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The Contribution of Electronically Excited
States to the Radiation Chemistry of Organic Systems

Progress Report

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Abstract

G values have been determined for the production of the lowest excited singlet states of seven saturated hydrocarbon liquids by direct measurement of the neat liquid fluorescence. Comparison with reported results obtained via a solute sensitization technique indicate that the solute technique may strongly underestimate the true G value.

The fluorescence of liquid bicyclohexyl excited both with β particles and 184.9 nm light has been studied as a function of concentration of perfluorocarbon scavengers. The results permit estimates of (a) the fraction of all excited singlet states that derive from geminate ion pairs and (b) the probability that a geminate pair will generate an excited singlet state on recombination.

A weak fluorescence has been observed from nine mono-olefinic hydrocarbons excited at 184.9 nm in vapor and/or liquid phases. Emission spectra and quantum yields have been obtained. For tetramethylethylene, additional studies have been made on effects of excitation wavelength, of quenchers and of solution in low-temperature matrices. A possible Rydberg assignment for the emission is considered.

Electron impact spectra have been obtained for eight saturated hydrocarbons at a scattering angle of 0° and an impact energy of 50 eV. Close agreement is obtained with spectra reported at higher energies and with optical spectra.

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Previous attempts to measure a G value for the production of the lowest excited singlet state of cyclohexane (S_1) have relied exclusively on a technique involving the sensitization of some solute by energy transfer from S_1 . The excited solute concentration is monitored either via its absorption or emission. $G(S_1)$ is then calculated by an extrapolation to infinite solute concentration assuming that each excited solute derives exclusively from a solvent S_1 and that at infinite concentration all S_1 is converted to excited solute. To circumvent some of the assumptions inherent in this technique we have recently measured $G(S_1)$ for cyclohexane and six other saturated hydrocarbons by a more direct technique. We excite the neat liquid with a high energy source (eg. ^{85}Kr) and determine the number of photons emitted by S_1 per 100 ev absorbed. The ratio of this to the probability that S_1 emits a photon (which is just the fluorescence quantum yield) gives directly $G(S_1)$. For cyclohexane we obtain a value about five times larger than obtained via a solute-sensitization technique. For the other liquids also rather large yields are obtained, approaching in some cases, the yields of geminate ions. Interestingly, for aromatic liquids we have found excellent agreement between the solute-sensitization technique and our more direct method. The source of difficulty with the saturated hydrocarbons is not yet understood. A manuscript describing this work has been accepted for publication in International Journal for Radiation Physics and Chemistry. A preprint is attached.

The yield of lowest excited singlet states of a hydrocarbon liquid, $G(S_1)$, derives mainly from two types of precursors (a) neutral excitations (S_n) which are generated directly by the high energy particle or other fast

particles produced in the course of its degradation and (b) geminate ion pairs which on recombination generate neutral excited species. All of the S_n , with some probability, β_n , convert to S_1 . In the presence of a solute which can both scavenge the geminate electrons and also directly quench the S_1 state, a simple analysis indicates that by comparison of the effect of the solute on both UV excited and high-energy excited solvent fluorescence, a determination can be made of the fraction of $G(S_1)$ that derives from the geminate ion recombination process. For this purpose we chose bicyclohexyl as solvent and perfluoroalkanes as solutes and found this fraction to be $\approx 0.9 \pm 0.1$, somewhat larger than had been anticipated. With this fraction known it was possible to proceed one step further and determine the probability for formation of a singlet state from the ion recombination process. A comparison of this with theoretical values indicate that, at least in bicyclohexyl, the geminate electron does not spin-relax prior to recombination. Preliminary results for p-xylene have also been obtained and important differences noted between the aromatic and saturated hydrocarbon systems. A manuscript describing this work has been submitted for publication to International Journal of Radiation Physics and Chemistry. A preprint is attached.

