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A Study of the Mechanism of the Conversion of Benzoyl Peroxide to Benzoic Anhydride by Triphenylphosphine[1]

BY MICHAEL A. GREENBAUM, DONALD B. DENNEY AND A. KENTARO HOFFMANN

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Benzoyl peroxide-carbonyl-O^{18} (I) reacts with triphenylphosphine to give triphenylphosphine oxide (III) and benzoic anhydride (II). All of the excess oxygen-18 is found in the anhydride II and none in the oxide III. Treatment of II with liquid ammonia affords benzamide (IV) and benzoic acid (V). Analysis of IV and V shows that in the anhydride one carbonyl was fully labeled and the other had half the original excess oxygen-18 (IIA). These results are consistent with a mechanism in which triphenylphosphine displaces on a peroxidic oxygen to give a benzoate ion and a phosphonium acylate ion which exist most probably as an ion pair VI. Collapse of VI gives the anhydride IIA and III. Further confirmation of this mechanism has been found by running the reaction in the presence of p-nitrobenzoate ion; under these conditions a mixture of anhydrides is formed.

The reaction of benzoyl peroxide (I) with triphenylphosphine to give benzoic anhydride (II) and triphenylphosphine oxide (III) was first discovered by Challenger and Wilson.[2] Later Schönberg[3] showed that dibenzoyl disulfide would react with triphenylphosphine to give dibenzoyl sulfide and triphenylphosphine sulfide. More recently Horner and Jurgeleit[4] have made a thorough study of the reactions of several types of peroxy compounds with trisubstituted phosphines. In general, these compounds react to give the phosphine oxide, and, for example, alcohols from hydroperoxides, ethers from alkyl peroxides and acids from peracids, etc. The reaction of acyl and aroyl peroxides with trisubstituted phosphines proceeds rapidly at room temperature in solvents such as pentane or ether. A free radical mechanism for these reactions does not seem likely as (1) there is no attack on solvent, (2) the products of the reactions do not correspond to those of the known radical decompositions of the peroxides, and (3) it has been shown that foreign ions in the medium can enter into the reaction. Horner has proposed that these reactions proceed by displacement on oxygen by the phosphine to give a phosphonium ion and an anion which can then combine to give the product and the phosphine oxide. Since the reactions of acyl peroxides proceed rapidly in non-polar solvents, conditions which are unfavorable for ionic reactions, it was decided to initiate an investigation which would determine how free any formed ions were, if indeed any ions were formed at all.

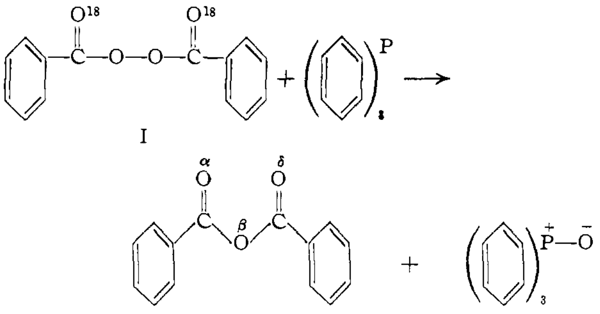
Benzoyl peroxide-carbonyl-O^{18} (I) was prepared according to the method of Doering and Greenbaum.[5] When I was allowed to react with triphenylphosphine, benzoic anhydride (II) containing all of the excess oxygen-18 was formed. The triphenylphosphine oxide (III) contained oxygen-18 corresponding to normal isotopic abundance. Table I summarizes the oxygen-18 analytical data.

TABLE I

OXYGEN-18 ANALYTICAL DATA[a]

Compound	Atom % oxygen-18 Found	Calcd. IIA	IIB	IIC
Benzoyl peroxide (I)[b]	3.42, 3.42			
Benzoic anhydride (II)	3.16, 3.16[c]	3.22	3.22	3.22
Triphenylphosphine oxide (III)	0.21, 0.21	0.20	0.20	0.20
Benzamide (IV)	1.15, 1.16	1.16	1.48	0.84
Benzoic acid (V)	2.00, 1.98	2.00	1.68	2.32

[a] Analyses were performed by the method of W. E. Doering and E. Dorfman, THIS JOURNAL, **75**, 5595 (1953). Normal isotopic abundance of oxygen-18 was taken as 0.204 atom %. [b] Each carbonyl oxygen of I contained 1.51 atom % oxygen-18; the peroxidic oxygens each had 0.20 atom %, *i.e.*, normal isotopic abundance. [c] In converting I to II, 0.26 atom % oxygen-18 was lost. III has normal abundance, 0.20 atom %, so 0.06 atom % cannot be accounted for. In calculating the distributions for IIA, B and C the found value for II was used. The mechanisms proposed lead quite simply to the calculated distributions.



