ionic effects in alkaline solutions is also obtained but is of slight significance because of the number of parameters involved. An independent proof of the partial nature of inhibition should be adduced before exploring this possibility further.

It is possible to represent the last step of the Michaelis–Menten mechanism by a sequence of reactions of the enzyme–substrate compound with hydrogen and hydroxyl ions, rather than with water. The electrolyte effect is then to be regarded as a kinetic, primary salt, effect. Such treatment, however, requires several parameters to describe the observed effect of *p*H on V^0_m and does not facilitate the interpretation of the ionic strength effect.

The failure of simple mechanisms to account for the effect of the ionic strength on enzymatic activity emphasizes the possibility that it may be an indirect result of the interaction of the entire molecule of urease, as a zwitterion, with the surrounding ionic atmosphere. The isoelectric point of urease has been observed at *p*H 5.1.[8] Thus ionic effects become noticeable only when the enzyme carries a large net negative charge. If similar effects are found in the as yet unexplored range of *p*H below 5, their correlation with the zwitterion properties of the enzyme would gain much in plausibility.

(8) J. B. Sumner and D. B. Hand, THIS JOURNAL, **31**, 1255 (1929).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MANCHESTER]

Oxidation of Aromatic Compounds in Aqueous Solution by Free Radicals Produced by Photo-excited Electron Transfer in Iron Complexes[1]

BY H. G. C. BATES[2] AND N. URI

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The kinetics of systems of the type $Fe^{3+}X^-$–aromatic substrate–ultraviolet light were investigated. The substrates chosen were benzoic acid and benzyl alcohol as monosubstituted benzene derivatives and *o*-, *m*- and *p*-toluic acids as disubstituted benzene derivatives. The kinetic scheme involves (1) light absorption, (2) primary dark back reaction, (3) dissociation of excited complex, (4) secondary dark back reaction, (5) free radical attack on the substrate, (6) oxidation of the free radical by the ferric ion pair and (7) combination of radicals at low ferric ion concentration. Benzyl alcohol was attacked in the side chain only and quantitatively oxidized to benzaldehyde. On the other hand, benzoic acid shows substitution in the benzene nucleus only. The respective ratios of *o*-, *m*- and *p*-hydroxybenzoic acid, were examined and under certain conditions these were found to be statistical (*i.e.*, 2:2:1). It appears that the benzene nucleus of *o*-toluic acid is not attacked (in contrast to the other toluic acids). Various ratios of the rate constants of the free radical reactions were evaluated quantitatively.

Introduction

In a recent paper concerned with the reactions of free radicals in aqueous solution Evans, Santappa and Uri[3] described in detail the system $Fe^{3+}X^-$–vinyl monomer–ultraviolet light (X^- being a monovalent anion such as OH^-, Cl^-, N_3^-). It was shown that the free radicals produced from the anion, X^-, by a photo-excited electron transfer reaction were capable of initiating polymerization. The work of Merz and Waters with Fenton's reagent[4] and particularly the very extensive examination by Stein and Weiss[5-8] of the reactions of aromatic compounds with OH radicals produced by this method and by the action of ionizing radiations, suggested a comparative study with the initiation system previously applied to the polymerization of vinyl compounds.[3,9-11]

A considerable advantage of this system over Fenton's reagent is that the production of free radicals is easily regulated by the variation of light intensity, and the problem of mixing conditions—important with Fenton's reagent—does not enter. The scope of this investigation was widened by the introduction, as substrates, of disubstituted benzene derivatives. The latter show interesting peculiarities which are not yet completely understood. Benzoic acid and benzyl alcohol were chosen as monosubstituted benzene derivatives and these two show remarkable differences in their behavior as substrates.

The problem of substitution in the benzene nucleus by organic free radicals was recently reviewed by Hey.[12] The whole field of aromatic substitution by free radicals is still largely undeveloped. This investigation does not fill the numerous gaps but merely supplies some more data, part of which seem to lend themselves to a satisfactory interpretation.

Experimental

Ferrous ion was determined colorimetrically as the *o*-phenanthroline complex in the presence of excess fluoride ion to avoid interference by ferric ion. The minimum excess of *o*-phenanthroline to ensure quantitative complex formation was calculated from the equilibrium measurements made by Lee, Kolthoff and Leussing.[13] The *p*H was regulated by addition of a biphthalate buffer. Ferric ion

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(1) Presented at the 122nd Meeting of the American Chemical Society held in Atlantic City, N. J., September 14–19, 1952.

