

## $\gamma$ -Radiolysis of Ferrocene in Cyclohexane and of Aqueous Solutions of Ferricinium Sulphate

By R. BLACKBURN and A. KABI

(Royal Military College of Science, Shrivenham, Wiltshire)

COLLINSON *et al.*<sup>1</sup> have shown that  $\gamma$ -radiolysis of a solution of ferrocene (dicyclopentadienyliron) in carbon tetrachloride leads to the formation of ferricinium chloride, presumably by the scavenging of chlorine atoms. Otherwise no investigation has been made of the radiolysis of solutions of ferrocene in organic solvents. This is surprising in view of the resistance of the solid compound towards degradation by ionising radiation,<sup>2</sup> an observation tentatively ascribed to the great stability conferred by the aromatic nature of the molecule. This conclusion would suggest that in solution ferrocene should act in a manner analogous to benzene and stabilise the system, either by 'sponge-type protection' in which energy is transferred to the solute molecules and dissipated without decomposition, by radical scavenging, or by a charge-transfer mechanism. Here we assess the ability of ferrocene to reduce radiolysis yields

in cyclohexane, and investigate the radiolysis of aqueous solutions of ferricinium sulphate.

Solutions of cyclohexane (B.D.H. Spectroscopic Grade dried over 3A Linde molecular sieve) containing different concentrations of ferrocene (purified by repeated vacuum sublimation), benzene (A.R.) and naphthalene (A.R.) were prepared and the yields of dicyclohexyl and cyclohexene resulting from a dose of 1.49 Mrad of <sup>60</sup>Co  $\gamma$ -radiation were measured by vapour-phase chromatography. It can be seen from Fig. 1 that the yield of dimer is relatively little affected by up to 0.1M concentration of benzene, while comparable concentrations of ferrocene and naphthalene result in a considerable reduction; the cyclohexene yield shows a similar trend. These results show that ferrocene is efficient in reducing radiolysis yields and it is possible that this property can be assigned to its aromatic

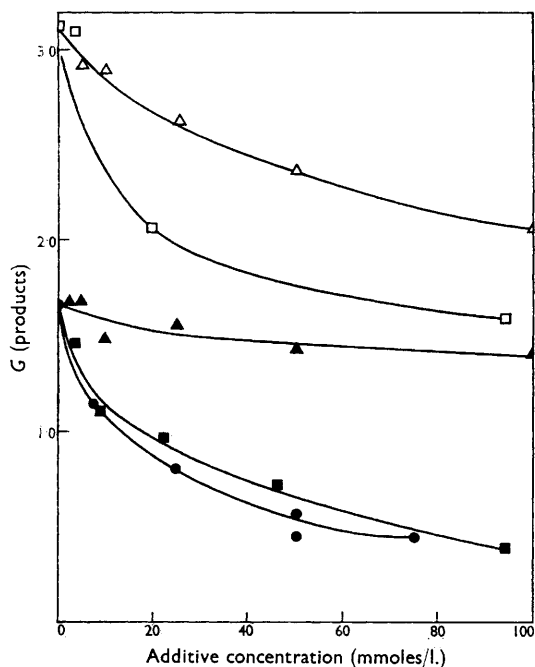


FIGURE 1

Cyclohexene yield:  $\Delta$  benzene additive,  
 $\square$  dicyclopentadienyl additive.  
 Dicyclohexyl yield:  $\blacktriangle$  benzene additive,  
 $\blacksquare$  dicyclopentadienyl additive,  
 $\bullet$  naphthalene additive.

character. The large difference, however, between benzene and naphthalene suggests that other factors are operative, and part of the difference may be due to positive charge transfer effects since the ionisation potentials of benzene (9.2 eV), naphthalene ( $\sim$ 8.0 eV) and ferrocene (7.6 eV) are lower than that of cyclohexane (11.0 eV). Radical scavenging effects also cannot be ruled out and it is probable that the reductions in yield are due to a combination of these factors. Irradiation of a dilute solution of ferrocene in cyclohexane to a dose of 8.9 Mrad produced no change in the optical density of the absorption peaks at 340  $m\mu$  and 490  $m\mu$  and no wavelength shift was observed. This would suggest that the ferrocene molecule is not consumed during irradiation and that radical attack is not of great importance. Absence of wavelength shift, however, cannot be regarded as an indication that no ferrocene derivatives are produced since such species absorb at virtually the same energy as the parent compound.<sup>3,4</sup>

