Laser flash photolysis study of *o*-tolyl vinyl ketone—methyl vinyl ketone copolymers. Electron donor properties of the intermediate macrobiradicals

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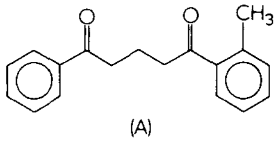
Laser excitation of solutions of *o*-tolyl vinyl ketone-methyl vinyl ketone copolymers leads to the formation of the short lived triplet state of the aromatic carbonyl chromophore. The decay of the triplet state yields 1,4-biradicals which have a lifetime of 310 ns (polar solvents) and are capable of transferring an electron to paraquat dications with a rate constant of $1.7 \times 10^9\ M^{-1}\ s^{-1}$. In the absence of electron acceptors these macrobiradicals decay to yield photoenols which eventually tautomerize to regenerate the original polymer.

INTRODUCTION

In recent publications from this laboratory, we have shown that the photoenolization of the *ortho*-methyl benzoyl group can be used to reduce, or prevent, the photodegradation of polymers containing phenyl vinyl ketone moieties[1,2]. We have also shown that triplet energy migration is an important process in polymers containing sequential aromatic carbonyl groups, such as poly(phenyl vinyl ketone)[3] and copolymers of phenyl vinyl ketone and *o*-tolyl vinyl ketone[1,2]. The same type of behaviour has also been observed in some diketones, e.g. 1-phenyl-5-*o*-tolyl-1, 5-pentanedione, (A), where we have shown that the photochemical behaviour is controlled by energy migration processes which lead to the efficient enolization of the *o*-methyl benzoyl group[4].



(A)

We have now examined the photochemistry of copolymers of methyl vinyl ketone and *o*-tolyl vinyl ketone (CoMT) using nanosecond laser flash photolysis techniques. The higher triplet energy and comparatively poor optical absorption characteristics make the methyl vinyl ketone moieties behave as inert units, while at the same time maintaining a relativity constant environment around the *o*-methyl benzoyl groups. These copolymers are also soluble in polar solvent mixtures; this property has allowed us to examine in some detail the electron donor reactions of the 1,4-biradicals, a process which has not been previously examined in macromolecular systems. *Scheme I* shows the main steps involved in the photochemistry of CoMT.

EXPERIMENTAL

Materials

Methyl vinyl ketone (Aldrich) was distilled prior to use. *o*-tolyl vinyl ketone was prepared from *o*-tolyl vinyl alcohol following a literature procedure[14].

The polymers were prepared by radical initiated polymerization of deaerated monomer mixtures in benzene. The initiator was always AIBN (azo-*bis*-isobutyronitrile), and the conversions were kept below 15% to avoid the depletion of the more reactive aromatic monomer from the reaction mixture. The polymers were then precipitated with cold methanol, separated and redissolved in benzene; this process was repeated five or six times and the sample was finally freeze-dried from benzene. The composition of the copolymers was determined by comparing their u.v. spectra with those of *o*-methylbutyrophenone solutions of known concentration.

Laser photolysis

The samples were contained in suprasil cells with an optical path of 3 mm. All experiments were carried out under oxygen-free conditions. Our instrument makes use of a Molectron u.v.—400 nitrogen laser for excitation. The use of computer averaging techniques allows the detection and analysis of rather weak signals; typically 10—30 laser shots were averaged to obtain each trace. Further details on the equipment have been given elsewhere[15].

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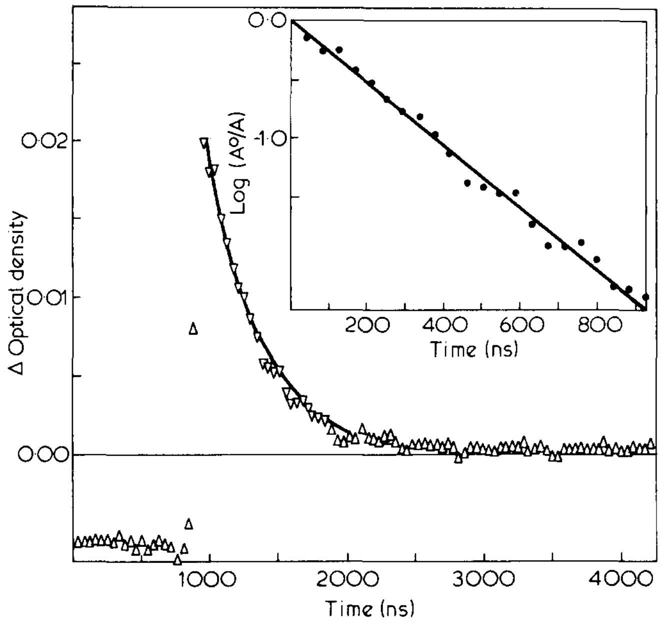


