QUENCHING EFFECT OF THIOPHENE AND METHYLMALEIC ANHYDRIDES ON THE PHOTOREDUCTION OF BENZOPHENONE: A MECHANISTIC STUDY OF THEIR PHOTOSENSITIZED CYCLOADDITION

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Summary

The photoaddition of methylmaleic anhydrides and their nitrogen analogues to thiophene has proved useful as a synthetic tool to prepare compounds containing cyclobutane. Nevertheless, no serious effort has been made thus far to study the role of each of the reactants as an energy acceptor.

The results obtained in the present investigation indicate that three species (the anhydride, thiophene and a charge transfer complex formed by the two addends) may act as energy acceptors in the sensitization process. The extent of their capacity as quenchers may depend upon the conditions of the reaction.

1. Introduction

The benzophenone-photosensitized cycloaddition of methylmaleic anhydrides to five-membered ring heterocycles (Fig. 1) has been an important area of research in this laboratory [1 - 4].

Historically, the sensitized photoaddition of 2,3-dimethylmaleic anhydride to thiophene was first studied by Schenk *et al.* [5]. Since these

X = O, S ; Y = O, NH, N—CH₃   I
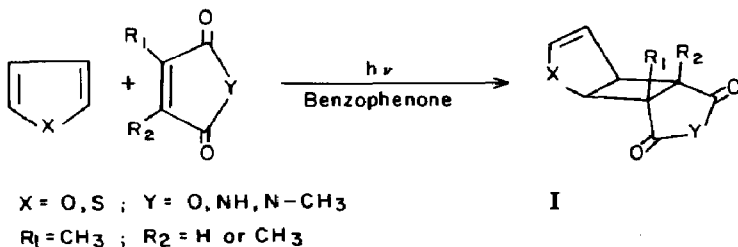
R₁ = CH₃ ; R₂ = H or CH₃

Fig. 1. Photosensitized cycloaddition of methylmaleic anhydrides and their analogues to yield heterocycles.

workers discovered the reaction in 1963 there has been no systematic effort to find clear evidence as to which of the reactants actually is the energy acceptor. This role has been unduly assigned to the maleic anhydride [4]. A comprehension of the extent to which each of the two addends acts as an energy acceptor may be very useful for a better understanding of the reaction. It will make possible an explanation of the product composition when compounds other than the expected adduct I are formed and it will also help suggest a mechanism for the process.

It is well known that the photochemical reactions of benzophenone and its photophysical processes, such as energy transfer, occur from its lowest excited triplet state [6]. Hence a reasonable approach for tackling the problem would be to investigate the quenching effect of the appropriate thiophene derivatives as well as that of the maleic anhydrides on one of the best known reactions of benzophenone, such as photoreduction [7]. A comparison of the rate of quenching for one reactant with that for the other would give a clear indication of the role played by each of them in the energy transfer process involved in the photoaddition reaction.

The quenching effect of thiophene and its methyl derivatives on the triplet state of benzophenone had already been studied in this laboratory in connection with reactions in which oxetane is formed [7, 8]. Therefore, the same technique used for the investigation of the oxetane heterocycles could be successfully applied to quenching experiments in which maleic anhydrides were employed.

Furthermore, in the course of this investigation evidence was found for the formation of a charge transfer complex between the methylmaleic anhydrides and thiophene in solution. In fact, when the UV spectrum of a solution of thiophene and anhydride is measured in cyclohexane a new absorption band, different from the characteristic bands of thiophene (238 nm) and of the anhydrides (citraconic (methylmaleic), 248 nm; 2,3-dimethylmaleic, 255 nm) in the same solvent, appears at 285 nm and 293 nm respectively. Therefore, this additional factor had to be taken into consideration as well. Consequently, a method based on nuclear magnetic resonance (NMR) techniques [9] was used to measure the equilibrium constants for the system thiophene–anhydride in equilibrium with the complex. In this way it was possible to estimate the concentrations of the three species (thiophene, anhydride and complex), all of these being capable of acting as energy acceptors.

