Tetrahedron Vol. 47, No. 18/19, pp. 3137-3154, 1991
Printed in Great Britain

0040-4020/91 $3.00+.00

THE PHOTOSENSITIZED DIMERIZATION OF 1,3-CYCLOHEXADIENE

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(Received in UK 7 January 1991)

Abstract. The quantum yield of formation of [4+2] and [2+2] cyclohexadiene dimers through photosensitization by aromatic nitriles is determined as a function of diene concentration, solvent polarity, presence of salts. A special effect by halides on the radical ion pair is observed, and is different from the general salt effect (increase of ionic strength) caused by perchlorates, fluophosphates, and fluoborates. A scheme based on two reactive intermediates, the exciplex and the radical ion pair (not the free radical ions) is proposed. The two species are in equilibrium and this causes the observed complex dependence of reaction quantum yield and product ratio on diene concentration. Intersystem crossing from the radical ion pair is the origin of a significant part of triplet 2+2 dimerization.

Introduction

Photochemical reactions between aromatic molecules and various π-donors (alkenes, alkynes, aromatics) are generally rationalized as involving either the intermediacy of excited complexes (exciplexes) or electron transfer to yield a radical ion pair.[1-5]

$$\begin{tikzcd}[column sep=small] & (A\text{----}D)^* \arrow[r] & \text{Products} & (1) \\ A^* + D \arrow[ur] \arrow[dr] & & & \\ & (A^{\cdot-} \quad D^{\cdot+}) \arrow[r] & \text{Products} & (2) \end{tikzcd}$$

Distinction between the two alternatives relies either on the chemistry observed (typically cycloaddition vs either ionic or radical addition or fragmentation) or on spectroscopic identification of transient intermediates.[2] We feel that also in view of synthetic applications, the important points to be attended to are selectivity and efficiency, and we presently report steady-state parameters for the photosensitized dimerization of 1,3-cyclohexadiene (CHD), and the implication that the observed medium effects, including an unprecedented salt effect, has on the mechanism.

We previously found that the reactions observed on irradiation of naphthalenenitriles in the presence of various dienes depend on the free energy change for electron transfer from the donor to the excited nitrile.[6] Thus, either 4+4 or 2+2 cycloadditions predominate for ΔG_{et} largely positive, or, respectively near to zero. Sensitized diene dimerization rather than cycloaddition takes place for largely negative ΔG_{et}.

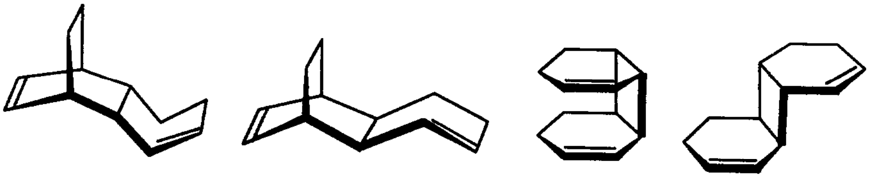
There has been a great interest in the mechanism of dienes dimerization and the situation is only briefly reviewed here as far the course of the reaction, not the detailed, and in some case controversial, mechanistic rationalization. Thus, while the thermal Diels-Alder reaction of CHD at 200°C gives only a low yield of products **1** and **2**, (Scheme I) the corresponding radical cation initiated process is efficient at room temperature. The latter course is observed either by γ-irradiation[9-11] or by treatment with the oxidant tris (p-bromophenyl)aminium hexachlorostibnate,[12-14] while cathodic oxidation is inefficient.[15] As for photochemical reactions, triplet sensitization yields mainly the 2+2 dimers **3** and **4**, with some of the exo 4+2 dimer **2**,[7] while with aromatic nitriles,[16-18] pyrilium salts[20] and some ketones[18-21] 4+2 dimers are mainly formed either via electron-transfer sensitization or via ternary excited complexes; direct irradiation gives intermediate results.[22]

Results

Three aromatic sensitizers, viz 1-naphthalenecarbonitrile (NN), 1,4-naphthalenedicarbonitrile (NDN), and 9,10-anthracenedicarbonitrile (ADN) have been considered in this study, and are expected to act via electron transfer from the singlet and energy transfer from the triplet state. For the sake of comparison, parallel experiments with 2,3,5,6-tetrachloro-p-benzoquinone (TCBQ) and 2-acetylnaphthalene (AN) as model triplet state electron-, and, respectively, energy-transfer sensitizers have also been carried out.

The quantum yields for the formation of the individual dimers have been determined in solvents of various polarity in a range of CHD concentrations (0.01 to 2M). Since it has been repeatedly confirmed in the literature[7], and here again, that the triplet pathway leads to products **3**, **4** and **2** in the ratio 3:1:1, and indeed with the nitrile the ratio **3** to **4** is consistently 3, the combined yield of these two products and the amount of **2** corresponding to that of **3** was formulated as the total quantum yield of triplet-derived dimers (Φ_T) while the remaining part of **2** together with **1** made up the total yield of radical cation-derived products (Φ_{RC}).

The nature of the "radical cation" process will be more fully discussed later, for the



