THE PHOTOCYCLOADDITION OF DICHLOROVINYLENE CARBONATE TO BENZENE AND NAPHTHALENE

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ABSTRACT

The mechanism of the photocycloadditions of dichlorovinylene carbonate (DCVC) to benzene and naphthalene, and the structures of the products, are described. Energy transfers from triplet-sensitizers ($E_T \geqslant 68$ kcal/mol) to DCVC as well as direct excitation of S_1^*-naphthalene initiate the sequence of reactions to give cycloadducts.

^{3}(DCVC)* leads to 1,2- and 1,4-adducts in a consecutive reaction pathway with either benzene or naphthalene, whereas the S_1^*-naphthalene gives the 1,2- and 1,4-adduct in parallel reactions via a common intermediate.

INTRODUCTION

Since the classical results of Angus and Bryce-Smith[1], and Schenck and Steinmetz[2] as well as Grovenstein, Rau and Taylor[3], who almost simultaneously discovered the photochemical cycloaddition of two molecules of maleic anhydride (MSA) to the benzene ring, which proceeds under either direct[1] or sensitized[2,4] irradiation of benzene solutions of MSA, many additional findings in this field have been published[5-15], reviewed[16], and treated theoretically[17]. Moreover acetylene derivatives[18,19], and more recently olefins[20,21] as well as 1,3-dienes[22,23] have been used as cycloaddition partners to benzene, benzonitrile[24,25], or anthracene[26,27]. In a number of cases the product formation proved to be a significant pathway of exciplex decay[28-30]. In addition the photochemistry of simple aromatic molecules including some heterocycles in the gaseous state has also been reviewed recently[31]. In the naphthalene series obviously 2-alcoxinaphthalene photochemically dimerizes in solution and shows excimer fluorescence[32-34]. Although maleic anhydride and naphthalene give no photoadducts[35], 1,3-dienes[36], acetylene dicarboxylic ester[37,38], cinnamic acid ester[39] and recently acrylonitrile[40-42] have been found to form significant photoadducts. Here again, exciplex formation seems to be an important factor in product formation.

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† Contribution of the preparative results in the naphthalene series.

Scheme 1
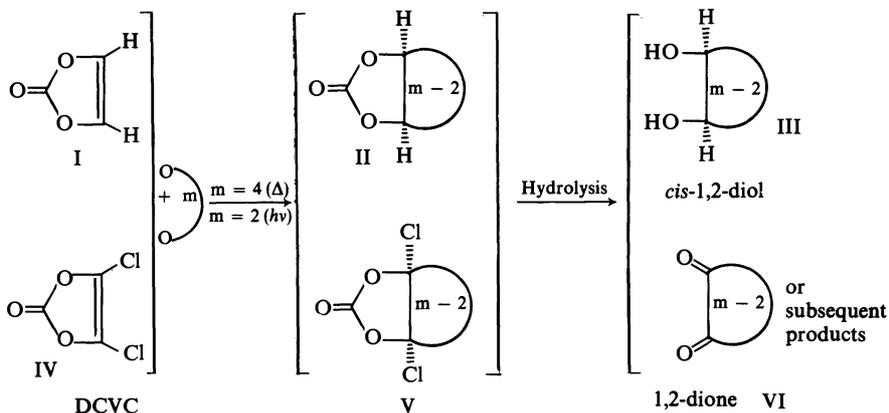
GENERAL APPLICATION OF VINYLENE CARBONATES AS CYCLOPHILES

From its first discovery by Newman and Addor in 1953 vinylene carbonate (I)[43] has been widely used as cyclophile in thermal as well as in photochemical cycloaddition reactions (reviewed in ref. 44).

As a synthetic tool I introduces an α-glycol function into the cycloadducts II when it reacts with a m-centred π-electron system as partner on either thermal or photochemical initiation. Dichlorovinylene carbonate IV is prepared by

Scheme 2
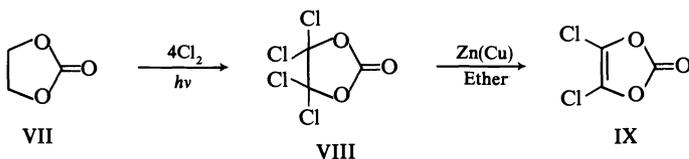
exhaustive chlorination of ethylene carbonate VII and subsequent treatment of the tetrachloroethylene carbonate VIII with zinc[45]. The dichloro derivative IV is a cyclophile with properties complementary to I. Cycloadducts V formed under analogous conditions contain a masked α-diketo function, from which subsequently the α-diketo function VI is liberated by simple hydrolysis of the adducts V. Thus various thermal and photochemical cycloadducts with olefins, dienes and acetylenes have been described in the past decade, which justifies the expectations put into their abilities to act as a quite common preparative tool in synthetic chemistry[44]. Contrary to their common applicability particularly in photochemical synthesis very little is known about the electronic structure of vinylene carbonates, or the question of excitation energy transfer to the compounds as well as kinetic data of the photochemical systems considered.

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To clear up these questions initially some experimental facts should be demonstrated.
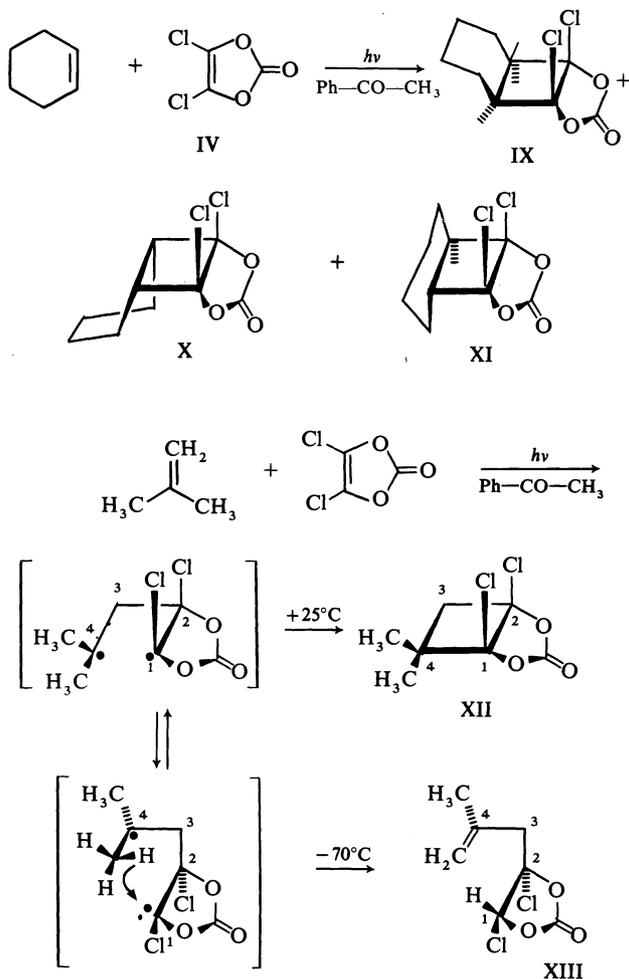
Scheme 3

