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Photochemical Cycloaddition of Olefins to Aromatic Compounds. 5. Formation and Deactivation of Exciplexes from Singlet Benzene or Toluene and 1,3-Dioxoles[†]

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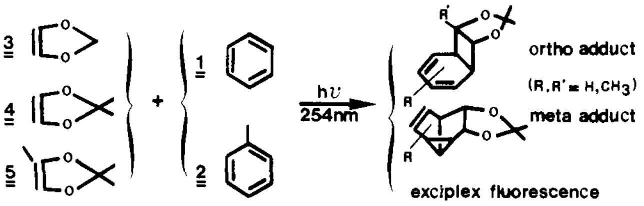
Abstract: Formation and deactivation of exciplexes from ^{1}S benzene or toluene and 1,3-dioxoles were tested with respect to ortho and meta adduct formation. The exciplexes are formed in a diffusion-controlled process in which dissociation plays a minor role. The small entropies of activation exclude restrictions to productlike geometries under formation of exciplexes. This coincides with the influence of solvent polarity and ionization potentials of the olefins, indicating that charge transfer effects play an important role not in exciplex but in product formation. Stern-Volmer analysis revealed that product formation requires interaction of the primarily formed exciplex with another dioxole molecule. The results are interpreted in the form of a general scheme for photoadduct formation in arene/olefin systems.

1. Introduction

Although exciplex intermediates were proven to be common intermediates in photochemical cycloadditions,[1-4] information about the role of exciplexes in photocycloadditions of benzene derivatives to ethylenic compounds is scarce. In all cases the lack of stereorandomization in product formation is interpreted by the existence of a geometrically fixed exciplex-like intermediate.[5-8] Only in the reaction of *cis*-enediol ethers with ^{1}S benzene[8,9] were fluorescent exciplexes observed.

In order to clarify the role of exciplex formation in these reactions, Stern-Volmer quenching experiments as well as temperature- and concentration-dependent lifetime measurements were performed on the following systems:



These favorable systems, which show both exciplex fluorescence and formation of two different cycloadducts,[8] should provide information about the elementary steps in photochemical cycloadditions of benzene derivatives to olefinic compounds.

2. The Problem

The application of the well-known photophysical scheme of exciplex formation and deactivation[10-12] (Scheme I) does not solve the question of parallel (route 3′) or consecutive (route 3) exciplex and product formation in an easy way:

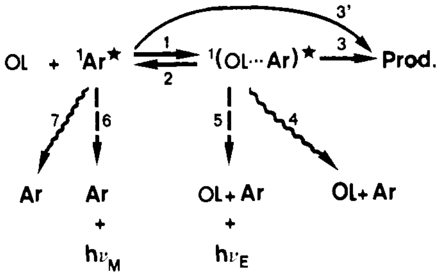
(i) Quenching experiments of exciplex fluorescence and product formation[1,13] indicated that the fluorescing exciplexes were intermediates in product formation. However, the advantage of this method is restricted, if the monomer is also quenched significantly and the quencher changes the solvent polarity.[13,30]

(ii) A negative temperature effect on product formation, which was assigned to a monomer/exciplex equilibrium preceeding the product formation,[3,15,16] could also be caused by ground-state interaction or change of some other competing rate constants.

(iii) The photochemical cleavage of photodimers showed that not only the corresponding excimers but also other intermediates like biradicals or the excited dimers can form minima on the reaction pathway between educts and product.[15,17,18,20]

In the photoaddition of ^{1}S benzene to dioxoles, application of the exciplex quenching (cf. (i)) method is not very promising, since quenchers that neither absorb 254 nm light, react with ^{1}S benzene or the dioxoles, nor quench ^{1}S benzene and do not form additional exciplexes proved to be scarce. Triethylamine, for example, which

Scheme I. Primary and Secondary Steps in Quenching of ^{1}Ar by Ol[a]



[a] Ar, 1 or 2 in ground state; Ol, olefinic ground-state partner 3-5; ^{1}Ar*, singlet excited 1 or 2; ^{1}(Ol···Ar)*, exciplex; *i*, rate constants k_i for formation of exciplex (1), exciplex dissociation (2), consecutive formation of product(s) (3), parallel formation of products (3′), radiationless deactivation of exciplex (4), exciplex fluorescence (5), monomer fluorescence (6), and radiationless deactivation of monomer, including intersystem crossing (7).

[†] Part 4: see ref 59.

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Table I. Parameters for Exciplex Formation and Deactivation from Lifetime Measurements in Aceotnitrile at 22 °C Compared to the Benzene–Triethylamine Exciplex[9a]

		system				
		1 + 3	**1 + 4**	**1 + 5**	**2 + 5**	**1** + NEt$_3$[a]
$10^{-8}k_1$, M^{-1} s	*b*	106 ± 5	126 ± 3	112 ± 14	89.6 ± 11	133 ± 6
	c	103 ± 3	102 ± 10	122 ± 6	94 ± 2	*d*
$10^{-8}k_2$, s^{-1}		0.02 ± 0.7	0.3 ± 0.5	0.98 ± 0.97	0.41 ± 0.57	3.8 ± 0.4
$10^{-8}(k_3 + k_4)$, s^{-1}		1.1 ± 0.06	5.5 ± 0.7	8.61 ± 0.09	7.94 ± 0.10	1.8 ± 0.5
$10^{-8}k_5$, s^{-1}		0.04 ± 0.03	0.05 ± 0.1	0.064 ± 0.007	0.041 ± 0.010	0.24 ± 0.04
ΔS_1^*, J mol^{-1} K^{-1}			−30 ± 3	−35 ± 5		−26 ± 5
ΔH_1^*, kJ mol^{-1}			7.5 ± 1	4.5 ± 1		7.5 ± 1.4
$\tau_E = 1/\sum_2^5 k_i$, ns	*e*	8.8 ± 5	1.7 ± 0.15	1.1 ± 0.1	1.3 ± 0.1	1.7 ± 1

[a] In cyclohexane.[9a,70] [b] Cf. eq 3 from biexponential exciplex decay. [c] Cf. eq 1a from monoexponential monomer decay. [d] Biexponential monomer decay.[70] [e] Exciplex lifetime.

