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MOLECULAR COMPLEXES OF MALEIC ANHYDRIDE WITH ACETONE AND BENZENE[1]

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Abstract—Concentration and temperature-dependent NMR chemical shifts for maleic anhydride in acetone and benzene solution are interpreted in terms of equilibria between monomers and solvent–solute molecular complexes. Calorimetric heats of dilution and heats of solution give thermodynamic parameters that agree with those determined in the NMR experiments. The thermodynamic parameters obtained are similar for both systems, and it is possible that the previously established role of a ground state complex in the benzene–maleic anhydride photochemical cycloaddition reaction can be extended to the acetone–maleic anhydride photocycloaddition.

Static quenching of excited states due to ground state complex formation is a well-recognized phenomenon[3–5] and the bimolecular requirement for photocycloaddition supports suggestions that ground state complexes could be important components of such additions.[6] In previous papers, we have reported equilibrium constants and thermodynamic properties of donor–acceptor complexes[7] and molecular dimers[8] of ketones and aromatic hydrocarbons in CCl_4 solution using an NMR spectroscopic technique. The association constants were small ($K = 0.01–0.40\ M^{-1}$), and we concluded that these types of ground state interactions may not be significant in photochemical processes at low concentrations of reactants.

In this paper we describe two additional systems, maleic anhydride–benzene and maleic anhydride–acetone, that are of interest in organic photochemistry. In these studies one of the reactive components, acetone or benzene, acts as the solvent and is therefore present in relatively high concentrations. We interpret concentration dependent and temperature dependent chemical shifts for maleic anhydride as being due to formation of equilibrium concentrations of donor-acceptor molecular complexes.

Donor (D) (Acetone or benzene)	+	Acceptor (A) (Maleic anhydride)	$\rightleftharpoons$	Complex (C)

Concentration dependent heats of dilution and heats of solution, determined calorimetrically, are in agreement with the equilibria parameters obtained in the NMR experiments.

In both cases, a substantial fraction of the maleic anhydride is present as complex. It is therefore possible that these ground state complexes are involved in the photocycloaddition reactions that take place in these systems. For the maleic anhydride–benzene case this contention supports previous descriptions of the mechanism for photoaddition,[9–13] where excitation into the charge-transfer band has been shown to lead to photo-adduct formation,[9] and where triplet sensitizers are presumed to be quenched by ground state complexes.[11] In the general case of oxetane formation from electron-deficient olefins and acetone,[14–18] the possibility that ground state olefin–ketone complexes mediate the photoreactivity has been dismissed, since no evidence has been found in the ultraviolet spectra for ground state charge transfer complexes.[17,18]

EXPERIMENTAL

Materials. Maleic anhydride (Eastman Organic Chemicals) was recrystalized twice from benzene–CCl_4 and sublimed, m.p. 53°. Analytical grade acetone, benzene, and cyclohexane gave single peaks in NMR spectra and gas chromatograms at high sensitivities. They were used without further purification. Solutions were prepared gravimetrically.

NMR measurements. Spectra were obtained with a Varian A-60 NMR Spectrometer equipped with the V-6040 variable temp. controller. Before taking spectra, each sample was maintained at probe temp. in a constant temp. bath for about 30 min. Temperatures were measured using the Varian standard MeOH and ethylene glycol samples. The ambient probe temp. was 39.8°. Sweep time was controlled at 1 Hz per sec and the narrowest possible sweep widths were used in order to secure the most accurate measurements.

Calorimetric measurements. The calorimeter used in these experiments was the Tronac Model 450 Adiabatic Calorimeter equipped for batch operation or thermometric titration. Neoprene O-rings used to seal the 100 and 200 ml glass reaction vessels to the calorimetric assembly had to be preswelled with the organic solvent before each run. The solns were blanketed with nitrogen saturated with the organic solvent being used. The bridge sensitivity is $(1.0 \times 10^{-5})°$. The titrant delivery system was calibrated weekely, and the calorimetric system was periodically calibrated electrically against a platinum resistance thermometer. Frequent checks of the calorimeter against standard values for the heat of soln of EtOH and KCl in water,[19,20] and the heat of reaction for NaOHaq with HCl[21] were carried out. More details of the experimental procedures are given elsewhere.[22]