Figure 1 Decay of the biradical (c) from CoMT15 in AAM as monitored at 395 nm. Insert – first order fit of the kinetics of the process

RESULTS AND DISCUSSION

The polymer samples employed were prepared by radical initiated polymerization of solutions of *o*-tolyl vinyl ketone and methyl vinyl ketone in benzene, using AIBN as initiator. The samples contained 3% (CoMT3) and 15% (CoMT15) of *o*-methyl benzoyl groups, as determined by u.v. spectroscopy. Assuming a random distribution, these compositions correspond to 94% and 74% isolated units for CoMT3 and CoMT15, respectively; the term 'isolated' is used for an *o*-methyl benzoyl group having as next neighbours two aliphatic carbonyl chromophores.

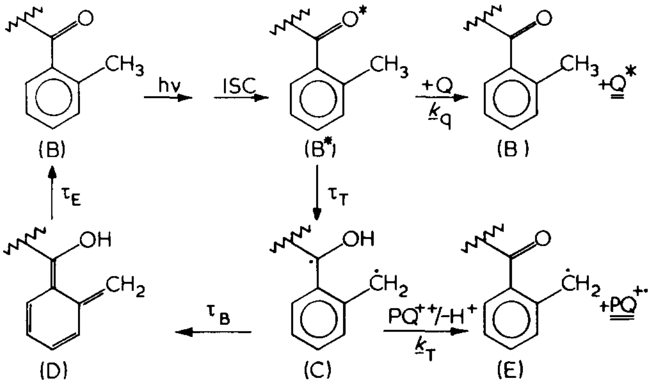
The samples were dissolved in either benzene or a mixture (AAM) of acetonitrile:acetone:methanol (30:30:40). This mixture was used because it dissolved the copolymers, as well as the electron acceptor, paraquat dichloride (see below).

The samples were excited with the pulses (337.1 nm, 8 ns, 3 mJ) from a nitrogen laser, and the transient optical absorptions which resulted were monitored using a detection system with nanosecond response.

Figure 1 shows a typical trace obtained by excitation of CoMT15 in AAM and monitoring the transient absorptions at 395 nm. The species decaying is the biradical (C), since the triplet state is very short lived (*vide infra*). The biradical lifetime determined by this method is 370 ns[5]. The final baseline position is quite different from the initial, or prepulse level. This difference is not uncommon[2], and should be attributed to the absorptions due to the photoenol, (D). The insert in *Figure 1* shows a first order kinetic fit of the data.

As pointed out above, the triplet state is quite short lived, and our instrument, having a resolution of only a few nanoseconds is not capable of directly time-resolving its behaviour. However, this problem can be overcome using a Stern–Volmer approach to the treatment of the laser data. For example, addition of 1-methylnaphthalene as a triplet energy acceptor leads to the formation of its easily detectable triplet state[6]. The transient absorbance due to the 1-methylnaphthalene triplet (A_N) and the value of $k_q\tau_T$ (see *Scheme I*) are related by equation (1), where a is an arbitrary constant[2,4]

$$\frac{1}{A_N} = a + \frac{a}{k_q\tau_T[Q]} \tag{1}$$



Scheme I

Figure 2 shows a plot according to equation 1 (Q ≡ 1-methylnaphthalene) for CoMT15 in AAM, from which we obtain $k_q\tau_T = 4.2\ M^{-1}$. If we take the rate of triplet quenching[7] as $k_q = 2.4 \times 10^9\ M^{-1}\ s^{-1}$, then $\tau_T = 1.8$ ns. The value of τ_T could be in error by as much as a factor of 2 because of the spectral interference due to absorptions (415 nm) by both the biradical and the photoenol.

In an alternative approach, one can add to the system a diene; i.e. a triplet quencher which does not yield an easily detectable triplet. In this case one monitors the intensity of the signals due to the biradical (see *Figure 1*)[8]. What we observe is that, while the kinetics of the decay do not change (i.e. as expected the quencher does not affect the biradical lifetime), the signal intensity due to the biradical decreases upon addition of quencher. The result points to a triplet state precursor. Stern–Volmer treatment of the data using 1,5-dimethyl-2,4-hexadiene as triplet quencher yields $k_q\tau_T = 2\ M^{-1}$. The difference with the value obtained using the 1-methylnaphthalene technique is not unusual in view of the large errors introduced in methods based on slope-to-intercept ratios.

