Mechanisms of Photochemical Reactions in Solution. XLIII.[1] Addition of Maleic Anhydride to Benzene

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Abstract: The photoaddition of maleic anhydride to benzene by both direct and sensitized excitation has been studied. Use of suitable quenchers and sensitizers and variation of the concentration of the reactants indicate that a triplet mechanism obtains. Key steps in the mechanism are: (1) excitation of the maleic anhydride–benzene complex to its triplet state, (2) collapse of the excited complex to a monoadduct, and (3) reaction of the first adduct with maleic anhydride in a thermal reaction. Study of quenching reactivities indicates that the triplet excitation energy of the maleic anhydride–benzene complex is at least 2 kcal/mole less than the excitation energy of maleic anhydride.

The photochemical addition of maleic anhydride to benzene was discovered almost simultaneously by three groups of workers.[2-4]

$$\text{(1)}$$
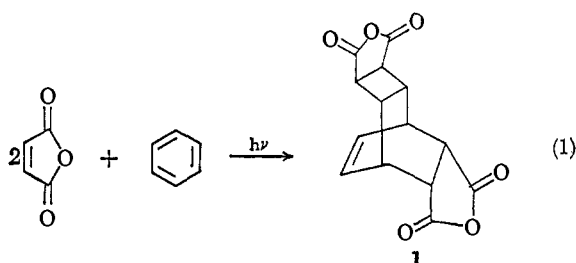
Schenck and Steinmetz[3] showed that the reaction could be conveniently carried out using benzophenone as a sensitizer and Bryce-Smith and Lodge[5] made a preliminary comparison of the sensitized and unsensitized reactions. Both groups suggested that the mechanisms of the direct and indirect reactions are distinctly different. Furthermore, the English workers reported some very unusual characteristics of the reactions[5] although one very important observation has since been reported by the same group[6] to have been in error. We should point out that quantitative studies of the reaction, including our own, have depended upon isolation of **1** which crystallizes from the reaction mixtures. Crystallization is slow and any isolated, negative result may be attributed to supersaturation.

Because of the complexity of the reaction and the provocative nature of the first suggestions concerning mechanism, we felt that the process deserved detailed study. A preliminary report of part of our results has already been published.[7]

Results and Discussion

Samples were irradiated in ampoules made from thin-walled Pyrex culture tubes in a merry-go-round ap-

paratus[8] so that a number of samples, including actinometric samples, could be irradiated simultaneously. The light source was a 450-w, medium-pressure mercury lamp. The 3130-, 3660-, and 4045-A lines from the source are transmitted to the extent of 78, 87, and 90% by the Pyrex tubes. In most experiments with sensitizers a uranium glass filter was used, eliminating essentially all source lines of wavelength shorter than 3300 A. Some measurements of quantum yields were made using a collimated beam from a high-pressure arc (Westinghouse SAH 800-C)[9] with glass filters chosen to isolate the 3660-A line. The reaction was monitored by isolating and weighing the insoluble product, **1**.

Sensitizers and Inhibitors. A survey of potential sensitizers was carried out, giving the results shown in Table I. The yields, given in milligrams, were determined at relatively low conversions (10 mg $\cong$ 2%) using 1.0 *M* maleic anhydride in benzene. The yields are not necessarily proportional to quantum yields since no corrections have been made for variation in either intersystem crossing efficiencies or variation in the absorption spectra of the additives. Although the experiments with compounds listed as "inhibitors" were not pursued exhaustively, there seems to be a clear-cut difference between these compounds and the effective sensitizers. None of the addition compound was formed even when the uranium glass filter was removed. Obviously the "inhibitors" not only fail to sensitize the reaction but also interfere with the unsensitized reaction. No attempt has been made to quantitatively dissect the effects into quenching and internal light filtering. Concentrations of the additives were adjusted so as to absorb essentially all incident light at 3660 A, where the benzene–maleic anhydride complex does not absorb. In the experiments with the uranium glass filter, 1–20% of the total incident light was estimated to be absorbed by the complex.

Separation of the sensitizers and inhibitors on the basis of triplet excitation energies is almost, but not quite, perfect. There seems to be a cutoff point with

(1) Paper XLII is L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Am. Chem. Soc.*, 88, 3665 (1966).

(2) H. J. F. Angus and D. Bryce-Smith, *Proc. Chem. Soc.*, 326 (1959).

(3) G. O. Schenck and R. Steinmetz, *Tetrahedron Letters*, No. 21, 1 (1960).

(4) E. Grovenstein, Jr., D. V. Rao, and J. W. Taylor, *J. Am. Chem. Soc.*, 83, 1705 (1961).

