

Figure 1.

the spectroscopic transition energy of *cis*-stilbene is about 57 kcal./mole and that of *trans*-stilbene is 50 kcal./mole,⁶ one would expect the value of k_2/k_1 to decrease as the energy of the sensitizer is lowered toward 57 kcal.⁹ This accounts for production of *cis*-rich mixtures with sensitizers having excitation energies of 54–62 kcal. However, we cannot account for the fact that the value k_2/k_1 apparently increases and finally becomes immeasurably large with sensitizers of still lower energy. We suggest that reaction 3, or some other process requiring less energy than transition to the spectroscopic *cis* triplet, must predominate. Since the ground state of *cis*-stilbene is unstable with respect to that of the *trans* isomer by 6 kcal./mole,¹¹ in any pair of processes in which two isomers undergo transitions to a common state, the reaction involving the *cis* isomer will be favored on energetic grounds. Figure 1 can be rationalized by the mechanism including reaction 3.

$$\frac{[trans]_s}{[cis]_s} = \frac{(k_2 + k_3)(k_3 + k_{-1}[S])}{k_1 k_3} \quad (9)$$

With high energy sensitizers, k_1 and k_2 , the rate constants for energy transfer with vertical excitation of the acceptor, have the magnitude for diffusion-controlled processes and are larger than k_3 . The value of k_2 falls off as the excitation energy of sensitizers approaches and falls below the $S_0 \rightarrow T_1$ excitation energy of *cis*-stilbene. As the energy of the sensitizers is lowered further, the value of k_1 falls sharply. Since k_3 , the rate of transfer with nonvertical excitation of *cis*-stilbene, depends on factors other than the excitation energy of the acceptor, $(k_2 + k_3)/k_1$ may be large with low energy sensitizers. Behavior in the 45–52 kcal. region will require further documentation prior to detailed discussion.

Sensitizers having energies close to that of *trans*-stilbene show pronounced concentration effects. The data fit eq. 9, implying that transfer of energy to *cis*-stilbene produces a species which can transfer energy to sensitizer molecules in their ground states. Confirmation was provided by experiments in which azulene was included in the reaction mixtures. The stationary states became more *trans*-rich and data for various azulene

(6) The energies are estimated from the singlet-triplet absorption spectra as reported.^{7,8}

(7) D. F. Evans, *J. Chem. Soc.*, 1351 (1957).

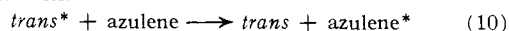
(8) R. H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36**, 2326 (1962).

(9) Transfers exothermic by more than 3–5 kcal. appear to be diffusion-controlled.¹⁰

(10) (a) G. Porter and F. Wilkinson, *Proc. Roy. Soc. (London)*, **A264**, 1 (1961); (b) K. Sandros and H. L. J. Bäckström, *Acta Chem. Scand.*, **16**, 958 (1962); (c) G. S. Hammond and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1148 (1962).

(11) R. B. Williams, *J. Am. Chem. Soc.*, **64**, 1395 (1942).

concentrations obeyed a law including reaction 10 in the mechanism.



The effect of azulene is observed irrespective of the energy of the sensitizers. Clearly, all energy transfer processes produce long-lived stilbene triplets which are quenched by azulene with the inevitable production of ground state *trans*-stilbene. This observation unequivocally demonstrates that reaction 3 does not deliver excitation to *cis*-stilbene as vibrational (thermal) energy.

Acknowledgment.—This research was supported by the National Science Foundation. We thank Professors J. D. Roberts and G. W. Robinson for fruitful discussions.