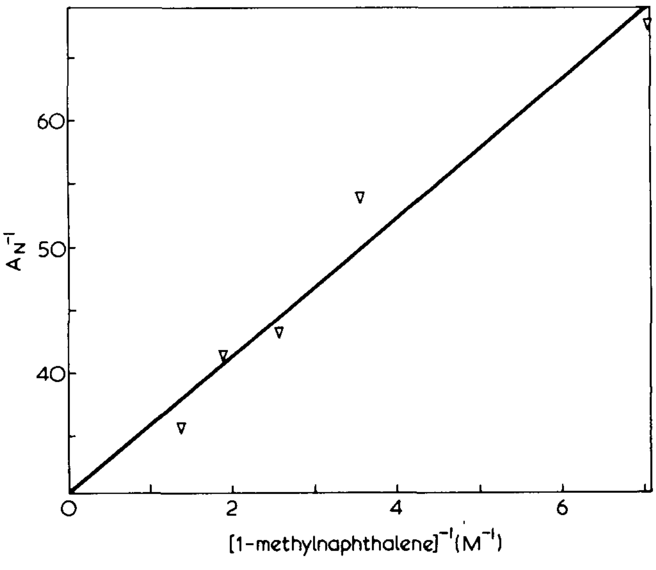


Figure 2 Plot according to equation 1 for CoMT15 in AAM. The transient absorbance due to the 10methylnaphthalene triplet was monitored at 415 nm

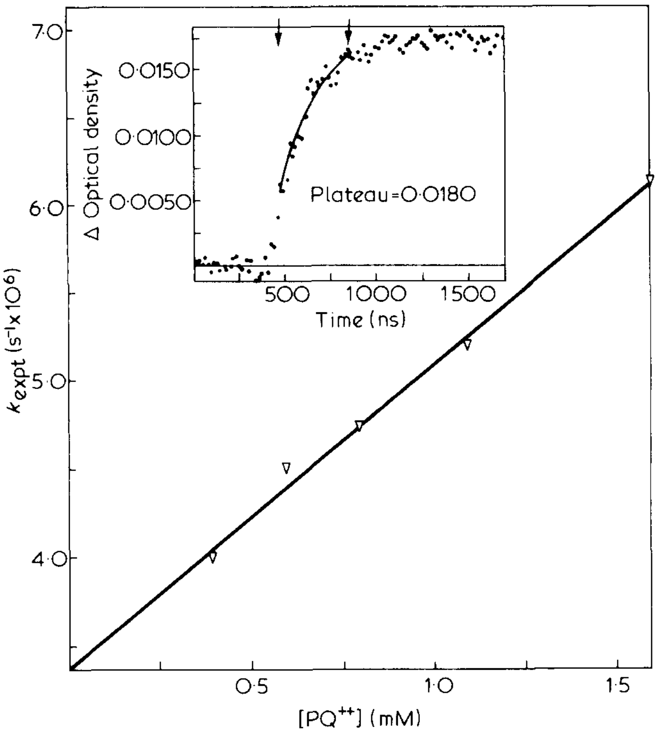
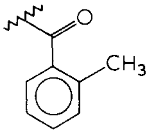
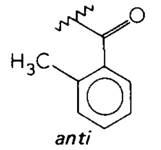


Figure 3 Data for the reaction of the biradicals from CoMT15 with paraquat dications, according to equation 3. Insert—typical time profile for the formation of PQ^{+} (603 nm) for $[PQ{+}{+}]$ = 0.0011 M

The Stern–Volmer plots obtained by both methods are reasonably linear. In other systems involving enolization of isolated *o*-methyl benzoyl groups, one usually obtains curved plots reflecting the intermediacy of two triplets; i.e. the *syn* and *anti* conformers[4,9]:



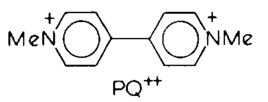
syn



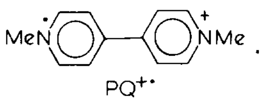
anti

The lifetime measured clearly corresponds to that of the *syn* triplet conformer[8–10], since lifetimes for the *anti* conformer tend to be substantially longer[8–10]. While a small curvature would be difficult to detect because of the relatively large errors previously mentioned, the difference in slopes is usually large enough to be easily detected[8]. The linearity of the plots suggests that the *anti* conformer must be relatively unimportant in the triplet manifold. A similar type of behaviour has also been observed in *o*-methylbenzophenone[11].

When the electron acceptor, paraquat (1,1′-dimethyl-4,4′-bipyridylium, PQ^{++}) is added to the samples, we observe the formation of the radical-cation, PQ^{+}.