(2) Shell Petroleum Co., Ltd., (CIM), St. Helen's Court, London, E. C. 3, England.

(3) M. G. Evans, M. Santappa and N. Uri, *J. Polymer Sci.*, **7**, 243 (1951).

(4) J. H. Merz and W. A. Waters, *J. Chem. Soc.*, 2427 (1949).

(5) G. Stein and J. Weiss, *Nature*, **161**, 650 (1948).

(6) H. Loebl, G. Stein and J. Weiss, *J. Chem. Soc.*, 2074 (1949).

(7) F. T. Farmer, G. Stein and J. Weiss, *ibid.*, 3241 (1949).

(8) (a) G. Stein and J. Weiss, *ibid.*, 3245 (1949); (b) 3254; (c) 3256.

(9) M. G. Evans and N. Uri, *Nature*, **164**, 404 (1949).

(10) *Idem*, *J. Soc. Dyers and Colourists*, **65**, 709 (1949).

(11) H. G. C. Bates, M.Sc. Thesis, University of Manchester, 1949.

(12) D. H. Hey, Tilden Lecture, Chemical Society, London and Leeds, 1951.

(13) T. S. Lee, I. M. Kolthoff and D. L. Leussing, THIS JOURNAL, **70**, 2348 (1948).

(always added as ferric perchlorate) was determined permanganometrically in accordance with the Zimmermann–Reinhardt standard procedure. Salicylic acid and methylsalicylic acid were determined colorimetrically as ferric complexes using a Hilger Spekker Colourimeter and a Chance OY 2 filter. Other hydroxybenzoic acids and diphenic acids were determined by algebraic analysis of the optical density at different wave lengths. The absorption spectra of the pure substances were ascertained by means of a Unicam Spectrophotometer model SP-500. This instrument was also used for all measurements of optical densities in the near ultraviolet. It is noteworthy that the steep absorption curves and the relative stability of the hydroxybenzoic acids make them suitable for use as liquid absorption filters when it is desired to remove the corresponding section of the near ultraviolet below a certain wave length. Numerical data can be worked out from the absorption spectra (*cf.* Figs. 2 and 3). Phenol was determined by measuring the absorption spectrum of an ether extract of the acidified irradiated solution (phenol shows a characteristic absorption peak at 273 mμ). Benzaldehyde was determined gravimetrically by precipitation with 2,4-dinitrophenylhydrazine.

A G.E.C. Osira 125-watt medium pressure mercury vapor lamp with a Wood glass envelope was used for practically all experiments. 95% of the lamp output is of the wave length 365 mμ. The lamp was fitted in a chromium plated housing and the light beam was made nearly parallel by means of a quartz condenser lens. The light intensity was adjusted with an iris diaphragm. The reaction vessels were cylindrical Pyrex cells (with flat Pyrex plates of 5 cm. diameter at both ends) fitted with two outlet tubes with standard B 14 ground cones. The length of the optical beam passing through the cell was 46 mm. Solutions were deaerated with nitrogen before irradiation and during the irradiation the cells were kept in a thermostat (made with quartz windows) at a temperature of 25 ± 0.1°. The lamp output was determined by chemical actinometry using the Leighton–Forbes uranyl oxalate actinometer. The procedure followed was that given by Bowen.[14]

Kinetic Results

1. The Photochemically Active Species.—In previous work on the photo-initiated polymerization of vinyl compounds it was conclusively demonstrated that with wave lengths >300 mμ it is the $Fe^{3+}OH^-$ ion pair and not the hydrated ferric ion $Fe(H_2O)_6^{3+}$ which is the photochemically active species. It was shown that the same applies to the oxidation of organic substrates. When an aqueous solution of 10^{-2} *M* $Fe(ClO_4)_3$, 2×10^{-2} *M* benzoic acid and 10^{-2} *M* $HClO_4$ was irradiated with light of wave length 365 mμ, the solution grew purple-violet as the result of the formation of salicylic acid and it could be shown by colorimetric analysis that ferrous ion was formed. Under similar conditions in the presence of normal perchloric acid practically no reaction occurred.

2. Variation of Substrates. I. Benzoic Acid as Substrate. (a) Formation of Ferrous Ion and Salicylic Acid.—Tables I and II show the dependence of the quantum yield on the concentrations of ferric ion and benzoic acid. It was observed that in both cases the quantum yield passes through a maximum. It was shown by a spectrophotometric examination that complex formation between ferric ion and benzoic acid is negligible in the concentration range in which these experiments were carried out. Table III shows that formation both of ferrous ion and salicylic acid vary linearly with the light intensity.