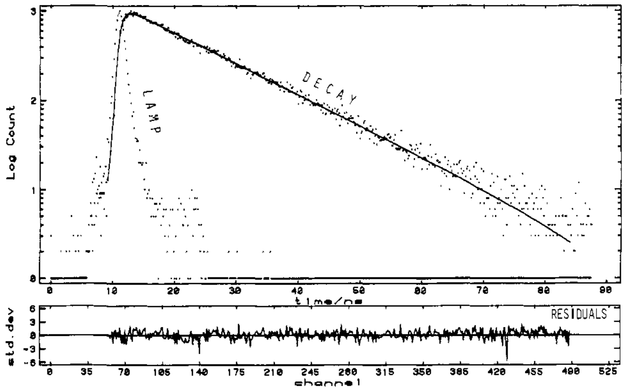

Figure 1. Fluorescence decay of benzene in acetonitrile at 22.5 °C, *c* 0.56, excitation at 250 nm, emission at 282 nm, spectral bandwidth Δλ = 10 nm (excitation, emission), $\tau = 12.5 \pm 0.07$ ns, $\chi^2 = 1.15$ ($\tau = 12.25 \pm 0.5$ ns from 10 independent measurements; see Figure 2).

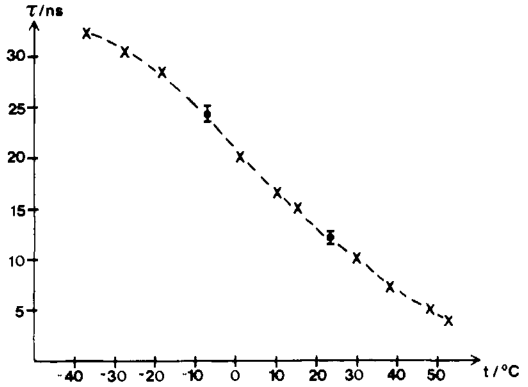

Figure 2. Temperature dependence of the fluorescence lifetime of benzene in acetonitrile, *c* 0.56. The indicated ranges of error at 22 and −9 °C are standard deviations of 10 and five independent measurements, respectively.

was used as a quencher for the system **1**/**4**,[8,21] is capable of quenching the benzene fluorescence,[8,9] exhibits exciplex fluorescence with benzene[9] (see Table I), and can also react with ^{1}S benzene chemically.[22]

There is no remarkable temperature effect on product formation (cf. (ii)) and photoexcitation of the products did not result in exciplex fluorescence (cf. (iii)). Thus rate constants and quantum yields should provide a more detailed mechanism.

3. Results and Discussion

(3.1) Concentration and Temperature Dependence of the Fluorescence Lifetime of Benzene. Since the preparative photoreactions usually require relatively high concentrations of benzene (0.56–1.1 M),[8,23] reliable photophysical measurements had to be performed under comparable conditions.

Lifetime measurements in the range of 0.05 M < [benzene] < 1.12 M resulted in monoexponential fluorescence decays up to 5 lifetime ranges (Figure 1) without a concentration effect. Neither in the fluorescence maximum nor in the long-wavelength range of the fluorescence spectrum were biexponential decays observed, so in our systems there is no participation of benzene excimers, which were observed in steady-state measurements at concentrations >2.0 M[24,25] or after laser flash excitation.[26-28]

However, temperature has a drastic effect on the fluorescence lifetime (Figure 2). Temperature change from 40 to −35 °C enhances the lifetime nearly 4-fold. This also could enhance the Stern–Volmer constant of fluorescence quenching and other bimolecular processes including photoadditions without any obligatory existence of an exciplex intermediate.

(3.2) Kinetic Measurements. The time evolution of monomer (I_m) and exciplex fluorescence (I_e) can be expressed as follows:[11,12]

$$I_m(t) = A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t) \qquad (1)$$

$$I_e(t) = A_3 \exp(-\lambda_1 t) - A_3 \exp(-\lambda_2 t) \qquad (2)$$

with

$$2\lambda_{1,2} = k_6 + k_7 + k_1[\mathrm{Ol}] + \sum_2^5 k_i \pm ((k_6 + k_7 + k_1[\mathrm{Ol}] - \sum_2^5 k_i)^2 + 4k_1k_2[\mathrm{Ol}])^{1/2}$$

and

$$\lambda_1 + \lambda_2 = k_6 + k_7 + \sum_2^5 k_i + k_1[\mathrm{Ol}] \qquad (3)$$

$$\lambda_1\lambda_2 = (k_6 + k_7)\sum_2^5 k_i + k_1\sum_3^5 k_i[\mathrm{Ol}] \qquad (4)$$

