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CONCENTRATION-DEPENDENT DEUTERIUM ISOTOPE EFFECTS ON THE QUANTUM YIELD OF ARENE–ALKENE META PHOTOCYCLOADDITION: THE ROLE OF EXCIMERS

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A deuterium isotope effect on the arene–alkene *meta* photocycloaddition, reported earlier for toluene/toluene-d_8 photoaddition to cyclopentene, was found to depend on the concentration of both arene and alkene. This phenomenon is explained in terms of an unbalanced dissociation of 'mixed' excimers, which play a role in the intermolecular competition experiments.

INTRODUCTION

Isotope effects on the quantum yield (quantum yield isotope effect, QIE) of a photoreaction are not always equal to the kinetic isotope effects (KIE).[1,2] The isotope effect on the quantum yield can have its origin in a diabatic process (internal conversion,[3] intersystem crossing,[4] fluorescence[5]), in the rate constant of the reaction under study,[6–8] or in other (bimolecular) competing decay processes of the excited state.[9–11]. The kinetic isotope effect depends on the rate constants of the reaction only.

With this in mind, we studied the isotope effect on the quantum yield of *meta* photocycloaddition of ring-deuterated arenes to cyclopentene in an intermolecular competition experiment.

Kinetic isotope effects on this type of reaction had been observed previously in the case of arenes deuterated at the carbon atoms to which bonds with the alkene are formed, and in the case of methyl-deuterated arenes. Both effects were determined in intramolecular competition experiments (see Figure 1 and Table 1, entries a–c).[12] Both effects can be explained in the usual way, common in ground-state chemistry:[13] the inverse effect observed with **1b** may be an α-secondary effect accompanying rehybridization of the carbon atoms towards which the new bonds are being formed; and the normal β-secondary effect observed with **1c** is in agreement with a polarized intermediate[14] in which the positive charge is stabilized by hyperconjugation with the methyl C—H bonds.[15]

The relationship between the kinetic isotope effect ($\mathrm{KIE} = k_H/k_D$) and the isotope effect on the quantum yield of adduct formation ($\mathrm{QIE} = \Phi_H/\Phi_D$) can easily be derived from equation (1). Here the assumption is made that the photoaddition is the only bimolecular process.

$$\Phi = \frac{k[\text{alkene}]}{k[\text{alkene}] + \Sigma k_x} \text{ or } \frac{\Phi}{1-\Phi} = k\frac{[\text{alkene}]}{\Sigma k_x} \quad (1)$$

where Σk_x is the sum of the rate constants of all unimolecular decay paths of the excited arene.

Because it is known that deuterium has no significant effect on singlet excited-state lifetimes of toluene ($\tau_H/\tau_D = 34$ ns/35 ns) and *p*-xylene ($\tau_H/\tau_D = 30$ ns/30·3 ns) in cyclohexane solutions[16,17] ($\tau_H = \tau_D = 1/\Sigma k_x$), the QIEs determined in these experiments are expected to be related to the KIEs according to the equation

$$\mathrm{KIE} = \mathrm{QIE} \times \frac{1-\Phi_D}{1-\Phi_H} \quad (2)$$

This means that the KIE will be nearly equal to the QIE if the quantum yields of product formation (Φ) are not extremely large, which is the case for the reactions which are subject of our studies ($\Phi < 0{\cdot}25$).

With the results of the intramolecular competition experiments and the above relationship between the KIE and the QIE in mind, the intermolecular competition experiments (Figure 2) between toluene (**4a**) and each of the labelled compounds 2,6-dideuteriotoluene (**4b**), 3,5-dideuteriotoluene (**4c**) and octadeuteriotoluene (**4d**), are expected to give the following isotope effects:

4a–4b: an α-secondary type effect as observed with **1b**, i.e. $\Phi_H/\Phi_D = 0{\cdot}93$;

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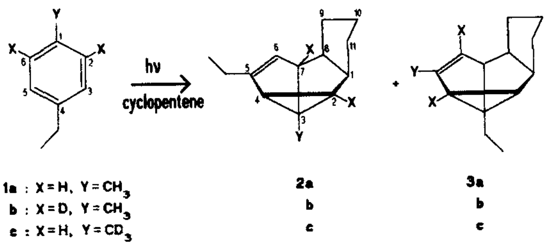


Figure 1. *Meta* photocycloaddition of 4-ethyltoluene and deuterated 4-ethyltoluenes to cyclopentene. Product distributions **2**:**3** are listed in Table 1, entries a–c

Table 1. Product distributions and isotope effects from intra- and intermolecular competition experiments

