energy" sensitizers. For these cases, involvement of T_2 states should be considered.

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Received December 20, 1967

9,10-Dichloroanthracene-Sensitized Isomerization of Stilbenes. The Question of Energy Transfer between Intimately Associated Molecular Pairs[1]

Sir:

The situation existing between the donor–acceptor pair, following transfer from the second triplet state of the donor,[1] appears ideal for further rapid "reversible" energy transfer.

$$D_{T_2} + A_{S_0} \longrightarrow D_{S_0} + A_{T_1} \longrightarrow D_{T_1} + A_{S_0}$$

Normally, the second transfer would only be reflected in the reduction of quantum yield of the reaction of A_{T_1}; thus its importance is experimentally difficult to determine. However, in stilbenes such quenching is expected to affect their photostationary-state (pss) compositions significantly.[2] We therefore studied this isomerization reaction sensitized by 9,10-dichloroanthracene (DCA = A).

The results can be successfully accounted for by the following scheme in which *only the DCA molecule in the T_2 state acts as donor.*

Excitation

$$A \xrightarrow{h\nu} A_{S_1} \longrightarrow A_{T_2}$$

Fate of T_2

$$A_{T_2} + t \xrightarrow{k_1} \overline{A + t^*} \qquad (1)$$

$$A_{T_2} + c \xrightarrow{k_2} \overline{A + t^*} \qquad (2)$$

$$A_{T_2} \xrightarrow{k_d} A_{T_1}$$

Fate of $\overline{A + t^*}$

$$\overline{A + t^*} \xrightarrow{k_3} \overline{A_{T_1} + t} \longrightarrow A_{T_1} + t \qquad (3)$$

$$\overline{A + t^*} \xrightarrow{k_4} A + t^* \qquad (4)$$

Fate of t*

$$t^* \xrightarrow{k_5} t \qquad (5)$$

$$t^* \xrightarrow{k_6} c \qquad (6)$$

$$t^* + A \xrightarrow{k_7} A_{T_1} + t \qquad (7)$$

Fate of A_{T_1}

$$A_{T_1} \xrightarrow{k_d'} A$$

Equation 7 differs from 3 by being diffusive in nature.[3]

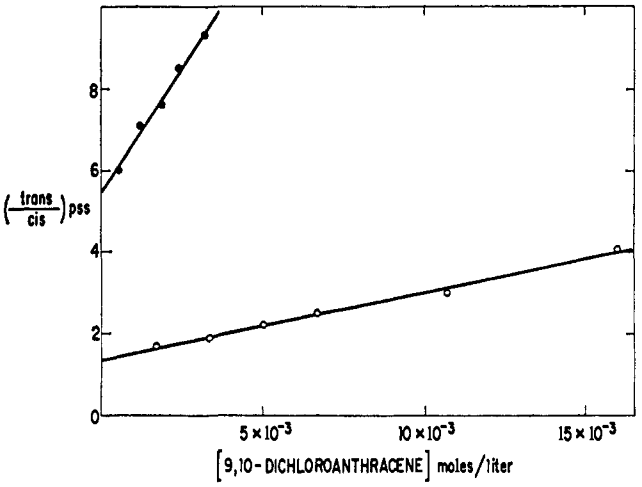

Figure 1. Photostationary-state composition of stilbenes (0.05 *M*) sensitized by 9,10-dichloroanthracene in benzene (○) and 1-propanol (●), irradiated at 26° in a "merry-go-round" apparatus, equipped with a 550-W Hanovia Hg lamp and Corning 0-51 filter.

By assuming a steady-state concentration of the intimately associated molecular pairs, $\overline{A_{T_1} + t}$, one arrives at an equation relating photostationary-state composition and concentration of DCA.

$$\frac{[t]_s}{[c]_s} = \frac{k_2}{k_1 k_6}\left(\frac{1}{1-b}\right)(k_6 b + k_5 + k_7[A]) \qquad (8)$$

where $b = k_3/(k_3 + k_4)$.