SENSITIZED PHOTOCHEMICAL CYCLOADDITION OF DCVC TO OLEFINS

Apart from cycloaddition to aromatic compounds, IV adds even more readily to simple olefins under sensitized conditions. In contrast to Barltrop's and Robson's observations on the system MSA–cyclohexene[46, 47] there is no CT-complex detectable between IV and cyclohexene; however, corresponding products IX–XI are formed[48, 49]. From these results two essential features of the reaction appear which demonstrate that a two-step ring-closure mechanism is involved:

(1) the appearance of a *trans*-fused adduct XI,

(2) the formation of an ENE-adduct XIII at $-70°C^{50}$, when isobutylene is used as an olefinic partner; that means, the decay of an intermediate 1,4-diradical species proceeds obviously through an intramolecular hydrogen-abstraction process at low temperatures, which establishes an alternative double bond within the adduct when the diradical conformation is not favoured for ring closure and rotational movement is hindered.

One can assume that a triplet energy-transfer mechanism initiates the reaction sequence, but one has to provide evidence as to which of the two partners accepts the energy from the excited sensitizer, and whether this happens in a diffusion-controlled process.

The electronic structure of dichlorovinylene carbonate
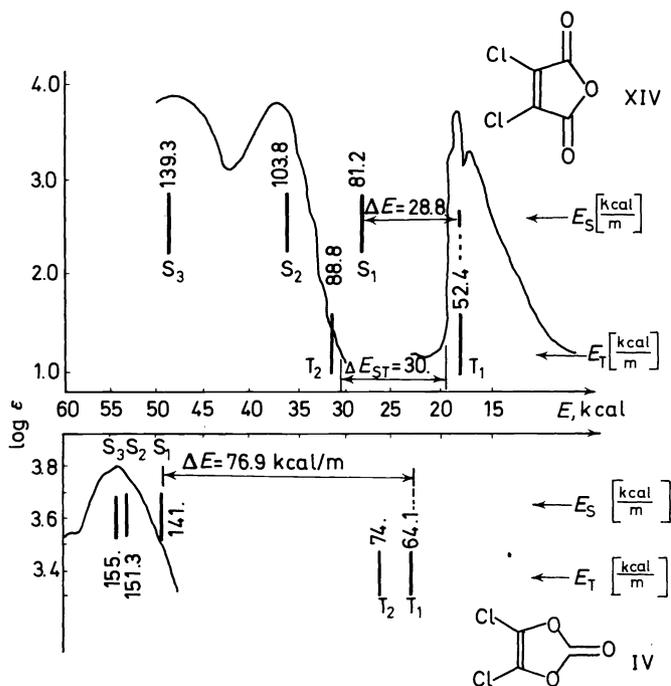
Figure 1. Experimental (curves) and calculated (bars) energy levels of IV and XIV.

Dichlorovinylene carbonate IV has its first absorption maximum below 200 nm (*Figure 1*) in the vacuum-u.v.[51]. Falsely attributed absorption above 300 nm proved to be originated by oxalyl chloride which contaminates IV when stored at room temperature (neat or in solution)[44, 48]. CT-absorption bands of IV and mesitylene which are described by Lechtken and Hesse[52], again are caused by oxalyl chloride and are completely absent if pure IV is

used[48]. Unfortunately pure IV shows neither fluorescence nor phosphorescence.

To get more information about the electronic structure of IV, the π-absorption and π-emission spectra of IV were calculated with a PPP-SCF-CI model[53]. Four different parameters have been considered:

(1) the valence state ionization potentials W_μ,
(2) the one-centre repulsion integrals $\gamma_{\mu\mu}$,
(3) the two-centre repulsion integrals $\gamma_{\mu\nu}$,
(4) the resonance integrals $\beta_{\mu\nu}$.

The evaluation of the two-centre repulsion integrals $\gamma_{\mu\nu}$ was accomplished in line with the Nishimoto approximation[54]. The other parameters were
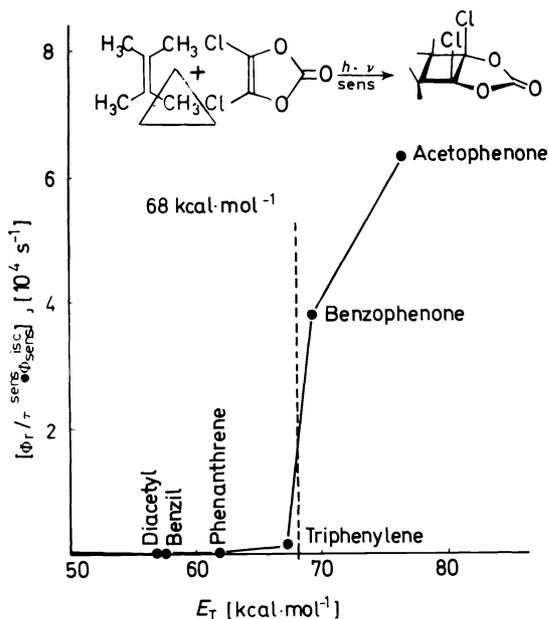
Figure 2. Sensitized cycloaddition of tetramethyl ethylene to IV in dioxan.

taken from Koutecky and Michl[55], Hinze and Jaffé[56], Prichard and Skinner[57], and Fabian[58]. The model has been proved on furan and phenol[59] with good agreement. To check the calculated results, dichloromaleic anhydride XIV which shows a pronounced phosphorescence emission[60] was used as test substance (Figure 1). Both the first singlet- and triplet-transition energies seem to appear at longer wavelengths than the measured 0,0 bands. Thus in the case of IV the lowest triplet level is calculated to exhibit at $> 64\,kcal/mole$ above the ground state. To support these calculations experimentally the sensitized cycloaddition of tetramethyl ethylene to IV in dioxan has been investigated applying sensitizers of decreasing triplet energy (Figure 2).

In the expression

$$k_{ET} \sim \Phi_r/(\tau_{sens}\Phi_{isc}^{sens})$$

in which Φ_r is the product quantum yield of the tetramethyl ethylene adduct to IV, τ_{sens} the phosphorescence lifetime, and Φ_{isc}^{sens} the quantum yield of intersystem crossing of the sensitizer, k_{ET} represents to a first approximation the rate of energy transfer from ^{3}sens* to IV. It is easily seen from *Figure 2*, that the energy of the lowest triplet level of IV at about 68 kcal/mole is a realistic approach, and corresponds fairly with the calculated result.

