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

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PROGRESS REPORT

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NOTICE

A. ABSTRACT

The photoionization current from anthracene in liquid hydrocarbons has been studied as a function of excitation energy. From the dependence of the photocurrent spectrum on the magnitude of an externally applied electric field, it is deduced that the appearance of a fine structure in these spectra is mainly attributable, not to variability in the electron yield probability as others have conjectured, but rather to an energy dependence of the electron's thermalization range parameter. Solvent effects on the diffuseness of this structure are also explainable on this basis.

By monitoring the fluorescence from hexafluorobenzene dissolved in the non–fluorescent hydrocarbon solvents, 2,2,4–trimethylpentane, 2,2–dimethylbutane, cyclopentane and tetramethylsilane excited with β^- particles, it has been possible to extract the geminate ion–pair scavenging probability, $p^\dagger$. This is found to have a dependence on hexafluorobenzene concentration, c, entirely similar to what has previously been reported for $p^\dagger$ extracted from quenching of solvent fluorescence by perfluorocarbon scavengers, i.e., $p^\dagger = (\alpha\ c)^{.7}/[1 + (\alpha\ c)^{.7}]$. Thus it is now demonstrated that two different fluorescent techniques provide an expression for $p^\dagger$ that is distinctly disparate from that initially introduced by Warman, Asmus and Schuler, i.e.

$$p^\dagger = \frac{(\alpha c)^{0.5}}{1 + (\alpha c)^{0.5}}$$

to explain their results on chemical scavenging . Origins for this difference are considered.

Preliminary attempts to locate a triplet–state emission from saturated hydrocarbons excited biphotonically with 307 nm XeCl excimer laser light have thus far been unsuccessful. Measurements are continuing with a more intense one–photon excitation at 193 nm obtained directly from ArF and at 179 nm obtained from its n=1 antiStokes Raman line in H_2.

B. RESEARCH

I. Photoconductivity of Anthracene in Liquid Hydrocarbons

The photoconductivity of an aromatic solute in a liquid hydrocarbon exhibits a strong dependence on the nature of the hydrocarbon solvent.(1,2) Both the energy threshold for photocurrent and the subsequent shape of the photocurrent spectrum are importantly altered by what would otherwise appear to be relatively minor changes in the nature of the solvent.

The effect of the solvent on the photocurrent threshold derives ultimately from its electronic polarization about the ion–pair. The contribution to the total polarization energy from the positive ion, although relatively large in magnitude, carries little solvent variability. On the other hand, the polarization energy deriving from the electron (which is essentially the negative of the "vertical" electron affinity of the solvent) appears to be very sensitive to molecular structure and accommodates almost all of the threshold shifting from one solvent to the next.(3)

The effect of the solvent on the structure of the photocurrent spectrum is less well understood. Holroyd, Preses, Bottcher, and Schmidt(2) have noted that for anthracene in neopentane (and for azulene and methylnaphthalene as well) the photocurrent structure corresponds closely to the positions of relatively sharp Rydberg transitions in the vapor phase and have suggested that their manifestation in neopentane and their absence in n–pentane is ultimately tied to differences in the mobility of the electron in these solvents. The argument follows essentially that of Fermi's(4) to explain the broadening of the spectral lines of high–lying Rydberg states of atoms by perturbers with large scattering amplitudes for slow electrons. By linking the electron's mobility in the solvent to the electron–solvent scattering amplitude, the argument for observation of the Rydberg transitions in neopentane and for their obscuration in n–pentane is made on the basis of a ca. 500 fold smaller electron mobility in n–pentane. To further support this, they note that with n–perfluorohexane added to anthracene (or benzanthracene) in neopentane, the photocurrent is quenched with an efficiency whose wavelength dependence exhibits a similar structure to that observed in the photocurrent spectrum.(2) The implication is that the photocurrent quenching will be maximal when a Rydberg state of anthracene is populated. Such a state, it is presumed, will transfer an electron to n–perfluorohexane to produce a geminate ion–pair with a separation distance smaller (and, therefore, with smaller escape probability) than is produced at other excitation energies by the simple ejection of an electron and its subsequent "epithermal" scavenging by the perfluorocarbon.(1,2)

In the present study we reinvestigated the photocurrent spectrum of anthracene. The results of some of these measurements were commented on briefly in last year's progress report and analyzed in a preliminary way in an attached write–up. During the past year some additional measurements were completed and a manuscript prepared and submitted. This manuscript has just recently been published and a reprint is attached.

