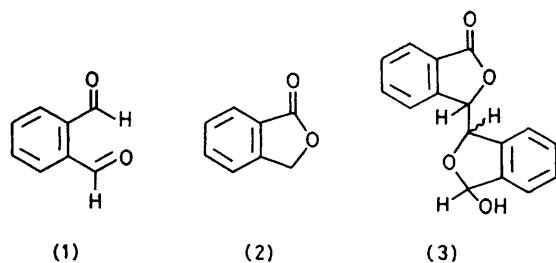


Photochemistry of *o*-Phthalaldehyde

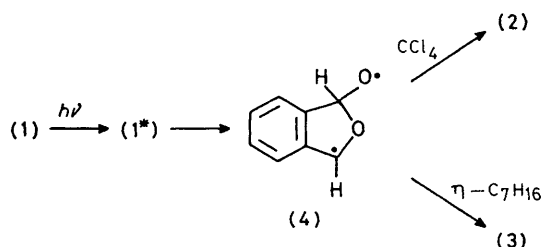
By Juan C. Scaiano,*† M. Victoria Encinas, and Manapurathu V. George, Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556, U.S.A.

U.v.-irradiation of *o*-phthalaldehyde leads to the formation of phthalide and dimeric products in varying yields and ratios depending on the solvent and reagent concentration. Laser flash photolysis studies show that the photochemistry of *o*-phthalaldehyde involves the intermediacy of a 1,4-biradical produced by intramolecular hydrogen transfer, and with a lifetime of 1.6 μ s. Two triplet states are the precursors of this biradical; they have lifetimes of 6 and 36 ns and are assigned to different rotational conformers. The triplet reaction path is not responsible for product formation; these arise *via* a parallel reaction path, apparently involving the singlet state.

SEVERAL investigators have examined the photochemical transformations of *o*-phthalaldehyde (1).¹⁻⁵ In general, it has been observed that the photolysis of (1) leads to the formation of the phthalide (2) and an isomeric mixture of dimeric products (3). Similar phototransformations have been observed in the case of other *o*-dialdehydes, namely 2,3- and 3,4-diformylpyridines,⁶ 2,3-diformylquinolines,⁶ and 2,3- and 3,4-diformyl-thiophens and -selenophens.⁷ It has been shown that the nature of the photoproducts formed from (1) depend largely on the solvent employed. Thus, dimer (3) is exclusively formed when the photolysis of (1) is carried out in *n*-heptane, while (2) is the major product in solvents like chloroform and carbon tetrachloride² and mixed products (2) and (3) are obtained in benzene.²



There is considerable controversy concerning the mechanism of the phototransformations of (1). Kagan² has suggested that the reaction proceeds through the diradical intermediate (4) (Scheme 1). Subsequently

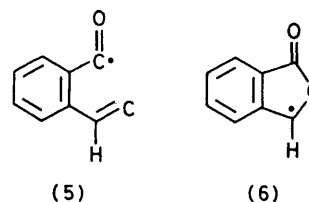


SCHEME 1 (1*) indicates the excited triplet state

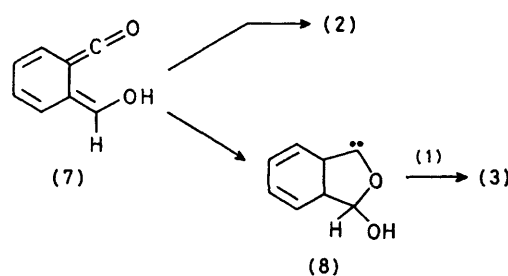
Harrison *et al.*⁵ reported that the irradiation of (1) at 77 K leads to the generation of radicals (5) and (6) which are relatively stable at this temperature. They have suggested that the observed photochemistry of (1),

† Present address: Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R6.

leading to products (2) and (3) may proceed from the short-lived singlet state of (1). In contrast, Pappas and Blackwell³ and Cohen *et al.*⁴ have suggested that the phototransformations of (1) may proceed through the



keten-enol intermediate (7) which can then undergo an intramolecular cyclization to give the phthalide (2). The formation of dimer (3), however, has been rationalized in terms of the oxacarbene intermediate (8) and its further reaction with (1) (Scheme 2).⁵

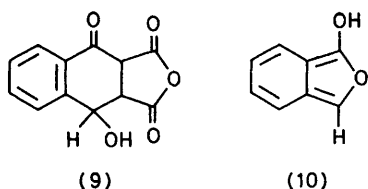


SCHEME 2

Enol (7) has been successfully trapped by maleic anhydride to give (9), which on base hydrolysis and treatment with diazomethane gave a mixture of α -naphthol derivatives.⁴

The object of the present study has been to understand the details of the mechanism of the phototransformations of (1). Recent reports from this laboratory⁹ have shown that the transient biradicals generated from the photoenolization of carbonyl compounds are excellent electron donors and that the study of these processes, using laser flash photolysis techniques can be used to investigate their behaviour and lifetimes. Using these techniques we have studied the conventional enolization path leading to (7) *via* an intramolecular hydrogen abstraction reaction. To our surprise, we find that this process, while quite efficient is not responsible for product formation, and that a different reaction path,

from the singlet state, and probably involving the cyclic enol (10) is responsible for the formation of (2) and (3).



