Induced Nonradiative Transitions in Benzene

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A nonradiative electronic transition in benzene occurs at about 2400 cm\(^{-1}\) above the zero-point vibration of the \(1B_{2u}\) electronic state. The rate-determining step may be the vibrational relaxation of the product or the nonradiative transition itself. The rate of the latter is limited to \(10^8 < k_{AC} < 10^{11}\) sec\(^{-1}\) in the vapor at 100 torr and \(k_{AC} \sim 10^{13}\) sec\(^{-1}\) in liquids. There are also limiting values in liquids for the threshold energy and the rate of vibrational relaxation of the initial state.

In liquid solutions, the observed transition rate increases with increasing intermolecular force, but it is not increased by alkyl substitutions. Symmetry perturbation and other sources of solvent-induced transitions are discussed. Also, means are suggested by which it may be possible to catalyse the formation of benzvalene.

Introduction

Two nonradiative transitions from the \(1B_{2u}\) electronic state of benzene have received attention. The first (rate \(k_1\)) dominates in the gas state when the excitation wavenumber is below 40,000 cm\(^{-1}\) and in liquid or glassy solutions below 200 °C K\(^{-1}\). This is an intersystem crossing that originates near the zero-point vibrational level, probably occurs in the isolated molecule, and is not obviously sensitive to changes of intermolecular forces. The second transition \(k_2\) dominates in the gas state with excitation just above 40,000 cm\(^{-1}\) and in liquids above 300 °C K\(^{-1}\). The two processes are related to the fluorescence quantum yield \(q\), the spontaneous emission rate \(k_0\), and the total nonradiative decay (rate \(\Sigma k_i\)) by

\[
\frac{1-q}{q} k_0 = \sum k_i \equiv k_1 + k_2,
\]

where \(k_2 = k_2^0 e^{-E_2/kT}\) (2)

although the second equality has yet to be demonstrated quantitatively. (We consider only transitions that occur below 42,000 cm\(^{-1}\) in the gas state.)

In liquid solutions at a given temperature the total rate of nonradiative decay increases regularly with increasing electrostatic- and London-interactions between benzene and the solvent. At 25 °C \(k_2\) constitutes over 70% of the total and an approximation with a single Arrhenius exponential gives

Theoretical Calculations

Because the temperature coefficients measured in mixed solvents are complicated by temperature-dependent changes of solvent structure, the activation energy \(E_2\) adopted here is the one measured in pure liquid solvents, i.e., n-hexane and methanol. Although the second equality has yet to be demonstrated quantitatively, the approach in the present report the author compares a few mechanisms for the effects that intermolecular forces may have on the second process (on \(k_2^0\) or \(E_2\)). The basic theory is given by Robinson and Burland. Some of the relevant data are summarized in Table 1 and Fig. 1.
### Table 1. The fluorescence yield of benzene dissolved in liquids. Key to Figs. 3 and 5.

