Arylcyclopropane Photochemistry. The Naphthalene-sensitized Isomerization of 1,2-Diarylcyclopropanes

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Summary Charge transfer from cyclopropane to sensitizer is important in the naphthalene-sensitized photochemical isomerization of 1,2-diarylcyclopropanes.

THE *cis–trans*-isomerization of 1,2-diphenylcyclopropane (**1**), sensitized by various naphthalene derivatives, was originally believed to proceed *via* triplet energy transfer.[1] Later work, however, showed the process involved instead an interaction of the singlet states of the naphthalenes with (**1**).[2] Since (a) the singlet energy of (**1**) is much greater than that of the naphthalenes and (b) some products arising from the singlet state of (**1**) (*via* direct photolysis) were not observed in the naphthalene-sensitized reactions, the energy transfer in these cases could not have been of the singlet–singlet type. Instead, an exciplex interaction was visualized,[2] but little quantitative data are available on this reaction.[1–3] We have, therefore, investigated this system and report here some of our initial findings.

Electronic effects in the sensitizer were investigated by studying the *cis-trans*-isomerization of *cis*-(**1**) (**1c**)† sensitized by the naphthalenes (**2**)—(**5**). The results, under conditions where only the sensitizer was absorbing the incident light, are in the Table. In all cases a sensitized isomerization was observed. Experiments in which the triplet states of (**2**)—(**5**) were generated in the presence of 0·25 M-(**1c**) by benzophenone sensitization resulted in no observable reaction, strongly indicating that the interactions between (**1c**) and (**2**)—(**5**) which lead to isomerization involve the singlet states of the latter as had previously been found for (**3**)[2] (though the involvement of sensitizer ^3T states cannot be ruled out). By analogy to the (**3**)-(**1**) system[2] we conclude that an exciplex interaction is most likely involved with (**2**), (**4**), and (**5**).

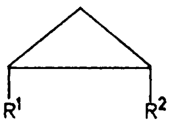
TABLE

Quantum yield of sensitized isomerization of 0·25 M (**1c**)[a]

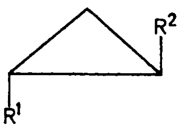
Sensitizer	Φ(**1t**) × 10^{-3} [b]	τ/ns[c]
1-Cyanonaphthalene (**2**)	85	26[d]
Naphthalene (**3**)	5·3	96[d]
2,6-Dimethylnaphthalene (**4**)	2·7	38[e]
1-Methoxynaphthalene (**5**)	2·1	49[d]

[a] Degassed benzene solutions. [b] Determined on a merry-go-round apparatus using benzophenone–benzhydrol actinometry. [c] Sensitizer singlet lifetime. [d] B. S. Solomon, C. Steel, and A. Weller, *Chem. Comm.*, 1969, 927. [e] I. B. Berlman, 'Handbook of Fluorescence Spectra of Aromatic Molecules,' 2nd edn., Academic Press, New York, 1971.

The reaction proceeds much more efficiently with the cyanonaphthalene sensitizer (**2**) than with (**3**)—(**5**). This increase in quantum yield is not simply due to a longer lifetime of (**2**) since in fact the lifetime of (**2**) is the shortest in the series (**2**)—(**5**) (see Table). Overall differences in quantum yields for the (**3**)—(**5**) sensitizations are small and may reflect in part sensitizer-lifetime differences.



(1c) $R^1 = R^2 = Ph$



(1t) $R^1 = R^2 = Ph$
(6) $R^1 = p\text{-}MeOC_6H_4, R^2 = Ph$
(7) $R^1 = R^2 = p\text{-}ClC_6H_4$

In accord with the observed differences in sensitization efficiencies for (**2**)—(**5**), only in the case of (**2**) did we observe any fluorescence quenching by (**1c**). (No new emission ascribable to an exciplex was observed.) These results, both chemical and spectroscopic, are consistent with the importance of an interaction involving charge-transfer from cyclopropane to sensitizer in exciplex formation and/or decay such has been found for other exciplex-forming systems.[4]

Because of the low quantum yields with (**3**)—(**5**) a reliable Stern-Volmer plot of 1/Φ(**1t**) *vs.* 1/[(**1c**)] could be obtained only with the (**1c**)—(**2**) system for which we obtained (see Scheme) $I = 6{\cdot}8$, $S = 2{\cdot}2$ mol l^{-1}, and $I/S = 3{\cdot}1$ l mol^{-1}. From this we calculate a value for k_q [$k_q = k_1(k_2 + k_3)/(k_{-1} + k_2 + k_3)$] of $1{\cdot}2 \times 10^8$ l mol^{-1} s^{-1}. We note that k_q represents the *minimum* value for the rate of exciplex formation k_1 and is equal to k_1 only if $k_{-1} \ll k_2 + k_3$. In addition, if we assume k_3 represents the rate of a cleavage step producing a biradical species for which $f = 0{\cdot}65$,‡ then we find that the fraction of exciplex which reacts by such bond cleavage, $k_3/(k_2 + k_3)$, is 0·23. On this basis >75% of the exciplex decays in another manner.