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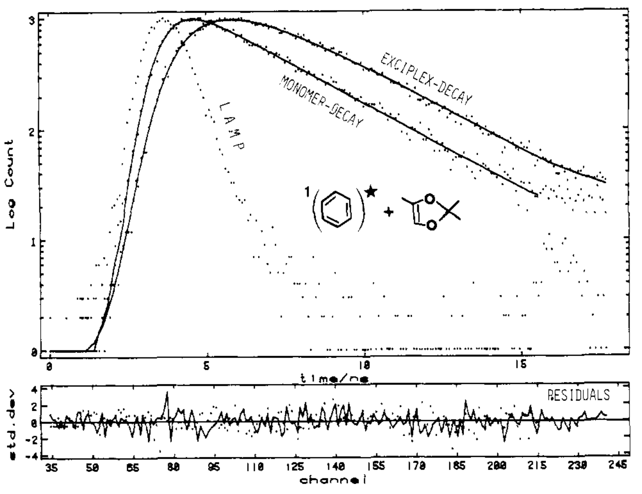

Figure 3. Monomer and exciplex decay of ^1S benzene in the presence of **5** in acetonitrile at 20 °C after excitation at 250 nm. Emissions at 282 (monomer) and 400 nm (exciplex); [**1**] = 0.56 M, [**5**] = 0.02 M. Deconvolution: monomer decay, $I_m(t) = 0.5 + 0.088\exp(-t/2.78\text{ (ns)})$, $\chi^2 = 1.19$; exciplex decay, $I_e(t) = 0.75 + 0.16\exp(-t/2.77\text{ (ns)}) - 0.14\exp(-t/1.15\text{ (ns)})$, $\chi^2 = 1.08$. Decay curves: (···) experimental, (—) fitted. Residuals: (···) monomer, (—) exciplex.

Equations 1 and 2 describe the behavior of the intensities of monomer and exciplex fluorescence after excitation by a δ-pulse. $I_m(t)$ and $I_e(t)$ are described by a sum and a difference of the same exponentials; the preexponential factors of the exciplex fluorescence are equal with reversed signs, indicating that no exciplex is present at $t = 0$.

An example is given in Figure 3, which exhibits the common decay patterns of the measured systems:

(i) The monomer decay is monoexponential in all cases. So it is not influenced by exciplex dissociation and $k_2 << k_3 + k_4 + k_5$ can be assumed. Then eq 1 degenerates to

$$I_m(t) = A_1\exp(-\lambda_1 t)$$

with

$$\lambda_1 = k_6 + k_7 + k_1[\text{Ol}] = 1/\tau_m \qquad (1a)$$

which equals the reciprocal of monomer lifetime.

(ii) The exciplex decay is biexponential in all cases and is described by eq 2 with

$$\lambda_1 = 1/\tau_m \qquad \lambda_2 = \sum_2^5 k_i = 1/\tau_e$$

which equals the reciprocal of exciplex lifetime.

So plots of λ_1 vs. olefin concentration (eq 1a, Figure 4a) yield k_1 from the slope, and plots of $\lambda_1\lambda_2$ vs. olefin concentration (eq 4, Figure 4b) give $\sum_3^5 k_i$ from the slope divided by k_1, so that k_2 can be calculated as the difference to $\lambda_2 = \sum_2^5 k_i$. k_5 is determined from additional steady-state data (intercept of eq 9, $x = 5$). From the temperature dependence of k_1, the activation parameters of exciplex formation could be calculated (Figure 5).

From the results shown in Table I the following conclusions can be drawn

(i) Formation of exciplexes is diffusion controlled, since k_1 values are in the range of 10^{10}; the most sterically hindered pair **2** + **5**, however, yields the smallest k_1. These values are in the same order of magnitude as measured for exciplexes in nonpolar and slightly polar solvents.[12]

(ii) The values of k_1 obtained by monomer lifetime quenching (*c* in Table I) agree with those obtained by exciplex fluorescence induction (*b* in Table I) within the limits of error, which means that the applied model is consistent.

(iii) The decay of the arene–olefin exciplexes occurs mainly via radiationless routes 3 and 4, while dissociation and fluorescence (routes 2 and 5) have a diminishing influence ($\lesssim$10%). Here the polar solvent acetonitrile enlarges the radiationless deactivation of the exciplex (for example, by enhancement of radical ion formation).[35,36] The exciplex with triethylamine yielded $\sum_3^5 k_i$ values in the range of k_2 corresponding to measurements on

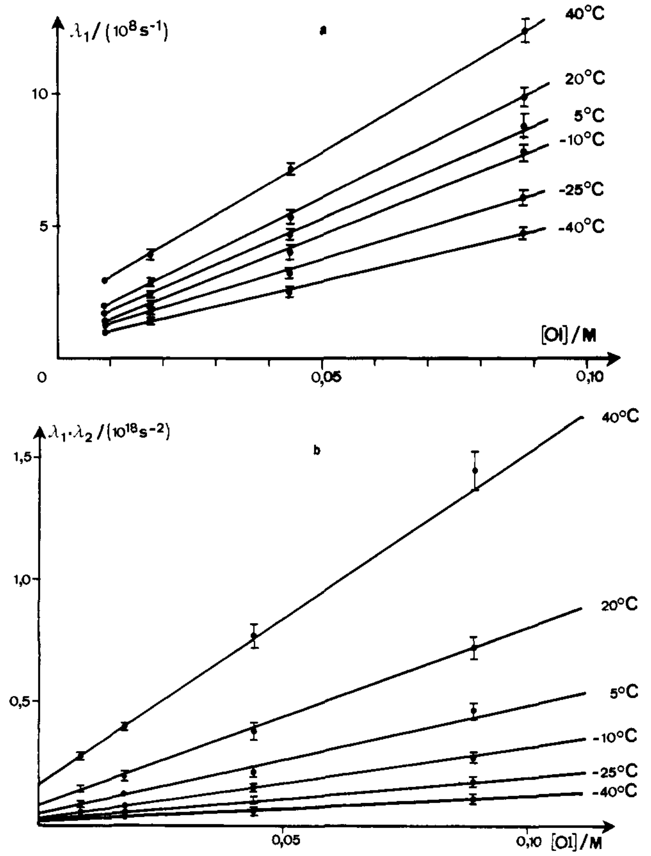

Figure 4. Concentration and temperature dependence of (a) λ_1 (eq 1a) and (b) $\lambda_1\lambda_2$ (eq 4) in acetonitrile, for the system **1** + **4**.

