the deuterium concentration of the gas phase. It is clear that the activated hydrogen produced by hydrogenase is not in immediate equilibrium with the water. This is consistent with our view of the hydrogenation process since we postulate that only one out of the two hydrogen atoms of the hydrogen molecule which interacts with the enzyme is immediately exchangeable with water. The amount of deuterium which will appear in the reduced compound will depend on the relative rates of reactions 3 and 5.

Hoberman and Rittenberg[7] have adduced evidence that hydrogenase is a ferrous protein complex and Waring and Werkman[17] have shown that hydrogenase activity is absent in bacteria grown in an iron-free medium.

There exist certain analogies to this enzyme. For example $Co_2(CO)_8$ undergoes hydrogenolysis to form a hydride. The reaction is reversible. Since

$$Co_2(CO)_8 + H_2 \rightleftarrows 2HCo(CO)_4 \qquad (6)$$

the hydrogen of $HCo(CO)_4$ is acidic and presumably, rapidly exchangeable with the hydrogen of water, the reaction should catalyze the exchange of hydrogen in the gas phase with hydrogen of the water. In addition, the hydride will reduce methylene blue.[18]

Any organism which possesses hydrogenase activity should be capable of carrying out both the conversion of parahydrogen and the exchange reaction. We have found that suspensions of Scenedesmus D-3 and Euglena,[19] which have been kept under hydrogen so as to activate the hydrogenase system,[20] catalyze both these reactions.

NEW YORK, N. Y.

[17] W. S. Waring and C. H. Werkman, *Arch. Biochem.*, **4**, 75 (1944).

[18] H. J. Emeléus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," 2nd edition, D. Van Nostrand Co., New York, N. Y., 1952, p. 426.

[19] Kindly supplied by Dr. Seymour Hutner of the Haskins Laboratories, N. Y. C.

[20] H. Gaffron, *J. Gen. Physiol.*, **26**, 195 (1942).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BOSTON UNIVERSITY]

The Oxygenation Reaction of Hexaarylethanes.[1] I. The Stoichiometry of the Reaction of Hexaphenylethane

BY NORMAN N. LICHTIN AND GEORGE R. THOMAS

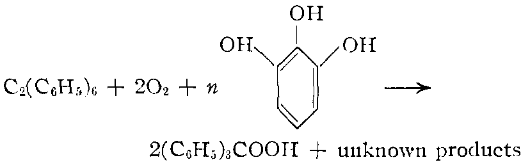
RECEIVED SEPTEMBER 16, 1953

The stoichiometry of the reaction of hexaphenylethane (I) with oxygen has been investigated in the presence and absence of pyrogallol by using numerous solid samples of identical history. In bromobenzene solution, in the absence of pyrogallol, with simultaneous dissolution of sample and reaction, consumption of oxygen decreases with increasing temperature and decreasing pressure of oxygen and, with air as reagent, appears to reach a limiting value in the vicinity of 25–30°. With samples of different history this limiting value was found to approach but never to exceed that expected on the basis of equation 1. Even under these conditions, however, bis-trityl peroxide (II) is not the sole product. The consumption of oxygen in the presence of pyrogallol was found to fall short of that expected on the basis of equation 2 in all experiments where dissolution of I and exposure to oxygen were simultaneous, regardless of variation in temperature, oxygen pressure, solvent and auxiliary reagents. The results of one set of experiments suggest that agreement is obtained if dissolution precedes reaction.

Introduction

That the reaction of hexaphenylethane (I) and related substances with oxygen is not a simple one has been recognized for some time. Thus, quantitative yields of bis-trityl peroxide[2] (II) and its congeners[3] have not been obtained. Furthermore, although Gomberg and his co-workers[4] as well as numerous other workers[5] employed oxygen absorption as a means of analyzing I and its congeners, several workers have reported that adherence to the stoichiometry exemplified by equation 1 is not exact and depends on such variables as nature of the solvent,[2b] structure of the ethane,[3] pressure of oxygen,[6,7] temperature[6] and ethane concentration.[6] Pyrogallol is particularly effective[7,8] in altering the stoichiometry and Ziegler and his associates have collected considerable evidence[9] in support of equation 2. Oxygen consumption falling short of that expected from 2 has been observed, however,[10] and the suggestion made that this might be due to dissolution of I and oxygenation being simultaneous. In addition, it has been established[11] that triphenylmethyl can initiate the autoxidation of readily oxidized aldehydes and olefins.

