THE CONTRIBUTION OF ELECTRONICALLY EXCITED STATES
TO THE RADIATION CHEMISTRY OF ORGANIC SYSTEMS

PROGRESS REPORT

SANFORD LIPSKY

Department of Chemistry

University of Minnesota

Minneapolis, MN 55455

June 30, 1989 - April 30, 1990

Prepared for the United States Department of Energy under Contract No.

DE-FG02-85ER13404

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED
22

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe privately owned rights.

A. ABSTRACT

The absorption of 160 nm light by cyclohexane in mixtures of cyclohexane, benzene and tetraphenylmethylenediamine results in an emission spectrum consisting of the simultaneous fluorescence from all three components. A mechanism for the development of this spectrum and its dependence on benzene concentration is constructed and shown to be quantitatively consistent with the results of independent measurements on the separate components. In the absence of tetraphenylmethylenediamine, the quenching of cyclohexane fluorescence by benzene is found to be well represented by the standard diffusion model but with important contributions from "transient" terms. However, the concomitant sensitization of benzene fluorescence via energy transfer from cyclohexane is found to occur with an efficiency factor of only 0.26 ± 0.02 per encounter.

The fluorescence from both cyclohexane and benzene in their irradiated mixtures has been studied as a function of benzene concentration from ≈ 0.005 M to 0.1 M. The quenching of the cyclohexane emission by benzene is found to be significantly greater than obtains under optical excitation conditions suggesting an important role for benzene as a scavenger of the geminate ion-pair precursor of the fluorescing state of cyclohexane. From diffusion models, a lower bound is established for the scavenging rate constant. An examination of the fluorescence from benzene leads to the conclusion that although the majority of benzene fluorescence derives from electronic energy transfer from excited cyclohexane, a large fraction (from ≈ 20 –50% over the concentration range studied) is generated by recombining molecular ions. The intrinsic efficiency with which the recombining ions generate fluorescent states of benzene, however, appears to be peculiarly low.

Minima have been located in the excitation spectra of neat cyclohexane and 2,3-dimethylbutane at approximately the positions of their ionization potentials. The implication is that electron + positive ion neutralizations generate excited neutral states at energies lower than the ionization threshold.

The emission spectrum of cyclohexane vapor is observed to red shift as the excitation energy is blue shifted from 175 nm to 150 nm. These results are qualitatively consistent with previous observations of the effect of excitation energy on the lifetimes of the vapor emission.

Preliminary results on the emission spectrum of cyclohexane liquid excited via 2-photon absorption at 308 nm seem to indicate a slight change in spectral distribution with increasing delay time. If verified, this would be consistent with a predicted long-lived excited metastable state of cyclohexane.

B. RESEARCH

1. The Transfer of Electronic Energy from Cyclohexane to Benzene to Tetramethylphenylenediamine

We have recently reported on a peculiar effect of solution composition on the fluorescence intensity of a solute (T) dissolved in a mixture of cyclohexane (C) and benzene (B) when primary light absorption is by the cyclohexane.^(1,2) In these studies, the fluorescing state of T (i.e., T*) is generated indirectly via the two electronic energy transfer channels

and

where C* and B* are the fluorescing states of C and B and B* is generated via

Since the channel II process should be more efficient than the channel I process (by virtue of the much longer lifetime of excited benzene), it was expected that the addition of small amounts of benzene to cyclohexane (at constant concentration of T) would cause an increase in the intensity of T* fluorescence. Instead, a rather dramatic decline was observed.

To explain this, it was noted that if there were a fundamental inefficiency in the channel III process, then the addition of benzene, by subverting some C^* from channel I to channel III, would indeed lower the yield of T^* so long as the product of the efficiencies of channels II and III was less than the efficiency of channel I. To account for the channel III inefficiency, it was proposed that in the transfer of energy from C^* to B, the propensity to preserve the total electronic energy of the system would cause there to be generated a large initial population of electronic states of benzene above B^* (by virtue of the ca. 2 eV disparity in electronic energies of C^* and B^*) which would then internally convert to B^* with low probability.^(3,4) In the present investigation we have more quantitatively established this mechanism by simultaneous observations on the fluorescence of all three components, cyclohexane, benzene and T as functions of benzene concentration when the cyclohexane is excited in its far UV absorption system at 160 nm. Additional to this we have demonstrated in this work that the quenching efficiency by benzene of cyclohexane fluorescence (excited at 160 nm) can be explained adequately by a 1-state standard diffusion quenching model that includes "transient" effects. There appears to be no evidence for contributions to the quenching by interception by benzene of upper excited states of cyclohexane as has been previously suggested.⁽⁵⁾ Rather, the state initially populated at $\lambda_e = 160$ nm is shown to convert rapidly to the emitting state of cyclohexane, with an efficiency of 0.65 and that the quenching action of benzene is exclusively on this emitting state. In this quenching encounter, no electronic excitation appears to be lost, i.e., for every excited cyclohexane that is quenched, an excited benzene is generated, albeit not one that necessarily internally converts to the emitting state of benzene. Indeed, the probability for the internal conversion to the emitting state from the distribution of states initially populated by the energy transfer process is only 0.26. Thus only about one in every four quenching encounters between excited cyclohexane and benzene results in the production of an emitting state of benzene.