RESULTS

Steady-state irradiation of n-heptane solutions of (1) has confirmed earlier results of Kagan² and Cohen *et al.*,⁴ showing that this process leads to the dimeric product (3). Addition of trifluoroacetic acid (0.025M) to the reaction mixture does not change significantly the course of reaction, although minor yields of (2) become detectable. The ¹³C n.m.r. spectrum of (3) is consistent with the assumption that it is a mixture of stereoisomers (see Experimental section). We had considered the possibility that the dimeric mixture (3) could arise through the secondary photolysis of the phthalide (2), the major products formed in other solvents. However, experiments in which the consumption of (1) and possible formation of (2) have been monitored by g.l.c. at different stages during the photolysis showed that this is not the case and that the phthalide (2) is not an important photoproduct in heptane, even when conversions are quite low. In benzene, both (2) and (3) are formed with significant yields.² We find that the ratio of products depends upon the initial concentration of (1) and follows a Stern-Volmer type of behaviour [equation (1) where Φ_2 is the

$$\Phi_2^{-1} = \Phi_p^{-1} \{1 + K_{SV}[(1)]\} \quad (1)$$

quantum yield for phthalide, Φ_p is the yield for the phthalide precursor [*i.e.* (10), see later] and K_{SV} is the Stern-Volmer slope, the significance of which will be discussed later}. Figure 1 shows a plot according to equation (1), from which we obtain K_{SV} 9.4 l mol⁻¹.

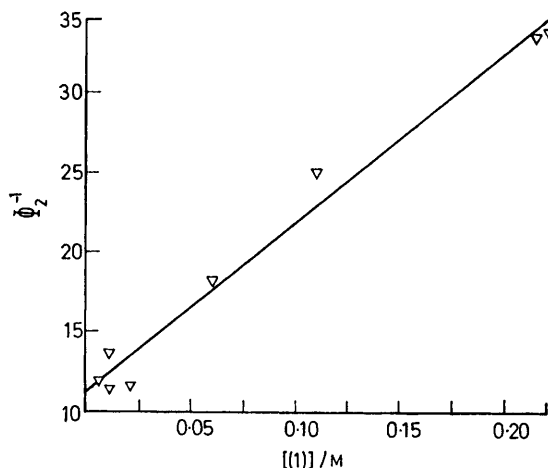
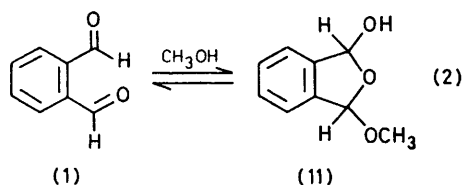


FIGURE 1 Effect of reagent concentration on the yield of phthalide in benzene. Plot drawn according to equation (1)

In polar solvents, methanol in particular, (2) is the only important product of reaction and is formed with Φ ca. 0.26.

Studies in methanol had to be carried out immediately after the solutions were prepared, since (1) undergoes a

solvation reaction (a dark process) leading to an addition product, which is tentatively assigned as (11), on the basis of analogy and the change in the u.v. spectra of the solu-



tions [reaction (2)]. Figure 2 shows a plot of the concentration of (1) as a function of time, as monitored by its u.v. absorption at 380 nm. When the equilibrium is reached, only ca. 4% of the initial concentration of (1)

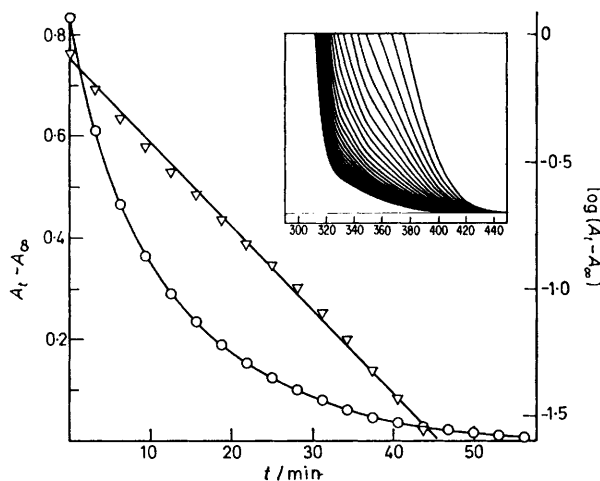


FIGURE 2 Solvation data for (1) in methanol, showing a linear (left) and logarithmic (right) plot of the difference in optical density at 380 nm between time and the equilibrium level. The insert shows a series of spectral scans at 188 s intervals

remains as such at room temperature. This process is reversible and evaporation of methanol leads to the regeneration of (1) (see Experimental section). We note that the lower intensity of the absorption spectrum of (1) in water or alcohol as compared to iso-octane has been attributed to its extensive solvation in hydroxylic solvents.¹⁰

