Some Aspects of the Oxidation of Di- and Tri-phenylmethane.

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Certain previous unusual results in the reaction of liquid diphenylmethane with oxygen are shown to be due to impurities. The purified hydrocarbon is oxidized, under various conditions, at rates which can be explained by a normal autoxidation mechanism involving hydroperoxides and a succession of free radicals, and the presence of such radicals was proved. The addition of organic acids markedly altered the form of the curves of oxygen-uptake and hydroperoxide yield, owing to catalysis of the ionic decomposition of the hydroperoxide. Some acids appear in addition to increase the rate of formation of the hydroperoxide.

The oxidation of triphenylmethane is complicated even in its initial stages.

THE reactions of the phenylmethanes with molecular oxygen in the liquid phase show a number of peculiarities. Waters (*J.*, 1946, 1151) found that the oxidation of triphenyl-methane catalyzed by chromic anhydride at 20—45° is slower than that of diphenyl-methane, although it might be expected that the methane hydrogen atom in the former would be easily removable. Also water inhibits the oxidation of tri- but not of di-phenyl-methane (Stevens and Roduta, *J. Amer. Chem. Soc.*, 1935, **57**, 2380). Larsen, Thorpe, and Anfield (*Ind. Eng. Chem.*, 1942, **34**, 282) state that the uptake of oxygen by diphenyl-methane at 110° stops completely after 500 ml./mole have been absorbed, and that the products are benzaldehyde plus residual inhibitors, in contrast to Stevens and Roduta (*loc. cit.*) who report only benzophenone as a product.

Because of the unusual results obtained by Larsen, Thorpe, and Anfield (*loc. cit.*), the oxygen-uptake characteristics of various specimens of diphenylmethane were studied at 105°. Typical curves are shown in Fig. 1. The rate of absorption accelerated from zero to a maximum, which occurred after ~0·02 mole of oxygen per mole of hydrocarbon had been taken up. This acceleration period was shortened or eliminated by not removing any " peroxide " initially present (due to exposure to air, sunlight, etc.), but the maximum rate was not affected : this was demonstrated by removal of peroxide, preferably by chrom-atography. With commercial diphenylmethane, purified by recrystallization or vacuum- or steam-distillation, or with specimens synthesized in various ways, oxygen-uptake ceased quite sharply after between 250 and 2000 ml. per mole of hydrocarbon had been absorbed (Fig. 1, *a* and *b*). The gas above the solution was still practically all oxygen, but the mixture had become dark brown and, as judged by smell, phenol and benzaldehyde were present. The hydroperoxide yield fell off rapidly from nearly 100%, just before the cessation of oxidation. However, when the diphenylmethane was purified by shaking it six times with concentrated sulphuric acid, washing it with water, drying it, and chrom-atography under nitrogen, the oxygen-uptake and hydroperoxide-yield curves (Fig. 1, *c*) resembled those for the oxidation of other hydrocarbons in the liquid phase. When the oxidation rate fell off from the maximum (0·75 ± 0·04 ml. at N.T.P. per g. of diphenyl-methane per hour) the solution again became brown and smelt of phenol and benzaldehyde. It seems that diphenylmethane as normally obtained or prepared contained an impurity, not removed by physical methods, and possibly anthracene (Orndorff, Gibbs, McNulty, and Shapiro, *J. Amer. Chem. Soc.*, 1927, **49**, 1541), which catalyzed the decomposition of the hydroperoxide, when this reached a critical concentration, producing a powerful inhibitor which prevented further oxygen-uptake. It is significant that, according to the literature, diphenylmethane has usually been purified for physical or chemical measure-ments by distillation or crystallization.

