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PHOTOPHYSICS AND PHOTOCHEMISTRY OF *o*-XYLENE SOLUTIONS
II. RADIATIONLESS PROCESSES

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SUMMARY

Data are presented for triplet yield measurements on *o*-xylene solutions as a function of temperature and concentration. Intersystem crossing from the excited singlet monomer is independent of temperature ($k_{\mathrm{ISCM}} = 7.2 \times 10^6$ s^{-1}). Internal conversion has temperature independent ($k^0{}_{\mathrm{ICM}} = 3.9 \times 10^6$ s^{-1}) and temperature dependent components. For the latter E_{ICM} is 0.207 eV and A 2.2 × 10^{10} s^{-1}). The results are interpreted on the basis of a recent model for radiationless decay. The intrinsic yields for intersystem crossing and internal conversion from the *o*-xylene excimer are also estimated.

INTRODUCTION

In this paper we give an account of measurement of triplet yields as a function of concentration and temperature. This allows evaluation of the parameters which govern the internal conversion $S_1 \rightarrow S_0$. The rate constant notation and general reaction scheme is that used previously[1,2].

EXPERIMENTAL

Materials

o-Xylene and methylcyclohexane were purified as described in Part I[1]. *cis*-Butene-2 (99.94%) was used without further purification other than trap-to-trap distillation. The major impurity was 0.05% *trans*-butene-2.

Apparatus and technique

Triplet yield measurements were made using equipment and technique similar to that described previously[3]. In most cases irradiation of the sample was made with the 254 nm Hg resonance line. In some instances another lamp was used to determine the effect, if any, of variation in light intensity on the system. In both cases actinometry was carried out, according to the recommendations of Forbes and Heidt[4], using uranyl oxalate solutions. The more intense lamp, operating with a 2 mm Chance OW1 filter to remove 185 nm light, gave absorbed intensity of about 1.7×10^{16} quanta s^{-1}. The lower intensity lamp run with a 5 cm $NiSO_4$ (120 g l^{-1}) filter gave a typical intensity of absorption of 1×10^{14} quanta s^{-1}. Both lamps had excellent short term stability; long term variations in intensity were corrected by monitoring the intensity with a reference photocell.

Determination of the butene-2 isomer ratio in irradiated samples was made by gas chromatography, using 1.2 m hexamethyl diphosphoramide (15% w/w on Chromosorb W) followed by 5.2 m of saturated silver nitrate/diethylene glycol (30% w/w) columns.

RESULTS

Studies of triplet quenching by butene-2 in 7.5×10^{-3} *M*, 4.8×10^{-1} *M*, 3.0 *M*, and 8.0 *M* solutions of *o*-xylene in methylcyclohexane at 60° C and 5×10^{-1} and 8.29 *M* at 30° C were made. The data are presented in Figs. 1, 2 and 3. The scatter in the results in Figs. 1 and 2 resulted from the considerable difficulty

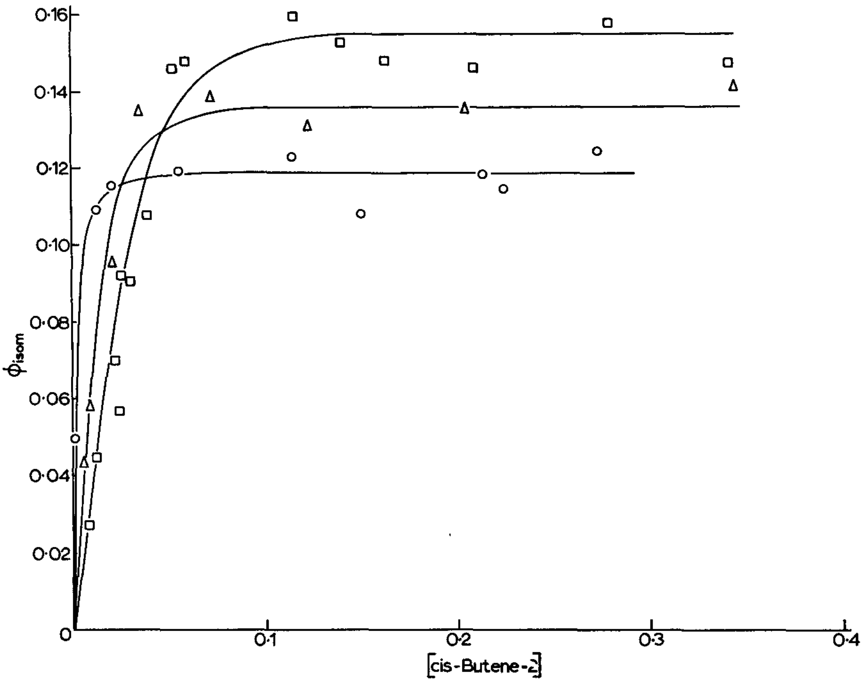

Fig. 1. *cis–trans* Isomerization of butene-2 yields as a function of olefin concentration at 60° C. *o*-Xylene concentrations: □, 8.0 *M*; △, 3.0 *M*; ○, 4.8×10^{-1} *M*.

