[A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Aromatic Substitution by Free Radicals. I. The Cleavage of Benzoyl Peroxide by the Triphenylmethyl Radical

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A quantitative investigation of the reaction between triphenylmethyl and benzoyl peroxide in benzene shows that the only products of the reaction are tetraphenylmethane, trityl benzoate and benzoic acid. A comparison is made between the reactions of benzoate radicals involved in this reaction with the reactions which are attributed to the same species when it is formed in the thermal decomposition of benzoyl peroxide. The failure of the radicals to undergo decarboxylation when produced in the cleavage of the peroxide by the triphenylmethyl radical is taken as a strong indication that reactions in which two free radicals make a concerted attack on a third molecule are of importance in at least one of the systems. It is suggested that such termolecular reactions may be involved frequently in aromatic radical substitution.

In 1937 Wieland and co-workers[1] reported that the reaction of triphenylmethyl with benzoyl peroxide in benzene solution yields tetraphenylmethane, benzoic acid and trityl benzoate. The reaction with other diaroyl peroxides and other aromatic solvents[2] gave rise to tetraarylmethanes in which one aryl group was clearly derived from the solvent. We were interested by the apparent absence of decarboxylation reactions which accompany the thermal decomposition of benzoyl peroxide in similar solvents.[3] Since Wieland's work was not quantitative, it seemed worthwhile to investigate this apparent anomaly by carrying out a careful material balance by suitable analysis of the reaction mixtures.

Experimental

The solution of triphenylmethyl in benzene was prepared and aliquots were assayed by titration with benzoyl peroxide. The details of the method are reported elsewhere[4] and serve to demonstrate the quantitative aspects of the reaction being studied. Aliquots of the radical solution were removed from the reaction vessel and added to a weighed amount of benzoyl peroxide either dry or contained in a known volume of benzene. In other runs in which the total amount of radical remaining after assaying was to be used in the reaction, the calculated amount, or an excess, of benzoyl peroxide was added to the reaction vessel. All reaction flasks had been evacuated and filled with nitrogen and transfers were accomplished by means of calibrated, nitrogen-filled syringes which were inserted through rubber serum stoppers. These precautions virtually eliminated air oxidation of the radical which, when it occurred, was indicated by the precipitation of slightly soluble ditrityl peroxide. The solutions were allowed to stand for periods of time which varied from one to 15 hours. The time was determined by waiting until no further change in color of the solution was noticeable. The final color of the solutions was always a very pale yellow. The reaction was very much faster in the more concentrated solutions and it was qualitatively observed that the rate of fading of the orange color is increased by increasing the concentration of either reactant. Excess peroxide was determined by the usual iodometric procedure.[5]

Isolation of Tetraphenylmethane.—An aliquot portion of the reaction mixture was poured onto a column of activated alumina and the tetraphenylmethane was eluted with 15% benzene in Skellysolve B. The melting point of the crude product was in the range 250–260°. Material melting at 280–283° was obtained by recrystallizing from benzene. Sublimation at atmospheric pressure at 400° gave a product melting at 285° (cor.). *Anal.* Calcd.: C, 93.61; H, 6.29. Found: C, 93.60; H, 6.60.

Determination of benzoic acid and trityl benzoate had to be carried out by volumetric procedures since the high solvolytic reactivity of trityl benzoate[6] precluded the possibility of its quantitative separation from benzoic acid. The analysis was carried out by two methods.

Method A.—An aliquot of the reaction mixture and an equal volume of absolute alcohol containing 0.0448 *N* potassium hydroxide were brought to temperature in a bath maintained at 54 ± 0.5°. The solutions were mixed and aliquots were withdrawn immediately and at intervals thereafter and titrated to the phenolphthalein end-point with standard aqueous hydrochloric acid. The immediate decrease in the titer was contributed to by the rapidly solvolyzed trityl chloride and benzoyl peroxide, if an excess remained, as well as benzoic acid. Separate experiments indicated that the halide consumes exactly one mole of hydroxide ion, as would be anticipated. However, benzoyl peroxide consumes about 0.6 mole of base immediately and takes up a considerable additional amount at a very slow rate. Since the peroxide was determined separately the initial acid titer was corrected by use of the empirical factor. Halide ion was determined in a separate aliquot by the Volhard method and was equated to the acid produced by solvolysis of trityl chloride. Free acid unaccounted for by trityl chloride and peroxide is reported as benzoic acid.