The oxygen-uptake characteristics of liquid triphenylmethane at 105° were studied, in order to compare them with those of diphenylmethane, and to see whether sudden cessation of the reaction occurred. Commercial triphenylmethane gave oxygen-uptake curves similar to those of the final specimen of diphenylmethane (Fig. 1*c*). The maximum rate

(about 0·53 ml. at N.T.P. per g. per hr.) occurred after approximately 0·01 mole of oxygen has been absorbed per mole of hydrocarbon, and the rate fell off again after about 0·04 mole per mole had been taken up. However, the " hydroperoxide " yield was always less than 60%, and fell off to zero after 0·10—0·15 mole of oxygen per mole of hydrocarbon had been absorbed, although the liquid was still taking up gas at 25—40% of the maximum rate. The products then were a dark brown crystalline solid and a red liquid condensate in the neck of the reaction flask. There was a phenolic and sometimes a sweet-scented smell. Stevens and Roduta (*loc. cit.*) found that benzophenone and phenol were produced during the oxidation of triphenylmethane. There was an indication that different methods of
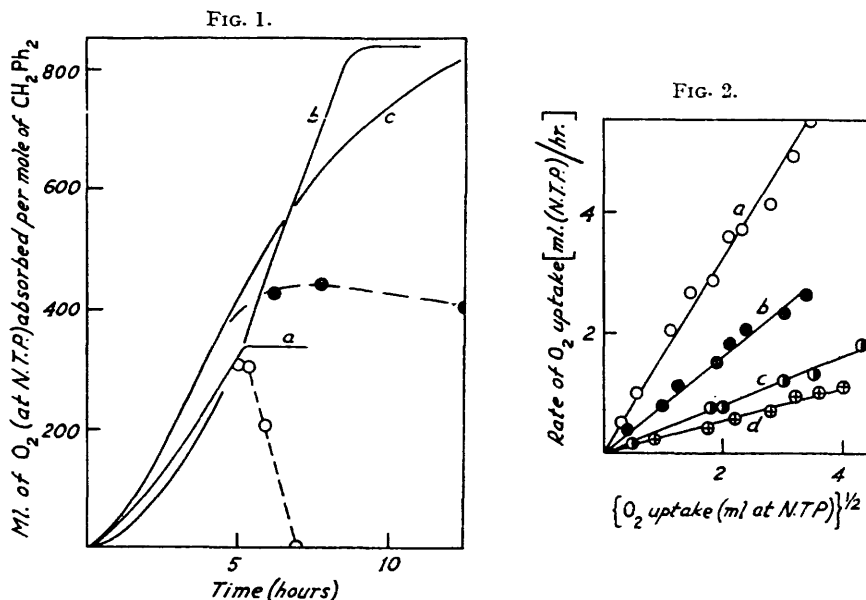

FIG. 1.

FIG. 2.

FIG. 1. *Oxygen-uptake curves for different samples of diphenylmethane.   Temp.* = 105°
O_2 *press.* = 760 mm.

a, CH_2Ph_2 *purified by vac. distn. and chromatographed under* N_2:   —○—, *oxygen as hydroperoxide.*
b, CH_2Ph_2 *prepared by reaction of* C_6H_6, $C_6H_5 \cdot CH_2 \cdot OH$, *AcOH, and conc.* H_2SO_4 c, CH_2Ph_2 *purified by treatment with conc.* H_2SO_4, *etc.* (*ordinates* × 5, *abscissæ* × 4).   —●—, *oxygen as hydroperoxide.*

FIG. 2. *Variation of rate of oxidation of diphenylmethane with amount of reaction during period of acceleration.*

a, 3 g. of CH_2Ph_2 at 115°, and 760 mm. of O_2.
b, 3 ,,   ,,   105°, ,,   ,,   ,,
c, 2 ,,   ,,   115°, ,,   67   ,,   (*abscissæ* × 0·5).
d, 3 ,,   ,,   +6·7 g. of PhCl at 115°, and 760 mm. of O_2 (*abscissæ* × 0·5).

peroxide determination gave somewhat different values of titratable oxygen at the same stage in the reaction, and possibly the products included some bistriphenylmethyl peroxide, unless these methods were not accurate for triphenylmethyl hydroperoxide. The oxidation even in the initial stages seems to be more complicated than that of diphenylmethane and was not studied further.