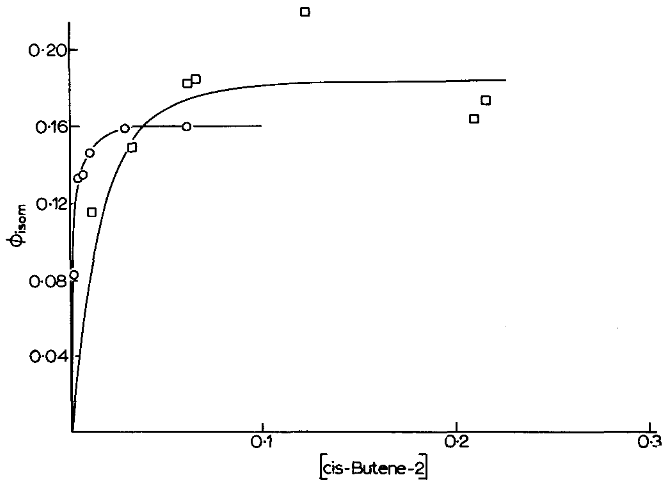

Fig. 2. As Fig. 1 at 30°C. *o*-Xylene concentrations: □, 8.29 *M*; ○, 5 × 10^{-1} *M*.

experienced in removing all of the dissolved olefin from the solution. Repeated refluxing of the irradiated sample onto a cold finger (−78°C) was necessary to remove completely the *trans*-butene-2 from the sample. In the case of Fig. 3 extremely small amounts of olefin were required for determination of the "fall-off" region of the plot, a major cause of experimental scatter. Nevertheless, in all cases the experimental points at the higher olefin concentrations are within 10% of the limiting isomerization yields obtained from an average of appropriate values. The variation in isomerization yield in 8.0 *M* (pure) *o*-xylene solution at 60°C is a combination of values at different light intensities. No intensity dependence of the iso-

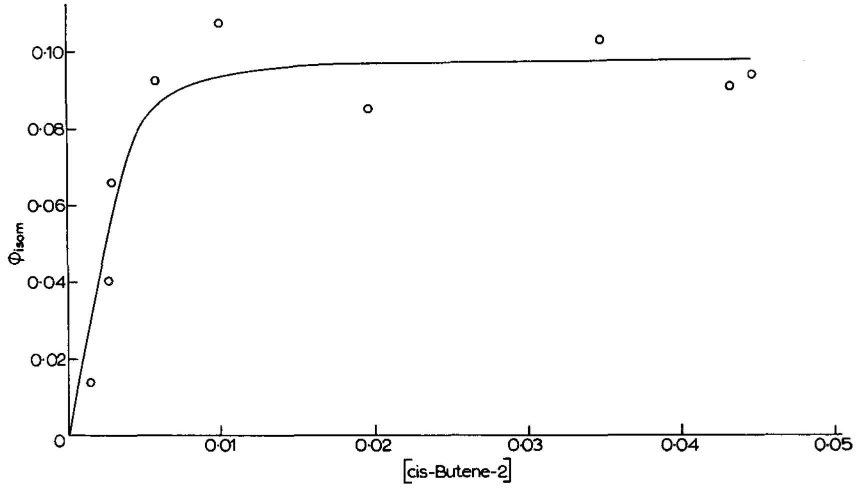

Fig. 3. As Fig. 1, 7.5 × 10^{-3} *M* *o*-xylene at 60°C.

merization yield outside the limit of experimental error ($\pm$ 10%) was ever observed. It should be noted that even at fixed incident light intensities the effective intensities of light absorbed varied considerably with changing *o*-xylene concentration.

The "fall-off" regions arise from competition between triplet energy transfer and other decay processes and the limiting value is reached when sufficient olefin is present to quench practically all the triplet species. The limiting isomerization yield values at the higher olefin concentrations are related to the triplet yields by the relative probabilities of the olefin triplet relaxing to either of the geometrical isomers. There are no indications that this ratio, unity within the limits of error, is a function of solvent, concentration or temperature.

