Journal of Photochemistry, 2 (1973/74) 239–246

PHOTOPHYSICS AND PHOTOCHEMISTRY OF *o*-XYLENE SOLUTIONS
III. PHOTOISOMERIZATION

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(Received May 3, 1973)

SUMMARY

The photoisomerization of *o*-xylene, in dilute hydrocarbon solutions, to the *meta* isomer, and to a slight extent to the *para*-form, has been studied as a function of temperature. The quantum yields are small, *e.g.* for formation of *m*-xylene $\Phi_m = 2.5 \times 10^{-3}$ at 30°C and formation of *p*-xylene Φ_p, is less than 10% of Φ_m. Using measured values of the fluorescence lifetimes a value for the energy of activation for isomerization is obtained. The effects of added xenon and butene-2 show that the first excited state is involved in the isomerization. A transient diradical of the "pre-fulvene" or "Jano" type may give rise to benzvalene or produce direct isomerization. Isomerization appears to result from a vibrational level of S_1 higher than that which is involved in internal conversion. The mechanism of isomerization is discussed.

INTRODUCTION

Attention has been directed to the possibility that formation, reversible or irreversible, of a non-aromatic photoisomer may explain the now well established observations that the sums of fluorescence and triplet yields in a number of photoexcited simple benzenoid hydrocarbons do not equal unity. The work described here was undertaken to examine the role of isomerization in the deactivation of the first excited singlet state of *o*-xylene in solution. Data on the fluorescence and triplet formation processes for *o*-xylene have been presented in earlier papers[1,2].

EXPERIMENTAL

Materials

o-Xylene and methylcyclohexane were purified as described previously[1]. Isopentane (B.D.H.) was acid washed and distilled through a silica gel packed column. The fraction distilling between 28.05 and 28.15° C was collected and stored under vacuum.

6,6′-Dimethylfulvene was provided by Dr. M. Dowe of Loughborough University and was used as received.

Xenon (B.O.C. Ltd. X grade) was used without further purification other than bulb-to-bulb distillation *in vacuo*. Phillips Research Grade *cis*- and *trans*-butene-2 were employed.

Apparatus and technique

The apparatus described in Part II was used. Reaction cells were 1 cm square cross-section fused silica, cleaned with boiling nitric acid and occasionally with dilute hydrofluoric acid to prevent accumulation of photoproduced polymer.

The samples were analyzed as follows: following irradiation liquid samples were distilled into small tubes and the contents of the latter were injected into a gas chromatograph at 100° C. One column, 2 m polyoxyethylene sorbitan monostearate (20% w/w on Chromosorb W), was used primarily for analyses of both *m*- and *p*-xylene in *o*-xylene. Another column, 2 m Bentone 34 (11.5%) and SFMS 550 (also 11.5% w/w) on Chromosorb W was used for the separation of *p*-xylene. All systems used for quantitative analyses were suitably calibrated with standard mixtures.

The fluorescence quenching experiments were carried out with the instrument mentioned in Part I using a stablized mercury resonance lamp instead of the xenon arc as the source of exciting radiation (254 nm).

RESULTS

The photoisomerization experiments were carried out, for analytical convenience, on 0.45 *M* solutions of *o*-xylene in isopentane. The fluorescence lifetimes, which form part of the monomer–excimer equilibrium studies on *o*-xylene were measured in methylcyclohexane. Though variation of solvent has some effect on the decay processes in benzenoid hydrocarbons[2,3] the difference between the two solvents in this case is slight. The fraction of excited singlet state molecules in 0.45 *M* solutions may be calculated from the data in Part I and is 0.98 at 30° C, and the measured lifetimes are those for the monomer τ_M. The data are presented in Table 1.

The yield of *p*-xylene produced in the photochemical reaction is lower than for *m*-xylene, which is itself only 2.5×10^{-3} at 30° C. Quantitative estimations of Φ_m were made with the polyoxyethylene sorbitan monostearate column which does not resolve *meta*- and *para*-isomers. Runs with the Bentone-34 column which resolves these isomers did not show the presence of *p*-xylene at the low conversions used in the experiments within the limits of experimental error. At low conversions Φ_p must be less than 10% of Φ_m. The yields of *m*-xylene were between 4 and

TABLE 1

TEMPERATURE DEPENDENCE OF *m*-XYLENE FORMATION YIELD (Φm) ISOPENTANE (0.45 *M*)

Temp./°C	τ_M/ns	Φ_m (× 10^3)
30	44.4	2.54
45	39.0	3.24
60	33.2	6.02
65	31.1	7.12
85	22.8	15.2
100		26.0

Lifetimes measured in methylcyclohexane.