Compound	Product ratio	Isotope effect
a 4-Ethyltoluene (**1a**)	**2a**:**3a** = 1·74	–
b 2,6-d_2-4-Ethyltoluene (**1b**)	**2b**:**3b** = 1·84	$k_H/k_D = 0{\cdot}93$
c α,α,α-d_3-4-Ethyltoluene (**1c**)	**2c**:**3c** = 1·64	$k_H/k_D = 1{\cdot}06$
d Toluene (**4a**)/2,6-d_2-toluene (**4b**) (1 : 1)	**5a**:**5b** = 1·10	$\Phi_H/\Phi_D = 1{\cdot}10$
e Toluene (**4a**)/3,5-d_2-toluene (**4c**) (1 : 1)	**5a**:**5c** = 1·17	$\Phi_H/\Phi_D = 1{\cdot}17$
f Toluene (**4a**)/toluene-d_8 (**4d**) (1 : 1)	**5a**:**5d** = 1·48	$\Phi_H/\Phi_D = 1{\cdot}48$

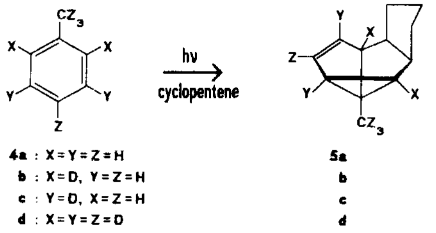


Figure 2. *Meta* photocycloaddition of toluene and deuterated toluenes to cyclopentene. Isotope effects from intermolecular competition experiments are listed in Table 1, entries d–f

4a–4c: no significant effect, i.e. $\Phi_H/\Phi_D = 1{\cdot}00$;
4a–4d: the net result of an α-secondary type effect as observed with **1b**($=0{\cdot}93$), and a β-secondary type effect as observed with **1c** ($=1{\cdot}06$), i.e. $\Phi_H/\Phi_D = 0{\cdot}99$, probably distorted by an effect due to the deuterium at position 4 in **4d**, which however, is not expected to be significant.

The isotope effects found with the experiments (1·10, 1·17 and 1·48, respectively), however, do not agree with these expectations (see Table 1, entries d, e and f).

At the time of publication of Ref. 12, we had no other data available which could give a clue to the origin of these unusual isotope effects. Two explanations are considered:

(A) It is possible that the usual explanation of the kinetic isotope effect fails in this case of a photochemical reaction. The isotope effects obtained in the intermolecular competition experiments may reflect the kinetic isotope effects. New theoretical insight would be required for a rationalization of these effects.
(B) The value from the intramolecular experiment with **1b** may represent the true KIE. In the intermolecular experiment an isotope effect on a process other than *meta* photocycloaddition then plays a role.

Explanation B seems the most likely. If the bonds between the arene and the alkene are being formed in the rate-determining step, an inverse isotope effect is expected in the case of 2,6-*meta* photocycloaddition of a 2,6-dideuterated arene. In such a process carbon atoms 2 and 6 change hybridization (from sp^2 to sp^3), leading to the inverse kinetic isotope effect[13] (0·93). On the other hand, carbon atoms 3 and 5 remain sp^2 hybridized initially, which results in a kinetic isotope effect of unity (1·00) for 3,5-dideuteriotoluene. In order to distinguish between explanations A and B of the effects, a series of additional experiments was performed as described below.

RESULTS

Competition experiments with toluene and toluene-d_8

In explanation B as described above there is one external factor on which the observed isotope effect may depend, viz. concentration. The *meta* photocycloaddition is a bimolecular process and its quantum yield depends on the cyclopentene concentration. Most other processes are unimolecular with no concentration dependence, or bimolecular with a dependence on a concentration other than that of cyclopentene, or a different dependence on the cyclopentene concentration. As a consequence, the QIE will change when other concentrations of reactants are chosen, for example when the ratio of labelled to unlabelled reactant is changed.

The usual method for determining isotope effects from intermolecular competition experiments [i.e. mass spectrometric (MS) determination of the isotopic product and substrate ratios] is very time consuming and

Table 2. Dependence of the QIE on the isotopic substrate ratio in the intermolecular competition experiment

	Toluene/toluene-d_8 ratio	$\Phi_H/\Phi_D = \frac{\mathbf{5a:5d}}{\mathbf{4a:4d}}$
a′	1 : 1	1·48(4) (determined by MS)[a]
a	1 : 1	1·46(2) (determined by GC)
b	2 : 1	1·54(2) (determined by GC)
c	1 : 2	1·36(2) (determined by GC)

[a] see Ref. 12.

not suitable for large series of experiments. Instead, the following method was chosen.