The lifetime of the triplet state (or states) of (1) can be determined from laser flash photolysis experiments even if these lifetimes are shorter than the resolution of the instrument employed. In these experiments, solutions of (1) in methanol were excited with the pulses (337.1 nm; 8 ns; ca. 3 mJ) from a nitrogen laser and the transient absorptions which resulted were monitored using a system with a nanosecond response. The signals observed in the absence of any other additives are discussed below. When the triplet quencher, 1-methylnaphthalene is added to the system, it leads to strong absorptions at 415 nm, which are characteristic of its triplet state.¹¹ These absorptions are strong enough that the corrections due to signal produced in the absence of 1-methylnaphthalene are minor. A plot of the reciprocal of the yield of 1-methylnaphthalene triplets (in arbitrary units) *versus* the quencher concentration (Figure 3) leads to two different slopes in the low and high quencher concentration region. This is indicative of two triplet states with different lifetimes. Proper kinetic analysis of the slopes and intercepts⁹ in the high and low concentration

regions leads to the corresponding $k_q\tau_T$ values for the two triplets in methanol as 30 and 182 l mol⁻¹; the triplets are produced in a 1.6 : 1.0 ratio. In the lower quencher concentration region equation (3a) simplifies to (3b) and, at the

$$A = \frac{\Phi_1 k_q[Q]}{\alpha k_q[Q] + \tau_1^{-1}} + \frac{\Phi_2 k_q[Q]}{\alpha k_q[Q] + \tau_2^{-1}} \quad (3a)$$

$$\frac{\alpha}{A} \sim \frac{\alpha}{\Phi_1} \left(1 + \frac{1}{k_q\tau_1[Q]} \right) \quad (3b)$$

$$\left(\frac{A}{\alpha} - \frac{\Phi_1}{\alpha} \right)^{-1} \sim 1 + \frac{1}{k_q\tau_2[Q]} \quad (3c)$$

high concentration limit, to (3c); where A is the optical density due to 1-methylnaphthalene triplets, τ_1 and τ_2 the triplet lifetimes for the long- and short-lived triplets, respectively, k_q the rate constant for quenching by Q , and α a constant ($\alpha = I_0\epsilon l$).

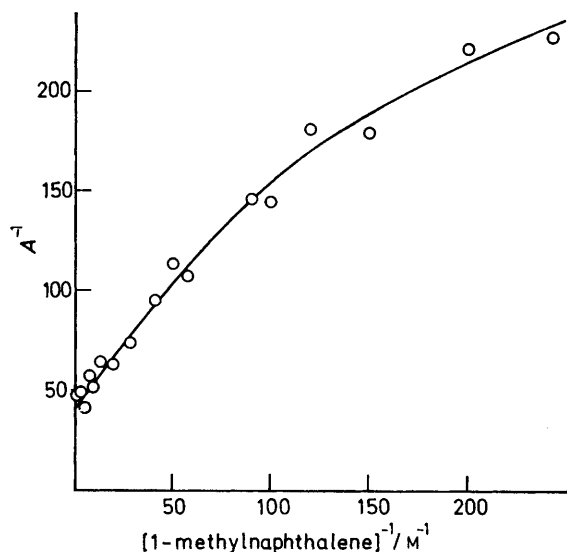
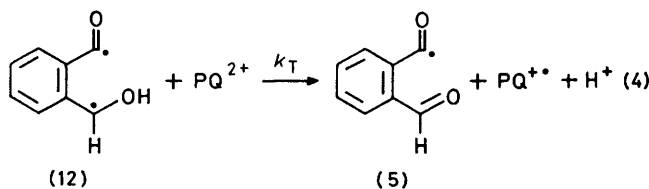


FIGURE 3 Sensitized formation of triplet 1-methylnaphthalene according to equation (3)

The suggestion of a mechanism of photoreaction involving intramolecular hydrogen abstraction by the triplet state of (1) requires the formation of the biradical (12) which can be expected to be a good electron donor. We have carried out a series of flash experiments in which (12) was trapped by



paraquat (1,1'-dimethyl-4,4'-bipyridylum) dication, PQ^{2+} , according to reaction (4). The formation of the radical cation, $\text{PQ}^{+\cdot}$, was monitored by its characteristic absorption at 603 nm.¹² The details of this technique have been discussed extensively elsewhere.¹³ A critical condition is that the triplet lifetime has to be considerably shorter than the biradical lifetime for the method to be applicable; our experimental measurements confirm that this criterion is met. The analysis of the time profiles for the formation of