$$C_2(C_6H_5)_6 + O_2 \dashrightarrow C_2(C_6H_5)_6{\cdot}O_2 \qquad (1)$$



$$C_2(C_6H_5)_6 + 2O_2 + n\,C_6H_3(OH)_3 \longrightarrow 2(C_6H_5)_3COOH + \text{unknown products} \qquad (2)$$

Ziegler and his associates have deduced from the kinetics[12] of the oxygenation of I that the reaction

---

[1] Presented in preliminary form before the Division of Organic Chemistry at the 123rd Meeting of the American Chemical Society, Los Angeles, March, 1953. *Cf.* p. 54 M of the Abstracts of Papers.

[2] (a) M. Gomberg, *Ber.*, **34**, 2726 (1901); (b) M. Gomberg and L. H. Cone, *ibid.*, **37**, 3538 (1904).

[3] J. B. Conant and M. W. Evans, THIS JOURNAL, **51**, 1925 (1929).

[4] M. Gomberg and C. S. Schoepfle, *ibid.*, **39**, 1652 (1917).

[5] (a) P. Walden, "Chemie der Freien Radikale," S. Hirzel, Leipzig, 1924, p. 87; (b) H. E. Bent, G. R. Cuthbertson, M. Dorfman and R. E. Leary, THIS JOURNAL, **58**, 165 (1936).

[6] K. Ziegler, L. Ewald and Ph. Orth, *Ann.*, **479**, 277 (1930).

[7] W. E. Bachmann and F. V. Wiselogle, *J. Org. Chem.*, **1**, 364 (1937).

[8] (a) H. W. Scherp, THIS JOURNAL, **58**, 576 (1936); (b) K. Ziegler and G. Ganicke, *Ann.*, **551**, 220 (1942).

[9] K. Ziegler, *Ann.*, **551**, 135 (1942).

[10] H. E. Bent and J. E. Cline, THIS JOURNAL, **58**, 1626 (1936).

[11] K. Ziegler and L. Ewald, *Ann.*, **504**, 162 (1933).

[12] *Cf.* W. A. Waters, "Chemistry of Free Radicals," Oxford University Press, London, 1948, pp. 45–49.

proceeds *via* a chain mechanism involving the attack of tritylperoxy radical on I. Complete elucidation of the reaction course has, nonetheless, not yet been accomplished since neither are the products fully established nor has the dependence of stoichiometry on conditions been examined sufficiently to provide a basis for chemical interpretation.

The present work constitutes a systematic investigation of the dependence on a limited number of variables of the stoichiometry of the oxygenation of I. In the absence of pyrogallol exploration has been largely, but not exclusively devoted to temperature dependence, a factor which has been considered only scantily by others.[6] In the presence of pyrogallol several variables have been scrutinized; of these, the state of solution of I has proved to be of dominant importance.

This work has been complicated by the lack of an unequivocal analysis for I. The uncertainties inherent in quantitative oxygenation[4,10] have already been noted. Other methods have been recommended on the basis of agreement with oxygenation[13] or have been subjected to only meagre tests of validity.[14] Because no method of analysis of I could be accepted without reservation, series of experiments have been carried out employing samples of identical history and, in view of the known occurrence of reactions between I and toluene[15] and nitrobenzene,[16] have been limited to those in which samples of I were dissolved either shortly before or simultaneous with oxygenation.