A solution of toluene and octadeuteriotoluene in cyclohexane in the presence of cyclopentene was irradiated, and at low conversion the mixture was analysed by capillary gas chromatography (GC). The chromatograms showed two product peaks of about equal height close to each other, due to the labelled and unlabelled photoproducts. Under optimized conditions the two peaks were almost baseline separated.

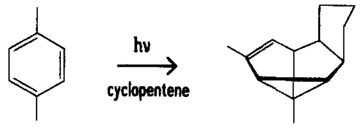
Competition experiments were performed with ratios of toluene/toluene-d_8 of 1, 2 and 0·5. The QIEs from these experiments are listed in Table 2. It can be seen from entries a and a′ that there is good agreement between the results of the GC method and the MS method.

Remarkably, the isotope effect increases with increasing toluene/toluene-d_8 ratio. This observation cannot be explained in terms of a kinetic isotope effect on the *meta* photocycloaddition reaction. The isotope effect is caused (at least partly) by a process which depends on the concentration of the substrate. In order to find out which process this might be, a series of competition experiments was performed in which the concentrations of the arene and the alkene were varied; *p*-xylene and *p*-xylene-d_{10} were used in these experiments because these arenes give very neat irradiation mixtures with only one product and no detectable by-products. Moreover, the peaks of the labelled and the unlabelled products are fully baseline separated in the gas chromatogram and the product ratio determined by integration of the two peaks is very reproducible (even better than with toluene/toluene-d_8).

Competition between *p*-xylene and *p*-xylene-d_{10}. Concentration dependence of the QIE

Competition experiments were performed with equimolar solutions of *p*-xylene (**6a**) and *p*-xylene-d_{10} (**6b**) in cyclohexane containing cyclopentene (Figure 3).

The QIE was determined by measuring the product ratio **7a**:**7b** at seven different xylene concentrations, ranging from 0·002 to 1·333 M, and two cyclopentene concentrations, 2·0 and 0·2 M. Lower concentrations of cyclopentene and xylene could not be used because impurities prevent an accurate determination of the product ratios at low conversion. The values of the QIEs determined in these experiments are listed in Table 3.



6a (= *para*-xylene)
b (= *para*-xylene-d_{10})

7a
b

Figure 3. *Meta* photocycloaddition of *p*-xylene and *p*-xylene-d_{10} to cyclopentene

Table 3. Concentration dependence of the QIE of *p*-xylene to cyclopentene *meta* photocycloaddition determined in intermolecular competition experiments

Xylene concentration (M)	Cyclopentene concentration (M)	Φ_H/Φ_D = **7a**/**7b**
1.333	2	1.51
0.444		1.51
0.133		1.40
0.044		1.22
0.013		1.02
0.004		1.01
0.002		1.01
1.333	0.2	1.61
0.444		1.51
0.133		1.51
0.044		1.34

Table 4. QIEs of *p*-xylene to cyclopentene *meta* photocycloaddition determined in a non-competition experiment (see text). Cyclopentene concentration, 2 M

Xylene concentration (M)	Φ_H/Φ_D = **7a**/**7b**
0·5	0·88
0·1	0·87
0·05	0·88

These values show that when both the concentrations of arene and alkene are high the QIE is constant (1·51). When the arene concentration decreases the QIE also decreases, but reaches a lower limit of 1·01 at very low concentrations. When the alkene concentration is lowered the QIE is even higher, but decreases with decreasing arene concentration.

In order to obtain more insight into the origin of the isotope effect, Φ_H/Φ_D was also determined in a non-competition experiment. This was done by irradiating solutions of *p*-xylene and *p*-xylene-d_{10}, both containing cyclopentene, in separate vessels. After several time intervals equal amounts of both solutions were mixed for analysis of the product ratios. The measured values are listed in Table 4. In contrast to the results of the competition experiments, here no concentration dependence is observed.

DISCUSSION

The origin of the concentration dependence observed with the competition experiments must be sought in a bimolecular process which competes with the *meta* photocycloaddition. With low alkene concentration, the quantum yield of the photoreaction is low and quantum yields of other decay paths are higher. The contribution of an isotope effect on such a decay path to the QIE will be proportionally higher.