TABLE I

[benzoic acid] = $1.5 \times 10^{-2} M$, [$HClO_4$] = 0.02 *M*, *I* = 6.2×10^{-7} *Nh* ν/min.

Concn. of Fe^{3+} ion, *M*	Net quantum yield of salicylic acid (γnet) × 10^2
10^{-1}	0.39
5×10^{-2}	.51
10^{-2}	.86
5×10^{-3}	.87
2×10^{-3}	.85
10^{-3}	.31

TABLE II

[Fe^{3+}] = $10^{-2} M$, [$HClO_4$] = 0.02 *M*, *I* = 6.2 × 10 *Nh*ν/min.

Concn. of benzoic acid, *M*	Net quantum yield of salicylic acid (γnet) × 10^2
1.5×10^{-2}	0.86
5×10^{-3}	1.02
2×10^{-3}	1.10
10^{-3}	1.00
5×10^{-4}	0.83
2×10^{-4}	.62
10^{-4}	.23

It was also observed that the rate of formation of salicylic acid decreased with increasing ferrous ion concentration. When the reciprocal value of the quantum yield was plotted against the mean ferrous ion concentration (*i.e.*, $[Fe^{2+}]_0 + 1/2\, \Delta[Fe^{2+}]/\Delta t$ where $[Fe^{2+}]_0$ denotes the concentration of initially added ferrous ion) a straight line was obtained. This is shown in Fig. 1. Under the experimental conditions of the results plotted in this diagram the ratio $d[Fe^{2+}]/dt/d[\text{salicylic acid}]/dt$ was ~5/1.

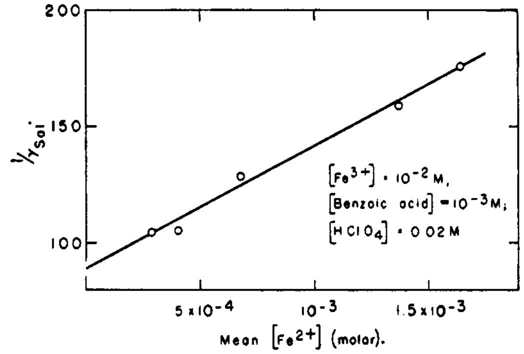

Fig. 1.

(b) Formation of *o*-, *m*- and *p*-Hydroxybenzoic Acids.—The absorption spectra of these acids and of benzoic acid in aqueous solution in the presence of $HClO_4$ were measured, and the data are presented in Fig. 2. The spectra of the corresponding ions in the presence of 10^{-2} *M* NaOH are shown in Fig. 3. The irradiated $Fe^{3+}OH^-$–benzoic acid system was subjected to spectrophotometric analysis after precipitation of the ferric ion as $Fe(OH)_3$ by neutralization with sodium hydroxide. At wave lengths >300 mμ the contribution of benzoic acid to the absorption spectrum was negligibly small. Thus, by measuring the light absorption at 300 and 310 mμ after adjusting the concentration of perchloric acid or sodium hydroxide to *p*H 0 and *p*H 12, respectively, four equations were obtained, which contain only three unknown magnitudes (*i.e.*, the concentrations of the

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[14] E. J. Bowen, "The Chemical Aspects of Light," Oxford University Press, 1942.

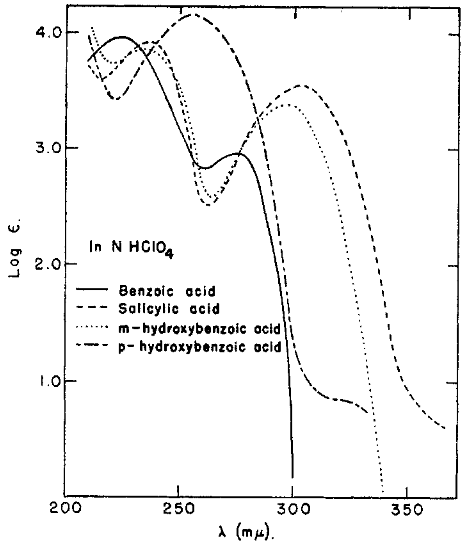

Fig. 2.

