Reactivity of Hydroxyl Radicals with Ferrocenyl-substituted Carboxylic Acids. A Radiation Chemical Study

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Radiation chemical studies demonstrate that the hydroxyl radical reacts readily with ferrocenyl-substituted carboxylic acids and that, when the ferrocenyl group and the carboxylate are separated by one or more methylene units, the reaction is principally an oxidation process. The nature of the reaction is less clear cut when the intervening group contains a double bond, a benzene ring, or is non-existent. Pulse-radiolysis studies indicate that the rate constants for the reaction of OH with 2-ferrocenylethanoate and 3-ferrocenylpropanoate are, respectively, $(2.2 \pm 0.2) \times 10^{10}$ and $(2.9 \pm 0.4) \times 10^{10}$ dm^3 mol^{-1} s^{-1}, while those of $(SCN)_2^-$ and of Br_2^- with the same anions are all less than 2×10^9 dm^3 mol^{-1} s^{-1}. It is deduced that the diffusion coefficient of the hydroxyl radical may be appreciably greater than that of the self-diffusion of water.

Previous photochemical studies [1-3] have shown that the illumination of aqueous solutions of carboxyalkylferrocenes, $Fc(CH_2)_nCO_2^-$, with u.v. light of *ca.* 250 nm produced little effect except when an electron acceptor such as N_2O was present, in which case the products detected were molecular nitrogen and the corresponding carboxyalkylferricenium dipolar ion. The conclusion [1,2] that the mechanism involved electron transfer to N_2O left unresolved the fate of the hydroxyl radical presumed to result from the reaction sequence (1)—(3). The most probable event appeared to be the occurrence of reaction (4), in which case the yields of the dipolar ion and of N_2 should have been in the molar ratio of 2 : 1. To resolve the matter it seemed desirable to apply the techniques of radiation chemistry.

$$Fc(CH_2)_nCO_2^- \xrightarrow{h\nu} [Fc(CH_2)_nCO_2^-]^* \qquad (1)$$

$$[Fc(CH_2)_nCO_2^-]^* + N_2O \longrightarrow \overset{+}{Fc}(CH_2)_nCO_2^- + N_2 + O^- \qquad (2)$$

$$O^- + H_2O \longrightarrow OH + OH^- \qquad (3)$$

$$OH + Fc(CH_2)_nCO_2^- \longrightarrow OH^- + \overset{+}{Fc}(CH_2)_nCO_2^- \qquad (4)$$

In aqueous solution containing N_2O, where the solvated electron reacts [4] by reaction (5), the predominant effect of ionizing radiation is the production of the OH radical with a *G* value [5] (*i.e.* yield of radicals per 100 eV of energy input [6]) of almost 6.

$$e_{aq}^- + N_2O \longrightarrow N_2 + O^- (\longrightarrow OH) \qquad (5)$$

It was thus desired to follow the spectral changes in aqueous solutions containing carboxyalkylferrocenes and saturated with N_2O to discover whether these indicated formation of the corresponding carboxyalkylferricenium dipolar ion, or of some other product. It was also desired to estimate the rate constant for the reaction with the OH radical.

Additionally, it was envisaged that the results of the above experiments might be compared with those in which bromide ion was also present at a concentration much higher than that of the carboxylate anion. In this case the formation of Br_2^- is expected by the sequence shown in reactions (6) and (7). Whereas the OH radical can conceivably be engaged in an H-atom abstraction reaction, either from the anion or from the ferricenium dipolar ion, the only probable reaction of Br_2^- is the oxidation process, reaction (8). Thus an observation of similar effects of γ-irradiation in the presence and the absence of an appreciable concentration of bromide ion would indicate that the hydroxyl radical is behaving purely as an oxidising species.

$$OH + Br^- \longrightarrow OH^- + Br \qquad (6)$$

$$Br + Br^- \longrightarrow Br_2^- \qquad (7)$$

$$Br_2^- + Fc(CH_2)_nCO_2^- \longrightarrow 2Br^- + \overset{+}{Fc}(CH_2)_nCO_2^- \qquad (8)$$

Experimental

Materials.—The ferrocenyl-substituted carboxylic acids were prepared as previously described [2,3,7] or were provided by Professor W. E. Watts. Other chemicals were of AnalaR grade and triply-distilled water was used. Unless otherwise stated solutions were buffered to pH 9 using 0.025 mol dm^{-3} borax.