| Solvent* | Symbol | Fluorescence Yield $q$ at 25°C | Nonradiative Decay $10^{-8} \sum k_i$ | Cohesive Energy Density, $\gamma^2$ (cal) |
|----------|--------|-------------------------------|--------------------------------------|--------------------------------|--------------------------------|
| 1) Vapor (> 10 torr) | — | $0 - 0.18$ | $> 0.11$ | 0 |
| 2) 2-Methylbutane | O | 0.044 | 0.54 | 46 |
| 3) 2,2,4-Trimethylpentane | O | 0.057 | 0.41 | 48 |
| 4) n-Pentane | O | 0.054 | 0.44 | 50 |
| 5) n-Hexane | O | 0.058 | 0.41 | 54 |
| 6) n-Octane | O | 0.057 | 0.41 | 58 |
| 7) n-Nonane | O | 0.059 | 0.40 | 60 |
| 8) Methylenechlorohexane | O | 0.046 | 0.52 | 62 |
| 9) n-Hexadecane | O | 0.063 | 0.37 | 67 |
| 10) Cyclopentane | O | 0.056 | 0.42 | 66 |
| 11) Cyclohexane | O | 0.061 | 0.38 | 68 |
| 14) Tetramethyilsilane | • | 0.054 | 0.44 | 38 |
| 15) 3-Methyl-1-Butanol | O | 0.045 | 0.53 | 100 |
| 16) 2-Methyl-2-Propanol | O | 0.031 | 0.78 | 113 |
| 17) 2-Methyl-1-Propanol | O | 0.042 | 0.57 | 112 |
| 19) 1-Butanol | O | 0.045 | 0.53 | 120 |
| 20) 2-Propanol | O | 0.037 | 0.65 | 132 |
| 22) Ethanol | O | 0.033 | 0.73 | 168 |
| 23) Diethylether | △ | 0.047 | 0.51 | 60 |
| 25) 1,2-Propanediol | O | 0.029 | 0.84 | 196 |
| 26) 1,2-Ethanediol | O | 0.029 | 0.84 | 212 |
| 27) Methanol | O | 0.027 | 0.90 | 212 |
| 29) 1,2-Dichloroethane | O | 0.031 | 0.78 | 100 |
| 30) Dichloromethane | O | 0.031 | 0.78 | 99 |
| 32) 1,4-Dioxane | △ | 0.044 | 0.54 | 96 |
| 34) 1,2,3-Propanetriol | O | 0.025 | 0.98 | 272 |
| 36) Acetonitrile | O | 0.029 | 0.84 | 141 |
| 37) Chloroform | □ | 0.005 | 5.1 | 87 |
| 39) Water | O | 0.006 | 4.3 | 552 |
| 40) D$_2$O | O | 0.005 | 5.0 | 568 |

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*See Ref. 12.

**Figures 3 and 5.**


Hypothetical limits only for a vapor with two vibrational levels in equilibrium; $\mathcal{S} s_k^i = \{ \sum k_i + k_2 e^{-E_2/kT} \}$ with $\sum k_i = 0.10 \times 10^8$ sec$^{-1}$, $E_2 / h c = 1600$ cm$^{-1}$, and $10^8 < k_2 < 10^{11}$ sec$^{-1}$.

If all molecules of the dissolved benzene were equivalent (see Ref. 40).

Table 2. Classifications for the effects of intermolecular forces on the second nonradiative transition [Eq. (2)]. $k_{\text{int}}$ and $k_{\text{ext}}$ are the vibrational relaxation rates in the initial and final electronic states of the nonradiative transition, respectively. $q_{\text{ac}}$ and $q_{\text{ca}}$ are the densities of vibronically coupled states in the final and initial electronic states, respectively. Under different circumstances, changing the solvent is expected to change the vibrational relaxation rate $k_{\text{int}}$, the nonradiative transition rate $k_{\text{ext}}$, or the activation energy $E_A$. The nonradiative transition rate may depend on the correlation time (not considered here) or the coupling probability where the latter may be factored into vibronic coupling energy $\beta$ and Franck-Condon $F$ factors.

<table>
<thead>
<tr>
<th>Nuclear Coupling Coordinate</th>
<th>Idealized Rate-Determining Step</th>
<th>Irreversibility</th>
<th>Potential Energy Surfaces</th>
<th>Electronic Energy Converted ($\Delta E$)</th>
<th>Anticipated Solvent Effect on:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intermolecular</td>
<td>I. Vibrational Relaxation</td>
<td>$k_{\text{int}} &gt; k_{\text{ext}}$</td>
<td>$q_{\text{ac}} &gt; q_{\text{ca}}$</td>
<td>$\Delta E$</td>
<td>Cross Small or Large $k_{\text{int}} = k_{\text{ext}}$, $E_A = E_A$</td>
</tr>
<tr>
<td></td>
<td>II A. Nonradiative Transition</td>
<td>$k_{\text{int}} &gt; k_{\text{ext}}$</td>
<td>$q_{\text{ac}} &gt; q_{\text{ca}}$</td>
<td>$\Delta E$</td>
<td>Nested Small Large $k_{\text{int}} = k_{\text{ext}}$, $E_A = E_A$, $F$</td>
</tr>
<tr>
<td>Intra-molecular</td>
<td>II B. Nonradiative Transition</td>
<td>$k_{\text{int}} &gt; k_{\text{ext}}$</td>
<td>$q_{\text{ac}} &gt; q_{\text{ca}}$</td>
<td>$\Delta E$</td>
<td>Cross Small Large $k_{\text{int}} = k_{\text{ext}}$, $E_A = E_A$, $F$</td>
</tr>
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</table>
Fig. 1. Energy-level diagram for benzene. Left (a): The fluorescence yield \( q \) of benzene vapor as a function of the excitation wavenumber (Ref. 4, 9). Right (b): Energy levels of benzene, including the zero-point vibrational level of the \( \text{B}_u \) electronic state, and the final sublevel of the perturbed \( 6^1 \text{IG} \) vibronic transition (Ref. 19); and the average activation energy measured in solution, dashed at \( E_q/h = 2400 \text{ cm}^{-1} \) above the zero-point level (Ref. 16, 11). [If excitation in (a) is due to hot bands, the plotted energy of the circles should be raised slightly.]