To ensure that the energy acceptor is really the dichlorovinylene carbonate IV rather than the olefinic partner, we have used the quenching of the type II cleavage of butyrophenone[61, 62] by IV and its various partners as a test. The results are shown in *Figure 3*. The diffusion controlled rate constant in
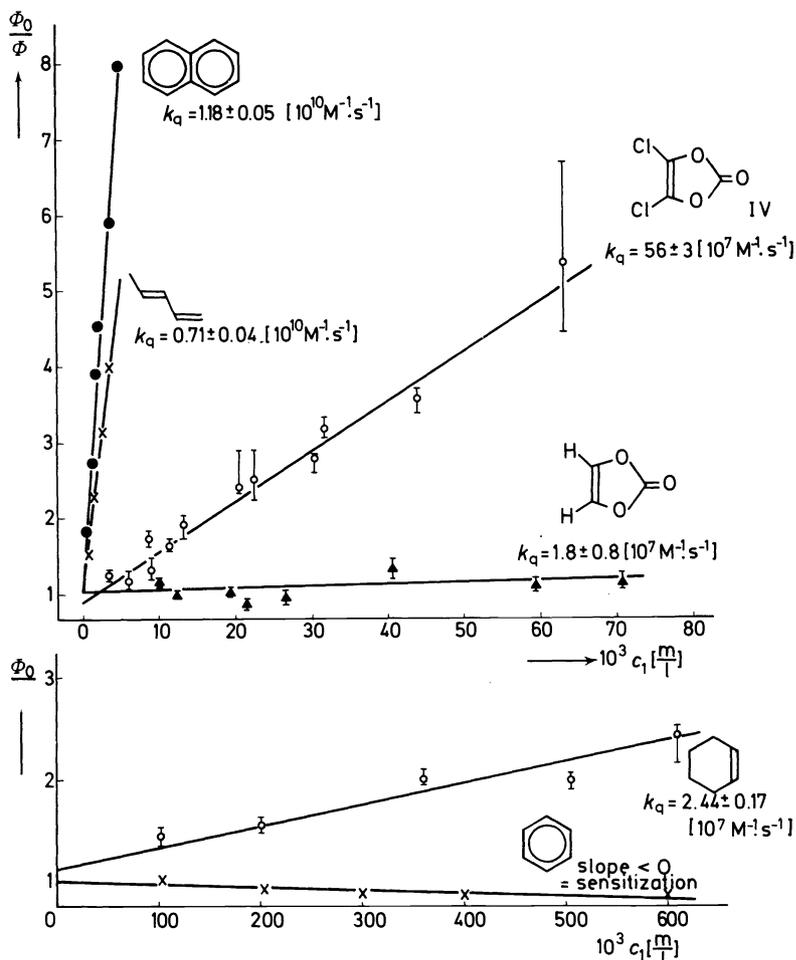
Figure 3. Quenching of the type II cleavage of butyrophenone in *n*-hexane by various materials.

n-hexane to be expected is $2 \times 10^{10}[M^{-1}s^{-1}]$. Therefore naphthalene quenches the type II cleavage of butyrophenone at an appropriate rate. Piperylene quenches nearly as well. The value corresponds to that determined in benzene ($0.5 \times 10^{10} [M^{-1} s^{-1}]$) by Kochevar and Wagner[62]. IV quenches the reaction about twenty times worse compared to naphthalene but far better than the parent compound vinylene carbonate I. It is strange that the phosphorescence of acetophenone is not quenched significantly by IV at 77 K in an ether–i-pentane glass.

Cyclohexene quenches the type II cleavage of butyrophenone as poorly as vinylene carbonate and thus is very unlikely to be the acceptor of triplet energy from the sensitizer in a mixture of IV and cyclohexene.

Benzene does not quench the type II reaction but obviously sensitizes it since the slope is negative.

Dichlorovinylene carbonate IV also quenches the fluorescence of benzene and naphthalene (*Figure 4*). The diffusion controlled quenching constant for dioxan is about $5.1 \times 10^9 [M^{-1} s^{-1}]$, with benzene IV it nearly reaches this value; however, naphthalene is far removed from it but corresponds to the value found for the fluorescence quenching of naphthalene by acrylonitrile[42]: $k_q^{acr.} = 2.3 \times 10^7 [M^{-1} s^{-1}]$ in t-butanol and $7.4 \times 10^6 [M^{-1} s^{-1}]$ in acetonitrile. The k_q value of IV compares with the quenching rate of *trans*-cyclooctene[63].

$\tau_F \approx 29 \times 10^{-9}$ s
$k_q\tau = 7.9 \pm 2$ M^{-1}
$k_q \approx 2.7 \times 10^8$ M$^{-1}\cdot$s^{-1}

$\tau_F \approx 69 \times 10^{-9}$ s
$k_q\tau = 0.63 \pm 0.01$ M^{-1}
$k_q \approx 6.5 \times 10^6$ M$^{-1}\cdot$s^{-1}

$\dfrac{\Phi_0^F}{\Phi^F}$

[DCVC] [m.l^{-1}]
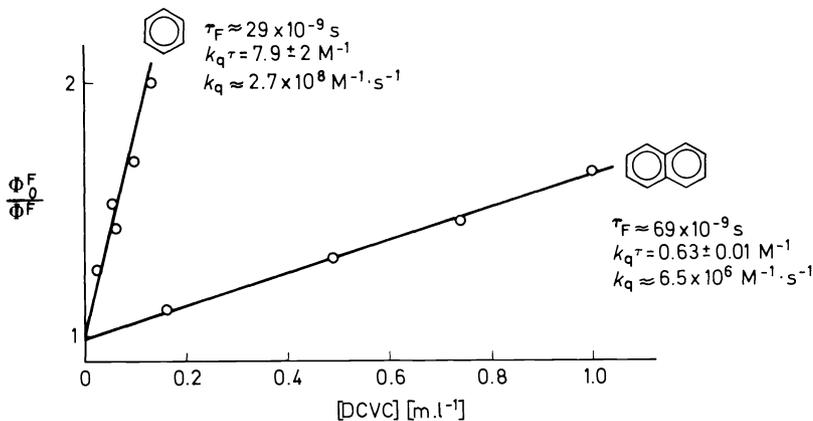
Figure 4. Quenching of naphthalene and benzene fluorescence by IV in dioxan (293 K).