1 **2** **3** **4**

Scheme I

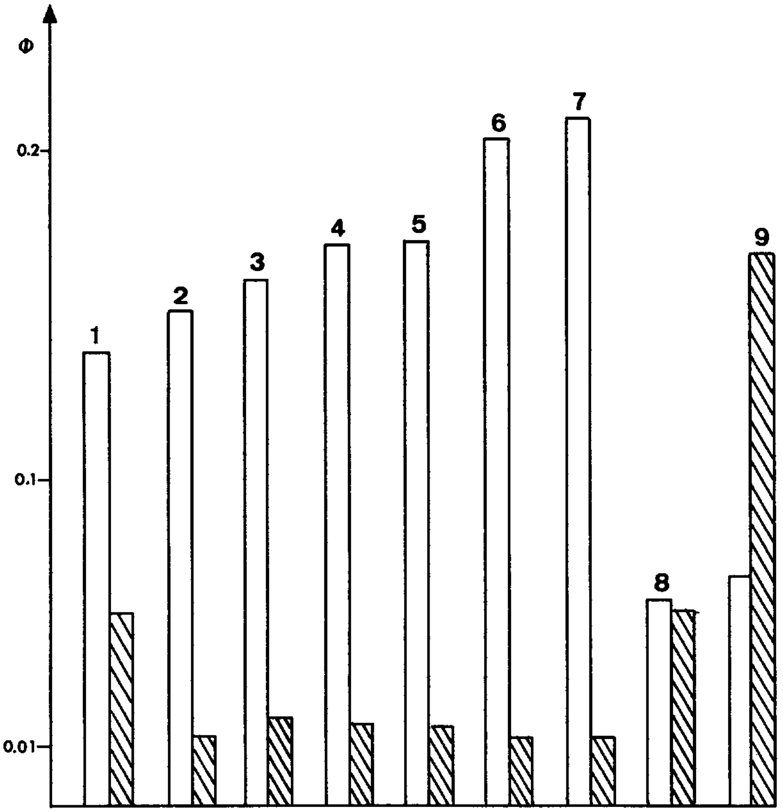


Figure 1. Quantum yield for phtosensitized CHD (0.1M) dimerization, viz. radical cation (Φ_{RC}, □) and triplet process (Φ_T, ▧), in the presence of the following salts (0.05M): 1, none; 2, $CsClO_4$; 3, $Mg(ClO_4)_2$; 4, $LiClO_4$; 5, *n*-Bu_4NBF_4; 6, Et_4NClO_4; 7, Et_4NPF_6; 8, *n*-Bu_4NCl; 9, *n*-Bu_4NBr

moment this is only a way for indicating the product not derived from the CHD triplet.

$$A^{*} + CHD \longrightarrow {}^{3}CHD^{*} \longrightarrow \mathbf{2}+\mathbf{3}+\mathbf{4} \qquad (3)$$

$$A^{*} + CHD \longrightarrow CHD^{+\cdot} \longrightarrow \mathbf{1}+\mathbf{2} \qquad (4)$$

These combined values are reported in Table I for 10^{-1} and 10^{-2}M [CHD].

The results are strongly dependent on conditions. Thus, with NN in acetonitrile path 4 predominates with 0.1 M CHD, and path 3 with 0.01 M CHD; the latter is likewise the major path both in benzene and in dichloromethane; notice further that in CH_2Cl_2 Φ_T increases with decreasing [CHD]. With NDN, Φ_{RC} Φ_T both in MeCN and in CH_2Cl_2 with 0.1 M CHD, while the order is reversed in the other cases. With ADN eq 4 is the main path, and Φ_{RC} is twice as much in CH_2Cl_2 than in MeCN; virtually no reaction takes place in benzene. The exclusively radical cation-initiated dimerization with TCBQ is strongly polarity dependent Table I also contains the value of the "corrected" 1 to 2 ratio **1**/**2**, were only the part of product **2** not arising from the triplet pathway has been considered.

Further representative results are presented in Table II where, together with Φ_T and Φ_{RC} for a more extensive range of CHD concentrations the quantum yield for the consumption of the sensitizer is also reported (the cycloadducts formed from NN and CHD in apolar medium have been previously described,[6] the same products as well as other ones are present in MeCN and the NDN-CHD addition has not been more clearly investigated). Over the range explored the **1**/**2** ratio grows and then drops again with both NN and NDN.

There are several reports in the literature about a favourable effect of dissolved salts on photochemical reactions via radical ions,[21-23-24] though generalisations are not supported by the scattered evidence available. Thus, an obvious extension was the study of salts effect. The results are presented in the histogram of Figure 1 for the case of NN with an extended series of salts, and in columns a and b in Table I for various sensitizers and two salts of opposite effect, viz. tetraethylammonium hexafluophosphate and tetra(n-butyl)ammonium chloride.

Indeed, the observed effect depends on the anion; thus, perchlorates, fluoborates, and hexafluophosphates increase, at least in some cases, Φ_{RC} and scarcely effect Φ_T, with no difference with the counter-ion (Li^+, Mg^{2+}, NR_4^+, Cs^+); on the other hand, tetrabutylammonium chloride and bromide tend to decrease Φ_{RC} and to increase (or to leave unaffected) Φ_T.

A sizeable ($>$ 10%) effect is observed only with a concentration of the salts greater

Table I. Quantum yield for the photosensitized dimerization of 1,3-cyclohexadiene via radical cation, (Φ_{RC}) and via triplet state (Φ_T)

		$\Phi_{RC} \times 10^2$								$\Phi_T \times 10^2$					
Sensitizer	Solvent	CHD, 0.1M	(a,	b)	$(1/2)^c$	0.01M	(a,	$b)^{zc}$	$(1/2)^{zc}$	0.1M	(a,	b)	0.01M	(a,	b)
NN	MeCN	14.2	(20,	0.65)	15	1.5	(1.5,	0.7)	4	2.2	(21,	5.7)	2.7	(2.1,	4.7)
	CH_4Cl_2	0.52	(0.4,	-)	1.5	1.2	(1.1,	1.2)		7.2	(7.3,	11)	12	(11,	17.6)
	$MeO(CH_2)_2OMe$	-				-				4.6			6.3		
	C_6H_6	0.15				0.1				3.1			2.9		
NDN	MeCN	12	(9,	-)	12.6	0.7	(0.6,	-)	5	0.62	(0.06,	-)	0.1	(0.4,	-)
	CH_2Cl_2	14	(24,	12)	3.8	0.58	(1.4,	0.3)	1.5	7.6	(6.2,	2.1	2.9	(3,	2.7)
	C_6H_6	1.7				0.7				3.2			1.6		
ADN	MeCN	3.7	(4.1,	-)	8.2	0.15	(-,	-)		-	(-,	1.3)	0.4	(0.5,	-)
	CH_2Cl_2	8.5	(17,	3.1)	4.2	1.4	(0.5,	-)		1	(3.5,	6.3)	-	(-,	-)
TCQ	MeCN	15	(23.2,	0.4)	17.5					-	(-,	-)			
	CH_2Cl_2	1.5	(2.7,	-)	4					-	(-,	-)			
AN	MeCN	-				-				80			8.3		
	C_6H_{12}	-				-				96			24		

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a, in the presence of 0.05 M $EtN_4^+ PF_6^-$

b, in the presence of 0.05 M $\underline{n}$-$Bu_4N^+Cl^-$

c, ratio of the yield of product **1** to **2**, the latter one corrected for the fraction arising from the triplet pathway, see text.