The only important bimolecular process of which the quantum yield does not decrease with decreasing alkene concentration is the formation of excimers. It is known (at least for benzene and toluene) that excimers are in equilibrium with the excited monomer,[18] and it can be imagined that this equilibrium lies more to the excimer side in the case of the deuterated arenes than in the case of the light isotopic species. The situation is much more complicated in our case, however. Because in the competition experiment both labelled and unlabelled xylene are present, three different excimers are possible, formed by interaction of an excited-state and a ground-state molecule of the same species (D_{HH} or D_{DD}), or from either kind of excited state molecule with a ground-state molecule of the other species (D_{HD}). Here the assumption is made that the 'mixed' excimers formed in the latter case are equal, i.e. it does not matter which of the two molecules was in the excited state before the interaction.[19]

The values of the QIEs found in the non-competition experiment contrast strongly with those found in the competition experiments. The QIE is inverse. No concentration dependence is observed in this case. This implies that the clue to the origin of the isotope effect must be sought in the difference between the two experiments. This difference lies in the absence of the processes involving the mixed excimers D_{HD}. The rationalization of the concentration dependence of the QIE in the competition experiment can be found in an unbalanced dissociation of the 'mixed' excimers. In that case these excimers would then give more excited *p*-xylene than excited *p*-xylene-d_{10} on dissociation. This can be viewed as excitation transfer from the labelled to the unlabelled xylene via an exciplex (i.e. the mixed excimer) of the two. Isotope effects on energy-transfer processes have been reported.[20,21] In several cases it has been shown that in mixtures of isotopic molecules the excitation energy will preferentially be located at the light isotopic species owing to differences in zero-point energy. This phenomenon, however, is only observed at very low temperatures and in crystals. In solution or at higher temperatures the excitation migration is fast and both isotopic species have their excited state equally populated. In our case the effect can therefore not originate from direct excitation migration, but may originate from the suggested energy-transfer process via the intermediacy of an excimer.

The fact that the isotope effect (1·01) no longer differs significantly from the KIE [i.e. the product (0·99) of the α-secondary (0·93) and β-secondary (1·06) effects shown in Table 1] at arene concentrations at which excimer fluorescence is no longer observed[22,23] supports this explanation. An energy diagram of the excimer equilibria is shown in Figure 4. It can be seen that the equilibrium constants of $A_H \rightleftharpoons D_{HH}$ and $A_D \rightleftharpoons D_{DD}$ will be equal.

Although the above qualitative interpretation of the experimental results is clear, it is tempting to try to express the concentration dependence of the QIE quantitatively in terms of the model proposed. A steady-state analysis of the processes which may influence the QIE should yield such an expression. Figure 5 depicts the processes which may affect the QIE, i.e. the ratio of **7a** to **7b**.

To make things not too complicated, it is assumed that $[A_H] = [A_D]$ and that the molar absorptivities E_H and E_D of the unlabelled and labelled arene are equal. In a steady-state approximation, it can be shown that the relationship between the QIE (Φ_H/Φ_D) and the KIE ($k_{R,H}/k_{R,D}$) is given by the following equation:

$$\frac{\Phi_H}{\Phi_D} = \frac{k_{R,H}}{k_{R,D}} \times \frac{k_{M,D} + k_{DD}k_{MDD}[A]\tau_{DD} + (k_{R,D} + k_{Q,D})[cp] + k_{DH}[A]\{1 + (k_{-HD} - k_{-DH})\tau_{HD}\}}{k_{M,H} + k_{HH}k_{MHH}[A]\tau_{HH} + (k_{R,H} + k_{Q,H})[cp] + k_{HD}[A]\{1 + (k_{-DH} - k_{-HD})\tau_{HD}\}} \qquad (3)$$

where

$$\tau_{HH} = 1/(k_{MHH} + k_{-HH}),\ \tau_{DD} = 1/(k_{MDD} + k_{-DD}) \text{ and } \tau_{HD} = 1/(k_{MHD} + k_{-HD} + k_{-DH})$$

Although the expression is very complex we can recognize two terms which depend on the arene concentration. One term stems from the formation and decay of

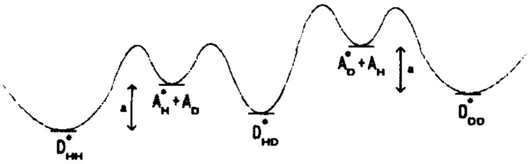


Figure 4. Energy diagram of monomer–excimer equilibria occurring in the intermolecular competition experiments