The reaction of " pure " diphenylmethane (*i.e.*, the hydrocarbon after treatment with concentrated sulphuric acid, etc.) with oxygen seems to follow the same course as those of olefin oxidations in solution (Bolland, *Quart. Reviews*, 1949, **3**, 1), in so far as the hydroperoxide is formed quantitatively at first but breaks down slowly later to form the stable products. The kinetics of the initial stages of the oxidation of the " pure " material were therefore studied to provide a further comparison.

It was found that, during the acceleration period, the rate of oxygen uptake at any time was proportional to the square root of the oxygen absorbed up to that time (Fig. 2, a and b). The rate during this period is therefore proportional to $[CHPh_2 \cdot O \cdot OH]^{\frac{1}{2}}$, the

hydrocarbon concentration being virtually constant. However, as can be seen from Fig. 1, the maximum rate was virtually independent of hydroperoxide concentration. Dilution of the diphenylmethane with chlorobenzene, an inert solvent, did not alter the square-root dependence of the rate during the acceleration period on hydroperoxide concentration (*e.g.*, Fig. 2*d*). Both the slope of this line and the maximum rate are proportional to the mole fraction of hydrocarbon at 115° (Fig. 3). A few experiments seemed to show that at 105° the dependence of the maximum rate on the concentration of diphenylmethane was about 1·5 rather than 1·0. The yield of hydroperoxide was again practically quantitative
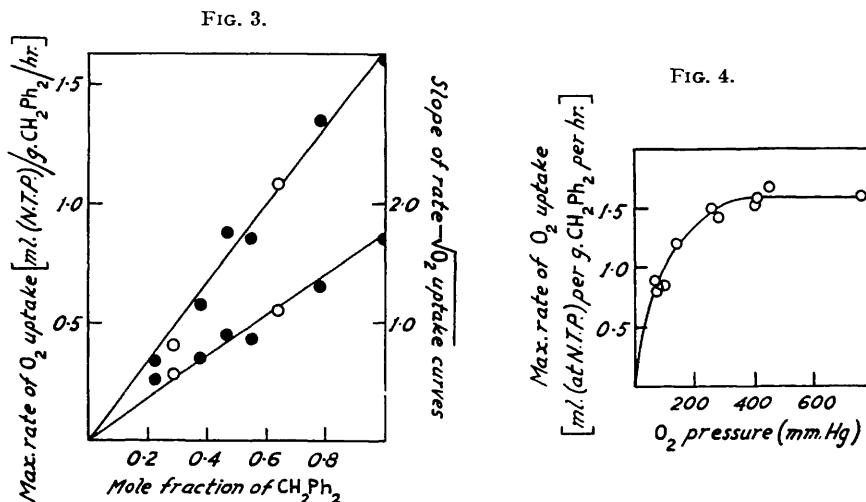
FIG. 3.

FIG. 4.

FIG. 3. *Variation of rate of oxidation of diphenylmethane with concentration in chlorobenzene solution.*
Temp. = 115°. O₂ press. = 760 mm.

Points marked ● represent the mean of several values.

FIG. 4. *Variation of maximum rate of oxidation of diphenylmethane with oxygen pressure.*
Temp. = 115°.

until the rate commenced to decrease from its maximum value. Above about 300 mm. the pressure of oxygen had little effect on the uptake curves, but below this value the rate began to fall off (Fig. 4). The plots for rate against (uptake)$^{\frac{1}{2}}$ remained linear as far as could be ascertained (*e.g.*, Fig. 2*c*), but the slope decreased in a manner parallel with the decrease in maximum rate.

