Energy Transfer between Aromatic Molecules

SEYMOUR SIEGEL AND KENNETH B. EISENTHAL
Materials Sciences Laboratory, Aerospace Corporation, El Segundo, California
(Received 7 January 1963)

THE mechanism of the transfer of electronic excitation energy from a molecule in its triplet excited state (donor) to another molecule in its ground state (acceptor) has received much discussion.[1-4] The discussion revolves about the nature of the interactions between excited donor and acceptor as a condition for the transfer of excitation. It was felt by the present authors that a careful study of the form of the decay curves of the donor and acceptor would yield some information about the strength of the interactions involved. If the interactions were stronger than ordinary van der Waals forces, i.e., complex formation, then one would expect the lifetimes to be altered for both the donor and acceptor molecules. In addition, if the normal donor decay constant (no acceptor present) is *competitive* with the transfer rate constant then for a system in which the donor has a lifetime greater than that of the acceptor one would expect a nonexponential acceptor decay pattern. The donor triplets would act as an auxiliary light source after the exciting source was removed. The experiments and the resulting decay patterns of a system of carbazole (donor, $\tau\sim 7$ sec) and diphenyl (acceptor, $\tau\sim 4.5$ sec) are described below.

The triplet-state concentration was monitored by means of Electron Paramagnetic Resonance. Samples were dissolved in ether–ethanol glasses at 77°K; therefore, it was the $\Delta M=\pm 2$ transitions[5] which were observed. Concentrations used were appropriately $0.1M$ in both constituents. The samples were not degassed but the reagents were purified. The EPR spectrometer used was the commercially available Varian instrument equipped with 100-kc/sec field modulation and the variable-purpose cavity. The latter cavity has a slotted end which allows *in situ* irradiation. Excitation sources were PEK–109 and PEK–502 compact high-pressure Hg arcs which were seated on a wooden optical bench along with a suitable filter and condensing lens system. A motor-actuated rotating slotted wheel placed between the lamp and the microwave cavity was used as a shutter. The spectrum was recorded on a Moseley X–Y recorder. To determine the form of the decay curves the field sweep was stopped at the appropriate field values, the shutter tripped and the decay curve recorded on the Moseley using the time-calibrated X function.

TABLE I. Lifetimes.

System	Molecule	τ(sec)	No. of runs
Biphenyl	Biphenyl	4.4±0.2	6
Carbazole	Carbazole	6.8±0.4	5
Biphenyl and carbazole	Biphenyl	4.6±0.2	5
Biphenyl and carbazole	Carbazole	6.7±0.4	4

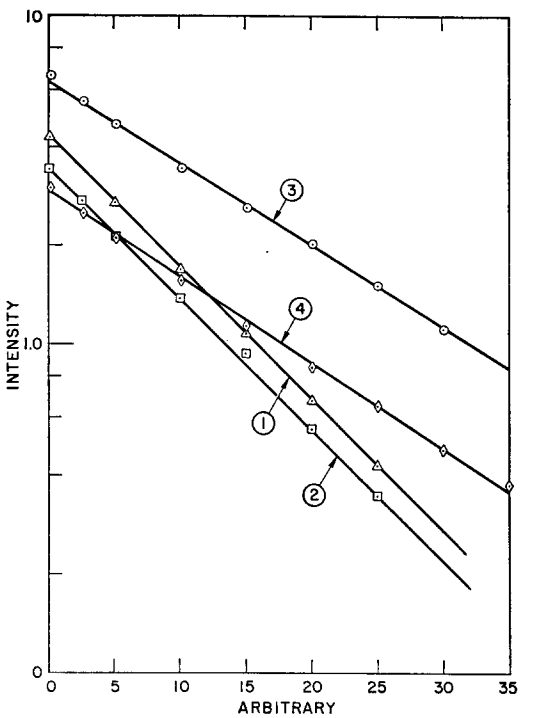

FIG. 1. Log intensity against time: The time scale is in arbitrary units (to convert to sec multiply by 0.394); the intensity scale is also in arbitrary units, and relative intensities between different curves have no meaning. Curves 1, 2, 3, and 4 correspond to the decay of biphenyl with no donor present, biphenyl with donor present, carbazole with no acceptor present, and carbazole with acceptor present, respectively.

The resulting decay curves were exponential in form both for the pure sample, i.e., diphenyl or carbazole alone, and for the binary mixtures. The characteristic lifetimes, given in Table I, were determined by replotting the experimental curves on semilog paper and taking the average over about 3 spans of τ in time. Representative curves are shown in Fig. 1. Maximum deviation from linearity was less than 5% in most runs.