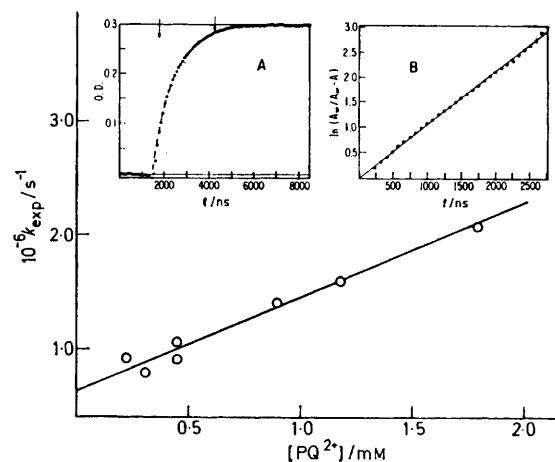


FIGURE 4 Plot of k_{exp} versus $[\text{PQ}^{2+}]$ according to equation (4). Inset A: typical buildup trace for $[\text{PQ}^{2+}] = 4.4 \times 10^{-4}\text{M}$ (average of two shots); inset B: derivation of k_{exp} for the data from insert A (between arrows), from a plot of $\ln [A_{\infty}/(A_{\infty} - A)]$ versus time, where A_{∞} and A are the optical densities in the plateau region and at time t

$\text{PQ}^{+\cdot}$ (see inserts A and B in Figure 4) leads to an experimental rate constant, k_{exp} , which is related to the biradical lifetime, τ_B , and the rate of trapping, according to equation (5). Figure 4 shows a plot of k_{exp} versus $[\text{PQ}^{2+}]$ in methanol

$$k_{\text{exp}} = \tau_B^{-1} + k_T[\text{PQ}^{2+}] \quad (5)$$

at room temperature, from which we derive $k_T = 7.6 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ and $\tau_B = 1600 \text{ ns}$. When a triplet quencher is added to a sample of (1) containing PQ^{2+} , the value of the absorbance in the plateau region (see insert A in Figure 4) changes, reflecting the quenching of the precursor triplet state, while the kinetics (as measured by k_{exp}) remain constant, showing thereby that biradical behaviour is independent of the triplet quencher added.

We were somewhat surprised at the low reactivity of (12) towards PQ^{2+} , when the value of k_T is compared with those for other biradicals,¹³ e.g. from γ -methylvalerophenone or *o*-methylacetophenone, typically in the $3-7 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ range; in fact, experiments in wet acetonitrile were unsuccessful because of an apparently lower reactivity. In this case we carried out a few exploratory experiments using also benzyl viologen as a possible electron acceptor. These experiments led to weak signals, which at least allowed us to confirm that the same process occurs in this solvent even if the small value of k_T prevented a detailed quantitative study.

In several earlier reports in which we used the paraquat technique we have been able to measure the quantum yields of biradical generation.¹⁴ In the system examined in this paper reaction (2) (which takes place in any of the solvents in which paraquat is soluble) prevented a truly quantitative measurement; nonetheless, our results do indicate that Φ_B , the quantum yield of biradical formation, probably exceeds 0.5.

Laser excitation of solutions of (1) leads to intense and long-lived transient absorptions which we initially thought should be assigned to the isomeric mixture of enols (7). To our surprise, the formation of the transient mentioned above could not be quenched by typical triplet quenchers, e.g. 2,5-dimethylhexa-2,4-diene, under conditions where the generation of the biradicals mentioned above could be easily quenched and where addition of 1-methylnaphthalene

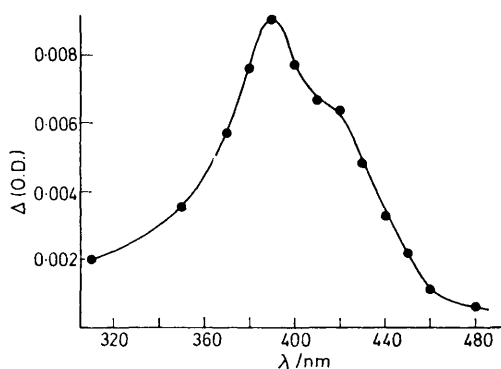


FIGURE 5 Transient spectra observed 5 μ s after laser excitation of dilute solutions of (1) in benzene