Analysis of the NMR data. The applicability of NMR chemical shift data[23] to the equilibrium depicted in eqn (1) depends upon the observation of a time-averaged chemical shift for a particular nucleus in two molecular environments.

$$\delta_A(\text{obs}) = \left[\frac{N_A{}^0 - N_C}{N_A{}^0}\right]\delta_A{}^0 + \left[\frac{N_C}{N_A{}^0}\right]\delta_C{}^0. \qquad (2)$$

In the present work, $\delta_A{}^0$ and $\delta_C{}^0$ are the shifts of maleic anhydride protons in uncomplexed and complexed form respectively, $N_A{}^0$ is the initial number of moles of maleic anhydride in the sample, and N_C is the number of moles of complexed maleic anhydride. Equation (2) can be rearranged to yield

$$\frac{N_C}{N_A{}^0} = \frac{\delta_A(\text{obs}) - \delta_A{}^0}{\delta_C{}^0 - \delta_A{}^0} = \frac{\Delta\,(\text{obs})}{\Delta_C}. \qquad (3)$$

Combining eqn (3) with the mole fraction equilibrium constant expression[24]

$$K = \frac{X_C}{X_A X_D} \quad (4)$$

leads to one of the algebraic expressions used to analyze NMR data obtained in this work.[25]

$$\frac{\Delta\,(\text{obs})}{X_D{}^0} = \frac{[\Delta\,(\text{obs})]^2 X_A{}^0}{\Delta_C X_D{}^0} + \frac{K\Delta_C}{1+K}. \quad (5)$$

The plot of $\Delta\,(\text{obs})/X_D{}^0$ vs $[\Delta\,(\text{obs})]^2 X_A{}^0/X_D{}^0$ gives a straight line whose slope and intercept determine values of Δ_C and the equilibrium constant. This equation has the advantage that no restrictions of concentrations limit its applicability as in Benesi–Hildebrand type equations,[26] but its use is confined to binary solns. A more complex treatment of the experimental data for the binary solns of benzene with maleic anhydride was required, and will be discussed later.

In solns where an inert solvent (cyclohexane) was mixed with the donor solvent, and the ratio of donor to maleic anhydride was large, an approximate equation was derived,

$$\frac{\Delta\,(\text{obs})(1 - X_A{}^0)}{X_D{}^0} = -K\Delta\,(\text{obs}) + K\Delta_C \quad (6)$$

where all symbols have the same meanings as in the previous equations. This equation is similar to previously derived equations[27,28] for treatment of complex formation constants. All data were treated by least squares regression analyses. All approximate equations were compared with a full treatment and tested with synthetic data to demonstrate their validity in the range of concentrations studied.

Analysis of the calorimetric data. Two types of experiments were carried out. In the first a conc soln of maleic anhydride was allowed to mix with pure donor solvent, and the heat of dilution Q(dil) was measured. If $N_C{}^0$ and N_C represent the number of moles of complexed maleic anhydride in the conc and dil solns respectively, then the heat associated with the dilution process is given by

$$Q(\text{dil}) = (N_C - N_C{}^0)\Delta H_R \quad (7)$$

where ΔH_R is the heat of complex formation. N_C and $N_C{}^0$ are related to the mole fraction equilibrium constant and to the respective number of moles of donor and acceptor molecules by quadratic expressions.

$$N_C = \frac{(N_A + N_D)}{2}\left[1 - \left\{1 - \frac{4KN_AN_D}{(1+K)(N_A+N_D)^2}\right\}^{1/2}\right] \quad (8)$$

$$N_C{}^0 = \frac{N_A{}^0 + N_D{}^0}{2}\left[1 - \left\{1 - \frac{4KN_A{}^0N_D{}^0}{(1+K)(N_A{}^0+N_D{}^0)^2}\right\}^{1/2}\right]. \quad (9)$$

In a series of dilution experiments, a single pair of values, ΔH_R and K, minimizes the sums of the squares of the deviation of calculated and observed Q's, $\Sigma[Q(\text{calc}) - Q(\text{obs})]^2$.