A plot of the isomer ratio at photostationary states, $[t]_s/[c]_s$, in benzene as solvent (○) (Figure 1) *vs.* DCA concentration gives an excellent linear correlation. The photostationary-state compositions are invariably richer in *trans;* this trend has not been observed previously.[2] The importance of "cage" quenching (eq 3) is evident. The constant *b*, a measure of the extent of t* quenched by the intimately associated anthracene molecule, can be calculated from the intercept with the added assumption that $k_1 = k_2$ and k_5/k_6 (the decay ratio) = 0.67.[2] The value for k_5/k_6 was obtained from the stationary-state composition produced by benzophenone.[4] In benzene $b = 0.28$. In addition, $k_2k_7/k_1k_6 = k_7/k_6$, obtained from the intercept and slope, is a measure of diffusive quenching. The calculated value of 120 ± 12 l./mole agrees well with values from similar studies with azulene as quencher (110–160 l./mole).[2] This result indicates that the quenching constants (k_7) in both cases are the same, and since E_{T_1} of DCA (40.2 kcal/mole) is much higher than that of azulene (31–39 kcal/mole),[5] it could only imply that they both approach k_D, the rate of diffusion.

The proposed scheme is further substantitated by the following observations. Results of parallel studies (Figure 1) in 1-propanol (●), a more viscous solvent (1.92 cP as compared with 0.616 cP for benzene), give a much larger value for the intercept indicating more molecular-pair quenching (calculated $b = 0.74$).[6]

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[1] The Role of Second Triplet States in Solution Photochemistry. III. For the previous papers in this series, see R. S. H. Liu and J. R. Edman, *J. Am. Chem. Soc.*, **90**, 213 (1968); R. S. H. Liu and D. M. Gale, *ibid.*, **90**, 1897 (1968).

[2] For the effect of a similar type of diffusive quenching uniquely shown in stilbene, *e.g.*, by azulene, see G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *ibid.*, **86**, 3197 (1964).

[3] We have observed a dependence of photostationary-state composition upon the concentration of stilbene. Evidently the present scheme does not accommodate such a dependence. The variation is, however, small over a wide range of stilbene concentration. In order to retain simplicity of the present scheme, and further, considering that the results presented here were carried out at a constant concentration of stilbene, no additional steps were introduced to account for this dependence.

[4] Although the exact T_2 energy level of DCA cannot be determined spectroscopically (see R. G. Bennett and P. J. McCartin, *J. Chem. Phys.*, **44**, 1969 (1966)), based on chemical evidence, we believe its energy is between 68 and 70 kcal/mole.

[5] A. A. Lamola, W. G. Herkstroeter, J. C. Dalton, and G. S. Hammond, *ibid.*, **42**, 1715 (1967).

Further, an experiment parallel to the azulene studies[2] using, instead, 9,10-dimethylanthracene[7] as quencher (sensitizer, Michler's ketone; solvent, benzene) gave a rate constant ratio, equivalent to k_7/k_6, of 115 ± 5 l./mole, which is the same within experimental error as that obtained in the azulene experiments.[2]

The extent of intimately associated molecular-pair quenching, as reflected in *b*, is surprisingly low, particularly in view of the notion that triplet–triplet energy transfer (eq 1 or 2) in solution involves actual contact of the donor–acceptor pair, leading to the impression that the efficiency of quenching step 3 should be close to unity.[8] Our results shed doubt on such a notion. If reactions 1 and 2 may take place with the donor–acceptor pair separated by at least one solvent molecule, the relatively small observed "cage" factors, *b*, become understandable. Our concept gains support when one considers that in glassy solution, such exchange interaction takes place with an average separation of 12–13 Å, a distance larger than the "average" separation between a neighboring donor–acceptor molecular pair.[9,9a]

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[6] The same decay ratio as in benzene was used in the calculation because the pss composition with benzophenone in either solvent was found the same.

[7] 9,10-Dimethylanthracene is chosen because of its low intersystem-crossing efficiency (<10%).

[8] The number of collisions of a set in a solvent cage is of the order 10–10²; see J. E. Leffler and E. Grunwald in "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p 59.