Experimental

Hexaphenylethane.—This was prepared by shaking a solution of one-tenth of a mole of triphenylchloromethane in 150 ml. of toluene with a tenfold excess of mercury for two hours. The reaction was carried out in a 250-cc. sealed flask shielded from light by wrapping with aluminum foil. Prior to sealing, the flask and contents were cooled to 0 or −80° and evacuated to the autogenous pressure of the reaction mixture. Shaking was carried out at room temperature by means of a "Burrell" model CC shaker set at speed 10. The sealed flask was next transferred to a vacuum dry-box equipped to carry out numerous chemical operations. Construction and operation of this apparatus are described elsewhere.[17] The dry-box was next evacuated to a pressure of 0.03 mm. and filled with "Seaford"[18] nitrogen which had been passed over copper turnings heated to 800°, cooled, and then passed over $CaCl_2$. During the ensuing manipulations light entering the dry-box was kept to a minimum with the aid of an orange-brown photographic safelight filter. After the flask was opened, the contents were filtered on a sintered glass disk with suction. The filtrate was evaporated under vacuum to dryness and the crystals of hexaphenylethane–toluene complex subjected to crystallization from acetone to yield the free ethane.[2a] In some cases, the product was recrystallized from acetone. The product obtained by so recrystallizing always assayed at least 95% pure by oxygen absorption in the absence of pyrogallol under "limiting conditions" (see below).

Reagents and Solvents.—Triphenylchloromethane was either Eastman "White Label" material recrystallized once,[19] or was prepared from Eastman "White Label" triphenylcarbinol.[20] The melting point was 111–112°. Mercury was usually triple-distilled C.P. grade although the degree of purity of this material had little influence on the results. The following solvents were of C.P. grade: toluene and benzene were dried over calcium hydride and filtered before use; bromobenzene and ethyl benzoate were distilled and a small forerun discarded; acetone was stored over "Drierite" for two weeks and distilled before use. Pyrogallol was Mallinckrodt Reagent Grade. Benzoic acid was C.P.

Preparation of Sample Bulbs.—After the product had been pumped overnight at 0.01 mm. to remove the last traces of acetone, it was divided into portions which were dropped with the aid of a funnel and glass sleeve through holes in the base plate of the dry-box into relatively thin walled glass bulbs of known weight. The mode of attachment of the bulbs to the dry-box is described[17] elsewhere. The bulb stems were wiped free of adhering ethane particles and sealed with the bulbs at a known temperature. The bulbs were then stored in a light-tight container in the refrigerator until needed. Sample weights were determined by weighing the grease-free, filled, sealed bulbs plus sealed off joints. Sample weights were of the order of $^1/_2$ gram. Numerous solid samples of identical history could be obtained in this way since twenty sample bulbs could be attached to the dry-box at one time. In the one case where a standard solution of ethane was employed, about 40 g. of toluene was transferred to a large weighed bulb, cooled to 0°, evacuated to 1 mm. pressure and sealed. The bulb containing a known weight of ethane and the toluene bulb were then transferred to the dry-box which was next filled with nitrogen as usual. The toluene bulb was broken and its contents poured into a beaker. The ethane bulb was broken while immersed in the toluene and the mixture stirred until dissolution was complete. Portions were pipetted into the usual sample bulbs, sealed off at 0° and weighed as usual. Insufficient care was, however, exercised in the attempted preliminary saturation of the 6 cu. ft. volume of the dry-box with toluene vapor. Toluene was boiled in a beaker in the dry-box for a few minutes prior to breaking the weighed bulb. It was later recognized that only a fraction of the required amount (about 18 g.) had been transferred to the gas phase. Thus a source of indeterminate error due to volatilization of the solvent toluene was introduced, and only a minimum limit to the concentration of the ethane solution was known (*cf.* Table III).

Preparation of Glassware.—The sample bulbs as well as all glassware employed in the preparation and handling of the ethane were subjected to the following treatment: (1) soaking in a hot sulfuric acid–nitric acid bath; (2) rinsing with tap water; (3) washing with "Alkanox"; (4) rinsing with dilute aqueous ammonia, tap water and finally three times with distilled water; (5) drying in an oven at 110° The sample bulbs were wiped with a slightly damp cloth and sparked before being weighed.

Oxygen Absorption Measurements.—The reaction vessel was a bomb of about 350-cc. capacity made of drawn aluminum equipped with a built in bulb holder and a bulb breaker, both of aluminum. The bulb breaker was a pointed rod fastened to a copper bellows which could be extended or contracted by means of a screw.[21] This breaking device was attached to the cap of the bomb. The cap was essentially an aluminum pressure plate which, in use, was held tightly to the bomb by means of set screws and a bomb-head which screwed onto the bomb. A neoprene O-ring served as gasket between the cap and bomb. The cap was also equipped with a brass nipple which was attached to a long helix of $^1/_{16}''$ i.d. aluminum tubing by means of a flare joint. This tubing connected with the upper end of a 50-ml.