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

(6) D. Bryce-Smith, A. Gilbert, and B. Vickery, *Chem. Ind.* (London), 2060 (1962).

(7) G. S. Hammond and W. M. Hardham, *Proc. Chem. Soc.*, 63 (1963).

(8) R. S. H. Liu, N. J. Turro, and G. S. Hammond, *J. Am. Chem. Soc.*, 87, 3406 (1965).

(9) W. M. Moore, G. S. Hammond, and R. P. Foss, *ibid.*, 83, 2789 (1961).

Table I. Yields of Addition Product Obtained by Irradiation of Solutions of Maleic Anhydride in Benzene in the Presence of Various Additives

Additive	Concn of additive, M	Yield of product,[a] mg	Triplet energy[b]
Sensitizers[c]			
Propiophenone	0.80	26	74.7
Xanthone	0.01	14	74.2
Acetophenone	0.80	41	73.6
Benzaldehyde	0.30	36	71.9
Benzophenone	0.050	46	68.5
4,4'-Dichlorobenzophenone	0.050	59	68.0
p-Diacetylbenzene	0.30	35	67.7
p-Cyanobenzophenone	0.050	40	66.4
Inhibitors[d]			
Triphenylene	0.10	0	66.6
Thioxanthone	0.05	0	65.5
Anthraquinone	0.010	0	62.4
2-Acetylfluorene	0.10	0	62.6
Naphthalene	0.10	0	60.9
2-Acetonaphthone	0.20	0	59.3
Chrysene	0.01	0	56.6
Benzil	0.050	0	53.7
Fluorenone	0.10	0	53.0

[a] 1.0 M maleic anhydride in benzene, irradiation for 50 hr in a merry-go-round apparatus (outside ring). [b] W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J Am. Chem. Soc.*, **86**, 4537 (1964). [c] All reported results with uranium glass filter. [d] Results reported were obtained without uranium glass filter.

sensitizers having about 66-kcal/mole excitation energy; those having higher excitation energies sensitize the reaction and those having less available energy do not. When energy transfer becomes insignificant, the rate of the process must fall below the first-order rate of decay of the sensitizer triplets. From our estimates of the concentrations of the complex (*vide infra*), the lifetimes of the various triplets in solution, and data from flash kinetic studies of triplet quenching,[10-12] we infer that energy transfer must be several kilocalories per mole endothermic at the cutoff point. The apparent anomalies with p-cyanobenzophenone and triphenylene may not be significant. Measurement of triplet excitation energies is not highly precise and we have observed other apparently deviant behavior with triphenylene.[13]

Triplet Excitation Energy of Maleic Anhydride.
The emission spectra from MCIP (5:1 methylcyclohexane-isopentane) glasses containing approximately 10^{-3} M maleic anhydride were measured at 77°K. A very weak, long-lived emission was observed. After subtraction of the background emission from the solvent the spectrum shown in Figure 1 was obtained. The spectrum was not very reproducible and that shown is the strongest obtained. Although other details varied, the first maximum (at 3980 A) was reproducible.[14] This indicates that the phosphorescent state has

(10) K. Sandros and H. L. J. Backström, *Acta Chem. Scand.*, **16**, 958 (1962).
(11) G. Porter and F. Wilkinson, *Proc. Roy. Soc.* (London), **A264**, 1 (1961).
(12) W. G. Herkstroeter and G. S. Hammond, *J. Am. Chem. Soc.*, in press.
(13) L. M. Coyne, unpublished observations.
(14) Factors known to effect the quality of a recorded spectrum are: (1) the purity of the constituents of the solvent, (2) variation in the amount of cracking in the glass, and (3) the phototube. The spectrum shown was the only one recorded with our best phototube.
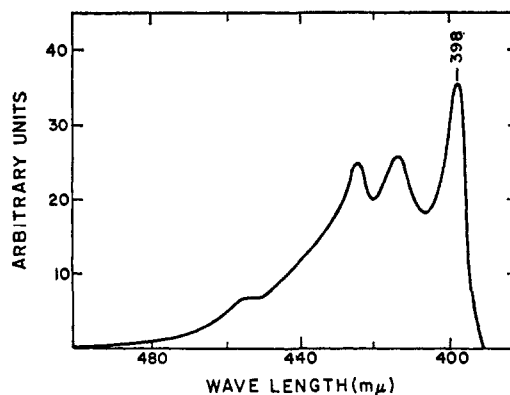

Figure 1. Emission spectrum of maleic anhydride in MCIP glass at 77°K. Weak emission from the glass has been subtracted.

an excitation energy of about 72 kcal/mole. Addition of benzene in amounts slightly greater than molar equivalence to the maleic anhydride led to complete disappearance of the phosphorescence. Apparently formation of the complex provides faster modes of decay for maleic anhydride triplets than are available to the uncomplexed molecule. The extent to which this is associated with the chemical reaction is not entirely clear.