The second type of experiment involved determinations of the heat of soln of maleic anhydride in the donor solvents. If complex formation takes place the heat change associated with the dissolution is

$$Q(\text{sol}) = N_A{}^0\Delta H_S + N_C\Delta H_R \quad (10)$$

where ΔH_S is the heat of solution and the other symbols retain their previous meanings. Given a value of the equilibrium constant, N_C can be obtained from eqn (7). In a series of experiments, a linear plot of $Q(\text{sol})/N_A{}^0$ vs $N_C/N_A{}^0$ has slope ΔH_R and intercept ΔH_S. In this approach, independent values of the equilibrium constant are obtained either from the NMR experiments or from the heat of dilution experiments. The values cannot be measured with sufficient precision to allow one to obtain simultaneous solns for the three independent constants in Eqns (7) and (10).

RESULTS

Maleic anhydride–acetone. The mole fraction of maleic anhydride in acetone was varied from 0.250 to 0.008, and the chemical shift of the maleic anhydride was obtained at 39.8° (NMR probe temp.). The shift position was found to vary from 427.2 to 431.0 Hz (TMS = 0.0 Hz). The chemical shift of uncomplexed maleic anhydride in cyclohexane is 403.2 Hz and is concentration independent at low concentrations. Figure 1 is a plot of the chemical shift data according to eqn 4 which assumes simple one-to-one complex formation. From the slope Δ_C is found to be 48.0 Hz, giving the resonance position of a complexed maleic anhydride molecule at 451.2 Hz, downfield from the uncomplexed molecule. The equilibrium constant is determined to be 1.37 (mole fraction units) and the correlation coefficient for the plotted data is 0.992.

The temperature dependence of the maleic anhydride chemical shift is illustrated in Table 1. In this experiment the mole fraction of maleic anhydride was maintained constant with only the temperature being varied.

Using the value of the chemical shift for the complex, $\Delta_C = 48.0$ Hz, and assuming its value to be invariant over the temperature range studied, equilibrium constants at each temperature can be calculated.[29] These constants are also given in Table 1. The temperature dependence of the equilibrium constant permits obtaining the enthalpy and entropy of complex formation. The values calculated are $\Delta H_R = -3.2$ kcal/mole, $\Delta S_R = -9.9$ e.u. The correlation coefficient for the fit of the data to the van't Hoff equation is a rather poor 0.959. Nevertheless, this type of experiment was not repeated since the thermodynamic parameters are more accurately obtained from the calorimetric experiments to be described.

Heats of dilution experiments were carried out as follows. Approximately 3.5 ml of a concentrated maleic anhydride solution in acetone was added during a 10 min period to a measured quantity of pure acetone. The titrant solution and the pure solvent were both maintained at 25° before addition. The total heat evolved during the mixing process was obtained at 5 equal increments of added solution. Using the data summarized in Table 2, optimum values of K and ΔH_R, obtained from the non-linear least squares treatment of eqns (7), (8) and

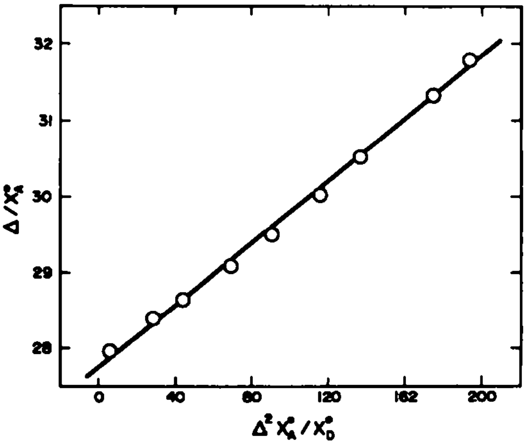


Fig. 1. Plot of eqn (5) for the system maleic anhydride (A)-Acetone (D).

Table 1. Temperature dependence of maleic anhydride NMR chemical shift in acetone[a]

Temperature (°K)	Chemical Shift (Hz)	Δ	K (Calculated)
313.0	430.7	27.5	1.36
290.8	432.8	29.6	1.63
278.3	434.8	31.6	1.95
268.3	437.1	33.9	2.41
255.2	440.0	36.8	3.26
244.0	444.4	41.2	6.14

[a] Mole fraction maleic anhydride = 0.0126.