Steady Irradiation Procedure.—The vessel employed for the γ-irradiation experiments was a test-tube of borosilicate glass with a side arm leading to a quartz spectrophotometer cell of 10 mm path length. The vessel was cleaned using permanganic acid followed by acidified hydrogen peroxide. The use [8] of a septum cap and syringe needles permitted solutions within the vessel to be readily de-aerated and saturated with N_2O.

Samples of 10.0 cm^3 were employed in the irradiation experiments. Spectra were recorded over the range 200—800 nm using a Pye Unicam SP8-100 spectrophotometer. Measurements were made before and after various periods of γ-irradiation with a ^{60}Co source of 2 000 Ci nominal activity. By using the Fricke dosimeter,[9] it was established that the dose rate was 1.68 krad min^{-1}.

Pulse Radiolysis.—This technique involves the measurement of time-resolved changes in the optical absorption spectrum of species produced in a sample by a short-duration pulse of ionizing radiation, usually provided by a beam of high-energy electrons.[10] The methods used in this laboratory have been described elsewhere.[11,12] An analysing light beam from a Xe arc lamp is passed through the sample cell and after passage through a monochromator falls on a photodetector, thus permitting measurements of optical absorption. The cells

Table. Initial values of $G\varepsilon$ from γ-irradiation

	$Fc(CH_2)_2CO_2^-$		$Fc(CH_2)_4CO_2^-$		$FcCH_2CO_2^-$	
Wavelength/nm	No KBr	With KBr[a]	No KBr	With KBr[a]	No KBr	With KBr[a]
625	1.5×10^3	1.7×10^3	1.3×10^3	1.8×10^3	1.4×10^3	1.7×10^3
284	3.7×10^4	4.1×10^4	3.6×10^4	4.5×10^4	2.8×10^4	4.0×10^4
256	4.8×10^4	5.2×10^4	4.9×10^4	6.0×10^4	3.5×10^4	4.7×10^4

[a] When KBr was added, the concentration was 10^{-2} mol dm^{-3}.

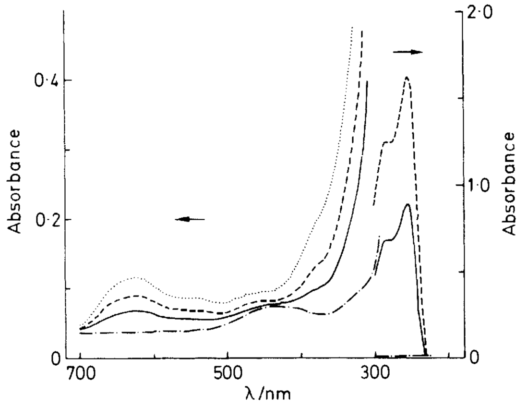

Figure 1. The change in the spectrum of an N_2O-saturated solution of $Fc(CH_2)_2CO_2^-$ produced by γ-irradiation. (— · — · —) initial spectrum; (——) after dose of 16.7 krad; (- - - -) after dose of 33.4 krad; (· · · ·) after dose of 66.8 krad. Below 300 nm, a cell containing unirradiated solution was used as a reference

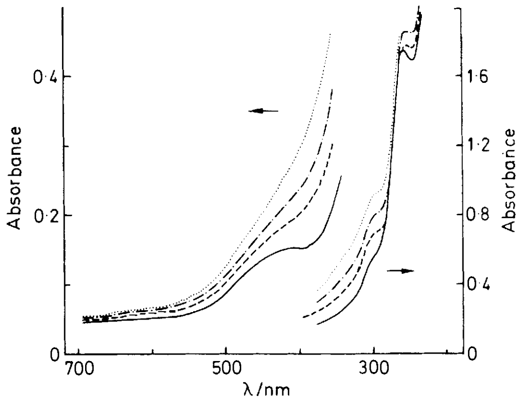

Figure 2. The change in the spectrum of an N_2O-saturated solution of ferrocenoate produced by γ-irradiation. (——) initial spectrum; (- - - -) after dose of 25.1 krad; (— · — · —) after dose of 51.1 krad; (· · · ·) after dose of 91.8 krad

were of Spectrosil grade silica and had optical path lengths of either 5 or 10 mm. Irradiation of the sample was by pulses of 3 MeV electrons generated by a Van de Graaff accelerator [High Voltage Engineering (Europa), KS-3000] and having durations of 25, 50, 100, or 600 ns depending on the requirements of the experiment.

Solutions for pulse-radiolysis experiments were de-aerated and saturated with N_2O by bubbling with this gas and were then stored in all-glass syringes. The irradiation cell could be filled from these syringes through a flow system which allowed the sample to be changed without contamination with air.