[9] For a detailed discussion, see R. G. Bennett and R. E. Kellogg, *Progr. Reaction Kinetics*, **4**, 215 (1967).

[9a] NOTE ADDED IN PROOF. Professor Jack Saltiel pointed out to us an error in the published azulene rate constant ratios (p 3207 of ref 2). Thus, a factor of 1.4, the decay ratio, must be multiplied for meaningful comparison with our values.

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Received January 6, 1968

The Synthesis of Perbromates[1]

Sir:

Past attempts to prepare perbromates, salts of heptavalent bromine, have been generally unsuccessful.[2–6] Very early reports of such compounds[7] could not be confirmed,[8–11] and several authors have discussed the reasons for their nonexistence.[12–15] In this communication we describe the successful synthesis of perbromates and the isolation of the rubidium salt.

We initially synthesized perbromate by a hot-atom process—the β decay of radioactive Se^{83} incorporated into a selenate. The process may be written

$$Se^{83}O_4^{2-} \longrightarrow Br^{83}O_4^{-} + \beta^-$$

Enriched Se^{82} (90%) was irradiated with thermal neutrons, dissolved in nitric acid, and oxidized to selenate by ozone in alkaline solution. After the 25-min Se^{83} activity had decayed, sodium perchlorate and bromate were added, and rubidium perchlorate was precipitated at 0° under conditions such that only about 1% of the bromate was coprecipitated. Approximately 14% of the 2.4-hr Br^{83} activity was found in the precipitate. This fraction was unchanged after extraction with Br_2 in CCl_4 or after treatment with iodide in 0.6 *M* HCl. However, after treatment with iodide in 6 *M* HCl, only 1% of the Br^{83} activity coprecipitated with rubidium perchlorate.

These results indicated the formation of a relatively unreactive perbromate ion and suggested that a determined effort might lead to the preparation of macro amounts of perbromates. We therefore attempted both chemical and electrolytic oxidation of bromate.

An electrolytic cell was set up with a platinum cathode immersed in 3 ml of 2.8 *M* $HClO_4$ in a porous porcelain cup. The anode was a rotating platinum microelectrode in a similar cup immersed in a slurry of Li_2CO_3 in 3 ml of 2.8 *M* $LiBrO_3$ tagged with 36-hr Br^{82}. The two cups were placed in a container of 2.8 *M* $LiClO_4$, which in turn was immersed in a cooling bath at −15°. The cell was run for about 1 A hr at an anodic current density of about 10 A/cm². Successive portions of Li_2CO_3 were added to the anolyte to maintain its neutrality, while the catholyte was periodically replaced to maintain its acidity.

At the end of the electrolysis about 2% of the bromine activity coprecipitated with $RbClO_4$ but did not coprecipitate with $Ba(BrO_3)_2$. When an electrolysis was carried out at a similar current density, but in an unpartitioned cell, with dichromate used to inhibit cathodic reduction, essentially all of the bromine activity could be coprecipitated with $Ba(BrO_3)_2$.

The following technique was developed to analyze for perbromate in the presence of bromate. The solution, no more than 0.15 *M* in bromate, was made 1.5 *M* in HBr to reduce the bromate. Argon was bubbled through until the bromine color disappeared and did not return upon standing. The solution was then diluted with four times its volume of saturated HBr. After 5 min it was diluted tenfold with 2% NaI and titrated with thiosulfate. The titer of the electrolyzed solution treated in this manner agreed with the tracer results, if we assume that each mole of perbromate consumed 8 equiv of thiosulfate.

Aqueous bromate is not appreciably oxidized by sodium perxenate or by persulfate at 100°, with or without silver catalyst. Aqueous xenon difluoride, however, does oxidize bromate to perbromate. After a solution 0.14 *M* in XeF_2 and 0.24 *M* in $NaBrO_3$ had stood until the XeF_2 had all reacted with water, analysis with HBr indicated the presence of 0.01 *M* perbromate. A solution 0.14 *M* in XeF_2 and 1.5 *M* in $LiBrO_3$ yielded 0.018 *M* perbromate.

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

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