---

[13] (a) J. B. Conant and B. F. Chow, THIS JOURNAL, **55**, 3758 (1933); (b) G. S. Hammond, A. Ravve and F. J. Modic, *Anal. Chem.*, **24**, 1373 (1952).

[14] (a) K. Ziegler, Ph. Orth and K. Weber, *Ann.*, **504**, 149 (1933); (b) R. Preckel and P. W. Selwood, THIS JOURNAL, **63**, 3399 (1941).

[15] R. M. Dobres and P. W. Selwood, THIS JOURNAL, **72**, 5731 (1950).

[16] G. S. Hammond and A. Ravve, *ibid.*, **73**, 1891 (1951).

[17] G. R. Thomas and N. N. Lichtin, *Rev. Sci. Inst.*, **23**, 738 (1952).

[18] Containing 1% hydrogen, supplied by Air Reduction Company.

[19] A. H. Blatt, Ed., "Organic Syntheses," Coll. Vol. 2, John Wiley and Sons, Inc. New York, N. Y., 1943, p. 609.

[20] *Org. Syntheses*, **23**, 100 (1943).

[21] Ziegler and his co-workers (ref. 14a, p. 153) determined that bombs constructed of aluminum were not attacked under the conditions prevailing during their work on the reaction of hexaphenylethane with *nitric oxide*. Copper was attacked under these conditions. No evidence of attack by components of the oxygenation mixtures on the bomb materials was observed in the present work, and results were obtained which are consistent with measurements obtained by other workers using glass equipment. Furthermore, experiments carried out in these laboratories by Mr. Peter Pappas have shown that with bromobenzene as the solvent, reaction at 35° in the absence of pyrogallol and air as the reagent, results obtained in glass apparatus are identical with those obtained in the metal bomb.

jacketed gas buret which was adapted from the apparatus of Gomberg and Schoepfle.[4] The lower end of the buret connected to a leveling bulb. Butyl phthalate, dyed with malachite green, was usually used as leveling and buret liquid. The jacket liquid was circulated from a thermostated bath by means of a pump.

While achieving thermal and oxygen solution equilibrium prior to a run, and during the course of the absorption measurements, the reaction vessel was immersed in a thermostat filled with kerosine and controlled to ±0.01°. After the bulb had been broken, the bomb was agitated with the aid of a "Burrell" model CC shaker at speed 10.

In addition to the sample, the reaction vessel was charged with 100 ml. of solvent, oxygen reagent and additional materials as indicated in the data summary. Shaking was begun immediately after breaking the bulb and continued for lengths of time that varied from five minutes to three hours depending on the reaction temperature. In all cases, oxygen absorption had ceased completely before shaking was stopped. In many cases the reaction temperature and buret temperature differed widely (since the buret was operated at about 25°). It can be easily demonstrated that the proper temperature to employ in reducing the volume of gas consumed to S.T.P. is the buret temperature. A further correction was necessary to compensate for change in the volume of the nitrogen in the bulbs in those cases where the reaction temperature differed widely from the temperature of the bulb when it was sealed. The bulb volumes were measured by water displacement. Since a change of atmospheric pressure amounting to 1 cm. during the course of a run would produce a change in gas volume of about 0.3 cc. it was occasionally necessary to make relevant corrections. This was particularly true in the few cases where less than 10 cc. of oxygen was consumed.

When measurements were carried out on samples initially in solution in the absence of pyrogallol (*cf.* Table III), the reaction bomb was immersed in a beaker of warm water and stirred by means of a glass sheathed iron rod which was activated from outside the bomb by a conventional magnetic stirring device. A 10-cc. buret was employed in all the measurements summarized in Table III.

Accuracy of Absorption Measurements.—In view of the sample sizes employed, the precision with which the burets could be read and the corrections which had to be made for change in volume of the nitrogen contained in the bulbs, the accuracy of the oxygen absorption measurements was about ±1%. Occasional better reproducibility was probably fortuitous.

