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PARTIAL RATE FACTORS IN PHOTOCHEMISTRY: THE *META* PHOTOCYCLOADDITION OF METHYLBENZENES TO CYCLOPENTENE

P. DE VAAL, G. LODDER* AND J. CORNELISSE*
Gorle aus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden (The Netherlands)

The partial rate factors of the four modes of *meta* photocycloaddition of methyl-substituted benzenes to cyclopentene have been determined by measuring quantum yields of formation of the most important *meta* photocycloadducts of benzene, toluene and the three xylenes. It is demonstrated that the results can be applied to predict quantum yields of any *meta* photocycloadduct of methylbenzenes to cyclopentene. The predicted yields agree very well with those determined experimentally, and it is shown that the effects of two or more methyl groups are fully additive. The method is promising for the investigation of mechanisms of photochemical reactions and can be used to predict regioselectivities.

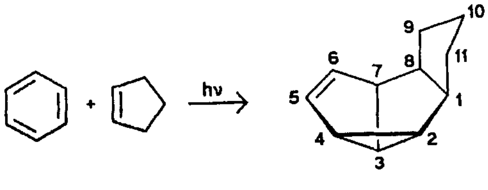
INTRODUCTION

Determination of partial rate factors has been of great help in the investigation of structure–reactivity relationships and reaction mechanisms[1] and the technique is well known in the case of (thermal) electrophilic aromatic substitution reactions.[2–4] An important item of discussion with this reaction has been the additivity principle.[5,6] It has been shown that in almost all cases the effects of more than one substituent are not fully additive, even when steric factors do not play a role.[3,7–9] The substituents always interact with each other, but this effect is weak if the substituent effects are not very large.[8,10]. This is the case with the methyl group, and the methylbenzenes have often been chosen for model studies.[9,11–13].

As far as we know, partial rate factors have not been used in the study of photochemical reactions. Also, very little is known about additivity of substituent effects in excited-state reactions.[14,15] Types of reactions for which partial rate factors might be defined are aromatic photosubstitution and aromatic photoaddition reactions.

These reactions involve the electronically excited states of the arenes, and this makes the kinetic analysis far more complicated than in the well known case of electrophilic aromatic substitution. Not only the photochemical reaction under study, but also the photophysical processes of the arene are influenced by substituents. This makes an accurate determination of relative reaction rates, needed for the calculation of the partial rate factors, difficult, although not in all cases impossible. If the substituent is a methyl group, difficulties can be overcome. The photophysics of all methylbenzenes are well known[16,17] and excited-state lifetimes have been determined accurately.[18] These lifetimes do not differ much from each other and from that of benzene, and this simplifies kinetic analysis of the photochemical reactions.

In this paper we describe the determination and application of partial rate factors in the *meta* photocycloaddition of benzenes to cyclopentene (see Scheme 1) (preliminary data on the experiments described in this paper have been published earlier,[19] but without any discussion of the kinetics, however). This type of reaction has been well studied, and is known to exhibit regioselectivity for a number of substituents.[20–24]



Scheme 1. The *meta* photocycloaddition of benzene to cyclopentene

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[*] Authors for correspondence.

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Special attention is paid to all aspects which should be taken into consideration when partial rate factors are determined from experimentally determined quantum yields. Another point of attention is the additivity of the effects of more than one methyl group.

PRELIMINARY CONSIDERATIONS AND DEFINITIONS

Prior to analysis of the kinetic relationships valid for the photochemical system under study and derivation of the relationship between the partial rate factors and the properties which will be determined experimentally (i.e. the quantum yields of photoaddition), some definitions have to be made.

A monosubstituted benzene can give *meta* photocycloaddition to a symmetrical alkene, in our case cyclopentene, in six ways,* of which two pairs are equivalent (1,3-addition = 1,5-addition and 2,4-addition = 4,6-addition). The four different regional modes of addition can be defined relative to the substituent. Similar to the case of aromatic substitution reactions, where the location of reaction is indicated with the terms *ortho*, *meta*, *para* and *ipso*, we can designate the four modes of *meta* photocycloaddition *ortho–ortho* (*OO*), *meta–ipso* (*MI*), *ortho–para* (*OP*) and *meta–meta* (*MM*), as depicted in Scheme 2. We shall call this the *relative* modes of addition (Z) of arene A with respect to substituent S.

This relative way of addressing can also be used for benzenes with more than one substituent. In some cases, however, the two *MI* and the two *OP* modes are not equivalent, and lead to different products. The *absolute* modes of addition (Y) are the six ways in which addition can take place, irrespective of symmetry. They are designated according to the IUPAC numbering of the arene ring (i.e. 1,3-, 1,5-, 2,4-, 2,6-, 3,5- and 4,6-addition).

