Inhibition of Charge-pair Recombination by Sulphuric Acid in Irradiated Aqueous Solution

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Summary Sulphuric acid species inhibit charge-pair recombination in irradiated aqueous solution and a reaction involving the charge pair can explain most of the apparent increase with acid concentration in primary radiolytic yields estimated from the iron(II) sulphate system.

The value of $G(Fe^{3+})$ from ^{60}Co γ-irradiated deaerated solutions of $FeSO_4$ in 0·4M sulphuric acid is only equal to the accepted value [1–3] of $2G(H_2O_2) + G(H) + G(OH)$ at a particular concentration of $FeSO_4$.[4] The marked dependence of $G(Fe^{3+})$ on the concentration of Fe^{2+} was attributed to reactions of Fe^{2+} with a species which oxidized Fe^{2+} to

Fe^{3+} or which decayed to water in the absence of Fe^{2+}. The species was postulated to be a geminate radical pair or an excited water species and the data were found to fit a model based on a significant yield of a comparatively long-lived excited water species.[4]

The alternative possibility of charge-pair recombination from the viewpoint of inhibition by sulphuric acid species has now been found to provide a good fit to the data at all acid concentrations studied. The yield of Fe^{3+} as a function of the concentration of Fe^{2+} in 1M H_2SO_4 and 0·04M H_2SO_4–0·1M Na_2SO_4 solutions was determined by the method previously described.[4] The results (Table) are shown together with the data for 0·4M acid in the Figure. The concentration of H^+, HSO_4^-, and SO_4^{2-} in these solutions were calculated from the data of Young, Maranville, and Smith[5] and from the data of Baes.[6]

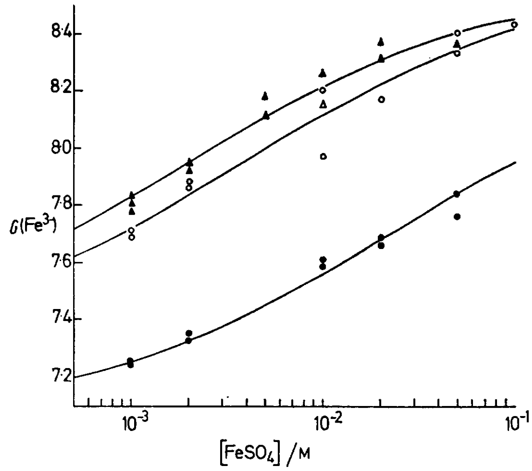

FIGURE. $G(Fe^{3+})$ *vs.* $[FeSO_4]$ in deaerated solutions: ● 0·04M H_2SO_4–0·1M Na_2SO_4; ○ 0·4M H_2SO_4; ▲ 1·0M H_2SO_4.

In addition to the usual reactions of hydrogen peroxide, hydroxyl radical, and hydrogen atom with Fe^{2+}, reaction (1) is also assumed to occur. The dependence of product yield

$$H_2O^+ \cdots e^- + HSO_4^- + Fe^{2+} \rightarrow FeSO_4^+ + H_2O + H\cdot \quad (1)$$

on solute concentration in irradiated cyclohexane solution has been shown by Schuler *et al.*[7] to be well described by expressions of the form $G_{gi}\sqrt{\alpha[S]}/(1+\sqrt{\alpha[S]})$. The yield of Fe^{3+} was found to fit expression (2) well, where $G^\circ_{1,2,3}$ =

$$G(Fe^{3+}) = G^\circ_{1,2,3} + 2G_X/\{1+1/(\alpha[HSO_4^-][Fe^{2+}])\} \quad (2)$$

$2G(H_2O_2) + G(H) + G(OH)$ in 1·0M H_2SO_4, 0·4 M H_2SO_4, and 0·04M H_2SO_4–0·1M Na_2SO_4 respectively, G_X = the yield (100 eV) of the charged pair, and α = the reactivity constant. The following parameters were obtained from expression (2) by least-squares methods: $G^\circ_{1,2,3} = 7{\cdot}22 \pm 0{\cdot}07,\ 7{\cdot}26 \pm 0{\cdot}07,\ 7{\cdot}03 \pm 0{\cdot}06$; $G_X = 0{\cdot}70 \pm 0{\cdot}03$; $\alpha = (8{\cdot}3 \pm 2{\cdot}6) \times 10^2\ l^{-2}\ mol^2$. The lines drawn through the points in the Figure are those calculated substituting the above parameters in expression (2).

TABLE

$[Fe^{2+}]$/mM	$[HSO_4^-]$/mM	$G(Fe^{3+})$ (exptl.)	$G(Fe^{3+})$ (calc.)
1	46	7·24, 7·25	7·256
2	46	7·33, 7·35	7·330
10	46	7·61, 7·59	7·560
20	46	7·66, 7·69	7·677
50	46	7·76, 7·84	7·836
1	290	7·69, 7·71	7·720
2	290	7·86, 7·88	7·832
10	290	7·97, 8·20	8·108
20	290	8·17	8·218
50	290	8·33, 8·40	8·342
100	290	8·43	8·418
1	720	7·78, 7·81, 7·83	7·827
2	720	7·92, 7·95	7·947
5	720	8·11, 8·18	8·102
10	720	8·15, 8·26	8·208
20	720	8·31, 8·37	8·300
50	720	8·36, 8·36	8·397

Similar reactions to (1) but involving H^+ or SO_4^{2-} in place of HSO_4^- may be written, requiring a corresponding substitution in expression (2). Application of least-squares methods using forms of expression (2) with $[H^+]$ and $[SO_4^{2-}]$ in place of the $[HSO_4^-]$ also provided good fits to the data. In the case of the $[H^+]$ form the values for $G^\circ_{1,2,3}$ were constant within standard error, so the analysis was repeated assuming a single value for $G^\circ_{1,2,3}$ in expression (2). The parameters obtained were: $G^\circ = 7{\cdot}04 \pm 0{\cdot}06$; $G_X = 0{\cdot}77 \pm 0{\cdot}03$; $\alpha = (8{\cdot}11 \pm 2{\cdot}2\ ) \times 10^2\ l^{-2}\ mol^2$.

These new estimates of G° are significantly lower than previous estimates and shows that most of the apparent increase in primary radical yields with increasing acid concentration may be due to inhibition of charge-pair recombination by acid species.

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