If the molecule was in the ionic state Sn^+Cl^- , the energy required to remove the electron from essentially Sn^+ , would be expected to be closer to the second I.P. of Sn, namely 14.6 eV, even allowing for an offsetting effect of the positive charge on the Sn by the negative charge on the Cl.

Hastie, *et al.*'s,⁹ opinion that PbCl is ionic, based on similar I.P. arguments, is, in our view, debatable.

This work tends to favor the value of 3.6 eV for D(Sn-Cl) though a recent paper¹⁵ favors that of 3.2 eV.

Acknowledgments. The authors wish to thank Dr. A. J. C. Nicholson and Dr. C. G. Barraclough for their many helpful discussions. Two of us, (A. S. B. & D. J. K.), would also like to thank Dr. A. L. G. Rees for the hospitality extended in the laboratories of the Division of Chemical Physics, C.S.I.R.O.

(15) Yu. Ya. Kuryakov, Vestn. Mosk. Univ. Khim., 23(3), 21 (1968).

Deuterium Sulfide as an Electron Scavenger in the Radiolysis of Liquid Saturated Hydrocarbons

by P. T. Holland and J. A. Stone

Chemistry Department, Queen's University, Kingston, Ontario, Canada (Received April 21, 1969)

The use of deuterium sulfide as a radical and ion scavenger in the radiolysis of organic liquids has been advocated by Henglein.^{1,2} Ausloos^{3,4} has used hydrogen sulfide as a free radical scavenger in gas phase radiolysis and photolysis of hydrocarbons. Bone and Futrell⁵ observed both proton transfer and charge transfer from propane ions to hydrogen sulfide in the ion source of a mass spectrometer. We have studied the radiolysis of saturated hydrocarbons in the liquid phase with varying concentrations of D₂S as solute and find that it is also an electron scavenger.

Von Meissner and Henglein¹ suggest that D_2S reacts by both H atom scavenging and charge transfer in liquids of low dielectric constant

$$H \cdot + D_2 S \longrightarrow HD + DS \cdot$$
 (1)

$$RH^+ + D_2S \longrightarrow RH + D_2S^+$$
(2)

$$D_2S^+ + e \longrightarrow D_2 + S$$
 (3)

In support of reaction 3 they find that the D_2 yield is reduced to a very low value by N₂O whereas the HD yield is relatively unchanged. In a single series of experiments it should therefore be possible to obtain the yields of both H atoms and positive ions. Our HD and D_2 yields from D_2S in *n*-hexane agree with those reported by von Meissner and Henglein.¹ However, we obtain similar HD and D₂ yields from D₂S in cyclohexane, the gas phase ionization potential of which is about 0.5 eV less than that of H₂S.⁶ In solid cyclohexane at 77°K, $G(D_2)$ is the same as in the liquid at 298°K, although G(HD) is lower. For example, $G(D_2)$ is 1.0 for 1 mol % of D₂S, a yield much higher than those usually associated with charge transfer processes occurring in the solid phase⁷ but one more consistent with electron scavenging.⁸ The usual diagnostic test for electron scavenging, which we have applied, is the reduction of $G(N_2)$ obtained when solutions containing N₂O are irradiated with a second solute.⁹



Figure 1. The yields of gaseous products from the radiolysis of liquid n-hexane containing N_2O (0.44 mol %) and D_2S at 298°K.

Liquid *n*-hexane containing 0.44 mol % N₂O was irradiated at 298°K with ⁶⁰Co γ rays at a dose rate of 6.2×10^{17} eV/ml min to a total dose of 9.5×10^{18} eV/ml. The gaseous volume in the Pyrex sample tube was less than 5% of the liquid volume. The yields of D₂, HD, H₂, and N₂ obtained with various D₂S concentrations are presented in Figure 1.

(1) Von G. Meissner and A. Henglein, Ber. Bunsenges. Phys. Chem., 69, 264 (1965).

(2) J. Pukies, A. Henglein, and G. Meissner, Z. Phys. Chem., 57, 177 (1968).

(3) P. Ausloos and S. G. Lias, J. Chem. Phys., 44, 521 (1966).

- (4) R. Gordon, Jr. and P. Ausloos, *ibid.*, 46, 4823 (1967).
- (5) L. I. Bone and J. H. Futrell, *ibid.*, 47, 4366 (1967).

(6) K. Watanabe, T. Nakayama, and J. Mottl, U. S. Department of Commerce Office Technical Service Report, **158**, 319, 1959.

(7) J. A. Stone, Can. J. Chem., 46, 3531 (1968).

- (8) N. H. Sagert, *ibid.*, **46**, 89 (1968).
- (9) W. V. Sherman, J. Chem. Soc., 599 (1966).