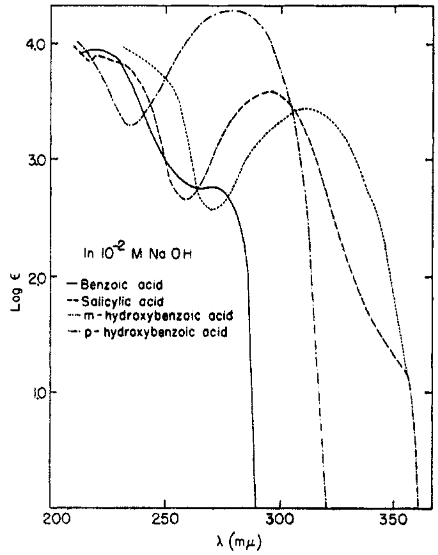

Fig. 3.

hydroxybenzoic acids). This allowed both the determination of the unknown concentrations from any three equations and, by verifications of these values from different combinations, the probable exclusion of unexpected components not taken into consideration. A further verification was made possible by the direct colorimetric determination of salicylic acid as ferric salicylate complex. The method itself was experimentally checked by analysis of known mixtures and proved very satisfactory. When the irradiations were carried out with solutions containing 10^{-2} *M* $Fe(ClO_4)_3$ the amounts of diphenic acid or phenol formed were negligible. The results of the spectrophotometric analysis indicated that under these conditions *o*-, *m*- and *p*-hydroxybenzoic acid isomers corresponded roughly to the statistical ratio of 2:2:1. This, however, did not hold when the ferric ion concentration was reduced to 10^{-3} *M*. The analysis under these conditions was more difficult as it appeared that the formation of diphenic acids could not be neglected.

(c) **$Fe^{3+}Cl^-$ as the Photochemically Active Species.**—When an aqueous solution containing $Fe(ClO_4)_3$, $HClO_4$, NaCl and benzoic acid at concentrations of 10^{-2} *M*, 1 *M*, 10^{-2} *M* and 2 × 10^{-3} *M*, respectively, was irradiated with light of wave length 365 mμ, ferrous ion but not hydroxybenzoic acids were formed which led us to the assumption that in analogy with OH radicals chlorine atoms would attack the benzene nucleus and produce chlorobenzoic acids. This was partially confirmed by the following analysis. An irradiated solution was extracted continuously with ether for 12 hours after the iron had been removed by precipitation with sodium hydroxide. When the ethereal extract was separated and the ether evaporated off under reduced pressure, a white residue with an aromatic odor was obtained which, on analysis, was found to contain 7.0% chlorine. A similar method of spectrophotometric analysis of isomers as in the case of hydroxybenzoic acids could not be applied as it was found that the chlorobenzoic acids have a very similar absorption spectrum to benzoic acid itself. It should however be possible to make such a determination by measuring the shifts and intensities of the infrared absorption bands.

The dependence of the rate of ferrous ion formation on the concentrations of initially added ferrous ion is similar to that in the case of $Fe^{3+}OH^-$ as initiator. It is very interesting to note that addition of benzoic acid actually decreases the rate of ferrous ion formation (as shown in Fig. 4). This could be due to the addition of a chlorine atom to the benzoic acid molecule and a very fast oxidation of ferrous ion by the radical thus formed.

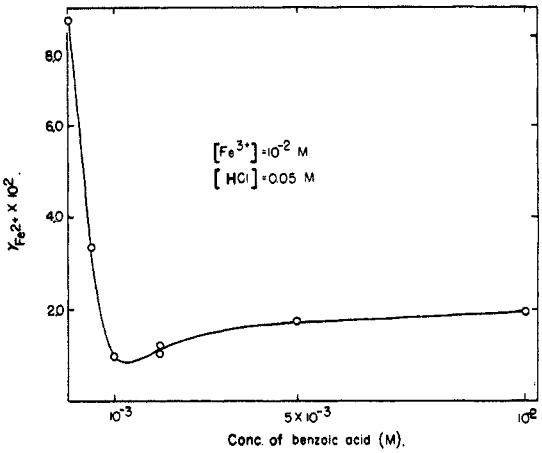

Fig. 4.