A manuscript describing these results has been submitted to *J. Phys. Chem.*

2. Energy Transfer From Cyclohexane to Benzene in Their Irradiated Mixtures

The formation of excited solute states in irradiated saturated hydrocarbon liquids derives from both neutral and ionic channels. The neutral channel involves the formation first of an excited solvent molecule (either formed directly or via geminate electron + positive ion recombination) followed by non-radiative transfer of this excitation to the solute. The ionic channels are more complex involving capture by the solute (hereafter referred to as B) of either the geminate electron, to form B^- , or of the positive charge of the solvent (hereafter referred to as C), to form B^+ , followed by some or all of the possible ionic recombination processes (i.e., $B^+ + B^-$, $B^+ + e^-$, $B^- + C^+$).

The relative contributions of these various channels to the observed yields of excited solute states has been considered by many investigators,⁽⁶⁻¹¹⁾ but remains generally unresolved. In only one case, that of biphenyl in cyclohexane, has there been some important progress made recently on this question using picosecond pulse radiolysis with analysis of both biphenyl negative ion and biphenyl fluorescence.⁽¹²⁾

In the case of benzene (or toluene or p-xylene) as solutes, the question of the mechanism of formation of excited aromatic takes on some additional relevance since the yields of these states (as deduced from their fluorescence) have been sometimes utilized to deduce G values for excited solvent states^(6,13,14) under the assumption that all of the ionic channels are ignorable. Neither benzene nor toluene or p-xylene are considered to form negative ions with any significant probability and their concentrations, in these studies, were kept sufficiently low as to avoid, presumably, any appreciable contribution from geminate positive charge transfer processes.^(13,14) However, the G values of excited solvent states thus obtained are found to be significantly lower than values determined by other methods.^(12,15,16,17) Although the question of possible origins for this disparity have been considered,^(14,16) there appears still no definitive answer.

By comparing the results obtained in our optical study of cyclohexane + benzene fluorescence (see section B1 of this Progress Report) with entirely similar experiments but using 0.22 MeV β^- particles as excitation source, we have been able to provide some new information pertinent to the mechanism of the formation of excited benzene. This information is summarized below.

Three possible mechanisms have been considered for the interaction of benzene with a recombining geminate $C^+ + e^-$ ion-pair in irradiated cyclohexane, namely (i) attachment of e^- to form B, (ii) electron transfer to C^+ to form $B^+ + C$ and (iii) formation of a temporary negative ion that decays to a thermal electron + B. It has been demonstrated that neither mechanism (ii) nor mechanism (iii) can be exclusively operating (i.e., there must be some non-trivial contribution from electron attachment). With the assumption that of the ionic routes to B^* , only $B^- + C^+$ or $B^- + B^+$ are important (i.e., $B + e^-$ is ignorable), it is concluded that the rate constant for electron attachment to benzene in cyclohexane cannot be less than ca. $7 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ and may be as large as $3 \times 10^{11} \text{ M}^{-1} \text{ sec}^{-1}$ if mechanism (iii) is ignorable. Also it is demonstrated that the annihilations of $B^+ + B^-$ and of $C^+ + B^-$ to give B^* are required to have efficiencies much less than unity if mechanism (iii) is ignorable.

The fraction of the total fluorescence from benzene that is attributable to electronic energy transfer from excited cyclohexane (formed by unperturbed $C^+ + e^-$ recombinations) is computed quite generally from the data to vary from 0.83 to 0.47 over the benzene concentration range from 0.0056 to 0.112 M. The remainder of this fluorescence is due to recombining molecular ions which clearly make a non-trivial contribution until concentrations much less than 0.0056 M are achieved. Accordingly, attempts to utilize benzene fluorescence to deduce the G value for excited cyclohexane by totally ignoring the ionic contributions, may be seriously in error.

