tions outlined will be discussed in a subsequent communication.

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THE REACTION OF TRIPHENYLMETHYL WITH NITROBENZENE

Sir:

It has been rather generally accepted[1,2,3] that aromatic nitro compounds are activated, relative to their unsubstituted analogs, toward attack by free radicals leading to aromatic substitution. Recent evidence concerning the inhibition of the peroxide induced polymerization of allyl acetate[4] by nitro compounds was taken to indicate that some other mode of reaction must be available to the growing chain radicals. A sequence of reactions involving attack on the nitro function was suggested as a likely alternative to nuclear substitution. We have undertaken a study of the reaction of triphenylmethyl with nitrobenzene in benzene solution and find that this radical and others which may be formed in the course of the reaction react only by abstracting oxygen from the nitro function.

When one mole equivalent of nitrobenzene is added to a benzene solution of triphenylmethyl, the solution immediately develops a red color. If such a solution is allowed to stand exposed to diffuse daylight for 24 hours, nearly a quantitative yield of triphenylcarbinol precipitates. The supernatant liquid is fractionated by adsorption on a a 5:1 Magnesol–Celite mixture followed by elution with mixtures of Skellysolve B, benzene and acetone or ethanol. Products isolated and characterized are unreacted nitrobenzene, azobenzene, azoxybenzene, nitrosobenzene, biphenyl and *p*-terphenyl. The nitrogen balance is quantitative but oxygen and hydrogen have not been entirely accounted for. Phenol is detected as its tribromo derivative in alkaline extracts of the original solutions. When the reaction is carried out in the dark a slower reaction produces a quantitative yield of ditriphenylmethyl peroxide and the same nitrobenzene reduction products. There is no evidence for attack on solvent in the dark reaction. Nitrosobenzene, which is found only in small amounts, reacts rapidly with triphenylmethyl, in separate experiments, to produce azobenzene and a trace of azoxybenzene (substantial amounts are produced from nitrobenzene) along with triphenylcarbinol, biphenyl and terphenyl. Azoxybenzene does not react to any appreciable extent in 72 hours.

It is not our intention to consider the mechanisms of these transformations in detail at this time since further study is in progress. However, certain important conclusions are apparent. It is clear that at least one radical, triphenylmethyl, is capable of effecting the reduction of nitrobenzene without bringing about nuclear substitution. The presence of phenol along with biphenyl and terphenyl suggests strongly that phenyl radicals are also produced and that they, too, abstract oxygen rather than attacking the nucleus of the nitro compounds. This is an entirely unexpected result in the light of previous work which indicates that phenyl radicals produced in the thermal decomposition of benzenediazoacetate[5] and benzoyl peroxide[6] attack nitrobenzene to give *p*-nitrobiphenyl. This difference in behavior may be taken to indicate that pairs of radicals produced in unimolecular decompositions are capable of making a concerted attack on solvent molecules in the short time interval in which they are held in the same cavity in the solution. A similar discrepency involving the fate of benzoate radicals[7] produced in different reactions has recently been observed.

This research was carried out under a contract with the Office of Naval Research.

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RADIATION CHEMISTRY OF FERROUS SULFATE SOLUTIONS

Sir:

Emphasis has been placed recently on *R*, the yield ratio, $\mathrm{Fe}^{+++}_{(\mathrm{O_2})}/\mathrm{Fe}^{+++}_{\mathrm{vac}}$, obtained by X-ray or γ-ray irradiation of dilute aqueous solutions of ferrous sulfate in the presence and absence of air.[1,2] These values vary from 2.55 to 4.0, as is shown in Table I.[1,2,3,4] The present communication demonstrates that theoretical values less than 4.0 are possible on the basis of the accepted ferrous sulfate oxidation mechanism.

According to present concepts reaction (1) occurs on the passage of ionizing particles through water. Reaction (2) also proceeds through free radical intermediates and occurs where the rate of energy loss is high and results from pairwise recombination of hydrogen atoms and hydroxyl radicals in zones of high free radical concentration. The mechanism for ferrous sulfate oxidation is:

$$\mathrm{H_2O = H + OH} \tag{1}$$

$$\mathrm{H_2O = {}^1/_2H_2 + {}^1/_2H_2O_2} \tag{2}$$

$$\mathrm{H + O_2 = HO_2} \tag{3}$$

$$\mathrm{Fe^{++} + OH = Fe^{+++} + OH^-} \tag{4}$$

$$\mathrm{Fe^{++} + HO_2 = Fe^{+++} + HO_2^-} \tag{5}$$

$$\mathrm{HO_2^- + H^+ = H_2O_2} \tag{6}$$

$$\mathrm{Fe^{++} + H_2O_2 = Fe^{+++} + OH + OH^-} \tag{7}$$

$$\mathrm{H + H = H_2} \tag{8}$$

In the absence of air the oxidation follows reactions (1), (2), (4), (7) and (8) and in the presence of

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