II. Benzyl Alcohol as Substrate.—With benzyl alcohol as substrate a stoichiometric ratio of γ 2:1 for ferrous ion:benzaldehyde formed was obtained (within the limits of experimental error) at a benzyl alcohol concentration of 5 × 10^{-2} *M*. This would indicate that practically no substitution occurs in the benzene nucleus. The ratio does not vary with time of irradiation (*cf.* Fig. 5). The rate of ferrous ion formation (at low ferrous ion concentrations) is not markedly effected by the concentration of benzyl alcohol. On the other hand, the rate of ferrous ion formation was found to be

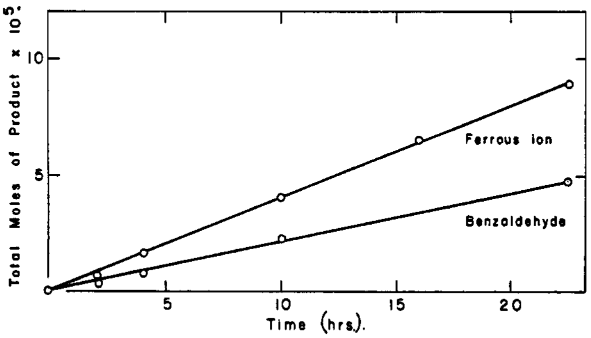

Fig. 5.—Benzyl alcohol, 5 × 10^{-2} *M*.

dependent on the concentration of the initiator $Fe^{3+}OH^-$ even when light absorption was practically complete. This is shown in Fig. 6. The rate of formation of benzaldehyde varies approximately in a parallel way. The rate of formation of benzaldehyde decreases (in analogy with many other substrates) with increasing ferrous ion concentration and a straight line was obtained when the reciprocal value of the quantum yield was plotted against the mean ferrous ion concentration (for a definition of the latter *cf.* Section 2, I, (a)) as shown in Fig. 7. Both the rates of formation of ferrous ion and benzaldehyde were found to vary linearly with light intensity.

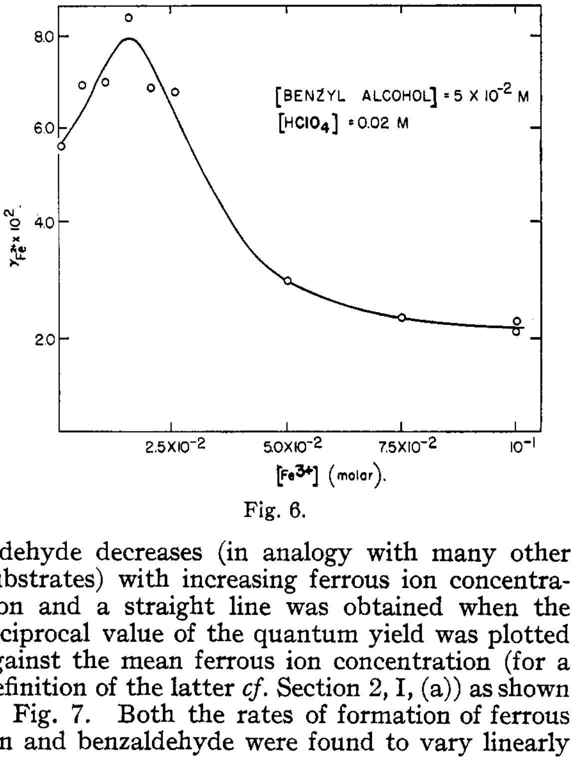

Fig. 6.

III. Toluic Acids as Substrates.—Some experiments were made with the system $Fe^{3+}OH^-$–toluic acid–light. It is known that the methylsalicylic acids form with ferric ion very similar complex compounds to those of salicylic acid, the violet color obtained being of similar intensity.[15] This was checked quantitatively with 4-methylsalicylic acid. It was found that the colorimetric calibration curve was undistinguishable from that of the ferric salicylate complex itself. This was expected, as the methyl group would hardly cause a considerable shift in the absorption spectrum in the visible region. It was assumed that, at least approximately, this would hold for the three other methylsalicylic acids that could be formed from *o*-, *m*- or *p*-toluic acid.

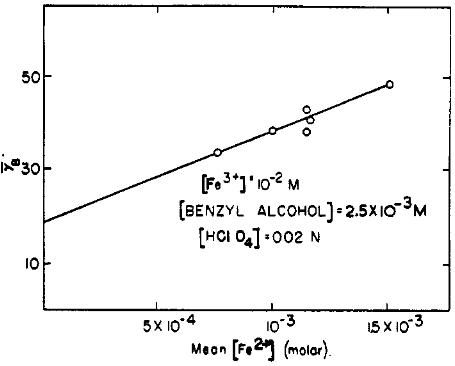

Fig. 7.

When the formation of methylsalicylic acids was compared with that of salicylic acid some surprising results were obtained (see Table IV). The experiments were carried out under identical conditions, *i.e.*, $[Fe(ClO_4)_3] = 10^{-2}$ *M*, [substrate] = 10^{-3} *M*, $[HClO_4] = 0.02$ *N* and similar intensities of the 365 mμ mercury line.