Melting Point of Hexaphenylethane.—A small portion of batch E was dropped directly into a melting point tube which was attached to the dry-box in the same way as the bulbs. The tube was then sealed off. The melting point of 150–152° (cor.) with preliminary darkening at 144° may be compared with the value, 145–147°, reported by Gomberg.[1] Batch E (*cf.* Table I) was 83% pure according to the limiting procedure in the absence of pyrogallol (*cf.* below).

Isolation of Products.—Bulbs containing ethane were broken in beakers containing enough benzene at the desired temperature to render the solutions approximately 0.005 *M*. This operation was carried out either in the open laboratory or in the nitrogen-filled dry-box. In the latter cases bulbs containing sufficient oxygen to give the desired final partial pressure were subsequently broken in the dry-box.

Data

The results of this research are summarized in Tables I–IV. From Table I, it is apparent that in bromobenzene solution, in the absence of pyrogallol, the amount of oxygen consumed per mole of I decreases with increasing temperature, and with air as the reagent appears to reach a limit in the vicinity of 25° or 30°. Under these conditions, oxygen in excess of the amount corresponding to equation 1 is absorbed at 0°. This equation is clearly incorrect under such conditions. With pure oxygen as the reagent, the excess absorption at 0° is considerably greater, and even at 36° the amount consumed is in excess of the limiting value obtained with air. It is significant that the limiting value with air reaches, but in no case exceeds, that expected according to equation 1.

TABLE I

EFFECT OF TEMPERATURE AND O_2 PRESSURE IN THE ABSENCE OF PYROGALLOL[a]

Preparative batch of $C_2(C_6H_5)_6$	No. of samples measured under indicated conditions	Temp., °C.	Theor. O_2 absorbed,[b] %
B	1	0.6	113
B	2	23.0	100 ± 1
E	2	0.5	92 ± 1.5
E	4	22.7	83.5 ± 1
E	2	34.5	83 ± 1
F	2	0.8	102.5 ± 1.5
F	2	14.5	95 ± 1
F	2	25.8	92.5 ± 1
F	2	36.3	91 ± 0.2
F	1[d]	0.8	123
F	1[d]	36.3	99
G	2	36.3	98 ± 0.5
H	3	36.1	95 ± 0.5
H[c]	1	0.3	129

[a] Solid samples weighing from 0.2 to 0.7 g. were employed. The solvent was bromobenzene and the reagent laboratory air, unless otherwise indicated. [b] On the basis of equation 1. [c] The solvent was ethyl benzoate. [d] The reagent was tank oxygen.

A further qualitative correlation with the dependence of the oxygen uptake on the reaction temperature was observed in the experiments with samples from batch F. It was found that the colors of solutions of the products varied regularly from a dark yellow in the one obtained at 0° to a pale lemon in that obtained at 36°.

The data obtained with batch H suggest that the amount of oxygen consumed using ethyl benzoate as the solvent is larger than the amount which would be taken up in bromobenzene solution under identical conditions. This can be demonstrated in spite of the absence of directly comparable data. Measurements in the latter solvent on batches B, E and F are in good agreement that the value at 0° is 112 ± 1% of the limiting value obtained at higher temperature. On this basis, an uptake of about 106.5% of the theoretical can be calculated for batch H in bromobenzene at 0°.

The data of Table II suggest that, in the presence of pyrogallol, oxygen consumption does not correspond to equation 2 when dissolution of the sample and absorption of oxygen are occurring simultaneously. Batches which, in the absence of pyrogallol, under limiting conditions, absorbed 95 to 100% of the amounts of oxygen expected on the basis of equation 1, in the presence of this reagent consumed only 70 to 80% of the amounts of oxygen expected on the basis of equation 2. No substantial change in this result could be obtained whether the solvent was ethyl benzoate, a mixture of the latter with toluene, or bromobenzene, the temperature 0 or 25°, the oxygen pressure one atmosphere or 0.2 atmosphere. Wide variations in the pyrogallol concentration (this substance is only slightly soluble in bromobenzene) had no significant effect nor did the use of benzoic acid as an auxiliary reagent or the use of the filtrate (bromobenzene) from one run as the solvent for another. The latter two expedients were employed by Ziegler, *et al.*,[22] in some of their kinetics studies.