led to the formation of its triplet, which is an unquestionable piece of evidence revealing triplet quenching. Further, the formation of (2) and (3), in benzene and heptane, could not be quenched by 0.4M-dienes. In addition, maleic anhydride, which quite clearly does trap (7) ⁴ does not seem to affect significantly the rate of decay of the transient signals. We believe that the species detected is (10); its transient spectrum is shown in Figure 5. The decay of (10) followed clean first-order kinetics, but its lifetime was dependent upon the concentration of *o*-phthalaldehyde. For example, in benzene changing [(1)] from 0.037 to 0.075M changes the lifetime of (10) from 90 to 76 μ s, and in dilute solutions we have measured lifetimes as long as 300 μ s. This transient can be scavenged by substances like trifluoroacetic acid, 2,5-dimethylhexa-2,4-diene, and dimethyl acetylenedicarboxylate, but, rather surprisingly, not maleic anhydride. Figure 6 shows pseudo-first-order plots according to equation (6) where the left term is the rate of decay. The

$$d[(10)]/dt = k_r [(10)] [\text{Scavenger}] \quad (6)$$

experimental pseudo-first-order rate constant, k_{decay} , is given by $k_{\text{decay}} = k_r [\text{Scavenger}]$. The corresponding rate constants are shown in the Table.

We have found that (10) can also be produced by irradiation of (1) in a methylcyclohexane glass at 77 K. The difference between the spectrum obtained in this manner

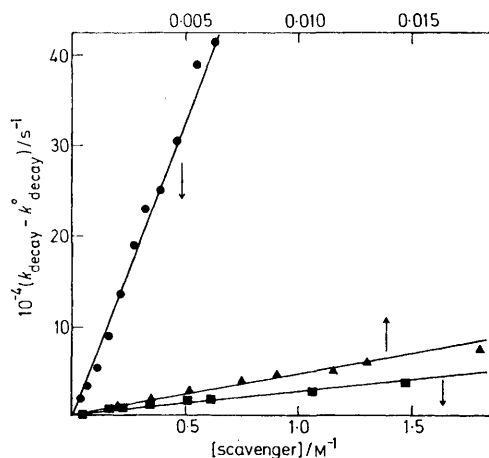


FIGURE 6 Scavenging of (10) in benzene by (●) 2,5-dimethylhexa-2,4-diene, (▲) trifluoroacetic acid, and (■) dimethyl acetylenedicarboxylate

and that of (1) agrees well with the transient spectrum shown in Figure 5.

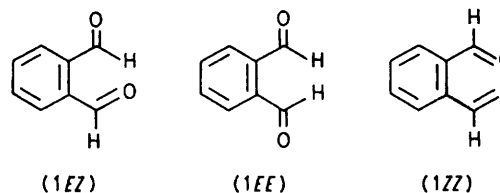
Scavenging of (10) in benzene at room temperature

Scavenger	$k_r/1 \text{ mol}^{-1} \text{ s}^{-1}$
2,5-Dimethylhexa-2,4-diene	6.7×10^5
Trifluoroacetic acid	4.3×10^6
Dimethyl acetylenedicarboxylate	2.4×10^4

Finally, we note that all the paraquat experiments carried out in methanol mentioned before were repeated several times, allowing for different delays between sample preparation and the flash experiments, in order to ensure that the solvation equilibrium discussed earlier had no effect on the measurement of lifetimes and rate constants. This was indeed confirmed by experiments which showed that the consumption of (1) to yield (11) changed the intensity of the signals observed, but not the kinetics associated with those processes.

DISCUSSION

The characterization of two triplet states with different lifetimes is consistent with similar observations in other systems which undergo photoenolization ^{8,9,15,16} and can be attributed to different triplet state conformations. In the case of (1), three different conformations, *EZ*, *EE*, and *ZZ*, are feasible.

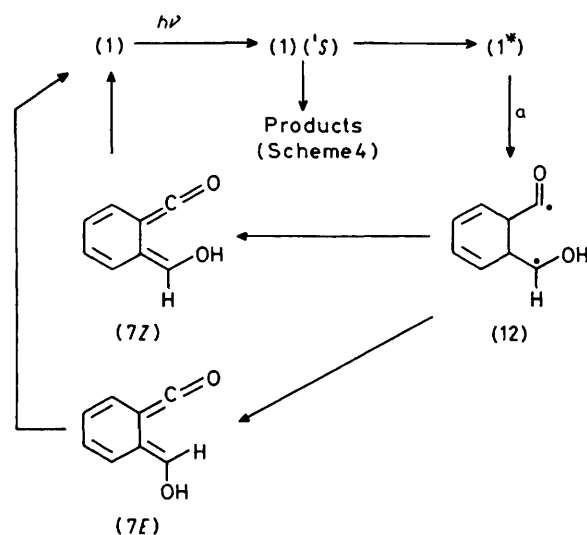


Our kinetic data suggests that one of the three triplets is not being formed, or is only formed in very low yield.* If we take the rate constant for quenching, k_q , as $5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ in benzene, then the corresponding triplet lifetimes are 6 and 36 ns and are referred to as the short and long triplet hereafter. The triplet state decays *via* hydrogen abstraction, step a in Scheme 3. The product of reaction, (12), can be described as the triplet state of the enols (7*) or as a biradical; we choose the latter because it describes best the properties exhibited in this work. Our electron transfer experiments show that (12) has a lifetime of 1 600 ns in methanol.