4398

 N_2O scavenges electrons to yield N_2 and O^{-10}

$$e + N_2 O \longrightarrow N_2 O^- \longrightarrow N_2 + O^- \qquad (4)$$

 $G(N_2)$ is reduced with increasing D_2S concentration but at the same time $G(H_2 + HD + D_2 + N_2)$ remains constant. A reaction of an electron with D_2S yielding D_2 and HD must be superceding a similar one with N_2O . The results of Sagert and Blair¹¹ show that at the N_2O concentration we employ, almost all the N_2 arises from reaction 4 and very little, if any, from the secondary reaction

$$O^- + N_2 O \longrightarrow N_2 + O_2^- \tag{5}$$

which increases $G(N_2)$ in gas phase radiolysis of saturated hydrocarbons by 55% above G(electrons).¹² It is to be noted that at 8 mol % D₂S, $G(N_2)$ is less than one half its value in the absence of D₂S. A Stern-Volmer type plot using the N₂ yields shown in the figure gives $k_{e+N_2O}/k_{e+D_2S} = 6$. The same value is obtained with cyclohexane as solvent.

A possible mechanism for the production of D_2 via electron capture is that given by von Meissner and Henglein¹ as the mechanism operating in irradiated aqueous D_2S solutions



The D atom will be scavenged by D_2S to give D_2 .

Von Meissner and Henglein¹ rejected the idea of electron capture by D_2S in saturated hydrocarbon solvents with low dielectric constants since the effects of solvation are not great enough to overcome the activation energy of 1.56 eV observed for the formation of SH^- in the gas phase.¹³ If this argument holds, then the extrapolation of the appearance potential of negative species from gas to liquid phase is not valid for the system under discussion.

Electron capture by D₂S explains two inconsistencies found in the radiolysis of this solute in cyclohexane and n-hexane. (a) Whereas the addition of the efficient proton acceptors ethanol-d and ammonia- d_3 to liquid cyclohexane does not lead to any increase in the total hydrogen yield^{14,15}, the addition of D₂S causes an increase which at 5 mol % is ~ 1 G unit. This increase can now be attributed to the reactions of D₂S with electrons which do not normally participate in hydrogen production. Such increased yields are found with HI16 and HCl17 as electron scavengers. (b) Freeman¹⁸ has made theoretical calculations of positive ion scavenging in liquid hydrocarbons. He finds that agreement between theory and experiment can be obtained for the D_2S -*n*-hexane system only if a reduced mobility is assumed for the negative entity. We have found that with the same basic theory the D₂ yields can be accounted for by an inefficient electron scavenging mechanism without any positive charge transfer.

Although we have shown that electron capture by D_2S occurs we cannot say whether positive charge scavenging occurs at the same time. The results of Bone and Futrell⁵ suggest that both charge exchange and proton transfer might occur. However a limiting $G(D_2)$ of ~ 3 at high D_2S concentration as found by von Meissner and Henglein¹ is consistent with electron scavenging being the sole process for the production of D_2 .

Acknowledgment. This work was supported by the National Research Council of Canada and Atomic Energy of Canada Ltd, Commercial Products.

- (10) G. R. A. Johnson and J. M. Warman, Trans. Faraday Soc., 61, 1709 (1965).
- (11) N. H. Sagert and A. S. Blair, Can. J. Chem., 45, 1351 (1967).
- (12) J. M. Warman, J. Phys. Chem., 71, 4066 (1967).
- (13) K. Jäger and A. Henglein, Z. Naturforsch., 21a, 1251 (1966).
- (14) F. Williams, J. Amer. Chem. Soc., 86, 3954 (1964).
- (15) J. W. Buchanan and F. Williams, J. Chem. Phys., 44, 4377 (1966).
- (16) J. R. Nash and W. H. Hamill, J. Phys. Chem., 66, 1097 (1962).
- (17) P. J. Dyne, Can. J. Chem., 43, 1080 (1965).
- (18) G. R. Freeman, J. Chem. Phys., 46, 2822 (1967).

Field Independence of Photoinjection

into Hydrocarbon Solution

by A. Prock and M. Djibelian

Department of Chemistry, Boston University, Boston, Massachusetts 02215 (Received April 31, 1969)

Photoinjection from rhodium electrode into hydrocarbon solutions has been reported previously,¹ where a simple thermodynamic analysis based on energy requirements led to an estimate of solvation energies of anionic species. Objections were later raised in private communication that the effect of the large applied electric field was not taken into account. That is, under high enough electric field strength there would be sufficient potential drop across the Helmholtz double layer for a nonnegligible amount of energy to be coupled into the electrode reaction. The solvation energy calculated without accounting for this energy would be too high. The question is, are we missing an energy term under the conditions of the experiment?

This note describes experiments on one of our previous systems which carries photoinjection measurements down to 1% of the original applied voltage, or

⁽¹⁾ A. Prock, M. Djibelian, and S. Sullivan, J. Phys. Chem., 71, 3378 (1967).