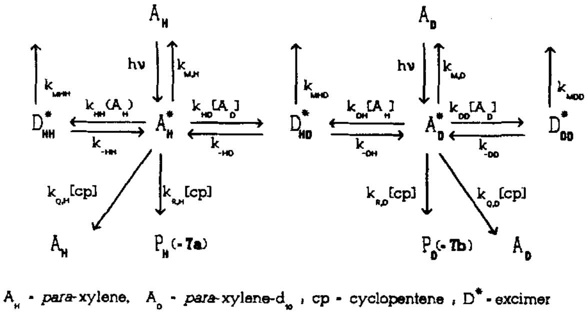


Figure 5. Schematic representation of excited-state processes occurring in intermolecular competition experiments (see text)

the excimers D_{HH} and D_{DD} and the other represents the contribution of the processes involving the mixed excimer D_{HD}. Rate constants of processes involving excimers of simple alkylbenzenes have been determined by Birks *et al.*[17,24] It can be shown by substituting these values for k_{HH}, k_{MHH} and τ_{HH} and the same values for the corresponding rate constants of deuterated or mixed species, that the term involving D_{HH} and D_{DD} is an order of magnitude smaller than any of the others, and so can be left out of the equation. This yields

$$\mathrm{QIE} = \mathrm{KIE} \times \frac{k_{M,D} + (k_{R,D} + k_{Q,D})[cp] + k_{DH}[A]\{1 + (k_{-HD} - k_{-DH})\tau_{HD}\}}{k_{M,H} + (k_{R,H} + k_{Q,H})[cp] + k_{HD}[A]\{1 + (k_{-DH} - k_{-HD})\tau_{HD}\}} \qquad (4)$$

The term involving the mixed excimer is eliminated when the two xylenes are irradiated in separate vessels, and the equation is then reduced to

$$\mathrm{QIE} = \mathrm{KIE} \times \frac{k_{M,D} + (k_{R,D} + k_{Q,D})[cp]}{k_{M,H} + (k_{R,H} + k_{Q,H})[cp]} \qquad (5)$$

The observation that in the non-competition experiment the QIE no longer depends on the arene concentration proves that such a dependence in the competition experiment stems entirely from the term caused by D_{HD}. At high arene concentration the QIE becomes larger, so $k_{DH}\{1 + (k_{-HD} - k_{-DH})\tau_{HD}\} > k_{HD}\{1 - (k_{-HD} - k_{-DH})\tau_{HD}\}$. This can be written as

$$\frac{k_{DH}}{k_{HD}} > \frac{1 - (k_{-HD} - k_{-DH})\tau_{HD}}{1 + (k_{-HD} - k_{-DH})\tau_{HD}} \qquad (6)$$

Because the processes involving the excimers D_{HH} and D_{DD} do not exhibit an isotope effect, as was concluded from the non-competition experiment, it seems very unlikely that the formation rate constants k_{DH} and k_{HD} of the mixed excimer from either side are different. In that case, the left-hand term in equation (6) is unity and it can be concluded that $k_{-HD} > k_{-DH}$.

It is known that $k_{M,H} = k_{M,D}$ [the fluorescence lifetimes (τ_0) of *p*-xylene and *p*-xylene-d_{10} are 30·0 and 30·3 ns, respectively[17]]. Equation (5) can therefore be rewritten as

$$\mathrm{QIE} = \mathrm{KIE} \times \frac{1 + \tau_0(k_{R,D} + k_{Q,D})[cp]}{1 + \tau_0(k_{R,H} + k_{Q,H})[cp]} \qquad (7)$$

If the assumption is made that $k_{Q,H} = k_{Q,D}$ then it can be seen from this equation that the QIE is greater than the KIE if KIE < 1. This is in agreement with the limiting value of 1·01 for the QIE at low arene concentration and the small inverse KIE effect which is expected for *p*-xylene.

All the observations are consistent with the above kinetic model and it can be concluded that the differences between the QIE and the KIE in the competition experiments are caused by asymmetric adiabatic dissociation of the mixed excimer.

EXPERIMENTAL

Toluene-d_8 and *p*-xylene-d_{10} were obtained from Aldrich and were used without further purification. Toluene and *p*-xylene (spectroscopic grade) were purified by shaking with concentrated sulphuric acid followed by repeated distillation.

The irradiations were carried out in a laboratory-made irradiation apparatus, fitted with a high-pressure mercury lamp (Philips HPLN) and a cooling block in which a quartz cuvette with the solution was placed.

The irradiation mixtures were analysed on a Packard Model 433 gas chromatograph with hydrogen as the carrier gas. The column temperature varied from 85 °C for the toluene irradiations to 95 °C for the *p*-xylene experiments. A chemically bonded, cross-linked methylsilicone column (25 m × 0·31 mm i.d., film-thickness 1·05 μm) was used.

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