<u>We find that the Rydberg–state hypothesis is not a viable explanation to explain the structure in photocurrent spectra.</u> Our measurements show that these structures reside not in the electron ejection probability but rather in the energy dependence of the thermalization range parameter of the electron. Considering the ejection as an autoionization from the valence states of the neutral that are initially populated by photon absorption, the structure is explainable in terms of final states of the process that leave the anthracene positive ion in some one of its vibrationally excited states. Solvent effects on the diffuseness of this structure can be qualitatively understood in terms of solvent modification of the autoionization amplitude either via alteration of the final state wavefunction of the quasi–free electron or via alteration of the Franck–Condon overlap of the valence and ion states due to differential shifts of the energies of these states. Also no evidence for structure in the photocurrent quenching efficiency by n–perfluorohexane for anthracene in isooctane was observed contrary to the reported appearance of such structure in neopentane solvent.

II. Dependence on Solute Concentration of the Efficiency of Scavenging of Electrons in Recombining Geminate Ion Pairs

When a simple hydrocarbon fluid is irradiated with fast electrons, an easily measurable fluorescence is observed which is identical to that produced by the absorption of non–ionizing photon radiation. The quenching of this fluorescence by added perfluorocarbons has been studied(5) and found to depend on the fluorocarbon concentration, c, in such a way that the ratio, Q_e, of the yield in the absence, G_0, and in the presence, G, of the scavenger (i.e., $Q_e = G_0/G$) is given by

$$Q_e = 1 + (\alpha c)^{0.7} \tag{1}$$

where α is some empirical parameter.

If one assumes that i) the high–energy induced fluorescence derives exclusively from recombining geminate ion–pairs, ii) the fluorescence quenching is a consequence of capture of the "geminate" electron by the perfluorodecalin and its subsequent non–radiative recombination with the "geminate" positive ion and iii) electrons that are thus scavenged would otherwise (i.e., had they not been scavenged) have recombined with an "intact" solvent positive ion to yield a fluorescent solvent state, then it is simple to derive that

$$Q_e = (1 - p^{\dagger})^{-1} \tag{2}$$

where $p^{\dagger}$ is the probability for scavenging of a geminate ion–pair (i.e., one that would have recombined in the absence of scavenger).(5) By substituting eq. (1) into eq. (2), it then follows that the scavenging probability, $p^{\dagger}$, is given by:

$$p^{\dagger} = \frac{(\alpha c)^{0.7}}{1 + (\alpha c)^{0.7}} \;. \tag{3}$$

Eq. (3) appears, however, to be at variance with earlier studies of $p^{\dagger}$ extracted from measurement of the yield of chemical product produced from the electron + scavenger attachment process over a similar range in c (i.e., $\simeq 10^{-4}$ to 10^{-1} M). From an analysis of a wide variety of such experiments, Warman, Asmus and Schuler(6) found that $p^{\dagger}$ could be represented by an equation similar to that of eq. (3) but with the power 0.7 replaced by 0.5, i.e.,

$$p^{\dagger} = \frac{(\alpha c)^{0.5}}{1 + (\alpha c)^{0.5}} \ . \tag{4}$$

Over the usual concentration range studied (of $\simeq 10^{-4}$ to 10^{-1} M), the difference between 0.7 and 0.5 would have been easily discernable.