Table 2. Heats of dilution, maleic anhydride and acetone

Total Acetone (Moles)	Total Maleic Anhydride (Moles)	Total Heat Evolved (Calories)	Calculated ΔH_R (Calories) K = 1.50	Calculated ΔH_R (Calories) K = 2.00
1.58691	0.0	0.0		
1.59585	0.00225	−0.5057	−3610.2	−3760.2
1.60479	0.00450	−1.0060	−3610.4	−3759.7
1.61373	0.00675	−1.5010	−3610.6	−3759.1
1.62267	0.00900	−1.9907	−3610.6	−3758.5
1.63151	0.01125	−2.4753	−3610.8	−3758.0

Table 3. Heats of solution, maleic anhydride in acetone

Acetone (Moles)	Maleic Anhydride (Moles	Heat Absorbed (Calories)	Uncorrected Heat of Solution (Calories/Mole)
1.77652	0.009097	9.4432	1038.1
1.69675	0.006174	6.4008	1036.7
1.70790	0.003446	3.5676	1035.3
1.74396	0.001465	1.5152	1034.3
1.80794	0.000838	0.8664	1033.9
1.73607	0.000344	0.3556	1033.7

(9), are $K = 1.58$, $\Delta H_R = -3.63$ kcal/mole, whence $\Delta S_R = -11.3$ e.u.

Given a value of the equilibrium constant, heat of complex formation values can be directly obtained from the data in Table 2. Quite a large variation in the equilibrium constant gives small changes in calculated heats of complex formation as illustrated in the table. However, even though the calculated ΔH_R values are relatively insensitive to the assumed K values, only a single optimum value of K does not lead to systematic small variations in the series of calculated ΔH_R values. Accordingly, we believe that the thermodynamic parameters, based on the chosen complex formation model, can be determined with high accuracy by this method.

Heats of solution at 25°, determined by measuring the heat associated with dissolution of small amounts of maleic anhydride in acetone, support the conclusion in the preceding paragraph. These data are given in Table 3, and can be very closely fitted by the linear eqn (10), suing the value $K = 1.58$ from the previous work. The calculated heat of complex formation (ΔH_R) is then -3.73 kcal/mole, and the heat of soln (ΔH_S) is $+3.32$ kcal/mole. The multiple correlation coefficient is -1.000, so a graph of the equation would not be informative, and is therefore not presented.

Maleic anhydride-benzene. The NMR chemical shift of maleic anhydride in benzene is highly dependent upon concentration. An upfield shift from uncomplexed maleic anhydride is observed, in contrast to the downfield shift in acetone. Relative chemical shifts at 30.8° are given in

Table 4. Chemical shifts in meleic anhydride–benzene solutions

Mole Fraction Benzene	Mole Fraction Maleic Anhydride	Chemical Shift (Hz)[a] Expt.	Chemical Shift (Hz)[a] Calc. Eq. 13
0.928538	.071462	-63.5	-63.1
0.942294	.057706	-66.5	-66.5
0.956308	.043692	-69.6	-69.9
0.964791	.035209	-71.4	-71.8
0.972753	.027247	-73.1	-73.6
0.981449	.018551	-75.6	-75.5
0.987449	.012551	-77.2	-76.8
0.990087	.009913	-77.6	-77.3

[a] Relative to Maleic Anhydride in Cyclohexane, δ = 403.2 Hz.

Table 4 for a binary series of solutions in which the mole fraction of maleic anhydride is less than 0.10. Also, in order to obtain a better understanding of the system, the NMR spectrum was examined in the presence of an inert solvent (cylohexane), varying the mole fraction of benzene from 0.50 to 0.955 while always maintaining a very large excess of benzene (20 fold–100 fold) over maleic anhydride. These data are illustrated in Fig. 2.

The data in Table 4 do not conform to the postulate of a simple mixture of donor, acceptor, and one-to-one donor–acceptor compelx. An irrational negative equilibrium constant is obtained when the data are treated according to eqn (5). In contrast, the data that gave rise to Fig. 2 are well-behaved; use of eqn (6) gives an equilibrium constant of 2.125 (Mole fraction units), a $\Delta_C = -118.2$ Hz, and correlation coefficient −0.995. Rather than ascribe these discordant results to failure of the mathematical treatment,[28,30,31] or solution nonideality,[24,32–36] we have examined alternate simple models of complex formation to rectify the data.