THE SENSITIZED PHOTOCYCLOADDITION OF DICHLOROVINYLENE CARBONATE TO BENZENE

Figure 5 shows the time-dependent product formation of the system: benzene–IV–acetophenone. Mixtures of both the endo- and exo-1,2-adducts XV and XVI are formed primarily at a very rapid rate. Later on the 1,4-cyclo-adduct XVII and the three stereoisomeric 2:1 cycloadducts XVIII–XX appear in the reaction mixture at the expense of the 1,2-adducts which disappear completely with time. Under sensitized conditions (*Figure 6*) the pure
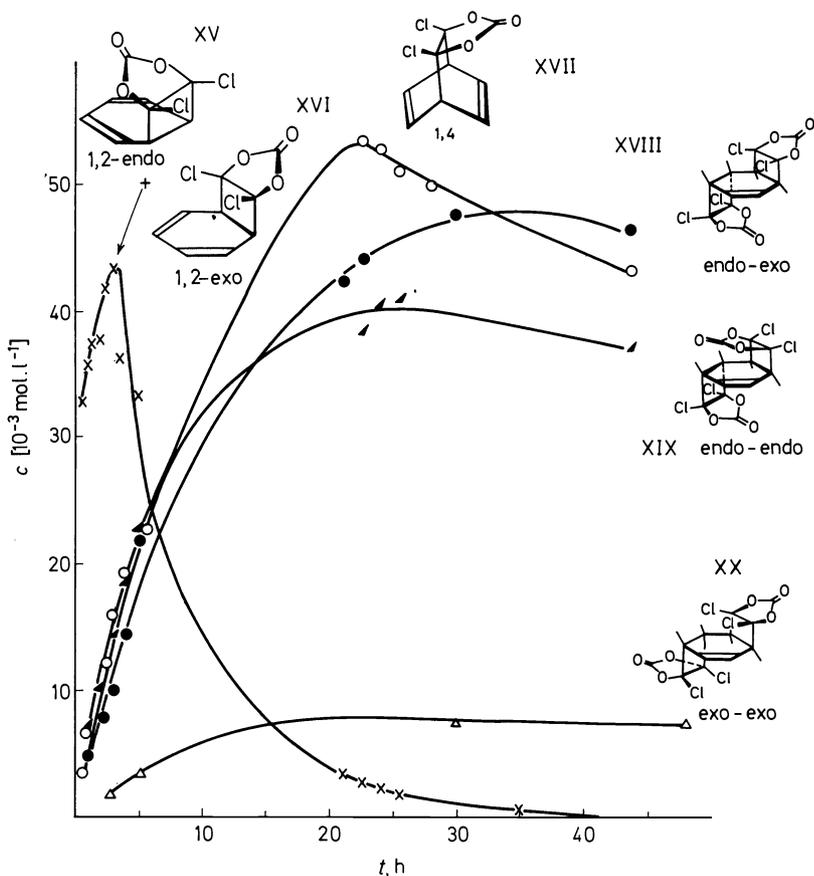
Figure 5. Time-dependent product formation during irradiation of acetophenone with benzene and IV[64, 65].

1,2-exo-adduct XVI rearranges to the 1,4-adduct XVII to the extent of about 20–25 per cent. The remaining amount of XVI cleaves to IV and benzene respectively dimerizes to 2:2-adducts of unknown structure. The relative amount of retrocleavage and dimerization is independent of the triplet energy of the sensitizer used. Down to the triplet energy of biacetyl (55 kcal/mole) nearly the same ratio of rearrangement, cleavage and dimerization is observed[70]. These results are in good agreement with a consecutive reaction pathway assumed from *Figure 5* and offer the possibility for selective preparations of the single adducts. After only short irradiation times the reaction mixtures contain nearly exclusively the 1,2-adducts XV and XVI. The exo-isomer XVI usually crystallizes from the mixture if it is concentrated by a distillation-flow irradiation apparatus[48, 52, 65], whereas the endo-isomer XV remains in solution and is obviously very sensitive to further reactions. The other adducts can be separated and isolated by thin layer chromatography[67].
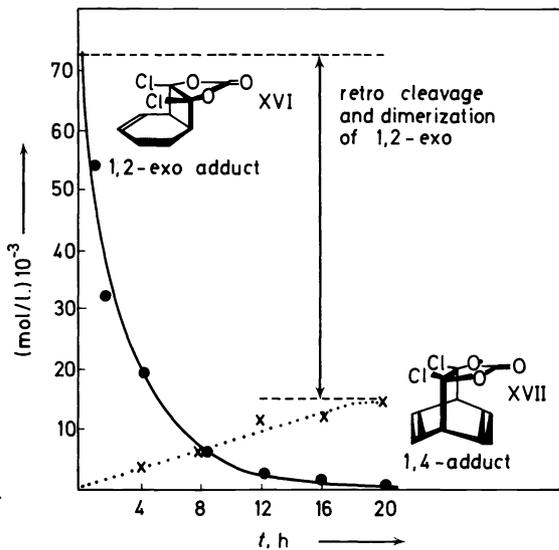
Figure 6. Sensitized rearrangement of the 1,2-exo-adduct → 1,4-adduct in benzene with acetophenone[66].
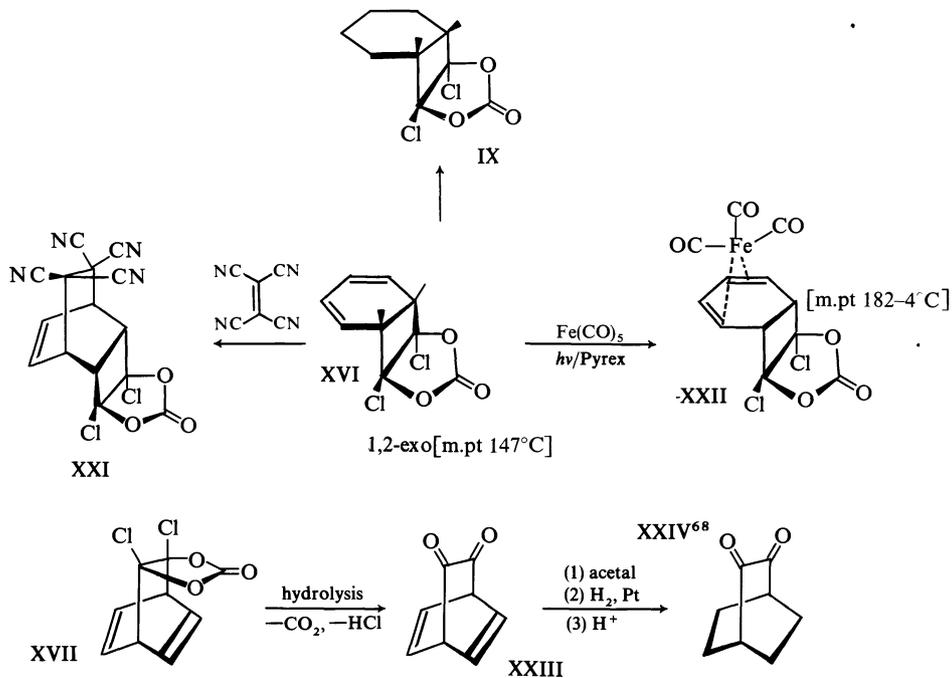
Scheme 4