The continuation of our measurements on the fluorescence of mono-olefinic hydrocarbons consumed a large fraction of Dr. Hirayama's time during this past year. The work was concluded shortly before his departure on July 1. A manuscript has recently been completed and will shortly be submitted for publication to Journal of Chemical Physics. A preprint is attached. The fluorescence quantum yields we have measured are all extremely small, even when compared to those of saturated hydrocarbons, and it is understandable,

therefore, why there have been no previous reports of emission from these compounds. The electronic state from which the emission originates, although still not unequivocally determined, seems most plausibly to be the 3s Rydberg state (R). For tetramethylethylene an excited state lifetime has been estimated from measurement of its quenching by added CCl_4 . The data indicate a very large contribution to the quenching from transient effects and an analysis gives an encounter distance of $10 \text{ \AA}$ and an excited state lifetime of 2×10^{-11} sec. This lifetime and a measured emission quantum yield of 2×10^{-4} are consistent with the $R \leftarrow N$ oscillator strength of 0.01-0.02. For less highly substituted ethylenes (*ie.* propylene, 1-butene, cis-2-butene, trans-2-butene, 1-hexene, cis-2-hexene, trans-2-hexene and 2-methyl-2-pentene) the fluorescence quantum yields are from one to three orders of magnitude smaller. Since, however, the $R \leftarrow N$ oscillator strengths for these compounds are similar to that for tetramethylethylene, the implication is that for these olefins the excited state lifetime is $\approx 10^{-12} - 10^{-14}$ sec. Since the 3s Rydberg state for many of these olefins lies energetically above that of the 90° twisted valence state (V), it is suggested that the predominating non-radiative decay channel of the R state is an $R \rightarrow V$ internal conversion. Peculiar differences in behavior of tetramethylethylene emission in glassy and crystalline low-temperature matrices also appear to be consistent with the Rydberg emission assignment.

Our electron-impact spectrometer is now operating for 0° scattering angle experiments with a resolution of 125 mv. We have begun to investigate the 50 ev impact spectra of a variety of saturated hydrocarbons and to date have examined methane, ethane, propane, n-butane, n-pentane, 2-methylpentane,

2,3-dimethylbutane and cyclohexane. The 50 ev spectra compare extremely well with optical spectra and with higher energy electron-impact spectra reported by others. With the exception of a shoulder on the low-energy side of the main peak in the n-alkane spectra, no additional features have been observed down to energy losses of 2 ev. The shoulder appears to be attributable to a predominantly C-C excitation. We have attached a brief progress report not intended for publication in its present form.

Additional to the work described above we have begun experiments on several other problems during the past year. Dr. Gregory completed construction of the double-beam spectrometer for measurement of optical absorption spectra to 1150 Å. Our initial concern was to determine whether or not vibrational structure would be resolved in saturated hydrocarbons (larger than ethane) when dissolved in low-temperature perfluoropentane matrices. In the vapor phase no structure has been detected. Our initial measurements were negative and we decided next to check whether in fact the vibrational structure of even benzene was being sharpened in these matrices. Much to our surprise the benzene structure was found to be appreciably broadened relative even to the spectrum obtained in liquid perfluoropentane. The reason for this broadening has occupied our attention now for several months and various possibilities are currently being experimentally explored. New equipment has been constructed to permit study of benzene in CF_4 , SF_6 and SiF_4 liquids since it has been anticipated that the more spherical the host molecule, the sharper should be the guest structure. This now indeed seems to be the case at least for liquid SF_6 which is the only spherical system thus far investigated. The double-beam equipment is also currently being used by Mr. Kenneth Johnson for measuring the absorption spectra of saturated hydro-

carbons in the vapor phase from 5-10 ev. The purpose here is to obtain spectra that can be better compared with our electron-impact results than current literature sources permit.

As remarked in last year's renewal request, we have become interested in studying the reactivity of Rydberg states. To this end, Mr. Larry Wilson has constructed equipment for repeating earlier measurements (by others) on the effects of rare gases to perturb the Rydberg series in Cs vapor. Following this we intend to study the perturbing effects of a variety of gases on molecular Rydberg states. Our first purpose is to attempt to confirm reports that the lowest Rydberg states of a molecule are asymmetrically broadened to the blue regardless of the nature of the perturber. For Cs this is certainly not the case. Both blue and red shifts are reported depending on the perturbing gas.

The liquid photoionization experiments (discussed last year) have been taken over by Mr. Kan Chu Wu using Dr. Hirayama's equipment. Mr. Wu is now attempting to repeat some of Dr. Hirayama's early results (see Report Number C00-913-47) and when and if successful will extend them as originally proposed.

Time Devoted to Project by Principal Investigator:

a) November 1, 1973 - June 15, 1974	50%
b) June 15, 1974 - September 15, 1974	100%
c) September 15, 1974 - October 31, 1974	50%

Meetings Attended by Scientific Personnel:

1. Fifth International Congress of Radiation Research, Seattle, Washington, July 14-20, 1974. S. Lipsky, participant.