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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[1] W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, Oxford, 1946, p. 151.

[2] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Co., New York, N. Y., 1940, p. 383.

[3] G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 670.

[4] G. S. Hammond and P. D. Bartlett, *J. Polymer Sci.*, in press.

[5] W. S. M. Grieve and D. H. Hey, *J. Chem. Soc.*, 1803 (1934).

[6] D. F. DeTar and H. J. Scheifele, *Abstracts, Chicago Meeting of Am. Chem. Soc.*, September, 1950.

[7] G. S. Hammond, J. T. Rudesill and F. J. Modic, THIS JOURNAL, manuscript submitted.

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RADIATION CHEMISTRY OF FERROUS SULFATE SOLUTIONS

Sir:

Emphasis has been placed recently on *R*, the yield ratio, $Fe^{+++}_{(O_2)}/Fe^{+++}_{vac}$, 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:

$$\begin{aligned}
H_2O &= H + OH && (1)\\
H_2O &= {}^1/_2H_2 + {}^1/_2H_2O_2 && (2)\\
H + O_2 &= HO_2 && (3)\\
Fe^{++} + OH &= Fe^{+++} + OH^- && (4)\\
Fe^{++} + HO_2 &= Fe^{+++} + HO_2^- && (5)\\
HO_2^- + H^+ &= H_2O_2 && (6)\\
Fe^{++} + H_2O_2 &= Fe^{+++} + OH + OH^- && (7)\\
H + H &= H_2 && (8)
\end{aligned}$$

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

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[1] N. Miller, *J. Chem. Phys.*, **18**, 79 (1950).

[2] F. H. Krenz and H. A. Dewhurst, *ibid.*, **17**, 1337 (1949).

[3] H. Fricke and S. Morse, *Am. J. Roent. and Rad. Ther.*, **18**, 430 (1927); H. Fricke and E. J. Hart, *J. Chem. Phys.*, **3**, 60 (1935).

[4] N. A. Shishacow, *Phil. Mag.*, **14**, 198 (1932).

oxygen reactions (1), (2), (3), (4), (5), (6) and (7) are followed. Therefore reaction (1) leads to the oxidation of four ferrous ions in the presence of oxygen and one ferrous ion in the absence of oxygen, whereas but one ferrous ion is oxidized per water molecule dissociated in reaction (2) whether oxygen is present or not. Let X equal fraction of total water molecules dissociated in (1) and $1 - X$ the fraction in (2) and we have for R: $R = 3X + 1$.

The fraction of radicals formed in the experiments of former investigators is compared in Table I with those of the present work using Co^{60} γ-rays and tritium β-rays.

TABLE I

EFFECT OF TYPE OF IONIZING RADIATION ON FREE RADICAL FORMATION IN THE OXIDATION OF FERROUS SULFATE IN 0.8 N SULFURIC ACID

	Radiation	(R)	Fraction of Radicals Formed in Reaction (1)	Reaction: (2)
Fricke, *et al.*[3]	X-Rays	2.55	0.52	0.48
Shishacow[4]	X-Rays	2.59	0.53	.47
Krenz and Dewhurst[2]	γ-Rays	4.0	1.00	.00
Miller[5]	γ-Rays	2.7	0.57	.43
Present work	γ-Rays	2.86	0.62	.38
Present work	β-Rays	2.59	0.53	.47

It is significant that the fractions of radicals formed in reaction (1) in the Fricke and Shishacow X-ray work and the present tritium β-ray work are similar and less than the fraction of radicals obtained for γ-rays. This is the expected trend, since the 5690 ev. electron from tritium disintegration has but one per cent. the energy of the recoil electron from the Co^{60} γ-ray interaction with water. Special mention must be made of the ratio 4.0 reported by Krenz and Dewhurst, who attributed lower values to traces of oxygen in evacuated samples. Here exhaustive means were taken to insure the removal of oxygen but it is possible, as was indicated by our work and as suggested by Miller,[5] that impurities suppressing the air-free reaction were introduced by their high vacuum method.

The present work was carried out on 0.5 mN ferrous sulfate in 0.8 N sulfuric acid using an evacuation technique[6] capable of reducing the oxygen content of dilute aqueous formic acid solutions to less than 10^{-6} M. The γ-ray dose-rate was 18000 r per hour and the tritium water activity was 0.157 curies per ml. Since R is very sensitive to methods of preparation and treatment of the ferrous sulfate solutions, the γ-ray irradiation was carried out on the tritium solution of ferrous sulfate and a correction for the tritium-induced oxidation made.

