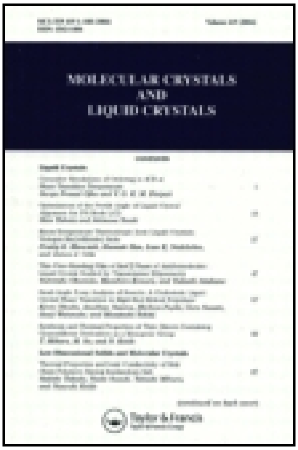

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On the Excited Cyclohexane Molecule as a Possible Excitation Donor in Luminescence Processes

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Abstract—Data on the kinetics of processes involving radiation protection, luminescence and luminescence quenching in cyclohexane solutions as well as on absorption spectra and luminescence of aliphatic glasses are briefly reviewed. It is concluded that energy transfer in a cyclohexane system cannot involve excitation transfer from single excited cyclohexane molecules. The Laor-Weinreb results[1] are explicable on the basis of charge transfer.

1. Introduction

One of the important questions both of radiation chemistry and of luminescence phenomena in condensed systems relates to the possibility of excitation transfer from an excited aliphatic hydrocarbon donor to an acceptor. In most cases the question refers to the experimental situation in cyclohexane solvent. On this question the work of Laor and Weinreb[1] on sensitized luminescence may be in the affirmative while that of similar work of Lipsky and Feinleib[2] seems definitely negative. On the other hand, the very detailed study by Merklin and Lipsky,[3] on cyclohexane-benzene mixtures, in which the kinetic treatment is formally in terms of "excited" cyclohexane, may be imagined to support the reality of such a process. However, in order to assess the actual physical situation properly, it is necessary to define the word "excited" in terms more precise than are required for mathematical formalism.

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For the purposes of the present discussion I define an electronically excited molecule in the conventional sense. It is a molecule in which one or more electrons are excited to a higher state, short of actual ionization. It is not a charge-separated or polaron state, such as may be produced in a condensed system. It is not excitation belonging to a molecule *and* its locale, such as may be invoked in condensed systems.[4] Further, it is not the type of delocalized excitation situation which exists briefly in a group of molecules ("spur" or "blob") such as is created along an ionization track in the high-energy irradiation of condensed systems;[5] in such cases, individual excited molecules resultant, perhaps, from secondary (localization) processes *are* included in the definition.

The *phenomenon* of energy transfer has been known for a long time in photosensitization processes. However, the *mechanism* itself has been subject to a variety of interpretations including the idea of excitation transfer in both non-adiabatic and adiabatic processes. The first cited case of protection in radiation chemistry (i.e., of liquid cyclohexane by benzene[6]) invoked the idea of energy transfer but carefully avoided a definitive statement as to the nature of the donor species—whether it was ionic or excited. Later interpretations have leaned heavily on charged aliphatic donors[7] or on secondary localization of energy directly in the protector species without intermediate involvement of individual protected aliphatic molecules. Usually, the question of the possible involvement of individual excited aliphatic molecules (i.e., in excitation transfer processes) has been carefully avoided.

It is the objective of this paper to show that information exists on the basis of which a decision can be made as to the involvement, or possible involvement, of excited cyclohexane molecules in excitation transfer processes in condensed systems.

2. Kinetics

Excitation transfer in liquids

The theoretically maximum rate of a bimolecular reaction corresponds to reaction on the first collision; i.e., no activation energy is required and there is no steric effect. Specific rates of such processes at room temperature are approximately 10^{10} M^{-1} sec^{-1}; they are diffusion controlled. For excitation transfer processes higher specific rates, k_t, have been reported;

they require the notion of increased radius of interaction without accompanying decrease in diffusion constant. The problem was solved by Förster,[8] who presented a model, based on dipole-dipole resonance interaction, in which transfer takes place typically over a distance of 40 A; in such case maximum values of k_t of $\sim 5 \times 10^{10}\, M^{-1}\,\mathrm{sec}^{-1}$ may be expected. Values of this magnitude, e.g., $3 \times 10^{10}\, M^{-1}\,\mathrm{sec}^{-1}$ for $^1B_{2u}$ benzene at very low concentration transferring to *p*-terphenyl in cyclohexane solution, have been observed and are in reasonable conformity with the Förster theory.[9]

A special problem is, however, presented by the same type of transfer (i.e., benzene donor to scintillator acceptor) in cyclohexane liquid of high benzene concentration and in pure benzene as solvent. Increased values of k_t approaching $6.6 \times 10^{10}\, M^{-1}\,\mathrm{sec}^{-1}$ suggest the participation of intermediate benzene molecules in the excitation transfer process and require a strong interaction between benzene molecules.[9] Strong interaction between benzene molecules involving the $^1B_{2u}$ state is required but is not to be expected as a dipole-dipole process. The suggestion was made, and it has been shown in calculations by Voltz, that the assumption of octupole-octupole interactions is adequate to explain the high specific rates characteristic of transfer between benzene molecules.[10]

The conclusion from this brief review of bimolecular reactions which proceed with high specific rate (i.e., $k_t \sim 5 \times 10^{10}\, M^{-1}\,\mathrm{sec}^{-1}$) is that they can be explained on the basis of long-range interactions of considerable magnitude. Values of k_t significantly in excess of such numbers are not to be expected on the basis of current theory. Consequently, very high values of experimentally determined specific rates merit special attention.