The absorption spectrum of a 0.067 M solution of maleic anhydride in ethyl iodide was measured in a 1-cm cell. The long wavelength spectrum shown in Figure 2 was obtained. The spectrum is probably due to a singlet–triplet transition induced by the external heavy-atom effect.[15] Although the spectrum is ab-
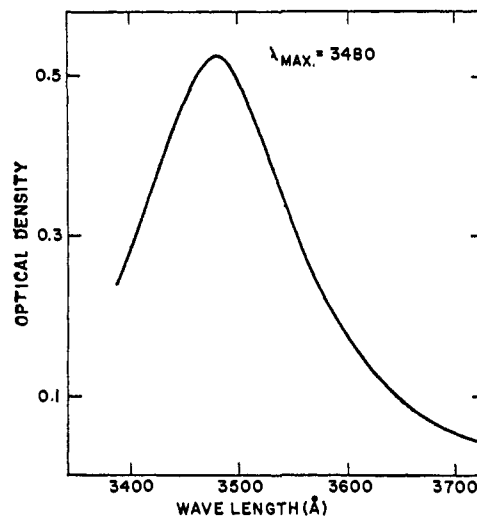

Figure 2. Long wavelength absorption spectrum of maleic anhydride in ethyl iodide solution.

solutely featureless, it is entirely possible that the long wavelength limit occurs close to 3900 A, the apparent position of the 0–0 band in the phosphorescence spectrum. If anything the absorption spectrum indicates a slightly higher value of the $S_0 \rightarrow T_1$ excitation energy.

Quenching of Triplets by Maleic Anhydride. The reaction of benzophenone with benzhydrol was used to

(15) M. Kasha, *J. Chem. Phys.*, **20**, 74 (1952).

measure the relative efficiency of maleic anhydride as a quencher for benzophenone triplets.[9,16] The spectroscopic studies reported above indicate that the excitation energy of maleic anhydride is too high to allow it to be a good quencher for benzophenone. However, an earlier measurement,[16] made in the course of a general survey, indicated that maleic anhydride is a good quencher *in benzene solution*. The study has been repeated in benzene and in nonaromatic solvents. The measurements in benzene are complicated by virtue of the fact that the addition reaction decreases the concentration of the quencher during the course of the runs. Correction for the change in concentration was made using data for the quantum yields of the addition reaction (*vide infra*). The results are shown in Table II.

Table II. Quenching of the Reaction of Benzophenone with Benzhydrol by Maleic Anhydride in Benzene[a]

Run	[Benz-hydrol]$_0$, M	[MA]$_0$ $\times 10^3$, M	Φ^b	$k_q/k_r{}^c$
A	0.100	2.0	0.341	79
B	0.100	1.0	0.517	56
C	0.050	1.0	0.314	59
D	0.200	2.0	0.536	70
E	0.100	0	0.731	. .
			Av	65

[a] Benzophenone was initially 0.100 M in each experiment. [b] The benzophenone–benzhydrol reaction without added quencher was used as an actinometer. The parameters reported in ref 18 were used in the calculations. [c] The average concentration of maleic anhydride was approximately 5% lower than the initial concentration in each run; k_q is the rate constant for quenching of benzophenone triplets by maleic anhydride and k_r is the rate constant for reaction of benzophenone triplets with benzhydrol.

The quenching reaction was also studied in carbon tetrachloride solution and a solvent consisting of 95% cyclohexane and 5% acetone. The values of $k_d/k_r{}^{17}$ were redetermined in each medium using Foss's method.[18] The value in cyclohexane–acetone was 0.036, well within experimental error of the value (0.033) for benzene solution; consequently, we infer that hydrogen abstraction from the solvent is unimportant in the former case. In carbon tetrachloride the value was 0.0526. While we have no way of dissecting the ratio, the increase is probably to be associated with an external heavy-atom effect on the radiationless decay rate in carbon tetrachloride. Adventitious quenchers could also be responsible. The quenching constants for maleic anhydride were too small for accurate measurement in both the nonaromatic solvents. In carbon tetrachloride the apparent values ranged from 1 to 9.6 with an average value of 5 ± 5. In cyclohexane–acetone the value was 8 ± 5. In the latter medium there can be no doubt that the quenching activity is real, but of an order of magnitude smaller than the activity in benzene.

