

## Short Communication

---

### Quencher effect of thiophene and its monomethyl derivatives on photo-reduction and photocycloaddition reactions of ketones

R. A. BOLÍVAR and C. RIVAS

*Centro de Química, Instituto Venezolano de Investigaciones Científicas, Apartado 1827, Caracas 1010-A (Venezuela)*

(Received August 24, 1981; in revised form November 2, 1981)

#### 1. Introduction

Some years ago the successful photoaddition of benzophenone to 2,5-dimethylthiophene to form an oxetane was carried out in this laboratory [1]. Later, the reaction was extended to other carbonyl compounds such as benzoylpyridines and 2-benzoylthiophene [2] as well as to other benzophenone and naphthaldehyde derivatives [3]. Nevertheless, it has always been puzzling that we have been unable to form oxetanes in this way with thiophene itself or with other thiophene derivatives such as 2-methylthiophene and 3-methylthiophene. Furthermore, the same behaviour has been observed in such systems as pyrrole [4], selenophene [5] and tellurophene [6]. In contrast with the lack of reactivity of all these five-membered heterocyclic ring systems, furan and its methyl derivatives [7] have always been found to be excellent substrates for excited carbonyl compounds.

Since the reactivity of these systems for ground state reactions is closely associated with their aromatic character, a number of workers have speculated that the inertness of thiophene [8] towards this kind of reaction may be due to this property. However, the lack of reactivity can be viewed from another angle: these compounds may behave as quenchers of the excited states of the ketones used in the cycloaddition reactions.

In order to test this hypothesis two types of experiments are currently being carried out with the aim of establishing a systematic method of predicting the reactivity towards oxetane formation in five-membered heterocyclic ring systems other than furan. In one series of experiments the quenching properties of these heterocyclic compounds with respect to the photoreduction of benzophenone are being examined, and in the second series the synthetic aspects of the reactions are being investigated.

The reason for choosing the photoreduction of benzophenone to test the quenching of oxetane formation is that the excited state of the aromatic ketones involved is the same for both types of reaction [9]. Thus the results obtained from these experiments can safely be applied to the Paterno-Buchi reaction.

## 2. Experimental details

Different concentrations of thiophene ranging from 0.625 to 6.25 M were added to a solution of benzophenone in isopropyl alcohol ( $5.04 \times 10^{-2}$  M). The reaction mixtures were irradiated by using a carousel apparatus in a Rayonet reactor equipped with a set of low pressure mercury lamps ( $\lambda = 300$  nm) with Pyrex filters. The disappearance of the  $\pi\pi^*$  band of benzophenone at 335 nm was followed by means of a Perkin-Elmer model 124 UV spectrometer. Similar experiments were carried out using 2-methylthiophene and 3-methylthiophene at concentrations of 0.02, 0.10, 0.25 and 0.50 M.

## 3. Results and discussion

When thiophene was added to the benzophenone solution before irradiation the photoreduction was strongly quenched. This effect gradually increased as the concentration of thiophene increased, and photoreduction was totally inhibited at the highest concentration used [10] (Fig. 1).

The following reaction scheme represents the mechanism of the benzophenone photoreduction:

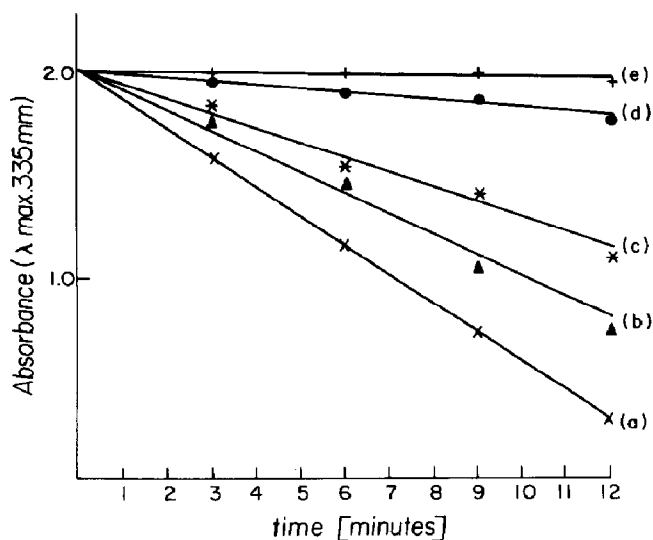
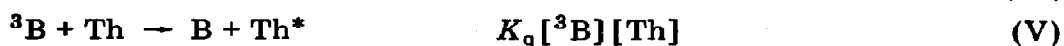
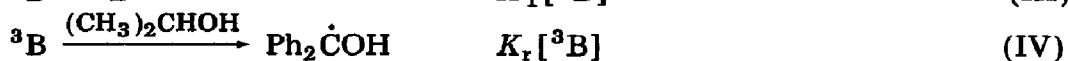
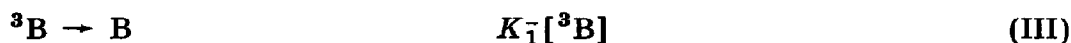