Aqueous solutions of ferricinium sulphate (prepared by the oxidation of ferrocene with

silver sulphate) irradiated to doses up to 0.48 Mrad were extracted with ether. The decrease in ferricinium sulphate concentration in irradiated sample was determined by measuring the u.v. absorption of the aqueous extract at 628  $m\mu$ . The corresponding increase in the absorption of the ethereal extract at 442  $m\mu$  was also measured, but for the reasons stated above, it is not possible to ascribe this solely to unsubstituted ferrocene. The bulk of the present work was carried out at pH = 1.0 and hence reactions of hydrated electrons in these solutions can be discounted since these species react preferentially with hydrogen ions to produce hydrogen atoms,<sup>5</sup> the residual reactive species are thus hydrogen atoms and hydroxyl radicals. Values of  $-G$  (ferricinium sulphate) and  $G$  (ferrocene), as calculated from the linear portions of Figs. 2 and 3, are respectively 4.27

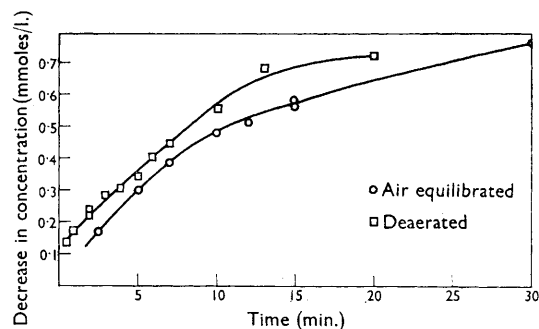


FIGURE 2

$\gamma$ -Irradiation of aqueous solutions of ferricinium sulphate ( $10^{-3}M$ , pH = 1.1). Decrease in concentration of ferricinium sulphate as a function of dose. Dose-rate = 16.05 Krad/min.

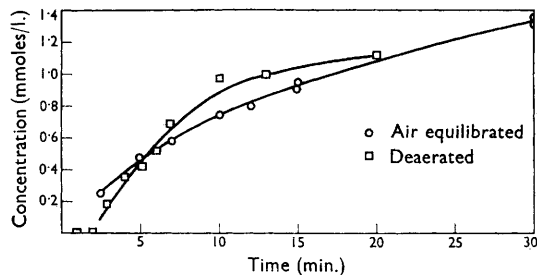


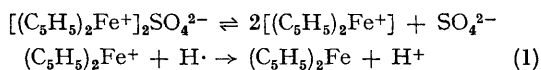
FIGURE 3

$\gamma$ -Irradiation of aqueous solutions of ferricinium sulphate ( $10^{-3}M$ , pH 1.1). Yield of ferrocene as a function of dose. Dose-rate = 16.05 Krad/min.

and 5.17 for air-equilibrated and 3.61 and 5.46 for deaerated solutions. A feature of the air-equilibrated results is the fact that the yield dose

curves for both ferricinium and ferrocene do not pass through the origin. It appears that while there is initially a rapid decrease in the ferricinium sulphate concentration, there is no corresponding rapid formation of ferrocene. It is to be noted that whereas in air-equilibrated solution a dark brown polymer was produced, no such material was formed in the absence of oxygen.

The lower yield of ferrocene in the presence of oxygen can be accounted for by the scavenging of hydrogen atoms in competition with the following reaction:



The relatively small difference between the ferrocene yields in air-equilibrated and deaerated solutions, however, suggests that the rate constant for reaction (1) is comparable in magnitude to

that for the reaction of oxygen with hydrogen atoms. The greater decrease in ferricinium sulphate concentration in air-equilibrated solutions is possibly due to the formation of polymeric material, but this point must await a detailed investigation of the constitution of the latter. Much of the marked falling off in the yield-dose curve for ferrocene in air-equilibrated solutions can be ascribed to depletion of oxygen. This process cannot, however, account for the similar but less pronounced change of slope in the curve for deaerated solution and it is necessary to invoke other reactions; the most likely appears to be that involving the oxidation of ferrocene back to ferricinium. These and other aspects of the radiation chemistry of ferricinium sulphate are being further investigated.

(Received, October 21st, 1966; Com. 803.)

<sup>1</sup> E. Collinson, F. S. Dainton, and H. Gillis, *J. Phys. Chem.*, 1961, **65**, 695.

<sup>2</sup> B. K. Krotoszynski, *J. Chem. Phys.*, 1964, **41**, 2220.

<sup>3</sup> M. Rosenblum, "Chemistry of the Iron Group Metallocenes", Part I, John Wiley, New York, 1965.

<sup>4</sup> M. Rosenblum, J. O. Santer, and W. G. Howells, *J. Amer. Chem. Soc.*, 1963, **85**, 1450.

<sup>5</sup> J. P. Keene, *Radiation Res.*, 1964, **22**, 1.