It is seen that with *m*-toluic acid the rate of methylsalicylic acid formation is of a similar order of magnitude as that of salicylic acid, with *p*-toluic acid it drops by 75% and with *o*-toluic acid *it could not be detected,* even qualitatively.

Although, statistically, a drop by 50% could be expected in the latter case as only one isomer of this methylsalicylic acid is feasible, the complete lack of the formation of the latter was remarkable. A turbidity was observed with *o*-toluic acid as substrate, presumably the corresponding dibenzyl dicarboxylic acid. However, the latter was not identified by us with certainty.

TABLE III

$[Fe^{3+}] = 10^{-2}$ *M*, [benzoic acid] = 2 × 10^{-3} *M*, $[HClO_4]$ = 0.02 *M*

Light intensity, *Nh*/min.	$d[Fe^{2+}]/dt$, moles/min. × 10^8	d[salicylic acid]/d*t*, mole/min. × 10^8
6.2 × 10^{-7}	3.7	0.68
2.7 × 10^{-7}	1.5	.32
1.18 × 10^{-7}	0.68	.16

TABLE IV

Substrate, acid	Quantum yields (×10²) of Ferrous ion formed	Quantum yields (×10²) of Salicylic acid
Benzoic	6.7	1.06
		Methylsalicylic acid
o-Toluic	7.7	0.00
m-Toluic	6.2	1.38
p-Toluic	5.2	0.28

Discussion

The following scheme was found to be consistent with the reaction kinetics.

1. Light absorption

$$Fe^{3+}X^- \underset{k\epsilon}{\xrightarrow{h\nu}} Fe^{2+}X$$

2. Primary dark back reaction

$$Fe^{2+}X \xrightarrow{k_d} Fe^{3+}X^-$$

3. Dissociation of excited complex

$$Fe^{2+}X \xrightarrow{k_s} Fe^{2+} + X$$

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[15] Beilstein, "Handbuch der organischer Chemie," 4th Ed., Vol. 10, Berlin, Germany, 1927, pp. 217, 220, 227, 233.

4. Secondary dark back reaction

$$\mathrm{Fe^{2+} + X \xrightarrow{k_0} Fe^{3+} + X^-}$$

5. Free radical attack on the substrate, RH

$$\mathrm{RH + X \xrightarrow{k_1} R\cdot + HX}$$

6. Oxidation of R· by the ferric ion pair

$$\mathrm{R\cdot + Fe^{3+}X^- \xrightarrow{k_t} RX + Fe^{2+}}$$

7. Termination at low ferric ion concentration

$$(\alpha)\mathrm{R\cdot + X \xrightarrow{k'_t} RX} \text{ and } (\beta)\ \mathrm{R\cdot + R\cdot \xrightarrow{k''_t} R_2}$$

The process of photoexcitation requires an energy which is higher by 40–50 kcal. than the thermal energy required for the electron transfer reaction $\mathrm{Fe^{3+} + X^- \rightarrow Fe^{2+} + X}$. This is best understood on the basis of the Franck–Condon principle. In the excited state $\mathrm{Fe^{2+}X}$ the internuclear distance will be that corresponding to the ion pair $\mathrm{Fe^{3+}X^-}$. A considerable repulsion energy is therefore not unexpected. In addition the hydration shell of $\mathrm{Fe^{2+}X}$ will be in a non-equilibrium state and will thus contribute to the apparent discrepancy in the energies required for the photo-excited electron transfer on the one hand and for thermal electron transfer on the other. Franck considers that the photo-excited $\mathrm{Fe^{2+}X}$ molecule formed in a cage of solvent molecules would undergo internal conversion to the effect that it becomes a "hot molecule" in its ground state.[16] The "hot molecule" will partially dissociate into $\mathrm{Fe^{2+} + X}$ and partially return to the (cold) $\mathrm{Fe^{3+}X^-}$ state accompanied by the release of heat. Such internal conversion might be the reason that no fluorescence is observed in the system.

