organic reactivity phenomena such as the chemical equilibrium, the rate of chemical reactions and the polymerization conversions (Hu et al., 2000) and so on. Organic chemists usually tried to explain the solvent effects by some physical properties of solvents.

It is well known that the frequencies of many vibrational modes depend not only on the molecular structure, but are also markedly affected by environmental factors. The infrared frequency shifts in dilute solutions reflect the solvent-solute interactions.

2-methyl-4, 5-dimethoxy-3-oxo-2H-pyridizine (MDOP) (Fig. 1) as the intermediate of fungicide and herbicide is an interesting molecule which can be used for mimicking protein interactions (Jan et al., 1993). Data obtained on the frequencies of the carbonyl stretching vibration $v(C=O)$ of MDOP in different solvents were correlated with the solvent acceptor numbers (AN) (Mayer, 1979) and the linear solvation energy relationships (LSER) (Kamlet, 1983; Reichardt, 1979).

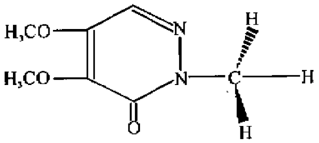

Fig. 1　Scheme of 2-methyl-4, 5-dimethoxy-3-oxo-2H-pyridizine

THEORIES

The solvent acceptor number (AN)

The acceptor number (AN) of a solvent was developed by Gutmann (Gutmann, 1978; Mayer, 1979) from the ^{31}P-NMR chemical shifts of triethylphosphane oxide (Gutmann, 1978) to study the solvent effects, and is reportedly a measure of the electrophilicity of the solvent.

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$$AN = [\delta(\text{solv}) - \delta(\text{hexane})] \times 2.348 = \Delta\delta \cdot 2.348 \quad (1)$$

δ(solv) and δ(hexane) are the ^{31}P-NMR chemical shifts of triethylphosphane oxide in a solvent and in hexane, respectively.

The solvent acceptor numbers (AN) have been found to be useful in the prediction of δ ^{13}C chemical shifts and infrared vibrational band shifts in different solvents for some simple molecules (Wohar, 1988). The infrared vibrational band shifts is shown in Eq.(2).

$$v = v_o + K \times AN \quad (2)$$

v_o is the infrared vibrational frequency of a solute in hexane. K is the sensitivities of infrared vibrating frequency v to the solvent acceptor numbers (AN).

The linear solvation energy relationships (LSER)

It can be shown that the correlations of equilibria and spectral properties are indeed significantly improved by multiparameter treatment which implicitly allows for various independent interaction mechanisms between solvent and solute ground transition and excited states. It was suggested that the solvatochromic solvent parameters α, β, and π^* could be used in the multiparameter equation proposed expressing so-called linear solvation energy relationships (LSER) (Kamlet, 1983).

$$v = v_0 + (s\pi^* + \mathrm{d}\delta) + a\alpha + b\beta \quad (3)$$

v_o and v are the infrared vibrating frequencies of a solute in cyclohexane and in a solvent respectively. π^* is an index of solvent dipolarity/polarizability which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect. δ is a discontinuous polarizability correction term for poly-chlorinesubstituted aliphatics and aromatic solvents. α is a measure of the solvent hydrogen-bond donor (HBD) acidity. It describes the ability of a solvent to accept an electron pair (or, vice versa, donate a proton) in a solvent-solute interaction. β is a measure of the solvent hydrogen-bond acceptor (HBA) basicity. It describes the ability of a solvent to be donor of an electron pair (or, vice versa, accept a proton) in a solvent-solute interaction.

EXPERIMEMTAL DETAILS

Material

2-methyl-4, 5-dimethoxy-3-oxo-2H-pyridizine (MDOP) was twice crystallized. All solvents were either of analytical or spectroscopic purity and were distilled prior to use. The concentrations of the solute in the pure solvents were 1.0×10^{-4} to 1.5×10^{-4} mol/L.

Spectroscopy

Infrared spectra were recorded on a Nicolet Nexus 670 FTIR spectrometer with a Ge/KBr beamsplitter and a DTGS detector. Sixty-four scans of all spectra recorded at 1 cm^{-1} resolution were averaged. Spectra were measured using 0.5 mm pathlength NaCl cells.

Analysis of spectra

In the case of strongly overlapping bands in the solution spectra, interactive spectral subtraction was performed. The Nicolet Omnic software Version 5.2 was used for all data manipulation. The data files were transferred to a computer for analysis using a digital curve-fitting program (origin 5.0).

RESULTS AND DISCUSSION

Table 1 lists the frequencies of the carbonyl stretching vibrations (v(C=O)) of MDOP in 12 solvents. The solvent acceptor number (AN)(Mayer, 1979) and the solvent parameters of LSER (α, β, δ, π^*) (Kamlet, 1983) are given for the solvents where the values are available.