Table II. Dependence of quantum yield of photosensitized dimerization on CHD concentration

Sensitizer	Solvent	[CHD], M	Φ_{RC}^{a}	Φ_{RC}	Φ_{T}^{a}	$(1/2)^{b}$	$\Phi_{-S}^{a,c}$
NN	MeCN	0.01	1.5	2.9	2.7	4	7.2
		0.02	3.6	5.2	2.2	9	
		0.05	8.2	9.6	2.2	19	
		0.1	14.2	15.5	2.2	15	14
		0.5	34.5	35.1	2.5	6.5	
		1	41	41.3	1.4	5.8	14
		2	49.4	49.6	3	5.3	14.8
	C_6H_6	0.01	0.12		2.9		
		0.05	0.15		3.2		8.4
		0.1	0.15		3.1		12.8
		0.5	-		6.3		13.1
		2	-		8		14.1
NDN	MeCN	0.01	0.7	1.2	0.06	5	1.2
		0.1	12	12.9	0.62	12.6	1.9
		0.5	26.7	27.1	0.4	10	2.6
		1	47.8	48.1	0.8	5.7	
		2	48.4	48.6	1	5.5	3.5

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a $\times 10^{2}$ b. Ratio of the yields of product **1** to **2**, the latter one corrected as in Table I

c quantum yield for the sensitizer consumption, the product found are 2+2 and 4+4 cycloadducts, see ref. 6

than 0.01 M. Table III shows the data for the N-CHD-$Et_4N^+ClO_4^-$ evidencing that the **1/2** ratio also increases somewhat with the concentration of the salt, at least up to a 0.05 M.

In order to check whether the effect of the salts was due to an interaction with the sensitizer's excited state, the quenching of the nitrile fluorescence by the salt and by CHD was compared (Table IV). The perchlorates cause no quenching, while chloride and bromide have a large effect. This does not explain the reaction quenching, though. Thus, e.g. with NDN - 0.1 M CHD - 0,05 M $Bu_4N^+Cl^-$ the proportion of the NN excited singlet quenched by CHD decreases from 82 (in the absence of the salt) to 71%, but Φ_{RC} decreases to 5% of the original value.

Further conditions explored were the addition of methanol and trifluoroacetic acid, in both cases resulting in a strong quenching of Φ_{RC}, and of 2,6-di-tert-butylpyridine, this one with the aim of recognizing Bronsted acid effect on the photoreaction, when the salts are added; this is not the case, since the pyridine causes a small increase of Φ_{RC} both in the presence and in the absence of $Et_4N^+ClO_4^-$ (Table V).

Discussion

There has been no shortage of studies on CHD dimerization in the last years (see the Introduction). A fraction of our experiments duplicates earlier work, and concurs in the results. Likewise the mechanistic discussion takes up again earlier proposals, though we think that the extended investigation presented here leads to a different overall picture.

Gross mechanistic scheme. The singlet excited state of aromatic nitriles is quenched by CHD at a rate near to diffusion controlled independently from the solvent polarity. However, only a charge transfer interaction leads to 4+2 dimers. The free energy change for electron transfer is evaluated by means of the Weller equation.[25]

$$\Delta G_{et} = E_{½}(A/A^{\bar{\cdot}}) - E_{½}(D/D^{\dot{+}}) - \Delta E_{exc} + \Delta E_{coul} \qquad (5)$$

$$\Delta E_{coul} = \frac{e\ N}{4\pi\epsilon a}\ (1/\epsilon - 2/37.2) \qquad (6)$$

The last term in eq 5, ΔE_{coul}, accounts for the coulombic interaction of the radical ions in solution, and is neglible in acetonitrile. However, in less polar solvents this term contributes significantly. Evaluation requires that an assumption of the ion separation distance, a, is made.[26] The values reported in Table VI (obtained with a = 0.7 nm) are only approximate, but may be useful for a classification, and show that 4+2 dimerization is the main process only for $\Delta G_{et} < -0.3$ eV. Besides, quenching of this process by electron donors such as trimethoxybenzenes as reported by other workers[17,18] and analogy with

Table III. NN-Sensitized photodimerization of CHD (0.1M) in MeCN. Dependence on $Et_4N^+ClO_4^-$ concentration

$[Et_4N^+ClO_4^-]$,M	Φ_{RC} x10^{-2}	Φ_T x 10^{-2}	1/2[a]
none	14.2	1.5	15
0.005	16	2.1	13.5
0.01	16.7	1.8	15.7
0.05	19.7	2.4	16.9
0.1	27.5	2.9	16.2

a Ratio of the yields of products 1 to 2, the latter one corrected as in Table I.

Table IV. Stern-Volmer constants, K_{SV},M^{-1}, for fluorescence quenching.

	Fluorophore		
Quencher	NN	NDN	ADN
CHD	110	134	123
$Et_4N^+ClO_4^-$	1	1	1
n-$Bu_4N^+Cl^-$	69		
n-$Bu_4N^+Br^-$	97	168	97

Table V. NN-Sensitized photodimerization of CHD (0.1M) in MeCN. Quantum yield in the presence of various additives.

Additive	Φ_{RC} x 10^2	Φ_T x10^2
none	14.2	2.2
MeOH,	5	3.1
CF_3COOH	5.1	2.2
2,6-(*t*-Bu)$_2C_5H_3N$	15.2	2
2,6-(*t*-Bu)$_2C_5H_3N$, $Et_4N^+ClO_4$,	21.3	2.4

dimerization induced by chemical[12-14] and electrochemical oxidation and by γ-irradiation[9,11] also support the intermediacy of the CHD radical cation, or of a charge transfer complex (see below), also in the photosensitization.

