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Temperature Dependence of Photocurrent in γ-Irradiated Alkaline Ice. Location of Energy Levels of Trapped Electrons

Sir:

Strongly alkaline solutions (5–10 *M* NaOH) form transparent glasses when rapidly frozen to 77°K. ^{60}Co γ radiolysis of this alkaline ice produces trapped electrons characterized by an epr singlet and an optical absorption with λ_{max} at 580 nm.[1] In this paper we report observation of photocurrent and its temperature dependence in this system. The photocurrent shows that the trapped electrons can be optically excited to a mobile state. The temperature dependence between 4 and 77°K indicates that the optical transition is from a bound ground state directly to the conduction band, and the temperature dependence above 77°K indicates the presence of shallow traps near the conduction band.

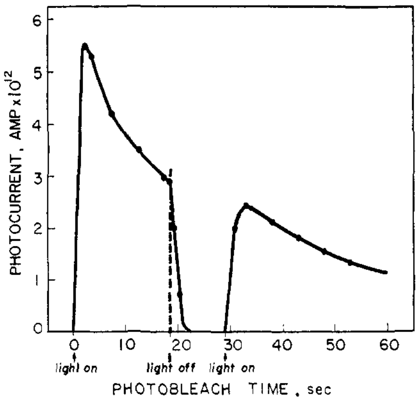

Figure 1. Time-dependent photocurrent in 10 *M* NaOH at 77°K with a radiation dose of 0.03 Mrad and an applied electric field of 4.5 kV/cm. The rise time of the photocurrent is due to the response time of the apparatus.

The alkaline ice sample was contained in a polyvinyl chloride sleeve (4.5-mm i.d.) into which two brass 4-mm diameter mesh electrodes were inserted. After γ irradiation at 77°K, the electrodes were connected to electrometer and voltage supply cables with gold pin connectors, and the sample was placed in an unsilvered dewar without allowing the sample to warm. The electrode distance was 2 mm and a typical applied voltage was 900 V. Light from a 500-W slide projector was passed through a water filter to remove infrared light and through a uv filter, and was directed perpendicular to a line between the electrodes. At 77°K and 0.03 Mrad, a peak photocurrent of 5×10^{-12} A is observed. The photocurrent varies with time as shown in Figure 1. Blanks verified that insignificant photocurrent was seen in unirradiated samples or in irradiated pure ice.

The peak photocurrent is linear with radiation dose from 0.006 to 0.06 Mrad, and is also linear with light intensity. When a monochromator is used, the peak photocurrent varies with wavelength in a manner similar to the known absorption spectrum of the trapped electron. The peak photocurrent is slightly higher at 4°K (liquid helium) than at 77°K (liquid nitrogen). However, between 74 and 111°K the peak photocurrent increases with temperature. A plot of peak photocurrent *vs.* reciprocal temperature is linear and gives an activation energy of 0.4 kcal/mole.

The fact that photocurrent is observed indicates that the trapped electrons in alkaline ice can be optically excited to a mobile state which can be considered as a type of conduction band level. The current is proportional to the number of electrons reaching the conduction band, their mobility, and their average lifetime in the conduction band. By analogy with trapped electrons in alkali halides (F centers), the mobility is expected to have a small negative temperature dependence.[2] The observation of a nearly temperature-independent photocurrent between 4 and 77°K indicates that the optical transition associated with the trapped electrons occurs directly to the conduction band or to a bound state that can cross over to the conduction band upon lattice relaxation.[3] There is no evidence for a strongly bound excited state. The negative temperature dependence of the electron mobility probably accounts for the slightly higher photocurrent at 4°K compared to 77°K. The positive temperature dependence of the photocurrent above 77°K indicates the presence of shallow traps. Above 77°K the electrons can be thermally excited out of these traps to effectively increase their lifetime in the conduction band and thus increase the photocurrent. This model implies that the temperature dependence of the net rate of loss of trapped electrons by optical bleaching will be negative near 77°K, because at higher temperatures there will be an increased probability for retrapping the electron in a deep trap. This negative temperature dependence has recently been confirmed in our laboratory.[4]

A number of calculations of the energy levels for trapped electrons in water and in ice have been made.[1,5–8] Although different approximations and both continuum and structural models have been used, all calculations predict that the first excited state is strongly bound by 1.8–3.0 eV with respect to the conduction band. Our experiments show that this value is much too large, and that the first excited state is probably not bound. Current calculations in our laboratory with a semicontinuum potential[9] appear to give a more weakly bound excited state which is in better agreement with experiment.

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Reaction between Molecular Hydrogen and Various Electron Donor-Acceptor Complexes of Aromatic Hydrocarbons with Sodium.
Their Electronic Properties[1]

Sir:

It was recently reported that molecular hydrogen was dissociatively chemisorbed over some electron donor-acceptor (EDA) complexes of alkali metals with aromatic compounds such as graphite,[2a] polycondensed hydrocarbons,[2b] and phthalocyanides,[2c] and the H_2–D_2 exchange reaction and hydrogenation of olefins took place markedly over these complex films at room temperature. It was also reported by Bank[3a] and van Tamelen[3b] that hydrogen was absorbed in the THF solution of sodium naphthalene at 25°, and sodium hydride was obtained stoichiometrically as a reaction product.