Unfortunately, it was not possible to measure the lifetime of (12) in non-polar solvents, *e.g.* benzene, because the insolubility of PQ^{2+} prevents the use of this technique, while our attempts to characterize (12) directly, using optical absorption, were not conclusive. Presumably, the strong absorption by (10) makes the direct detection of (12) difficult.

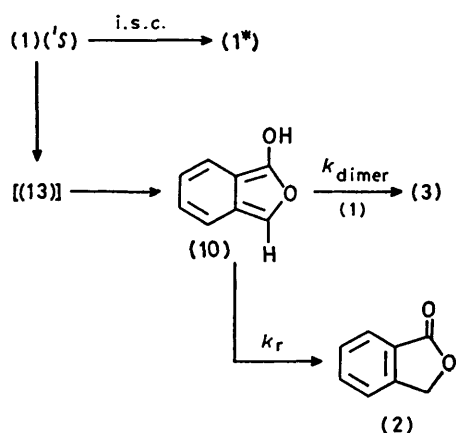
As pointed out before, the formation of (2) and (3) cannot be quenched by triplet quenchers under conditions where other experiments provide conclusive evidence for

* Another explanation would be that two of the triplets have very similar lifetimes; however, this seems unlikely.



SCHEME 3

triplet quenching. Therefore, we believe that (2) and (3) are formed in a singlet state reaction, although it should be clear that our results cannot distinguish between a singlet process and one taking place from an unusually short triplet (*i.e.* if $\tau_T \leq 100$ ps). Scheme 4



SCHEME 4

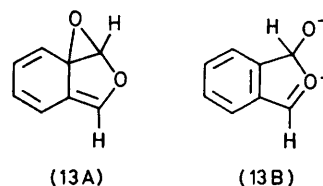
illustrates the mechanism proposed for the reaction; intermediate (13) has been tentatively included in the mechanism, and its possible structure (and even existence!) will be discussed below. The evidence for (10) is based on our spectroscopic evidence, derived from both laser experiments and irradiation at 77 K, its behaviour towards dienophiles, and its reactivity towards (1) to produce (3), as shown by the dependence of its lifetime on the concentration of (1) and the dependence of the yield of phthalide, as illustrated in Figure 1 [see equation (1)]. The Stern-Volmer slope K_{SV} ($=k_{\text{dimer}}/k_r = 9.4 \text{ l mol}^{-1}$) corresponds to the ratio of rate constants (see Scheme 4).

The lower relative yield of dimer in polar solvents should probably be attributed to a small value of K_{SV} , as well as to the fact that the solvation equilibrium tends to favour the unimolecular decay of (10) by maintaining a low steady-state concentration of (1).

The limiting quantum yield for phthalide formation at infinite dilution is given by the reciprocal of the intercept in Figure 1 [see equation (1)] and corresponds to $\Phi_p \text{ lim}_{c \rightarrow 0} \Phi_2$.

Two questions still remain, what is the structure of (13), and which conformations of (1) are responsible for the different reaction pathways? On both these, we can only speculate at present. Concerning the latter, we tentatively suggest that (1ZZ) is relatively unimportant on steric grounds; (1EE) cannot reasonably be expected to yield (10) and we assume that the main pathway for its singlet state is intersystem crossing; (1EZ) has the correct conformation to yield (10) from the singlet state and (12) from the triplet state and we believe the singlet partitions between (10) and intersystem crossing. In summary (1ZZ) is unimportant, (1EE) undergoes intersystem crossing to yield the long lived triplet (rotation must precede reaction), and (1EE) yields (10) from its singlet state, which *via* intersystem crossing also leads to the short-lived triplet.

Concerning the other question, namely the structure of the intermediate (13), we have been unable to arrive at a satisfactory answer. First, one would like to know whether the reaction from (1) (1S) to (10) involves any kind of intermediate or proceeds *via* a cyclic concerted mechanism? If the reaction is not proceeding through a concerted mode, then from our laser experiments we conclude that the lifetime of (13) is shorter than 5 ns ['instantaneous' formation of (10) in our time scale]. Could (13) be the *Z*-enol [*i.e.* (13) \equiv (7Z)]? Since the yields of (10) and the final products are independent of the presence of triplet quenchers, it is clear that the formation of (10) does not involve triplet state precursors. If biradical (12) can be expected to yield (7Z and E), then the above suggestion can be ruled out because at least partial quenching by triplet quenchers would be expected. Some of the other possible structures for (13) could include the isobenzofuran epoxide (13A), and the dipolar species (13B). The formation of the isobenzofuran epoxide (13A) from (1), for example can be visualized in terms of a symmetry allowed



$[\pi^4_s + \pi^2_a]$ type of reaction, occurring under photochemical conditions. However, it is unlikely that such a reaction is occurring in the case of (1), wherein the π^4 system incorporates an aromatic double bond.