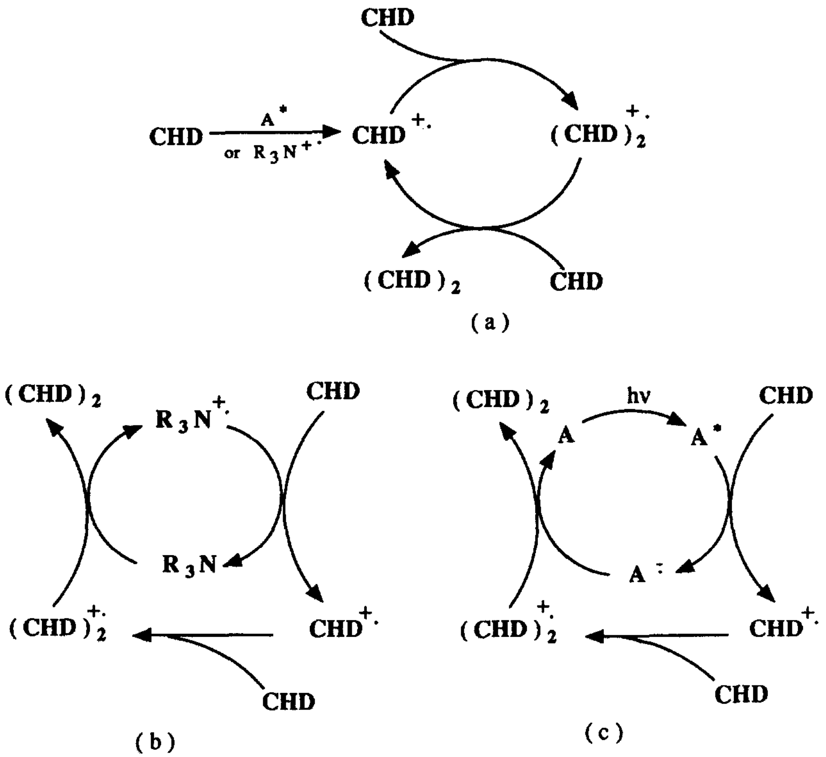
On the other hand a single intermediate does not adequately explain the results. Mattay and Turro noted that the **1** to **2** ratio decreases with increasing CHD concentration (and applied pressure),[19] and suggested two intermediates, the exciplex and the free radical ions. In fact examination over a large concentration range show a more complex behaviour, with the **1/2** ratio maximizing at ca 0.1 M CHD and decreasing at both higher and lower values (Table II). For a proper discussion of the concentration effect on quantum yield, it is better to make reference to the corrected value Φ' (see Table II), where the fraction of the sensitizer's singlet quenched by CHD (α_s, as independently determined by fluorescence quenching measurements) is taken into account.

$$\Phi' = \Phi / \alpha_s \qquad (7)$$

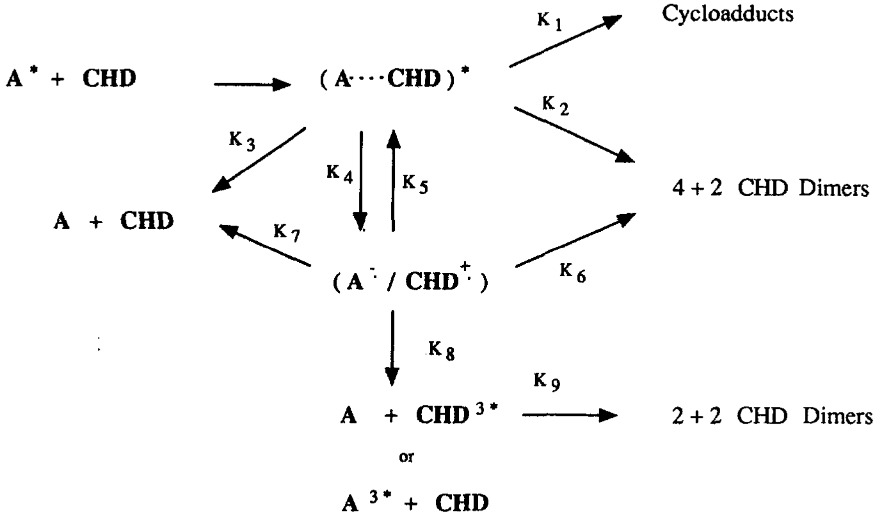
The double reciprocal plot of Φ'_{RC} vs [CHD] is linear at low concentration, but show some downward curvature at high (> 0.5 M) [CHD].

Other points relevant for the formulation of the mechanism are as follows. There is no indication for a ground state complex between the sensitizer and CHD. The dimerization quantum yield at high CHD concentration slightly exceeds 0.5 and under this condition the quantum yield for diene-senstizer addition is about 0.15; thus, while chemical reactions account for the greater part of excitation, with physical decay as a less important pathway, the total quantum yield is below **1**, and there is no reason to postulate a radical cation chain mechanism (Scheme IIa), also because the corresponding electrochemical process is inefficient[15] and recent evidence shows that in the R_3N^+ catalyzed process chain transfer is effected by the amine, not the diene (Scheme IIb). Therefore, if the radical cation is an intermediate, the reaction would be a classical (electron transfer) photosensitized process (Scheme IIc).[28-29]

The way we envisage the reaction is depicted in Scheme III, where two reactive intermediates, which for the moment are designed as exciplex and radical ion pair are considered (see below for nearer characterization), and these are in equilibrium, with back electron transfer within the pair faster (k_5) than charge separation (k_4). The ion pair gives almost exclusively the endo[4+2]dimer **1**, and the exciplex (besides the cycloadducts, among which the endo adduct at positions 1,2 predominates) the [4+2]dimers with a much larger proportion of exo dimer **2**. Intersystem crossing from the ion pair leads to the



Scheme I,I



Scheme III

lowest lying triplet (this is CHD^{3*} with both NN and NDN, but not with ADN, Table VI).

Effect of the experimental parameters on the competing processes. The case of NN as sensitizer has been more fully investigated and is discussed first. In the range of concentration explored three situations arise. With $[CHD] > 0.5$ M, $k_2\ [CHD] \geq k_4$; thus a substantial part of the exciplex is quenched and yields the dimers via an excited termolecular complex according to the model proposed by Schuster.[17,30,31]

$$(A{-}{-}{-}CHD)^* + CHD \longrightarrow (A{-}{-}{-}CHD{-}{-}{-}CHD)^* \longrightarrow A + (CHD)_2 \qquad (8)$$

and the 1/2 ratio is relatively low. With [CHD] between 0.5 and 0.05 M; $k_4 > k_2\ [CHD]$ and $k_6\ [CHD] > k_5$. Hence dimerization essentially involves the ion pair, and the 1/2 ratio reaches the highest values. The results imply that $k_6 > k_5$. From the effect of quenchers on the 4+2 dimerization Schuster[17] obtained the value of $3x10^8 M^{-1}\ s^{-1}$ for the rate constant of the process.