**Mechanism**

We consider only an idealized stepwise mechanism (Fig. 2) in which either the vibrational relaxation of the primary product (Case I in Table 2) or the nonradiative transition itself (Case II) determines the rate \( k \). This idealization of independent steps will break down in a more complete treatment, for the duration of the rate-determining interaction will depend at least partly on the average rate of the other fast process.17

In the gas state (Fig. 2 A) the excitation (I) near 40,000 cm\(^{-1}\) (to \( A_2 \)) populates excited vibrational sublevels of the \( \text{B}_u \) electronic state.18-22 In vapors of moderate pressure (up to 100 torr)9 no subsequent fluorescence is found. The corresponding


18 This may be seen by the analysis of the vibrational fine-structure in the UV absorption spectrum of benzene.19, 20 One unexpected shift of 20 cm\(^{-1}\) occurs at a somewhat lower energy,19 and the corresponding sublevel excited \( (v_4 + 2 v_{10}) \) is indicated in Fig. 1. The relative ease of assigning the fine structure in the UV absorption to benzene vibrations indicates that physically the initial and final states of the nonradiative transition derive from characteristic but overlapping potential energy surfaces of their own, rather than from a common surface with a double minimum. However, the assignment should be re-examined with respect to considerations summarized by Herzberg.21


22 The threshold of the transition at 40,000 cm\(^{-1}\) may be due to (1) the increasing of the density of final states \( \rho_\infty \) with increasing energy (\( \Delta E \) large), (2) the occurrence of an electronic state not available at a lower energy (\( \Delta E \approx 0 \)), or (3) a crossing of potential energy surfaces (large change in geometry or force-constant, or small changes with \( \Delta E \) large). (\( \Delta E \) is the electronic energy converted to vibrational energy.)
nonradiative transition occurs with a rate $k_{AC}$ where $k_{AC} > (k_{r0} + k_T + k_{AX}) \approx k_{r0}$. (The definitions of the various rate constants are given in Fig. 2.) The vibrational relaxation rate $k_{r0}$ is pressure dependent and is slightly different for different vibrational sublevels. However, in all observed cases it is near the hard-sphere collision rate $^6, ^{23}$ At 100 torr this gives a lower limit of $k_{AC} > 10^8$ sec$^{-1}$. An upper limit is obtained from the linewidth $\delta E/\hbar c < 1$ cm$^{-1}$ in the fine structure of the UV absorption of benzene. Using the uncertainty relation, $k_{AC} \approx \delta E/\hbar \approx 10^{11}$ sec$^{-1}$.

In liquid solutions (Fig. 2B) the fluorescence quantum yield $\eta$ is independent of the frequency of the exciting light $^{25, 26}$ so that $k_{AC} < k_{r0}$, and $[A_o] = [A_e] \exp (-k_{AX}/k_B)$, where the brackets indicate concentrations and $E_A$ is the thermal activation energy.

**Rate-Determining Step.** The activation energy in solution $E_2/\hbar c = 2400$ cm$^{-1}$ agrees with the threshold energy in the gas state (Fig. 1) so little thermally-excited back reaction ($k_{r0}$) occurs in liquids. Otherwise the activation energy would have been the difference $E_2 = (E_A - E_C)$ $^{27}$. The measured $E_2$ becomes $E_A$ of the mechanism, and the pre-exponential $k_2^0$ becomes the rate $k$ of the rate-determining step.