The results are neatly accommodated by the hypothesis that the effective quencher in benzene solution is

the benzene–maleic anhydride complex.[19,20] Attempts were made to use the data of Andrews and Keefer[19] for benzene–chloroform mixtures to evaluate the fraction of the anhydride that is in complexed form in neat benzene. The ultraviolet spectra of 1×10^{-3} and 2×10^{-3} M solutions indicated 42.5 and 51.0% complex, respectively, if the reported value of ϵ_{2700} for the complex is used. On the other hand, use of the reported equilibrium constant indicates that the anhydride should be 88% complexed. If the absorbance of the solutions at 2700 A is taken as a measure of the amount of complex, the value of k_q/k_r for that species is about 130, a factor of 5 smaller than the largest constants that have been measured.[9,16] If the value of k_d reported by Bell and Linschitz[21] is used as a reference point, the value of k_q for the complex is calculated to be 4×10^8 l. mole^{-1} sec^{-1}.

As an ancillary study we measured the reactivity of maleic anhydride as a quencher for acetophenone triplets which have more available excitation energy than benzophenone triplets (73.6 *vs.* 68.5 kcal/mole). The photoreduction of acetophenone by isopropyl alcohol[22,23] was used as a reference system. The reaction was carried out in cyclohexane. The quenching constant, k_q/k_r, for maleic anhydride was evaluated by standard procedures. The results scattered more than is usual but the average value was 193 ± 78. The fact that maleic anhydride *in an aliphatic solvent* is a good quencher for acetophenone triplets is clear from inspection of any of the experiments. This is in agreement with the assignment of the excitation energy of the uncomplexed anhydride as 72 kcal/mole.

The quenching experiments indicate that the excitation energy of the complex is close to that of benzophenone (68 kcal), about 4 kcal lower than that of the uncomplexed anhydride. This indicates that the binding energy of the complex is greater in the excited state than in the ground state. The triplet excitation is probably partly delocalized between the two partners in the complex. Chemical intuition indicates that charge transfer is probably not a principal factor in stabilization of the excited state since the complex excitation is probably much more closely related to excitation of the acceptor (maleic anhydride) than to that of the donor (benzene). Delocalization of singlet excitation in symmetrical systems has recently been discussed extensively in connection with excimer fluorescence.[24]

Quantum Yields. Preliminary measurements showed that quantum yields in the sensitized reaction increased with increasing maleic anhydride concentration in benzene solution. A series of carefully matched runs were then carried out, giving the results shown in Table III. The results are reported in terms of milligrams of product since measurement of relative quantum yields is more accurate than measurement of absolute quantum yields. Actinometric measurements indicate that the highest quantum yields are approximately 0.1.

(16) G. S. Hammond and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1148 (1962).
(17) The constant k_r is the specific rate constant for abstraction of hydrogen from benzhydrol and k_d is the rate constant for radiationless decay by benzophenone triplets.
(18) G. S. Hammond and R. P. Foss, *J. Phys. Chem.*, **68**, 3739 (1964).

(19) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **75**, 3776 (1953).
(20) W. G. Barb, *Trans. Faraday Soc.*, **49**, 143 (1953).
(21) J. A. Bell and H. Linschitz, *ibid.*, **85**, 528 (1963).
(22) S. G. Cohen, D. A. Laufer, and W. V. Sherman, *ibid.*, **86**, 3060 (1964).
(23) J. N. Pitts, *et al.*, *ibid.*, 81, 1068 (1959).
(24) See, for example, T. Azumi, A. T. Armstrong, and S. P. McGlynn, *J. Chem. Phys.*, 41, 3939 (1964).

Table III. Effect of Variation of Maleic Anhydride Concentration on Quantum Yields[a]

Sensitizer[b]	[MA]$_0$, M	Run no. 1	Run no. 2	Run no. 3
Benzophenone	0.05	8.6 ± 0.2	9.6 ± 0.1	7.5 ± 0.5
(0.10 M)	0.10	17.5 ± 1.0	19.5 ± 0.2	15.7 ± 0.5
	0.25			28.4 ± 1.5
	0.50	25.3 ± 4.0	41.6 ± 1.0	31.9 ± 1.0
	1.00	25.0 ± 4.0	47.7 ± 1.5	35.4 ± 1.0
	1.50		49.1 ± 3.0	33.8 ± 3.0
Acetophenone	0.05	12.3 ± 0.8	11.5 ± 1.0	
(1.00 M)	0.10	21.8 ± 0.5	37.0 ± 2.0	
	0.25	25.8 ± 2.0	42.1 ± 1.5	
	0.50	22.0 ± 1.5	45.6 ± 3	
	1.00	28.3 ± 0.5	45.5 ± 3	
	1.50	25.2 ± 3.0	39.5 ± 2	
Xanthone	0.05		14.0 ± 1.0	
(0.050 M)	0.10		25.4 ± 0.5	
	0.25		31.6 ± 1.0	
	0.50		33.0 ± 1.5	
	1.00		30.0 ± 2.0	
	1.50		25.9 ± 1.0	