Results

γ-Irradiation Experiments.—When solutions of 3-ferrocenylpropanoate at pH 9.5 and saturated with N_2O were γ-irradiated, they turned perceptibly green. Spectrophotometric monitoring showed the development of peaks at *ca*. 625, 284, and 256 nm, at rates which slowed down as irradiation was continued, as illustrated in Figure 1. Within the limits of experimental error, there was no dependence of the initial rate on anion concentration over the range 10^{-3}—10^{-4} mol dm^{-3}. The initial values of $G\varepsilon$ † are shown in the Table.

With KBr also present, very similar effects were observed from γ-radiolysis, with slightly higher $G\varepsilon$ values, as shown in the Table. Thus the hydroxyl radical oxidises the 3-ferrocenylpropanoate anion to the corresponding ferricenium dipolar ion and this is virtually the exclusive mode of reaction.

The Table also summarises the results of similar experiments with 5-ferrocenylpentanoate and with 2-ferrocenylethanoate, where γ-irradiation produced spectral changes very similar to those shown in Figure 1. In both cases the initial $G\varepsilon$ values are enhanced by the addition of KBr, suggesting that in its reactions with these anions the OH radical behaves predominantly, but not exclusively as an oxidising species.

The γ-radiolysis of N_2O-saturated solutions of ferrocenoate at pH 9 produced an increase in absorbance over the whole spectral range, particularly around 300 nm, as shown in Figure 2. With 10^{-2} mol dm^{-3} KBr added, there was a more apparent peak at 620 nm and at lower wavelengths the greatest increases were at 284 ($G\varepsilon = 1.7 \times 10^4$) and 256 nm ($1.6 \times 10^4$). Thus oxidation did not seem to be an important mode of reaction of OH with ferrocenoate anion.

The γ-radiolysis of N_2O-saturated solutions of *trans*-3-ferrocenylacrylate anion at pH 9 produced a very slight increase in absorbance at 600 nm ($G\varepsilon < 300$) but a steady decrease over the remainder of the spectrum, which was specially marked at the 460 nm peak ($G\varepsilon = -500$) and at 320 nm. With KBr added, increases in absorbance were apparent throughout most of the spectral region with peaks at 700 ($G\varepsilon = 1.0 \times 10^3$), 400 ($2.2 \times 10^3$), 325 ($7.9 \times 10^3$), 265 ($2.2 \times 10^4$), and 228 nm ($1.6 \times 10^4$) and a decrease at 460 nm ($G\varepsilon = -1.7 \times 10^3$). Thus the reaction of the hydroxyl radical with the 3-ferrocenylacrylate anion is not principally an oxidation process.

The γ-irradiation of the N_2O-saturated solution of 2-ferrocenylbenzoate anion caused increases in absorbance at 740, 300, and 255 nm with initial $G\varepsilon$ values of 1.3×10^3, 1.85×10^4, and 1.7×10^4, respectively. With the addition of KBr these were increased to 2.3×10^3, 2.9×10^4, and 2.7×10^4. It may be concluded that the hydroxyl radical oxidises this anion, but that Br_2^- ion does so more efficiently.

Pulse-radiolysis Studies.—In the pulse-radiolysis experi-

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† $G\varepsilon$ is the product of the radiolytic yield of the product species (molecules per 100 eV) and its molar decadic extinction coefficient (dm^3 mol^{-1} cm^{-1}).

ments, it was desired to find out whether the absorbance detectable at the end of the pulse corresponded with that observed on the much longer time scale after γ-radiolysis.

The major peak produced by irradiation, at 256 nm, is at a wavelength where appreciable photolysis of these solutions is known [1,2,3,7] to occur. It was found that in order to observe the effect of pulse irradiation in this wavelength range, it was necessary to keep the light shutter closed between pulses. It was also desirable to refill the irradiation cell frequently with fresh solution, since successive pulses on one aliquot of solution did not reproduce the same absorbance change.

(i) *Spectra and kinetics.* Pulse experiments using N_2O-saturated solutions of 3-ferrocenylpropanoate at pH 9 showed that absorbance changes similar to those described above for γ-radiolysis grew in very quickly (<1 μs) after the pulse. In some cases a slight decay of this absorbance occurred over the next 30 μs, but this was less than 10% of the initial absorbance. The extent of this decay varied with the number of pulses to which the sample had previously been subjected, and so it was difficult accurately to determine its dependence on wavelength.