The Arrhenius pre-exponential measured in liquids $k_2^0$ must be equal to or less than the nonradiative transition rate $k_{AC}$, $k_2^0 \leq k_{AC}$, and also $k_{AC} < k_{r0}$. Various measurements on other systems would place $k_{r0} \approx 10^{11}$ sec$^{-1}$ (see Refs. $^{28-32}$), but the resulting inequality $k_2^0 < k_{r0} \approx 10^{11}$ sec$^{-1}$ is not consistent with the activation energy $E_2/\hbar c = 2400$ cm$^{-1}$ and the degree of fluorescence quenching, which gives $k_2^0 > 10^{11}$ sec$^{-1}$ (see Ref. $^{19}$). We must either abandon the simple Arrhenius approximation and use a more exact representation of the rate $^{33}$, or use a higher rate for vibrational relaxation $^{34}$. $k_{r0} \approx 5 \times 10^{12}$ sec$^{-1}$. In the first case, the levels drawn in Fig. 2 must represent a manifold of vibrational sublevels extending upward from a threshold wavenumber of about 1600 cm$^{-1}$ and leading to an average $E_2/\hbar c = 2400$ cm$^{-1}$.

The rate-values ($k_2^0 = k$) obtained both in the vapor and in the liquid are similar to the rates expected for vibrational relaxation in the product. If this is the rate-determining step (Case I, Table 2), $k_2^0 = k = k_{no}$, and in the macroscopic vapor under steady-state illumination

$$[C_n]/[A_o] = k_{AC}/k_{CA} = q_{ac}/q_{ca}.$$  
$q_{ac}$ and $q_{ca}$ are the densities of coupled states for the forward and reverse nonradiative transitions, respectively. Also, in liquids

$$[C_n] = [A_o] \langle q_{ac}/q_{ca} \rangle \exp \{-E_A/k_B T\}.$$  

Although vibrational relaxation of the product has been invoked as a rate-determining step in photochemical tautomerizations $^{36, 37}$, in the present case there is a quantitative difficulty. When 2537 A excitation is used, the vibrational relaxation of the populated benzene levels requires few hard-sphere collisions $^6$. If we apply this result to both the initial ($A_o$) and final ($C_n$) resonant levels under consideration ($k_{no} \approx k_{r0}$, about 450 cm$^{-1}$ higher than reached

$^{23}$ In a vapor of moderate pressure, it is also known that $(k_T + k_{AX}) > k_{r0}$, because no thermal quenching of fluorescence or of triplet state formation is found (up to 700 torr of propane gas) $^{24}$, when low-energy excitation (to a partially equilibrated $A_o$) is used. Using $(k_T + k_{AX}) = 1.4 \times 10^8$ sec$^{-1}$ (sec $^5, ^{12}$) shows that the upward vibrational excitation of about 2000 cm$^{-1}$ ($k_{AX}$) requires more than $10^9$ hard-sphere collisions.


$^{27}$ The location of state $C_n$ in Fig. 2 is immaterial as long as it is not close to state $A_o$, and even then the Boltzmann population factor is near unity and the backward step can be neglected.

$^{28}$ The rate for vibrational relaxation in the $^{1}B_2u$ state of benzene dissolved in liquids is not known. However in the ground state of benzene it is reported to be about $10^9$ sec$^{-1}$ (sec $^{39-41}$). In an excited state of azulene it is reported to be about $10^{11}$ sec$^{-1}$ (sec $^{38}$).
with 2537 Å excitation), there is little room to explain the irreversibility of the transition in the gas state, which requires \( k_{\text{rs}} > k_{\text{sr}} \). One may expect the irreversibility to appear more naturally when the rate-determining step is the nonradiative transition itself, \( k_{\text{rs}} = k = k_{\text{AC}} \) (Table 2, Case II). A forward bias in the densities of states \( \rho_{\text{ac}} > \rho_{\text{ca}} \) then drives the reaction.

### Solvent Effect

In the liquid solutions studied the distance between the molecules does not change much when the solvent is changed, so the intermolecular force is approximately proportional to the minimum depth of the bimolecular potential. As a convenient measure of this depth we take the cohesive energy density \( \delta^2 \) of the solvent. It correlates increasing nonradiative decay rates with increasing intermolecular force. Fig. 3. (A straight line is predicted if the coupling energy of the rate-determining step is proportional to the intermolecular force.)