Stationary state kinetics based on equations 1–6 lead to the following equation for the net quantum yield of ferrous ion formation.

$$\gamma = \frac{d\mathrm{Fe}^{2+}}{dt}\Big/ k\epsilon I = 2\,\frac{k_s}{k_d + k_s}\,\frac{k_1[\mathrm{HR}]}{k_0[\mathrm{Fe}^{2+}] + k_1[\mathrm{HR}]} \qquad \text{(A)}$$

where [HR] represents the concentration of the substrate. The assumptions are $d[\mathrm{Fe^{2+}X}]/dt = 0$, $d[\mathrm{X}]/dt = 0$ and $d[\mathrm{R}]/dt = 0$. The kinetic treatment is similar to that applied for monomers as substrates. While the maximum yield with monomers as substrates was ~ 0.05 $(= k_s/(k_d + k_s))$, the maximum quantum yield obtained with aromatic substrates was ~ 0.09. This leads us to the assumption that termination occurs by the ferric ion pair and the maximum quantum yield of ferrous ion formation therefore corresponds to $2k_s/(k_d + k_s)$. This is also borne out by the observation that at very low ferric ion concentrations the quantum yield drops to $k_s/(k_d + k_s)$. Under these conditions termination occurs by reaction 7α or 7β. The drop of the quantum yield at larger ferric ion concentration (*cf.* Table I and Fig. 6) requires further clarification. A possible explanation could be a competition of ferric ion or the ferric ion pair with the substrate for OH radicals. The formation of ferryl ion was first suggested by Bray and Gorin.[17] A more likely mechanism of its formation was recently introduced by Barb, Baxendale, George and Hargrave[18] who postulated the reaction $\mathrm{Fe^{3+} + OH \rightarrow FeO^2 + H^+}$. A similar reaction would be feasible with the ion pair, *i.e.*, $\mathrm{Fe^3OH^- + OH \rightarrow FeO^{2+} + HOH}$. If ferryl ion were to oxidize ferrous ion rather than react with the substrate the decrease of the quantum yield could be accounted for. This explanation should be considered as speculative. According to Uri[19,20] $\mathrm{Fe^{3+}OH^-}$ could also compete with the substrate to produce the Haber–Weiss back reaction $\mathrm{Fe^{3+}OH^- + OH \rightarrow Fe^{2+} + H_2O_2}$. The formation of $\mathrm{H_2O_2}$ would increase the number of possible reactions in this system to such an extent that it would make the kinetic equations incalculable. In the absence of any substrate OH radicals react with impurities in the distilled water. Figure 8 shows the dependence of ferrous ion formation on the ferric ion concentration in the absence of any substrate. This curve shows that a similar effect of ferric ion to that discussed above is also obtained when the substrate is replaced by the volatile organic impurities of the distilled water. Hence it should be expected that the absolute rate of ferrous ion formation, which occurs on standing in diffused daylight, is less pronounced with concentrated ferric salt solutions than with dilute ones (at $[\mathrm{Fe^{3+}}] < 5 \times 10^{-2}$ *M*). This is confirmed by experience.

The importance of impurities in distilled water at low substrate concentrations should not be neglected. Water which was distilled twice from glass vessels was used for most experiments, but even distillation from alkaline permanganate solutions did not inhibit the photochemical reduction of ferric ion in the absence of a substrate without accompanying oxygen evolution. The initial quantum yield of ferrous ion formation with $\mathrm{Fe^{3+}Cl^-}$ is larger than with $\mathrm{Fe^{3+}OH^-}$ in the absence of added substrate—as it is in its presence—in view of the different $k_s/(k_d + k_s)$ values applying to the two ion pair complexes.

While benzyl alcohol as substrate has no marked effect on the rate of ferrous ion formation, the latter is suppressed at higher concentrations of benzoic acids. This can be explained by a radical ion transfer of the type $\mathrm{OH + C_6H_5COO^- \rightarrow OH^- + C_6H_5COO\cdot}$ followed by $\mathrm{C_6H_5COO\cdot + Fe^{2+} \rightarrow C_6H_5COO^- + Fe^{3+}}$. The latter oxidation of $\mathrm{Fe^{2+}}$ is relatively more favored than that with OH radicals because, on the one hand, the electron affinities in solution of the two radicals would be expected to be very similar but, on the other hand, the energy gain resulting from the abstraction of hydrogen by the formation of the $\mathrm{C_6H_5COO\cdot\cdot\cdot H}$ bond is at least 15 kcal. smaller than that for the formation of the $\mathrm{HO\cdot\cdot\cdot H}$ bond. In a recent review[20] "promoter" and "suppressor" effects with Fenton's reagent, including the apparent non-oxidation of some carboxylic acids, were interpreted on this basis. A similar "suppressor" effect on ferrous ion formation is observed with $\mathrm{Fe^{3+}Cl^-}$ as photo-initiator and an alternative explanation has been suggested (*cf.* Section 2, I, (c)). The

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[16] J. Franck, private discussion.