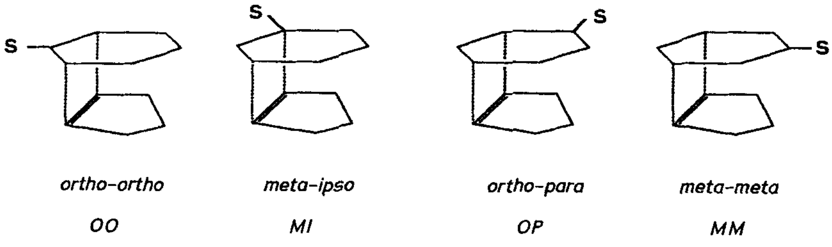
Following the formation of the bonds between the arene and the alkene, closure of a three-membered ring leads to the final product(s);[19,24] for example, *OO*-addition leads to a product as shown in Scheme 1, with the substituent attached to C-3.

ANALYSIS OF THE KINETICS

It has been demonstrated that the reaction takes place from the first excited singlet state of the arene.[25] Thus, in the systems used in our studies, i.e. the aromatic compound (A) in a solution of cyclohexane containing cyclopentene (cp), the processes shown in Scheme 3 should be taken into consideration.

1.	$A^* \xrightarrow{k_f} A$	fluorescence
2.	$A^* \xrightarrow{k_{ic}} A$	internal conversion
3.	$A^* \xrightarrow{k_{isc}} {}^3A^*$	intersystem crossing
4.	$A^* \xrightarrow{k_{vi}} B$	valence isomerization[26]
5.	$A^* + cp \xrightarrow{k_r} \text{product}$	*meta* photocycloaddition
6.	$A^* + cp \xrightarrow{k_{other}} \text{other products}$	e.g. *ortho* or *para* photocycloaddition[27]
7.	$A^* + cp \xrightarrow{k_q} A$	quenching by cyclopentene
8.	$A^* + O_2 \xrightarrow{k_{q,ox}} A$	quenching by oxygen
9.	$A^* + A \xrightarrow{k_d} [AA]^*$	excimer formation

Scheme 3. Pathways of decay of singlet excited arenes in cyclohexane solution and in the presence of cyclopentene (cp) and atmospheric oxygen



Scheme 2. The four modes of *meta* photocycloaddition of a monosubstituted benzene to cyclopentene

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* In fact there are twice as many modes of addition: six with the cyclopentene ring in the *endo* orientation and six with this ring being in the *exo* orientation. The *exo* modes, however, are of minor importance in the case of methylbenzenes. Only in the case of benzene, toluene and 1,2,4-trimethylbenzene is a minor amount of an *exo* adduct found. These will not be considered in this paper.

For the *meta* photocycloaddition reaction the partial rate factors $f_{S,Z}$ can be defined as follows:

$$f_{S,Z} = \frac{k_{S,Z}}{k_H} \times \frac{n_H}{n_{S,Z}} \qquad (1)$$

where k_H is the rate constant of product formation (k_r in Scheme 3) from an arene not bearing substituent S, and $k_{S,Z}$ that of formation of product from the arene substituted with S, via reaction mode Z with respect to substituent S; n is the number of equivalent modes. Benzene has, owing to its symmetry, six equivalent modes, whatever type of reaction is under consideration, so $n = 6$ for benzene. For a substituted arene n depends on the substitution pattern and on Z. For example, 2,6- and 3,5-*meta* photocycloaddition of *p*-xylene to cyclopentene are equivalent (both *OO* with respect to one methyl group and *MM* with respect to the other) and lead to the same product. In this case $n = 2$.

The partial rate factors for the four modes of addition will be designated by f_{oo}, f_{mm}, f_{mi} and f_{op}, without reference to the substituent because only one substituent will be considered, i.e. the methyl group.

The ratio of the reaction rate constants $k_{S,Z}$ and k_H will be obtained from the quantum yields $\Phi_{S,Z}$ and Φ_H. If the other decay paths are unimolecular processes (entries 1–4 in Scheme 3) and no other bimolecular processes (entries 6–9 in Scheme 3) play a significant role, then the equation relating the reaction rate constant k_r and the quantum yield Φ_r of the reaction is

$$\Phi_r = \frac{k_r[\mathrm{cp}]}{k_f + k_{ic} + k_{isc} + k_{vi} + k_r[\mathrm{cp}]} \qquad (2)$$

Because $k_f + k_{ic} + k_{isc} + k_{vi} = 1/\tau_M = k_M$ (where τ_M is the fluorescence lifetime of the arene in dilute cyclohexane solution), this equation can also be written as

$$(1 - \Phi_r)k_r = \frac{\Phi_r}{\tau_M[\mathrm{cp}]} \quad \text{or} \quad k_r = \frac{\Phi_r}{(1 - \Phi_r)\tau_M[\mathrm{cp}]} \qquad (3)$$

Because quantum yields have been obtained in the experiments under identical conditions (same cyclopentene concentrations), the partial rate factor is

$$f_{S,Z} = \frac{n_H}{n_{S,Z}} \times \frac{\tau_{M,H}}{\tau_{M,S}} \times \frac{\Phi_{S,Z}}{\Phi_H} \times \frac{(1 - \Phi_H)}{(1 - \Phi_{S,Z})} \qquad (4)$$

The τ_M values for all methylbenzenes have been reported (see Table 1, second column).[18] Therefore, only quantum yields have to be measured for the determination of the partial rate factors.