TABLE II

RESULTS IN THE PRESENCE OF PYROGALLOL UNDER A VARIETY OF CONDITIONS[a]

Preparative batch of $C_2(C_6H_5)_6$	Samples meas. under indicated cond.	Temp., °C.	Solvent[e]	Wt. of pyrogallol, g.	Wt. of benzoic acid, g.	Theor. O_2 absorbed,[f] %
B[b]	2	24.6	Bromobenzene	2	1	80.5 ± 1.5
B[b]	1	24.0	Ethyl benzoate	2.5	1	73
B[b]	1	0.6	Bromobenzene	1	1	80
B[b]	1	0.6	Filtrate from above run			72
G[c]	1	36.3	Ethyl benzoate	3.5	0.2	70
G[c]	2	0.0	Ethyl benzoate	3.5	1	73.5 ± 0.5
G[c]	1	0.3	Ethyl benzoate	6.3	None	73.5
H[d]	1	0.3	Ethyl benzoate	4	0.2	74
H[d]	1	0.3	23% Toluene 77% Ethyl benzoate	4	0.2	76
H[d]	1	0.3	Ethyl benzoate	4	None	66
H[d,g]	1	3.3	Bromobenzene	4	None	72

[a] Sample weights were 0.3–0.6 g. Dissolution and exposure to oxygen were simultaneous. Laboratory air was employed unless otherwise indicated. [b] This batch may be taken as 100% pure; *cf.* Table I. [c] This batch may be taken as 98% pure; *cf.* Table I. [d] This batch may be taken as 95% pure; *cf.* Table I. [e] Homogeneous solutions of reagents were obtained with ethyl benzoate; 2 g. of pyrogallol was found not to dissolve in 100 cc. of bromobenzene even on boiling. [f] On the basis of equation 2. [g] Tank oxygen was employed.

Table III compares experiments in which aliquots of an approximately 0.02 *M* solution of I in toluene were, on the one hand, simultaneously diluted with about 20 volumes of bromobenzene and exposed to air at 30–50° and, on the other, were simultaneously diluted with about 20 volumes of ethyl benzoate containing pyrogallol and benzoic acid and exposed to oxygen at one atmosphere pressure at 0°. The latter conditions are essentially those employed by Ziegler, *et al.*, in many of their studies of kinetics.[22] The concentration of the standard solution was calculated from the former data with the aid of equation 1 and from the latter on the basis of equation 2. The results are in good agreement with each other. The fact that the concentration was found to be 9% greater than was expected on the basis of the weights of toluene and ethane taken and the purity of the ethane (as indicated in Table I) is consistent with the evaporation error discussed in the Experimental section.

TABLE III

DIRECT COMPARISON OF RESULTS IN THE PRESENCE AND ABSENCE OF PYROGALLOL USING ALIQUOTS OF A STANDARD SOLUTION[a,b]

Samples meas. under indicated cond.[b]	Reagents	Temp., °C.	Solvent	Mmoles ethane g. of standard soln.
2	Laboratory air	30–50[c]	Bromobenzene	0.0205 ± 0.003[d]
2	Tank oxygen Pyrogallol, 2 g. Benzoic acid, 0.2 g.	0.6	Ethyl benzoate	0.0205 ± .005[e]

[a] The solution was prepared by dissolving in toluene a sample of batch H (*cf.* Table I). The quantities of solute and solvent initially taken were such as to yield a solution containing 0.0198 mmole per gram, assuming pure ethane, or 0.0188 mmole per gram on the basis of 95% purity. [b] Aliquot weights were 4 to 7 g., corresponding to 0.04 to 0.07 g. of ethane. The pyrogallol was in approximately one hundred fifty-fold molar excess. [c] For an explanation of this temperature range see the Experimental section. [d] Calculated on the basis of equation 1. [e] Calculated on the basis of equation 2.

