QUENCHING OF THE NORRISH TYPE II REACTION OF BUTYROPHENONE BY THIOPHENIC COMPOUNDS

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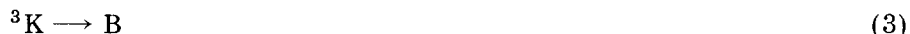
(Received May 3, 1975)

Summary

The acetophenone production from excited butyrophenone, in cyclo-hexane solution, at 25 °C, was quenched by thiophene, 3-methylthiophene, 2-chlorothiophene, and 2-methylthiophene. The determined rate constants correlate well with the ionization potentials calculated for the quenchers from charge transfer complexes studies. A mechanism involving a charge transfer complex between the excited butyrophenone and the quencher is proposed.

Introduction

As part of the study of the kinetics and mechanism of the interaction of excited carbonyl compounds with several groups of substrates, we have examined the photochemistry of butyrophenone in the presence of thiophene and substituted thiophenes.

The following reaction scheme represents the mechanism of the photochemical type II process in butyrophenone:

$$K \xrightarrow{h\nu} {}^1K \qquad (1)$$

$$^1K \longrightarrow {}^3K \qquad (2)$$

$$^3K \longrightarrow B \qquad (3)$$

$$B \longrightarrow K \qquad (4)$$

$$B \longrightarrow CH_3COPh + C_2H_4 \qquad (5)$$

$$B \longrightarrow \text{(cyclobutanol)} - OH \qquad (6)$$

Ph

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where K represents butyrophenone and B the intermediate biradical resulting from intramolecular γ hydrogen abstraction. The quantum yield of intersystem crossing to the triplet state can be taken as unity; therefore other reactions of the singlet state do not need to be considered.

Preliminary quenching experiments were carried out in benzene as solvent. This led to serious deviations from linearity in the Stern–Volmer plots. In particular, this effect was quite large for 2-methylthiophene as the quenching species. This result can be attributed to the formation of a complex with the solvent, evidence for which was obtained from the presence of a new band in the absorption spectrum of the mixture, which could neither be attributed to 2-methylthiophene, nor to the solvent [1]. We have therefore preferred to avoid aromatic solvents and all the kinetic results reported here were obtained in cyclohexane, whose reaction (7) also needs to be considered.

$$^3K + C_6H_{12} \rightarrow \dot{K}H + C_6H_{11} \cdot \tag{7}$$

The rate for reaction (7) is k_7 [2] = $3.95 \times 10^5 \, M^{-1} \, s^{-1}$ at room temperature. The lifetime of butyrophenone triplets is therefore given by:

$$\tau^{-1} = k_3 + k_7 [C_6H_{12}] \tag{8}$$

In neat cyclohexane (9.4 M) at 25 °C τ^{-1} = $12.15 \times 10^6 \, s^{-1}$, using k_3 [3] = $8.45 \times 10^6 \, s^{-1}$. Reaction (9) takes into account the quenching process by the thiophenic compound, (Th):

$$^3K + Th \rightarrow quenching \tag{9}$$

Experimental

The photolyses were carried out in a laboratory made merry-go-round where the filled tubes were located, the whole system being immersed in a thermostatic bath kept at 25 ± 1 °C. The radiation source used was a 400 W Osram medium pressure mercury arc. Its emission was not filtered. Taking into account the cut-off of the Pyrex glass, the wavelength used was λ > 300 nm.

Solutions were prepared using cyclohexane as solvent and the tubes were degassed in a conventional grease free, mercury free high vacuum line down to a pressure of 1 μm. When photolyzing care was taken to avoid gas phase photolysis. After photolyzing a series of tubes containing different concentrations of the used thiophenic compound, the amount of acetophenone produced in each tube, related to the amount of butyrophenone, were measured in an Acromat gas chromatograph using a hydrogen flame detector. The column used was ¼ in. diameter × 6 ft. long 20% Apiezon L over Chromosorb W and the N_2 flow rate was 50 cm³/min. The irradiation time was always around 60 min assuring conversion under 5%. U.v. spectra were taken with a Beckman DB-GT grating spectrophotometer.

Reagents

Cyclohexane (Erba "RS") was distilled and the middle fraction was used as solvent. Butyrophenone (Aldrich) was used and its purity was checked by gas–liquid chromatography. All the thiophenic compounds, from Merck, were distilled and the middle fraction was used. In every case a u.v. spectrum of the thiophenic compound in cyclohexane was taken, making sure that there was no absorption in the region where the butyrophenone was to be excited.

Results and Discussion

From the proposed mechanism the following Stern–Volmer equation holds:

$$\frac{\Phi_0}{\Phi} = 1 + k_9 \tau [Th] \tag{10}$$

where Φ_0 and Φ are the quantum yields of acetophenone production in the absence and presence of added quencher. The equation is valid provided that the thiophenic compound does not affect the ratio $k_5/(k_4 + k_5 + k_6)$ and that its concentration is low enough so that it does not significantly affect the concentration of cyclohexane (see eqn. 8). The latter condition is certainly met, while the linearity of the plots (see Fig. 1) suggests that the former assumption also holds. Table 1 gives a summary of results. All the rate constants are around one order of magnitude below the rate for a diffusion controlled process.