Under steady-state conditions the carbazole has transferred approximately 40% of its excitation energy to the diphenyl at the concentrations employed. However, as seen from Table I and Fig. 1 the decay patterns of both the acceptor and donor molecules are not appreciably affected by each other's presence. If the energy transfer rate has a dependence upon the D–A intermolecular distance, then the observed absence of transfer after the light has been extinguished indicates that the function has a relatively sharp cut-

off point. For about 95% of D–A pairs (the latter number is estimated from the experimentally reliability of the decay curves) the slowest time of transfer is much faster than the normal decay processes at these low temperatures. The latter conclusion is in agreement with some of the previously published work.[1,3]

However, the constancy of the observed decay patterns for both acceptor and donor indicates that the interaction between the molecules is quite weak. If a true complex were formed between donor and acceptor, then, since the excited acceptor has a donor molecule associated with it in intimate nearest-neighbor contact, one would expect that the lifetime of the acceptor molecule would be affected, in contradiction to the experimental results. To further test the conclusion that there are no complexes formed, several experiments were run in which the sample was first cooled to ~248°, ~203° and then to 77°K. There were no appreciable differences in the percent of energy transfer in these experiments compared to the experiments in which the sample was cooled directly to 77°K. Since a complex would have a temperature-dependent equilibrium constant, the latter experimental results support the absence of a chemical complex. Hence, in agreement with the work of Brandon, Gerkin, and Hutchison,[6] one may conclude that complex formation is not necessary for triplet–triplet energy transfer. These results, however, do not rule out exchange interactions[1–3] (not necessarily between nearest neighbors) as the mechanism of energy exchange. Rather, the exponential behavior of the decay curves discussed above supports this latter mechanism.

[1] B. Smaller and J. R. Remko, Organic Crystal Symposium, National Research Council, Ottawa, October 1962.
[2] T. Förster, Discussions Faraday Soc. **27,** 7 (1959).
[3] A. Terenin and V. Ermalaev, Izv. Akad. Nauk, SSSR Ser. Fiz. **26,** 121 (1962); Trans. Faraday Soc. **52,** 1042 (1956).
[4] G. Porter and F. Wilkinson, Proc. Roy. Soc. (London) **A264,** 1–18 (1961).
[5] M. S. de Groot and J. H. van der Waals, Mol. Phys. **2,** 333 (1959).
[6] R. W. Brandon, R. E. Gerkin, and C. A. Hutchison, Jr., J. Chem. Phys. **37,** 447 (1962).

Evidence for Triplet–Triplet Transfer from Benzene to Biacetyl in Cyclohexane Solution*

SANFORD LIPSKY
Department of Chemistry, University of Minnesota, Minneapolis 14, Minnesota
(Received 31 January 1963)

THE emission from biacetyl, optically excited in its first absorption band, consists of both triplet and singlet transitions to ground state with intensity ratio, ϕ_0, phosphorescence to fluorescence, estimated at 60:1.[1] This emission may also be sensitized by electronic energy transfer from suitably chosen donors.[2–5] If the excited singlet state of the donor lies energetically above the biacetyl singlet (e.g., benzene), sensitization may occur by singlet–singlet and/or triplet–triplet mechanisms. Evidence for contribution from the triplet–triplet mechanism obtains if the sensitized phosphorescence to fluorescence ratio, ϕ, exceeds ϕ_0. Ishikawa and Noyes[5] have recently demonstrated such an increase for a benzene–biacetyl gas mixture. This now has been observed in degassed cyclohexane solution at low biacetyl concentration (e.g., $\phi/\phi_0>10$ at $c\simeq 10^{-4}M$). However, for quantitative study of triplet–triplet efficiency, the weakness of biacetyl fluorescence has made it necessary to rely instead on the concentration dependence of the intensity ratio of biacetyl phosphorescence to *benzene* fluorescence.

Studies were made at 25°C on degassed solutions of $0.0110M$ benzene in cyclohexane containing biacetyl varying from 0.325×10^{-4} to $11.6\times10^{-4}M$. The 2550-Å emission of a 1000-W Xe arc was isolated with grating monochromator operating at 100 Å spectral half-width and made incident at approximately 45° on the face of a 1-cm quartz cell. Emission was observed from the opposite face and monitored with Beckman DU monochromator (0.5-mm slit) for benzene fluorescence (2780–3100 Å) and biacetyl phosphorescence (5200 Å). The purification of benzene and cyclohexane, the degassing procedure, and the filling techniques have been described elsewhere.[6] Biacetyl was purified by four bulb-to-bulb vacuum distillations.

The nonradiative transfer probabilities/sec from excited singlet and triplet states of benzene are represented respectively, by k_sc and k_tc. Biacetyl has at least two singlet states (around 2.8, 3.9 eV)[7] and two triplet states (both ~2.5 eV)[7] lying below the corresponding benzene singlet (about 4.7 eV) and triplet (approximately 3.6 eV). Whereas k_sc represents transfer probability/sec from benzene to *some* singlet biacetyl state, p_sk_sc is used to denote probability/sec for ultimate production of the *lowest* excited biacetyl singlet. Thus, p_s may be regarded as the probability for internal conversion to the 2.8-eV state. Similarly, p_tk_tc represents probability/sec for a process in which triplet benzene ultimately produces the lowest biacetyl triplet. In terms of these rates, the ratio, R, of biacetyl phosphorescence to benzene fluorescence should be proportional to

$$R\sim c[p_sk_s\Phi+\nu p_tk_t\tau_t/(1+k_t\tau_tc)], \qquad (1)$$

where Φ is the probability for the intersystem crossing in biacetyl from lowest singlet to triplet, ν is the probability/sec for intersystem crossing in benzene, and τ_t is the lifetime of triplet benzene in the absence of biacetyl. The proportionality constant involves emission quantum yield ratios and an instrument spectral discrimination factor not yet determined. For $c<2\times10^{-4}M$, the first term in the bracket of (1) arising from singlet–