If one or more of the processes 6–9 in Scheme 3 are of importance, the relationship between k_r and Φ_r becomes more complicated. The following should be considered:

A. The formation of other photoproducts (process 6) is negligible in the case of benzene and toluene.[19] Our experiments show that this is also the case with the other methylbenzenes. It can therefore be left out of the discussion.

B. The first excited singlet state of an arene is quenched by oxygen. Because of the experimental difficulty of excluding oxygen and at the same time accurately maintaining the composition of the mixture, the experiments are performed in the presence of atmospheric oxygen. The quantum yields of *meta* photocycloaddition are altered by oxygen quenching as follows:

$$\Phi_r^c = \frac{\Phi_r}{1 + \tau k_{q,ox}[O_2]} \qquad (5)$$

Substitution in equation (4) leads to the following correction to the partial rate factor:

$$f^c_{S,Z} = f_{S,Z}c_{q,ox} \qquad (6)$$

where

$$c_{q,ox} = \frac{1 + \tau_S k_{q,ox,S}[O_2]}{1 + \tau_H k_{q,ox,H}[O_2]}$$

In this equation τ_S is the excited-state lifetime if *meta* cycloadditions were to be the only bimolecular processes. Thus $\tau_S = 1/(k_M + k_r[\mathrm{cp}])$. The value for benzene can be calculated to be 14 ns (with [cp] = 1 M), using the k_r value reported by Osselton *et al.*[25] ($3{\cdot}5 \times 10^7$ dm^{3}mol^{-1}s^{-1}) and the k_M ($= 1/\tau_M$) value from Table 1.

The concentration of oxygen in cyclohexane solutions at room temperature is known[28] to be 2×10^{-3} M. Oxygen quenching rate constants for the different methylbenzenes are in close proximity to each other,[29] and amount to *ca* $2{\cdot}4 \times 10^{10}$ dm^{3}mol^{-1}s^{-1}. This means that the term $k_{q,ox}[O_2]$ is of the same order of magnitude as $k_M + k_r[\mathrm{cp}]$ ($= 1/\tau$). The correction terms $c_{q,ox}$ might therefore become significant. Not until the k_r values for the different methylbenzenes have been

Table 1. Lifetimes[18] and concentration quenching parameters[31,32] of excited benzene and methylbenzenes (cyclohexane, room temperature)

Compound	τ_M (ns)	$[A]_{1/2}$ (mole l^{-1})
Benzene	29	2·1
Toluene	32	4·2
o-Xylene	32	10·9
m-Xylene	29	10·9
p-Xylene	29	10·9
1,2,3-Trimethylbenzene	35	
1,2,4-Trimethylbenzene	27	
1,3,5-Trimethylbenzene	36	6·7
1,2,3,4-Tetramethylbenzene	24	
1,2,3,5-Tetramethylbenzene	30	
1,2,4,5-Tetramethylbenzene	25	
Pentamethylbenzene	17	
Hexamethylbenzene	4	

determined can the τ values be calculated. Only then can it be judged whether these correction terms are small enough to be neglected.

C. Benzene fluorescence is reported to be quenched by cyclopentene with a higher efficiency than that of the *meta* photocycloaddition reaction. Physical quenching (process 7) must therefore be partly responsible for it. It has been found that k_q and k_r are of the same order of magnitude in the case of benzene.[25] Physical quenching by cyclopentene will reduce the quantum yield of *meta* photocycloaddition in a comparable way to oxygen quenching. We can write a combined correction term for both phenomena:

$$c_q = \frac{1 + \tau_S(k_{q,S}[\mathrm{cp}] + k_{q,ox,S}[\mathrm{O_2}])}{1 + \tau_H(k_{q,H}[\mathrm{cp}] + k_{q,ox,H}[\mathrm{O_2}])}$$

Thus

$$f^c_{S,Z} = f_{S,Z}c_q \tag{7}$$

If it is assumed that k_q is always of the same order of magnitude as k_r (which is the case for benzene),[25] then c_q can also be expressed in terms of quantum yields and monomolecular lifetimes τ_M instead of ks and the above defined τs. By assuming $k_q = k_r$, the expressions for the numerator and denominator of c_q have the following form, with $k_{q,ox}[\mathrm{O_2}] = 4 \cdot 8 \times 10^7$ and $k_M = 1/\tau_M$:

$$c_X = \frac{k_{M,X} + k_{q,ox}[\mathrm{O_2}]}{(1 - \Phi_X)(k_{M,X} + \Phi_X k_{q,ox}[\mathrm{O_2}])} \qquad (X = H, S)$$

Thus

$$c_q = \frac{c_S}{c_H} \tag{7a}$$

It should be noted that here the Φs are the sums of quantum yields of all *meta* photocycloaddition reactions from the corresponding substrate X.