Reaction (9) might take place by two different mechanisms: (i) a resonance energy transfer leading to the thiophenic compound in the triplet state. Such a reaction would need to be endothermic as suggested by the values of the rate constants; and (ii) the formation of an exciplex between the carbonyl compound and the substrate, represented by the following resonance structures [4]:

$$[K^*, Th] \rightleftarrows [K, Th^*] \rightleftarrows [K^+, Th^-] \rightleftarrows [K^-, Th^+]$$
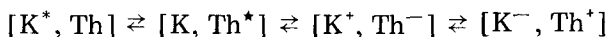
where the first and the last one would be the structures being important contributors. The latter mechanism would be expected to lead to a good correlation between $\log k_9$ and the ionization potential of the different quenchers. When the experimental ionization potentials were used the correlation was fairly poor, although a trend was observed. The experimental ionization potentials are included in Table 1 and were taken from refs. 5, 6 and 7. For thiophene two different values were found and both are included in the Table. It was impossible for us to surely prefer one of them. However, a good correlation was obtained (see Fig. 2) when calculated ionization potentials (*IP*) were used. They were obtained as

$$IP = a + b \, \bar{\nu}_{CT} \tag{11}$$

This is an empirical relationship between *IP* and the maximum wavenumber
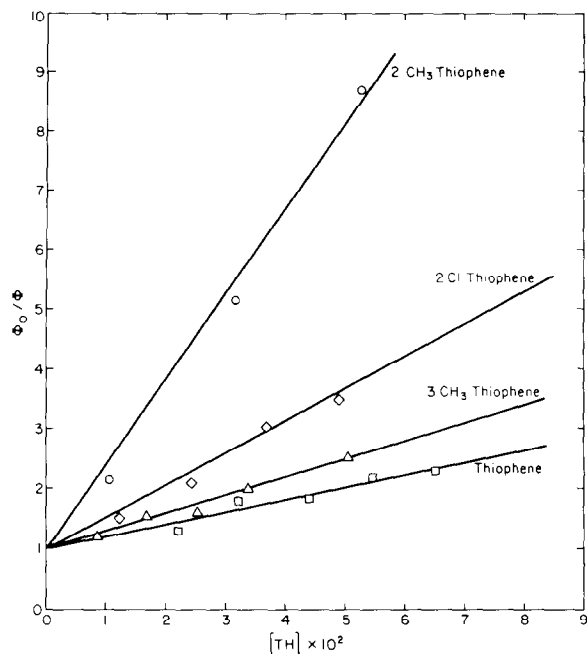
Fig. 1. Stern–Volmer plots for the quenching of acetophenone production from the photolysis of butyrophenone by thiophenic compounds.

TABLE 1

Values calculated from the slopes of Fig. 1 for the quenching constants of the triplet states of butyrophenone (k_9) by thiophenic quenchers, at 25 °C in cyclohexane.

Quencher	$k_9 \times 10^{-8}$ ($M^{-1}s^{-1}$)	IP (experimental) (eV)
Thiophene	2.66	9.12 [5] - 8.86 [7]
3-methylthiophene	3.88	8.72 [6]
2-chlorothiophene	6.65	9.06 [5]
2-methylthiophene	17.32	8.63 [5]

The experimental ionization potentials for the different quenchers are included.

of the charge transfer band for a given donor and a series of acceptors [8, 9] a and b are experimentally determined constants. These calculated IP should rather be regarded as parameters measuring the donor ability of the substrates in solution and therefore as a good measure of this property under our experimental conditions, since they presumably take into account solvent and steric effect. From the correlation shown in Fig. 2, done using the IP calculated by Aloisi et al. [6] with the preceding formula relating IP and $\bar{\nu}_{CT}$, for the thiophenic compounds acting as π donors, we conclude that the charge transfer mechanism is probably operative.

In an earlier study performed by Braslavsky and Heicklen [10] on the reaction of thiophene with electronically excited SO_2 two kinds of products
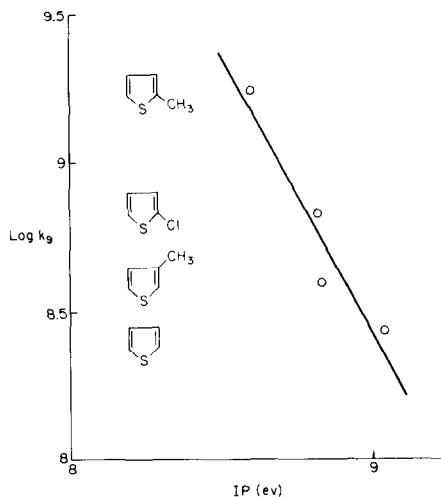
Fig. 2. Log k_9 *vs.* calculated *IP* (see text).

were observed. One kind were the same as those found in the photolyses of pure thiophene and the proposed detailed mechanism included an energy transfer process between excited SO_2 and thiophene giving rise to excited thiophene which in turn decomposed giving the observed products. The other kind of reaction products were new products and it was said that they came mainly from SO_2^* (a non-emitting excited state of SO_2) through the following reaction:

$$SO_2^* + Th \rightarrow SO_2 + Th^{II}$$
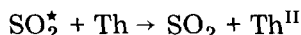
Th^{II} being an intermediate species. It is possible that this last reaction occurs *via* a charge transfer complex, not giving rise to an excited thiophene molecule. In this charge transfer complex thiophene could act as a donor and the excited SO_2 as an acceptor, being the case similar to the one studied in this paper between thiophenic compounds and excited butyrophenone. The role of excited SO_2 as acceptor in the formation of charge transfer complex has been already pointed out by Jones and Adelman [11].

Finally, it should be pointed out that the mechanism proposed for the quenching process cannot be distinguished kinetically from an alternative one where the formation of the exciplex is diffusion controlled but reversible [replacing reaction (9) by reaction (12)]:
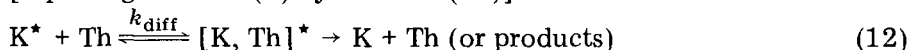
$$K^* + Th \xrightleftharpoons{k_{diff}} [K, Th]^* \rightarrow K + Th \text{ (or products)} \tag{12}$$

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