It is seen that the nonradiative transitions are exceptionally rapid in water and chloroform. Much of this acceleration is caused by energetic electrostatic- and London-interactions, as shown by the correlation between the nonradiative transition rate and the \( (0 - 0) \ ^1\text{B}_{2g} - ^1\text{A}_{1g} \) UV absorption intensity, which increases with increasing electrostatic- and London-interactions and for the solvents considered is most intense in water and chloroform. The high rate in water is to be expected from the high dipole moment. In chloroform, however, the rate is far above that expected. In this solvent, the integrated UV absorption suggests that complexes with benzene are present. In such complexes the effects of electrostatic- and London-interactions may be greater than they are in randomly oriented spheres of solution.

### Intramolecular Coupling

**Symmetry Rules.** If the rate-determining step is a nonradiative electronic transition coupled through intramolecular vibrations (Case II B, Table 2), the intramolecular forces may induce or accelerate the transition by removing restrictions of symmetry. For example, the primary product may be the \( ^1\text{A}_{1g} \) ground state. (A relatively large density of final states \( \rho_{\text{ac}} \) favors such an internal conversion at 40,000 cm\(^{-1}\) (see 14, 43). In this case, the geometry change that accompanies the nonradiative transition is small, and the corresponding vibronic selection rules show that the transition is coupled by the \( b_{2g} \) \((r_{14} \text{ or } r_{15})\) vibrations in the isolated molecule. In the presence of neighboring molecules the electronic transitions are altered by the solvent and benzene in chloroform at 25 °C. Considerably more than 8% of the benzene molecules must be present as complexes in the excited state to account for the difference between this predicted yield and the observed \( q = 0.005 \). Additional complexes are formed in the excited state.

41 M. LUDWIG and C. D. AMATA, J. Phys. Chem. 72, 3725 [1968].
wave functions of benzene are perturbed so that the forbidden \((0 - 0)^{1}B_{2u} - ^{1}A_{1g}\) UV absorption appears. At the same time, nonradiative transitions coupled by \(e_{1u}\) and \(e_{2g}\) vibrations (for example) are introduced. (We have been led to look in particular for transitions coupled by the \(v_6\ e_{2g}\) and \(v_{10}\ e_{1g}\) vibrations because their UV-excitation near 40,000 \(\text{cm}^{-1}\) (Fig. 1) is perturbed.)

Benzvalene (Fig. 4) is a photochemical product obtained from benzene\(^{36, 45}\) (see “Discussion” below) and the corresponding vibronic rules are given in

![Fig. 4. Equilibrium nuclear configurations for the tautomerization of benzene to benzvalene.](image)

Table 3. If the \(^{1}A_{1}\) ground state of benzvalene is the primary product there are eleven vibrations of four symmetries (including the \(e_{2g}\)) that couple the transition in the isolated molecule. Intermolecular forces may induce coupling by some of the remaining vibrations. Also, another symmetry restriction may apply. This is the \textsc{Woodward-Hoffmann} correlation\(^{46}\), which is invoked in tautomerizations for which the geometry change is relatively large. The correlation does not favor the \(^{1}B_{2u} - ^{1}A_{1}\) transition, but does favor that of \(^{1}B_{1u}\)-benzene to \(^{3}B_{1}\)-benzvalene\(^{37}\). Again the intermolecular forces may induce the transition by introducing some \(^{1}B_{1u}\) and \(^{1}B_{1}\) symmetry into the initial and final states, respectively.

\textbf{Substitution Effects.} Perturbations that are caused by intramolecular substitution exceed the intermolecular ones, even when the former are as weak as those produced by alkyl-substitution. For example, alkyl substitutions cause the \((0 - 0)\) absorption peak in the \(^{1}B_{2u} - ^{1}A_{1g}\) UV absorption spectrum to appear\(^{47}\), and in so doing they are considerably more effective than intermolecular forces\(^{39}\). Also as expected the alkyl substitutions cause an increase in the spontaneous emission rate, and this is shown in Fig. 5\(^{48}\). However, the total nonradiative decay rate \((\geq k_1 + k_2)\) is not increased by the substitution\(^{49-51}\). Clearly the solvent perturbation that leads to increasing nonradiative transition rates is different from the in-plane perturbations that lead to enhanced \((0 - 0)\) UV absorption and enhanced spontaneous emission.