8×10^{-8} mol in the 2.5 ml samples. In this region the rate of production of *m*-xylene is linear with time, as shown in Fig. 1. At higher conversions the apparent variation in yield of *m*-xylene with time may not be linear due to polymer deposition on the cell wall and production of some species, *e.g.* a substituted fulvene, which inhibits photoisomerization. The formation of polymer was readily obvious above 80°C even at the lowest conversions which could be used. The quantum yield of *m*-xylene was slightly lower for pure liquid *o*-xylene than in the case of dilute solutions.

The quenching of both fluorescence and *m*-xylene formation from *o*-xylene at various concentrations of xenon at 60°C gave the results presented in Table 2. When the data are plotted in the Stern–Volmer form, *i.e.* Φ^0_{FM}/Φ_{FM} or Φ^0_m/Φ_m *vs.* [Xe], both plots yield the same quenching rate constant of $2.1 \times 10^8\ M^{-1}\ s^{-1}$ within the limits of error.

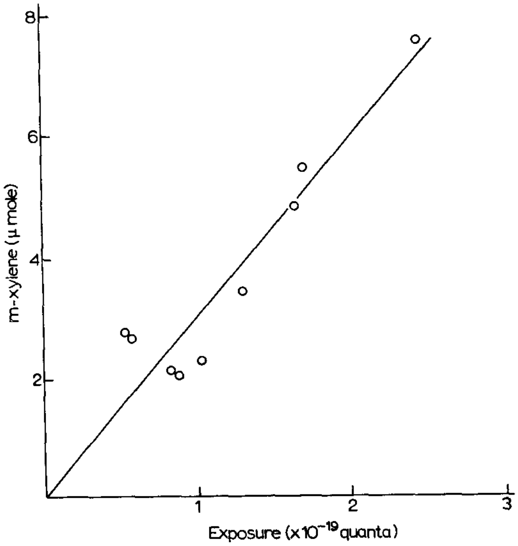


Fig. 1. Yield of *m*-xylene with quanta absorbed for 0.45 *M* solutions of *o*-xylene in isopentane at 30°C.

TABLE 2

EFFECT OF XENON CONCENTRATION ON FLUORESCENCE (Φ_{FM}) AND ISOMERIZATION (Φ_m) YIELDS OF *o*-XYLENE IN ISOPENTANE (0.45 *M*)

[Xe] (*M*) at 60°C	Φ	Φ°/Φ_{FM}	Φ_m ($\times 10^3$)	Φ°_m/Φ_m
0	0.110	1.00	6.20	1.00
0.034	0.087	1.27	7.00	0.89
0.074	0.051	2.18	3.46	1.79
0.199	0.046	2.38	2.30	2.69
0.269	0.031	3.57	1.74	3.56
0.440	0.020	5.56	0.97	6.37

In solutions with 5×10^{-1} *M* *trans*-butene-2 present the yield of *m*-xylene was increased threefold. The ratio of the fluorescence yields of 0.5 *M* solutions of *o*-xylene in isopentane and *trans*-butene-2 was 1.068, and the olefin does not appreciably affect the excited singlet state.

The effect of fulvene derivatives which may arise from photochemical reactions, on excited states of *o*-xylene was examined with 6,6′-dimethylfulvene which is convenient since it polymerizes relatively slowly. Its quenching properties are probably very similar to the other more reactive dimethylfulvenes which could be formed from *o*-xylene. Stern–Volmer plots at different *o*-xylene concentrations are shown in Fig. 2. Using measured lifetimes quoted in Part I quenching rate constants for 5×10^{-2}, 5×10^{-1} and 8.2 *M* solutions are 5.7, 2.3 and 1.9×10^{11}

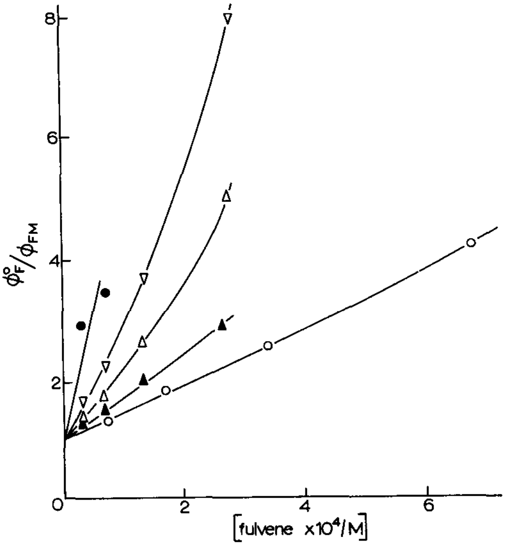


Fig. 2. Stern–Volmer quenching plots for the effect of 6,6′-dimethylfulvene on *o*-xylene fluorescence at different *o*-xylene concentrations (30°C). ●, 0.01 *M*; ▽, 0.05 *M*; △, 0.10 *M*; ▲, 0.50 *M*; ○, 8.27 *M*.