Two-to-one molecular complexes have been identified as the source of anomalies in equilibrium constant determinations in several previous studies.[37–40] However, the data of Table 4 still give a negative equilibrium constant when treated by an equation derived on the basis of termolecular complex formation. Approximate forms of the termolecular equation can be obtained by making the usual assumptions of the Benesi–Hildebrand method. It is interesting to note that the approximate equations do give positive values of equilibrium constants with high correlation coefficients. The fact is that the full termolecular equation does not confirm these values. This may indicate that previous work of this type ought to be reinvestigated.

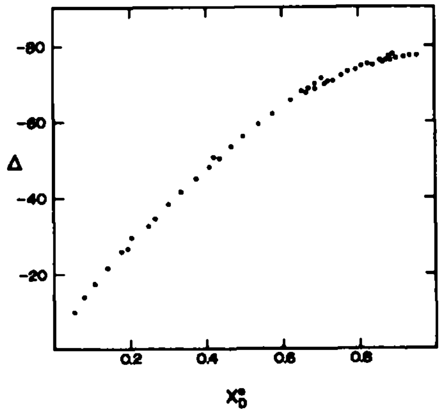


Fig. 2. Plot of Δ(maleic anhydride) vs mole fraction of benzene for the system maleic anhydride–benzene–cyclohexane.

Self-association[41] of either donor or acceptor is also possible in these solutions. An equilibrium constant for molecular dimerization of benzene is available from our previous work,[8,42] $K = 0.0063\ M^{-1}$ in CCl_4 soln at 37°. This constant is very small, which is in agreement with calculated estimates of the interaction energy between two benzene molecules (less than kT at room temperature).[43,44] Therefore we consider that the self-association of maleic anhydride is the only possibility of this type. Assuming simultaneous equilibrium concentrations of molecular dimers and donor acceptor complexes

$$K_1 = \frac{X_{\text{Dimer}}}{(X_A)^2} \tag{11}$$

$$K_2 = \frac{X_{\text{Complex}}}{X_A X_D} \tag{12}$$

an equation relating chemical shifts for dimer Δ_1 and complex Δ_2 to the observed average chemical shift Δ of maleic anhydride can be derived.

$$\frac{\Delta}{X_D{}^0} = \frac{X_A{}^0}{X_D{}^0}\left\{\frac{1+K_2X_A{}^0}{1+K_2X_D{}^0}\right\}\left\{\frac{2K_1\Delta_1}{1+K_2}\right\} + \frac{K_2\Delta_2}{1+K_2}. \tag{13}$$

An important assumption leading to this equation is that dimer concentration is much smaller than complex concentration, a circumstance highly likely to be fulfilled because of the high ratio of benzene to maleic anhydride present in all of our studies.[45]

The data in Table 4 are precisely correlated with this equation using the value $K_2 = 2.125$ in the second term of the dependent variable. The slope of eqn (13) is 381.51, the intercept is −79.34, and the multiple correlation coefficient is 0.995. The resulting calculated chemical shifts for maleic anhydride are listed in the fourth column of Table 4. The value of the intercept can be

Table 5. Heats of solution, maleic anhydride in benzene[a]

Benzene (Moles)	Maleic Anhydride (Moles)	Heat Absorbed (Calories)	Uncorrected Heat of Solution (Calories/Mole)
1.104932	0.000397	0.1599	402.8
1.108127	0.000602	0.2426	403.0
1.096134	0.000938	0.3783	403.3
1.109175	0.001214	0.4899	403.5
1.103932	0.001515	0.6117	403.8
1.106238	0.002397	0.9695	404.5
1.091828	0.002840	1.1498	404.9

[a]Experiments carried out at 39.8°.

independently obtained from the equilibrium constant and complex chemical shift determined by the experiments in cyclohexane as a cosolvent. From those experiments $(K_2\Delta_2)/(1+K_2) = -80.38$, a value in close agreement with the binary solution value. The agreement is supportive of the assumptions that have been made, but of course is not absolute proof for the monomers-dimers-complexes molecular model.

Calorimetric data for heats of dilution in this system would be very difficult to interpret. Four independent thermodynamic parameters would govern the dilution heats, and accurate determination of this amny parameters from calorimetric data is not feasible. We did carry out heats of solution experiments at very small final mole fractions of maleic anhydride in benzene. The data are listed in Table 5. Under these conditions, eqn (10) can be used to treat the data with concurrent use of the equilibrium constant for complex formation from the NMR studies. The heat of solution for maleic anhydride in benzene is found to be +3.26 kcal/mole, and the heat of complex formation is determined to be −4.20 kcal/mole. The correlation coefficient for the data fit is −0.999. Finally, the entropy change for complex formation is calculated as $\Delta S_R = -11.7$ e.u.