CONTRIBUTION No. 2992

GATES AND CRELLIN LABORATORIES OF CHEMISTRY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

JACK SALTIEL

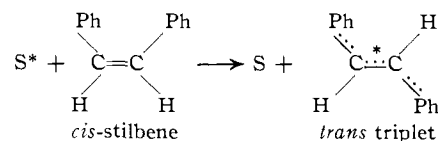
GEORGE S. HAMMOND

RECEIVED JUNE 17, 1963

Mechanisms of Photoreactions in Solution. XVIII. Energy Transfer with Nonvertical Transitions

Sir:

In the accompanying communication¹ we have given evidence for the occurrence of a process that was formulated as



The product of the excitation transfer may be a triplet having a transoid configuration or it may be some other triplet having a noncisoid configuration. If such a

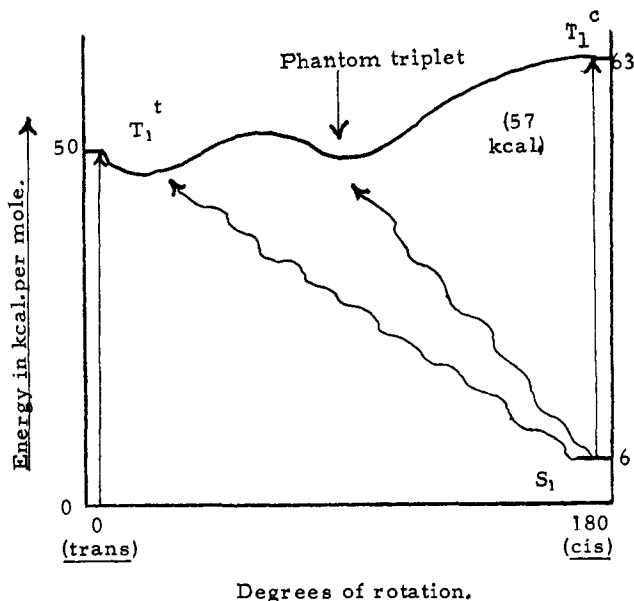


Fig. 1.—Possible potential function for rotation about the central bond in the stilbene triplet states.

“phantom” triplet is involved it must be both readily interconvertible with the *trans* triplet and rather close to isoenergetic with it. The potential function for twisting about the central bond might look as is shown in Fig. 1. However, we should stress the fact that the two possibilities, *trans* triplet only or *trans* triplet and phantom triplet in equilibrium, cannot be distinguished on the basis of presently available information.

(1) J. Saltiel and G. S. Hammond, *J. Am. Chem. Soc.*, **85**, 2515 (1963).

The two possible nonvertical transitions of *cis*-stilbene are indicated by wavy arrows and spectroscopic transitions by straight arrows in the figure. Excitation of *cis*-stilbene by low energy sensitizer triplets cannot involve the spectroscopic *cis* triplet because the sensitizers do not possess the requisite energy content and the processes do not have significant activation energies.¹

We believe that production of nonspectroscopic states by energy transfer is a common process and a number of examples now have been observed in our Laboratory. Therefore, we should examine the details of the process which we are suggesting. It appears to us that reaction 1 and similar transfers in which acceptors are not promoted in accordance to the Franck-Condon principle have some of the characteristics of both thermal and spectroscopic processes but are identical with neither. The process is not spectroscopic since the restrictions imposed by the Franck-Condon principle are removed. On the other hand, the behavior is unlike that of common thermal reactions because the donor-acceptor system does not come to equilibrium with the surrounding medium. The electronic excitation energy of the sensitizer triplet is handed over to the acceptor and the latter then is released in a long-lived excited state.² Since the lifetime of the excited acceptor is long enough to allow it to encounter other solutes present in low concentration, we may be reasonably certain that energy transfer has not become a pure thermal process, *i.e.*, the excitation does not appear in the acceptor as vibrational excitation. If this were the case, vibrational relaxation should deactivate the molecule before it could move from its original solution site. Further evidence of the fact that the energy transfer does not merely involve vibrational excitation of the acceptor comes from consideration of the special role of *cis*-stilbene as an acceptor. The sensitized reactions have been carried on in benzene solution and measurements of quantum yields show that *cis*-stilbene is enormously more active as an energy acceptor (by at least a factor of 2500) than benzene. Even this estimate of the relative reactivities probably vastly underestimates the difference in reactivity since it treats the radiationless decay of species such as fluorenone triplets as though deactivation were entirely due to transfer of vibrational excitation to individual solvent molecules, a most unlikely circumstance.³

Even though the donor-acceptor complex does not become equilibrated with its surroundings, the over-all change may be effected by passage through many "internal equilibrium" states which effectively mix vibrational and electronic states of the donor-acceptor system. In other words, the electronic systems of the two components must interact and some vibrational motions of the two molecules must become strongly coupled. In this respect discussion of the configuration of the system at the time the energy is being transferred should resemble discussions of the transition states involved in ordinary thermal reactions.