2. Experimental details

2.1. Kinetics

Different concentrations of thiophene ranging from 0.060 to 6.25 M were added to a solution of benzophenone in isopropyl alcohol (5.04×10^{-2} M). The reaction mixtures were irradiated by means of a carousel apparatus placed in a Rayonet reactor equipped with a set of low pressure mercury

lamps (λ = 300 nm) with Pyrex filters. The disappearance of the n,π^* band of benzophenone at 335 nm was monitored by using a Perkin–Elmer model 124 UV spectrometer. Similar experiments were carried out using citraconic anhydride and 2,3-dimethylmaleic anhydride. The concentrations used in these experiments were in the range (1.0×10^{-3}) - (25×10^{-3}) M. In order to equalize the volumes of all the solutions, varying amounts of an inert solvent such as benzene were added when thiophene was used as a quencher.
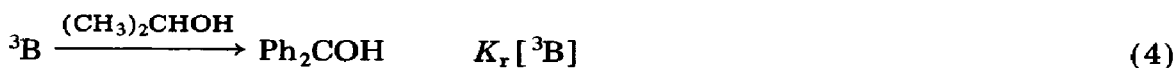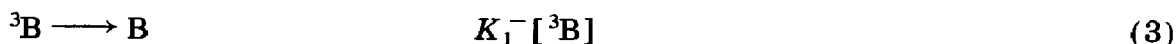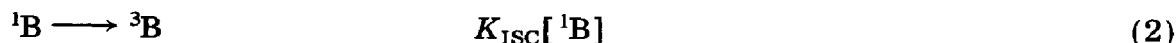
In the experiments with maleic anhydrides, dichloromethane was used for this purpose instead of benzene in order to avoid complexes being formed with the solvent [10]. Complete inhibition of photoreduction was attained when the maximum concentration given above for each of the quenchers was employed. The data obtained were subjected to the analysis previously reported [7, 8] in order to obtain the Stern–Volmer plots.

2.2. NMR measurements for the determination of the K_{eq}

Several sets of solutions of the methyl-substituted maleic anhydride under study and thiophene in carbon tetrachloride with 1% tetramethylsilane (TMS) were prepared. In each set of solutions the concentration of the anhydride was kept constant while that of thiophene was varied from 2.5 to 7.5 M. The concentrations of citraconic anhydride used were in the range (2.0×10^{-3}) - (21.3×10^{-3}) M and those for 2,3-dimethylmaleic anhydride were in the range (1.6×10^{-3}) - (3.9×10^{-3}) M. In each determination the displacement upfield of the anhydride methyl group resonance relative to the TMS resonance, as the thiophene concentration increased, was observed and measured. The data were analysed according to Foster's adaptation [9] of the Benesi–Hildebrand equation.

3. Results and discussion

As reported previously [7, 8], and confirmed once more in this investigation, the following reaction scheme illustrates the mechanism of the benzophenone photoreduction in isopropyl alcohol in the presence of a quencher such as thiophene or the maleic anhydrides.

$$B \longrightarrow {}^1B \qquad\qquad \text{Rate } I \tag{1}$$

$$^1B \longrightarrow {}^3B \qquad\qquad K_{ISC}[{}^1B] \tag{2}$$

$$^3B \longrightarrow B \qquad\qquad K_1^-[{}^3B] \tag{3}$$

$$^3B \xrightarrow{\text{(CH}_3)_2\text{CHOH}} Ph_2COH \qquad K_r[{}^3B] \tag{4}$$

$$^3B + Q \longrightarrow B + Q \qquad K_q[{}^3B][Q] \tag{5}$$

(Q $\equiv$ quencher (thiophene (Th) or anhydride (A)); B $\equiv$ benzophenone.)

TABLE 1

Quencher	Slope	Correlation coefficient	K_q ($\times 10^8 M^{-1} s^{-1}$)
Thiophene	7.35	0.997	1.3
Citraconic anhydride	53.30	0.949 (0.987)	9.35
2,3-Dimethylmaleic anhydride	74.26	0.955 (0.986)	13.03

The values in parentheses are for very dilute solutions between zero and 9.1×10^{-3} M for citraconic anhydride and between zero and 13×10^{-3} M for 2,3-dimethylmaleic anhydride.