DISCUSSION AND CONCLUSIONS

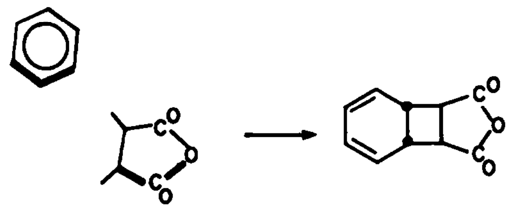
The results obtained in these NMR and calorimetric studies are summarized in Table 6. We wish to emphasize that the data obtained cannot be interpreted without the assumption of a molecular model. We have assumed that these solutions consist of mixtures of solvent and solute molecules in equilibrium with molecular complexes. It should be noted that the experimental data *per se* yield no evidence concerning the existence of complexes in these systems. Alternate interpretations in terms of solution nonideality[46] could probably describe the properties of these solutions. We believe the discrete molecular complex model is reasonable,[47] and that the consonant results obtained are supportive of the assumptions that have been made.

The data in Table 6 can be compared with previous work on the benzene–maleic anhydride complex. A study of the charge-transfer spectrum in $CHCl_3$ soln gave a wave-length dependent equilibrium constant K = 0.60–0.85 at room temp.[48] A correction for benzene concentration in terms of the well-known association of benzene with solvent $CHCl_3$[25,49–56] could account for the discrepancy with our results. Our previously reported NMR value for K in CCl_4 soln is 0.21 M^{-1} at 27°.[7] The molal volume of CCl_4 is 0.1011 at this temperature, giving an approximate value of K = 2.08 in mole fraction units. Recalculation of NMR data from a temperature study of maleic anhydride in benzene,[57] using our values of δ^0 (maleic anhydride) and Δ_C, gives $\Delta H = -2.9$ kcal/mole and $\Delta S = -7.8$ e.u., in approximate agreement with our calorimetric data.

Table 6. Thermodynamic parameters and NMR chemical shifts for maleic anhydride complexes

Maleic Anhydride - Acetone	
K (39.8°C) = 1.37	NMR
K (25.0°C) = 1.58	Heats of Dilution
ΔH_R = −3.2 kcal/mole	NMR
ΔH_R = −3.63 kcal/mole	Heats of Dilution
ΔH_R = −3.73 kcal/mole	Heats of Solution
ΔS_R = −9.9 e.u.	NMR and van't Hoff Eq.
ΔS_R = −11.3 e.u.	Calorimetry and van't Hoff Eq.
ΔH_S = +3.32 kcal/mole	Heats of Solution
Δ_C = +48.0 Hz	NMR
Maleic Anhydride - Benzene	
K (39.8°C) = 2.13	NMR
ΔH_R = −4.20 kcal/mole	Heats of Solution
ΔS_R = −11.7 e.u.	van't Hoff Eq.
ΔH_S = +3.26 kcal/mole	Heats of Solution
Δ_C = −118.2 Hz	NMR
Maleic Anhydride Molecular Dimer	
$K_1\Delta_1$ = 597	NMR

The nature of the ground-state interaction between maleic anhydride and benzene, in connection with photochemical studies has been the subject of several papers.[9–13,58,59] The pronounced upfield NMR shift of the maleic anhydride protons has been interpreted in terms of a closely associated *exo* complex (1),[12,59] corresponding in structure to the initial photocycloadduct.



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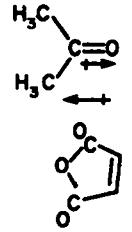
Our NMR and thermodynamic data indicate that 25% of maleic anhydride is present as complex under the reported conditions[60] of photocycloaddition. The fraction of complex would only decrease to 10% at 80°, and this doesn't seem to be a sufficient decrease to explain the complete absence of cycloaddition at this temperature.[9] Inefficiency of cycloaddition in an excited complex (increasing with temperature) might account for these observations. The detailed mechanism previously proposed[11] contains a step for deactivation of excited molecular complexes, competing with cycloaddition to yield the reactive intermediate.