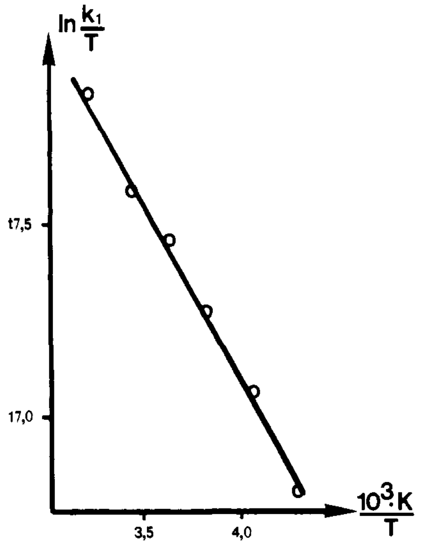

Figure 5. Eyring plot for the calculation of ΔH_1^* and ΔS_1^* in the system **1** + **4** in acetonitrile.

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Table II. Steady-State Data Corresponding to Eq 8 and 9[a]

	system									
	1 + **3**		**1** + **4**			**1** + **5**		**2** + **5**		
solvent	AN	DIOX	AN	DIOX	CY	AN	CY	AN	CY	calcd from
K_{av}, M^{-1}	116 ± 2	123 ± 3	125 ± 3	115 ± 3	180 ± 11	138 ± 6	210 ± 10	215 ± 16	242 ± 11	eq 8
$k_1\tau_0$, M^{-1}	132 ± 12		157 ± 10			140 ± 20		141 ± 23		eq 3
K'_{sv}	114 ± 48		168 ± 20			139 ± 10		212 ± 20		eq 9, exciplex fluorescence
		31 ± 3	74 ± 15	21 ± 10	105 ± 34		69 ± 10			ortho adduct formation
		18 ± 2	22 ± 20	23 ± 3	270 ± 64					meta adduct formation
$\phi_5^{max}10^4$	9.3 ± 3		74.9 ± 0.4			70 ± 5		60 ± 8		exciplex fluorescence
ϕ_{add}^{max}		0.11	0.18	0.39	0.40		0.42			ortho adduct formation
		0.31	0.032	0.11	0.28		≲0.05			meta adduct formation

[a] In acetonitrile (AN), dioxane (DIOX), and cyclohexane (CY). Definition of quantum yields and constants, see text.

different systems fluorescing in nonpolar and slightly polar solvents.[12]

(iv) The efficiencies of radiationless deactivation of the exciplexes $\eta_3 + \eta_4 = (k_3 + k_4)/\sum_2^5 k_i$ are ≈0.3 and >0.9 for NEt$_3$ and **3**–**5**, respectively. The larger value for the olefins reflects their enhanced reactivity against ^{1}S benzene compared to triethylamine.[9a]

(v) The enthalpy and entropy changes of activation reflect the temperature dependence of the solvent viscosity. The entropy changes are much less negative then activation entropies in thermal cycloadditions with productlike transition states (120–160 J mol^{-1} K^{-1}),[31,32] so the fluorescing exciplexes must not necessarily have the geometries of the products.

(3.3) Steady-State Measurements. As reported earlier[8,9] the systems under discussion exhibit exciplex fluorescence only in polar solvents (e.g., acetonitrile, dioxane) and not in cyclohexane. The largest fluorescence yield was obtained in acetonitrile. Isoemissive points indicate stochiometric relations between monomer quenching and exciplex generation.

The example in Figure 6 allows the following conclusions:

(i) The fluorescence of benzene is partly quenched by self-absorption, caused by the applied high concentration, so that only the longest wavelength band of the fluorescence can be monitored.

(ii) The olefin at high concentrations (c >0.1) causes deformations in the monomer fluorescence band by absorption in its long wavelength tail; so only concentrations c <0.1 could be used for mechanistic studies.

(iii) The exciplex spectra are not structureless as reported for the other exciplexes with benzene,[8,9] but there is no deformation at high olefin concentration, which could indicate triple exciplex formation.[33,34]

The relations between the rate constants in Scheme I and the quantum yields of fluorescence and product formation can be expressed as follows:[29] monomer fluorescence

$$\phi_6 = \eta_6 \sum_{n=0}^{\infty} (\eta_1\eta_2)^n = \frac{\eta_6}{1 - \eta_1\eta_2} \tag{5}$$

exciplex fluorescence

$$\phi_5 = \eta_1\eta_5 \sum_{n=0}^{\infty} (\eta_1\eta_2)^n = \frac{\eta_1\eta_5}{1 - \eta_1\eta_2} \tag{6}$$

product formation

$$\phi_3 = \eta_1\eta_3 \sum_{n=0}^{\infty} (\eta_1\eta_2)^n = \frac{\eta_1\eta_3}{1 - \eta_1\eta_2} \tag{7}$$