A manuscript describing these results has been submitted for publication in *Rad. Phys. Chem.*

3. Other Work in Progress

(a) Studies of Positive Ion + Electron Recombination Fluorescence in Hydrocarbon Liquids

Quantum yields of fluorescence have thus far been obtained at 20 °C from cyclohexane, 2,3-dimethylbutane and cis-decalin as functions of excitation energy from 150 to 130 nm. In cyclohexane and 2,3-dimethylbutane, the quantum yields decline rapidly from 160 to 140 nm and then slowly increase to 130 nm. The ionization potentials of these liquids lie at about 140 nm. For cis-decalin the yield remains flat for 160 to 130 nm. Measurements at lower temperatures and at shorter wavelengths are being planned.

(b) Studies of the Fluorescence Spectra of Simple Hydrocarbon Vapors

A red shift has been observed in the emission spectrum of cyclohexane vapor (at 54 torr) as the excitation energy is shifted from 175 nm to 150 nm. The effect of pressure on this red shift is being examined and measurements on other vapors are planned.

(c) Studies on the 2-Photon Emission Spectrum of Cyclohexane Liquid

The emission spectrum of cyclohexane liquid has been obtained with 2-photon excitation using the 308 nm output of a XeCl laser. The emission spectrum is being examined as a function of delay time in order to seek evidence for a previously postulated long-lived metastable state of cyclohexane. A very weak emission has recently been observed at delays of up to 1 μ sec with a spectral distribution similar to but somewhat broader than that of the prompt fluorescence. The origin of this emission remains to be determined but the long delay would be consistent with previous estimates of the lifetime of the metastable of ca. 1 μ sec.

REFERENCES

1. Y. Yoshida, L. Walter and S. Lipsky, *Radiat. Phys. Chem.* 1988, **32**, 449.
2. Y. Yoshida and S. Lipsky, *J. Phys. Chem.* 1988, **92**, 2240.
3. C. L. Braun, S. Kato and S. Lipsky, *J. Chem. Phys.* 1963, **39**, 1645.
4. C. W. Lawson, F. Hirayama and S. Lipsky, *J. Chem. Phys.* 1969, **51**, 1590.
5. K. Kimura and J. Hormes, *J. Chem. Phys.* 1983, **79**, 2756.
6. G. A. Salmon, *Radiat. Phys. Chem.* 1976, **8**, 13.
7. F. Busi and L. Flamigni and G. Orlando, *Radiat. Phys. Chem.* 1979, **13**, 165.
8. R. Hermann, O. Brede, J. Bös and R. Mehnert, *Ber. Bunsenges. Phys. Chem.* 1980, **84**, 814.
9. S. Tagawa, Y. Katsumura and Y. Tabata, *Radiat. Phys. Chem.* 1982, **19**, 125.
10. B. Brocklehurst, *Int. Rev. Phys. Chem.* 1985, **4**, 279.
11. W. R. Appleton and B. Brocklehurst, *Radiat. Phys. Chem.* 1988, **32**, 245.
12. Y. Yoshida, S. Tagawa, M. Washio, H. Kobayashi and Y. Tabata, *Radiat. Phys. Chem.* 1989, **4**, 493.
13. J. H. Baxendale and J. Mayer, *Chem. Phys. Lett.* 1972, **17**, 458.
14. F. Busi and G. Casalbore, *Gaz. Chim. Ital.* 1983, **113**, 83.
15. L. Walter and S. Lipsky, *Int. Radiat. Phys. Chem.* 1975, **7**, 175.
16. H. T. Choi, D. Askew and S. Lipsky, *Radiat. Phys. Chem.* 1982, **19**, 313.
17. L. Wojnarovits and G. Földiák, *Acta Chim. Acad. Sci. Hung.* 1980, **105**, 27.

C. SUMMARY OF ATTACHMENTS

1. D. W. Tweeten, K. Lee and S. Lipsky, "Dependence on Solute Concentration of the Efficiency of Scavenging of Electrons in Recombining Geminate Ion-Pairs", *Radiat. Phys. Chem.*, **34**, 771 (1989).
2. D. B. Johnston and S. Lipsky, "Energy Transfer from Cyclohexane to Benzene in Their Irradiated Mixtures", *Radiat. Phys. Chem.*, submitted for publication.
3. D. B. Johnston and S. Lipsky, "Electronic Energy Transfer from Cyclohexane to Benzene to Tetramethylphenylenediamine", *J. Phys. Chem.*, submitted for publication.

D. TIME DEVOTED TO PROPOSAL BY PRINCIPAL INVESTIGATOR

I.	Academic Year	50%
II.	Summer	50%

END

DATE FILMED

11 / 07 / 90