[a] Four-milliliter samples irradiated using the uranium glass filter in the merry-go-round apparatus. [b] Concentrations chosen to absorb equally at 3660 A. [c] Samples having the same run number were irradiated at the same time. Irradiation was continued until enough 1 separated from tubes containing 0.05 M anhydride to permit accurate weighing. The results given are averages of triplicate samples.

The results, especially in experiments with the higher concentrations of maleic anhydride, are frustratingly erratic. A number of factors may contribute, including slow deposition of the crystalline product and scattering of light by crystals deposited on the walls of the tubes. At least a major source of error must arise from reasons entirely independent of the light intensity delivered to the tubes since there were significant variations in the amounts of product collected from duplicate samples within any run. However, the general trend of the results seems reproducible. The yields increase with increasing maleic anhydride concentration up to the level of about 0.25 M and then become constant within any series. Absorbance by the different sensitizers was equalized at 3660 A and concentrations were high enough to give essentially complete absorption at that wavelength, although there is some difference in the fractions of the weaker source lines between 3700 and 4100 A absorbed by the three sensitizers. The data in Table IV show that there is only a small dependence of yield on sensitizer concentration, indicating close to complete absorption of effective incident light and that energy transfer is not appreciably reversible.

Table IV. Variation in Yield as a Function of Benzophenone Concentration[a]

[Benzophenone]$_0$, M	Yield of adduct[b]
0.03	24.9 ± 1.2
0.06	24.2 ± 1.2
0.10	25.4 ± 1.2
0.15	26.1 ± 1.3
0.20	28.3 ± 1.3
0.30	29.1 ± 1.3

[a] The initial concentration of maleic anhydride was 1.00 M in all samples. [b] Milligrams of product formed by irradiation of 4-ml samples as described in the Experimental Section for 8 hr.

Reduction of the light intensity was accomplished by placing an 80-mesh, stainless-steel screen around the lamp. This reduced the transmission to 32.5% of the unscreened value and reduced the yield to 33 ± 3% of the value in control experiments. The quantum yield is apparently independent of light intensity.

The concentrations of maleic anhydride were large enough in all experiments to assure quantitative transfer of the triplet excitation of the sensitizers (see Quenching of Triplets above). Consequently dependence of the quantum yield on the concentration of maleic anhyride must be due to competition at some step other than energy transfer. Two likely candidates come to mind: (1) capture of intermediate in a thermal reaction and (2) a two-photon process. The latter possibility is ruled out by the linear response to a change in light intensity. The first possibility is the one that would have been anticipated on the basis of all suggested mechanisms.

$$C^{*(3)} \xrightarrow{k_2} C \qquad (3)$$

$$2 + MA \xrightarrow{k_4} 1 \qquad (5)$$

$$2 \xrightarrow{k_5} C_6H_6 + MA \qquad (6)$$
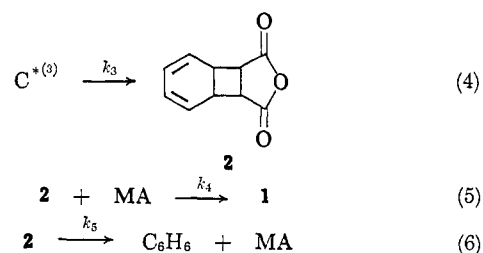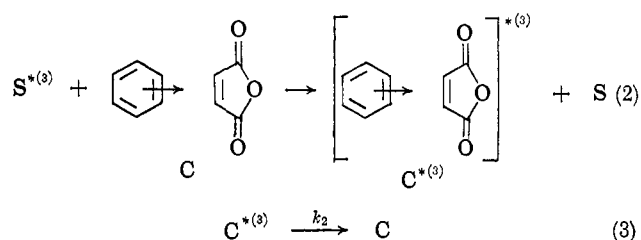
The dependence of quantum yields on the concentration of maleic anhydride is attributed to competition between reactions 5 and 6, two thermal processes. The above mechanism, with the assumption that energy transfer (reaction 2) is quantitative, yields the following rate law

$$\Phi = \Phi_{ic} \frac{k_2 k_4 [MA]}{(k_2 + k_3)(k_4[MA] + k_5)} \qquad (7)$$

where Φ_{ic} is the quantum yield for intersystem crossing by the sensitizer.