\(^{45}\) I. E. \textsc{DenBesten}, L. \textsc{Kaplan}, and K. E. \textsc{Wilzbach}, J. Amer. Chem. Soc. \textbf{90}, 5868 [1968].

\(^{46}\) R. \textsc{Hoffmann} and R. B. \textsc{Woodward}, Accounts Chem. Res. \textbf{1}, 17 [1968].


\(^{49}\) That nonradiative transitions of alkyl-benzenes and benzene itself may be usefully compared is indicated by the close resemblance in the gas state of the nonradiative transitions of toluene and benzene\(^{50, 51}\).\(^{50}\) C. S. \textsc{Burton} and W. A. \textsc{Noyes, Jr.}, J. Chem. Phys. \textbf{49}, 1705 [1968].

The intermolecular forces might mix in planar-antisymmetric states not available from alkyl-substitution. For example, out-of-plane vibrational modes may couple the $1^2B_2u$ and $1^1A_1g$ benzene states in the presence of intermolecular forces. However, this mechanism cannot account for the solvent effect if benzvalene is the primary product. Consider the data for mesitylene. In the mesitylene tautomer both the $\sigma_{xy}$ and $\sigma_{xz}$-symmetric symmetries of benzvalene are removed to some degree by the alkyl groups. However, the nonradiative transition rate (Fig. 5) is affected less by the substitution than it is by a polar solvent. That the $\sigma_{xz}$-symmetry is not crucial to induced tautomerization is also indicated by the isolation of both 1,2,4-tri-t-butyl and 1,3,6-tri-t-butylbenzalenes. The latter, but not the former, is symmetric about the $\sigma_{xz}$ plane.

We are led to believe that (1) if the primary product of the nonradiative transition is a valence tautomer such as benzvalene, the solvent-induced nonradiative transitions are probably not caused by a breakdown of symmetry, and (2) if the intermolecular forces do break down a crucial symmetry (related to the vibronic rules), the primary product is probably planar (for example, $1^1A_{1g}$-benzene), and the solvent perturbs this symmetry.

**Discussion**

**Solvent Effects.** In the nonradiative transition step, the particular initial and final states that interact at a given energy will depend on the solvent if the energy of one state shifts with respect to the other when the solvent is changed. However, in liquid solutions there is a large inhomogeneous broadening of the energy levels. The broadening is not much different from the frequency shifts that can be induced in the electronic energy of a nonpolar molecule by changing the solvent. As the shift does not greatly exceed the width, we do not expect the coupled initial and final states to change much when the solvent is changed. In particular, if the nonradiative transition is a $1^2B_{2u} \rightarrow 1^1A_{1g}$ internal conversion, the effect of solvent on the nonradiative transition does not derive from the relative shift of the electronic energies of the coupled states. The solvent-induced shift of the $1^2B_{2u} \rightarrow 1^1A_{1g}$ electronic absorption frequency has been measured, and it does not correlate with the rate of the nonradiative transition as a function of solvent.

If the vibrational relaxation of the primary product is the rate-determining step (Case I), the coupling energy and the observed transition rate should increase with increasing intermolecular force and should be comparatively insensitive to molecular symmetry, in accord with the experimental data. Similarly the data are in accord with a mechanism in which the rate-determining step is a nonradiative electronic transition (Case II) coupled through the

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52 This mechanism can be checked by calculation of the sort carried out by ALBRECHT on vibronic absorption and by YOUNG on nonradiative transitions. The matrix elements are known in general, and trial wave functions are available, and accurate methods to include solvent perturbations have been developed.

55 O. V. SVERDLOVA, Opt. Spectry. 6, 223 [1959].
intermolecular coordinate (IIA) 57-59. (In this latter case the competition between the nonradiative transition and the vibrational relaxation must be considered in detail as a function of the distance between the molecules.)