Table IV summarizes yields of products obtained with low pressures of oxygen, elevated temperature and no pyrogallol. These conditions constitute a somewhat extreme version of the limiting conditions which appear to give oxygen absorption in agreement with equation 1. The yields of solid product were higher than those reported by Gomberg[1,2] but were not in quantitative agreement with equation 1. Furthermore, the low melting points (Gomberg[23] reports 185–186° uncor.) indicate that the solid products were not pure bis-trityl peroxide. The soluble residues were light brown oils with phenolic odors. The present work is in agreement with Gomberg's observation[1] that the *total* yield of oxygenation product is greater than would be expected from equation 1.

TABLE IV

PRODUCTS FROM THE OXYGENATION REACTION USING PRE-DISSOLVED SAMPLES IN BENZENE SOLUTION

Expt. no.	Purity of sample, %[a]	Temp. of reacn., °C.	O_2 pressure, atm.	Initial solid residue[b] % of theor.[c]	M.p. of solid residue[b] (cor.), °C.	Residue[d] from mother or wash liquors, % of theor.[c]	Total products, % of theor.[c]
1	91	60	0.2	95.6	180[f]	..	....
2[h]	99.5	25	.003	92.8	172–173[g]	..	....
3[h]	99.5	55	.003	95.2	172–173[g]	7.8[e]	103.0[e]
4[h]	99.5	55	.003	97.6	......	4.2[e]	101.0[e]

[a] Based on oxygen absorption in the absence of pyrogallol under limiting conditions. [b] For expts. 1–3, obtained by evaporating the solution to 10 cc. under vacuum, chilling in refrigerator, filtering with suction, and weighing. For expt. 4, obtained by evaporating solution to dryness under vacuum and washing with 30–60° petroleum ether. [c] Theoretical amounts are based on the assumption that bis-trityl peroxide is the sole product and on an amount of ethane calculated from the sample weights and the purity determined as indicated in note *a*. [d] Obtained by evaporating the appropriate liquor under vacuum and pumping at 0.2 mm. for 1/2 hour. [e] These should include approximately 0.5% of inert material from ethane sample. Thus the total yield should be approximately 100.5% of theoretical on basis of note *c*. [f] Not improved on recrystallization from benzene. [g] Increased to 177–178 on recrystallization from benzene. [h] Reaction carried on for two hours in the dark.

Discussion of Results

Prior observations that the amount of oxygen consumed per unit weight of I depends on conditions have been confirmed. This holds for the reaction both in the presence of excess pyrogallol and in its absence. The observation that the molar consumption of oxygen in the absence of pyrogallol, with oxygen absorption accompanying dissolution of ethane in bromobenzene, reaches a limiting value which in no case exceeds that expected from equation 1, although it approaches or coincides with it, suggests that under the limiting conditions (air as the reagent and a temperature of 25–30° or higher) the stoichiometry of equation 1

---

(22) K. Ziegler, A. Seib, K. Knoevenagel, P. Herte and F. Andreas, *Ann.*, **551**, 179 (1942).

(23) M. Gomberg, *Ber.*, **33**, 3150 (1900).

maintains. Equation 1a does not, however, represent the sole course of the reaction, even under

$$C_2(C_6H_5)_6 + O_2 \longrightarrow (C_6H_5)_3COOC(C_6H_5)_3 \quad (1a)$$

limiting conditions, since bis-trityl peroxide is not produced quantitatively. Because of the mildness of the isolation procedure, and in view of the concordance of the experiments with reaction at 25 and 55°, this result cannot be ascribed to decomposition of the relatively stable peroxide[24] subsequent to its formation. The isolation of total oxygenation product, produced under limiting conditions, in excess of the quantity predicted by equation 1a is further evidence of the inadequacy of this equation. Nevertheless, the reaction under limiting conditions appears to constitute a valid procedure for analysis of hexaphenylethane assuming the stoichiometry of equation 1.

If the above conclusion is accepted, it follows that the stoichiometry of the reaction in the presence of pyrogallol, with simultaneous exposure to oxygen and dissolution, is intermediate between those of equations 1 and 2. An alternative conclusion is that the stoichiometry of equation 2 maintains under these conditions but that the ethane employed was highly impure, and further, that, in the absence of pyrogallol, even the limiting consumption of oxygen exceeds that expected from equation 1. This proposal is rendered improbable by the data of Table III which are consistent with the conclusions that, in the absence of pyrogallol, the stoichiometry of equation 1 holds under limiting conditions, whether dissolution of the ethane precedes or is simultaneous with its exposure to oxygen, and that in the presence of pyrogallol the stoichiometry of equation 2 maintains when dissolution of the ethane precedes oxygenation. These conclusions cannot, however, be extended to other hexaarylethanes in the absence of similar experiments.