$$CHD^{+\cdot} + CHD \longrightarrow (CHD)_2^{+\cdot} \qquad (9)$$

Given the relatively high CHD concentrations he used, this would correspond in our scheme to k_4 rather than k_6. That the latter constant may be even higher than that does not appear unreasonable in view of the extreme reactivity of the polarized diene. Also the relatively high values obtained for O' imply that neither exciplex decay (k_3) nor dissociative back electron transfer (k_7) are very fast, $k_3 \leq k_7 \leq k_6/20$. literature analogy[32] support that k_3 does not exceed $2x10^7\ s^{-1}$. As for back electron transfer, the span of measured values is relatively large, and the upper limit is over $10^{10} s^{-1}$.[33] We suggest that this process is slower in the present case, probably because of the high energy of the radical ion pair (see Table II), and indeed a decrease of two or three order of magnitude have been observed for ion pair of comparable energy.[33] Finally, for [CHD] < 0.05M the radical ion pair is less efficiently trapped, and a significant part of the reaction occurs from the exciplex again (with decreasing 1/2 ratio).

The medium polarity affects both the rates of reaction, k_2 and k_6, which is reasonable since the Diels Alder process requires that the complexed diene is strongly polarized, but not the rate of the diene-NN addition where there is no such demand) and the equilibrium k_4/k_5. In apolar benzene both effects are observed, and sensitized dimerization proceeds with a poor quantum yield. In solvents of intermediate polarity such as dichloromethane and dimethoxyethane, on the other hand, 4+2 dimerization is substantially quenched, but 2+2 dimerization is enhanced. This is not due to sensitization of CHD by NN^{3*} formed by direct inter system crossing from NN^{1*}, since this would not give a Φ_T higher than in benzene and acetonitrile (considering that the fluorescence quantum yield of NN drops by only a 24% from acetonitrile to dichloromethane, viz. from 0.21 to 0.16, and thus the increase in k_{isc} in the heavy atom-containing solvent does not explain the observed effect, viz. at least a trebling of Φ_T). Rather, this is an indication that equilibration to the radical ion pair remains operating, and intersystem crossing from there now overcomes reaction with a second CHD molecule (this is not due to the effect of the chlorine atoms, since dimethoxyethane gives virtually the same results, and thus a decrease in k_6 rather than an increase in k_8 is involved). The increase of Φ_T is obviously larger at low [CHD], and does not go beyond a certain limit because competition with k_7 remains important.

As for the two different salt effects observed, the first one (with perchlorates, fluophosphates, fluoborates) has the characteristics of a general salt effect; with enhanced ionic strength both k_3 and the reaction rates increase beyond the value in neat acetonitrile. The effect is fully comparable to an increase in solvent polarity, and here again the ratio 1/2 (Table III) does not increase regularly with the salt concentration, an indication that also k_2, and not only k_3 and k_6 is affected.

A different situation arises with the strongly coordinating chloride and bromide anions. As reported in the results section, the observed effect (dramatic drop of Φ_{RC}, increase of Φ_T) is only in part due to quenching and induced i.s.c. of NN^{1*} by the salt. The major part is rather due to binding of both exciplex and radical ion pair by the strongly complexating anions. The end result is both unproductive decay to the ground state and increased intersystem crossing

$$(A\text{---}CHD)^* \text{ or } (A^{\cdot-}/CHD^{\cdot+}) + Cl^- \longrightarrow (A/CHD/Cl)^- \qquad (10)$$

$$(A/CHD/Cl)^- \longrightarrow A + CHD + Cl^- \qquad (11)$$

$$(A/CHD/Cl)^- \longrightarrow A + CHD^{3*} + Cl^- \qquad (12)$$

In our systems the cation present has little importance, even when an high atomic weight ion (cesium) is used. Thus the phenomenon is related to the specific complexation of the polarized diene.

Other additives also affect the process. Thus, protonation by trifluoroacetic acid and presence of methanol (acting either as nucleophile or as protonating agent) quench the 4+2, but scarcely the 2+2 dimerization, showing that the effect is mainly on the radical ion pair, substituting of different process for k_6 but leaving k_8 unchanged. Quenching by protonation of a complexed excited acceptor or of the corresponding radical anion has ample precedent,[34] and likewise the small enhancement of Φ_{RC} by a pyridine has a precedent in another cycloaddition via radical ions.[35]

Effect of the sensitizer's structure. In general, the same trend of NN is observed also with NDN as far as the dimerization is concerned, though in the latter case the naphthalene-diene photoaddition is less efficient, due to the greater polarity of the exciplex.[6] ADN is a relatively poor sensitizer. Competition between the various processes as well as the relative effect of the additive depend on the sensitizer used. A (possibly naive) attempt to correlate the reaction output with ΔG_{et}, as determined by the reagents redox parameters and solvent dielectric constant (see eqs 5,6 and Table VI) is discussed in the following and, for some parameters, graphically expressed in Figure 2 for the case of [CHD]=0.1 M.

Thus, high quantum yield for 4+2 dimerization and high 1 to 2 ratio require $\Delta G_{et} \leq -0,4$ eV. Enhancing ionic strength has a positive effect for an intermediate degree of charge transfer (NN in MeCN, NDN and ADN in CH_2Cl_2), where indeed there is room for medium effect, whereas for $\Delta G_{et} \leq -0,65$ or ≥ -0.25 the effect is scarce because the limit of polarization has already been attained in the first case, and in the latter one charge separation (k_3) remains unfavourable even under this forcing conditions. The special salt effect of halides is likewise dependent on ΔG_{et}; for very negative values (NDN and ADN in MeCN) quenching of both Φ_{RC} and Φ_T is observed (Table I, column b); apparently in these case the fully ionized complex reacts only according to eq. 11. On the other hand with moderate charge transfer quenching of Φ_{RC} is less important (consistently with the idea that the more separate are the charges the stronger is the complexation) and Φ_T tend to increase (eq. 12 takes over).

The free energy change for electron transfer to the excited state is not the only important parameter, however, as is apparent from the low quantum yield of ADN-sensitized dimerization, in comparison with the results with the naphthalene derivatives with comparable ΔG_{et}. This is explained by the higher rate for back electron transfer (k_7) in the former case reasonably related to the lower energy of the radical ion pair (Table VI, compare ref. 33).

Some 2+2 dimerization is induced by the chloride even with ADN, though this has a triplet energy lower than CHD. In the case of TCBQ, spin slows down back electron transfer.