The kinetics of the initial stages of the oxidation of diphenylmethane can be summarized in two equations : during the acceleration period,

$$\text{rate} = k[\text{CHPh}_2\text{·O·OH}]^{\frac{1}{2}} . [\text{CH}_2\text{Ph}_2][\text{O}_2]/(\alpha + [\text{O}_2])$$

and max. rate = $k'[\text{CH}_2\text{Ph}_2][\text{O}_2]/(\beta + [\text{O}_2])$ (in any case at 115°), where k, k', α, and β are constants.

The overall activation energies, calculated from the average slopes of the plots for rate against (uptake)$^{\frac{1}{2}}$ or from the average maximum rates at 105° and 115°, are the same within experimental error, *viz.*, 21·2 and 21·9 kcal./mole, respectively.

The first equation can readily be explained by postulating a reaction scheme, which is a special case of the general free-radical chain mechanism put forward by Bolland (*loc. cit.*), auto-catalysis being due to the decomposition of a small proportion of the hydroperoxide formed :

(1) $\text{CHPh}_2\text{·O·OH} \longrightarrow$ radicals R· (first-order reaction)

(2) $\text{R·} + \text{CH}_2\text{Ph}_2 \longrightarrow \text{RH} + \text{Ph}_2\text{CH·}$

(3) $\text{Ph}_2\text{CH·} + \text{O}_2 \longrightarrow \text{CHPh}_2\text{·O·O·}$

(4) $\text{CHPh}_2\text{·O·O·} + \text{CH}_2\text{Ph}_2 \longrightarrow \text{CHPh}_2\text{·O·OH} + \text{Ph}_2\text{CH·}$

(5) $2\text{CHPh}_2\text{·O·O·} \longrightarrow$ inert products (termination at " high " oxygen pressures)

Assuming that the chains are long, we have

$$-d[O_2]/dt = k_3[Ph_2CH\cdot][O_2] = k_4[CHPh_2\cdot O\cdot O\cdot][CH_2Ph_2]$$

Strictly, $[CHPh_2\cdot O\cdot O\cdot]$ is not constant, since the rate is increasing, but this increase is very slow compared with the rate of the radical reactions and so $d[CHPh_2\cdot O\cdot O\cdot]/dt$ can be taken as zero. Then at any time before the maximum rate is reached

$$-d[O_2]/dt = (k_1/k_5)^{\frac{1}{2}}k_4[CHPh_2\cdot O\cdot OH]^{\frac{1}{2}}[CH_2Ph_2]$$

The fall-off in the rate at " low " oxygen pressures would be due to reaction (3) becoming so slow that $Ph_2CH\cdot$ radicals can take part in termination reactions. Although the unimolecular decomposition of $CHPh_2\cdot O\cdot OH$ is postulated to obtain agreement with the experimental kinetics, it is known that the decomposition of hydroperoxides, unstable only above 100°, is generally of the first order (*e.g.*, Bell, Raley, Rust, Senbold, and Vaughan, *Discuss. Faraday Soc.*, 1951, **10**, 242; Tipper, *J.*, 1953, 1675).

Tobolsky, Metz, and Mesrobian (*J. Amer. Chem. Soc.*, 1950, **72**, 1942) have shown that a straightforward mathematical extension of Bolland's mechanism can account for the phenomenon of maximum rates in the autoxidation of hydrocarbons in solution. However, they predicted that the maximum rate of an uncatalyzed oxidation should depend on the square of the hydrocarbon concentration and be accompanied by a steady concentration of hydroperoxide. This was not so in the present work, a feature of which was that the uptake (in moles of oxygen per mole of diphenylmethane) before the maximum rate was reached was small compared with that during the autoxidations of many other hydrocarbons (*e.g.*, Bolam and Sim, *J. Soc. Chem. Ind.*, 1941, **60**, 51; Larsen, Thorpe, and Anfield, *loc. cit.*; Bolland, *Proc. Roy. Soc.*, 1946, *A*, **186**, 218; Robertson and Waters, *Trans. Faraday Soc.*, 1946, **42**, 201). Since the maximum rate of diphenylmethane oxidation was independent of the concentration of hydroperoxide, this must be involved in both the initiation and the termination step at this stage in the oxidation. Robertson and Waters (*J.*, 1948, 1585) have suggested the reaction