We wish to report that the activities of some aromatic mono- and dianions for the uptake of hydrogen are correlated with their electronic properties such as reduction potentials and localization energies, and the formation of the monohydro anion.

Each stoichiometric (1:1 and 1:2) EDA-complex film of aromatic hydrocarbons (*ca.* 3×10^{-3} mol) with sodium was deposited over a silica wool or gel from its THF solution by evacuating the solvent. Their characteristic electronic spectra show the formation of the stoichiometric EDA complexes. When hydrogen gas (10–35 cm) was admitted onto each film in the temperature range between 20 and 100°, a considerable amount of hydrogen was taken up rapidly, whereas its desorption took place very slowly under the reaction conditions. If the initial rates of uptake of hydrogen by some stoichiometric EDA-complex films at 71°, $P_{H_2} = 27$ cm were plotted against the reduction potentials for anion radicals and dianions of the corresponding hydrocarbons ($-E'$, volts),[4a] which have been measured by Hoijtink, *et al.*,[4b] a volcano shaped curve was obtained as given in Figure 1. Hydrogen was also absorbed in the THF solution of each EDA complex in the temperature range between 20 and 60°, and the rate of the uptake of hydrogen was correlated similarly with their reduction potentials as well as those over their complex films.

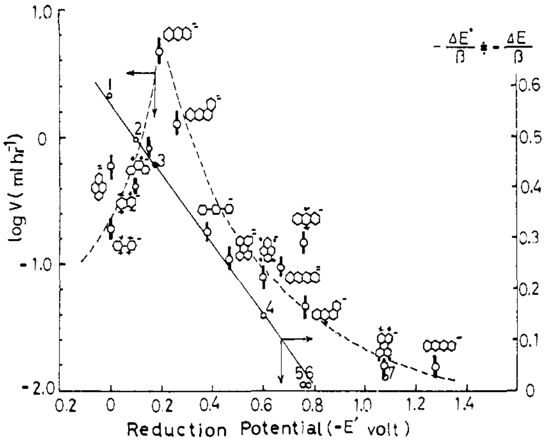

Figure 1. ---○---, the plot of the rate of hydrogen adsorption against the reduction potential for each anion radical and dianion; —○—, the plot of the localization energy of each acceptor molecule against the reduction potential for its anion radical; (1) biphenyl, (2) naphthalene, (3) phenanthrene, (4) pyrene, (5) anthracene, (6) 1,2-benzoanthracene, (7) perylene.

When hydrogen gas was introduced into each of the EDA-complex solutions of biphenyl-, naphthalene-, phenanthrene-, and anthracene- (1:1 and 1:2) sodium at 20°, it was found spectroscopically that new peaks appeared rapidly soon after the introduction of hydrogen at 425 and 500, 435, 565, and 430[5] mμ, respectively, which might be attributed to the formation of the corresponding monohydro anions, AH^-Na^+, where A denotes each of the aromatic hydrocarbons. For sodium–biphenyl, –naphthalene, and –phenanthrene complexes, the corresponding new absorption peaks decreased gradually and disappeared considerably in several hours, and a small amount of sodium hydride was detected in the reaction systems.[5] For the complex films (deposited over a silica wool) of biphenyl-, naphthalene-, phenanthrene-, anthracene- (1:1 and 1:2), and pyrene- (1:1 and 1:2) sodium, sodium hydride was also obtained considerably in the complex films when hydrogen was sorbed in the temperatures above 60°.

Monohydro anions of anthracene (430 mμ), pyrene (455 and 525 mμ), and perylene (470 mμ) were comparatively stable in the solution at 20°, and similar absorption peaks of the corresponding monohydro anions were also observed when hydrogen was admitted onto the thin films of the EDA complex of sodium with anthracene (1:1 and 1:2), pyrene (1:1 and 1:2), and perylene (1:2) in the temperature range between 40 and 110° in several hours. On the other hand, no peaks of monohydro anions of biphenyl, naphthalene, and phenanthrene were detected in the films probably due to their instability even when hydrogen was introduced.

Hydrogen molecule seems to be activated by the EDA complexes *via* the following steps

$$A^{2-} + H_2 = AH^- + H^- \qquad (1)$$

$$2A^- + H_2 = (2AH^-) \longrightarrow 2A + 2H^- \qquad (2)$$

The stabilities of those monohydro anions (AH^-) might

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[1] This communication was scheduled to be published simultaneously with a communication by Bank, *et al.* (S. Bank, T. A. Lois, and M. C. Prislopski, *J. Amer. Chem. Soc.*, **91**, 5407 (1969)).

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