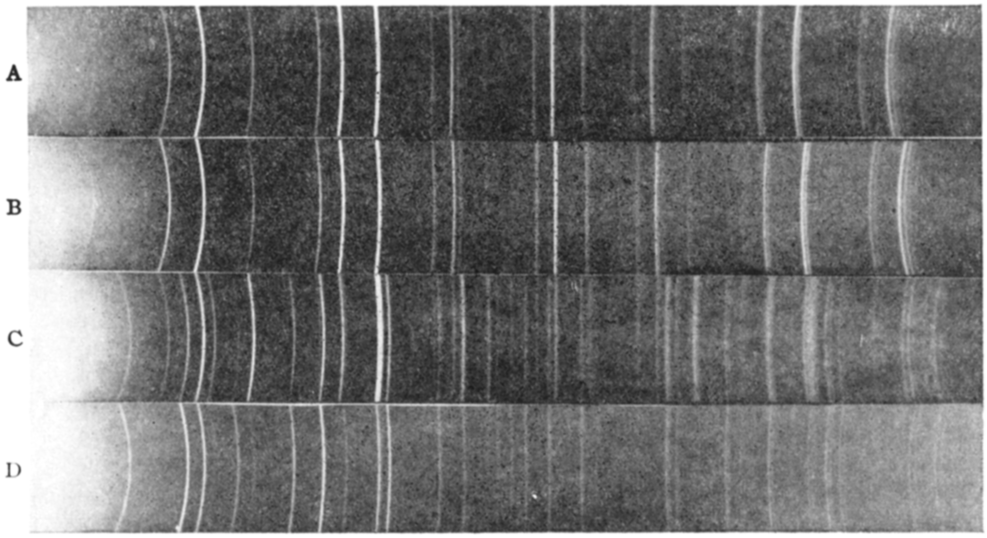

Fig. 1.—X-Ray diffraction patterns of (A) Zn_2TiO_4, (B) $ZnO:NiO:TiO_2 = 1.1:0.9:1$, (C) $ZnO:NiO:TiO_2 = 0.3:1.7:1$, (D) $NiTiO_3$. A pronounced change in the unit cell size is evident from (A) to (B) as solid solution occurs. The lack of such change from (D) to (C) is indicative of the inability of zinc to enter the $NiTiO_3$ lattice. The additional lines present in pattern C are those of nickel oxide.

and nickel form only one titanate by direct heating at temperatures up to 1200°, was substantiated by our own work. Furthermore, from our own X-ray data we concluded: (1) Zn_2TiO_4 forms more readily than $NiTiO_3$ under comparative conditions. (2) NiO readily substitutes for ZnO in Zn_2TiO_4 to the extent of approximately 45 mole per cent. as calculated by Vegard's law.[3] (3) ZnO will not enter the $NiTiO_3$ unit cell to any measurable extent. Attempts to obtain substitution of this type results in the formation of pure $NiTiO_3$ and the limit of substitution of NiO in Zn_2TiO_4. The fact that the "d" values of pattern C are slightly smaller than the corresponding "d" values of pattern B indicates that the actual limit of solid solution is slightly greater than the 45 mole per cent. NiO calculated on the basis of the contraction of the Zn_2TiO_4 unit cell. (4) $NiTiO_3$ is a yellow pigment of poor brilliance, and any green tinge in the absence of ZnO is due to unreacted NiO. (5) Zn_2TiO_4 is white. Substitution of zinc by nickel in the crystal lattice results in pure green pigments. The depth of shade depends solely on the extent of the substitution of NiO for ZnO. Nickel oxide present in excess of the limit of solid solution results in a gradual change of color to an olive green, due to the presence of $NiTiO_3$ and NiO.

Experimental

Since metal oxides do not react too rapidly in the dry state, it was considered advantageous to use the sulfates of the divalent metals. The reagents therefore used were: $ZnSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 6H_2O$, TiO_2.

From these compounds compositions were prepared having the mole ratios: $ZnO:NiO:TiO_2$, 2.0:0.0:1 (zinc orthotitanate), Pattern A; 1.1:0.9:1 (substitutional solid solution), Pattern B; 0.3:1.7:1 (mixed titanates), Pattern C; 0.0:1.0:1 (nickel metatitanate), Pattern D; Those mixtures of the sulfates and TiO_2 were ground to a fine powder, digested twice with concentrated sulfuric acid, evaporated to dryness each time and heated to 1050° for extended periods. From time to time the reaction products were removed from the furnace for visual inspection and preparation of X-ray diffraction patterns. The heating was continued until the reaction was complete. However, in the case of mixtures where $NiTiO_3$ was one of the end products, the reaction temperature of 1200° was maintained until the uncombined NiO was reduced to an estimated 1%. Diffraction patterns were made by the Debye–Scherrer method, using a powder wedge in a cylindrical camera of 14.32 cm. diameter. A copper target tube was used with heavy filtration Kβ radiation.