[17] W. C. Bray and M. H. Gorin, THIS JOURNAL, **54**, 2124 (1932).

[18] W. J. Barb, J. H. Baxendale, P. George and K. R. Hargrave, *Trans. Faraday Soc.*, **47**, 591 (1951).

[19] N. Uri, "L. Farkas Memorial Volume," Research Council of Israel, Jerusalem, 1952, p. 193.

[20] N. Uri, *Chem. Revs.*, **50**, 357 (1952).

results obtained with $Fe^{3+}Cl^-$ as initiator, *i.e.*, the lack of formation of hydroxybenzoic acids clearly indicates that neither the reaction (α) $Cl + OH^- \rightarrow Cl^- + OH$ nor (β) $Cl + H_2O \rightarrow Cl^- + H^+ + OH$ effectively compete with the direct reaction of chlorine atoms with the substrate. This is not unexpected since as far as reaction (α) is concerned, the low OH^- concentration at the *p*H of $\sim$2 of the reaction mixtures would make it ineffective in spite of its exothermicity and a ΔS of +20 e.u., and as far as (β) is concerned, it can be calculated that it is endothermic to an extent of $\sim$10 kcal., which implies an activation energy of $\geq$10 kcal.

The statistical ratio of hydroxybenzoic acids is somewhat different from the observations made by Stein and Weis[5–8] who always found the *p*-isomer preponderant. On the other hand, with our system the termination step is different from the one assumed to occur when solutions of benzene derivatives are subjected to ionizing radiations or oxidized by Fenton reagent. The latter system was however re-examined recently.[21,22] The theoretical background of the mechanism of substitution in aromatic nuclei by free radicals is still largely unexplored. It is understood that the material balance in this substitution is given by two ferric ions reduced for each molecule of hydroxybenzoic acid formed.

The factors k_0/k_1 were ascertained by utilizing equation (A). When the reciprocal value of the quantum yield was plotted against the mean ferrous ion concentration a straight line was obtained. From the slope k_0/k_1 was evaluated for benzoic acid as 0.60 (Fig. 1) and for benzyl alcohol as 2.4 (Fig. 7). The same method was applied by Evans, Santappa and Uri[3] to vinyl monomers. The values of k_0/k_1 are slightly different from, but of a similar order of magnitude to, those obtained by Merz and Waters[4] with Fenton reagent (with which the reaction mechanism is probably more complex). The intercepts in Figs. 1 and 7 are different, as in both figures the plot is one of the quantum yield of the formation of the oxidation product (not of ferrous ion). In the case of benzaldehyde formation the stoichiometric ratio (benzaldehyde formed):(ferrous ion formed) was always 1:2. The intercept of this plot corresponds in accordance with the mechanism to $(k_d + k_s)/k_s = 20$. The similar plot for salicylic acid would be less valuable for the evaluation of this ratio as the constancy of the fraction (salicylic acid formed):(ferrous ion formed) is merely an approximation.

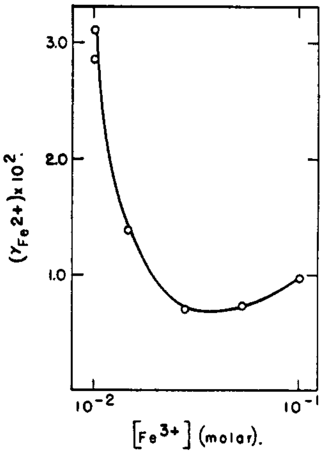

Fig. 8.

It is interesting to note that with benzyl alcohol only the side chain is attacked. This indicates that the neighboring hydroxyl group makes the C· · ·H bond in the side chain a very labile one. A similar effect is obtained with a COOH group in the ortho-position. Also in this case it appears that the C· · ·H bond in the methyl side chain is so labile that no substitution in the nucleus occurs. The turbidity observed in this case (*cf.* p. 2757) could be due to the formation of dibenzyldicarboxylic acid. A minor weakening of the C· · ·H bond in the side chain appears to be exerted by the COOH in the para-position. On the other hand in *m*-toluic acid no such effect is observed.[23]

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[22] J. H. Baxendale and J. Magee, *Discussions Faraday Soc.*, No. 14, "Reactivity of Free Radicals," in press.

[23] M. Szwyrc (*ibid.*, in press) suggested a different interpretation.