In the absence of the salts, the triplet pathway is important for moderate charge transfer (NN in CH_2Cl_2) rather than when either there is no radical ion pair (reaction in

Table VI. Parameter for electron transfer from the sensitizers to CHD, eV

Substracts	E(S)	$E_{½}(A/A^{\overline{\cdot}})$	E(T)	$\Delta G_{et}(S)^{a}$	(b,	c)	$\Delta G_{et}(T)^{a}$	$E(A^{\overline{\cdot}}, D^{\overset{+}{\cdot}})^{d}$
NN	3,75	-1.98^{e}	2.49	-0.42	-0.22	0.28		3.33
NDN	3,45	-1.28^{e}	2.41	-0.82	-0.62	-0.12		2.63
ADN	2,88	-0.89^{e}	2.03	-0.64	-0.42	0.06		224
TCBQ		0.02^{e}	2.70				-1.33	1.33
CHD		1.35	2.29					

a disregarding the E_{coul} term (see eq. 7): this makes little difference in MeCN

b ΔG_{et} (S) in dichloromethane, see text for the approximation used

c ΔG_{et} (S) n benzene, see note b

d energy of the ion pair with $CHD^{\overset{+}{\cdot}}$, simply calculated from the algebraic sum of the redox potential, not taking in account any stabilization

e vs SCE, Farid, S.; Mattes, S.L. Org.Photochem. 1983, 6, 233

f E½ $(D/D^{\overset{+}{\cdot}})$ vs SCE; Baltes, H.; Steckhan, E.; Schafer, H.J. Chem.Ber. 1978, 111, 1294.

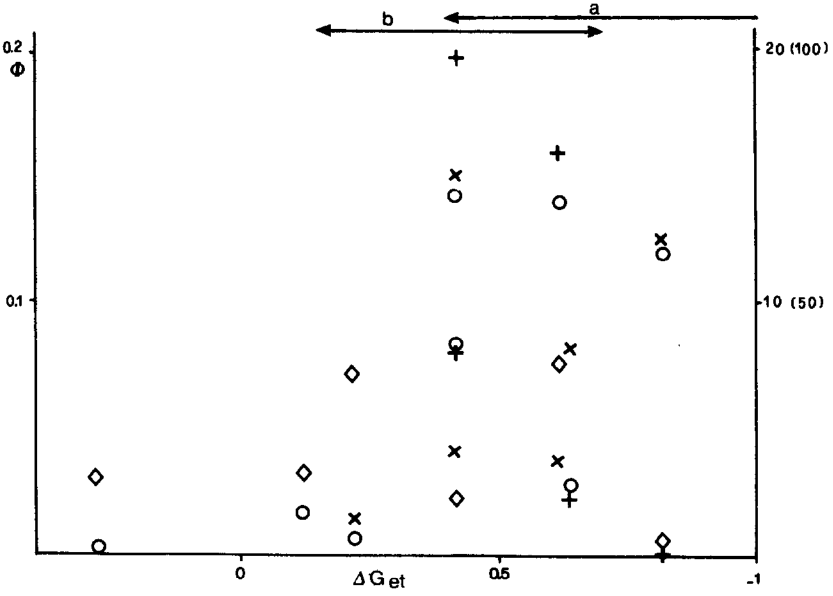


Figure 2. Relation of the steady-state parameters for photosensitized CHD (0.1M) dimerization with ΔG_{et} (eV). Quantum yield for radical cation (Φ_{RC}, ○) and triplet (Φ_{T}, ◇) dimerization (see left-hand units); 1/2 ratio (x, right hand units); % increment of Φ_{RC} in the presence of 0.05 N Et_4NClO_4 or Et_4NPF_6 (+, right hand units in parentheses). For $\Delta G_{et} < -0.35$ eV (region a) Φ_{RC} and the 1/2 are mostly (but not necessarily) high, and involve both intermediates, exciplex and radical ion pair (region b) triplet dimerization and increment of Φ_{RC} with the salts maximize. In the regio 0.1 to -0.3 eV 2+2 cycloaddition between the naphthalene and the diene takes also place (not reported here) through the same exciplex intervening in the dimerization (via the triplex) and at $\Delta G_{et} > 0.1$ eV only 4+4 cycloaddition though a different exciplex occurs.

benzene) or charge separation is predominant (NDN in MeCN), again showing the role of the ion pair in the triplet pathway.

Structure of the intermediate. Though the change in the product distribution demands the intermediacy of two different sensitizer-CHD complexes, the question of their structure remains open between the extreme hypotheses of they being two conformationally different exciplexes (this is sufficient to explain the different 1 to 2 ratio obtained and there is precedent for the conformation of the exciplex being conserved in the photoadduct configuration)[36] and of one of them being a covalent exciplex and the other corresponding to the free solvated ions. It appears to us that the results agree rather with intermediate structures, possibly with a continuous variation. On one hand, occurring of a Diels Alder reaction via a ternary complex demands that the exciplex is polarized, and the medium polarity on k_2 is consistent with this idea. Furthermore, it has been previously shown on the basis of the phoadducts effect structure that the NN-CHD exciplex (and a fortiori this holds for the other nitriles) has a pronounced charge transfer character and is different from the covalent complexes formed e.g. by naphthalene and CHD[6]. The extensive studies by Schuster of the triplex Diels-Alder reaction also points to polar exciplexes as the first intermediates.

On the other hand, though free radical ions might be indicated by some features of the reaction, e.g. the leveling of Φ_{RC} for $\Delta G_{et} < -0.3$ eV, some difference with the sensitizer structure do remain, and furthermore the effect of sone additives, in particular that of acids, is well explained by a radical ion pair where some mutual influence of the opposite charged ion remains (quite possibly a solvent penetrated ion pair as described by Farid),[33] whereas protonation of $A^{\cdot-}$ should not affect negatively the reaction of $CHD^{\cdot+}$ were the independent solvated species involved. Likewise, the magnesium, but not the tetraethylammonium, cation is known to prolonge the radical anion lifetime in the NDN-trans-stilbene system by a factor of 10,[24b] and again this find no correspondence in the salt effect on the present reaction.