On the other hand, the dipolar species (13B) appears to be an attractive precursor for the cyclic enol (10). However, one wonders why (13B) is not formed under thermal conditions also. In the present studies, we have shown that (1) does not undergo thermal trans-

formation to give either (2) or (3) readily. Refluxing a solution of (1) in mesitylene (160°; 8 h) did not lead to any phthalide formation; most of the starting material remained unchanged, as detected by g.l.c.

At this point our experimental evidence does not lead to any conclusive answer as to the possible structure of (13).

Conclusions.—The chemistry of the triplet states of *o*-phthalaldehyde parallels that of many other *o*-alkyl-substituted carbonyl compounds, *e.g.* *o*-methylbenzaldehyde or *o*-methylacetophenone, *i.e.* the decay of two isomeric triplet states leads to the same biradical, which then decays presumably to an isomeric mixture of enols. These enols apparently revert back to (1) quite efficiently.

Biradical (12) is the first example examined of a biradical having an acyl centre. The presence of this α -radical site seems to have only a minor effect on the lifetime of the biradical, while the electron donor properties (compare with *o*-methylbenzaldehyde or *o*-methylacetophenone)⁹ decrease considerably.

The products of the photochemistry of *o*-phthalaldehyde, *phthalide and the dimeric products* (3), arise from an independent reaction path which does not involve a triplet state precursor. We propose that (2) and (3) are produced *via* the intermediacy of the cyclic enol (10) which can rearrange to (2) or react with a second molecule of (1) to yield the dimer to (3).

EXPERIMENTAL

Starting.—All solvents employed were from Aldrich (Gold Label) and were used as received. *o*-Phthalaldehyde (Aldrich) was freshly sublimed under high vacuum, before use. Paraquat dichloride (K and K) was purified by a reported procedure.^{13b} Trifluoroacetic acid, 2,5-dimethylhexa-2,4-diene, and 1-methylnaphthalene (all Aldrich) were used as received.

Quantum Yield Measurements.—The samples (1 or 2 ml) were contained in matched tubes made of precision bore tubing (i.d. 0.250 0 ± 0.000 2 in; Corning 7740 glass; Lab Crest Scientific). They were deaerated by bubbling oxygen-free argon or, by three freeze-pump-thaw cycles to a residual pressure of <10⁻⁴ Torr when they contained volatile substrates. The samples were irradiated in a merry-go-round apparatus, using a Rayonet reactor fitted with sixteen RPR-3500 or RPR-3000 lamps. The latter were used only to measure the quantum yield for (2) in methanol.

Conversions in the quantum yield measurements [based on (1)] were kept below 1%.

Actinometry.—The photofragmentation of valerophenone in benzene ($\Phi = 0.30$)¹⁷ was used as an actinometer.

Preparative Photolyses and Related Studies.—(1) *Photolysis of o-phthalaldehyde in n-heptane.* A solution of *o*-phthalaldehyde (1.005 g, 7.5 mmol) in *n*-heptane (500 ml) was irradiated under nitrogen for 1 h using a 450 W medium pressure mercury lamp (Hanovia). Removal of the solvent under vacuum gave the dimer (3) (0.92 g, 91%), m.p. 185–186° (softens around 181°), δ_C (CDCl₃) 81.84, 81.99, 82.85, 82.98, 101.37, 101.60, 121.56, 122.16, 122.65, 123.01, 123.17, 125.60, 125.94, 126.78, 129.10, 129.23, 129.51, 129.59, 129.79, 133.68, 133.88, 135.72, 137.6, 139.91, 140.37, 145.50, 146.15, and 169.13 p.p.m. The signals at δ_C 81.84,

81.99, 82.85, 82.89, 101.37, and 101.60 p.p.m. appear as three distinct pairs and they can be assigned to the three *sp*³ carbon atoms in (3). The fact that these signals appear in pairs (six in all) is strongly indicative of the fact that (3) is a mixture of stereoisomers. The signal at δ_C 169.13 p.p.m. should be assigned to the carbon bearing the lactone carbonyl in (3); the corresponding lactone carbonyl in (2) shows a signal at δ_C 170.81 p.p.m. In contrast, the ¹³C spectrum of *o*-phthalaldehyde (CDCl₃) showed signals at δ_C 130.98, 133.59, 136.27, and 192.04 p.p.m.

(2) *Attempted photolysis of phthalide* (2). A solution of phthalide (1.005 g, 7.5 mmol) in methanol (400 ml) was photolysed for 3 h under nitrogen. Removal of the solvent under vacuum and recrystallization of the residue from Skellysolve B gave unchanged starting material (0.88 g, 87%), m.p. and mixed m.p. 70°.