If the data in Table III are averaged and corrected for consumption of the reactant the numbers can be fitted surprisingly well to a function of the form of eq 7. The scatter of the numbers before averaging discourages us from a serious attempt to extract a value of the critical reactivity ratio, k_4/k_5, from the data although it must be on the order of ten.

The mechanism suggested predicts that the yields should fall off if the concentration of complex is reduced, at constant total maleic anhydride concentration, by dilution of the benzene with a cosolvent. The decrease should become significant when the concentration of the complex becomes small enough to allow radiationless decay of sensitizer triplets to compete with energy transfer. The data for experiments using dioxane, chloroform, and acetonitrile as cosolvents are

gathered in Table V. The data in the three series cannot be directly cross-compared because the light intensity was different in the three runs.

Table V. Effect of Dilution with Cosolvents[a]

[Benzene]$_0$, M	Dioxane	Yield of product[b] Chloroform	Acetonitrile
1.1	0		
2.3		9.1 ± 0.4	15.0 ± 1.9
3.4	0		
4.5		15.3 ± 0.2	42.1 ± 1.9
5.6	23.2 ± 3		
6.8		19.0 ± 0.5	65.9 ± 1.0
7.9	65.2 ± 4		82.7 ± 3.0
9.0		27.1 ± 1.0	94.3 ± 3.0
10.7	81.8	33.5 ± 1.5	98.9 ± 1.0

[a] [Benzophenone] = 0.10 M, [MA]$_0$ = 1.0 M. [b] Milligrams of product obtained from 3-ml samples irradiated as described in the Experimental Section for 7 hr.

The effect of variation of the concentration of benzene is surprising. If the value of Andrews and Keefer[19] for the dissociation constant is even close to correct, there should be enough of the complex in all solutions to effect complete quenching of benzophenone triplets. Consequently, there must be some reversible interaction with benzene *after* the energy-transfer step. The simplest way that we can see to include such a step is as follows

$$C^{*(3)} \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} MA^* + B \qquad (8)$$

$$MA^* \xrightarrow{k_7} MA \qquad (9)$$
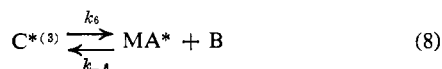
The excitation energies of the complex and monomeric maleic anhydride inferred from quenching studies (*vide supra*) would indicate that reaction 8 should be endothermic. The small decrease in quantum yield with increasing temperature reported by Angus and Bryce-Smith[2] may be due to change in the equilibrium constant for reaction 8. Another possibility is that the excited complex is stabilized by interaction with a second molecule of benzene to form a ternary triplet complex.

$$C^{*(3)} + B \rightleftharpoons C'^{*(3)} \qquad (10)$$

$$C'^{*(3)} \longrightarrow B + 2 \qquad (11)$$
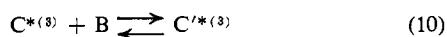
Formation of such a ternary complex might well be expected to effect unusual stabilization of the excited triplet. McGlynn and his co-workers[25] have pointed out that the excited singlet state of a complex should lie lower than the triplet if charge transfer is dominant in the excitation process. With two acceptor molecules in the complex, the triplet should be stabilized. It is even conceivable that the complex responsible for the quenching action is a 2:1 complex in the first place. Andrews and Keefer[19] found no evidence for such a species but their experiments were carried out with diluents and, as was previously mentioned, extrapolation of the spectroscopic properties of the complex as observed in chloroform solution to pure benzene is not very accurate.

(25) S. P. McGlynn and J. D. Boggus, *J. Am. Chem. Soc.*, **80**, 5096 (1958); S. P. McGlynn, J. D. Boggus, and E. Elder, *J. Chem. Phys.*, **32**, 357 (1960).

Attempts to Capture an Intermediate. The proposed intermediate, **2**, should be a reactive diene so (unsuccessful) attempts were made to intercept the species with dienophiles. Irradiation of a benzene solution containing 1.0 M maleic anhydride, 2.5 M methyl acrylate, and 0.10 M benzophenone gave only the usual adduct although a viscous yellow oil, probably a polymeric material, was also formed. A toluene solution containing 0.5 M maleic anhydride and 0.05 M benzophenone was irradiated for 15 hr at $-77°$ with the hope that **2** would accumulate. The contents of the tubes were then added quickly to concentrated solutions of tetracyanoethylene. No adducts could be isolated.