In attempts to estimate the second-order rate constant of the reaction of the hydroxyl radical with 3-ferrocenylpropanoate, it was observed that an enhanced level of light was recorded just after the onset of the pulse, presumably because of fluorescence emission. Thus the kinetic analysis was considered unreliable.

The $G\varepsilon$ values measured 10 μs after the pulse were 2.6×10^3 and 6.1×10^4 at 625 and 255 nm, respectively. In the presence of 10^{-2} mol dm^{-3} KBr, virtually identical values were found.

In the experiments on the solutions containing KBr, a large transient peak was observed at 360 nm, attributable to the Br_2^- ion. The decay of this peak was pseudo-first-order, and gave a value of 1.7×10^9 dm^3 mol^{-1} s^{-1} for the rate constant of the reaction of $Fc(CH_2)_2CO_2^-$ with Br_2^-. This reaction could also be monitored from the growth in absorbance at 285 nm, due to the product zwitterion. Some light emission was detectable at this wavelength and this may be an important factor in the rather poor agreement of the value of 2.6×10^9 dm^3 mol^{-1} s^{-1} for the second-order rate constant, derived from the formation of the peak at 285 nm, with that obtained from the decay of the Br_2^- ion absorption.

In experiments with N_2O-saturated solutions of ferrocenylethanoate anion, absorbance changes were found to grow in quickly after the electron pulse and to persist with only a very slight decrease over 1 ms. From the plateau values, $G\varepsilon$ was estimated as 1.4×10^3 (625), 4.8×10^4 (285), and 2.6×10^4 (255 nm). When KBr was also present, these values became 1.7×10^3, 3.8×10^4, and 4.3×10^4, respectively. They thus show very close agreement with the data from γ-irradiation, except that in the pulse study in the absence of bromide a larger absorption was observed at 285 than at 255 nm.

From the work on solutions containing bromide, values of the bimolecular rate constant for the reaction of Br_2^- with $FcCH_2CO_2^-$ were estimated as 1.8×10^9 dm^3 mol^{-1} s^{-1} from the decay of the Br_2^- peak at 360 nm and as 2.0×10^9 dm^3 mol^{-1} s^{-1} from the rate of formation of the absorption of the zwitterion at 285 nm.

N_2O-saturated solutions of $FcCO_2^-$ yielded long-lived absorptions over most of the spectral range. The peak at 625 nm corresponded to a $G\varepsilon$ value of 3.4×10^4, while very large absorptions were found below 300 nm with a $G\varepsilon$ value of 5.5×10^5 at 260 nm.

With N_2O-saturated solutions of 3-ferrocenylacrylate containing KBr, it was confirmed that absorptions were detected at the wavelengths of the peaks observed from γ-irradiation, with $G\varepsilon$ values of 5.9×10^3 (230), 1.0×10^4 (265), 8.0×10^3 (320), and 1.1×10^3 (720 nm), and with decreased absorbance at 460 nm with $G\varepsilon = -1.5 \times 10^3$. With bromide absent, $G\varepsilon$ was found to be 5.2×10^3 at 230 nm.

In similar studies with N_2O saturated solutions of 2-ferrocenylbenzoate, the absorptions that appeared within a few μs after the electron pulse all decreased by about one-quarter over the next 40 μs. In the presence of KBr, such a change is masked at certain wavelengths by the absorption due to Br_2^-, but it appears that the decrease is much smaller. In the absence of KBr, $G\varepsilon$ values after 40 μs were determined as 0.7×10^3 (750), 2.2×10^3 (420), 1.2×10^3 (300), and 1.0×10^3 (260 nm) while in the presence of KBr the values were 1.7×10^3 (720), 2.7×10^3 (420), 1.1×10^4 (320), 2.3×10^4 (300), and 1.7×10^4 (260 nm). These values are, perhaps surprisingly, about one quarter less than those obtained on the minute time scale after γ-irradiation.

(ii) *Competition studies.* Competition methods have been used extensively [13,14] to measure the rate constants for the reaction of ·OH with solutes using the pulse-radiolysis method. Hydroxyl radicals generated by pulse radiolysis of N_2O-saturated solutions are allowed to compete with the solute concerned (S_1) and a reference solute (S_2) which on reaction produces a strongly absorbing species (B), reactions (9) and (10). If D_0 is the optical density due to B when only S_2 is present and D the optical density when solute S_1 is also present then we obtain equation (I).

$$OH + S_1 \longrightarrow \text{A (non-absorbing)} \qquad (9)$$

$$OH + S_2 \longrightarrow \text{B (absorbing species)} \qquad (10)$$

$$\frac{D_0}{D} - 1 = \frac{k_9[S_1]}{k_{10}[S_2]} \qquad \text{(I)}$$

For equation (I) properly to reflect the competition between S_1 and S_2 it is necessary that B be sufficiently stable that the extent of its decay during the pulse is negligible. If the decay of B is significant, say by reaction with S_1, then D may be corrected for the amount of decay occurring during the time required for B to reach its maximum concentration,[15] provided the kinetics of decay of B are known and the extent of decay is not excessive.