We may, as an example, consider without prejudice values of k_t determined for transfer of excitation to a scintillator in pure cyclohexane solvent as compared with benzene solvent. Two cases have been measured[4]

	k_t, $M^{-1}\,\mathrm{sec}^{-1}$, in	
Scintillator	Benzene	Cyclohexane
p-terphenyl	5×10^{10}	$>1.2 \times 10^{12}$
PPO	$\sim 7 \times 10^{10}$	$>1.6 \times 10^{12}$

Precise values of k_t were determined from decay-time data; limiting data (i.e., for cyclohexane solvent) were determined from such data and more recently determined Q' values.[11] It is noteworthy that the numbers and the acceptors are precisely known, that the donor is established as the state excited by light of 2537 A (i.e., the ${}^1B_{2u}$ state of the single benzene molecule) in the case of benzene,[12] but that the donor state in cyclohexane solvent is simply *not* known. It can, however, be said that one may view with considerable suspicion, as explanation of the extraordinarily high value of k_t in cyclohexane, the suggestion that the mechanism of excitation localization in the scintillator in cyclohexane solvent is a conventional bimolecular reaction involving one donor molecule and one acceptor molecule.

Luminescence quenching in high-energy irradiated systems

Details of luminescence quenching in cyclohexane scintillator solutions are not thoroughly known. However, it is established that the quenching process involves the solvent (not the scintillator). In the case of carbon tetrachloride as quencher the specific rate k_q has been established to be $> 3.0 \times 10^{11}$; i.e., it is abnormally high—higher than that corresponding to any bimolecular collision process.[13] Furthermore, in this case, the concept of excitation transfer at a distance is not helpful because no evident resonances can be invoked. Thus, the inference again is that in a case where cyclohexane acts as the principal primary absorber of energy it loses that energy, this time to a quencher species, in a process which does not involve excitation transfer.

3. Spectra

In the cases of the aliphatic hydrocarbon molecules structured absorption spectra do not appear to have been observed.[14]

The proper inference is that the lifetime of the excited state is $< 10^{-11}$ sec; photochemists generally assume $\sim 10^{-13}$ sec. It is interesting that Dr. Lipsky[2] reports that when solutions of *p*-terphenyl in cyclohexane are irradiated by a xenon or krypton lamp in the range of wavelength absorbed by cyclohexane, but not importantly by the scintillator directly, no significant luminescence is produced.

Work on luminescence from pure aliphatic glasses at temperatures in the neighborhood of 77°K indicates that although excited states may be produced very late in the history of events (in electron capture by a positive hole) and emit light, those states belong *not* to a single molecule but to a molecule and its entire locale.[15] Such states have *not* been found to be involved in sensitized luminescence phenomena; they are not even produced if trace amounts of scintillator species are present.[15b] In such case, the excitation is localized in the scintillator, which emits its own characteristic luminescence, without any evidence of the production of excited states characteristic of the pure glass.[15b,16]

4. Conclusion

The only reasonable conclusions from this set of facts are that the established, extraordinarily large values for k_t and k_q in cyclohexane imply that the process in cyclohexane *cannot* involve simple excitation transfer from an excited donor molecule to an acceptor, that the process involves a type of reaction in which, quite probably, charge transfer (or electron capture) occurs in an initial act requiring about 10^{-13} sec or less and that the values of k_t and k_q have only formal significance and do not relate to an isolable (chemical) mechanism.

The Laor-Weinreb results[1] cannot be considered independently of the entire set of kinetic and spectral data. Any mechanism suggested must be compatible with all that is known as well as with the facts there reported. It is noteworthy that, in the work reported for luminescence of PPO in cyclohexane (or hexane), the luminescence decreases to a minimum in the wavelength region where the aliphatic hydrocarbon absorbs and then rises slightly as the wavelength is decreased. At the low wavelength, photoionization of the aliphatic molecules becomes important. Thus, on the reasonable assumption that the data themselves are trustworthy, one interpretation of the Laor-Weinreb results is that the luminescence observed is the consequence of charge transfer from cyclohexane C to scintillator X in a series of reactions which may be written[17]

$$
\begin{aligned}
&\mathrm{C} \rightsquigarrow \begin{cases}\text{Products}\\ \mathrm{C}^{+} + e\end{cases}\\
&\mathrm{C}^{+} + \mathrm{X} \rightarrow \mathrm{C} + \mathrm{X}^{+}\\
&\mathrm{X}^{+} + e \rightarrow \mathrm{X}^{*}\\
&\mathrm{X}^{*} \rightarrow \mathrm{X} + h\nu
\end{aligned}
$$

Other reactions very probably also take place but these explain the Laor-Weinreb results without the unacceptable assumption of excitation transfer. Actually, the kinetics of high-energy induced processes are very much more complicated than represented by this simple set of equations. The donor state of excitation or ionization is probably not localized[4, 18] nor can the kinetics of homogeneous systems be employed in interpretation of the results.[19]

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