Structural assignments

The stereochemistry of the easily isolable 1,2-exo-adduct XVI was confirmed by hydrogenation and identification with the exo-1,2-adduct of IV to cyclohexene IX[48]. With tetracyanoethylene, XVI reacts thermally to the Diels–Alder adduct XXI having the structural assignments of the benzene–maleic anhydride photoadduct[65]. The low dienophilic activity of IV[69] prevents the subsequent Diels–Alder adduct formation of XVI and XV with IV in the reaction mixture in a (4 + 2)-cycloaddition. Irradiation of XVI in the presence of iron pentacarbonyl yields a yellow complex probably having the stereochemistry of XXII; also the endo-adduct XV yields a corresponding complex (m.pt 177°C dec.)[70]. Hydrolysis of XVII leads to the barrelene quinone XXIII[65] which is hydrogenated to the bicyclo[2,2,2]octane-dione XXIV described by Alder *et al.*[68].

The structures of the 2:1-adducts XVIII–XX have been elucidated by [1]H-n.m.r.-spectroscopy[65].
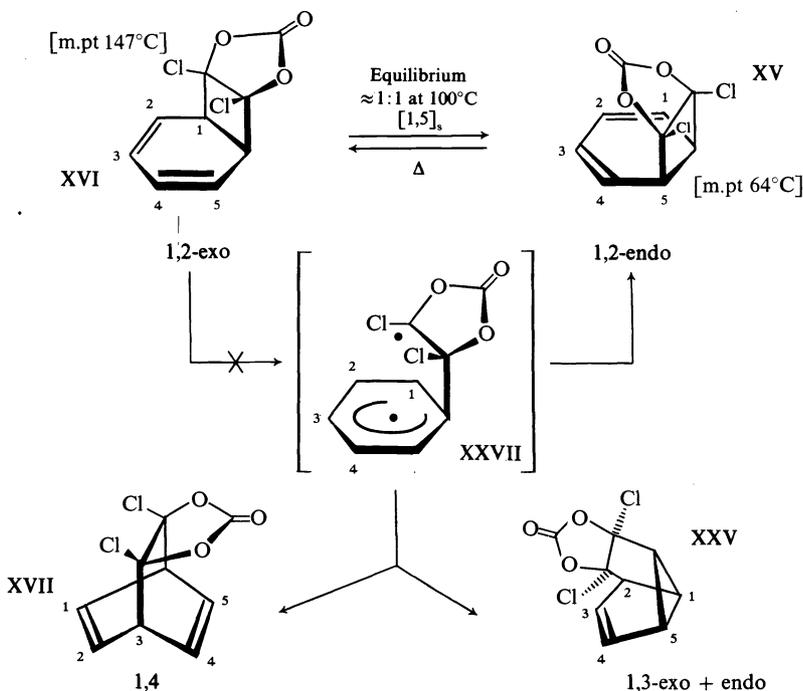
Scheme 5

Under thermal conditions both 1,2-adducts equilibrate to a 1:1 mixture of XV and XVI. The 1,2-endo-adduct XV can thus be isolated because of its higher volatility. Since no byproducts are formed, especially no XVII or XXV, we prefer a [1,5]$_s$-shift mechanism[71] rather than a biradical intermediate (*Scheme 5*) for this rearrangement.
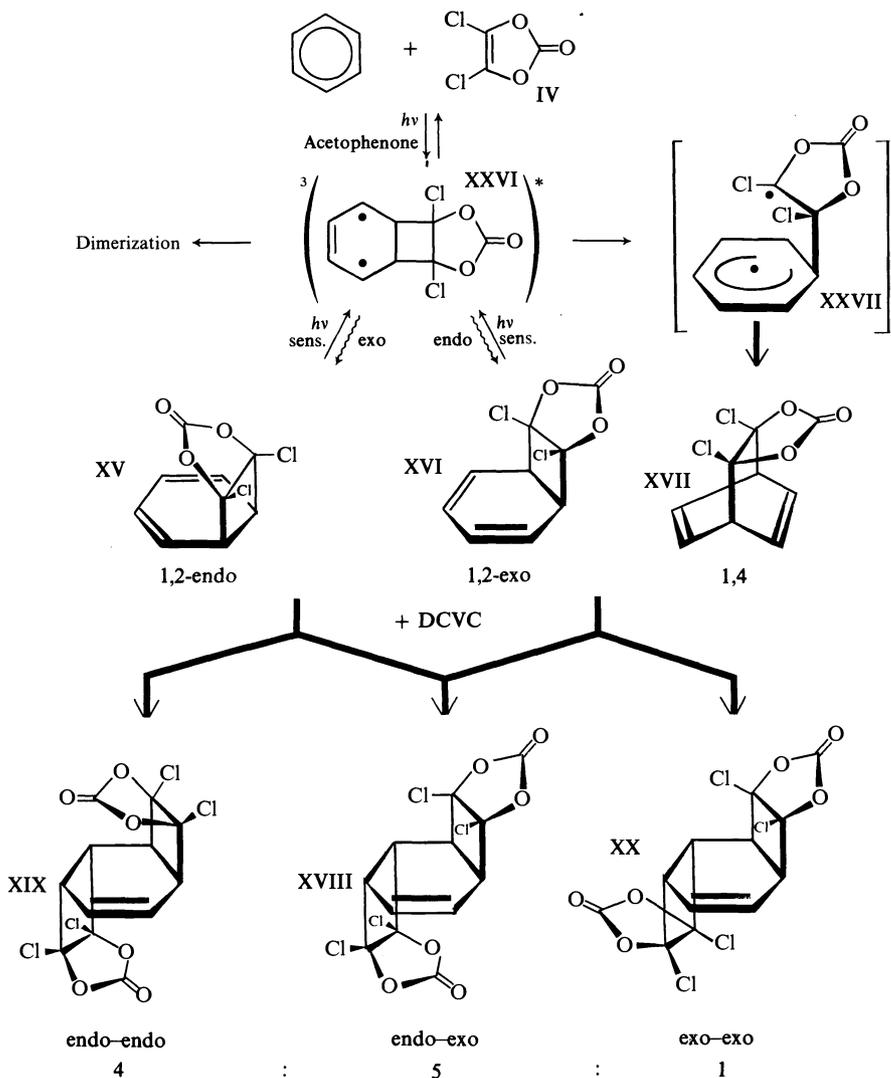
Scheme 6

Conclusion

In accordance with *Scheme 6* primarily the sensitizer transfers its energy to IV, which attacks the benzene nucleus under formation of the two stereo-isomeric 1,2-adducts XV and XVI.