The following Stern–Volmer equation holds for the proposed mechanism.

$$\frac{\phi_0}{\phi} = 1 + K_q \tau [Q]$$

The data obtained from the Stern–Volmer plots are given in Table 1.
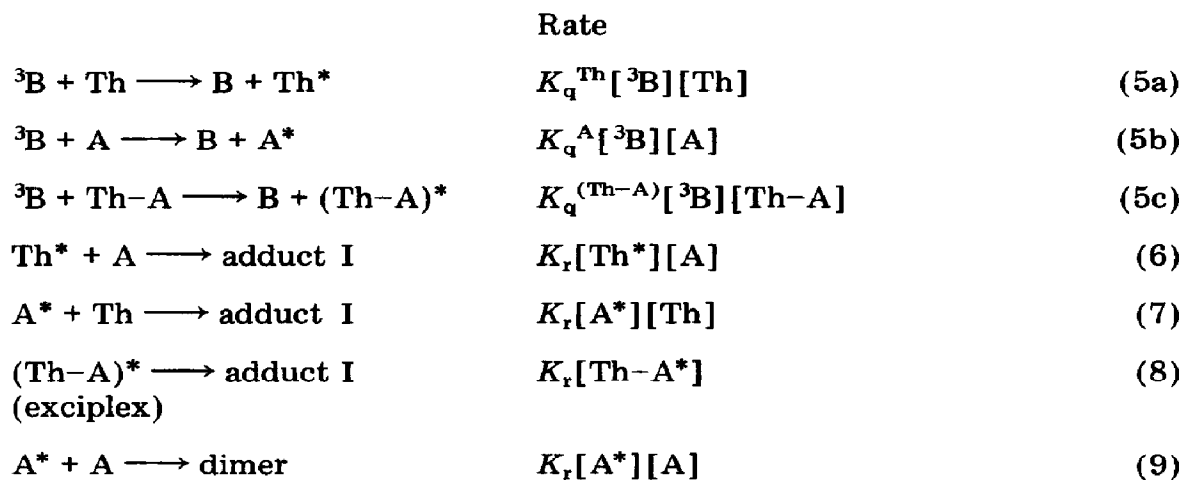
The correlation coefficients given for the anhydrides were calculated by taking into consideration all the points found (a total of nine) between a zero concentration of quencher and 25×10^{-3} M. The values in Table 1 show a slight deviation from linearity. When only five points are considered, namely between zero and 9.1×10^{-3} M for citraconic anhydride and from zero to 13×10^{-3} M for 2,3-dimethylmaleic anhydride, the correlation coefficient found was 0.987. At low concentrations of quencher the Stern–Volmer plot is a straight line but as the concentration increases there is the possibility that an exciplex between the anhydride and benzophenone may be formed. Once this new excited species appears the quencher starts quenching two excited species and as a consequence the Stern–Volmer plot starts to deviate from linearity [11].

However, for the system involving citraconic anhydride–thiophene in equilibrium with their complex, $K_{eq} = 0.10 \pm 0.02$ M^{-1} was found from the above-mentioned Benesi–Hildebrand equation; for the system involving 2,3-dimethylmaleic anhydride the calculated value for the equilibrium constant was $K_{eq} = 0.088 \pm 0.002$ M^{-1}. These values indicate that (a) when thiophene is in large excess ([Th] $\gg$ [A], e.g. thiophene is used as the solvent in the photochemical reaction), i.e. the ratio of the concentration of thiophene to that of the anhydride is about 370 to 1 ([Th]/[A] = 370), about 50% of the anhydride present in solution is associated with thiophene in the form of a charge transfer complex, and (b) when equal concentrations of both species are present ([Th] = [A]) only a small amount of the anhydride is in the form of a complex ([Th–A] $\ll$ [A]).