D. The last process which needs discussion is excimer formation.[30-33] Because excimers, after being formed, can dissociate into an excited singlet-state molecule and a ground-state molecule, they are in equilibrium with the monomeric excited state. The quantum yield of the reaction allowing for excimer formation is[30]

$$\Phi^c_r = \frac{\Phi_r}{1 + [A]/[A]_{1/2}} \tag{8}$$

where $[A]_{1/2}$ is the concentration at which $\Phi^c_r = 0 \cdot 5\ \Phi_r$. The correction on the partial rate factor becomes

$$c_{exc} = \frac{1 + [A_S]/[A_S]_{1/2}}{1 + [A_H]/[A_H]_{1/2}}$$

Thus

$$f^c_{S,Z} = f_{S,Z}c_{exc} \tag{9}$$

Because the 'half-value concentrations' $[A]_{1/2}$ are reported to be higher than 2 M for benzene, toluene, *p*-xylene and mesitylene,[31,32] the correction term will never differ from unity by more than a factor of 0·66. In the case where A_H is benzene and A_S is toluene, for example, the half-values $[A]_{1/2}$ are 2·1 and 4·2, respectively, and the correction term is 0·83 (with [A] = 1 M). Half-value concentrations are listed in Table 1.

In conclusion, it can be said that all difficulties in the kinetic analysis can be overcome and that values for the partial rate factors can be obtained from quantum yields of product formation.

When values for the partial rate factors have been determined, they can be applied to predict quantum yields of formation of other *meta* photocycloadducts of methylbenzenes to cyclopentene assuming additivity of the substituent effects. The quantum yield of products from one absolute mode of *meta* photoaddition to an (m)-methylbenzene (m = number of methyl groups) is a function of the quantum yield of formation of benzene–cyclopentene adduct **1**, and the product of the m partial rate factors due to each methyl group. For example, the total quantum yield of the products from 2,6-addition of 1,2,4-trimethylbenzene to cyclopentene is a function of the product $f_{oo} \times f_{mi} \times f_{mm}$. The addition takes place *OO* with respect to the methyl group at position 1 and *MI* and *MM* relative to the methyl groups 2 and 4, respectively.

The relationship, derived from equations (4), (7a) and (9), assuming additivity of the effects, is

$$\prod_{i=1,m} f_{S,Z(i)} = \frac{\tau_{M,H}}{\tau_{M,S}} \times \frac{\Phi_{X,Y}}{\Phi_H} \times \frac{n_H}{n_{X,Y}} \times \frac{(1 - \Phi_H)}{(1 - \Phi_{X,Y})} \times c_{exc} \times c_q \tag{10}$$

where Z(i) is the *relative* mode of addition with respect to the ith methyl group and Y is the *absolute* mode of addition to substrate X. Because now the effects of all methyl groups present in the molecule are taken into account, the subscript H refers to the unsubstituted compound, i.e. benzene. Using literature values for τ_H (29 ns), Φ_H (0·16) and $[A]_{1/2,H}$ (2·1) and 6 for n_H results in the following equation for the quantum yield of adducts from substrate X and absolute mode of addition Y:

$$\Phi_{X,Y} = \frac{\prod_{i=1,m} f_{S,Z(i)}}{\frac{(1 + 1/[A]_{1/2,S})}{\tau_S n_{X,Y}} \times c_q \times 6 \cdot 09 \times 10^{-7} + \prod_{i=1,m} f_{S,Z(i)}} \tag{11}$$

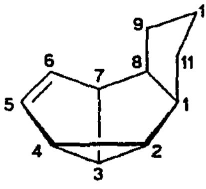
An illustrative example can be found in the next section.

RESULTS AND DISCUSSION

Quantum yields have been published for the *meta* photocycloaddition of benzene (0·16), toluene (0·21) and the xylenes (0·12, 0·08 and 0·05 for *p*-, *o*- and *m*-xylene, respectively) to cyclopentene ([cp] = 1 M).[19,34] Because relative reaction rate constants (or relative quantum yields) are needed for the calculation of partial rate factors, the value of the quantum yield (0·16) of formation of product **1** from benzene–cyclopentene *meta* photocycloaddition is taken as reference relative to which other values have been determined. Structures of the adducts are listed in Table 2. The measured quantum yields of all identified adducts found upon UV irradiation of all methylbenzenes are listed in Table 3.