Initial studies at pH 8.6 on the competition between ferrocenylethanoate and HCO_3^-/CO_3^- indicated that $CO_3^{-\cdot}$ reacts so rapidly with the ferrocene compound that the system was unsuitable for the competition study. Consequently all subsequent studies were made using potassium thiocyanate as the reference solute.[14]

With $[SCN^-] = 2.6 \times 10^{-3}$ mol dm^{-3} and $[FcCH_2CO_2^-]$ in the range 9.7×10^{-4}—2.4×10^{-3} mol dm^{-3}, large absorptions due to $(SCN)_2^-$ were observed at the end of the 25 ns pulse. The decay of $(SCN)_2^-$ was observed to follow first-order kinetics and the observed rate constant increased linearly with $[FcCH_2CO_2^-]$, giving $k_{11} = (1.51 \pm 0.07) \times 10^9$ dm^3 mol^{-1} s^{-1}. Calculations indicate that reaction (11) caused significant decay of $(SCN)_2^-$ during its period of formation and therefore corrections were made as indicated above when applying equation (I). The magnitude of the corrections were quite significant ranging from 14% for a solution with $[FcCH_2CO_2^-] = 4.84 \times 10^{-4}$ to 33% for $[FcCH_2CO_2^-] = 1.86 \times 10^{-3}$ mol dm^{-3}. The corrected values of D were plotted according to equation (I) and yielded a straight line with $k_{12}/k_{13} = (2.0 \pm 0.2)$. Taking the value [14,15] of (1.08 ± 0.10)

$$(SCN)_2^- + FcCH_2CO_2^- \longrightarrow \overset{+}{Fc}CH_2CO_2^- + 2SCN^- \qquad (11)$$

$\times 10^{10}$ dm^3 mol^{-1} s^{-1} for k_{13}, this gives $k_{12} = (2.2 \pm 0.2) \times 10^{10}$ dm^3 mol^{-1} s^{-1} [equations (12)—(14)].

$$\mathrm{OH} + \mathrm{FcCH_2CO_2^-} \longrightarrow \text{product} \qquad (12)$$

$$\mathrm{OH} + \mathrm{SCN^-} \longrightarrow \mathrm{SCN} + \mathrm{OH^-} \qquad (13)$$

$$\mathrm{SCN} + \mathrm{SCN^-} \longrightarrow \mathrm{(SCN)_2^-} \qquad (14)$$

Similar experiments with ferrocenylpropanoate indicated that this solute is oxidised by $(SCN)_2^-$ with a rate constant of $(1.75 \pm 0.13) \times 10^9$ dm^3 mol^{-1} s^{-1}. Again, the corrections to be applied to the optical densities to be used in equation (I) were very significant ranging from 17.5 to 38.5%. However, the corrected values gave a good straight line when plotted according to equation (I) and yielded $k_{15}/k_{13} = 2.70 \pm 0.36$ and hence the value of $(2.9 \pm 0.4) \times 10^{10}$ dm^3 mol^{-1} s^{-1} for k_{15} [equation (15)].

$$\mathrm{OH} + \mathrm{Fc(CH_2)_2CO_2^-} \longrightarrow \text{product} \qquad (15)$$

Discussion

These experiments show that the hydroxyl radical reacts with the anions $Fc(CH_2)_nCO_2^-$ with rate constants in excess of 10^{10} dm^3 mol^{-1} s^{-1}. The similarity of the spectral changes produced by OH and by Br_2^- indicate that the main reaction of OH with these solutes is oxidation to the corresponding ferricenium dipolar ion and that side-reactions are of relatively minor importance. Possible side-reactions are H-atom abstraction from one of the methylene groups or addition to the cyclopentadienyl rings. It is, perhaps, not surprising that of these processes the former is unimportant since the rate constant for the reaction of OH with the anions of the unsubstituted acids, $H(CH_2)_nCO_2^-$, are[14] very low for small values of n and reach 10^9 dm^3 mol^{-1} s^{-1} only when $n = 3$. In the γ-irradiation of 5-ferrocenylpentanoate, the increase in the $G\varepsilon$ values brought about by the addition of KBr suggests that in this case H-atom abstraction may be a significant, if minor, mode of reaction of the hydroxyl radical with this solute. For the solutes with $n > 1$, there seems to be no evidence that OH addition to the cyclopentadienyl rings is important.