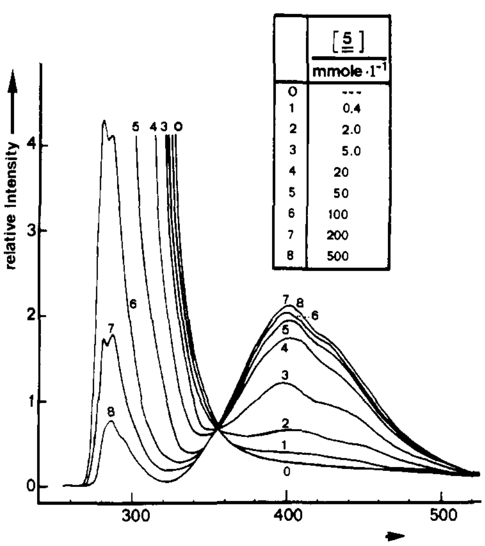

Figure 6. Monomer and exciplex fluorescence of **1** and **5** in acetonitrile at 22 °C, [**1**] = 0.56 M, spectra uncorrected for detector sensitivity.

where η_x is the efficiency of a single deactivation process x of an excited species (x = 1–7). With $k_{3'} << k_3$ and $k_2 << \sum_2^5 k_i$ (see Table I), the following useful expressions are obtained: Stern–Volmer relation

$$\frac{\phi_6{}^{\circ}}{\phi_6{}^{\mathrm{Ol}}} = 1 + \frac{k_1}{k_6 + k_7}[\mathrm{Ol}] \tag{8}$$

dilution relation for exciplex fluorescence (x = 5) and product formation (x = 3)

$$\frac{1}{\phi_x} = \frac{\sum_2^5 k_i}{k_x} + \frac{(k_6 + k_7)\sum_2^5 k_i}{k_1 k_x}[\mathrm{Ol}]^{-1} \tag{9}$$

intensity ratio plot for exciplex and monomer fluorescence

$$\frac{\phi_5}{\phi_6} = \frac{k_1 k_5}{k_6 \sum_2^5 k_i}[\mathrm{Ol}] \tag{10}$$

Equation 8 gives the Stern–Volmer constant for fluorescence quenching $K_{sv} = k_1/(k_6 + k_7)$, eq (9) the maximum quantum yields ($\phi_x{}^{max}$ = intercept$_x{}^{-1}$) and the Stern–Volmer constant for generation of exciplex fluorescence or product(s) (K'_{sv} = intercept$_x$/slope$_x$).

The results of the systems under research are summarized in Table II for acetonitrile, dioxane, and cyclohexane. These data fit the exciplex mechanism (Scheme I) with respect to fluorescence quenching and generation of exciplex fluorescence: the Stern–Volmer constants calculated by eq 8 and 9 are the same within the limits of error and are similar to those calculated by kinetic results via eq 3. Only in one case (toluene/**5**) the steady-state

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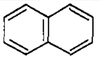
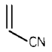
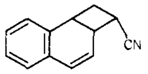
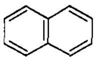
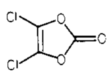
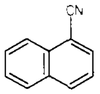
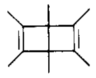
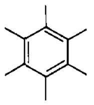
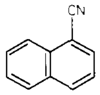
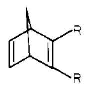
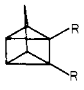
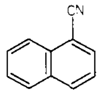
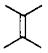
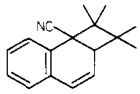
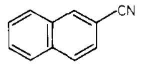
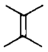
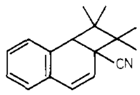
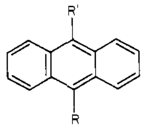
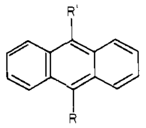
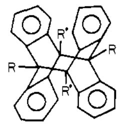
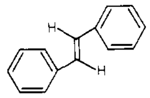
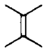
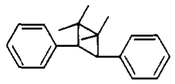
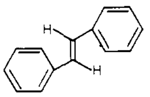
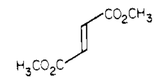
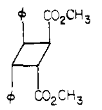
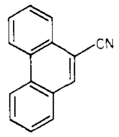
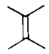
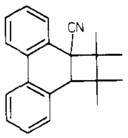
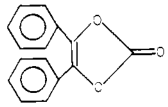
Table III. Comparison of Photoreactive Systems Ar + $h\nu$ + Ol → Product(s) with Respect to Stern–Volmer Constants K_{sv}[a]

Ar	Ol	product(s)	ic/sl = K'_{sv}	exciplex fluorescence	ref/solvent
			$=K_{sv}$	–	38/T
		1,2- and 1,4-adducts	$=K_{sv}$	–	39/D
			$=K_{sv}$	+	40/H
			$<K_{sv}$	–	41/H
			$<K_{sv}$	+	42/B
			$=K_{sv}$	–	42/B
			$\leq K_{sv}$	+, –	43/B
			$=K_{sv}$	–	44/H
			$<K_{sv}$	+	47/B
			$=K_{sv}$ $<K_{sv}$	– –	2/B, 48/C 2/A
	conjugated dienes	cyclobutane formation	$=K_{sv}$	+	45/B

[a] Solvents: hexane (H), benzene (B), acetonitrile (A), dioxane (D), *tert*-butyl alcohol (T). Exciplex fluorescence: observed (+), not observed (–). Discussion, see text.

value lies far above the kinetic Stern–Volmer constant, obviously caused by static quenching effects.[12,37]

However, the Stern–Volmer constants calculated from adduct formation are commonly much smaller than expected from the exciplex scheme. Such a discrepancy was reported earlier for some other reactions (Table III). From the data in Table III, no systematic correlation between Stern–Volmer coincidence, type of solvent, and existence of exciplex fluorescence can be concluded. So for $K'_{sv} \neq K_{sv}$ the exciplex hypothesis (Scheme I) for adduct formation has to be improved.