(6) $RO_2 + OH$ (from the hydroperoxide) $\longrightarrow ROH + O_2$
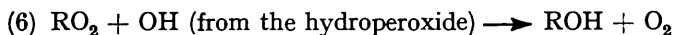
to account for the levelling-off in the rate during the autoxidation of tetralin. This requires that the maximum rate be again proportional to the square of the hydrocarbon concentration, however. Possibly traces of a retarder were being formed by a very small amount of hydroperoxide decomposition, and the reaction

(7) $CHPh_2\cdot O\cdot O\cdot +$ retarder $\longrightarrow$ inert products
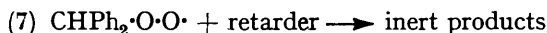
replaced reaction (5). If the concentration of retarder was proportional to the hydroperoxide concentration, the observed kinetics at 115° would be explained. The higher order with respect to the concentration of diphenylmethane at 105° may have been due to the occurrence of reaction (6) as well as (7). The decrease in the maximum rate at " low " oxygen pressures was again probably the result of $Ph_2CH\cdot$ radicals beginning to take part in termination reactions.

The presence of free radicals during the oxidation was confirmed by the addition of 8 mg. of β-naphthol, known to be an inhibitor of radical reactions, to 2 g. of diphenylmethane. This completely prevented oxygen uptake at 115° for at least 54 hr. Addition of 10 mg. of phenol to 2 g. of diphenylmethane caused the absorption of gas to be very slow for about 15 hr., after which the oxidation proceeded normally. The rôle of phenol in the autoxidation of diphenylmethane is difficult to assess, since it is probably formed in some quantity during the later stages of the reaction which is still proceeding at $\sim\frac{1}{3}$ to $\frac{1}{2}$ of the maximum rate. It can therefore scarcely be responsible for the sudden cessation of the oxidation of " impure " diphenylmethane, but it might have acted as the retarder in reaction (7). There appears, however, to be a difference between the effect of phenol added initially and that formed during the oxidation.

The decomposition of hydroperoxides is greatly affected by conditions, especially the presence of acids or bases, and therefore it would be expected that these substances would

have an effect on the course of the oxidation of a hydrocarbon in solution. There have been few investigations of the effect of the solvent on such an oxidation. Some patents record different products from the use of different solvents, and Bolam and Sim (*loc. cit.*) found that there was a marked difference in the oxidation characteristics of methyl linoleate in neutral and in acidic or basic solvents. Morrell and Davis (*J. Soc. Chem. Ind.*, 1936, **55**, 237) and Paquot (*Bull. Soc. chim.*, 1941, **8**, 695) have also noted the marked effect of acetic acid on autoxidations in solution.

In the presence of 70 moles % of acetic acid the oxidation of " pure " diphenylmethane was very slow (~0·05 ml./g./hr.) and the concentration of hydroperoxide was negligible. With 65 moles % of butyric acid added, at 115° or 105° the uptake of oxygen appeared
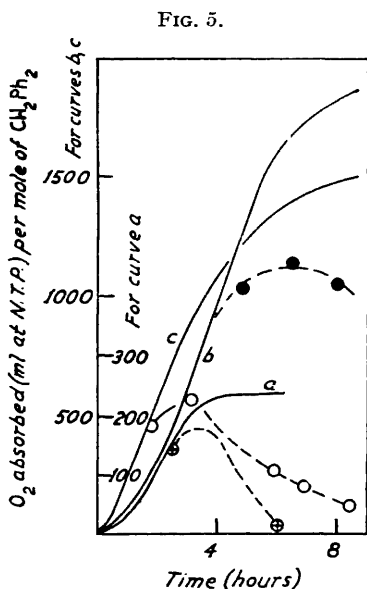
FIG. 5.

FIG. 6.