Positive evidence for the free radical ions is not unambigous; although Schuster detected the $NDN^{\cdot-}$ absorbtion after flash photolysis of a solution containing 0.58 2M CHD,[17] we notice that, when CHD is in the range 0.05 or below both $NDN^{\cdot-}$ and $ADN^{\cdot-}$ absorptions are less than 15 times as intense as observed with the same experimental setting when the donor is trans-stilbene. Since at these concentrations the quantum yield of reaction remains high, it is unlikely that, whould the free anions be on the main path of reaction (Figure 2c), their absorption would not be more intense. Therefore, it appears more likely that small amounts of the free ions are formed in a side pathway.

A further element is that while several Diels-Alder reaction between different dienes have been reported, cross-addition is not always successful. It has been previously reported,[16-18] and we confirm here, that this is the case for the CHD-2,5-dimethylhexadiene (DMHD) system with aromatic nitriles as sensitizers. Thus, the normal dimerization is quenched while cross-adducts are found only in traces; in contrast, cross addition works well with aminium salts initiation[13] and pyrilium salts photosensitization.[20] While quenching of CHD dimerization is easily rationalized on the basis of the low oxidation potential of DMHD, failure of CHD-DMHD addition which is actually obtained in conditions more favourable for the formation of the free radical ions (see above) shows that a different situation obtains with the aromatic sensitizer. Indeed, we showed that the DMHD (a s-trans diene) complexes with naphthalenenitriles have a different geometry from the CHD complexes.[6] This conformation leads to adducts with the CN group of the sensitizers and not on the ring and it appears reasonable that, being the donor in a peripheric position it is not suited for diene dimerization, which probably requires parallel stacking of the aromatic rings. Thus again indicates the influence of $A^{\overline{\cdot}}$ on $D^{\ddagger}$ reactivity, and thus a radical ion pair.

At very negative ΔG_{et} value, or with triplet (e.g. TCBQ) or charged (e.g. pyrilium salts) acceptors the free ions limit is probably reached.

A tentative rationalization of the pressure effect reported by Turro and Mattay[33] in the frame of this scheme would be that in acetonitrile pressure affects the k_4/k_5 equilibrium towards the more compact exciplex (small positive effect on the **2/1** ratio), and in benzene the [4+2] to [2+2] dimers ratio increases because again the exciplex reaction is favoured in comparison to solvent penetration and collapse of the radical ion pair to the CHD triplet (k_8).

Conclusion

We think that the present results, together with other ones, e.g. those concerning the photoreaction between acceptors and alkylbenzenes,[37] identify the radical ion pair as an intermediate different from both the exciplex and the free solvated radical ions, with a chemistry of its own. With respect to previous studies new aspects have been evidenced, viz. that the equilibrium between the transient intermediates and the complex salt effect upon them.

The equilibrium between two species, the exciplex and the (solvent penetrated?) ion pair explains these results and probably a sizeable part of the bimolecular photochemistry of aromatics. Collapse of the pair to free solvated radical ions is important either when the radical cation has available a mechanism for stabilization (this is the case e.g. with the extensively delocalized, non planar stilbene radical cation),[33,38] or when other factors favour separation (e.g. with a charged acceptor such as pyrilium salts).[20] In the other cases stabilizing interaction of the π-systems of donor and acceptor remain the dominating factor, even with a strong charge transfer character.

Experimental section

Materials. 1,3-Cyclohexadiene (Aldrich) was fractionally distilled from $NaBH_4$ shortly before use. 1,4-Naphthalenedicarbonitrile and 9,10-anthracenedicarbonitrile were prepared from the corresponding bromides by heating with CuCN; these materials, as well as commercial (Aldrich) 1-naphthalenecarbonitrile were purified by alumina chromatography and recrystallization. 2,3,4,5-Tetrachlorobenzoquinone, 2-acetonaphthone (Merck), and the lithium, magnesium, tetraethylammonium and tetrabutylammonium salts were recrystallized commercial samples (Fluka or Carlo Erba). Cesium perchlorate was prepared by treating the carbonate with $HClO_4$ and recrystallization. Acetonitrile and benzene were distilled from CaH_2. *Endo*- and *exo*-tricyclo[6.2.2.0^{2,7}] dodeca-3,9-diene (2) were prepared by the tris (*p*-bromophenyl)ammoniumyl hexachloroantimonate catalized dimerization according to Bauld.[13b] Dimer 2 as well as *trans* (3) and *cis*-tricyclo[6.4.0.0.^{2,7}]dodeca-3,H-diene (4) were prepared by 2-acetonaphthone photosensitization.[7]

Quantum Yield Measurement. Irradiations were effected either by means of an Applied Photophysics multilamp apparatus fitted with phosphor-coated lamps centered at 320 (NN, NDN, TCBQ, AN) or 360 nm (ADN), using tubes arranged in a merry-go-round apparatus, or by means of a focalized high pressure mercury arc fitted with an interference filter (centered at 313, or, respectively, at 365 nm), using spectrophotometric cuvettes. Solutions were degassed by the freeze-degas-thaw procedure. Ferrioxalate actinometry was used in the experiments with cuvettes. The CHD dimers were determined by glc using a nonpolar capillary column (HP1, 25 m), maintaining the injector temperature at 150°C in order to avoid thermal decomposition or interconversion. The observed photosensitized dimerization was linear with time in the range explored (up to $2x10^{-5}$ mM consumed CHD). The initial concentration of the sensitizer was $5x10^{-3}$ M. The consumption of the sensitizers was determined by hplc and by direct spectrophotometric measurement in the couvette.

Fluorescence Measurements. Fluorescence spectra and intensities were measured by means of Aminco-Bowman MPF spectrophotofluorometer using degassed samples. The fluorescence quantum yield of NN was determined by comparison with 2-methoxynaphthalene (literature value 0.42 in toluene),[39] and resulted: 0.21 (MeCN); 0,205 (C_6H_6); 0.17 ($CH_3O(CH_2)_2OCH_3$), 0.16 (CH_2Cl_2). Fluorescence quenching experiments gave linear Stern-Volmer plots.

Aknowledgement. This work was supported by Consiglio Nazionale delle Ricerche, Roma.