With 12.46 years half-life and average β-energy of 5690 ev.[7] for tritium, these experiments show that one radial pair in water requires 17.9 ev. in the absence of oxygen and 17.6 ev. in the presence of oxygen. These values are lower than the 32.5 ev. generally assumed for ion-pair formation in gases.

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(5) N. Miller, private communication, December 2, 1950.

(6) E. J. Hart, THIS JOURNAL, **73**, 68 (1951).

(7) G. H. Jenks, F. H. Sweeton and J. A. Ghormley, ORNL-333 (March 28, 1950).

ON THE STRUCTURE OF ELEMENTARY BORON[1]

Sir:

We have found an approximate structure for one modification of elementary boron from a study of the needle-like single crystals prepared earlier in this Laboratory.[2] Complete (CuKα) Weissenberg photographic X-ray data together with the density,[2] 2.31 g./cc., establish a tetragonal unit with $a = 8.73 \pm 0.02$, $c = 5.03 \pm 0.02$ Å., containing fifty atoms. The observed symmetry and glide plane vanishings are characteristic of D_{4h}^{14}–$P4/mnm$, C_{4v}^{4}–$P4nm$, and D_{2d}^{8}–$P\bar{4}n2$, but the absence of peaks in the Patterson section P(00Z) virtually eliminates D_{4h}^{14}. In terms of D_{2d}^{8} the "ideal" structure uses the positions 2(b): 00 $^1/_2$; $^1/_2$ $^1/_2$ 0 and 8(i) with the parameters:

	x	y	z		x	y	z
I	0.328	0.095	0.395	IV	0.078	0.223	0.105
II	.095	.328	.395	V	.127	.127	.395
III	.223	.078	.105	VI	.250	.250	−.078

The same arrangement with a different grouping of equivalent atoms is obtainable from C_{4v}^{4} (but not from D_{4h}^{14}). The forty-eight atoms in general positions are arranged at the vertices of four nearly regular icosahedra centered at $^1/_4$ $^1/_4$ $^1/_4$; $^3/_4$ $^3/_4$ $^1/_4$; $^1/_4$ $^3/_4$ $^3/_4$; $^3/_4$ $^1/_4$ $^3/_4$. These icosahedra are linked together so that every boron atom of a group forms six bonds directed toward the corners of a pentagonal pyramid. The two atoms in 2(b) form only four tetrahedrally directed bonds, but are needed to complete in detail the three-dimensional network.

This structure accounts remarkably well for numerous Patterson sections. A Fourier synthesis of ($hk0$) amplitudes, $h + k$ even, nearly reproduces the ideal structure in projection on (001). The phases of the few weakly observable ($hk0$) reflections with $h + k$ odd differ for C_{4v}^{4} and D_{2d}^{8}, but no basis for a choice is as yet apparent. A second Fourier projection along $[1\bar{1}0]$, assumed centrosymmetric on the basis of D_{2d}^{8}, also shows the structure to be approximately correct. This projection, however, could be interpreted as an approximation to the real part of a complex synthesis based on C_{4v}^{4}, the imaginary contribution being small. To resolve the space-group ambiguity and to improve the quality and range of the data we plan to measure intensities on our spectrometer with MoKα radiation. We have begun also a study of the more complex plate-like crystals obtained in the earlier study.[2] It seems probable that this modification, with a unit volume about four times that of the tetragonal form, is present in the usual microcrystalline preparations.

The average bond distance in tetragonal boron appears to lie in the range 1.75–1.80 Å., somewhat smaller than Godfrey and Warren's 1.89 Å. (obtained from a Fourier integral analysis of powder data[3]), but agreeing with the data for boron car-

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(1) Supported in part by a grant from the Research Corporation, in part by the Atomic Energy Commission under contract with Cornell University.

(2) A. W. Laubengayer, D. T. Hurd, A. E. Newkirk and J. L. Hoard, THIS JOURNAL, **65**, 1924 (1943).

(3) T. N. Godfrey and B. E. Warren, *J. Chem. Phys.*, **18**, 1121 (1950)