Although a biradical intermediate cannot be excluded we prefer the formulation of an adiabatic reaction pathway leading to triplet excited products which subsequently deactivate to the ground states of XV and XVI. This is favoured by the condition $E_T^{sens} > E_T^{product}$[72]. As the result from *Figure 6* indicates there must be a diabatic pathway from XXVI to XVII and byproducts via XXVII under sensitized conditions.

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Further addition of a molecule IV to XV and XVI yields the 2:1 adducts XVIII–XX. If one starts with pure XV one only obtains the isomers XVIII and XIX. Vice versa with XVI under the same conditions one obtains exclusively XVIII and XX.

The minor amount of the 1,2-endo-adduct XV compared to XVI in the reaction mixture obtained by irradiation of IV in benzene–acetophenone (*Figure 5*) corresponds to the dominant amounts of the 2:1 isomers XIX and XVIII.

THE PHOTOCYCLOADDITION OF DICHLOROVINYLENE CARBONATE TO NAPHTHALENE
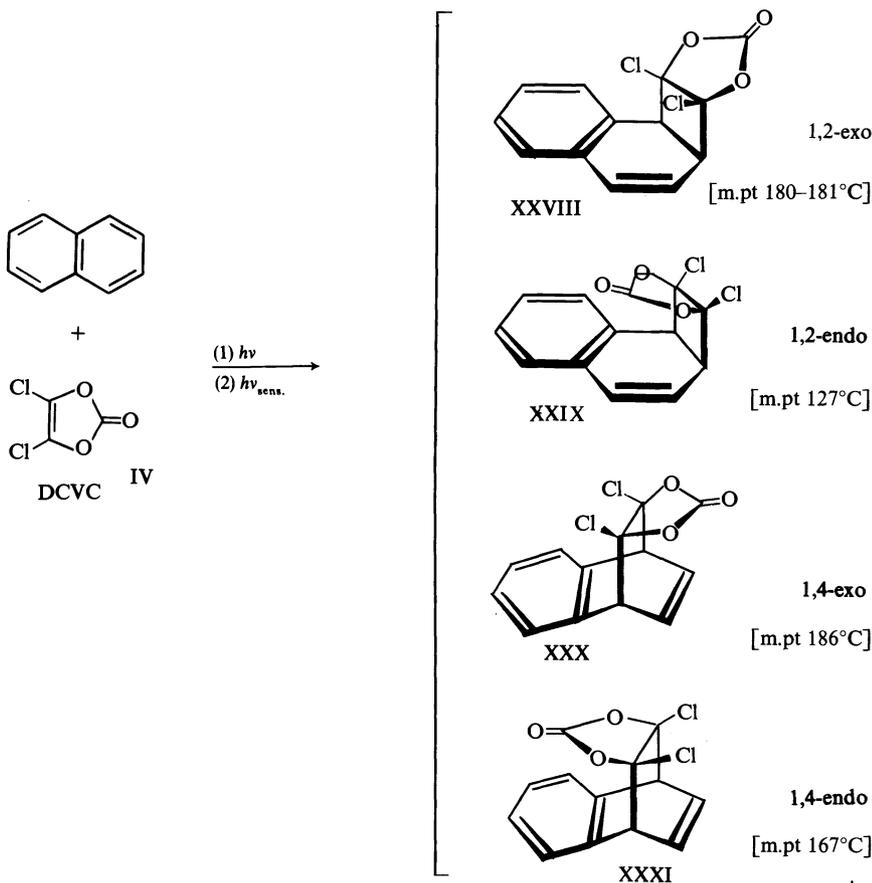
Scheme 7

Sensitized as well as non-sensitized photoaddition of IV to naphthalene yields the 1,2- and the 1,4-adducts XXVIII–XXXI (*Scheme 7*).

Since endo- and exo-adducts show nearly identical electronic-, vibrational-, and ^{1}H-n.m.r.-spectra in the 1,2- and the 1,4-pairs, structural assignments

were made by means of Eu(fod)$_3$-shifting experiments[73]. On the assumption that complex association occurs to the carbonyl oxygen, significant differences between the induced shifts of the signals of the olefinic and the tertiary protons were observed, and led to the structural assignments given.

Pathways of product formation

Contrary to the system IV–benzene–acetophenone naphthalene quenches the triplet of appropriate sensitizers very efficiently (*Figure 3*). Therefore we have to take into account the following cases A, B, C (*Scheme 8*).

$$^3(\text{Naphthalene})^* + (\text{DCVC})_0 \qquad (\text{Naphthalene})_0 + {}^3(\text{DCVC})^* \qquad {}^1(\text{Naphthalene})^* + (\text{DCVC})_0$$

A	B	C
$\Phi_{336\text{nm}} < 10^{-4}$	$\Phi_{336\text{nm}} = 3.2 \times 10^{-2}$	$\Phi_{312\text{nm}} = 3.8 \times 10^{-2}$
Traces of products	Products XXVIII–XXXI	Products XXVIII–XXXI

Scheme 8

However, variation of reaction conditions (*Table 1*) reveals that the photo-addition considered occurs either via the excited triplet state of IV or the excited singlet state of naphthalene, whereas the naphthalene triplet is quite unreactive (*Scheme 8*).

Table 1. Selective reaction conditions (*Scheme 8*)

Route	[Naphth.] M	[DCVC] M	Benzo-phenone M	[Piperylene] M	$\lambda_{\text{irrad.}}$ nm	Φ_{prod}
A	0.5	0.01	0.016	—	336	$< 10^{-4}$
B	0.01	1.0	0.016	—	336	3.2×10^{-2}
C	0.01	1.0	—	—	312	3.8×10^{-2}
D	0.01	1.0	—	0.02	312	4.7×10^{-3}

Φ_{prod} denotes quantum yield of product formation.

Addition of piperylene to solution C not only completely suppresses any reaction from excited triplet states[61] but also quenches the excited singlet state of naphthalene ($k_q = 10^8$ [M^{-1} s^{-1}])[74]. This explains the low quantum yield of solution D (*Table 1*). On the basis of these results one can restrict investigations to cases B and C.