The most obvious way for obtaining the partial rate factors is the determination of the quantum yields (relative to that of product **1**) of products resulting from the four modes of addition of toluene to cyclopentene. In practice (see Table 2, entry 2 and Table 3, entry 2) the product resulting from *OO*-addition (compound **2**) dominates the product mixture. Minor quantities of adducts from the *MM* and *MI* modes of addition are also present, but no products are found resulting from the *OP* mode of addition. Moreover, the *MI* mode is expected to give two different adducts (differing in direction of closure of the three-membered ring), but only one could be found. For this reason only the f_{oo} will be calculated from the quantum yields of a toluene–cyclopentene addition product (**2**); the other three partial rate factors can be obtained using quantum yields of *meta* photocycloaddition of the three xylene isomers.

Table 2. Structures of products from the *meta* photocycloaddition of benzene and the methylbenzenes to cyclopentene



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Product	Substrate	Methyl groups at positions
1	Benzene	–
2	Toluene	3
3	Toluene	5
4	Toluene	7
5[a]	Toluene	2
6	*o*-Xylene	3, 7
7	*o*-Xylene	2, 3
8	*m*-Xylene	3, 4
9	*m*-Xylene	3, 6
10	*m*-Xylene	5, 7
11	*m*-Xylene	2, 5
12	*p*-Xylene	3, 5
13	1,3,5-Trimethylbenzene	3, 4, 6
14	1,3,5-Trimethylbenzene	2, 5, 7
15	1,2,4-Trimethylbenzene	3, 5, 7
16	1,2,4-Trimethylbenzene	2, 3, 5
17	1,2,4-Trimethylbenzene	3, 5, 6
18	1,2,4-Trimethylbenzene	3, 4, 5
19	1,2,4-Trimethylbenzene	3, 4, 7
20	1,2,3-Trimethylbenzene	2, 3, 7
21	1,2,3-Trimethylbenzene	3, 6, 7
22	1,2,3-Trimethylbenzene	2, 3, 4
23	1,2,3,5-Tetramethylbenzene	2, 3, 5, 7
24	1,2,4,5-Tetramethylbenzene	3, 4, 5, 7
25	1,2,4,5-Tetramethylbenzene	2, 3, 5, 6
26	1,2,3,4-Tetramethylbenzene	3, 5, 6, 7
27	1,2,3,4-Tetramethylbenzene	2, 3, 4, 5
28	1,2,3,4-Tetramethylbenzene	2, 3, 6, 7
29	1,2,3,4-Tetramethylbenzene	2, 3, 4, 7

[a] This adduct has not been detected, but its formation is assumed.

The partial rate factor for *OO*-addition is calculated from the quantum yields of products **1** and **2** (Table 3) using equation (4):

$$f_{oo} = \frac{n_H}{n_{oo}} \times \frac{\Phi_2}{\Phi_1} \times \frac{\tau_{M,\text{benzene}}}{\tau_{M,\text{toluene}}} \times \frac{(1-\Phi_1)}{(1-\Phi_2)}$$

$$= \frac{6}{1} \times \frac{0{\cdot}21}{0{\cdot}16} \times \frac{29}{32} \times \frac{0{\cdot}84}{0{\cdot}79} = 7{\cdot}6$$

where Φ_1 and Φ_2 denote the quantum yields of formation of the products **1** and **2**, respectively. The correction terms for excimer formation, c_{exc}, and quenching, c_q, are calculated with equations (9) and (7a) to be 0·84 and 1·05, respectively. This results in the corrected partial rate factor $f^c_{oo} = 7{\cdot}6 \times 0{\cdot}84 \times 1{\cdot}05 = 6{\cdot}67$. Hence the methyl group has an activating effect of 6·67 on *OO-meta* photocycloaddition.

The other three partial rate factors can be calculated using the product quantum yields of the *meta* photocycloaddition of the xylenes to cyclopentene. Assuming additivity of the effects of two methyl groups, these quantum yields are taken relative to that of product **2** from toluene. Addition of a xylene to cyclopentene will take place, as in the case of toluene, preferentially *OO* with respect to one of the methyl groups. The effect of the second methyl group will be expressed by a higher or lower yield of products from the xylene with respect to toluene.