If a rate-determining nonradiative electronic transition arises from the vibronic coupling of intramolecular vibrations (II B), there are a number of additional mechanisms possible. Increasing rates will result from increased coupling probability that is related in turn either to increasing vibronic coupling energy [β in Table 2] or increasing Franck-Condon overlap (F) 33, 64, 65. The coupling energy β will increase when symmetry restrictions are removed (treated above) or when a change in the shape of the electronic wave functions occurs without reduction of symmetry 44. A sensitivity of the Franck-Condon overlap F to intermolecular forces (Table 2) is expected only when the potential energy surfaces of the initial and final states are nested and when ΔE, the amount of electronic energy converted to vibrational energy, is large. ΔE should be large because the vibrational wave functions are most sensitive to intermolecular forces at high amplitudes of vibration 16, 66. If the potential energy surfaces are not nested, E2 = E1 is lowered when the vibrational anharmonicities added by intermolecular forces lower the energy of the intersection (F remaining about the same).

Benzvalene as Product. In the gas state with increasing wavenumber of excitation, increasing amounts of 1B2u-benzene disappear (Fig. 1 a) 8, 9 and increasing amounts of benzvalene are isolated 36. Also, the amount of benzene that disappears and the amount of benzvalene isolated from the vapor both increase when added gases are introduced 67, 68. In liquid solutions, both the disappearance of the 1B2u state of benzene 55 and the isolation of benzvalene 36 are independent of the excitation wavenumber. In addition, neither the observed nonradiative transition rate (Fig. 5 and Ref. 50) nor the isolation of benzvalene 45 are markedly sensitive to alkyl-group substitution. These correlations suggest that benzvalene is a product of the induced or partially-induced transition discussed (rate k3 69). The primary product of the nonradiative transition may be the 1A1g ground state of benzvalene, the 1A1g ground state of benzene that subsequently converts to the tautomer 78, or other intermediates 69.

Conclusions

Rate-determining Step. In an idealized step-wise mechanism (Fig. 2), the rate-determining step may be the vibrational relaxation of the primary product (Table 2, Case I, induced by intermolecular forces and bearing no particular relation to the intramolecular symmetry of benzene), or the nonradiative transition [Case II, caused by displacements in the intermolecular coordinate with symmetry again irrelevant (II A), or by intramolecular vibrational displacements related to molecular symmetry (II B)]. In the vapor 108 < kAC < 1011 sec−1 at 100 torr, and kAC > k0. If vibrational relaxation of the product is rate-determining, kCA > k00, and k00 > k0. However, vibrational relaxation of the initial resonant
sublevel \((A_r)\) and the final level \((C_n)\) may both require only a few collisions, so \(k_{n0} \sim k_{r0}\). In such a case, the nonradiative transition \((k_{AC})\) must be the rate-determining step. Such an irreversible nonradiative transition requires both that \(k_{AC}/k_{r0} > 1\) and \(k_{CA}/k_{n0} < 1\), so \(k_{AC} \gg k_{CA}\). This can be caused by a forward bias in the density of states \(\omega_{AC} > \omega_{CA}\).

In liquids \(k_{AC} < k_{r0}\) and the measurements on fluorescence quenching give \(k_2^0 = k \sim 10^{11} - 10^{13}\) sec\(^{-1}\) when a single activation energy \(E_A/hc = 2400\) cm\(^{-1}\) is adopted. These data are not consistent with values of \(k_{r0}\) that have been measured for the ground state of benzene and for an excited state in azulene, \(k_{r0} \sim 10^{10} - 10^{11}\) sec\(^{-1}\). Either the vibrational relaxation of the levels coupled by the nonradiative transition in benzene is considerably more rapid, \(k_{r0} \sim 10^{12}\) sec\(^{-1}\) in liquids, or the activation energy should be spread over several levels starting above a threshold of about 1600 cm\(^{-1}\).