Fig. 1. The effect of thiophene on the photoreduction of benzophenone. Five solutions of benzophenone ( $5.04 \times 10^{-2}$  M) in isopropyl alcohol containing various thiophene concentrations were irradiated: (a) 0.00 M; (b) 0.625 M; (c) 1.25 M; (d) 2.50 M; (e) 6.25 M.

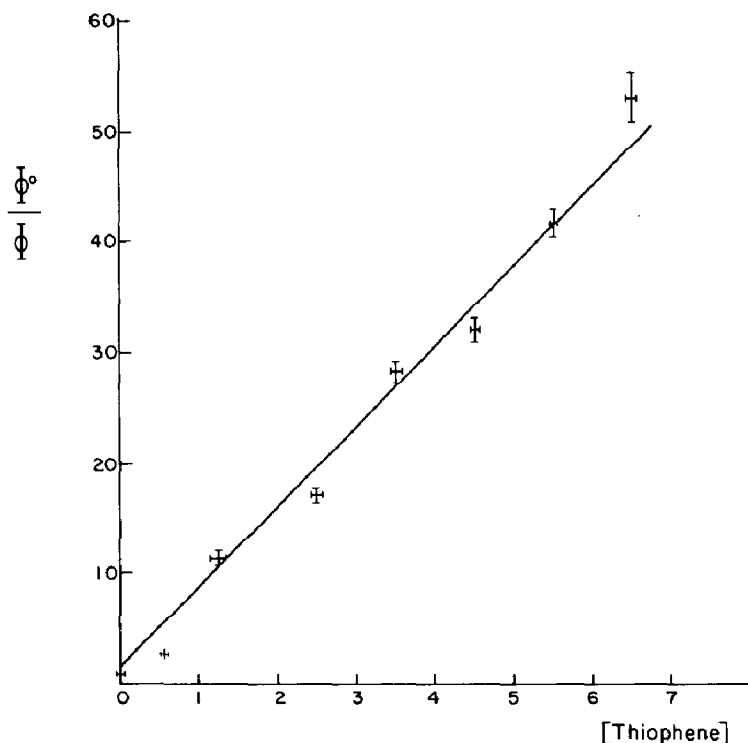


Fig. 2. Stern-Volmer plots for the quenching of benzophenone photoreduction by thiophene. Similar plots are obtained for the effects of the quencher on the monomethyl derivatives of thiophene.

where Ph denotes phenyl, B denotes  $\text{Ph}_2\text{CO}$ , Th denotes thiophene and  $I$  is the intensity. The following Stern-Volmer equation holds for the proposed mechanism:

$$\phi_0/\phi = 1 + K_q\tau[\text{Th}] \quad (1)$$

where  $\phi_0$  and  $\phi$  are the quantum yields for the photoreduction of benzophenone in the absence and the presence of the quencher respectively (Fig. 2).

2-methylthiophene and 3-methylthiophene are more efficient quenchers than thiophene itself since lower concentrations are required to produce total inhibition of the reaction. Under the same conditions concentrations of 0.5 M of thiophene are required to quench photoreduction completely.