Acknowledgment.—The authors wish to thank Dr. S. S. Sidhu of the University of Pittsburgh for his interest in their study.

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Received October 20, 1949

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[3] Vegard, *Z. Physik*, **5**, 16 (1921).

Structure Proof of 2,2-Bis-(4-fluorophenyl)-1,1-dichloroethane[1]

By R. C. Blinn and F. A. Gunther

Müller[2] reported the preparation of 2,2-bis-(4-fluorophenyl)-1,1-dichloroethane (I) by treating dichloroacetal with fluorobenzene in concentrated sulfuric acid. Bradlow and VanderWerf[3] subsequently reported that they had also prepared this compound by the catalytic hydrogenation of 2,2-bis-(4-fluorophenyl)-1,1-dichloroethylene (II). The compound prepared by

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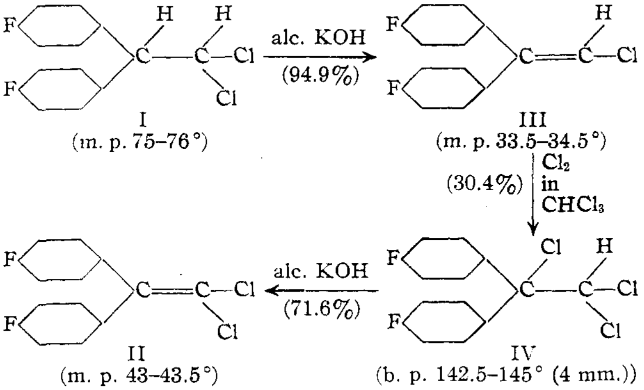
[1] Paper number 618 from University of California Citrus Experiment Station.

[2] Müller, *Helv. Chim. Acta*, **29**, 1560 (1946).

[3] Bradlow and VanderWerf, This Journal, **69**, 662 (1947).

Müller melted at 77°, whereas that prepared by Bradlow and VanderWerf melted at 45°. A sample of Müller's compound,[4] when mixed in this Laboratory with an equal weight of that prepared by Bradlow and VanderWerf,[5] melted at 64–68°.

Verification of the structure of the compound reported by Müller as that of I has been obtained in this Laboratory by the series of reactions



A mixed melting point of II with an authentic sample prepared by dehydrochlorination of 2,2-bis-(4-fluorophenyl)-1,1,1-trichloroethane was undepressed. The compound reported as I by Bradlow and VanderWerf proved to be unconverted II, as shown by mixed melting-point determinations and by ultraviolet absorption characteristics. Bradlow and VanderWerf's compound, m. p. 42–43.5°, mixed with authentic II, m. p. 43–43.5°, obtained as above, melted at 42.5–43°. These compounds in cyclohexane gave the ultraviolet spectra shown in Fig. 1. Maximum extinction coefficients at 258 mμ were 12,110 for II and 11,242 for Bradlow and VanderWerf's compound. This discrepancy undoubtedly is occasioned by the higher purity of II. The hydrogenation procedure reported by Bradlow and VanderWerf was repeated in this Laboratory, to afford 71.6% unconverted II, melting at 42–43.5°, plus 16.1% of a non-crystallizing oil, b. p. 99–106° (3 mm.), $n^{16}\text{D}$ 1.5249.

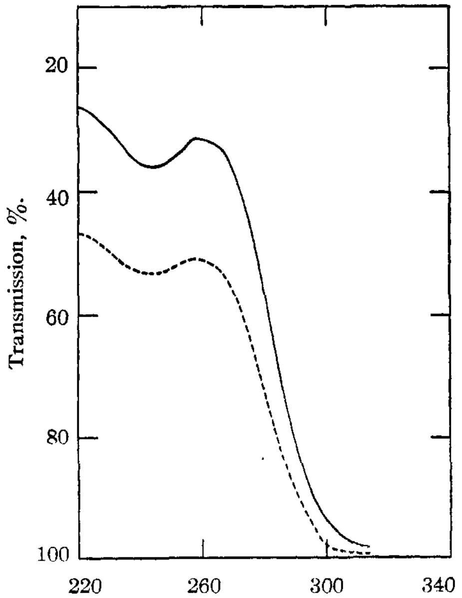


Fig. 1.—Absorption spectra of 2,2-bis-(4-fluorophenyl)-1,1-dichloroethylene, 4.10 × 10^{-5} molar, ———; compound reported by Bradlow and VanderWerf, 2.60 × 10^{-5} molar, - - - - -; (in cyclohexane).

