

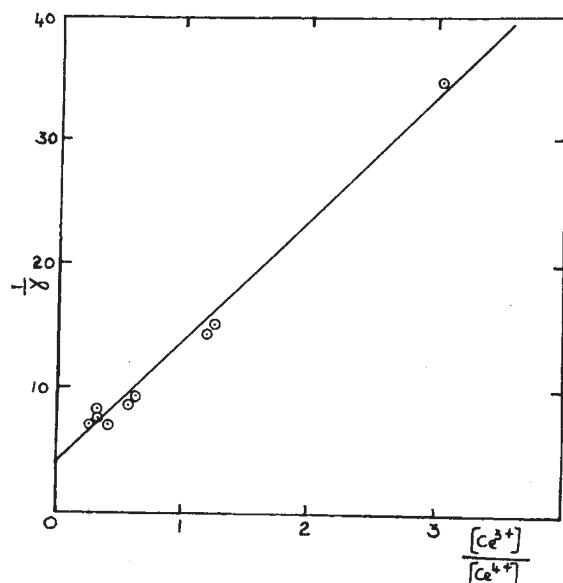
The net quantum yield with regard to  $Ce^{3+}$  ion formation is:

$$\gamma_{\text{net}} = \frac{dCe^{3+}}{dt} k_s I = \frac{4k_s}{k_d + k_s} \times \frac{k_1 [Ce^{4+} OH^-]}{k_0 [Ce^{3+}] + k_1 [Ce^{4+} OH^-]}$$

The maximum quantum yield is  $4k_s/(k_d + k_s)$ . The experimental observations would lead to a value of  $\sim 5 \times 10^{-2}$  for  $k_s/(k_d + k_s)$ , that is, of a similar order to that observed for  $Fe^{3+}OH^-$ . It is obvious that

$$\frac{dO_2}{dt} = \frac{1}{4} \frac{dCe^{3+}}{dt}$$

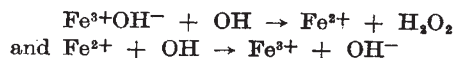
When the results obtained by Heidt and Smith are utilized for a plot of  $1/\gamma$  against the ratio  $[Ce^{3+}]/[Ce^{4+}]$ , a straight line is obtained leading to values of  $\sim 5 \times 10^{-2}$  for  $k_s/(k_d + k_s)$  and 10 for  $k_0/k_1$ . This is shown in the accompanying graph. Heidt and Smith (*loc. cit.*) plotted instead the quantum yield against  $[Ce^{4+}]/[Ce^{3+}]$  and obtained a hyperbola. It must be understood that, at very low ceric ion concentrations (less than  $\sim 2 \times 10^{-3} M$ ), hydroxyl radicals would react with impurities in the distilled water. Under these conditions the maximum quantum yield will be  $k_s/(k_d + k_s) \simeq 5 \times 10^{-2}$ .



We note that both reactions (3) and (4) are considerably exothermic. The ionization potential of cerous ion in aqueous solution may be estimated as  $\sim 110$  k.cal. (from the oxidation-reduction potential and the expected entropy change). With the values obtained by Evans and Uri<sup>5</sup>, the heat of the reaction  $Ce^{3+} + OH^- \rightarrow Ce^{4+} + OH^-$  and  $Ce^{4+}OH^- + OH^- \rightarrow Ce^{3+} + H_2O_2$  may be calculated as  $\sim 25$  k.cal. and  $\sim 20$  k.cal. respectively. The experimental observations show that the respective rate constants differ at the most by one power of 10; which in energy terms means a difference as small as 1.5 k.cal. in the activation energy, assuming similar temperature-independent factors (which considerations of the entropy of activation would not make unlikely).

We would expect that this action of hydroxyl radicals which we discuss above will be found to be

important in many reaction systems in aqueous solution. The relative rates of



may well account for the high light-intensities required for the measurement of oxygen evolution from water and  $Fe^{3+}OH^-$  complex.

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<sup>1</sup> Rabinowitch, "Photosynthesis", 1, 69 (New York and London: Interscience Publishers, 1945).

<sup>2</sup> Weiss and Porret, *Nature*, **139**, 1019 (1937).

<sup>3</sup> Baur, *Z. phys. Chem.*, **63**, 683 (1908).

<sup>4</sup> Heidt and Smith, *J. Amer. Chem. Soc.*, **70**, 2476 (1948).

<sup>5</sup> Evans and Uri, *Nature*, **164**, 404 (1949).

<sup>6</sup> Evans and Uri, *J. Soc. Dyers and Colour.*, **65**, 709 (1949).

<sup>7</sup> Bates, Evans and Uri (in the course of publication).

<sup>8</sup> Evans and Uri, *Trans. Farad. Soc.*, **45**, 224 (1949).

### Photochemical Conversion of Stilbene to Phenanthrene

SMAKULA<sup>1</sup> noticed that irradiation of solutions of *cis*-stilbene with ultra-violet light caused the formation of material different from *trans*-stilbene, and this observation was confirmed by Lewis, Magel and Lipkin<sup>2</sup>. To our knowledge, the nature of this photochemical reaction has never been elucidated, nor have any products been identified.

We have succeeded in isolating a single product in good yield from cyclohexane solutions of *trans*-stilbene irradiated with ultra-violet light, and have unequivocally identified the product as phenanthrene.

Eventually we will present more extensive information concerning this reaction and its occurrence with *cis*-stilbene and  $\alpha$ -phenyleinnamic acid.

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<sup>1</sup> Smakula, *Z. physik. Chem.*, **B**, **25**, 90 (1934).

<sup>2</sup> Lewis, Magel and Lipkin, *J. Amer. Chem. Soc.*, **62**, 2973 (1940).

### Ferric Soaps as Catalysts for Vinyl Polymerization

IN the course of work on the effect of metallic soaps on polymerization<sup>1</sup>, we found ferric oleate to possess a fairly strong catalytic power for the polymerization of styrene and methyl methacrylate. As the problem presents some very unusual features, a detailed account of which will be published elsewhere, we report here some salient features about this new catalyst.

It might be suspected that some spurious peroxidic impurities likely to be present in the oleic acid were responsible for this catalytic property. This, however, was disproved by the following experiments. Ferric oleate solution in benzene was heated *in vacuo* at 80° C. for several days in order to decompose any peroxide present, and this pretreated solution was found to retain the power to catalyse the polymerization of styrene. Further, specially purified ferric laurate and ferric stearate were successfully used as catalysts in these polymerization experiments. Lastly,