The present results serve also as a clear warning that prior work, the significance of which depends on establishment of purity of I or a congener by means of quantitative oxygenation, must be approached critically and with close attention to experimental details.

A hypothesis which is consistent with data in the absence of pyrogallol reported here, as well as with the observations of others, involves attack by trityl peroxy radical[12] ($TO_2\cdot$) on the solvent (SH). The formation of TO_2H plus TO_2S under conditions such that little $TO_2\cdot$ is removed by combination with trityl radical ($T\cdot$) would account for the observed consumption of oxygen in excess of Equation (1). When conditions are conducive to combination of $TO_2\cdot$ and $T\cdot$, even to the exclusion of direct reaction of $TO_2\cdot$ with I,[12] attack by $TO_2\cdot$ and $T\cdot$ on SH to yield products such as TO_2H plus TS would account for non-quantitative yields of II accompanied by adherence to the stoichiometry of equation 1. The results in the presence of pyrogallol when oxygenation and dissolution are simultaneous suggest that the reaction may be partially heterogeneous in the sense that $TO_2\cdot$ may attack undissolved as well as dissolved ethane.[12] Solid hexaphenylethane undergoes a rapid surface reaction with atmospheric oxygen yielding a yellow product. A highly reactive radical such as $TO_2\cdot$ would be expected to attack the crystal surface even more rapidly. Further work directed toward the elucidation of these systems is continuing in these laboratories.

Acknowledgment.—This work was made possible through support extended by the Geophysics Research Division of the Air Force Cambridge Research Center, under Contract AF 19(122)-405. The authors wish to acknowledge valuable discussions with Prof. Paul D. Bartlett, Dr. John H. Ridd and Dr. Leonard Spialter, and the assistance of Dr. Martha Bergin and Mr. Edward Zdanuk in some of the experiments.

BOSTON, MASSACHUSETTS

---

[24] The peroxide can be recrystallized from hot chloroform or carbon disulfide, *cf.* M. Gomberg, *Ber.*, **33**, 3154 (1900).

[CONTRIBUTION NO. 343 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & COMPANY]

Olefin–Carbon Monoxide–Alcohol Copolymers

BY T. L. CAIRNS, D. D. COFFMAN, RICHARD CRAMER, A. W. LARCHAR AND B. C. MCKUSICK

RECEIVED JANUARY 7, 1954

The radical-initiated copolymerization of ethylene and carbon monoxide in methanol at high pressures gives copolymers containing chemically-bound methanol. Absorption spectra and chemical studies suggest that the methanol is combined in α-hydroxy ester units, $-C(OH)(CO_2CH_3)CH_2CH_2-$. Such units appear to predominate over $-CH_2CH_2-$ and $-C(=O)-$ units in certain copolymers made at 8000 atm. The replacement of ethylene by other olefins or of methanol by other alcohols gives analogous copolymers.

Recent publications from this Laboratory describe a new class of polyketones obtained by the radical-initiated copolymerization of ethylene with carbon monoxide.[1,2] Subsequent study of the effect of polymerization medium on this copolymerization has resulted in the surprising observation that copolymers prepared in alcohols are quite different in character. These new copolymers contain alkoxyl groups due to chemically-bound alcohol molecules. This paper discusses the conditions under which these copolymers are formed and proposes a structure for them.

Copolymers of this new class are obtained when ethylene and carbon monoxide are copolymerized in methanol, ethanol, 2-propanol, *t*-butyl alcohol, benzyl alcohol or 2-(*p*-chlorophenoxy)-ethanol and

---

[1] M. M. Brubaker, D. D. Coffman and H. H. Hoehn, THIS JOURNAL, **74**, 1509 (1952).

[2] D. D. Coffman, P. S. Pinkney, F. T. Wall, W. H. Wood and H. S. Young, *ibid.*, **74**, 3391 (1952).