Experimental

2,2-Bis-(4-fluorophenyl)-1,1-dichloroethane (I).—A mixture of 8 ml. of concentrated sulfuric acid (d. 1.84) and 4.5 ml. of 30% fuming sulfuric acid was added with efficient stirring to a cold mixture of 5 g. of fluorobenzene and 5 g. of dichlorodiethylacetal at such a rate as to keep the reaction temperature below 10°. The reaction mixture was stirred at room temperature for twelve hours, then poured into ice-water mixture. After removal of steam-volatile material, the residual white solid was filtered, dried, and recrystallized from petroleum ether (b. p. 60–80°); yield, 4.84 g. (64.5% of the theoretical), m. p. 75–76° (Müller[2] reported 77°).

2,2-Bis-(4-fluorophenyl)-1-chloroethylene (III).—A solution of 2.0 g. of I in 20 ml. of hot 95% ethanol was mixed with 2.0 g. of potassium hydroxide in 50 ml. of 95% ethanol. This mixture was refluxed for 15 minutes, then poured into 500 ml. of ice–water mixture and acidified with dilute nitric acid. The crystalline solid so obtained was filtered, dried, and recrystallized from petroleum ether (b. p. 30–60°); yield, 1.69 g. (94.9% of the theoretical), m. p. 33.5–34.5°.

Anal. Calcd. for $C_{14}H_9ClF_2$: C, 67.08; H, 3.62. Found: C, 67.36; H, 3.96.

2,2-Bis-(4-fluorophenyl)-1,1,2-trichloroethane (IV).—A solution of 5.0 g. of III in 150 ml. of chloroform was chlorinated in the dark for 10 hours at room temperature. This chlorinated solution was then washed successively with 5% sodium bisulfite solution, water, concentrated sulfuric acid (d. 1.84) till colorless, then again with water. The solution was then dried and solvent removed, affording a colorless oil, b. p. 142.5–145° (4 mm.), $n^{26}\text{D}$ 1.5775; yield, 1.95 g. (30.4% of the theoretical).

Anal. Calcd. for $C_{14}H_9Cl_3F_2$: C, 52.28; H, 2.82; mol. wt., 321.6. Found: C, 52.47; H, 2.89; mol. wt., 324.2 (Rast).

2,2-Bis-(4-fluorophenyl)-1,1-dichloroethylene (II).—When 1.44 g. of IV was dehydrochlorinated, as above, there was obtained 0.92 g. (71.6% of the theoretical) of II, m. p. 43–43.5°. A mixed melting point with an authentic specimen was undepressed.

Hydrogenation of II.—A solution of 9.0 g. of II in 50 ml. of carefully purified methanol and 0.1 g. of Adams catalyst was hydrogenated at 30 pounds initial pressure, as described by Bradlow and VanderWerf,[3] to afford 8.1 g. of an oily solid. Recrystallization from ethanol yielded 4.7 g. of white crystals, m. p. 42.5–43.5°; mixed m. p. with II, 42–42.5°. The residual oil was fractionated to yield 1.65 g. of II, b. p. 130–132° (3 mm.), m. p. 39–40°, recrystallized from ethanol, m. p. 41.5–42.5°; mixed m. p. with authentic specimen 42–42.5°. The total recovery of II was 71.6%. This fractionation also yielded a colorless oil, b. p. 99–106° (3 mm.), $n^{16}\text{D}$ 1.5249; yield, 1.45 g. (16.1% by weight).

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[4] Generously supplied by Dr. Paul Müller.

[5] Generously supplied by Dr. H. L. Bradlow.

Acknowledgment.—The authors thank Dr. R. L. Metcalf for bringing to their attention the apparent discrepancy in the two reports on 2,2-bis-(4-fluorophenyl)-1,1-dichloroethane.

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RECEIVED JUNE 4, 1949

Ferric Catalyzed Hydrogen Peroxide Decomposition Inhibition by Acetanilide

BY WILLIAM C. BRAY[1] AND SIGFRED PETERSON[2]

The several reported studies of the ferric catalyzed hydrogen peroxide decomposition have been reviewed recently by Abel.[3] A variety of conflicting mechanisms have been proposed, in most of which, in analogy to the bromine–bromide catalysis,[4] two oxidations states of iron, either ferrous and ferric or one of these with an unstable higher state,[5] reduce and oxidize the peroxide. This work is being published after some delay because it shows confirmation of a chain mechanism as proposed by Haber and Weiss[6] and amplified by Baxendale and coworkers[7] but discounted in recent reports.[3,8]

Certain student experiments had demonstrated that sometimes hydrogen peroxide decomposition in ferric solutions is delayed during an induction period. This investigation sought to determine the cause of this induction period and use it to further elucidate the mechanism of the reaction. It was found that the induction period was due to the inhibition of the reaction by acetanilide present as a preservative in commercial hydrogen peroxide and could be duplicated by adding acetanilide to the solutions of pure hydrogen peroxide. The rate of peroxide disappearance during this period is only a few per cent. of the maximum rate attained after the induction period ends.