PQ^{++}



$PQ^{+\bullet}$

The build-up of the radical-cation concentration can be time-resolved in experiments similar to those already reported for biradicals in small molecules[12,13]. The insert in *Figure 3* shows a typical build-up profile. Proper kinetic analysis (equation 3) leads to k_{expt}, a pseudo-first order experimental rate constant, which is related to τ_B and k_t according to equation 3:

$$\ln \frac{A_\infty}{A_\infty - A} = k_{\text{expt}} \times t \qquad (2)$$

$$k_{\text{expt}} = \tau_B^{-1} + k_t [PQ^{++}] \qquad (3)$$

A and A_∞ are the transient absorptions due to $PQ^{+\bullet}$ at time t and in the plateau region, respectively. *Figure 3* shows a plot according to equation 3, which leads to k_t = $1.7 \times 10^9\ M^{-1}\ s^{-1}$ and τ_B = 310 ns. This value is in good agreement with that obtained from direct measurements (*Figure 1*). The lifetime of the macrobiradical is comparable with those obtained for similar structures in small molecules[4,8,10], while the rate constant for electron transfer (k_t) is significantly smaller in the case of the polymer. This difference probably reflects a smaller diffusion coefficient for the polymer as well as the effect of a hindered radical centre.

In benzene the overall behaviour is quite similar to that observed in polar media; while the biradical lifetime is slightly shorter (τ_B = 320 ns, by direct detection), the triplet lifetime is almost identical. The corresponding $k_q\tau_T$ values in benzene are 3.0 (1-methylnaphthalene) and 1.2 M^{-1} (diene).

The experiments described above were all carried out using CoMT15. A few experiments with CoMT3 led to substantially weaker signals, as a result of the lower abundance of absorbing chromophores. The behaviour as far as triplet and biradical lifetime is concerned, was, within experimental error, the same for both copolymers, though we note that the experimental errors are considerably larger for CoMT3.

The photoenol (D) in *Scheme 1* is shown as the *cis* or Z-enol, but, as in the case of other photoenolizable carbonyl compounds[5,11], one can expect both isomers to be formed, with the *trans* or E-enol being longer lived as a result of the unfavourable conformation for reketonization. The species detected following biradical decay is very long lived (outside the range of our instrument) and should almost certainly be assigned to the E-enol. It is possible that the small difference between the biradical lifetimes measured by direct detection and by the paraquat technique may be due to underlying absorptions due to the short lived Z-enol in the direct method.

CONCLUSION

The behaviour of *o*-methylbenzoyl chromophores in copolymers containing mostly aliphatic carbonyl chromophores is similar to that observed in both the homopolymer, poly(*o*-tolyl vinyl ketone)[2] and in small molecules like *o*-methylacetophenone[8] and (A)[4]. The solubility of the copolymers examined in this work has allowed us to examine the redox properties of a macrobiradical for the first time. We find that the rate of electron transfer is about one third of that observed in small biradicals of similar structure[8].

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REFERENCES

1 Bays, J. P., Encinas, M. V. and Scaiano, J. C. *Macromolecules* 1974, **12**, 348

2 Bays, J. P., Encinas, M. V. and Scaiano, J. C. *Macromolecules* (submitted for publication)

3 Encinas, M. V., Funabashi, K. and Scaiano, J. C. *Macromolecules* (submitted for publication)

4 Bays, J. P., Encinas, M. V., Small Jr., R. D. and Scaiano, J. C. *J. Am. Chem. Soc.* (submitted for publication)

5 Haag, R., Wirz, J. and Wagner, P. J. *Helv. Chim. Acta* 1977, **60**, 2595

6 Porter, G. and Windsor, M. W. *Proc. R. Soc., Ser. A.* 1958, **256**, 238

7 Encinas, M. V. and Scaiano, J. C. (unpublished work)

8 Das, P. K., Encinas, M. V., Small Jr., R. D. and Scaiano, J. C. *J. Am. Chem. Soc.* (in press)

9 Wagner, P. J. *Pure Appl. Chem.* 1977, **49**, 259

10 Small Jr., R. D. and Scaiano, J. C. *J. Am. Chem. Soc.* 1977, **99**, 7713

11 Das, P. K. and Scaiano, J. C. *J. Photochem.* (in press)

12 Small Jr., R. D. and Scaiano, J. C. *J. Phys. Chem.* 1977, **81**, 828; *ibid* 1977, **81**, 2126; *ibid* 1978, **82**, 2662

13 Encinas, M. V. and Scaiano, J. C. *J. Am. Chem. Soc.* 1978, **100**, 7108

14 Thorsett, E. D., Stermited, F. R. and O'Donnel, C. M. *Synth. Commun.* 1972, **2**, 375

15 Encinas, M. V. and Scaiano, J. C. *J. Am. Chem. Soc.* 1979, **101**, 2146; Patterson, L. K. and Scaiano, J. C. (to be published)