There are no previous studies on complexes of maleic anhydride with acetone. The downfield shift of the maleic anhydride protons in the complex, $\Delta_C = +48.0$ Hz, is consistent with a structure in which a major contributing force to the intermolecular interaction is dipolar in nature (3). After excitation of the ground state, a reorientation of the two molecules would be required so that the addends could undergo the concerted cycloaddition reaction favored by perturbational MO calculations.[61,62]



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At 25°, in a solution of maleic anhydride (0.25 mole fraction) in acetone 55% of the solute exists as complex, and this fraction slowly increases with decreasing mole fraction of maleic anhydride to 61% at infinite dilution. We therefore consider it sensible to postulate that this complex is involved in the photochemical cycloaddition. Since photochemicals studies have not been carried out with this possibility in mind, extended further discussion is not warranted.

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REFERENCES

[1] Taken in part from the Ph.D. thesis (1971) of E. Silber, and the M.Sc. thesis (1972) of S.-M. Park, Texas Tech University, Lubbock, Texas. Preliminary communication: E. Silber, S.-M. Park and W. C. Herndon, *Chem. Comm.* 933 (1978).

[2] Deceased, Argentina (1976).

[3] A. Weller, *Progr. Reaction Kinetics* 1, 189 (1961).

[4] P. J. Wagner and I. Kochevar, *J. Am. Chem. Soc.* 90, 2232 (1968).

[5] C. Lewis and W. R. Ware, *Chem. Phys. Lett.* 15, 290 (1972).

[6] Examples: R. Robson, P. W. Grubb and J. A. Barltrop, *J. Chem. Soc.* 2153 (1964); Y. L. Bahurel, D. J. MacGregor, T. L. Penner and G. S. Hammond, *J. Am. Chem. Soc.* 94, 637 (1972); J. G. Otten, C. S. Yeh, S. Byrn and H. Morrison, *Ibid.* 99, 6353 (1977). Also see papers on benzenemaleic anhydride photocycloaddition to be cited.

[7] S.-M. Park and W. C. Herndon, *Tetrahedron* 34, 3201 (1978).

[8] S.-M. Park and W. C. Herndon, *Tetrahedron Letters* 2363 (1978).

[9] D. Bryce-Smith and J. E. Lodge, *J. Chem. Soc.* 2675 (1962).

[10] D. Bryce-Smith and A. Gilbert, *Ibid.* 918 (1965).

[11] W. M. Hardham and G. S. Hammond, *J. Am. Chem. Soc.* 89, 3200 (1967).

[12] D. Bryce-Smith and M. A. Hems, *J. Chem. Soc.* (B), 812 (1968).

[13] D. Bryce-Smith, B. E. Connett and A. Gilbert, *Ibid.* (B), 816 (1968).

[14] J. J. Beereboom and M. S. V. Wittenau, *J. Org. Chem.* 30, 1231 (1965).

[15] N. J. Turro, P. Wriede, J. C. Dalton, D. Arnold and A. Glick, *J. Am. Chem. Soc.* 89, 3950 (1967).

[16] N. J. Turro, P. A. Wriede and J. C. Dalton, *Ibid.* 90, 3274 (1968).

[17] J. A. Barltrop and H. A. J. Carless, *Tetrahedron Letters* 3901 (1968).

[18] J. C. Dalton, P. A. Wriede and N. J. Turro, *J. Am. Chem. Soc.* 92, 1318 (1970).

[19] F. Franks and B. Watson, *J. Sci. Instrum.* [2] 1, 940 (1968).

[20] R. J. Irvine and I. Wadsö, *Acta Chem. Scand.* 18, 195 (1964).

[21] H. S. Harned and R. A. Robinson, *Trans. Faraday Soc.* 36, 973 (1940).

[22] W. C. Herndon, J. Feuer and R. E. Mitchell, *Analytical Calorimetry* (Edited by R. S. Porter and J. F. Johnson), Vol. 3, pp. 245–281. Pleunum Press, New York (1974).

[23] J. C. Davis, Jr. and K. K. Deb, *Advan. Magnetic Resonance* 4, 201 (1970).

[24] The ratio of activity coefficients $\gamma_C/\gamma_A\gamma_D$ is assumed to be unity or constant over the range of solutions studied. See M. W. Hanna and A. L. Ashbaugh, *J. Phys. Chem.* 68, 811 (1964).