The results for ferrocenoate anion, where large absorptions are seen on the μs time scale but very little on the time scale of minutes, are consistent with the photochemical studies.[3] The differing products of the reactions of OH and of Br_2^- with ferrocenoate suggest that in this case the reaction of OH involves addition to a cyclopentadienyl ring.

With ferrocenylethanoate, it is difficult to explain the larger $G\varepsilon$ values in the presence of KBr as being due to H-atom abstraction by OH, since ethanoate is so unreactive[14] with OH ($k = 8.5 \times 10^7$ dm^3 mol^{-1} s^{-1}). On the other hand, the pulse-radiolysis studies suggest that there is something unusual about the reaction of OH with this anion since, on the μs time scale, $G\varepsilon$ at 255 nm is less than at 285 nm and less than is detected several minutes after γ-irradiation.

In the reaction of OH with ferrocenylacrylate, an alternative to oxidation is to be expected since OH reacts readily with acrylate ion. With 2-ferrocenylbenzoate, much the same applies since the rate constant[14] of OH with benzoate ion is 6×10^9 dm^3 mol^{-1} s^{-1}. The decays of the transient absorptions produced from 2-ferrocenylbenzoate in the absence of KBr are perhaps due to further reactions of the radicals produced by the addition of OH to the benzene ring. Comparable reactions would be expected in the ferrocenylacrylate system and may explain why so little sign of oxidation is detected after γ-irradiation, whereas a strong absorption was seen at 230 nm on the μs time scale.

The rate constants for the reactions of the hydroxyl radical with ferrocenylethanoate and with ferrocenylpropanoate anions, 2.2×10^{10} and 3.0×10^{10} dm^3 mol^{-1} s^{-1}, respectively, are extremely high for reactions in water involving one uncharged species. It is likely that they occur virtually on the first collision.

The steady-state treatment of diffusion-controlled reactions[16] leads, using the lower boundary condition of von Smoluchowski,[17] to the expression, $k_D = 4\pi\sigma D_{AB}$ for the second-order rate constant, where σ is the separation of the centres of the two reactants when reaction occurs and D_{AB} is the sum of the diffusion coefficients of the two reactants.

On geometrical consideration, it would seem, from the known inter-nuclear distances of the ferrocene molecule[18] and disregarding electron tunnelling, that the centre of the hydroxyl radical must approach within about 4.5 Å of the centre of the iron atom in the ferrocenyl group for reaction to occur. Applying the von Smoluchowski relation, a rate constant of 3×10^{10} dm^3 mol^{-1} s^{-1} requires that if $\sigma = 4.5$ Å then $D_{AB} = 8.8 \times 10^{-5}$ cm^2 s^{-1}. The diffusion coefficient of the ferrocenylpropanoate anion might be expected to be closer to 1×10^{-5} than to 2×10^{-5} cm^2 s^{-1}, which would imply that the diffusion coefficient of the OH radical would most probably have to exceed 7×10^{-5} cm^2 s^{-1}. This is more than three times the minimum values suggested by Henglein *et al.*,[19] on the basis of the reactivity of OH with catalase.

A very high rate constant has been found[20] for the reaction of OH with tyrosine, with $k = 2.2 \times 10^{10}$ dm^3 mol^{-1} s^{-1}. It is not improbable that the diffusion coefficient of the hydroxyl radical in water is significantly higher than the value[21] of 3.0×10^{-5} cm^2 s^{-1}, which pertains to the water molecules themselves as measured by ^{18}O labelling. However, in redox reactions it is difficult to eliminate the possibility that an electron-tunnelling mechanism produces an additional contribution to the reaction parameter, σ.

The rate constants for the reactions of $(SCN)_2^-$ and Br_2^- with ferrocenylethanoate and ferrocenylpropanoate are all close to 2×10^9 dm^3 mol^{-1} s^{-1}. Since in each case both reactants are anions, this value is not far short of the diffusion controlled limit which, for the ionic strength in question and assuming that σ is the sum of the Stokes radii of each reactant, may be estimated[22] to be $(3.5—5.0) \times 10^9$ dm^3 mol^{-1} s^{-1} for such a reaction.

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