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SOLVENT EFFECTS ON THE C=O AND THE S=O STRETCHING VIBRATIONS IN CYCLOPROPANONE AND IN ETHYLENE EPISULFOXIDE

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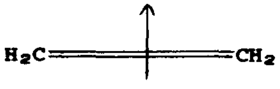
The shift to lower carbonyl stretching frequencies in ketones with increasing solvent polarity has been attributed to the stabilization of the dipolar structures (1). Hydrogen bonding with protonic solvents (2-6) also lowers the carbonyl stretching frequency. Presently all reported carbonyl shifts are to lower frequencies with an increase in solvent polarity. The same is also true for the S=O bond in sulfoxides (7).

We wish to report that the stretching frequencies (8) in cyclopropanone, $(CH_2)_2C=O$, and in ethylene episulfoxide, $(CH_2)_2S=O$, both shift to higher frequencies in more polar solvents. The data are presented in Table I.

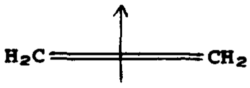
The shift to higher frequencies seems to be a characteristic property of the three-membered ring ketone. Thus, cyclobutanone and ketene show the same solvent behavior as does acetone. The carbonyl shift in cyclopropanone is not due to molecular association and/or hydrogen bonding since the values are independent of the concentration.

The $(CH_2)_2X=Y$ system is rather unique. Based on spectroscopic and dipole moment data, Walsh has suggested dipolar structures for cyclopropane and ethylene epoxide (9, 10).



(I)

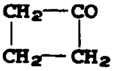
(Ia)



(II)

TABLE I

Stretching Frequencies in cm.$^{-1}$

		SOLVENT				
Compound	Vapor	n-C_6H_{14}	CCl_4	$CHCl_3$	CH_2Cl_2	ETHER
$(CH_2)_2CO$	1815[a]	1817	1822[e]	1823	-	1825
$(CH_2)_2SO$	1050 1065(sh)	1056 1065 (sh)	1062 (sh) 1078	1050 (sh) 1074	1057 1068	- -
	1816[b]	1798	1790	1774	-	-
$(CH_3)_2CO$[c]	1738	1724	1719	1713	-	1721
$CH_2=C=O$	1251[d]	2140	2138	2136	-	2130

All spectra were recorded at 24±0.5°C using calibrated spectrometers (Perkin-Elmer 421 and Hitachi-Perkin-Elmer 125) (sh, shoulder).

a) W. B. DeMore, H. O. Pritchard and N. Davidson, J. Am. Chem. Soc., 81, 5874 (1959).

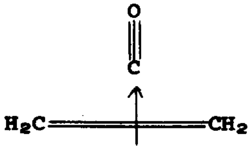
b) K. Frei and Hs. H. Gunthard, J. Mol. Spec. 5, 218 (1960).

c) L. J. Bellamy and R. L. Williams, Trans. Faraday Soc. 55, 15 (1959).

d) W. F. Arendale and W. H. Fletcher, J. Chem. Phys. 26, 793 (1957).

e) Note that this value in CCl_4 should be used rather than the value in the vapor. C. S. Foote, J. Am. Chem. Soc., 86, 1583 (1964).

The same type of structure (III) also can be used to represent the ground state of cyclopropanone. The more polar the solvent, the more important the polar canonical structure. Hence the carbonyl frequency shifts towards that



(III)

of carbon monoxide, 2143 cm.$^{-1}$ Another example of such a shift is that of the stretching vibration of the N=O bond in nitrosyl chloride. This has been explained by the increase in importance of the ionic canonical form: $(O\equiv\overset{+}{N})\ Cl^-$, in polar solvents (1). The triple bond forms as III (or $\overset{+}{O}\equiv N$) would have higher valence force constants.

Ethylene episulfoxide behaves in a somewhat different manner from cyclopropanone, but a definite shift to higher frequency can be observed by going from the vapor to solution and by changing the solvent from *n*-hexane to carbon tetrachloride. The shifts from carbon tetrachloride to chloroform and to dichloromethane could be due to hydrogen-bonding (7, 12, 13) or association. Variation of the concentration from 1.0 *M* to 0.02 M in CCl_4 shows that the shoulder (1062 cm^{-1} band) decreases at a faster rate than does the 1078 cm^{-1} band.

This suggests that the high frequency band is the monomer and the low frequency band is due to associated, mutually-solvated molecules. In the neat liquid there is only a broad band centered at 1042 $cm.^{-1}$

In the vapor phase the 1065 cm^{-1} band intensity of ethylene sulfoxide relative to the 1050 cm^{-1} band increases noticeably upon heating from 20° to 60°C. Similar association has been described for acetic acid (14). The solvent and temperature effects would seem to rule out a doublet due to Fermi resonance.

Conclusion — The unique electronic properties of the three-membered rings are observed in the infrared spectra of these molecules. The relevance of the cyclopropanone data to the vibrational behavior of the cyclopropyl cation will be discussed in further papers (15).

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8. Cyclopropanone was prepared by the reaction of diazomethane with ketene. Since it is known that carbon-carbon double bonds *exo* to small rings also absorb near the 1800 cm^{-1} region, NMR spectra were run on the solutions in carbon tetrachloride. No olefinic protons were observed; only a singlet at δ equal to 2.04 was seen in the spectra. Dilute solutions (1 to 5%) of cyclopropanone (better than 95% purity) were stable at -77°C but decomposed slowly with a half time of 30 minutes at room temperature. See footnote (a) of Table I. Refer to N. J. Turro and W. B. Hammond, *J. Am. Chem. Soc.*, **89**, 1028 (1967).

   The sulfoxide was prepared by careful oxidation with perbenzoic acid. The detailed procedure will be published by Ohno and coworkers. The compound obtained was of high purity. (> 99%) after repeated high vacuum transfers.

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15. This paper represents paper V in our series on Vibrational Effects. Paper IV. *Tetrahedron*, in press.