$$S + h\nu \longrightarrow {}^1S$$

$${}^1S \xrightarrow{1/\tau_S} S,\ {}^3S,\ \ldots$$

$${}^1S + C \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Ex$$

$$Ex \xrightarrow{k_2} S + C$$

$$Ex \xrightarrow{k_3} S + bi$$

$$bi \longrightarrow C' + C$$

$$1/\Phi(\mathbf{1t}) = (k_2 + k_3)/fk_3 + (k_{-1} + k_2 + k_3)/fk_1k_3\tau_S[\mathrm{c}]$$

S = sensitizer

C = cyclopropane

C′ = isomerized cyclopropane

Ex = exciplex

bi = biradical

f = fraction of biradical forming C

intercept $(I) = (k_2 + k_3)/(fk_3)$

slope $(S) = (k_{-1} + k_2 + k_3)/(fk_1k_3\tau_S)$

$$I/S = k_1\left(\frac{k_2 + k_3}{k_{-1} + k_2 + k_3}\right)\tau_S$$

SCHEME

We have also investigated the *trans–cis*-isomerization of the *trans-para*-substituted cyclopropanes (**6**) and (**7**) sensitised by (**2**). Again, consistent with the importance of a charge-transfer interaction in exciplex formation and decay, we find the isomerization of the methoxy compound (**6**) to be the more efficient of the two. Linear Stern-Volmer plots were obtained. Analysis of the data according to the Scheme gives, for (**6**), $I = 19{\cdot}2$, $S = 1{\cdot}2$ mol l^{-1}, $I/S = 16{\cdot}0$ l mol^{-1}, $k_q = 6{\cdot}2 \times 10^8$ l mol^{-1} s^{-1}; making assumptions similar to those above for k_3, we find $k_3/k_2 + k_3 = 0{\cdot}15$. For the dichloro-compound (**7**), $I = 40$, S = 5·0 mol l^{-1}, $I/S = 8{\cdot}0$ l mol^{-1}, $k_q = 3{\cdot}1 \times 10^8$ l mol^{-1} s^{-1}) $k_3/(k_2 + k_3 = 0{\cdot}07$.

We find, as expected, that k_q for (**6**) is greater than that for (**7**). However, the difference in k_q's is small and, in fact, much of the observed difference in isomerization efficiency between (**6**) and (**7**) is due to a more favourable partioning of exciplex to products (1/I) with the former. As noted by Hammond *et al.*,[4] the difference in k_q may reflect differences in rates of exciplex association and dissociation (k_1 and k_{-1})

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† We used the *cis*- rather than the *trans*-isomer of (**1**) because, being crystalline at room temperature, (**1c**) is much easier to purify in large quantities to the purity required for these experiments.

‡ This was found by Cole[2a] for the sensitization of (**1t**) by a naphthalene derivative. Matzke's results[3] differ.

and/or in the rates of exciplex decay ($k_2 + k_3$). Furthermore, it seems probable that exciplex association–dissociation (and possibly k_2 and k_3) is related to charge-transfer capability and that exciplex decay (both k_2 and k_3) involves significant stretching of the C-1–C-2 ring bond. One would therefore expect isomerization of the dichloro-derivative (**7**) to be relatively disfavoured, certainly by less favourable k_1 and k_{-1} values and probably by a lower value for $k_2 + k_3$.§ Our results are consistent with this, though the fact that the k_q's differ by a factor of only two is somewhat surprising. [The data for (**6**) and (**7**) should not be compared with that for (**1c**) since the steric interactions are greatly different.]

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§ The rate of the thermal *cis–trans*-isomerization for (**7c**) is slower than that for (**1c**).[5] One would expect a *p*-OMe group to have a rate-enhancing effect.

[1] (a) C. D. De Boer, Ph.D. Thesis, California Institute of Technology, 1966; (b) G. S. Hammond and R. S. Cole, *J. Amer. Chem. Soc.*, 1965, **87**, 3256.

[2] (a) R. S. Cole, Ph.D. Thesis, California Institute of Technology, 1968; (b) S. L. Murov, R. S. Cole, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1968, **90**, 2957.

[3] T. A. Matzke, Ph.D. Thesis, University of Texas at Austin, 1971.

[4] A good leading reference is F. A. Carroll, M. T. McCall, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1973, **95**, 315.

[5] L. B. Rodewald and C. H. DePuy, *Tetrahedron Letters*, 1964, 2951.