Photoreactions in which product formation requires quenching of the primarily formed exciplex or excimer by a third molecule have been reported elsewhere.[47-53] For the systems in this paper such a mechanism would suggest the following extension of Scheme I.

Scheme Ia. Termolecular Deactivation of the Exciplex

$$^1(\text{Ol}\cdots\text{Ar})^* + \text{Ol} \xrightarrow{k_a} \text{adduct} + \text{Ol} \quad \text{adduct formation}$$

$$\xrightarrow{k_q} 2\text{Ol} + \text{Ar} \quad \text{quenching}$$

The quantum yield of adduct formation now has to be expressed by the product of the efficiencies of exciplex and adduct formation:

$$\phi_{\text{adduct}} = \eta_1\eta_a = \frac{k_1[\text{Ol}]}{k_6 + k_7 + k_1[\text{Ol}]}\,\frac{k_a[\text{Ol}]}{\sum_2^5 k_i + (k_a + k_q)[\text{Ol}]}$$

which gives the extended relation 9a,

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(51) Yang, N. C.; Shold, D. M.; Kim, B. *J. Am. Chem. Soc.* **1976**, *98*, 6587.

(52) Ohta, H.; Creed, D.; Wine, P. H.; Caldwell, R. A.; Melton, L. A. *J. Am. Chem. Soc.* **1976**, *98*, 2002.

(53) Saltiel, J.; Townsend, D. E.; Watson, B. D.; Shannon, P.; Finson, St. L. *J. Am. Chem. Soc.* **1977**, *99*, 884.

(54) Taylor, G. N.; Hammond, G. S. *J. Am. Chem. Soc.* **1972**, *94*, 3684.

(55) McCullough, J. J.; Wu, W. S. *J. Chem. Soc., Chem. Commun.* **1972**, 1136.

$$\frac{1}{\phi_{\text{adduct}}} = \frac{k_a + k_q}{k_a} + \frac{(k_1\sum_2^5 k_i) + (k_6 + k_7)(k_a + k_q)}{k_1 k_a}[\mathrm{Ol}]^{-1} + \frac{(k_6 + k_7)\sum_2^5 k_i}{k_1 k_a}[\mathrm{Ol}]^{-2} \quad (9a)$$

describing the adduct formation exclusively via exciplex quenching. At sufficiently high concentrations, used for monitoring product formation ([Ol] = 1–0.12 M),[8] the quadratic term is minimal, dilution plots are linear (Figure 7), and the ratio of intercepts and slopes can decrease below the K_{sv} values, obtained by fluorescence quenching.

$$K'_{sv} = \frac{\text{intercept}}{\text{slope}} = \frac{K_{sv}}{1 + K_{sv}\sum_2^5 k_i/(k_a + k_q)} \leq K_{sv} \quad (11)$$

These processes quench the routes $x = 2$–5 (Scheme I) with the quenching constant $(k_q + k_a) = k_q^E$ and thus change the dilution relation (eq 9) for direct exciplex processes as follows:

$$\frac{1}{\phi_x} = (\eta_1\eta_x)^{-1} =$$

$$\frac{k_q^E(k_6 + k_7) + k_1\sum_2^5 k_i}{k_1 k_x} + \frac{(k_6 + k_7)\sum_2^5 k_i}{k_1 k_x}[\mathrm{Ol}]^{-1} + \frac{k_q^E}{k_x}[\mathrm{Ol}] \quad (9b)$$

Low concentrations ([Ol] < 0.15 M) yield linear dilution plots[8] under minimization of the linear concentration term, which leads to

$$K'_{sv} = \frac{\text{intercept}}{\text{slope}} = K_{sv} + \frac{k_q^E}{\sum_2^5 k_i} > K_{sv} \quad (12)$$

for the exciplex processes 2–5.

According to the data in Table II, relation 11 holds for product formation and relation 12 for exciplex fluorescence ($x = 5$). The influence of the above-described mechanism is additive for exciplex quenching (12) and thus much lower than for product formation (11), where it is multiplicative.

(3.4) Solvent and Charge Transfer Effects. As stated earlier exciplex fluorescence of dioxole–benzene systems is only observable in polar solvents like acetonitrile,[8,9] dimethyl sulfoxide, or dioxane. With the exception of acetonitrile (Table II), quantum yields are usually less than about 10^{-4} in the other solvents. So no dipole moment of the exciplexes could be estimated by solvent shift experiments.

Furthermore the existence of exciplex-like intermediates in nonpolar solvents has to be proved by indirect methods. Nonfluorescent exciplexes can be detected (i) by enhancement of the Stern–Volmer quenching constant if a second quencher is present and the exciplex is reversible,[16,56] (ii) by energy transfer to a fluorescing acceptor,[57] or (iii) by changes of dilution plots, cf. eq 9 and 9a, in the presence of a second quencher.[58] The first two methods could not be applied, since no reversible exciplex could be detected by lifetime measurements and possible energy acceptors would also absorb in the benzene absorption region.