To accommodate this disparity, Jonah and Sauer(7) have recently suggested that not all geminate postive ion plus electron recombinations have the same probability for generating a solvent fluorescent state (i.e., assumption iii is violated). As a possible mechanism for this, they propose that solvent positive ions are initially generated in electronically excited states whose recombination with the electron gives neutral chemical products rather than fluorescence. Accordingly, only that fraction of the electron population which thermalizes sufficiently distant from the positive ion and whose recombination is therefore sufficiently slow to allow the positive ion to electronically relax, would give fluorescence. The consequence of this, they argue, is that whereas the technique for determining $p^{\dagger}$ via measurement of the product formed from the scavenging reaction samples the entire population of electrons, the fluorescence quenching technique looks only at a smaller sub–population. From this they demonstrate that if the "total" scavenging probability is indeed given by eq. (4) then the $p^{\dagger}$ extracted from the fluorescence quenching measurement must be of higher power than 0.5 in c, and, with not unreasonable choices of some pertinent parameters, could be as large as 0.7.(7)

Since the chemical product technique is itself subject to the validity of some crucial approximations, we have attempted this past year to utilize another technique for extracting $p^{\dagger}$. In the case that recombination of the solvent positive ion and the solute negative ion generates a fluorescent state of the solute, it is possible, with some assumptions to extract another measure of $p^{\dagger}$ from the concentration dependence of the intensity of this solute fluorescence.(8) For this purpose, however, it is important that solute excited states derive predominately from the recombining ions and, therefore, that contributions from electronic energy transfer from neutral excited solvent states be kept negligible. To ensure this, we have employed three non–polar solvents from which no fluorescence has yet been observed (i.e., quantum yield less than 10^{-6}),(9,10) namely 2,2–dimethylbutane (neohexane), 2,2,4–trimethylpentane (isooctane) and tetramethylsilane and one solvent, cyclopentane, which emits only a very weak fluorescence (quantum yield $\simeq 5 \times 10^{-6}$).(10) These solvents were also chosen to span a large range in the mobility of the electron, and, therefore, a large range of rate constants for the electron attachment to the scavenger.

The choice of scavenger was dictated by three considerations. It should i) have a sufficiently large ionization potential to prevent transfer of an electron to the solvent positive ion (since if this were permitted to occur it would provide another channel for formation of solute excited states via recombination of scavenger positive and negative ions and thus complicate the experimental analysis), ii) have a sufficiently large electron affinity so as to favor the formation of the excited state of the scavenger over that of the solvent upon recombination of the scavenger negative and solvent positive ions, and iii) have an adequately large fluorescence quantum yield to permit its reliable observation above background levels. For these purposes, the scavenger of choice was hexafluorobenzene with an adiabatic ionization potential of $\simeq$ 9.9 eV,(11) an electron affinity of at least 0.5 eV(12) and a fluorescence quantum yield of $\simeq$ 0.034.(13)

The results of this work are presented in an accompanying preprint. The manuscript has been accepted by *Rad. Phys. and Chem.* and will be published sometime this year. In essence, what we find is that the $p^{\dagger}$ that we extract by the present technique continues to be well represented by eq. (3), contrary to the predictions of Jonah and Sauer.(7) Thus there remains a serious discrepancy between all of the fluorescence results and those obtained from chemical scavenging studies. Some possible origins of this discrepancy are considered in the manuscript.

III. Excited States of Saturated Hydrocarbons

As we discussed in our Proposal of last year, there are a number of indirect indications for a metastable state of saturated hydrocarbons that i) lies slightly lower in energy than the lowest state observed in optical absorptions (i.e., Si) and ii) has a lifetime of ca. 100–1000 nsec.(14) The only assignment for such a state from theoretical studies (at least at the equilibrium geometry of the ground state) is as the lowest spin triplet state – but so long a lifetime for such a state in a saturated molecule would be rather surprising.