The trityl benzoate could not be estimated accurately by simply taking an infinity titer in the samples which contained excess peroxide because of the slow uptake of base by substances derived from the latter compound. This process continues without any apparent limit and is probably due in part to the peroxide-catalyzed air oxidation of the ethanol in the solvent. The trityl ester was estimated by plotting the decrease in hydroxide ion concentration against time and reading off the value at the known half time for the first order solvolysis of trityl benzoate[6] in the solvent medium at the ionic strength represented by the initial potassium hydroxide concentration. By using the value for total ester estimated in this manner it was possible to show that the consumption of base followed first order kinetics to over 80% reaction with a rate constant of 0.030 ± 0.001 min.$^{-1}$ in all runs which were considered to be acceptable.

Method B, which was developed later is simpler and probably more precise because it avoids interference by peroxide. Free acid is determined by adding an aliquot from the reaction mixture to at least twice its volume of ethanol and titrating with aqueous base at room temperature. Another aliquot was added to two volumes of alcohol, diluted with water after a few minutes, and filtered. Halide ion was determined in the filtrate by a Volhard titration. The difference between the total free acid and the halide was assumed to be equal to the benzoic acid since it was shown that neither trityl benzoate nor benzoyl peroxide is affected by the treatment and that trityl chloride is solvolyzed quantitatively.

In the estimation of trityl benzoate an aliquot from the reaction mixture was added to at least two volumes of alcohol and one or two milliliters of standard 0.1 *N* aqueous hydrochloric acid was added. The solution was then heated at 54° for 20–30 minutes and back-titrated with base. Investigation showed that this treatment was more than sufficient to effect the quantitative solvolysis of trityl benzoate but that only a negligible amount of acid was produced from peroxide. After correction for the added hydrochloric acid and the free acid found by the titration at room temperature, the sodium hydroxide titer was equated to trityl benzoate in the aliquot.

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(1) H. Wieland, T. Ploetz and H. Indest, *Ann.*, **532**, 166 (1937).

(2) H. Wieland and A. Meyer, *ibid.*, **551**, 249 (1942).

(3) (a) B. Barnett and W. E. Vaughan, *J. Phys. Colloid Chem.*, **51**, 926 (1947); (b) P. F. Hartmann, H. G. Sellers and D. Turnbull, THIS JOURNAL, **69**, 2416 (1947).

(4) G. S. Hammond, A. Ravve and F. J. Modic, *Anal. Chem.*, in press.

(5) G. S. Hammond, THIS JOURNAL, **72**, 3737 (1950).

(6.) G. S Hammond and J. T. Rudesill, *ibid.*, **72**, 2769 (1950).

TABLE I

YIELDS OF BENZOIC ACID AND TRITYL BENZOATE

Run	Equivalents triphenylmethyl × 10^3	Equivalents peroxide × 10^3	Equivalents $T\cdot$/liter[a]	Order of addition[b]	Method of analysis[c]	Acid, %	Ester, %	Ester/acid
B-5	12.0	12.0	0.167	A	A	30	65	2.16
B-7	9.3	11.7	.0348	A	A	35	63	1.80
C-1	6.86	7.45	.0249	B	B	34	61	1.80
C-2	7.11	6.6	.285	B	B	29	70	2.42
C-3[d]	7.78	7.90	.0336	B	B	32	70	2.18
C-4	7.90	7.90	.395	B	B	24	72	2.92

[a] Calculated using final volume of reaction mixture. [b] A, peroxide added to radical; B, radical added to peroxide. [c] See experimental. [d] Runs C-3 and C-4 were carried out in parallel using the same radical preparation.

TABLE II

YIELDS OF TETRAPHENYLMETHANE

Run	Equivalents triphenylmethyl × 10^3	Equivalents $T\cdot$ per liter	$(C_6H_5)_4C$ %
A-1	5.6	0.083	20
A-2	9.3	.14	27
A-3	4.9	.033	30
A-4	7.0	.117	26
A-5	8.9	.137	30
C-3	7.78	.0336	25

The absence of biphenyl in the reaction mixture was established by ascertaining, by the study of artificial mixtures, that this substance, if present, would have been eluted from the chromatogram along with tetraphenylmethane. Exhaustive steam distillation of one of the hydrocarbon fractions gave only a trace of triphenylmethane although controls showed that biphenyl was readily recovered from a mixture by this method.