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The photoaddition of ^{3}(DCVC)* to naphthalene (case B)
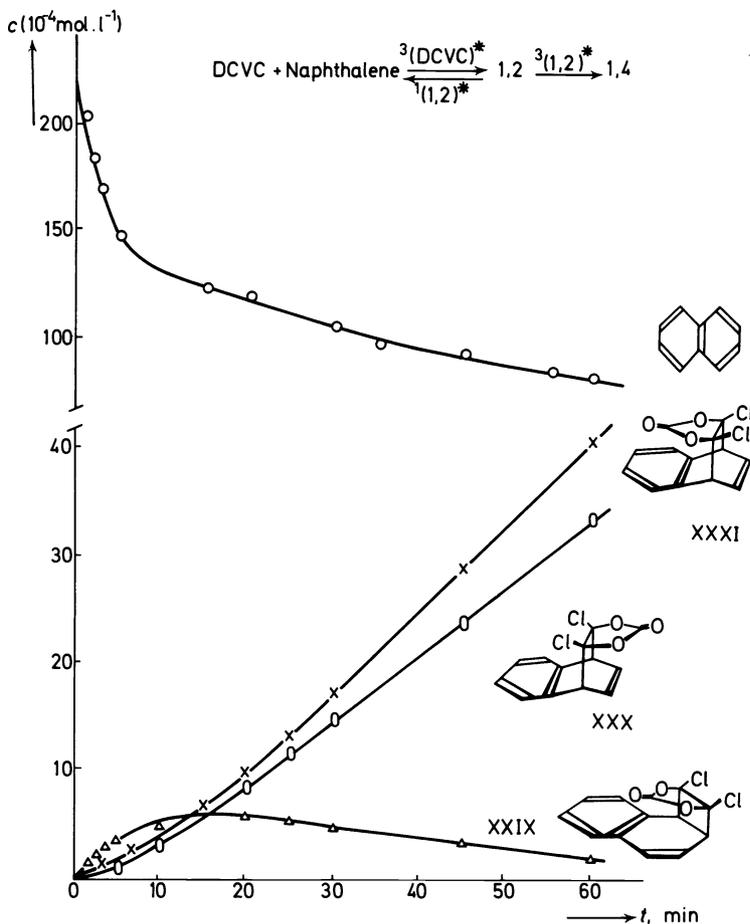
Figure 7. Time-dependent product formation during irradiation of 0.15 M acetophenone in dioxan in the presence of IV and naphthalene[75].

The variation of substance concentration with time (*Figure 7*) suggests a reversible generation of the 1,2-adduct as an intermediate in 1,4-adduct formation[76]. This is confirmed by the following facts:

(i) The 1,2-adducts decompose to naphthalene and DCVC from the S_1 with a high quantum yield (*Scheme 9*);

(ii) This retro cleavage is quenched by piperylene with a k_q due to its quenching of singlets[74] (*Figure 8*);

(iii) The 1,4-adducts are only formed via the triplet states of the 1,2-adducts sensitized by acetophenone as well as by naphthalene (*Figure 9, Scheme 9*) which proceeds highly stereospecifically;

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$$(1)\,\Phi_{312nm}^{Naphthalene} = 1.2 \times 10^{-2}$$

$$(2)\,\Phi_{312nm}^{Acetophenone} = 2.3 \times 10^{-2}$$

T_1

XXXI

S_1

$\Phi_{312nm} = 0.8$

XXIX

IV

Scheme 9

$$k_q \tau_{S_1}(1,2\ \text{Add.}) = 3\,(\text{l.}\,\text{mol}^{-1})$$

$$\tau_{S_1} \approx 10^{-8}\text{s} \Leftrightarrow k_q \approx 3 \times 10^8\,(\text{l.}\,\text{mol}^{-1}\text{s}^{-1})$$

$$\frac{^{Fl}\Phi_{285}^{1,2}}{^{Ph}\Phi_{285}^{1,2}} = 700\,(77\ \text{K})$$

$[Q], \left[\dfrac{mol}{l}\right]$

Figure 8. Quenching of naphthalene formation by piperylene in dioxan at room temperature.

(iv) The fluorescence quantum yield of 1,2-adducts is $700 \times$ the phosphorescence yield at 77 K in ether–isopentane glass, whereas no cleavage is observed in triplet sensitized rearrangement of 1,2-adducts (*Figure 9*).

XXX

XXVIII

t, h

Figure 9. Sensitized rearrangement of the 1,2-exo-adduct → 1,4-exo-adduct in dioxan with acetophenone.

(i)–(iv) corroborate the exclusive singlet or triplet pathway. The emission spectra of XXIX are distinct from those of naphthalene (*Figure 10*). The deviation of the excitation spectrum of XXIX from its u.v.-absorption spectrum is independent of concentration and may well be caused by the high decomposition probability (*Scheme 9*). The triplet energy of 60 kcal/mole is in the range of that of styrene (62 kcal/mole)[77].
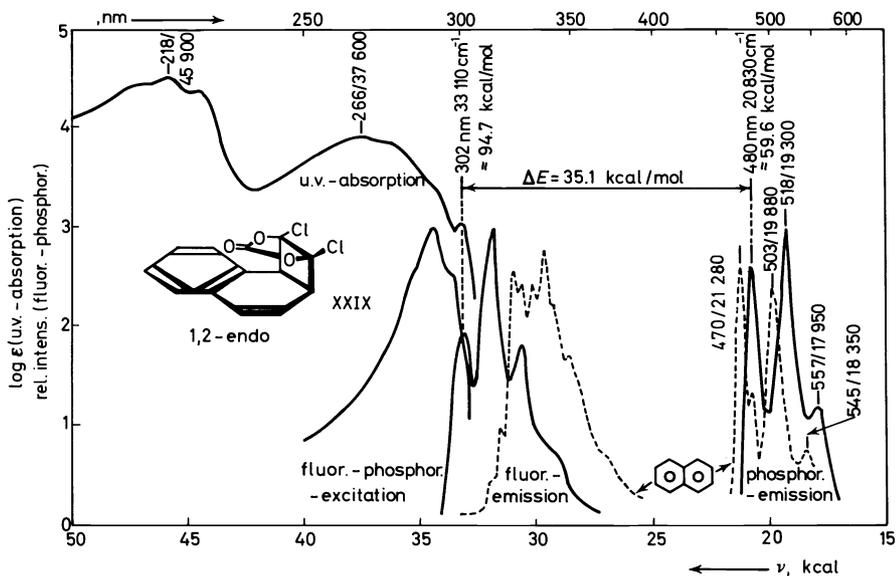
Figure 10. Absorption and emission spectra of the 1,2-endo adduct (solid line) and naphthalene (broken line)—u.v.: in acetonitrile/295 K/Cary 14. Luminescence: in ether–isopentane 1:1/77 K/Aminco SPF $\tau_{ph} = 0.0255$ s

The phosphorescence lifetime of 25 ms and the singlet–triplet splitting of 35 kcal/mole are consistent with a $\pi\pi^*$-triplet state.