References

1 Mattes, S.L.; Farid, S. *Acc.Chem.Res.*, 1982, *15*, 80.
2 Fox, M.A.; Chanon, M., eds., Photoinduced Electron Transfer, Elsevier, Amsterdam, 1988.
3 Kavarnos, G.J.; Turro, N.J. *Chem.Rev.*, 1986, *86*, 401.
4 Lewis, F.D., Carbon-Carbon Multiple Bonds, in ref. 2, vol. C, p.1.
5 Albini, A.; Sulpizio, A. Aromatics, in ref. 2, vol. C, p. 88.
6 Albini, A.; Fasani, E.; Giavarini, F. *J.Org.Chem.*, 1988, *53*, 5601.
7 Valentine, D.; Turro, N.J.; Hammond, G.S. *J.Am.Chem.Soc.*, 1964, *86*, 5202.
8 Alder, K.; Stein, G. *Justus Liebigs Ann.Chem.*, 1932, *496*, 197.
9 Schenk, G.O.; Mannsfeld, S.P.; Schomburg, G.; Krauch, C.H. *Z.Naturforsch. Teil B*, 1964,

19, 18.

10 Schutte, R.; Freeman, G.R. J.Am.Chem.Soc., 1969, 91, 3715.

11 Penner, T.L.; Whitten, D.G.; Hammond, G.S. J.Am.Chem.Soc., 1970, 92, 2861.

12 Bellville, D.J.; Wirth, D.D.; Bauld, N.L. J.Am.Chem.Soc., 1981, 103, 718.

13 (a) Bauld, N.L.; Bellville, D.J.; Harirchian, B.; Lorenz, K.T.; Pabon, R.A.; Rehynolds, D.W.; Wirth, D.D.; Chiou, H.S.; Marsh, B.K. Acc.Chem.Res., 1987, 20, 371 (b) Reynolds, D.W.; Lorenz, K.T.; Chiou, H.S.; Bellville, D.J.; Pabon, R.A.; Bauld, N.L. J.Am.Chem.Soc., 1987, 109, 4960 (c) Lorenz, K.T.; Bauld, N.L. J.Am.Chem.Soc., 1987, 109, 1157.

14 Gassman, P.G.; Singleton, D.A. J.Am.Chem.Soc., 1984, 106, 6085; ibid., 7993.

15 Nigenda, S.E.; Sleich, D.M.; Narange, S.C.; Keumi, T. J.Electrochem.Soc., 1987, 134, 2465.

16 Jones, C.R.; Allman, B.J.; Mooring, A.; Spahic, B. J.Am.Chem.Soc. 1983, 105, 652.

17 Calhoun, G.C.; Schuster, G.B. J.Am.Chem.Soc., 1984, 106, 6870.

18 Mattay, J.; Trampe, G.; Runsirk, J. Chem.Ber., 1988, 121, 1991.

19 Chung, W.S.; Turro, N.J.; Mertes, J.; Mattay, J. J.Org.Chem., 1989, 54, 4881.

20 Mlcoch, J.; Steckhan, E. Angew.Chem. Int.Ed.Engl., 1985, 24, 412.

21 Mattay, J;, Gersdorf, J;, Mertes, J. J.Chem.Soc., Chem.Commun., 1985, 1088.

22 Bahurel, Y.L.; Mac Gregor, D.J.; Penner, T.L.; Hammond, G.S. J.Am.Chem.Soc., 1972, 94, 637.

23 Santamaria, J., in ref. 2, vol. B, p. 483.

24 (a) Goodman, J.L.; Peters, K.S. J.Am.Chem.Soc., 1986, 108, 1700. (b) Goodson, B.; Schuster, G.B. Tetrahedron lett., 1986, 3123. (c) Mc Cullough, J.J.; Yeroushalmi, S J.Chem.Soc. Chem.Commun., 1983, 254 (d) Kitamura, N.; Imabayashi; S., Tazuke, S. Chem.Lett. 1983, 455 (c) Masnovi, J.M.; Levine, A.; Kochi, J.K. J.Am.Chem.Soc., 1985, 107, 4356.

25 Rehm, D.; Weller, A. Isr.J.Chem., 1970, 8, 259.

26 Weller, A.; Z.Phys.Chem. (Munich), 1982, 133, 93.

27 Eberson, L.; Olofsson, B. Acta Chem.Scand., 1988, B42, 336.

28 Arnold, D.R.; Maroulis, A.J. J.Am.Chem.Soc., 1976, 98, 5931.

29 Albini, A. Synthesis, 1981, 249.

30 Calhoun, G.C.; Schuster, G.B. J.Am.Chem.Soc., 1986, 108, 8021.

31 Akbulut, N.; Hartsough, D.; Kim J.I.; Schuster, G.B. J.Org.Chem., 1989, 54, 2549.

32 (a) Caldwell, R.A., Creed, D., Acc.Chem.Res., 1980, 13, 45 (b) Stevens, B., Adv.Photochem., 1971, 8, 161.

33 (a) Gould I.R.; Ege, D.; Mattes, S.L.; Farid, S. J.Am.Chem.Soc., 1987, 109, 3794. (b) Gould, I.R.; Moser, J.E.; Ege, D;, Farid, S. J.Am.Chem.Soc., 1988, 110, 1991. (c) Gould, I.R.; Moody, R.; Farid, S. J.Am.Chem.Soc., 1988, 110, 7242. (d) Gould, I.R.; Farid, S. J.Am.Chem.Soc., 1988, 110, 7883. (e) Gould, I.R., Moser, J.E.; Armitage, B.; Farid, S.; Goodman, J.L.; Herman, M.S. J.Am.Chem.Soc., 1989, 111, 1917.

34 See e.g. Albini, A.; Fasani, E.; Oberti, R. Tetrahedron, 1982, 38, 1027.

35 Mattes, S.L.; Farid, S. J.Chem.Soc., Chem.Commun., 1980, 457.

36 Yang, N.C.; Libman, J.; Savitzky, M. J.Am.Chem.Soc., 1972, 94, 9226.

37 (a) Albini, A.; Fasani, E.; Mella, M. J.Am.Chem.Soc., 1986, 108, 4119. (b) Albini, A.; Fasani, E.; Sulpizio, A. J.Am.Chem.Soc., 1984, 106, 3562. (c) Sulpizio, A.; Albini, A,; d'Alessando, N.; Fasani, E.; Pietra, S. J.Am.Chem.Soc., 1989, 111, 5773.

38 Spada, L.T.; Foote, C.S. J.Am.Chem.Soc., 1980, 102, 391.

39 Laposa, J.D.; Lim, E.C.; Kellog, R.E. J.Chem.Phys., 1965, 42, 3025.