Reactions of the Hydrated Electron with Alcohol Radicals

By JACK BARRETT,* M. F. FOX,† and A. L. MANSELL

(*Department of Chemistry and Biology, Hatfield College of Technology, Hatfield, Herts.*)

IT has been shown[1-3] that the effect of 1849Å radiation upon the aqueous sulphate ion is to produce a hydrated electron and a sulphate ion-radical. In the presence of a specific electron-scavenger such as H_3O^+ ion and an alcohol (to scavenge the sulphate ion-radical) the quantum yield of hydrogen gas-production as a result of absorption of radiation by sulphate ion was found to be **0·64**. In the absence of an electron scavenger the quantum yield is dependent upon the alcohol present. Values of 0·37, 0·16, and zero for the quantum yield were observed in the presence of methanol, ethanol, and propan-2-ol respectively.

These observations are not consistent with hydrogen atom scavenging and can be interpreted in terms of reactions between the hydrated electron and the alcohol radical produced as a result of sulphate ion-radical scavenging. These reactions may be written:

$$SO_4^- = RH \text{ (alcohol)} \rightarrow HSO_4^- + R \text{ (alcohol radical)} \quad (1)$$

$$R + e^-_{aq} \rightarrow R^- \quad (2)$$

$$R^- + H_2O \rightarrow RH + OH^- \quad (3)$$

* Present address: Department of Chemistry, Chelsea College of Science and Technology, Manresa Road, Chelsea, London, S.W.3.

† Present address: Department of Chemistry, University of Leicester.

The overall effect of these reactions would be to suppress the observed quantum yield since Reaction (2) would compete with the hydrogen gas-forming processes:

$$e^-_{aq} + H_2O \rightarrow H + OH^-$$

$$H + RH \rightarrow H_2 + R$$

$$e^-_{aq} + e^-_{aq} \rightarrow H_2 + 2OH^-$$

For reactions such as (2), which have been predicted by Hart *et al.*,[4] it would be necessary for the relative rates to increase in the order $Me_2COH > MeCH{\cdot}OH > CH_2{\cdot}OH$. Evidence which supports this order comes from the observation[5] that the electron density on the α-carbon atom increases along the above series.

(*Received, March 14th*, 1966; *Com.* 156.)

[1] J. Barrettt, M. F. Fox, and A. L. Mansell, *J. Phys. Chem.*, 1965, **69**, 2996.
[2] F. S. Dainton and P. Fowles, *Proc. Roy. Soc.*, 1965, *A*, **287**, 312.
[3] J. Barrett, M. F. Fox, and A. L. Mansell, to be published.
[4] E. J. Hart, S. Gordon, and E. M. Fielden, *J. Phys. Chem.*, 1966, **70**, 150.
[5] M. C. R. Symons, "Identification of Organic Free Radicals", in *Adv. Phys. Org. Chem.*, 1962, **1**, 284.