The experimental techniques used in this work were essentially similar to those used by Andersen,[8] except, of course, that acetanilide when used was dissolved in the hydrogen peroxide stock solution. Chemicals used were of the highest quality available. Iron perchlorate solutions were obtained from reprecipitated ferric hydroxide and reagent grade perchloric acid or ferrous sulfate and barium perchlorate solutions.

Since the nature of the anions present influences the reaction rate,[9] only nitrate and perchlorate, those anions which form fewest metal complexes, were present. Experiments with nitrate present showed deviations from first order decomposition qualitatively like those found by Andersen[8] although the ferric and hydrogen ion concentrations were in a different range of magnitudes. In perchlorate solutions (nitrate absent) the decomposition was first order in agreement with the rate equation first proposed by Bertalan.[10] This nitrate effect is probably related to the inhibition by nitrate found by Taube and Bray[11] for the reaction between ozone and hydrogen peroxide, since the same free radical intermediates, OH and HO_2 are involved.

TABLE I

EFFECT OF CONDITIONS ON INDUCTION PERIOD

Expt.	t, °C.	$10^4 \times$ (acnd)[a]	(H^+)[a]	Induction, min.
1	20	2.0	0.18	14
2	23.5	2.0	.18	9
3	25	2.0	.18	6
4	20	3.5	.20	25
5	20	5.2	.18	55
6	25	5.2	.18	21
7	20	5.3	.32	145
8	25	5.3	.32	55
9	25	26.7[b]	.32	55

[a] Concentrations in moles/l. also $(Fe^{+++}) = 0.11$ and initial $(H_2O_2) = 0.060$. [b] Initial $(H_2O_2) = 0.30$.

Table I shows how the length of the induction period depends on certain conditions of the reaction. Comparing the expts. 1, 4 and 5 or 3 and 6 shows that the induction period is increased by increasing the acetanilide concentration at constant peroxide concentration in agreement with the hypothesis that acetanilide is being used up by reaction with chain carrying intermediates. But because the number of chain starting reactions is proportional to the initial peroxide concentration, the five-fold increase in acetanilide concentration in expt. 9 over expt. 8 is compensated for by the similar increase in peroxide concentration.

A comparison of expts. 1, 2 and 3, 5 and 6 or 7 and 8, shows that the inhibition of the reaction has an unusually high temperature coefficient, the rate of disappearance of acetanilide being increased by a factor of 2.5 for a 5° temperature rise. A comparison of expts. 5 and 7 or 6 and 8, shows that hydrogen ion slows down the disappearance of acetanilide by about the same factor as its slows down the hydrogen peroxide decomposition. This is consistent with the suggestion of Haber and Weiss[6] that the chain is started by a reaction of HO_2^- with ferric ion.

The magnitude of the temperature coefficient of the induction period suggests that the destruction of the inhibitor involves two steps with normal temperature coefficients. Since it is unbelievable that the reaction between an inhibitor and a chain-carrying radical have an

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(1) Based on work done under the direction of the late W. C. Bray.

(2) Present address: University of Louisville, Louisville 8, Kentucky.

(3) Abel, *Monatsh.*, **79**, 457 (1948).

(4) Bray and Livingston, THIS JOURNAL, **45**, 1251 (1923).

(5) Bohnson and Robertson, *ibid.*, **45**, 2493 (1923); Bray and Gorin, *ibid.*, **54**, 2124 (1932).

(6) Haber and Weiss, *Proc. Roy. Soc.* (*London*), **A147**, 332 (1934).

(7) Barb, Baxendale, George and Hargrave, *Nature*, **163**, 692 (1949).

(8) Andersen, *Acta Chem. Scand.*, **2**, 1 (1948).

(9) Simon, Haufe, Reetz and Preissler, *Z. anorg. allgem. Chem.*, **230**, 129 (1936).

(10) Bertalan, *Z. physik. Chem.*, **95**, 328 (1920).

(11) Taube and Bray, THIS JOURNAL, **62**, 3357–3373 (1940).