Quenching the Unsensitized Reaction. Bryce-Smith and Lodge reported that the unsensitized reaction is not quenched by oxygen.[5] We irradiated samples sealed under oxygen at a pressure of 1 atm in parallel with degassed samples and found unmistakable evidence for quenching. The results are summarized in Table VI.

Table VI. Quenching of the Unsensitized Reaction by Oxygen

Series	[MA]$_0$[a]	Percentage of reaction quenched[b]
1	2.00	23 ± 5
2	1.50	20 ± 7
3	0.20	31 ± 7

[a] Benzene solution. [b] Average results obtained from irradiation in parallel of five samples under oxygen and five degassed samples.

The effect is small but unmistakable. Other common quenchers, such as anthracene and azulene, were also tried but because of competitive absorption could not be used at concentrations greater than 5×10^{-4} M. Although some quenching was probably observed, the effect was not clearly outside the limits of experimental error. If the saturation solubility of oxygen in toluene is similar to that in benzene,[26] the oxygen concentration was about 5×10^{-3} M. Since quenching was observed, the rate constants for competitive reactions, including collapse to **2**, must be of the order of 5×10^7 moles l.$^{-1}$ sec^{-1}.

The experiment has considerable signficance since it indicates that at least part of the unsensitized reaction goes by way of triplets. Since it is not feasible to do studies involving varying concentrations of a quencher, we cannot be sure that the triplet path is the only one.[27]

Experimental Section

Materials. Acetonaphthone (Matheson Coleman and Bell, reagent grade) was recrystallized from acetic acid–water, mp 54.0°. Anthroquinone was recrystallized twice from acetic acid, mp 284–285°. Benzene (Matheson Coleman and Bell, Spectro quality) was generally used without purification. The material did not give a color on contact with sulfuric acid and less than 0.1% impurities was found by vapor chromatography. Benzaldehyde (Matheson Coleman and Bell, reagent grade) was distilled twice, the second

(26) M. Reznikovskii, Z. Tarasova, and B. Dogadkin, *Zh. Obshch. Khim.* **20**, 63 (1950); *Chem. Abstr.*, **44**, 4754 (1950).

(27) NOTE ADDED IN PROOF. We now find that maleic anhydride is an efficient quencher of the fluorescence of triphenylene and naphthalene (see ref 1 for similar observations). Consequently the significance of inhibition by those compounds (Table I) should be reevaluated. This removes the apparent anomaly presented by the cases of triphenylene and *p*-cyanobenzophenone. An attempt to reproduce the spectrum shown in Figure 1, with a less sensitive instrument, gave no resolvable emission so we cannot be entirely certain that the original result was not due to the presence of an impurity.

time through a spinning-band column, bp 65° (25 mm). Benzil (Matheson Coleman and Bell, reagent grade) was recrystallized from ethanol–water and then from ligroin, mp 96.5–96.8°. Chloroform (Matheson Coleman and Bell, Spectro quality) was used without further purification. Chrysene, recrystallized and sublimed, was supplied by Dr. J. R. Fox. p-Cyanobenzophenone was obtained from Dr. C.-H. Wu; it was recrystallized from ligroin–benzene, mp 115.5–116°. p-Diacetylbenzene (Aldrich, research grade) had been chromatographed on alumina and then recrystallized twice by Dr. A. A. Lamola. 4,4′-Dichlorobenzophenone (K and K Laboratories) was used without further purification; its phosphorescence spectrum was taken by Dr. A. A. Lamola and showed no trace of benzophenone. Fluorenone (Matheson Coleman and Bell, reagent grade) was recrystallized once from ligroin and once from ethanol, mp 83.8–84.5°. Maleic anhydride (Matheson Coleman and Bell, reagent grade) was sublimed at 45° (0.5 mm) immediately before use. Naphthalene (Matheson Coleman and Bell) was recrystallized twice from ethanol. Propiophenone (Matheson Coleman and Bell, reagent grade) was recrystallized from ligroin at −5° and then distilled at 0.5 mm through a Vigreux column; the fraction boiling at 63–64° was collected for use. Tetracyanoethylene (Aldrich, research grade) was recrystallized from ethyl acetate–chloroform. Thioxanthone was treated with carbon black and then recrystallized twice from methanol, mp 209°. Toluene (Matheson Coleman and Bell reagent grade) was shaken three times with concentrated sulfuric acid, dried over calcium chloride, and distilled from sodium. Triphenylene (Aldrich, research grade) was sublimed, mp 194–198°. Xanthone (Aldrich) was passed through an alumina column, eluted with benzene, and then recrystallized twice from methanol.