M^{-1} s^{-1} respectively. Part of the trend with *o*-xylene concentration arises from the partial absorption of the incident exciting light by the dimethylfulvene itself ($\varepsilon_{250} \approx 7000$ M cm^{-1}). This also accounts for the slight curvature evident in the Stern–Volmer plots. None of the fluorescence quenchers used affected the shape of the *o*-xylene emission spectrum.

DISCUSSION

The yields for the photoisomerization of *o*-xylene to the *m*- and *p*-isomer in solution are so low that their formation cannot significantly interfere with the mechanism which has been used to describe the photophysical effects. Isomers of the benzovalene, prismane or Dewar type formed from *o*-xylene would have lifetimes of many hours at room temperature but should be completely re-aromatized with formation of some *meta*-isomer under the conditions of injection into the gas chromatograph. It must be concluded that such isomers are also formed in low yield. The yield of dimethylfulvene and the polymer formed from it is also small. It is unlikely that formation of these products, which can act as quenchers of excited singlet states is responsible for the important process ascribed, in the absence of other explanations, to internal conversion.

The effect of additives

Xenon

Xenon is an efficient quencher of the singlet excited states of aromatic hydrocarbons, promoting intersystem crossing by enhancement of spin-orbit coupling by the external heavy atom effect[4]. Cundall and Tippett have shown for liquid benzene that the xenon enhanced $S_1 \rightarrow T_1$ (or T_2) transition proceeds with a rate constant of 2×10^8 M^{-1} s^{-1}. The rate constant for xenon quenching of the S_1 state of xylene is the same as for benzene, 2.1×10^8 M^{-1} s^{-1}. The fact that the same rate constant is deduced from the reduction of isomerization shows that fluorescence and isomerization arise from the same state. Photoisomerization proceeding through the triplet would probably be enhanced by xenon. This effect could be counteracted by the fact that xenon also promotes triplet state decay. Under the experimental conditions the xylene triplet is short lived[2] due to self quenching; the rate constant of the order of 3×10^8 M^{-1} s^{-1} for xenon catalysis of the $T_1 \rightarrow S_0$ transition in benzene deduced by Cundall and Tippett[5] is probably that for intersystem crossing of the triplet dimer.

Butene-2

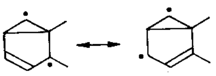
Noyes and Harter[6] found that butene-2 reduced the yield of *m*-xylene from *o*-xylene in the vapour phase and considered that the triplet state was involved. Dunnicliff[7], in contrast, has observed a small enhancement of the $o \rightarrow m$ isomerization in the vapour phase by the addition of *cis*-butene-2 after 254 nm excitation. This could be due to vibrational stabilization of the excited singlet states on some action of the xylene triplet or olefin on the precursor of the *m*-xylene. The first effect would be unimportant for liquid phase system. In our experiments with sufficient butene-2 (0.5 *M*) to quench virtually all the triplet states present a marked increase in the yield of *m*-xylene occurred. The triplet xylene interacting with precursor is rather unlikely in view of the short lifetime of the aromatic triplet and low concentration of precursor. It is more probable that a product of the triplet degradation reacts with the isomer precursor. A species, which is probably diradical, has been observed by Thomas[8] with a longer lifetime than the parent triplet. A reaction of olefin with the intermediate to form a product which gives an enhanced yield of *m*-xylene seems an unlikely alternative. Kaplan and Wilzbach[9] find that addition of butene-2 to benzene vapour increases the steady state concentration of benzvalene from $2 \times 10^{-3}\%$ to 1.3% at 254 nm. Benzvalene can re-aromatize[10] and may be one of the precursors of *m*-xylene. A reaction of benzvalene with a triplet derived product is the most plausible explanation.

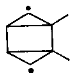
Irrespective of the mechanism of butene-2 enhancement of *m*-xylene formation it is clear that the triplet state is not the photoisomerization precursor.

