The nickel–cyclopropenyl ring bonding can probably best be described using an MO model similar to that initially invoked[8] for symmetrically bonded cyclobutadiene complexes. Assuming C_{3v} localized symmetry, the a_1 and e combinations of the three $p\pi$ atomic orbitals of the cyclopropenyl ring interact with the nickel atomic orbitals to give bonding and antibonding molecular orbitals. An electron pair, which is formally donated from the cyclopropenyl ring to the nickel atom, resides in the a_1 bonding nickel–cyclopropenyl ring orbital, and the antibonding e orbital combination provides a pathway for electron density drift back to the cyclopropenyl ring. Using this formalism, the complex attains the inert gas configuration. An interesting result of this work is an internally consistent experimental determination of 1.33 Å for the tetrahedral Ni(0) covalent radius. This is based upon the Ni–N and Ni–Cl bond lengths which would not be affected by appreciable multiple bond character.

Acknowledgments. We wish to thank E. W. Gowling for a generous supply of triphenylcyclopropenyl chloride. We gratefully acknowledge the National Science Foundation for financial support of this research.

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Optical Detection of Transient Solvated Electrons in Pulse-Irradiated Viscous Squalane[1]

Sir:

Considerable physical and chemical evidence exists for the formation of ionic species in irradiated hydrocarbon glasses and liquids.[2] Optical and electron spin resonance studies[3] show that electrons can be stabilized in glasses at −196° with *G* values near unity. Chemical scavenging experiments[4] on liquids indicate that ion pairs are produced with yields approaching 4 per 100 eV, most of which recombine geminately, but some become uniformly distributed before reacting. Conductivity measurements[5] on these liquids provide direct evidence for such separated free ions. In the interest of linking together the glass and liquid results, viscous squalane ($C_{30}H_{62}$, mp $\sim$−80°, $\eta_{-80°}$ $\sim 10^6$ P) was pulse irradiated in an intermediate temperature–viscosity region and optically monitored in the near-infrared. This preliminary report deals briefly with the main observations and consequent implications for the nature of electrons in hydrocarbons and the mechanism of their neutralization.

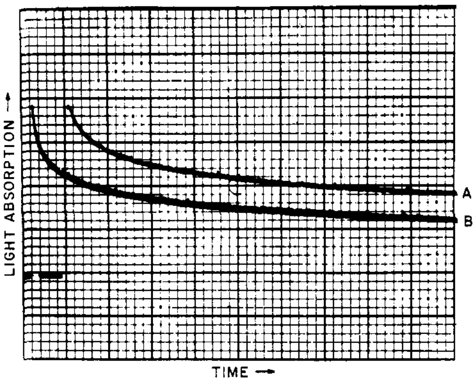

Figure 1. Decay of the solvated electron absorption at 1.6 μ in squalane at −140°. Light absorption scale: 8%/large division; time scales: (A) 50 μsec/large division, (B) 200 μsec/large division; optical path length: 2 cm; pulse duration: 5 μsec; delay between oscilloscope and accelerator triggering: 25 μsec.

In these experiments pulses of 3-MeV electrons with currents of approximately 50 mA and with durations ranging from 0.5 to 20 μsec impinged on purified squalane in a Suprasil cell mounted in a polystyrene cryostat. The dose received by a sample for a typical 1-μsec pulse was about 2×10^{17} eV/cc, and the variation in dose from pulse to pulse was monitored with charge collection devices external to the cell. A tungsten lamp, a grating spectrometer, wide-band filters, and an InAs detector comprised the optical system.

Squalane upon pulse irradiation below −70° exhibits a near-infrared absorption corresponding to a nontrivial yield of a species that decays with complex kinetics in times longer than 10^{-6} sec.

Identification of this species as a "solvated electron," e_s^-, rests on spectral and kinetic considerations.[6] The optical spectrum, determined at −130°, is very broad and appears to have a maximum in the 1.6–1.7-μ region. It is similar to trapped electron absorptions[3] found in other saturated hydrocarbons at −196°, for which confirmatory esr data exist. Moreover, in the presence of CCl_4 or C_2H_5Br, which are efficient electron scavengers, the absorption intensity and lifetime are both reduced.

The yield of e_s^- at −140° is estimated roughly as 0.6 per 100 eV by taking $\epsilon_{1.6\mu} \sim 3 \times 10^4\ M^{-1}\ \text{cm}^{-1}$.[7] With increasing temperature the dose-normalized initial optical density decreases, but this effect may be related more to electron decay during the pulse than to any inherent diminution in the yield.

The electron decay in squalane has certain features indicative of an inhomogeneous neutralization of spatially correlated ion pairs. Figure 1 shows a typical decay, the rate of which is initially very fast but becomes

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(1) Supported in part by the U. S. Atomic Energy Commission.

(2) Reviews of these subjects have appeared recently: see (a) J. E. Willard in "Fundamentals of Radiation Chemistry," P. Ausloos, Ed., John Wiley and Sons, Inc., New York, N. Y., 1968, Chapter 9; (b) R. A. Holroyd, *ibid.*, Chapter 7; (c) W. H. Hamill in "Radical Ions," E. T. Kaiser and L. Kevan, Ed., John Wiley and Sons, Inc., New York, N. Y., 1968, Chapter 9.

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(4) For a review, see J. M. Warman, K.-D. Asmus, and R. H. Schuler in "Radiation Chemistry-II," Advances in Chemistry Series, No. 82, American Chemical Society, Washington, D. C., 1968, pp 25–57.