The quantum yields determined of products from *o*-, *m*- and *p*-xylene are listed in Table 3, entries 3, 4 and 5, respectively. Both products **6** and **7** of *o*-xylene (see Table 2 for their structures) result from the *MI* mode of addition with respect to the second methyl group (they differ only in the direction of closure of the three-membered ring in the subsequent reaction step). The sum of their quantum yields can be used for the calculation of f_{mi}. The products **8** and **9** from *m*-xylene result from *OP*-addition with respect to the second methyl group, and with their quantum yields the f_{op} may be obtained. Finally, product **12**, the only adduct from

Table 3. Measured and calculated quantum yields of *meta* photocycloadducts of methylbenzenes (1 M) with cyclopentene (1 M)

Arene	Addition to carbons	*n*	Adduct no.	Φ	Φ/mode	Φ_{calc}/mode
1. Benzene	1 + 3	6	**1**	0·16	0·16	–
2. Toluene	2 + 6	1	**2**	0·21	0·21	0·21
	3 + 5	1	**3**	0·013	0·013	0·018
	1 + 3	2	**4**	0·008	0·013[a]	0·030
			5[a]	?		
3. *o*-Xylene	1 + 3	2	**6**	0·09	0·14	0·18
			7	0·05		
4. *m*-Xylene	2 + 4	2	**8**	0·012	0·026	0·042
			9	0·014		
	1 + 5	2	**10**	0·009	0·014	0·013
			11	0·005		
5. *p*-Xylene	2 + 6	2	**12**	0·13	0·13	0·19
6. 1,3,5-Trimethylbenzene	2 + 4	3	**13**	0·007	0·007	0·006
	1 + 3	3	**14**	0·004	0·004	0·008
7. 1,2,4-Trimethylbenzene	2 + 6	1	**15**	0·026	0·043	0·036
			16	0·017		
	3 + 5	1	**17**	0·004	0·008	0·008
			18	0·004		
	1 + 3	1	**19**[b]	0·003	0·005[b]	0·007
8. 1,2,3-Trimethylbenzene	1 + 3	1	**20**	0·030	0·030	0·038
	2 + 4	2	**21**	0·010	0·015	0·018
			22	0·005		
9. 1,2,3,5-Tetramethylbenzene	1 + 3	1	**23**	0·011	0·011	0·015
10. 1,2,4,5-Tetramethylbenzene	1 + 3	4	**24**	0·010	0·017	0·011
			25	0·007		
11. 1,2,3,4-Tetramethylbenzene	2 + 6	2	**26**	0·002	0·003	0·005
			27	0·001		
	1 + 3	2	**28**	0·001	0·002	0·004
			29	0·001		
12. Pentamethylbenzene	1 + 3	2	?	–	–	0·0015
13. Hexamethylbenzene	1 + 3	6		–	–	0·00007

[a] Because the quantum yield of product **5** could not be determined, the isomer ratio **4**:**5** is assumed to be the same as the ratio **6**:**7**.

[b] The isomer of **19** with methyls at positions 2, 3 and 6 was not found, but its formation is assumed to take place in the same ratio to **19** as **7**:**6**.

p-xylene, results from *MM*-addition with respect to the second methyl group, and may be used to obtain f_{mm}. Application of equations (4), (7a) and (9), with $\Phi_{mi} = \Phi_6 + \Phi_7$, $\Phi_{op} = \Phi_8 + \Phi_9$ and $\Phi_{mm} = \Phi_{12}$, gives the values of the corresponding partial rate factors as listed in Table 4, first data column. These values agree fairly well with the observed composition of the product mixture of the toluene irradiation. Especially the absence of products from the *OP* mode of addition in this mixture can easily be understood.

Table 4. Partial rate factors for the four modes of *meta* photocycloaddition

Mode of addition Z	f_Z	f_Z^{average}
ortho–ortho (*OO*)	6·67	6·2 ± 0·6
meta–meta (*MM*)	0·26	0·41 ± 0·15
meta–ipso (*MI*)	0·27	0·37 ± 0·16
ortho–para (*OP*)	0·05	0·08 ± 0·04

As mentioned earlier, the partial rate factors for *MM*-, *MI*- and *OP*-addition are calculated assuming additivity of the effects of the two methyl groups present in the xylenes. In order to obtain support for this assumption, we can calculate the partial rate factors from other pairs of substrates which differ by only one methyl substituent. For example, we can use for the calculation of f_{mm} the substrate pair benzene–toluene and the quantum yields of the products **1** and **3** instead of the pair toluene–*p*-xylene (products **2** and **12**). In that case, we find a value of $f_{mm} = 0{\cdot}33$, which agrees reasonably with the 0·26 as listed above.