Solvent acceptor number(AN)

Fig.2 is a plot of v(C=O) for MDOP versus the solvent acceptor number (AN). The linear regression equation from Fig. 1 shows good linear correlation between the data and AN(R = 0.98). The points for the v(C=O) band almost fall on the linear regression line and the carbonyl stretching bands decrease in frequency with the increase of the solvent acceptor number (AN). The result indicates that the solvent acceptor number is applicable to not only NMR chemical shifts but also the solvent-induced stretching frequency shifts in infrared spectra.

$$v(C=O)=1654.27-0.71881\,AN \quad (4)$$
$$R=0.98 \quad SD=1.32\text{cm}^{-1}$$

Table 1 The $\nu(C=O)$ and solvent parameters

No.	Solvent	$v(C=O)^a$	AN	β	α	π^*	δ	$v(C=O)^b_{cal}$	Δv^c
1	Chloroform	1636.34	23.1	0	0.44	0.58	0.9	1636.37	0.03
2	Dichloromethane	1639.51	20.4	0	0.3	0.82	0.19	1639.64	0.13
3	1,2-dichloroethane	1641.73	16.7	0	0	0.81	0.6	1641.91	0.18
4	Acetonitrile	1643.24	18.9	0.31	0.19	0.75	0	1643.04	−0.20
5	1,4-dixone	1646.65	10.8	0.37	0	0.55	0	1646.16	−0.49
6	Benzene	1646.93	8.2	0.1	0	0.59	0	1646.71	−0.22
7	Tetrahydrofuran	1648.74	8.8	0.55	0	0.58	0	1647.78	−0.96
8	Toluene	1648.63	−	0.11	0	0.54	0	1648.34	−0.29
9	Tetrachloromethane	1646.64	8.6	0	0	0.28	0.9	1646.46	−0.18
10	Diethyl ether	1651.51	3.9	0.47	0	0.27	0	1651.23	−0.28
11	Cyclohexane	1654.16	0	0	0	0	0	1654.34	0.18
12	n-hexane	1655.17	0	0	0	−0.08	0	1655.23	0.06

[a] the frequencies of the carbonyl stretching vibration of MDOP. measured by experiment; [b] calculated from Eq(5); [c] $\Delta v = v(C=O)_{cal} - v(C=O)$

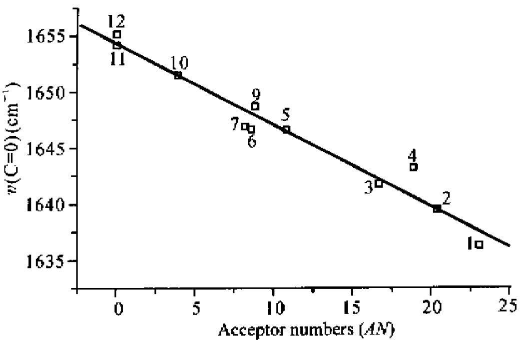

Fig.2 A plot of $\nu(C=O)$ vs the solvent acceptor number (AN).

Linear solvation energy relationships (LSER)

Besides the solvent's dielectric effects (measured by π^*), solvent molecules interact directly with the carbonyl via two kinds of attractive forces (Fig. 3). The first attractive force induces the solvent as Lewis acid (measured by α) to form a hydrogen bond with the oxygen atom of the carbonyl. The second causes the solvent, which has electronegative atoms, such as O, N, S, X(F, Cl, Br, I), to interact as Lewis base (measured by β) with the positive carbon atom of the carbonyl owing to nucleophilic attack of electronegative atoms.

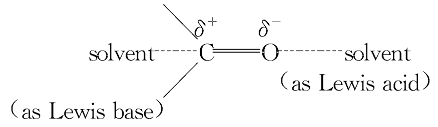

Fig. 3 Both interactions between solvent molecules and the carbonyl.

$v(C=O)$ data and solvent parameters for the 12 kinds of solvent systems in Table 1 were used to compute Eq(5)'s the LSER regression coefficients(correlation coefficients $R=0.99$, standard deviation is 0.71cm^{-1}), showing excellent correlationship. The infrared vibrational frequencies calculated by Eq. (5) and listed in Table 1 deviated very little from the experimentally obtained frequencies.

$$v(C=O) = 1654.34 - 0.25\beta - 15.40\alpha - (11.06\pi^* + 5.32\delta) \quad (5)$$
$$R=0.99 \quad SD=0.71\text{cm}^{-1}$$

How solvents interact with the carbonyl can be determined from the coefficients of Eq.5. The v(C=O) shifts being the most sensitive to the solvent acidity (α) means that the hydrogen bond between solvent and the carbonyl has the strongest influence on the solvent-induced stretching frequency shifts. Therefore, the frequencies of the carbonyl stretching band are lower in dichloromethane and chloroform owing to the hydrogen bonding. The influence of the solvent basicity (β) on the solvent-induced stretching frequency shifts is negligible. This indicates that the interaction between the electron-donor solvent and the positive carbon atom is very weak. For aproton solvents, the solvent dipolarity/polarizability (π^*) plays a major role in interaction between solvent and the carbonyl.

CONCLUSIONS

There was good correlation between the carbonyl vibration frequencies and the solvent acceptor number (AN). Though the solvent acceptor number (AN) is simple for application, a physically meaningful explanation of solvent-induced stretching frequency shifts can not be obtained.

The observed excellent correlation between the carbonyl stretching frequencies and the LSER parameters of the solvents enables the prediction of the frequency of the carbonyl stretching band of MDOP in other solvents if the LSER parameters of these solvents are obtained. It indicates that the linear solvation energy relationships (LSER) are quantitatively accurate and provide physically meaningful explanation for solvent-induced stretching frequency shifts.

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