At the concentrations used *cis*-butene-2 had practically no effect on the first excited singlet state of *o*-xylene.

DISCUSSION

Dilute solutions

The extent to which 0.5 *M* *o*-xylene solution represents the intrinsic monomeric situation can be estimated from knowledge of the fraction of singlet excited molecules in the monomer form, f_{M}. This is given by the expression[6]:

$$f_{\mathrm{M}} = \frac{\tau_{\mathrm{M}} c_{\mathrm{n}}}{\tau_{\mathrm{M}} c_{\mathrm{n}} + \tau_{\mathrm{D}} c} \qquad (1)$$

Use of data calculated in Part I for the parameters in eqn. (1) shows that for 0.5 *M* solutions of *o*-xylene in methylcyclohexane $f_{\mathrm{M}} = 0.982$ at 60° C and 0.964 at 30° C. It is therefore proposed to use the triplet data at this concentration to represent the intrinsic yield from monomer rather than the 7.5×10^{-3} *M* solution where experimental uncertainty is greater. The rate constant for intersystem crossing was evaluated from:

$$\Phi_{\mathrm{T}} = k_{\mathrm{ISCM}}/\tau_{\mathrm{M}} \qquad (2)$$

The τ_{M} values are given in Table 1.

From the data for 0.5 *M* solutions it is calculated that k_{ISCM} is $7.22 \times 10^{6}\ \mathrm{s}^{-1}$ and $7.11 \times 10^{6}\ \mathrm{s}^{-1}$ at 30 and 60° C respectively. The constancy of the intersystem crossing rate constant with respect to temperature agrees with the results for toluene, a molecule which belongs to the same symmetry point group. This behaviour has been explained[7] on the basis of transitions from S_1 to both T_1 and T_2 which appear to be independent of temperature in the case of toluene. The $S_1 \rightarrow T_2$ transition in benzene[3] requires vibrational perturbation and intersystem crossing is noticeably temperature dependent.

If k_{ISCM} is independent of temperature the limiting triplet yield at low temperatures may be estimated from the lifetime measurements of Cundall and Pereira[8]. The fluorescence lifetime (10^{-2} *o*-xylene in methylcyclohexane) tends

TABLE 1

EFFECT OF TEMPERATURE ON THE RATE CONSTANT FOR INTERNAL CONVERSION IN *o*-XYLENE

Temp. (°C)	τ_M (ns)	$1/\tau_M = \Sigma k_M$ $\times 10^{-6}$ (s^{-1})	Σk_{ICM} $\times 10^{-6}$ (s^{-1})	k_{ICM} $\times 10^{-6}$ (s^{-1})
20	47.2	21.2	10.6	6.7
30	44.4	22.5	11.9	8.0
40	41.0	24.4	13.8	9.9
50	37.1	27.0	16.4	12.5
60	33.2	30.1	19.5	15.6
70	29.3	34.1	23.5	19.6
80	25.1	39.8	29.2	25.3

to be a low temperature limit of about 67 ns. Accepting a rate constant for intersystem crossing of 7.2×10^6 s^{-1} a limiting triplet yield of 0.50 at low temperature is obtained. Similarly, assuming a temperature independent fluorescence rate constant[1] of 3.45×10^6 s^{-1} a limiting fluorescence yield of 0.23 is estimated. Therefore, the sum of the low temperature fluorescence and triplet yields falls short of unity by 0.27. This deficit is tentatively assigned to a temperature independent internal conversion process, the nature of which will be discussed. The existence of such a process is borne out by the behaviour of the total internal conversion "rate constant" abstracted from the temperature dependence of the fluorescence lifetime:

$$\tau_M = (k_{FM} + k_{ISCM} + \Sigma k_{ICM})^{-1} \qquad (3)$$

$\tau_M{}^{-1} - (k_{FM} + k_{ISCM})$ gives Σk_{ICM}, which if it represents a single decay process should follow a simple Arrhenius relationship. Figure 4 shows that such a plot is curved. If Σk_{ICM} is represented as:

$$\Sigma k_{ICM} = k^0{}_{ICM} + k'{}_{ICM}$$

where $k^0{}_{ICM}$ is the temperature independent rate constant abstracted from the quantum deficit at low temperature and the limiting fluorescence lifetime, and $k'{}_{ICM}$ is a temperature dependent parameter which could obey an Arrhenius relationship. Figure 4 shows the variation of $\log_{10}k'{}_{ICM}$ with T^{-1}. The plot shows reasonable linearity within the limits of experimental error and the probable oversimplication of the model. An activation energy of 0.21 eV and a pre-exponential factor of 2.2×10^{10} s^{-1} are found for $k'{}_{ICM}$. The radiationless $S_1 \rightarrow S_0$ process may be represented by

$$\Sigma k_{ICM} = 3.9 \times 10^6 + 2.2 \times 10^{10} \exp(-0.21/RT) \qquad (5)$$