(3) *Attempted reaction of o-phthalaldehyde with methanol.* A solution of *o*-phthalaldehyde (0.27 g) in absolute methanol (15 ml) was refluxed for 2 h under nitrogen. Removal of the solvent under vacuum gave a residue which was treated with Skellysolve B to give unchanged starting material (0.12 g), m.p. and mixed m.p. 50–51°. Evaporation of the Skellysolve solution under vacuum gave a residue consisting mostly of unchanged starting material, as revealed by its n.m.r. spectrum.

(4) *Attempted thermal transformation of o-phthalaldehyde.* A solution (8 ml, 0.26M) of (1) in mesitylene was refluxed under nitrogen for 8 h, and examined by g.l.c. No phthalide (2) could be detected.

Analyses.—The measurement of the yields of (2) was carried out by g.l.c. using a column of 5% Apiezon L on Chromosorb W and a Beckman GC-5 instrument equipped with flame ionization detectors.

Spectra.—U.v.-visible spectra were recorded using a Cary-219 spectrometer. N.m.r. spectra were recorded on either Varian A-60 or XL 100 instruments.

Laser Flash Photolysis.—The instrument makes use of the pulses (337.1 nm; *ca.* 8 ns; 3 mJ) from a Molecron UV-400 nitrogen laser for excitation. The monitoring system consisted of a monochromator and an RCA-4840 photomultiplier tube. The signals were terminated into 93 ohm and into a Tektronix R-7912 transient digitizer; they were then transmitted to a PDP 11/55 computer, which controlled the experiment, averaged signals, and processed the data. The rise time of the system was *ca.* 2 ns. Further details have been given elsewhere.^{14,18}

We thank the Office of Basic Energy Sciences of the Department of Energy, Washington D.C., for support.

[9/694 Received, 4th May, 1979]

REFERENCES

- 1 A. Schönberg and A. Mustafa, *J. Amer. Chem. Soc.*, 1955, **77**, 5755.
- 2 J. Kagan, *Tetrahedron Letters*, 1966, 6097.
- 3 S. P. Pappas and J. E. Blackwell, jun., *Tetrahedron Letters*, 1968, 3337.
- 4 K. F. Cohen, J. T. Pinhey, and R. J. Smith, *Tetrahedron Letters*, 1968, 4729.
- 5 D. A. Harrison, R. N. Schwartz, and J. Kagan, *J. Amer. Chem. Soc.*, 1970, **92**, 5793.
- 6 G. Quequiner and A. Gôdard, *Compt. rend.*, 1969, **C269**, 1648.
- 7 C. Paulmier, J. Bourguignon, J. Morel, and P. Pastour, *Compt. rend.*, 1970, **C270**, 494.
- 8 R. D. Small, jun., and J. C. Scaiano, *J. Amer. Chem. Soc.*, 1977, **99**, 7113.

⁹ P. K. Das, M. V. Encinas, R. D. Small, jun., and J. C. Scaiano, *J. Amer. Chem. Soc.*, 1979, **101**, 6965.

¹⁰ M. Carmack, M. B. Moore, and M. E. Balis, *J. Amer. Chem. Soc.*, 1950, **72**, 844.

¹¹ G. Porter and M. W. Windsor, *Proc. Roy. Soc.*, 1958, **A245**, 238.

¹² (a) P. Hyde and A. Ledwith, *J.C.S. Perkin II*, 1974, 1768; (b) J. A. Farrington, M. Ebert, E. J. Land, and K. Fletcher, *Biochim. Biophys. Acta*, 1973, **314**, 372; (c) L. K. Patterson, R. D. Small, jun., and J. C. Scaiano, *Radiation Res.*, 1977, **72**, 218.

¹³ R. D. Small, jun., and J. C. Scaiano, *J. Phys. Chem.* (a) 1977, **81**, 828, 2126; (b) 1978, **82**, 2662.

¹⁴ M. V. Encinas and J. C. Scaiano, *J. Amer. Chem. Soc.*, 1978, **100**, 7109; *ibid.*, 1979, **101**, 2146; *J.C.S. Perkin II*, 1980, 56.

¹⁵ P. J. Wagner, *Pure Appl. Chem.*, 1977, **49**, 259; P. J. Wagner and C.-P. Chen, *J. Amer. Chem. Soc.*, 1976, **98**, 239.

¹⁶ R. Haag, J. Wirz, and P. J. Wagner, *Helv. Chim. Acta*, 1977, **60**, 2595.

¹⁷ P. J. Wagner, P. A. Keslo, A. E. Kemppainen, J. M. McGrath, H. N. Schott, and R. G. Zepp, *J. Amer. Chem. Soc.*, 1972, **94**, 7506.

¹⁸ L. K. Patterson and J. C. Scaiano, to be published.