Time (hours)

FIG. 5. *Oxygen-uptake curves for diphenylmethane in presence of some organic acids.* *Temp.* = 115°. O₂ *press.* = 760 *mm.*

a, CH₂Ph₂ + 65 *moles* % *of butyric acid.* —⊕—, *oxygen as hydroperoxide.*
b, CH₂Ph₂ + 58 *moles* % *of benzoic acid.* —●—, *oxygen as hydroperoxide.*
c, CH₂Ph₂ + 55 *moles* % *of phenylacetic acid.* —○—, *oxygen as hydroperoxide.*
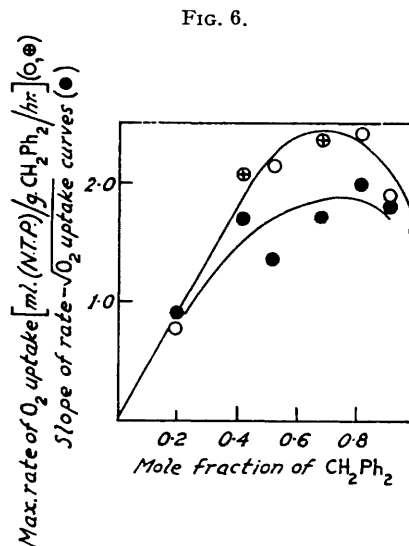
FIG. 6. *Variation of rate of oxidation of diphenylmethane with concentration in the presence of benzoic acid.* *Temp.* = 115°. O₂ *press.* = 760 *mm.*

Points marked ⊕ *represent the mean of several values.*

to follow the same course as with the same concentration of chlorobenzene as diluent until there was a sudden reduction in the rate of absorption to a low value (<0·09 ml./g./hr.), and at the same time the yield of hydroperoxide which had been nearly quantitative dropped sharply (Fig. 5a). Addition of 1·4 moles % of trichloroacetic acid, a strong acid, to a 38 mole % solution of diphenylmethane in chlorobenzene caused practically complete inhibition at 116° (~0·05 ml. of O₂ absorbed/g./hr.) and no hydroperoxide was present. The lack of uptake was real, since the gas above the solution at the end of an experiment was still practically all oxygen. The acids were obviously catalyzing the hydroperoxide decomposition in such a way that no fresh chain centres were formed, presumably to give ions; with butyric acid this only occurred after a certain amount of hydroperoxide had accumulated. The autocatalysis by the hydroperoxide was cut out, and the very slow uptake may have been due to a chain reaction initiated by a direct reaction with a high activation energy between diphenylmethane and oxygen.

With benzoic acid or phenylacetic acid as diluent the results are somewhat different. With the former there was a short acceleration period to a maximum rate much greater

than that with the same concentration of chlorobenzene as diluent, but the rate began to decrease at a lower uptake. The yield of hydroperoxide, which was practically quantitative during the acceleration period, fell off, and the hydroperoxide concentration reached a maximum during the period of maximum rate (Fig. 5b). A plot of rate against (O_2 uptake)$^{\frac{1}{2}}$ was again a straight line through the origin up to the attainment of the maximum rate. The variation of the slope of this line and of the maximum rate with hydrocarbon concentration is shown in Fig. 6. There is a maximum in both curves at about 75 moles % of diphenylmethane. When more than about 40 moles % of phenylacetic acid were added, the rate of oxygen uptake accelerated very rapidly from zero to its maximum value, and this rate was again very much greater than with an inert diluent. The rate of absorption tailed off sharply and the hydroperoxide yield, which was nearly 100% at the beginning, fell rapidly to a low level (Fig. 5c). With progressively less acid an increasingly long acceleration period occurred and the tail-off was more gradual. Neither acid absorbed oxygen by itself. Two effects were probably competing when diphenylmethane was oxidized in the presence of these two acids. At the beginning of the reaction there was rapid chain transfer to give reactive solvent radicals, leading to an increased rate in the initial stages; but later, acid-catalyzed decomposition of the hydroperoxide became increasingly prominent. With phenylacetic acid presumably a hydrogen atom from the CH_2 group would be removed in the solvent-transfer reaction but, although benzoic acid has never been considered prone to attack by free radicals, it seems likely that in these circumstances $Ph \cdot CO \cdot O \cdot$ radicals were formed, since chlorobenzene was inert. From the results it appears that the order of increasing reactivity towards $CHPh_2 \cdot O \cdot O \cdot$ radicals is $CH_2Ph_2 < Ph \cdot CO_2H \ll CH_2Ph \cdot CO_2H$. It is possible that the sudden cessation of oxygen-uptake with impure diphenylmethane was due to the formation of an acid. Waters and Wickham-Jones (*J.*, 1951, 812) found that the addition of benzoic or trichloroacetic acid to benzaldehyde eliminated autocatalysis by the perbenzoic acid formed.