**Solvent Effects.** Concerning the effects of intermolecular forces, the conclusions may be summarized as follows. First, when the rate-determining step is the vibrational relaxation of the primary product (Case I) or a nonradiative transition coupled by intermolecular motion (II A), the increasing rate with increasing intermolecular force is expected, for the intermolecular coordinate enters explicitly in the transition probability. In either of these cases the induced nonradiative decay becomes slower than spontaneous emission at very low pressures in the gas phase. If nonradiative transitions persist at low pressure, the induced decay may arise from an acceleration of nonradiative transitions already coupled by intramolecular vibrations in the isolated molecule (II B). This may be caused by reductions of molecular symmetry, with respect to which the following conclusions may be drawn:

1) If the primary product is benzvalene, and if either the Woodward-Hoffmann or vibronic symmetry rules are valid, the intermolecular forces do not act to break the symmetry restrictions. This is because the rate is not significantly accelerated by alkyl-substitutions, and these perturb the relevant symmetry more than the intermolecular forces.

2) When the primary product is planar (for example, benzene \(^1\)A\(_{1g}\)) the intermolecular forces may mix in planar-antisymmetric states and introduce coupling by out-of-plane vibrations.

Also the effects of intermolecular forces (under II) may not be due to a breakdown of symmetry but to variations in:

- \(\Delta E\), the electronic energy converted to vibrational energy during the transition. However in liquids the inhomogeneous broadening of the vibronic levels is so large that this seems unlikely. If the primary product is \(^1\)A\(_{1g}\)-benzene, the variation in \(\Delta E\) does not explain the solvent effect observed, for there is no correlation between the nonradiative transition rate and the changes in \(\Delta E\), which have been measured;

- Franck-Condon overlap, \(F\). A solvent is expected to significantly affect \(F\) only when \(\Delta E\) is large and the potential energy curves are nested at the transition energy (possible when the product is the ground electronic state of benzene and the threshold energy derives from the increasing density of states with increasing energy);

- The energy at which two potential energy surfaces intersect, as expected when \(\Delta E\) and the geometry change (or force constant change) are both large (for example, when \(^1\)A\(_{1g}\)-benzvalene is the primary product).

The mechanisms ii) and iii) depend on anharmonicities in the potential energy surfaces and their sensitivity to intermolecular forces.

**Benzvalene.** Correlations between the nonradiative transition (rate \(k_2\)) and the formation of benzvalene suggest that the tautomer is a product of the transition. If so, the activation energy for its formation in liquids should be 2400 cm\(^{-1}\) (see \(^{71}\), \(^{72}\)), and the formation may be catalyzed by carbon tetra-chloride, chloroform, possibly 1,3-pentadiene, or other complex-forming compounds, as well as by molecules of high dipole moment and polarizability (Fig. 3). The geometry change that occurs in the tautomerization is relatively large, so the Franck-Condon overlap may require many vibrational excitations in the primary product of the initial nonradiative transition step. This product may be the

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\(^{71}\) Measurement of the activation energy may be possible in solvents such as glycerol or water that are rigid enough to trap the benzvalene before it reconverts to benzene. The amount of trapped benzvalene may be determined after conversion to more stable derivatives.

\(^{72}\) This may also be the activation energy for the disappearance of triplet states of benzene in liquids.
ground state of benzvalene or the ground state of benzene that leads in turn to the tautomer. In the latter case, if the rate-determining step is the $^1A_{1g} \rightarrow ^1B_{2u}$ internal conversion coupled by intramolecular vibrations, the formation of benzvalene might be catalyzed by chemical substitutions that reduce the planar-symmetric symmetry.

Nonradiative transitions are exceptionally rapid in benzyl-vibrations, the formation of benzvalene might be accepted. The mean travelling distance of the excitons in the three host lattices was found to be 250—300 mean molecular distances.

I. Einleitung


Die Grundgitter- und Gastsubstanzen wurden so gewählt, daß sich ihre Fluoreszenzspektren mit Hilfe geeigneter Filterkombinationen trennen lassen. Als Grundgitter wurden die Verbindungen 2,3-Dimethylanthrynalanilin (2,3 DN), Phenanthren (Ph) und p-Terphenyl (p-Tp) gewählt, als Dotierungen dienten Anthracen (A) und Tetracen (T).

In diesen ternären Systemen kann durch gezielte Anregung der einzelnen Komponenten untersucht werden, ob die beiden Dotierungen ihre Anregungsenergie unabhängig voneinander aus dem Excitonenband des Wirtes beziehen, oder ob auch eine Energieübertragung von der einen zur anderen Gastkomponente stattfindet. Letzterer Prozeß könnte bei

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