Since it would be difficult to determine the K_q for these complexes, they could be approximated to the maximum value permitted for a diffusion-controlled process, and on the assumption that there are two

chromophores in the complex, the latter should be an even better quencher than either of the two chromophores separately. Thus the approximate value for $K_q[Th–A]$ would be $5 \times 10^9 \, M^{-1} \, s^{-1}$. An analogy to this reasoning may be found in the work of Hammond and Hardham [12] on the photosensitized addition of maleic anhydride to benzene. They inferred from their results that the complex maleic anhydride–benzene should be a better quencher than the uncomplexed material for the photoreduction of benzophenone in benzene solution.

Knowing all the quenchers involved, it is possible, beginning with reaction (5) of the scheme above and substituting for Q with the individual quenchers, to write a mechanism for the sensitized process under study.

<div align="center">Rate</div>

$$^3B + Th \longrightarrow B + Th^* \qquad\qquad K_q^{Th}[^3B][Th] \qquad\qquad (5a)$$

$$^3B + A \longrightarrow B + A^* \qquad\qquad K_q^{A}[^3B][A] \qquad\qquad (5b)$$

$$^3B + Th–A \longrightarrow B + (Th–A)^* \qquad\qquad K_q^{(Th–A)}[^3B][Th–A] \qquad\qquad (5c)$$

$$Th^* + A \longrightarrow adduct\ I \qquad\qquad K_r[Th^*][A] \qquad\qquad (6)$$

$$A^* + Th \longrightarrow adduct\ I \qquad\qquad K_r[A^*][Th] \qquad\qquad (7)$$

$$(Th–A)^* \longrightarrow adduct\ I \qquad\qquad K_r[Th–A^*] \qquad\qquad (8)$$
(exciplex)

$$A^* + A \longrightarrow dimer \qquad\qquad K_r[A^*][A] \qquad\qquad (9)$$

Knowing the concentrations for the different species and the values of K_q it is possible to calculate the relative rates for the different quenching processes. Since they are known under the same experimental conditions the relative rates for any two can be calculated as illustrated for reaction (5a) relative to reaction (5b) as

$$\frac{R_{5a}}{R_{5b}} = \frac{K_q^{Th}[^3B][Th]}{K_q^{A}[^3B][A]}$$

where R is the rate of the process.

However, in order to visualize more clearly the contribution of each species to the overall reaction, the fraction of quenching from each specific quencher rather than their relative ratios is depicted in Table 2.

With these values it would be reasonable to propose that different mechanisms operate at the same time. They have been summarized above and the appropriate steps for the predominant mechanism can be selected according to the concentrations of the different species involved.

From the values given for the K_q it may be inferred that the anhydrides as well as the charge transfer complex are better quenchers than thiophene. From Table 2 it is easily visualized that the predominance of the anhydride as a quencher depends on its concentration relative to that of the thiophene.

TABLE 2

Fraction of quenching due to each specific quencher under different conditions

Concentration (M)				Fraction of quenching		
Thiophene	Citraconic anhydride	2,3-dimethyl-maleic anhydride	Thiophene–anhydride	Thiophene	Anhydride	Thiophene–anhydride
12.34	0.14	—	0.16	0.630	0.050	0.320
0.914	0.914	—	0.086	0.084	0.601	0.308
12.46	—	0.27	0.03	0.763	0.166	0.071
0.92	—	0.918	0.08	0.069	0.697	0.233

Thus, the dimer of the anhydride is formed only when thiophene and the anhydride are in a 1:1 ratio. When thiophene is in excess process (5a) competes favourably with process (5b). It can be stated that these processes as well as reaction (5c) operate in the photoreaction and that one or two of these predominate according to the reaction conditions. Nevertheless, when thiophene is in excess, the synthetic result is that no other products apart from the cycloaddition compound are formed.

The dimer of citraconic anhydride was not obtained; the reason why it was not isolated may be found in the work of Boule et al. [10]. Perhaps the use of a solvent of low complexing ability, such as dichloromethane [10], influenced the results.

Boule's studies also revealed that the more substituted the anhydride the more easily are dimers formed. Thus, the order of increasing reactivity of the anhydrides is maleic < citraconic < 2,3-dimethylmaleic.

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