Mechanism of photoisomerization

Bryce-Smith and Lonquet-Higgins[10–12] have argued that a diradical intermediate "prefulvene" is the precursor of the benzvalene and fulvene, and symmetry requirements necessitate that this arises from the ${}^1B_{2u}$ state. Another diradical from the ${}^1B_{1u}$ or ${}^3B_{1u}$ states gives rise to prismane or Dewar isomers.

Kaplan *et al.*[13] have reported that photoisomerization of the xylenes in the gas phase produced only 1,2-migration of methyl groups whereas in the liquid state both 1,2- and 1,3-shifts (7%) occurred. In experiments with mesitylene the shifting methyl groups were accompanied by their ring carbons. They concluded that benzvalene is an intermediate in the gas phase and prismane or Dewar forms are intermediates in the liquid phase. The group theory predictions would require that in the latter case triplet state be involved; this is not found to be the case although the slight extent of 1,3-shifts observed is at the extreme limit of error. Jano[14] has suggested that two other diradicals may be involved:


(I)


(II)

(I) is favoured in the gas phase and can only give the *m*-isomer. (II) is considered to form also in the liquid phase and can produce *p*-xylene.

The yields of *m*-xylene from *o*-xylene are comparable with[15] 1.3×10^{-2} for benzvalene and 1.5×10^{-3} for fulvene in the 254 nm photolysis of dilute solutions of benzene particularly when it is borne in mind that re-aromatization to *m*-xylene arises from only a fraction of the intermediate involved and the formation of the u.v. opaque film due to polymerization of fulvene derivatives reduces the measured quantum yield.

The data of Anderson[16] on the liquid phase isomerization of the xylenes are not strictly comparable with those reported here. The conversions were very much greater than in our work, secondary reactions are possible and considerable amounts of polymer must have formed under his conditions.

Further, the method of data analyses used by Anderson in fitting the variation of isomer quantum yield with temperature to an Arrhenius relationship is inaccurate because it fails to take account of the temperature behaviour of the remaining rate constants included in the expression for isomer quantum yield.

The quantum yield for *m*-xylene formation is temperature dependent and accumulative rate constant for isomerization may be derived from Φ_M/τ_M. When this rate constant is plotted in Arrhenius form an activation energy of 0.44 eV is obtained. In terms of the formation of intermediate, such as benzvalene:

$$k_m = \beta\, k_{INT}$$

where k_{INT} is the rate constant for intermediate, probably a dimethyl benzvalene, formation and β is the branching ratio for *m*-xylene formation from this metastable intermediate. The latter is assumed in the absence of other evidence to be invariant under the experimental conditions. If benzvalene is involved, the re-aromatization occurs on injection into the gas chromatograph.

E_{ICM} is 0.21 eV and isomerization must be a different process from internal conversion. Both processes originate from different vibrational levels of the S_1 state.

The slight lowering of the isomerization yield in the pure liquid is consistent with a reaction proceeding from a high vibrational level of the monomeric excited state, as the fraction of excited molecules in the monomeric state decreases with increase in concentration.

Fulvence derivatives might act as a quencher, reducing the apparent yield of *m*-xylene, although the maximum quenching rate constant $k_{Q_{max}}$ is 6×10^{11} $M^{-1}\,s^{-1}$, the dilute solutions and low conversions used in these experiments would result in very low concentrations of substituted fulvenes and therefore the quenching would not seriously affect the measured isomerization yield. The quenching rate constant is more than ten times greater than diffusion controlled and dipole–dipole interaction must be involved.

The simplified kinetic scheme is affected by the occurrence of triplet, or product originating from the triplet, induced distruction of the *m*-xylene precursor. Part of the temperature dependence could arise from this.

Since this paper was prepared, we have been informed by Professor G. Stein[17] that in the case of benzene solutions in water there is kinetic evidence that benzvalene is removed by this type of process.

CONCLUSIONS

The results discussed in this and the two previous papers have allowed evaluation of a large number of rate constants for photophysical and photochemical processes arising from electronic excitation of *o*-xylene. A non-radiative $S_1 \rightarrow S_0$ conversion is very important and does not involve isomerization. The isomerization to the *m*-isomer involves an intermediate, perhaps benzvalene, which is formed from a higher vibrational level of the S_1 state. It is possible that the isomerization may occur through an intermediate formed by excitation of the transient such as a (σ,π^*) state involved in internal conversion, though there is no direct experimental evidence to suggest the existence of such an intermediate.

ACKNOWLEDGEMENTS

We are grateful to the S.R.C. for a grant to D.A.R. and the University of Nottingham for a post-graduate scholarship (A.J.R.V).

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