The absence of phenyl benzoate was indicated by the following experiment. It was shown in a control experiment that phenyl benzoate in an artificial mixture was eluted from the chromatograms along with some triphenylcarbinol by washing with 20% acetone in benzene. One of the chromatograms was washed exhaustively with this solvent and the residue, after evaporation of the solvent, was refluxed with 10% sodium hydroxide in aqueous alcohol for two hours. The resulting mixture was extracted with benzene and then acidified and extracted with ether. The ether extract was evaporated to dryness and the residue dissolved in water. Addition of bromine water to the resulting solution gave only a very faint cloudiness indicating the presence of no more than a trace of phenol.

Results and Discussion.—Our results are in complete accord with those of Wieland, *et al.*, and further demonstrate, both by material balance and through the demonstrated absence of other products which might have been expected, that no products other than the three noted are formed. The results of typical experiments are summarized in Tables I and II. The yields of tetraphenylmethane were not determined in later runs which were conducted for the purpose of improving the accuracy of the analyses for the other products. Since the former was not readily isolated in pure form without some loss, the precision of the trityl balance is not high. However, it is apparent that the results are consistent with the view that the yield of hydrocarbon is equal to that of benzoic acid. The benzoate balance is excellent and, within the expected over-all accuracy of the work, indicates a quantitative conversion of benzoyl peroxide to benzoic acid and trityl benzoate.

It is not difficult to formulate a simple mechanism to account for the observed course of the reaction

$$T\cdot + (BzO)_2 \longrightarrow BzOT + BzO\cdot \quad (1)$$

$$BzO\cdot + T\cdot \xrightarrow{k_2} BzOT \quad (2)$$

$$BzO\cdot + ArH \longrightarrow BzOH + Ar\cdot \quad (3)$$

$$Ar\cdot + T\cdot \longrightarrow ArT \quad (4)$$

This sequence is the same as that proposed by Waters,[7] except that we feel that the fact that the reaction proceeds smoothly at room temperature indicates that no appreciable amount of peroxide undergoes thermal dissociation. The real difficulty arises when one attempts to reconcile the fate of the benzoate radical in this reaction with reactions which must be attributed to this species when it is produced in the thermal decomposition of benzoyl peroxide in the same solvent. It has been demonstrated[5,8] by trapping the radicals with iodine, that the yield of benzoate radicals in the primary process of thermal decomposition is very high, reaching 100% in carbon tetrachloride and being at least 90% in benzene. Despite this fact, a large amount of decarboxylation of the thermal radicals occurs.[3] Some benzoic acid is produced but the maximum yield is about 20%.[3,8] The discrepancy cannot be laid to the reactions of aryl radicals produced in reaction (3) since this would require that one mole of benzoic acid should be produced for every aryl radical formed. Even if every aryl radical were to react in such a way as to effect the decarboxylation of one benzoate function the yield of acid would have to be 50% of the theoretical. Confusion because of the chain decomposition involved in the thermal decomposition is avoided since Barnett and Vaughan have found that the yield of carbon dioxide *increases* with increasing dilution and consequent *diminution of the importance of the induced reaction.* It is likewise possible to rule out the difference in temperature as a source of the discrepancy. Hartman and coworkers[3] found that the yield of carbon dioxide is only slightly dependent on temperature. Furthermore, we found in an experiment which is not reported in detail that the reaction of triphenylmethyl with benzoyl peroxide at 54° did not produce any appreciable amount of carbon dioxide.

If benzoate radicals are involved in both reactions, it appears that the only significant difference in their environment is to be found in the nature of the other radicals present in the solution. Since benzoate has been clearly shown to react with the solvent in both reactions, it follows that if other

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(7) W. A. Waters, "Physical Aspects of Organic Chemistry," 4th ed., D. Van Nostrand Co., New York, N. Y., 1950, p. 170.