The nature of so-called internal conversion processes in aromatic molecules are uncertain. The valence isomer model[9–11] involves an isomeric intermediate thought to originate from a transient diradical. Berenfeld and Krongauz[12] measured a quantum yield for radical formation in *o*-xylene in cyclohexane of 0.02 by reaction

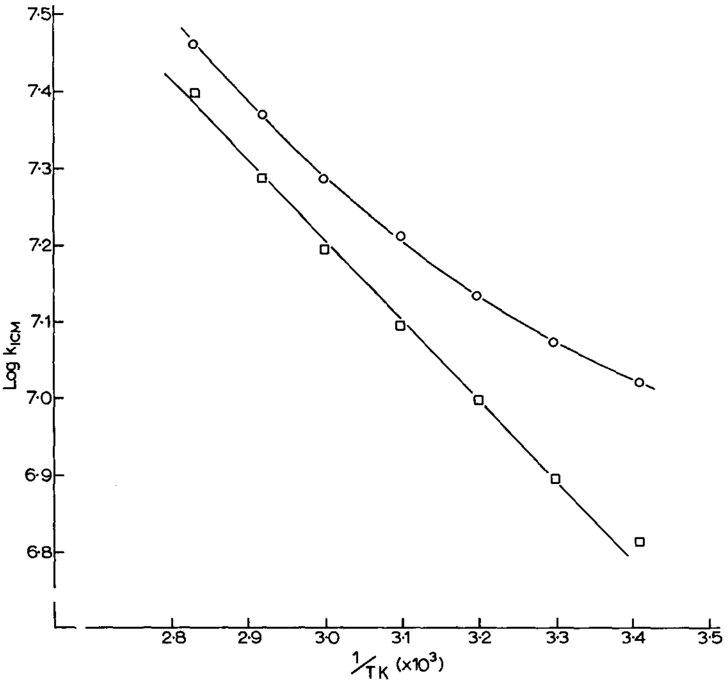

Fig. 4. Plots of T^{-1} *vs.* $\Sigma\, k_{\mathrm{ICM}}$ and k'_{ICM}.

with diphenylpicryl hydrazyl. This is unlikely, in spite of the experimental difficulties, to be in error by the factor of 15 necessary to explain the temperature dependent internal conversion quantum deficit at room temperature. Photochemical reactions which accompany excitation at 254 nm will be examined elsewhere[13].

Callomon *et al.*[14] have suggested the participation of (σ–π^*) states in "internal conversion". Of the six states[1,3] (A_{1u}, A_{2u}, E_{2u}), which arise from the promotion of an e_{2g} σ electron to an e_{2u} π^* orbital they predict that the $^3E_{2u}$ (σ–π^*) state should be the most important. Adopting this model, Cundall *et al.*[7] have suggested that a singlet (σ–π^*) state is more probable in toluene in view of the high A factor for the transition and inability of butene-2 to quench the state formed. The lowering in activation energy for internal conversion in toluene compared to benzene has been accounted for in terms of the relative inductive effect[15,16] of the methyl group on the σ and π levels. In the case of *o*-xylene, the high A factor for the temperature dependent part of Σk_{ICM} also favours a singlet–singlet transition.

The lifetime of the aromatic triplet state may be estimated from the "fall-off" of the butene-2 quenching plots. It has been shown[17] that butene-2 isomerization may not measure all of the triplet species in the benzene system under all conditions: participation of the triplet excimer can lead to a situation where triplet excitation energy is lost through a state not quenched by butene-2. The general kinetics of this situation is complex. In dilute solution, where singlet excimer is not present to any appreciable extent the situation is simple and a plot of $\Phi^{-1}_{\mathrm{ISOM}}$ against $[cis\text{-}\mathrm{C_4H_8\text{-}2}]^{-1}$ should be linear according to:

$$\frac{1}{\Phi_{\mathrm{ISOM}}} = \frac{1}{\Phi_{\mathrm{T}}b} + \frac{k_{\mathrm{TDyM}}}{\Phi_{\mathrm{T}}bk_{\mathrm{ET}}[\mathrm{Bu}]} \tag{6}$$

where k_{TDyM} is the rate constant for non-radiative decay of the triplet monomer and k_{ET} the electronic energy transfer rate constant. Plots have been made for 0.48 *M* and 0.0075 *M* solutions at 60°C and for 0.50 *M* solutions at 30°C. The ratio of intercept to slope gives $k_{\mathrm{ET}}/k_{\mathrm{TDyM}}$. The energy transfer rate constant, k_{ET}, is evaluated from published viscosity data using the equation given by Wagner and Kochevar[18], based on the Osborne–Porter[19] modification of the Debye formula:

$$k_{\mathrm{ET}} = pk_{\mathrm{DIFF}} = p(8RT/2000\eta) \tag{7}$$

The empirical factor p was assumed to be the same as that for cyclohexane (0.60).

