Progress Report on the Present Year's Work

The purpose of this year's work was to do electron spin resonance (ESR) studies on trapped species in irradiated solids. Several different projects of this type were begun to provide a broad base of experience in the field.

1. Reactions of Gaseous H Atoms with 77°K Solid Substrates

H atoms can be readily generated from hydrogen gas in a microwave discharge. Furthermore, atomic hydrogen at pressures below 1 Torr will pass through several meters of a boric acid coated glass tube without recombining. This property permits H atom bombardment of substrates frozen on a 77°K cold finger directly in the ESR cavity, and an apparatus to accomplish these ends was constructed.

We felt that some questions about reactions of H atoms in irradiated solids might be cleared up by using the essentially thermal H atoms produced in the above apparatus. For example, in liquid alkaline water the following reaction occurs.[1]

$$H + OH^{-} \rightsquigarrow HOH + e_{s}$$

Alkaline ice at 77°K was therefore bombarded with H atoms to see if the same reaction would occur in the solid phase, whence a trapped electron would be observed. After a variety of experiments failed to produce any significant yield of trapped electrons, we concluded that either the reaction was not occurring or our experimental technique was inadequate.

Another question considered was the reactions of H atoms with frozen alcohols at 77°K. Conflicting results had been obtained in that a flow system

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like ours[2] had shown reaction while a static system using a hot wire for dissociation had showed ethanol at 77°K to be inert to H atoms.[3] We bombarded some frozen solutions of saturated alcohols mixed with some unsaturated organic molecules to establish the reactivity of the saturated alcohols relative to molecules that were surely known to react with atomic H. The results showed that the saturated alcohols were less reactive than the standard compounds but not completely inert.

At this point we decided to more carefully consider what was happening in our experimental set-up. It was clear that H atoms were being generated in high yields because they could be monitored by ESR. We then turned to the substrate and wondered if the roughly 0.5 Torr of hydrogen being pumped by it were warming the surface where the reaction was taking place. A thermocouple cemented to the cold finger showed a 30° rise in temperature when the hydrogen was turned on. The temperature of the first few microns of substrate surface is no doubt considerably higher than this measurement indicated, so in actuality equipment like ours does not run reactions at 77°K, but rather at temperatures many tens of degrees K warmer. Static H atom sources do show reactivity for saturated alcohols at these higher temperatures, so our results agree with the static ones but do not test the 77°K case.

Another aspect of the higher surface temperature is that it may be responsible for the failure to produce trapped electrons by reacting H with alkaline ice, since trapped electrons in such systems are unstable above 160°K.[4]

Because of the uncertainty of the substrate temperature, the preliminary experiments on this project were not followed up. The apparatus is now used for less precise work such as doping crystals with hydrogen.

2. Spatial Distributions of Trapped Species in Alkali Halides

This laboratory has developed a technique for determining spatial distribution of trapped irradiation products by using ESR measurements.[5] The technique has been used on trapped electrons and H atoms in ices and organic glasses. Comparisons for different types of radiation have also been made.[6] One parameter that was invariant in these experiments is that they were all done on materials containing atoms from the first two rows of the periodic table. Recently some evidence has indicated that some gamma ray absorbers with atomic numbers higher than 10 will give drastically different spatial distributions of initially produced species.[7] This effect was ascribed to higher cross sections for inner shell ionization by fast electrons in heavier atoms. Inner shell ions of intermediate atomic number emit Auger electrons of several hundred eV with high probability, and these electrons are of higher energy than those produced by direct ionization of valence electrons by the high energy Compton electrons. The high linear energy transfer of such low energy electrons will mean that many ionizations will be caused by them in a small region. Such "spurs" caused by Auger electrons will, of course, be larger and contain more species than those resulting from direct ionization of valence electrons.

An attempt was thus made to measure some spatial distributions in alkali halides, which were selected to give the maximum possible density of absorbing matter in various atomic number ranges (e.g., NaF, KCl, RbBr, CsI). At first F-centers were selected to be the trapped irradiation product. These normally cannot be produced in sufficiently high concentrations to be suitable, but it was reported that doping alkali halides with ions like Ca^{++} greatly enhanced F-center production.[8] So, some crystals were doped by melting the impurity salt with the alkali halide in a platinum crucible and then quick-cooling to get polycrystalline material. However, the yield of F-centers in the materials was still too low to be sure their distribution would reflect the initial distribution produced by the radiation. Hence an effective electron trapping species was sought that could be densely substituted in an alkali halide crystal. Since we had already had some favorable experience with silver ions as electron traps,[9] some Ag^+ doped crystals were prepared.

A variety of alkali halides were tested, and of these only KCl and RbCl showed the ESR spectrum of Ag atoms upon irradiation with Co-60. KCl gave a higher yield and showed hyperfine structure indicating Ag^+ was in the lattice substitutionally, so saturation measurements were done on quenched powder samples of silver ion doped KCl. The saturation time vs. dose curve obtained indicates an inhomogeneous distribution of Ag atoms with the radius of the average spur being about 80 Å. Contrast this with 30 Å spurs for electrons in alkaline ice, in which all the absorbing atoms have lower cross sections for inner shell ionization than those in KCl do. The KCl number is actually larger than its face value indicates because spur size varies inversely with matrix polarity.[5]

Experiments are now in progress to measure spatial distribution of Ag^0 in CsI and NaF (using purchased crystals). The Auger electron yield should be quite small in NaF, which should thus show spur sizes even less than those for ice systems (NaF being more polar). CsI, on the other hand, would be expected to show spurs with average size at least as large as seen in KCl and possible larger, depending on the cross sections for ionization of the various inner electron shells.

3. Energy Levels of Trapped Electrons in Irradiated Alkaline Ice

Simple theoretical treatments predict that the optical transition of the trapped electron in irradiated 10 M NaOH at 77°K goes to an excited state which is still bound by more than an eV.[4] This prediction was put to the experimental test by studying the bleaching rate of the trapped electron as a function of temperature. If the theoretical treatments are correct, the thermal activation required for removing the electron from the excited state will give rise to a positive temperature dependence of the bleaching rate.

Measurements by both ESR and (for confirmation) optical spectrometry show a small <u>negative</u> dependence of the bleaching rate (E_a = -0.5 Kcal/mole). This result shows that the first optically allowed excited state of the trapped electron in alkaline ice is weakly bound if bound at all. A similar study on irradiated glassy methanol near 77°K gives the same conclusion for that system. The negative temperature dependence observed may be due to a slight temperature dependence for retrapping delectrons from the conduction band.

As a further check on this work, measurements of the already known temperature dependence of the bleaching rate for F-centers in KCl were undertaken. Samples irradiated at room temperature give a large positive temperature effect, which is reassuring. The literature values for KCl, however, are for the 77-150°K region,[10] and measurements in this range are now in progress.