Using as many substrate pairs and product pairs as possible we have calculated three values for f_{oo}, six values for f_{mm}, eleven values for f_{mi} and eight values for f_{op} (see Table 5). The values of the different partial

Table 5. Partial rate factors calculated from different product pairs

Mode Z	Product pair used for the calculation of f_Z	f_Z
OO	**1/2**	6·67
	3/12	5·26
	10 + 11/15 + 16	6·53
MM	**1/3**	0·33
	2/12	0·26
	6 + 7/15 + 16	0·61
	8 + 9/17 + 18	0·62
	20/23	0·39
	21 + 22/26 + 27	0·24
MI	**2/6 + 7**	0·27
	3/10 + 11	0·51
	12/15 + 16	0·63
	6 + 7/20	0·37
	8 + 9/19	0·39
	8 + 9/21 + 22	0·52
	10 + 11/14	0·18
	15 + 16/23	0·24
	17 + 18/24 + 25	0·56
	17 + 18/26 + 27	0·20
	21 + 22/28 + 29	0·16
OP	**2/8 + 9**	0·047
	12/17 + 18	0·113
	6 + 7/19	0·068
	6 + 7/21 + 22	0·092
	8 + 9/13	0·171
	15 + 16/24 + 25	0·101
	15 + 16/26 + 27	0·036
	20/28 + 29	0·039

rate factors thus obtained do not show an increase or decrease with increasing number of methyl substituents, so the assumption of complete additivity of the effects seems to be justified. Now a best fitting set of partial rate factors can be obtained by averaging all values found for one mode. Values are listed in the last column of Table 4.

Mechanistic consequences

The results are in good agreement with the mechanism (see Scheme 4) proposed in earlier papers.[24,35]

The methyl group stabilizes partial positive charge which develops at carbon C-1 on *OO*-addition. With *OP*-addition, on the other hand, this atom becomes partly negatively charged, and this is destabilized by the methyl group. The charge separation is not very large, however. This can be concluded from the relatively weak effect of the methyl group, as expressed by the partial rate factors.

Additivity of the effects

The seventh column of Table 3 lists quantum yields calculated with equation (11) using the averaged values of the partial rate factors as listed in Table 4, and τ_M and $[A]_{1/2}$ values from Table 1. In the cases where $[A]_{1/2}$ was not reported a value of 10·9 was assumed, which will not be far from reality. As an example the quantum yield of product **13** (from mesitylene) is calculated to be

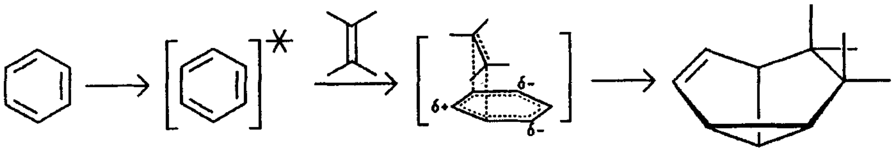
$$\Phi_{13} = \frac{f_{oo} \times f_{op} \times f_{op}}{\dfrac{(1 + 1/[A]_{1/2,S})}{3 \times \tau_{M,S}} \times c_q \times 6\cdot19 \times 10^{-7} + f_{oo} \times f_{op}^2}$$

$$= \frac{6\cdot2 \times 0\cdot08^2}{\dfrac{1\cdot19}{3 \times 35} \times 619 + 6\cdot2 \times 0\cdot08^2} = 0\cdot006$$

This value agrees very well with the measured value (0·007). Although many other calculated values are also in agreement with experimental values, it should be noted that a number of measured quantum yields are about a factor or two higher than the calculated values. However, because these 'deviating' cases are randomly distributed in the series and no relationship with the number of methyl substituents can be found, it can be assumed that the deviation has its origin in experimental inaccuracy and not in non-additivity.

CONCLUSIONS AND PROSPECTS FOR FUTURE RESEARCH

Our investigations have shown that in analogy with ground-state reactions it is possible to determine partial rate factors for excited-state reactions of aromatic compounds. When attention is paid to all excited-state processes which may occur, it is possible to calculate relative reaction rates from product quantum yields if excited-state lifetimes are known.



A

Scheme 4. Mechanism of the *meta* photocycloaddition of arenes to alkenes

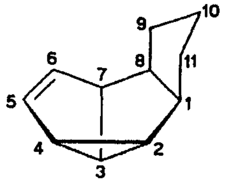
In the case of the investigated substituent, the methyl group, full additivity of the effects is observed. This implies that there is little resonance interaction between the methyl groups in the excited arene. It would be interesting to establish whether this also holds for substituents with a stronger effect. Therefore, it would be worthwhile to extend this study to other substituents, other, electron-richer or more electron-deficient alkenes. An example from the first group is anisole. It is of interest to know if the partial rate factors of methyl substitution of anisole are equal to those of benzene. If they are not, they may be a measure of the degree of charge transfer between the alkene and the arene in the 'transition state' (i.e. complex A in Scheme 4). The same holds for addition of benzene to different alkenes. Thus, measuring more partial rate factors can give information about the role of charge transfer in this reaction, as suggested to be important by Mattay *et al.*[36–38]

EXPERIMENTAL

All methylbenzenes used in the experiments were commercially available. The sample of 1,2,3,5-tetramethylbenzene (obtained from Aldrich) was contaminated with 15% of isomers, but could be purified by means of preparative gas–liquid chromatography. Cyclopentene (Merck) was redistilled twice before use.