On this basis it is found that $\tau_{\mathrm{T}} = 66$ ns and 120 ns for 5×10^{-1} solutions at 60° and 30° C respectively. This behaviour of the triplet in dilute solution is in agreement with the prediction of Cundall and Robinson[17] who derived the equation:

$$\tau_{\mathrm{T}} = \left[k_{\mathrm{TDyM}} + \frac{k_{\mathrm{TDyD}}\,k_{\mathrm{TDTM}}c}{k_{\mathrm{TDyD}} + k_{\mathrm{TMTD}}}\right]^{-1} \tag{8}$$

where c is [*o*-xylene]. This implies that even at very low solute concentrations triplet decay may occur via formation of a triplet excimer and subsequent rapid decay of this species. Experiments with the most dilute *o*-xylene solution failed to establish any "fall off" within the limits of the experimental technique. This means that τ_{T} at 30°C for this solution is > 900 ns. It can be concluded with certainty that the true monomeric triplet lifetime is $\sim 1\ \mu$s.

The uncertainty about the efficiency of energy transfer from *o*-xylene triplet excimer makes it difficult to determine the exact mechanism of triplet deactivation. If $k_{\mathrm{TDyD}} \gg k_{\mathrm{TMTD}}c$ the kinetics should follow Stern–Volmer type quenching:

$$\tau_{\mathrm{T}}^{-1} = k_{\mathrm{TDyM}} + k_{\mathrm{TDTM}}c$$

Treating the limited amount of data in this way it can be deduced that k_{TDTM} is 2.4×10^7 m^{-1} s^{-1} at 60°C and 6×10^6 *M*$^{-1}$ s^{-1} at 30°C.

It should be stressed that this k_{TDyM} is, on this basis, about 10^6 s^{-1} but the simplified mechanism is probably not valid over the whole range of experimental conditions. Furthermore $\tau_{\mathrm{T}-1}$ is not simply determined from $\Phi^{-1}_{\mathrm{ISOM}}$ against $[\mathrm{C_4H_8\text{-}2}]^{-1}$ plots[17].

Concentrated solutions

If Φ^0_{TM} and Φ^0_{TD} are the intrinsic yields of triplet from monomer and *from* excimer, and f_{M} and f_{D} are the fractions of excited singlet molecules in the monomeric and excimer forms, it can be deduced that:

TABLE 2

INTRINSIC QUANTUM YIELDS FOR THE PRIMARY PROCESSES IN *o*-XYLENE AT 60° C

Monomer processes	Excimer processes
$\Phi^{\circ}_{\mathrm{FM}} = 0.118$	$\Phi^{\circ}_{\mathrm{FD}} = 0.018$
$\Phi^{\circ}_{\mathrm{TM}} = 0.28$	$\Phi^{\circ}_{\mathrm{TD}} = 0.56$
$\Phi^{\circ}_{\mathrm{ICM}} = 0.60$	$\Phi^{\circ}_{\mathrm{ICD}} = 0.42$

$$\Phi_{\mathrm{T\ (total)}} = (\Phi^0{}_{\mathrm{TM}} - \Phi^0{}_{\mathrm{TD}})f_{\mathrm{M}} + \Phi^0{}_{\mathrm{TD}} \tag{9}$$

f_{M} is calculated as described previously, and plotted against the data for the triplet yield at 60°C for four concentrations. The plot is linear, as anticipated from the mechanism, giving 0.56 (± 0.06) as the intrinsic yield of triplet *from* excimer. This is only a lower limit since at this temperature butene-2 may not quench all the triplet species but nevertheless it considerably exceeds the intrinsic yield of triplet from monomer.

CONCLUSIONS

From the data presented in this work and in Part I, it is possible to evaluate the intrinsic quantum yields for the major decay processes in both the excited *o*-xylene monomer and excimer states. These are presented in Table 2. It is clear that radiationless deactivation, not involving a scavengable triplet state, also plays a major role in the deactivation of the first excited singlet.

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