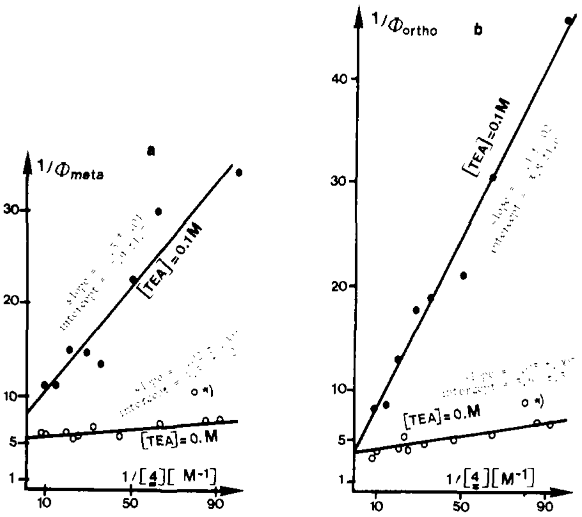

Figure 7. Dilution plots for the formation of the meta and ortho adducts in the system benzene + **4** with and without triethylamine (TEA) as a quencher; solvent = cyclohexane, $t = 22$ °C, *not used for calculations.

The third method has been applied to the system benzene + **4** in cyclohexane with and without triethylamine as a quencher (Figure 7). The plots show that even at extremely high concentrations of **4** the formation of the meta adduct can be quenched (Figure 7a), since the added amine increases the intercept beyond the limits of error. So in the benzene–dioxole system a quenchable intermediate must have been formed in a primary step. This is not the case with the ortho adduct formation (Figure 7b), where only the slope but not the intercept is changed by the added quencher. So the ortho adduct may be formed directly or via a different short-lived intermediate. These results need further investigations, since in dioxane the ortho adduct formation is quenched faster than the meta adduct formation.[8]

There is no correlation between the ionization potentials of the dioxoles and the benzene fluorescence quenching,[8,9] the exciplex formation (Tables I and II), and the wavelength of the exciplex fluorescence maximum.[9] Additionally changes of the solvent from a polar to a less polar one do not exhibit the characteristics of charge-transfer quenching, e.g., reduction of the K_{sv} value by at least an order of magnitude.[2,10,35,54,55] Instead Table II shows increasing Stern–Volmer constants with decreasing solvent polarity. This behavior is not observed with triethylamine although its oxidation potential (0.98 V)[10b] coincides with that of **4** (0.99 V);[70] here the Stern–Volmer constant for quenching of benzene fluorescence decreases with decreasing solvent polarity:

$$K_{sv} = 26\ (\text{cyclohexane})^9 < 87\ (\text{dioxane})^8 < 110\ (\text{acetonitrile})$$

The absence of such a solvent effect in the case of the dioxoles **3–5** is most probably caused by a minor contribution of charge transfer to exciplex formation.[10c,d] This property was assigned by Weller to "mixed excimers", which show fluorescence even in strongly polar solvents and a weaker dependence of exciplex emission maxima on donor oxidation potentials.[10c]

Whereas there is only a small influence of the charge-transfer properties of dioxoles and solvents on exciplex formation, strong effects on adduct formation can be observed. Figure 8 demonstrates, that better donor properties of the olefins indicated by lower ionization potentials favor the ortho adduct formation. Steric effects can be excluded, since all adducts are predominantly formed in the exo conformation.[59]

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(56) Charlton, J. L.; Townsend, D. E.; Watson, B. D.; Shannon, P.; Kowaleswska, J.; Saltiel, J. *J. Am. Chem. Soc.* **1977**, *99*, 5992.

(57) Bendig, J.; Kreysing, D. *J. Prakt. Chem.* **1978**, *320*, 732.

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(70) Gersdorf, J. Diplomarbeit Aachen, 1983. Half-wave potentials by cyclic voltammetry in acetonitrile/0.1 M $LiClO_4$ vs. SCE.

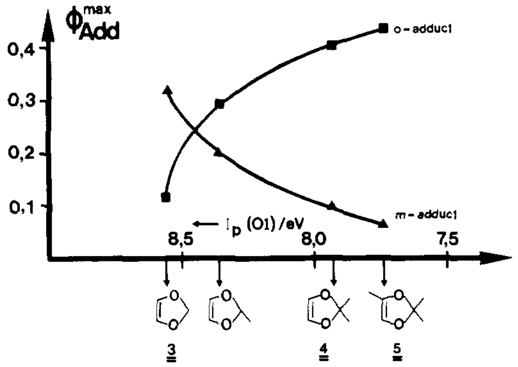


Figure 8. Change of adduct quantum yields with ionization potential of the dioxoles in dioxane at 22 °C; ϕ_{Add}^{max} = maximum quantum yields cf. Table II.

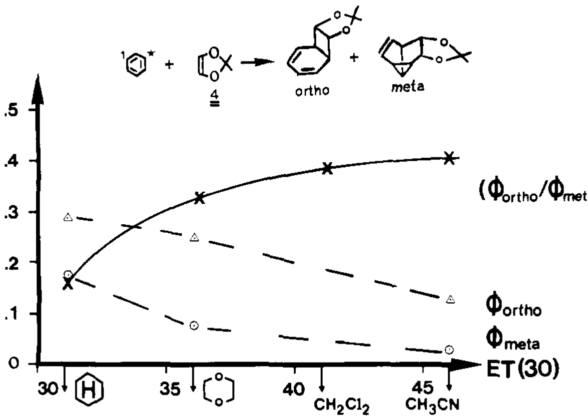


Figure 9. Solvent dependence of the quantum yields for ortho and meta adduct formation. System: benzene, *c* 1.1; **4**, *c* 0.1; *t* = 22 °C; *x* axis, solvent polarity scale.[60]

This change in regioselectivity is supported by the solvent effect (Figure 9): here the more polar solvents which are able to enhance charge-transfer processes also favor the ortho relative to meta adduct formation. But there is another influence of the solvent, which reduces the total quantum yield of adduct formation with increasing polarity. This happens most probably by stabilizing the separated charges and hence quenching formation of neutral species.