The photoaddition of ^{1}(naphthalene)* to DCVC (case C)

Under irradiation conditions (*Table 1*), where only singlet naphthalene is the reactive species (see *Scheme 8*), there is no indication of a consecutive reaction pathway in contrast to case B (see *Figure 7*). The assumption of parallel generation of the products leads to the following kinetic scheme.

$$^1(\text{naphthalene}) \xrightarrow{K_{IC}, \, K_{ISC}} \begin{array}{l}\text{radiationless}\\ \text{deactivation}\end{array}$$

$$^1(\text{naphthalene}) \xrightarrow{K_F} \text{fluorescence}$$

$$\text{DCVC} + {}^1(\text{naphthalene})^*(1) \xrightarrow{\sum\limits_{1}^{4} K_i} \begin{array}{l}\text{direct formation of}\\ \text{products}\end{array}$$

$$(2) \xrightarrow{K_{im}} \text{formation of intermediate}$$

$$\text{intermediate (2)} \xrightarrow{\overset{4}{\underset{1}{\sum K_p}}} \text{formation of products}$$
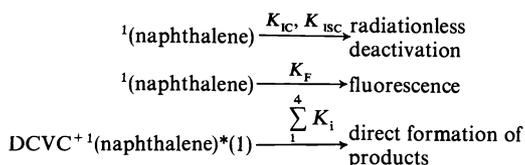
$$\text{intermediate (2)} \xrightarrow{K_d} \text{deactivation of the intermediate}$$
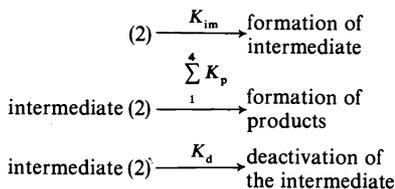
Scheme 10. Pathways of product formation via intermediate (2) or direct (1)

Scheme 10 results in the following equations for fluorescence quantum yield Φ_F and the different quantum yields of product formation $\Phi_p^{(1)}$ and $\Phi_p^{(2)}$:

$$\frac{1}{\Phi_F} = \frac{K_F + K_{IC} + K_{IsC}}{K_F} - \frac{K_{im}}{K_F}[DCVC], \quad \text{(plot A in } \textit{Figure 11)}$$

$$\frac{1}{\Phi_p^{(1)}} = 1 + \frac{K_F + K_{IC} + K_{IsC}}{\Sigma K_i} \times \frac{1}{[DCVC]}, \quad \text{(plot B in } \textit{Figure 11)}$$

$$\frac{1}{\Phi_p^{(2)}} = \frac{\Sigma K_p + K_d}{\Sigma K_p} + \frac{(\Sigma K_p + K_d) \times (K_F + K_{ISC} + K_{IC})}{K_{im} \times \Sigma K_p} \times \frac{1}{[DCVC]}$$
(plot B in *Figure 11*)

Plots of Φ_F^{-1} versus the concentration of DCVC and of Φ_p^{-1} versus the reciprocal value of DCVC-concentration (*Figure 11*, A and B) fit pathway (2) since:

(i) the intercept of plot B is not equal to unity, and

(ii) the product of the intercept of plots A and B is equal to the product of the slopes under consideration within the limit of error[42].
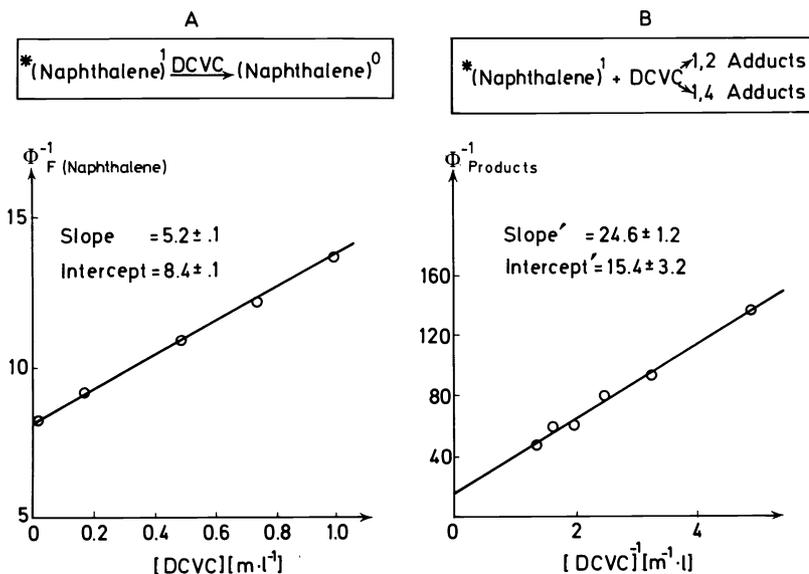
Figure 11. Dependence of [1](naphthalene)* fluorescence and product formation on DCVC concentration in dioxan[78]

This means that product formation proceeds via an intermediate.

Furthermore the intercept of plot B yields the reverse quantum yield of product formation from the intermediate

$$1 + K_d/\Sigma K_p = 15.4$$

and thus the ratio of intermediate deactivation and product formation amounts to $K_d/\Sigma K_p = 14.4$. This may explain the very low product quantum yields (see *Scheme 8*).

ACKNOWLEDGEMENTS

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[64] Reaction solution: 0.468 M DCVC, 0.27 M acetophenone in benzene at 20°C
Lamp: Philips HPK 125 W
Filter: pyrex

Determination of concentrations by v.p.c.:
standard: *n*-eicosan
apparatus: Carlo Erba Fractovap 2200

column: 3 m × 2 mm glass   injection: 280°C
           5% apiezon L on Gaschrom Q 80/100   carrier: N$_2$, 1.8 at
           210°C   detector: FID, 280°C

The deviations to the results in ref. 65 are due to partial decomposition of the products in metal columns.

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Lamp: Philips HPK 125 W
Filter: pyrex
Apparatus: merry
Determination of concentration by v.p.c.[65]

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ether/benzene 8:2
Carrier:
Kieselgel 60, F$_{254}$ (Merck)

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[75] Reaction solution:
0.223 M DCVC, 0.022 M naphthalene, 0.153 M acetophenone in dioxan at 20°C
Lamp: Philips HPK 125 W
Filter: pyrex
Determination of concentrations by v.p.c.:
standard: *n*-eicosan
apparatus: Carlo Erba Fractovap 2200
column: 5 m × 2 mm glass
             5% apiezon L on Gaschrom Q 80/100
             190°C (adducts), 100°C (naphthalene)
injection: 250°C
carrier: N$_2$, 4.5 at
detector: FID, 250°C

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[78] plot A: quenching of naphthalene fluorescence by DCVC (see *Figure 4*) Φ_F^0 (naphthalene, 293 K) = 0.12 [79].
plot B: variation of product formation with DCVC concentration in dioxan
        conditions: lamp = Original Hanau Q 700
                    [naphthalene] = 0.1 M
                    [piperylene] = 0.2 M
                    2.5 cm filter solution of 1.45×10^{-4} M fluorene in dioxan to avoid retrocleavage of $^1(1, 2)^*$.
                    (fluorene and the 1,2-adduct have a nearly identical long wavelength absorption onset)

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