

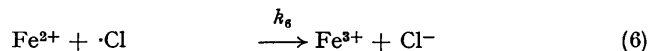
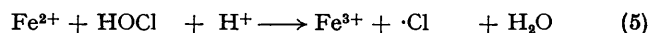
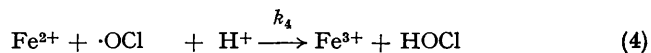
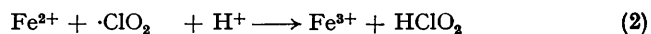
Formation of Free Radicals in the Reduction of Chlorate by the Iron(II) Cation in Dilute Aqueous Acid Solution

By WILLIAM C. E. HIGGINSON* and (Mrs.) MARGARET E. SIMPSON
(Chemistry Department, Hull University, Hull HU6 7RX)

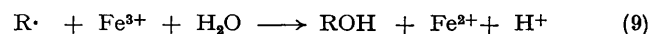
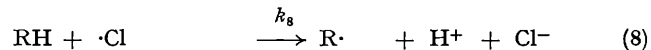
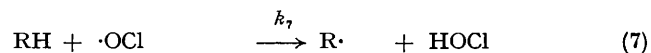
Summary The effect of alcohols on the rate of oxidation of the iron(II) cation by chlorate provides evidence for the intermediate formation of the active free radicals $\cdot\text{OCl}$ and $\cdot\text{Cl}$.

ALTHOUGH the kinetics of oxidation of the iron(II) cation by chlorate in dilute aqueous acid solution have previously been investigated,¹ the mechanism is uncertain. We have obtained new information by following the kinetics of formation of Fe^{3+} spectrophotometrically under nitrogen in the presence and absence of various alcohols and of chloride ions. At 25.0 °C, $I = 2.0\text{M}$ (NaClO_4), $[\text{H}^+] = 0.050\text{M}$, $[\text{ClO}_3^-] = 0.039\text{M}$, $[\text{Fe}^{2+}] = \text{ca. } 0.004\text{M}$, we find $k = -[\text{ClO}_3^-]^{-1} \text{d} \ln[\text{Fe}^{2+}]/\text{d}t = 0.01091 \text{ mol}^{-1} \text{ s}^{-1}$. This reference value of k is denoted k_0 . In the presence of alcohols, plots of $\ln [\text{Fe}^{2+}]$ against t show slight curvature, and k obtained from the gradient at half-reaction is less than k_0 .

We interpret our results in terms of the mechanism in reactions (1)–(6). We consider that reactions between two



free radicals are unimportant in this system. If free radicals only are able to react rapidly with alcohols (RH) in the presence of Fe^{2+} , we may include reactions (7)–(9).



When RH is methanol (1—2M) k assumes a limiting value of almost exactly $\frac{2}{3}k_0$. We attribute this to the complete replacement of reaction (6) by (8) and (9). With propan-1-ol, propan-2-ol, or allyl alcohol, the value of k becomes $\frac{2}{3}k_0$ at [RH] = 0.05—0.1M, but a further drop in k to *ca.* $\frac{1}{2}k_0$ occurs as [RH] is increased to 1.0M. We ascribe this further drop to the partial replacement of reaction (4) by reactions (7) and (9). Thus, the free radical $\cdot\text{OCl}$ is insufficiently active to react with methanol in the presence of Fe^{2+} . This radical, well known in the gas phase, has been studied in condensed phases,² but there is little previous evidence for its occurrence in aqueous solution.³

The evidence for the particular free radicals cited is, first, that $\cdot\text{ClO}_2$ does not react with these alcohols. Secondly, the reactivity ratio $N = k_7/k_4$ or k_8/k_6 for the more reactive of the two remaining free radicals is *ca.* 0.1 for propan-1-ol and propan-2-ol, and *ca.* 0.03 for methanol. These values are much smaller than those obtained with $\cdot\text{OH}$, an alternative possibility for the free-radical product of reaction (5), but are similar to, although somewhat smaller than, those obtained in the reduction of HOCl by Fe^{2+} and ascribed⁴ to the formation of $\cdot\text{Cl}$. The less reactive free radical is therefore $\cdot\text{OCl}$, and we note its greater selectivity compared with $\cdot\text{Cl}$. For the latter, N values for propan-2-ol and methanol are in the ratio 3:1; the corresponding ratio for OCl exceeds 25:1.

Finally, in the absence of alcohols the presence of up to 1.2M- Cl^- has only a minor effect upon k . The addition of 0.4M- Cl^- to a reaction at 1.15M-methanol restores k from

$\frac{2}{3}k_0$, back to k_0 . Evidently $\cdot\text{Cl}$ is reacting completely with Cl^- to produce a species ($\cdot\text{Cl}_2^-$) which does not abstract a hydrogen atom from methanol in the presence of Fe^{2+} . Similar experiments with 0.38M-propan-2-ol, where $k = 0.44k_0$ in absence of Cl^- , gave an increase to $k = 0.78k_0$ at 0.73M- and 1.22M- Cl^- . This difference of $\frac{1}{3}k_0$ again shows the removal of the more active $\cdot\text{Cl}$, but the effect of $\cdot\text{OCl}$ remains. Calculations following Weiss,⁵ and using the standard reduction potential⁶ for $\cdot\text{Cl}_2^-/2\text{Cl}^-$ suggest, in accordance with our results, that Cl^- should not scavenge $\cdot\text{OCl}$ by reaction (10) because this is endothermic by *ca.* 30 kJ mol⁻¹.



In principle, our conclusions could more simply be obtained by measurements of the consumption ratio $\Delta[\text{Fe}^{2+}]/\Delta[\text{ClO}_3^-]$ in the absence and presence of alcohols and chloride ion. We intend to investigate this approach since it is likely to prove more convenient than kinetic measurements in other systems in which $\cdot\text{OCl}$ may be involved. The method should be of even wider application, because bond-energy considerations suggest that free radicals such as $\cdot\text{OBr}$ and $\cdot\text{OI}$ may be detectable, provided their competing disappearance by electron transfer is not too rapid.

We thank the S.R.C. for their support.

(Received, 23rd July 1974; Com. 928.)

¹ A. M. Azzam and I. A. W. Shimi, *Z. phys. Chem. (Frankfurt)*, 1962, **33**, 190; K. P. Ang, G. A. Creak, and W. L. Kwik, *J.C.S. Dalton*, 1972, 2560.

² D. D. Tanner and N. Nychka, *J. Amer. Chem. Soc.*, 1967, **89**, 121; F. K. Chi and L. Andrews, *J. Phys. Chem.*, 1973, **77**, 3062.

³ J. C. Mialocq, F. Barat, L. Gilles, B. Hickel, and B. Lesigne, *J. Phys. Chem.*, 1973, **77**, 742; G. Gordon, R. G. Kieffer, and D. H. Rosenblatt, *Progr. Inorg. Chem.*, 1972, **15**, 201.

⁴ D. J. Mackinnon and W. A. Waters, *J. Chem. Soc.*, 1953, 323.

⁵ J. Weiss, *Trans. Faraday Soc.*, 1947, **43**, 173, 675.

⁶ A. T. Thornton and G. S. Laurence, *J.C.S. Dalton*, 1973, 1632.