Efficiencies in energy transfer involving nonvertical excitation of an acceptor are characteristically lower than corresponding transfers in which the sensitizer triplet has sufficient excitation to promote the acceptor to a spectroscopic state. However, if the acceptor is

present in the solution in high concentration, the overall quantum yields in a photoprocess may be very high. This merely reflects the fact that donor triplets may have sufficiently long lifetimes to allow them to undergo many collisions with potential acceptor molecules. Since the transfer rates typically fall below the diffusion controlled rates by one or more orders of magnitude, and since pairs of molecules remain nearest neighbors in solution for times of the order of 10^{-9} sec., it is evident that the time constants for the nonvertical excitation process must be of the order of 10^{-8} sec. or longer. In view of this fact, it is not surprising that considerable adjustment of nuclear positions may be coupled with the transfer of "electronic" energy.

It is interesting to speculate that similar considerations may be important in the description of other "slow" electronic processes such as radiationless decay of excited states, such as S_1 or T_1 , to ground states. For example, we have suggested that stilbene triplets having transoid configurations may decay to give both *cis* and *trans* ground state molecules. It is very likely that if a molecule exists in several, closely-related, isomeric ground state configurations, excited states having the geometry of any of the ground states will explore all of the various ground state geometries in attempts to find suitable routes for radiationless deactivation. Such a pseudo-thermal behavior may be largely responsible for the fact that excitation of many molecules seems to be followed by decay to high energy isomers of the original substrate.

Acknowledgment.—This research was supported by the National Science Foundation. We wish to thank Professor G. W. Robinson for many long and useful discussions.

CONTRIBUTION NO. 2978
GATES AND CRELLIN LABORATORIES OF CHEMISTRY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

GEORGE S. HAMMOND

JACK SALTIEL

RECEIVED JUNE 17, 1963

Inner- and Outer-Sphere Mechanisms in the Oxidation of Pentacyanocobaltate(II) by Pentaamminecobalt(III) Complexes

Sir:

Only in a relatively few favorable cases has it been possible to establish unambiguously whether the mechanism of electron transfer between two metal complexes is of the inner- or outer-sphere type.^{1,2} We report here studies on another such system which is of special interest, in that both types of mechanism appear to operate, the contribution of each being separately measurable. A particularly promising opportunity thereby is afforded for the systematic examination of the factors influencing the choice between these two mechanisms.

Our studies relate to the stoichiometry and kinetics of the $\text{Co}(\text{CN})_5^{3-}$ -catalyzed substitution of various pentaamminecobalt(III) complexes by CN^- , which apparently proceeds through an electron transfer mechanism. The products of substitution were identified spectrophotometrically and the kinetics, which are rapid, were measured with a stopped-flow apparatus.

Two distinct types of substitution behavior, differing both in stoichiometry and kinetics, were observed, depending on the nature of the ligand X in the pentaamminecobalt(III) complex, $\text{Co}(\text{NH}_3)_5\text{X}$. For $\text{X} = \text{Cl}^-$, N_3^- , NCS^- , and OH^- , the stoichiometry of the substitution reaction was found to be (as previously

(2) The long lifetime of the triplet produced by nonvertical excitation of *cis*-stilbene is evidenced by its ability to enter into reversible energy exchange with certain sensitizers and to be quenched to *trans*-stilbene by low concentrations ($<10^{-2} M$) of azulene.¹

(3) The theories of Robinson and Frosch⁴ and Gouterman⁵ both indicate that an important feature of radiationless deactivation of excited states is direct transfer of energy into solvent phonon bands.

(4) G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **37**, 1962 (1962).

(5) M. Gouterman, *ibid.*, **36**, 2846 (1962).

(1) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

(2) J. Halpern, *Quart. Rev. (London)*, **15**, 207 (1961).