Irradiations for analytical purposes were carried out in quartz cuvettes in a laboratory-made irradiation box fitted with a Philips HPLN lamp from which the glass bulb was removed, a focusing lens and a metal cooling

Table 6. NMR chemical shifts of the most important protons in the *meta* photocycloadducts **1**–**29**



	δ (ppm) of skeletal protons							δ (ppm) of methyl protons					
Product	H-1	H-2	H-3	H-5	H-6	H-7	H-8	2	3	4	5	6	7
1	2·95	1·66	2·75	5·70	5·62	2·90	3·25						
2	2·94	1·68		5·71	5·59	2·63	3·26		1·20				
3	2·96	1·63	2·74		5·14	2·87	3·19				1·51		
4	2·94	1·63	2·43	5·65	5·39		2·94						1·21
6	2·85	1·55		5·63	5·33		2·87		1·28				1·06
7	2·68			5·68	5·58	2·64	3·12	1·09	1·29				
8	2·92	1·61		5·54	5·55	2·63	3·20		1·27	1·12			
9	2·98	1·80		5·31		2·32	3·22		1·36			1·73	
10	2·92	1·74	2·40		4·91		2·85				1·79		1·10
11	2·85		2·40		4·88	2·63	3·20	1·10			1·79		
12	2·95	1·78			5·10	2·54	3·18		1·37		1·79		
13	2·98	1·73		5·14		2·33	3·18		1·24	1·04		1·73	
14	2·70		2·28		4·91		2·86	1·07			1·74		1·12
15	2·82	1·63			4·84		2·82		1·24		1·73		1·00
16	2·67				5·10	2·57	3·07	1·08	1·27		1·76		
17	2·99	1·6				2·39	3·20		1·33		1·65	1·60	
18	2·85	1·67			5·19	2·52	3·15		1·27	1·08	1·78		
19	2·99	1·6		4·60	4·50		3·20		1·20	1·02			1·12
20	2·62			5·60	5·30		2·78	1·04	1·18				1·09
21	2·84	1·61		5·31			2·87		1·24			1·66	1·04
22	2·82			5·29	5·55	2·68	3·08	1·02	1·25	1·08			
23	2·65				4·84		2·68	0·99	1·16		1·72		1·08
24	2·78	1·73			4·90		2·78		1·17	0·99	1·70		1·02
25	2·71					2·41	3·03	1·05	1·23		1·62	1·59	
26	2·80						2·85		1·22		1·66	1·66	1·02
27	2·69				4·70	2·59	3·05	0·98	1·10	1·05	1·70		
28				5·05				1·01	1·20			1·70	1·10
29	2·6			5·30	5·38		2·7	0·97	1·08	1·00			1·05

block as container for the cuvettes. No attempt was made to use monochromatic light because the absorption maxima, extinction coefficients and shapes of the UV spectra do not differ much for the different methylbenzenes. No attempt was made to exclude oxygen for reasons mentioned earlier. For the analytical irradiations solutions of 1 M arene and 1 M cyclopentene in cyclohexane (spectroscopic grade) were used.

Preparative irradiations were carried out in a Rayonet Photochemical Reactor RPR 200 fitted with seven 254 nm arc lamps. All preparative irradiations were carried out with 25 ml of solutions of 1 M arene and 2 M cyclopentene in cyclohexane (analytical-reagent grade) in a quartz tube.

All products were identified as follows. The mixtures from preparative irradiations were separated by means of preparative gas chromatography on a Varian Aerograph 90-P chromatograph (glass column, 20% SE-30 on Chromosorb WAW, 40–60 mesh, 6 m × 8 mm i.d., carrier gas hydrogen, temperature 100–170 °C). The purity of the samples thus obtained was checked by means of analytical gas chromatography and then a ^{1}H NMR spectrum was recorded at 300 MHz. The structures of the products could be affirmed by means of homonuclear decoupling experiments. Chemical shifts of skeletal protons and methyl protons of adducts **1–29** are listed in Table 6.

Product ratios and relative quantum yields were determined with the help of a Packard 433 capillary gas chromatograph (glass column, 40 m, 0·4% OV-101, carrier gas hydrogen) as follows. Two cuvettes, one containing a solution of the polymethylbenzene under study and the other containing toluene, were irradiated simultaneously in the irradiation box. Their positions were interchanged several times to be sure that both samples received the same light flux. After several time intervals, samples with equal volumes were taken from both cuvettes and after mixing they were analysed by analytical gas chromatography. The strong product peak at relatively low retention time (from the major adduct from toluene and cyclopentene) was used as an internal standard to express the peak areas from the polymethylbenzene adducts. In this way the toluene–cyclopentene *meta* photocycloaddition was used as an actinometer and quantum yields could be calculated easily using the product ratios obtained.

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