[25] W.-C. Lin and S.-J. Tsay, *J. Phys. Chem.* 74, 1037 (1970).

[26] H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.* 70, 3832 (1948); 71, 2703 (1949).

[27] W. R. Carper, C. M. Buess and Gary R. Hipp, *J. Phys. Chem.* 74, 4229 (1970).

[28] D. A. Deranleau, *J. Am. Chem. Soc.* 91, 4044 (1969).

[29] P. Laszlo and D. H. Williams, *Ibid.* 88, 2799 (1966).

[30] W. B. Person, *Ibid.* 87, 167 (1965).

[31] R. M. Guidry and R. S. Drago, *Ibid.* 95, 6645 (1973).

[32] S. Carter, J. N. Murrell and E. J. Rosch, *J. Chem. Soc.* 2048 (1965).

[33] P. J. Trotter and M. W. Hanna, *J. Am. Chem. Soc.* 88, 3724 (1966).

[34] F. L. Slejko and R. S. Drago, *Ibid.* 94, 6546 (1972).

[35] E. H. Lane, S. D. Christian and J. D. Childs, *Ibid.* 96, 38 (1974).

[36] M. H. Litt and J. Wellinghoff, *J. Phys. Chem.* 81, 2644 (1977).

[37] G. D. Johnson and R. E. Bowen, *J. Am. Chem. Soc.* 87, 1655 (1965).

[38] D. A. Deranleau, *Ibid.* 91, 4050 (1969).

[39] B. Dodson, R. Foster and A. A. S. Bright, *J. Chem. Soc.* (B), 1284 (1971).

[40] N. Kulevsky and R. Foster, *J. Phys. Chem.* 70, 3816 (1966).

[41] D. W. Tanner and T. C. Bruice, *Ibid.* 70, 3816 (1966).

[42] Unpublished calorimetric studies, William C. Herndon.

[43] R. S. Mulliken, *J. Am. Chem. Soc.* 72, 600 (1950); 74, 811 (1952).

[44] K. E. Shuler, *J. Chem. Phys.* 21, 765 (1953).

[45] The maximum possible ratio of dimer to complex is equal to $K_1K_A{}^0/K_2X_D{}^0$.

[46] J. H. Hildebrand, J. M. Prausnitz and R. L. Scott, *Regular and Related Solutions.* Van Nostrand Reinhold, New York (1970).

[47] For a strongly documented opposing viewpoint, see E. M. Engler and P. Laszlo, *J. Am. Chem. Soc.* 93, 1317 (1971).

[48] L. J. Andrews and R. M. Keefer, *Ibid.* 75, 3776 (1953).

[49] L. W. Reeves and W. G. Schneider, *Can. J. Chem.* 35, 251 (1957).
[50] J. Hurwic and J. Michalczyk, *Roczniki Chemii* 34, 1423 (1960).
[51] N. C. Perrins and J. P. Simons, *Trans. Far. Soc.* 65, 390 (1969).
[52] J. Homer and M. C. Cooke, *J. Chem. Soc.* (A), 73 (1969).
[53] J. Homer, C. F. Jackson, P. M. Whitney and M. H. Everdell, *Chem. Comm.* 965 (1971).
[54] J. Homer, M. H. Everdell, C. J. Jackson and P. M. Whitney, *J. Chem. Soc.* Far. Trans. II 874 (1972).
[55] L. Abella, *J. Chem. Phys.* 70, 1355 (1973).
[56] R. P. Rastogi and R. R. Misra, *Indian J. Chem.* 14A, 521 (1976).
[57] T. Matsuo, *Can. J. Chem.* 45, 1829 (1967).
[58] D. Bryce-Smith, A. Gilbert and H. M. Tyrrell, *Chem. Comm.* 699 (1974).
[59] D. Bryce-Smith and A. Gilbert, *Tetrahedron* 33, 2459 (1977).
[60] H. J. F. Angus and D. Bryce-Smith, *J. Chem. Soc.* 4791 (1960).
[61] W. C. Herndon and W. B. Giles, *Mol. Photochemistry* 2, 277 (1970).
[62] W. C. Herndon, *Tetrahedron Letters* 125 (1971).