

ents almost a constant proportion of the heat of combustion of the inflamed gas, namely, 2 per cent. Yet at all flame radii the reaction is more complete with the wet mixture, as shown by the mean gas temperatures, and we estimate that the total chemiluminescent radiation emitted from the wet mixture will be approximately a quarter of that from the dry mixture after the reaction is completed.

A continuation of this work using carbon monoxide-oxygen and carbon disulphide-air mixtures has shown that chemiluminescence again occurs, but forms a smaller proportion of the total radiation due to the higher mean gas temperatures attained.

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<sup>1</sup> David, *Phil. Trans. Roy. Soc.*, Ser. A., **211**, 375 (1912); *Phil. Mag.*, **39**, 84 (1920). David and Parkinson, *Phil. Mag.*, Ser. 7, **15**, 177 (1933).

<sup>2</sup> Garner, *Indust. Eng. Chem.*, **20**, 1008 (1928). Garner and Roffey, *J. Chem. Soc.*, 1123 (1929).

<sup>3</sup> See Blinov, V. I., *J. Phys. Chem.*, U.S.S.R., **5**, 1333 (1934).

<sup>4</sup> Leah, *Phil. Mag.*, Ser. 7, **34**, 795 (1943).

<sup>5</sup> Leah, Rounthwaite and Bradley, *Phil. Mag.*, Ser. 7, **41**, 468 (1950).

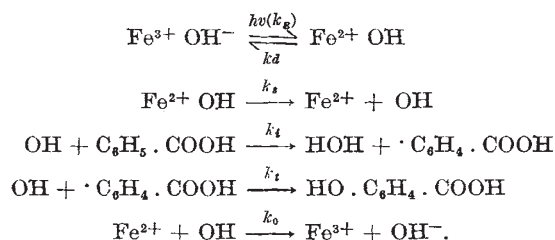
<sup>6</sup> Leah, Rounthwaite and Bradley, *Phil. Mag.*, Ser. 7, **41**, 478 (1950).

<sup>7</sup> Leah, *Phil. Mag.*, Ser. 7, **38**, 657 (1947).

### Oxidation by Photochemical Electron Transfer Excitation

Stein and Weiss<sup>1</sup> have shown that hydroxyl radicals can be detected in solution by their ability to oxidize the benzene nucleus, leading to the formation of phenol derivatives. These hydroxyl radicals were produced *in situ* both by irradiation of aqueous substrate solutions with X-rays,  $\alpha$ -rays, etc., and by the use of Fenton's reagent. Similar results were obtained with the latter by Merz and Waters<sup>2</sup>. Evans and Uri<sup>3</sup> have shown that irradiation of aqueous solutions of ion pair complexes such as  $\text{Fe}^{3+}\text{OH}^-$ ,  $\text{Fe}^{3+}\text{Cl}^-$ ,  $\text{Fe}^{3+}\text{F}^-$ , etc., with ultra-violet light (300–400  $\text{m}\mu$ ) produces atoms or free radicals in solution able to initiate the polymerization of vinyl compounds. Experimental evidence indicates that the ion-pair complexes postulated by Rabinowitch and Stockmayer<sup>4</sup> are the photochemically active entities in ferric salt solutions. In the light of these findings, we investigated the effect of monochromatic light of wave-length 365  $\text{m}\mu$  on aqueous solutions of benzoic acid in the presence of ferric ion-pair complexes. Benzoic acid was chosen as substrate because the formation of the very intensely coloured ferric salicylate complex is convenient for a photometric determination.

The kinetics of ferrous ion formation and of salicylate complex formation can be interpreted on the basis of the scheme:



Stationary state kinetics would lead to the following equations (assuming  $k_t \gg k_i$ ):

$$-\frac{d[S]}{dt} = \frac{1}{2} \cdot \frac{d[\text{Fe}^{2+}]}{dt} = \frac{1}{2} \cdot \frac{k_s k_e I}{k_d + k_s} \left( \frac{2k_i[S]}{k_0[\text{Fe}^{2+}] + 2k_i[S]} \right)$$

Ferrous ion and salicylic acid in the reaction mixture were determined colorimetrically, the former with *o*-phenanthroline in the presence of excess fluoride and the latter by measuring the concentration of the ferric salicylate complex formed. At a concentration  $\geq 10^{-3} M$  of benzoic acid, the ratio of ferrous ion and salicylic acid formed is found to be about 5.

Spectroscopic analysis of the reaction mixture shows that not only salicylic acid but also the meta- and para-hydroxy acids are formed and are present in the molar ratio of approximately 2:2:1. This is in keeping with the above ratio of  $d[\text{Fe}^{2+}]/d[\text{salicylate}] \sim 5$ . It seems that the probability of free radical attack is independent of the position in the nucleus of benzoic acid. We have not been able to detect the formation of diphenic acids under these conditions.

The following additional features throw some light on both the identity of the photochemically active species and the free radical substitution in the benzene nucleus.

In the presence of *N* perchloric acid, no salicylic acid is formed, giving further evidence that  $\text{Fe}^{3+}\text{OH}^-$  is the active species and not the hydrated ferric ion. Irradiation of  $\text{Fe}^{3+}\text{Cl}^-$  or  $\text{Fe}^{3+}\text{F}^-$  which led to the polymerization of vinyl compounds does not produce salicylic acid but presumably halogeno-benzoic acids, while ferric ion is being reduced to ferrous ion. This shows that under these conditions the reactions  $\text{Cl} + \text{OH}^- \rightarrow \text{Cl}^- + \text{OH}$  ( $\Delta H \approx -3$  kcal.,  $\Delta S \approx +20$  e.u.), and  $\text{F} + \text{OH}^- \rightarrow \text{F}^- + \text{OH}$  ( $\Delta H \approx -30$  kcal.,  $\Delta S \approx 0$ ) are too slow to compete with the direct attack of the substrate. This might be expected when taking into consideration the low concentration of  $\text{OH}^-$ . Moreover, one may conclude that the reactions  $\text{Cl} + \text{H}_2\text{O} \rightarrow \text{Cl}^- + \text{OH} + \text{H}^+$  and  $\text{F} + \text{H}_2\text{O} \rightarrow \text{F}^- + \text{OH} + \text{H}^+$  are also too slow to compete with the atom + substrate reaction.

When *p*-toluic acid is used instead of benzoic acid, 4-methylsalicylic acid (producing a similar complex with ferric ion) is formed. The amount, however, is considerably less than that found in the case of benzoic acid, although the formation of ferrous ion is similar under comparable conditions. This observation might suggest that side-chain oxidation is occurring.

A more detailed account of this study will be published later.

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<sup>1</sup> Stein and Weiss, *Nature*, **161**, 650 (1948); *J. Chem. Soc.*, 2074 (1949). (with Loebel, H.); *ibid.*, 3241 (with Farmer, F. T.); *ibid.*, 3245, 3254, 3256 (1949).

<sup>2</sup> Merz and Waters, *J. Chem. Soc.*, 2427 (1949).

<sup>3</sup> Evans and Uri, *Nature*, **164**, 404 (1949); *J. Soc. Dyers and Colourists*, **65**, 709 (1949).

<sup>4</sup> Rabinowitch and Stockmayer, *J. Amer. Chem. Soc.*, **64**, 335 (1942).