Procedures. Most irradiations were carried out in the "merry-go-round," an apparatus in which a number of tubes are rotated about a Hanovia immersion reactor containing a 450-w, medium-pressure lamp. The entire apparatus is placed in a constant-temperature water bath. The samples were placed in Pyrex culture tubes (13 mm o.d.) which had been constricted. The tubes were washed with Orvus soap, rinsed five times with distilled water and once with methanol, and dried at 125°. Solutions were prepared in volumetric flasks and 3- or 4-ml aliquots were added to the individual tubes. The samples were then degassed using three freeze–thaw cycles, with pumping at 5×10^{-4} mm, before being sealed off. The Pyrex tubes passed very little of the 2753- and 2804-A lines from the source and in most experiments with sensitizers a uranium–glass filter having virtually no transmission below 3300 A was used. No filter was used in experiments involving direct irradiation.

After irradiation the tubes were opened and the product was collected by suction filtration, washed with a few milliliters of cold reaction solvent, dried for 20 min at 115°, and weighed. The solubility of the adduct in all reaction solvents is too low for convenient measurement. However, varying amounts of product may have remained in the supernatant liquid by supersaturation, since crystal growth is very slow.

Some measurements of quantum yields were made using the collimated beam provided by the apparatus previously described.[9] Actinometry for runs with both systems was carried out by monitoring the reaction of benzophenone by benzhydrol.[9]

Radical Additions of Cl–CCl₃ to cis-Cyclooctene[1,2]

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Abstract: Both photo- and thermally initiated additions of carbon tetrachloride to cis-cyclooctene give mainly stereoisomeric 1-chloro-4-(trichloromethyl)cyclooctanes, products of transannular addition. Small amounts of the stereoisomeric 1,2-addition products and several other minor products containing less chlorine per molecule are also formed. Peroxide-initiated addition of trichloromethanesulfonyl chloride (net addition of Cl–CCl₃) produces the 1,2- and 1,4-addition products in the ratio 30:70. The activation energy requirement for transannular hydrogen atom shift in this system is estimated to be approximately 18 kcal/mole. Selective dehydrochlorinations of the addition products have been achieved; potassium hydroxide in alcoholic dimethyl sulfoxide produces mostly chloro-(dichloromethylene)cyclooctanes, but alcoholic silver nitrate leads to (trichloromethyl)cyclooctenes.

Transannular hydride shifts during cationic reactions of medium-ring compounds were first reported in 1952[3] and are now considered to be characteristic of those compounds.[4] Although these rearrangements occur to small extents in unsubstituted cycloalkyl cations, they become extensive when the initial carbonium ion center is flanked by an electron-withdrawing substituent.[4] Examples of transannular reactions involving radical intermediates have been far fewer in number than those involving cationic intermediates. Some[5] but not all[6] radical additions to 1,5-cyclooctadiene yield mostly substituted bicyclo[3.3.0]octanes as products (transannular C=C participation), and thiol addition to norbornadiene gives both normal and transannular products.[7] Recently, reports of transannular hydrogen abstraction by the intermediate alkoxy radical formed during decomposition of 1-methylcyclooctyl hypochlorite[8] and transannular hydrogen migration to a

(1) (a) Presented in part at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965; Abstracts, p 6S. (b) Based upon the Ph.D. dissertation submitted by T. M. C., Louisiana State University, Jan 1966. (c) A preliminary account of part of this research has been published: J. G. Traynham and T. M. Couvillon, J. Am. Chem. Soc., 87, 5806 (1965).

(2) Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research (Grant No. 1817-A.)

(3) (a) A. C. Cope, S. W. Fenton, and C. F. Spencer, J. Am. Chem. Soc., 74, 5884 (1952); (b) V. Prelog, K. Schenker, and H. A. Gunthard, Helv. Chim. Acta, 35, 1598 (1952).

(4) (a) V. Prelog and J. G. Traynham in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Division of John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 9; (b) A. C. Cope, M. M. Martin, and M. A. McKervey, Quart. Rev. (London), 20, 119 (1966).

(5) R. Dowbenko, J. Am. Chem. Soc., 86, 946 (1964).

(6) J. M. Locke and E. W. Duck, Chem. Commun., 151 (1965).

(7) S. J. Cristol, G. D. Brindell, and J. A. Reeder, J. Am. Chem. Soc., 80, 635 (1958).

(8) A. C. Cope, R. S. Bly, M. M. Martin, and R. C. Petterson, ibid. 87, 3111 (1965).