Table 1 gives the data obtained from the Stern-Volmer plots for the quenchers at 25 °C in isopropyl alcohol. All the quenching rate constants  $K_q$  are about an order of magnitude less than the rate for a diffusion-controlled process. From these results it is clear that (1) the lowest triplet energy of thiophene ( $T_{1T}$ ) is lower than that of benzophenone ( $T_{1B}$ ) (according to literature sources the values of  $T_1$  for both compounds are the same ( $T_{1T} = T_{1B} = 69 \text{ kcal mol}^{-1}$ ) [11]) and (2) the gap between the lowest triplet energy

TABLE 1

Quencher	Slope	Correlation coefficient	$K_q$ ( $M^{-1} s^{-1}$ )
Thiophene	7.35	0.997	$1.3 \times 10^8$
2-methylthiophene	19.05	0.999	$3.3 \times 10^8$
3-methylthiophene	9.33	0.990	$1.6 \times 10^8$

level of the methylthiophenes and  $T_{1B}$  should be smaller than that between  $T_{1T}$  and  $T_{1B}$ .

These results should not be surprising in view of the fact that the attachment of electron-donating groups to a conjugated diene system should raise its lowest triplet energy level to a higher value above the ground state than that of the unsubstituted diene [9]. Thus the substitution of one methyl group in the thiophene nucleus raises its lowest triplet energy level  $T_{1T}$  closer to that of benzophenone  $T_{1B}$  but still not high enough to change it from a quencher to an acceptor of the excited ketone such that an oxetane is formed. The substitution of two methyl groups in the ring as is the case for 2,5-dimethylthiophene raises  $T_{1T}$  to a higher level than  $T_{1B}$ ; the energy transfer then becomes inefficient or perhaps zero and the reaction takes place. In order to test this hypothesis, which is based on the reactivity of one compound only, 2,3-dimethylthiophene was synthesized and used as a substrate for the excited benzophenone. After irradiation of the ketone in the presence of this thiophene derivative an oxetane was obtained with a good yield [12].

Preliminary studies of the quenching properties of pyrrole indicate that when pyrrole itself is used as the solvent for the photoaddition reaction it darkens very quickly and acts as a light filter preventing the reaction from taking place. However, when it is used in small concentrations, as in the experiments with the thiophene derivatives, the darkening is not appreciable and it also behaves as a quencher of the excited state of benzophenone. The only way in which oxetanes have been produced from pyrrole has been by attaching electron-attracting groups such as benzoyl to the nitrogen atom [4, 13].

The quenching experiments initiated with the thiophene series will be extended to pyrrole derivatives as well as to selenophene and tellurophene derivatives in order to use these results for more successful synthesis work which thus far has mostly been carried out by trial and error.

- 1 C. Rivas, M. Velez and O. Crescente, *Chem. Commun.*, (1970) 1474.
- 2 C. Rivas and R. A. Bolívar, *J. Heterocycl. Chem.*, 10 (1973) 967.
- 3 C. Rivas, R. A. Bolívar and M. Cucarella, submitted to *J. Heterocycl. Chem.*
- 4 C. Rivas, M. Velez, M. Cucarella, R. A. Bolívar and S. E. Flores, *Acta Cient. Venez.*, 22 (1971) 145.
- 5 C. Rivas, D. Pacheco and F. Vargas, *J. Heterocycl. Chem.*, 17 (1980) 1151.
- 6 C. Rivas, D. Pacheco and F. Vargas, unpublished work, 1980.

- 7 C. Rivas and E. Payo, *J. Org. Chem.*, **32** (1967) 2918.
- 8 G. R. Evanega and E. B. Whipple, *Tetrahedron Lett.*, (1967) 2163.
- 9 D. R. Arnold, *Adv. Photochem.*, **6** (1968) 301.
- 10 R. A. Bolívar and C. Rivas, *J. Photochem.*, **17** (1981) 91.
- 11 N. J. Turro, *Molecular Photochemistry*, Benjamin, New York, 1965, p. 132.
- 12 C. Rivas, D. Pacheco, F. Vargas and J. Ascanio, *J. Heterocycl. Chem.*, **18** (1981) 1065.
- 13 C. Rivas and R. A. Bolívar, *J. Heterocycl. Chem.*, **13** (1976) 1037.