(8) G. S. Hammond and L. M. Soffer, THIS JOURNAL, **72**, 4711 (1950).

radicals influence these reactions, they must do so in concerted reactions in which two radicals attack the solvent simultaneously. Since triphenylmethyl is present at relatively high concentrations, we were prejudiced in favor of the view that it is responsible for the fate of the benzoate even in the solvent reaction and that reactions (3) and (4) actually occur in one step rather than two.

$$\mathrm{T}\cdot + \mathrm{ArH} + \mathrm{BzO} \xrightarrow{k_5} \mathrm{BzOH} + \mathrm{ArT} \qquad (5)$$

If such is the case, it is clear that the relative yields of benzoic acid and trityl benzoate should be independent of the concentrations of peroxide and triphenylmethyl since

$$\frac{\mathrm{d}[\mathrm{BzOT}]}{\mathrm{d}[\mathrm{BzOH}]} = \frac{2k_2}{k_5[\mathrm{ArH}]} + 1 \qquad (6)$$

We therefore carried out the reaction over a wide range of initial concentrations of reactants, and, as is seen from Table I, the relative yield of benzoic acid is significantly higher in the more dilute solutions. The relative yields can have no exact quantitative significance since the rate of the reaction in the most concentrated solutions was so rapid that when the triphenylmethyl solutions were added to the peroxide in two portions, the color of the aliquot first delivered was entirely discharged before the syringe could be refilled and the addition completed. Furthermore, the kinetics of the reaction give promise of being rather complex since the rate of the overall reaction in concentrated solutions is sufficiently high to invalidate the assumption that triphenylmethyl and its dimer are in equilibrium. On the other hand, the persistence of the color in reactions in dilute solution shows that the dissociation of hexaphenylethane is not rate controlling under these circumstances. The increase in yield of benzoic acid is consonant with reactions (1) through (4), but leaves us with the original problem of explaining the decarboxylation of thermal benzoate radicals.

Two of a number of possible solutions seem worthy of mention. The first involves the possibility that trityl benzoate is produced both by reaction (1) and by the simultaneous attack of two trityl radicals on a molecule of peroxide.

$$2\mathrm{T}\cdot + (\mathrm{BzO})_2 \longrightarrow 2\mathrm{BzOT} \qquad (7)$$

If this reaction occurs, it would then allow us to assume that benzoate radicals produced in reaction (1) are consumed after a very short life time in reaction (5). The relatively longer life of the thermal radicals would then admit the possibility of their undergoing other reactions involving decarboxylation.

The second possibility is that a "proximity effect" allows benzoate radicals produced in thermal decomposition to react in pairs with the solvent before they diffuse away from each other. The kinetics of this situation are identical to those used by Matheson[9] in discussing "cage effect." In fact, the only difference between the two cases is the necessity of assuming that "caged" radicals react with each other through the agency of the walls of the cage rather than directly in radical union or disproportionation reactions. Evidence that this last reaction does not occur has been summarized previously. A variety of concerted reactions may be formulated to account for the products of the thermal reaction.

It should be noted that these two explanations are not mutually exclusive and that it is entirely possible that concerted radical attacks on solvent occur in both the systems discussed. We feel that such a possibility should be considered for many of the reactions in which free radicals attack aromatic compounds to give nuclear substitution. Confirmation of such a view would lead to the resolution of certain anomalies which develop in the consideration of nuclear alkylations and arylations. For example, triphenylmethyl[10] and polyallylacetate[11] radicals apparently attack aromatic nitro compounds at the nitro function whereas the radicals produced in the thermal decomposition of benzeneisodiazotate,[12] benzoyl peroxide[13] and lead tetraacetate[14] attack the nucleus of such compounds. A related phenomenon which has concerned us is the nature of the attack on toluene which leads to the formation of *p*-tolyltriphenylmethane when benzoyl peroxide is cleaved by trityl in toluene solution.[2] If hydrogen abstraction is considered to be the product-determining reaction, it is surprising that a nuclear hydrogen is removed rather than one of the methyl hydrogens, since the latter process should be aided considerably by the resonance energy of the benzyl radical produced. If the hydrogen is removed at the same time that a new bond is being formed, the nuclear attack is readily understood since the transition state may derive considerable stabilization from structures in which both the old and new bonds are intact.

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

[13] D. F. DeTar and H. J. Scheifele, THIS JOURNAL, **73**, 1442 (1951).

[14] L. F. Fieser, R. C. Clapp and W. H. Daudt, THIS JOURNAL, **64**, 2052 (1942).