It may be mentioned that initial addition of small amounts of mercury ($\sim$1 mole %) inhibited the autoxidation; and when it was added during the course of a normal reaction, complete cessation of oxygen uptake took place, and the hydroperoxide concentration dropped rapidly.

In conclusion it can be said that, while the oxidation of triphenylmethane is complicated even in its initial stages, that of diphenylmethane fits into the general pattern of autoxidations in solution. However, the results illustrate again the vital rôle of hydroperoxides, and their modes of formation and decomposition, in the liquid-phase oxidation of hydrocarbons.

EXPERIMENTAL

The uptake of oxygen was followed by means of a conventional constant-pressure apparatus. Up to four 25-ml. flasks at a time contained the hydrocarbon with or without additive. They were immersed in an oil thermostat, constant to $\pm 0 \cdot 1°$ during an experiment, and were shaken about 400 times per min. The rate of shaking, unless low ($<$100 per min.), had no effect on the uptake curves within the experimental error. The flasks were connected to constant-pressure gas burettes by capillary tubing and the smallest lengths of pressure tubing possible. They were cleaned before use by washing them successively with soap and water, boiling alcoholic potash (EtOH 90, H_2O 5, KOH 5 parts), concentrated nitric acid, water, concentrated nitric acid, distilled water, and " AnalaR " acetone, and dried by heating them in a stream of air. Pipettes, etc., were cleaned as above but not heated. The air in the apparatus was swept out by pure oxygen before an experiment.

The " peroxide " content was determined by the iodometric method of either Skellon and Wills (*Analyst*, 1948, **73**, 78) or Wagner, Smith, and Peters (*Ind. Eng. Chem. Anal.*, 1947, **19**, 976). Gas samples were removed from above the reaction mixture by connecting the flask to an evacuated tube, and analyzed in a Bone and Wheeler apparatus.

The methods of purification of diphenylmethane have been discussed. The hydrocarbon was synthesized by three methods : reduction of benzophenone by sodium and alcohol; condensation of benzene and benzyl chloride in presence of mercuric chloride and aluminium; condensation of benzene and benzyl alcohol by acetic and concentrated sulphuric acids [see Beilstein's " Handbuch," V (Syst. No. 479), p. 589]. The alumina used for chromatography

was B.D.H. special. Triphenylmethane was recrystallized twice from alcohol and stored in a continually evacuated desiccator for some hours before use. Chlorobenzene was distilled twice, kept under nitrogen, and chromatographed under nitrogen before use. " AnalaR " acetic acid was distilled with 1% " AnalaR " acetic anhydride. " AnalaR " trichloroacetic acid was used directly. Butyric acid was distilled in a nitrogen atmosphere. Benzoic acid was recrystallized three times from water, and phenylacetic acid three times from light petroleum, and kept in an evacuated desiccator for several hours. B.P. phenol and β-naphthol were used directly. Mercury was freshly distilled.

Oxygen was purified by passage through a liquid-oxygen trap, and nitrogen by passage over heated copper and through a liquid-oxygen trap.