Energy Transfer between Aromatic Molecules

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(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, \( \tau \approx 7 \) sec) and diphenyl (acceptor, \( \tau \approx 4.5 \) 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°C; therefore, it was the \( \Delta M = \pm 2 \) transitions 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 \( \textit{in situ} \) 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.

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 replottting the experimental curves on semilog paper and taking the average over about 3 spans of \( \tau \) 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-

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**Table I. Lifetimes.**

<table>
<thead>
<tr>
<th>System</th>
<th>Molecule</th>
<th>( \tau ) (sec)</th>
<th>No. of runs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biphenyl</td>
<td>Biphenyl</td>
<td>4.4±0.2</td>
<td>6</td>
</tr>
<tr>
<td>Carbazole</td>
<td>Carbazole</td>
<td>6.8±0.4</td>
<td>5</td>
</tr>
<tr>
<td>Biphenyl and carbazole</td>
<td>Biphenyl</td>
<td>4.6±0.2</td>
<td>5</td>
</tr>
<tr>
<td>Biphenyl and carbazole</td>
<td>Carbazole</td>
<td>6.7±0.4</td>
<td>4</td>
</tr>
</tbody>
</table>
Evidence for Triplet–Triplet Transfer from Benzene to Biacetyl in Cyclohexane Solution

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(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, \( \phi_0 \), phosphorescence to fluorescence, estimated at 60:1.\(^1\)

This emission may also be sensitized by electronic energy transfer from suitably chosen donors.\(^2\)-\(^3\) 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, \( \Phi \), exceeds \( \phi_0 \). Ishikawa and Noyes\(^4\) 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., \( \phi_0/\Phi > 10 \) at \( c \approx 10^{-4} M \)). 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 0.0110 M benzene in cyclohexane containing biacetyl varying from 0.325 \( \times 10^{-4} \) to 11.6 \( \times 10^{-4} M \). The 2500 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.\(^5\) 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 \( k_{SE} \) and \( k_{SC} \). Biacetyl has at least two singlet states (around 2.8, 3.9 eV)\(^7\) and two triplet states (both \( \approx 2.5 \) eV)\(^7\) lying below the corresponding benzene singlet (about 4.7 eV) and triplet (approximately 3.6 eV). Whereas \( k_{SE} \) represents transfer probability/sec from benzene to some singlet biacetyl state, \( p k_{SC} \) 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, \( p k_{SC} \) 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

\[
R \sim c[p k_{SC}/(1 + k_{SE} c)],
\]

where \( \Phi \) is the probability for the intersystem crossing in biacetyl from lowest singlet to triplet, \( \nu \) is the probability/sec for intersystem crossing in benzene, and \( \tau_i \) 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 \( c < 2 \times 10^{-4} M \), the first term in the bracket of (1) arising from singlet–