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(6) The term "solvated electron" as used here refers to a matrix-stabilized or localized electron, irrespective of its lifetime, in contradistinction to a quasi-free or delocalized electron (see J. Jortner in "Radiation Chemistry of Aqueous Systems," G. Stein, Ed., John Wiley and Sons, Inc., New York, N. Y., 1968, p 91).

(7) Williams and coworkers[3a] found excellent agreement in the *G* value of electrons trapped at −196° as determined by both esr measurements and optical measurements based on this value of ε determined by Gallivan and Hamill,[3c] thereby adding confidence in its use here.

progressively slower. As expected for such kinetics,[8] the reciprocal optical density is approximately linear with $(\text{time})^{1/2}$. Most indicative is that the lifetime does not depend on initial concentration. If the fraction of the initial optical density remaining at any time is plotted against time, then the resulting curves for runs differing 30-fold in dose can be superimposed over as much as 70% of the decay.[9]

The rate of neutralization, moreover, depends on temperature. For example, $(\tau_{1/2})_0$, the time for the initial optical density to decrease by 50%, changes from 4 msec to <2 μsec as the temperature is raised from -165 to $-70°$. A phenomenological activation energy of 2–4 kcal/mole is estimated from an observed linear dependence of $\log (\tau_{1/2})_0^{-1}$ on T^{-1}.

Comparison of the electron decay in squalane and in 3-methyloctane, where this species has also been observed, suggests that medium viscosity is an unimportant kinetic factor. At $-150°$ $(\tau_{1/2})_0$ is the same in both systems even though the viscosity of the latter is only $\sim 10^{-10}$ as high as that of the former.[10] Furthermore, the activation energy for decay in either case (~8 kcal/mole in 3-methyloctane) is much less than the respective Arrhenius term for viscosity change.

The observation of an electron absorption at these temperatures implies the persistence of suitable binding sites, even in the thermodynamically stable liquid phase. These sites presumably are always present and do not necessarily correspond to the ultimate stabilization depth achieved following electron trapping. A temperature-dependent, dynamic distribution of sites of different depths, which conceivably widens and shifts to lower energies with increasing temperature, should be considered.

The observation of a G for e_s^- that is smaller than G for total ion pairs[11] means that, unless most of the e_s^- escape detection, only some of the thermalized electrons become solvated. Possibly either the concentration of binding sites is too low or the stabilization process is too slow for solvation to compete effectively against recombination. As a consequence of inefficient trapping, the mean separation distance from the positive ions for the e_s^- is most likely longer than the corresponding distance for the original thermalized electrons.

The observation of an electron decay representing neutralization of correlated, inhomogeneously distributed ion pairs in the 10^{-6}–10^{-3}-sec time range under these conditions, and apparently with negligible viscosity dependence, tends to rule out structural diffusion as a means for migration of charge. It may be that there are in equilibrium bound and unbound electrons, e_s^- and e_m^-, the latter migrating and reacting, or that charge migration occurs by a tunneling mechanism.

The kinetic data obtained in this study, moreover, should provide a means for testing recent theoretical and empirical descriptions[8,12] of such neutralization reactions, since electron concentration–time profiles are directly indicated. Assessment of certain of these theories is in progress.

Acknowledgment. The authors are grateful to Professor William H. Hamill for bringing to our attention the useful physical properties of squalane.

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[10] The viscosity of squalane below $-80°$ has been estimated from the data of Leone and Hamill[9b] and T. Sawai and W. H. Hamill, private communication. Viscosity data for 3-methyloctane are available from A. C. Ling and J. E. Willard, *J. Phys. Chem.*, **72**, 3349 (1968).

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Observation of Phosphorescence in Pyridines[1]

Sir:

Pyridine may be considered as the prototype nitrogen heteroaromatic, yet its electronic properties have remained for many years an enigma to the spectroscopist.[2] The apparent absence of phosphorescence has been one of the most puzzling items. The lowest triplet state was observed in absorption[3] under oxygen pressure and labeled $^3A_1(\pi\pi^*)$. The intersystem crossing yield has been measured to be 0.3 by photochemical studies.[4] Moreover, it might be expected that the lowest $\pi\pi^*$ triplet states of pyridine and benzene should have similar radiative capabilities. In spite of attempts by many researchers, using many different samples, methods of purification, and deoxygenating procedures, no authentic phosphorescence of pyridine has been reported.

Since pyridine has several low-lying $n\pi^*$ singlet states, it is possible that the lowest triplet state is in fact $n\pi^*$ and not $\pi\pi^*$. To investigate this possibility a careful study was made of the luminescence properties of a series of substituted pyridines, especially with cyano and methyl groups. We have observed either strong $\pi\pi^*$ (long lifetime) or strong $n\pi^*$ (short lifetime) phosphorescence with appropriate substitution. These results lead to the conclusion that the lowest triplet state in pyridine is the orbitally[5] forbidden $^3A_2(n\pi_5^*)$ state. The explanation of the absence of phosphorescence in pyridine itself, and its presence in substituted pyridines, is then given in terms of specific state ordering.

The low-lying triplet states of pyridine (Figure 1) in orbital classification are $^3A_1(\pi_2\pi_4^*-\pi_3\pi_5^*)$, $^3B_1(n\pi_4^*)$, and $^3A_2(n\pi_5^*)$. The n-orbital electron after excitation is localized partly on the N atom in the $^3B_1(n\pi_4^*)$ state, and on carbon atoms 2,6 in the $^3A_2(n\pi_5^*)$ state.

Methyl substitution at the 2,6 positions should blue shift the A_2 state more than the B_1 state. If the A_2

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