A search for more direct evidence for this metastable state began this past summer when Professor F. Hirayama (Dept. Physics, Miyazaki University, Miyazaki, Japan) visited with us for a short period. Our first attempt was to seek a long–lived fluorescence (or phosphorescence) from the metastable state. For this purpose, samples of decalin and bicyclohexyl were slowly cooled to dry ice temperature and the resulting glasses were illuminated with 308 nm pulses of light from a XeCl excimer laser. Two photon absorptions generated a previously characterized fluorescence emission(15) (coincident with the pulse from Si) but no delayed emission was obtained in <u>any</u> spectral region. Although these initial experiments were unsuccessful, they were nevertheless important in suggesting several avenues for improvement. We have now altered the collection geometry of our analyzing system to improve its efficiency and have moved our exciting pulse to 193 nm using the ArF excimer emission. Although 193 nm is barely on the absorption edge of our sample, a substantial gain is still achieved in excited state population by virtue of now being able to utilize a 1 vs. 2–photon excitation process. An H_2 cell for Raman upshifting the 193 nm line is also being constructed and an unstable resonator is being added to the excimer optics to improve the upshifting efficiency. This will permit a somewhat deeper penetration into the one–photon absorption systems.

With regard to our project for obtaining the emission spectra and emission quantum yields of very weakly fluorescent saturated hydrocarbons, we have had some problems with a newly constructed system. The problem was ultimately located in improper coating of the gratings that we had purchased from Spex Industries. These have now been successfully recoated at Acton. The apparatus is now working extremely well and we can <u>routinely</u> obtain emissions with quantum yields at the 10^{-5}–10^{-6} level.

IV. Ionized States of Saturated Hydrocarbons

We have made essentially no progress with this aspect of our program during the past year. Dr. Yoshida, who had begun work on this project, left to return to Japan prematurely in order to assume a newly created academic position at the University of Tokyo. Dr. Tweeten opted not to take over the "ionized state" project but rather to continue his work on the Projects I and II of this Report until they were concluded. However, immediately after they were finished he took a position in the Research Laboratories at 3M. Negotiations with a potential new post–doc from the Radiation Laboratory at Notre Dame broke down and another new post–doc from Beijing has delayed his arrival to August 1989. However, our intention to pursue this part of our program remains fully intact.

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12. The electron affinity of C_6F_6 in the gas phase as determined by electron transfer equilibria in 0.52 eV: S. Chowdhury, E. P. Grimsrud, T. Heinis and P. Kebarle, *J. Am. Chem. Soc.* 1986, 108, 3630. A higher value of 1.09 eV has been reported in non–polar liquids as determined by photodetachment: U. Sowada and R. A. Holroyd, *J. Phys. Chem.* 1980, 84, 1150.
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C. SUMMARY OF ATTACHMENTS *

1. G. A. Howell, K. Lee, D. W. Tweeten and S. Lipsky, "Photocurrent Enhancement in Non–Polar Liquids by the Addition of Electron Scavengers", *J. Phys. Chem.* 1988, 92, 4241. (Reprint)
2. Y. Yoshida, L. Walter and S. Lipsky, "The Scintillation Process in Three Component Systems: The Luminescence Minimum Revisited", *Radiat. Phys. Chem.*, 1988, 32, 449. (Reprint)
3. Y. Yoshida and S. Lipsky, "Scintillation Process in Three Component Systems: Mechanism of the Luminescence Minimum", *J. Phys. Chem.* 1988, 92, 2240. (Reprint)
4. D. W. Tweeten and S. Lipsky, "Photoconductivity of Anthracene in Liquid Hydrocarbons", *J. Chem. Phys.* 1989, 93, 2683. (Reprint)
5. 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.*, Accepted for publication. (Preprint)

D. TIME DEVOTED TO PROPOSAL BY PRINCIPAL INVESTIGATOR

I.	Academic Year	50%
II.	Summer	50%

E. OTHER ACTIVITIES OF PRINCIPAL INVESTIGATOR

I. Teaching

Fall 1988	Thermodynamics (8512)
Winter 1989	Stat. Mech. & Reaction Kinetics (5535)
Spring 1989	General Chemistry (1004)

II. Extra–University Activities

1. Chairman of Evaluation Panel of Notre Dame Radiation Laboratory
2. Member of Physical Chemistry Subcommittee of the American Chemical Society for Graduate Level Placement Exams

* removed and cycled separately.