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CHEMISTRY

Thermoluminescence from Recombination of Organic Ions

THE trapping of positive and negative ions in γ -irradiated organic glasses at 77° K has been extensively studied by Hamill *et al.*¹ The products of the recombination of ions are of considerable interest in the elucidation of reaction mechanisms in radiation chemistry. We have shown previously² that ion recombination in solutions of naphthalene in a hydrocarbon glass (2 parts methyl-cyclohexane : 3 parts isopentane) leads to luminescence on warming—thermoluminescence (TL)—or on stimulation by infra-red radiation (IRSE). This work has been extended and we report here some new results.

A more careful estimate of the thermoluminescence yield leads to a G value for emitted quanta of the order of magnitude of 0.1: our previous estimate² of 10^{-6} (based on the manufacturer's data for the photomultiplier sensitivity) was in error—the result partly of a faulty photomultiplier circuit and partly of a numerical mistake in the calculations: the new value depends on a comparison of the intensity of thermoluminescent emission with a standard scintillation solution containing carbon-14 (ref. 3). The G value for trapped ions is about 1: because the luminescence yield of excited naphthalene is low⁴, the majority of the recombining ions probably produce excited states. Luminescence is therefore a useful tool for studying ion recombination in this system.

Further study of the emission spectrum has shown that in addition to naphthalene fluorescence and phosphorescence, emission from the excimer⁵ ($C_{10}H_8$)₂*⁻ also occurs. This band was at first thought to be caused by the solvent, but the band is narrower than the emission spectrum of the impure solvent and its intensity increases rapidly with increasing concentration (maximum used was 10^{-2} molar). The excimer band is stronger in TL than in IRSE; this probably accounts for the apparent difference in phosphorescence/fluorescence ratio described previously² as the filter used to measure fluorescence intensities also transmitted the excimer band.

In addition to $C_{10}H_8^-$ and the $C_{10}H_9$ radical, we have now detected $C_{10}H_8^+$ (ref. 6) in the visible absorption spectrum after irradiation. At low solute concentrations (for example, 10^{-4} molar) in hard glasses, trapped electrons can be detected by their infra-red absorption^{1,2,7}, but at 10^{-2} molar concentration the only negative species observed was $C_{10}H_8^-$; therefore it seems reasonable to suppose that luminescence results from recombination of $C_{10}H_8^+$ and $C_{10}H_8^-$ which diffuse together on warming the solvent. Because emission is observed both from excimers and single molecules, it is possible that the negative ion dissociates into $C_{10}H_8$ and an electron during the diffusion process (perhaps as a result of the field of the positive ion). The previously suggested reaction between $C_{10}H_8^-$ and a solvent cation, however, cannot yet be ruled out. The concentration dependence² of the yield of TL remains puzzling.

Johnson and Albrecht⁸ have recently shown that CO_2^-

may play an important part in the photolysis of similar glassy solutions because carbon dioxide is not removed by the usual freeze-pump-thaw degassing procedure. Experiments with added carbon dioxide and with solutions degassed by bubbling pure nitrogen through them show that our previous results were not affected by the presence of carbon dioxide: naphthalene competes efficiently for the electrons. Addition of large amounts of carbon dioxide (several hundred mm of mercury), however, removes the $C_{10}H_8^-$ absorption leaving $C_{10}H_8^+$: TL is somewhat weakened and consists of phosphorescence alone. This suggests that recombination of $C_{10}H_8^+$ with CO_2^- can lead to excitation, but there is insufficient energy available to produce the excited singlet state. The singlet and triplet excitation energies are 3.9 and 2.6 eV. The electron affinity of carbon dioxide (or, rather, the vertical ionization potential of the ion) has been estimated to be between 2.3 and 2.9 eV⁹. The ionization potential of $C_{10}H_8$ is 8.1 eV in the gas phase⁹: it may be 1–2 eV less in solution. This leaves 4.2–5.8 eV for recombination, which may be further reduced if coulombic energy is lost in collisions during the approach of the ions.

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Kinetics of Proton-transfer Reactions

THE kinetics of proton-transfer reactions have been studied, using a number of methods, by Eigen *et al.*¹ and by Ertl and Gerischer², and this communication reports the application of yet another technique—pulse radiolysis—to the study of the reaction between H_3O^+ and OH^- .

Pulse radiolysis of water and aqueous solutions produces transient changes in composition, and the subsequent relaxation of the system can be studied in various ways, for example, by measuring the electrical conductivity. The latter method is, of course, applicable only to reactions involving ionic species. In irradiated water the ionic products are H_3O^+ , H_2O^- and OH^- and the behaviour of the hydrated electron (H_2O^-) has been extensively studied by absorption spectroscopy³. Conductimetry, however, can be applied to all these ions and thus, in conjunction with pulse radiolysis, can be used to study fast homogeneous reactions involving H_3O^+ . The overall effect is the sudden production of these three ionic species (along with uncharged radicals) and the relaxation of the H_3O^+ concentration can be followed under appropriate conditions.

In dilute ammonia the hydrated electron is relatively long lived, and if the concentration of OH^- is substantially larger than those of the H_3O^+ and OH^- produced by