Maleic Anhydride–Benzene and Maleic Anhydride–Acetone Molecular Complexes

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Summary Concentration- and temperature-dependent n.m.r. chemical shifts, and concentration-dependent heats of dilution and solution, for maleic anhydride in acetone or benzene, are interpreted in terms of equilibria between monomers and solvent–solute molecular complexes, and these complexes are presumed to be involved in photocycloaddition reactions.

GROUND state molecular complexes may be involved in static quenching of excited states,[1] photodimerization of uracil derivatives,[2] and photodimerization of cyclohexadiene.[3] Excitation into the charge-transfer band of the ground state donor–acceptor complex of benzene with

maleic anhydride leads to photo-adduct formation.[4] However, in the case of photochemical oxetan formation from electron-deficient olefins and acetone, the possibility that ground state olefin–ketone complexes mediate the photochemistry has been dismissed,[5] since no evidence for charge-transfer complexes has been found in the u.v. spectra.

The n.m.r. chemical shift of maleic anhydride dissolved in either benzene or acetone is concentration- and temperature-dependent. Heats of solution and heats of dilution for maleic anhydride in either solvent are also concentration-dependent. The data can be interpreted with high precision in terms of equilibria between solvent, solute, and solvent–solute molecular complexes. The results are summarized in Tables 1 and 2. Δ_c in both Tables refers to

TABLE 1. Maleic anhydride–acetone molecular complex.

Result[a]	Experimental method	Correl. coeff.
$K = 1.37$ (mol fraction^{-1})	N.m.r. (39.8 °C)	0.992
$K = 1.58$ (mol fraction^{-1})	Heats of dilution (25.0 °C)	0.999
$\Delta H = -3.2$ kcal mol^{-1}	N.m.r. (temperature variation)	0.959
$\Delta S = -9.9$ cal mol^{-1} K^{-1}	van't Hoff equation	
$\Delta H = -3.63$ kcal mol^{-1}	Heats of dilution (25.0 °C)	0.999
$\Delta H = -3.73$ kcal mol^{-1}	Heats of solution (25.0 °C)	-0.999
$\Delta S = -11.3$ cal mol^{-1} K^{-1}	van't Hoff equation	
$\Delta_c = +48.0$ Hz	N.m.r. (39.8 °C)	0.992

[a] 1 cal = 4.184 J.

TABLE 2. Maleic anhydride–benzene molecular complex.

Result[a]	Experimental method	Correl. coeff.
$K = 2\cdot13$ (mol fraction^{-1})	N.m.r. (39·8 °C)	0·995
$\Delta H = -4\cdot2$ kcal mol^{-1}	Heats of solution (39·8 °C)	$-0\cdot999$
$\Delta S = -11\cdot7$ cal mol^{-1} K^{-1}	van't Hoff equation	
$\Delta_{\text{C}} = -118\cdot2$ Hz	N.m.r. (39·8 °C)	0·995

[a] 1 cal $= 4\cdot184$ J.

the chemical shift of maleic anhydride in the respective pure molecular complex, with the chemical shift of uncomplexed maleic anhydride taken as 403·2 Hz (60 MHz). The correlation coefficients refer to the fit of experimental results to the exact quadratic expressions that relate mole fractions of donor and acceptor to chemical shift[6] or calorimetric data.[7]

The tabulated results are in reasonable agreement with previous studies of the benzene–maleic anhydride system.[8] The consonant results by the two techniques support the assumption of the molecular complex model in the maleic anhydride–acetone case. In both systems, a substantial fraction of the maleic anhydride is present as complex under the reported conditions of photocycloaddition, e.g. 55% for acetone solutions.

The primary conclusion from this work is straightforward and is in agreement with the accepted description of the mechanism for benzene–maleic anhydride photocycloaddition.[9] Ground state complexes are important components of both solvent–solute systems investigated, and it is likely that these complexes are involved in the observed photochemical reactions.

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