The absolute quantum yields with methylene chloride are less than 0.1, most probably caused by enhancement of intersystem crossing and chlorine abstraction reactions.

4. Conclusions

The above-gathered data suggest the following conclusions:

(i) Formation of exciplex in benzene–dioxole systems does not exhibit predominant charge-transfer interaction.

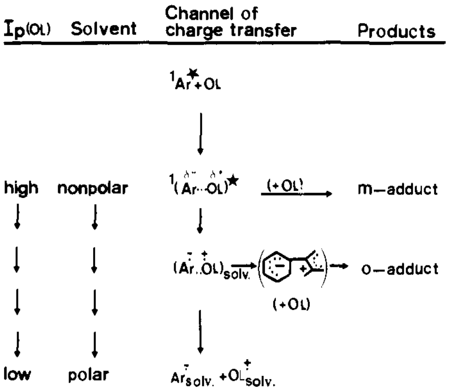
(ii) The primarily formed exciplex is a necessary but not a direct percursor of the products, since another molecule is required for product formation (Scheme Ia).

(iii) Increasing charge transfer between the two exciplex partners influences strongly both the mode of reaction and the absolute quantum yield.

The complete description of possible processes in arene–olefin photocycloaddition is as in Scheme II. Increasing charge separation in the exciplex, caused by decreasing ionization potentials of the olefins, can lead to zwitterionic intermediates, which are able to form ortho adducts,[61] corresponding to a similar pathway in thermal reactions of donor/acceptor pairs.[62] Increasing solvent polarity can reduce the formation of adducts by propagating the formation of radical ion pairs.[36,37] This channel is supported by the fact that no meta or ortho adducts are observed with benzonitrile instead of benzene.

The role of the second olefinic partner, which enhances the formation of adducts, may be a catalytic one: donation of charge to the cationic olefinic site of the exciplex may weaken the solvent stabilization of exciplex and zwitterionic species and thus reduce the solvent-induced quenching of the adduct formation. This mechanism can also be valid in nonpolar cyclohexane, since the added benzene is able to stabilize exciplexes to a surprisingly large extent,[63] most probably caused by the high polarizability of the benzene molecule.[69]

Scheme II. Formation of the Arene/Olefin Exciplex and Its Deactivation Directed by Charge-Transfer Effects Induced by Changes of Olefin I_p and Solvent Polarity



However, a mechanism including additional product formation by direct collapse of the exciplex cannot be excluded. Such a mixed mechanism will most probably occur under minimal exciplex stabilization in cyclohexane resulting in increasing K'_{sv} values (Table II; system **1**–**4** in cyclohexane).

An influence of the olefin concentration on the reaction mode as expected from product formation by exciplex quenching, cf. Scheme II, was not observed.[8] The ratio of ortho/meta adducts keeps constant at the applied concentrations within the limits of error, which may be caused by changes of solvent polarity at high olefin concentrations.

Further work dealing with the influence of solvents and substitution is in progress in this laboratory.

5. Experimental Section

Fluorescence spectra were measured with a Perkin-Elmer MPF3-L spectrometer in a triangular cuvette as described earlier.[9] The standard concentrations of benzene and toluene were 0.56 and 0.47 M, respectively, unless otherwise noted. The wavelength response of the emission detector was determined by a calibration lamp Model 245 C, Optronic Laboratories Inc., Orlando, FL. The spectral bandwidth was 5 nm for excitation and emission. Fluorescence quantum yields were determined relative to those of benzene (0.05)[9] and toluene (0.12). Fluorescence lifetimes were measured by the single-photon counting method on an Edinburgh Instruments 199 M Fluorescence lifetime spectrometer with a hydrogen-filled nanosecond flashlamp.[64] The fitted values were obtained by a least-squares reconvolution using a nonlinear χ-squared minimization technique.[65,66] The fitting procedure included background and relative position of the time scales for fluorescence and lamp decay. Biexponential fits, cf. eq 2, gave identical A_3 values within the limits of error, while the monoexponential fitted lifetimes of the monomer decays coincided with one of the lifetimes calculated from the exciplex decay, cf. eq 2, within ±0.2 ns. So for the calculations, cf. eq 3 and 4, the lifetimes from eq 2 were used. The quoted errors are standard deviations, which are enlarged for calculated values by differential propagation of errors.

The dioxoles **3**–**5** and their photoadducts were prepared as described earlier,[8,67] the applied solvents ("uvasol") were used as purchased from Merck, and benzene and toluene (Merck "uvasol") were destilled prior to use. All samples were purged with argon until was no change in fluorescence intensity or lifetime. The lifetime of benzene in acetonitrile (12.25 ns) is slightly shorter than that reported previously (15 ns),[68] however, there no limits of error are given.

Quantum yields of reactions were determined as described earlier.[8]

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Registry No. 1, 71-43-2; **2**, 108-88-3; **3**, 288-53-9; **4**, 22945-10-4; **5**, 51494-95-2.