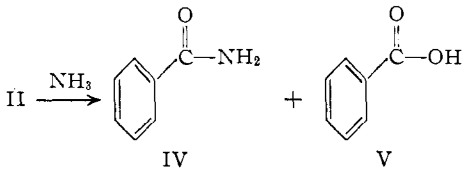
I

III

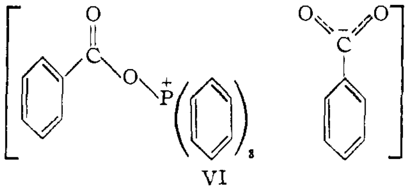
IIA, $\alpha = O^{18}$; $\beta = \gamma = \frac{O^{18}}{2}$

B, $\alpha = O^{18}$; $\beta = O^{16}$; $\gamma = O^{18}$

C, $\alpha = O^{18}$; $\beta = O^{18}$; $\gamma = O^{16}$



IV V



VI

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[1] Requests for reprints should be sent to D. B. Denney, School of Chemistry, Rutgers University, New Brunswick, N. J.

[2] F. Challenger and V. Wilson, *J. Chem. Soc.*, 209 (1927).

[3] A. Schönberg, *Ber.*, **68**, 163 (1935).

[4] L. Horner and W. Jurgeleit, *Ann.*, **591**, 138 (1955).

[5] W. E. Doering and M. A. Greenbaum unpublished work from the Sterling Chemistry Laboratory, Yale University. The carbonyl labeled benzoyl peroxide was prepared by the reaction of sodium peroxide with carbonyl labeled benzoyl chloride. That all of the excess oxygen-18 is in the carbonyl groups of the peroxide has been demonstrated by Doering and Greenbaum by conversion of the peroxide to methyl benzoate with sodium methoxide. Analysis of the ester indicated complete retention of the oxygen-18 in the carbonyl groups.

Clearly these results eliminate any mechanism which requires the transfer of a carbonyl oxygen to the phosphorus atom with formation of III. Such a mechanism might have been an SN2′ type of attack on the carbonyl oxygen. Having established that peroxidic oxygen is found in the phosphine oxide, attention was directed to an elucidation of the distribution of the oxygen-18 in II. Three possibilities were considered as represented by IIA, IIB and IIC. In IIA, the α-oxygen contains the original amount of oxygen-18 while the β- and γ-oxygens contain equal amounts, *i.e.*, each has half of the remaining oxygen-18. Such an anhydride could arise through an ion pair exemplified by VI. Formation of VI would proceed by nucleophilic displacement on oxygen by the phosphine to give the benzoate ion and the phosphonium ion. Since the two oxygens of the benzoate ion in VI are equivalent, collapse leads to IIA and III. IIB, in which the α- and γ-oxygens are oxygen-18, could arise by displacement on oxygen by the phosphine. As the displacement occurs the benzoate group could then migrate to the adjacent carbonyl carbon yielding in a concerted reaction IIB and III. IIC could arise by a similar process. However, in this case the carbonyl oxygen of the benzoate being displaced would attack the carbonyl carbon through a quasi five-membered ring to become the ether oxygen of II. These three possibilities lead to three different positional distributions of oxygen-18 in II (see Table I). In order to ascertain the oxygen-18 distribution in II, it was treated with liquid ammonia to give benzamide (IV) and benzoic acid (V). It has been shown that in this reaction all of the carbonyl oxygen in IV was carbonyl oxygen in the starting anhydride.[6] The analytical data on IV and V completely rule out IIB and IIC as the structures of the anhydride and moreover point unequivocally to IIA as the correct structure. Any mechanism which is used to account for the formation of II must then lead to the oxygen-18 distribution shown by IIA. An ion pair such as VI, which is formed as discussed earlier, is in complete agreement with these results. The collapse of VI most probably proceeds by displacement on the carbonyl carbon of the phosphonium benzoylate ion by the benzoate ion. The rate of this collapse will be dependent to a large degree on the polarity of the solvent in which it is formed. In solvents such as pentane or ether this collapse will be quite rapid as compared to more polar solvents.

In order to test this ion-pair hypothesis, it was decided to run the reaction in the presence of *p*-nitrobenzoate ion. In this reaction the solvent was the more polar chloroform. When I was treated with triphenylphosphine in chloroform in the presence of an equivalent quantity of trimethylammonium *p*-nitrobenzoate, the crude product was a mixture of anhydrides which contained nitrogen in an amount which leads to a calculated ratio of 1.2 moles of benzoic anhydride to 1.0 mole of *p*-nitrobenzoic benzoic anhydride. It was shown also that benzoyl peroxide did not undergo exchange with *p*-nitrobenzoate ion under these conditions. Benzoic anhydride does exchange with *p*-nitrobenzoate ion, but under comparable conditions the ratio of anhydrides isolated is 21 moles of benzoic anhydride to 1 mole of *p*-nitrobenzoic benzoic anhydride. In the solvent chloroform, then, the ion-pair is "loose" enough so that a foreign anion can intervene to a large degree and alter the nature of the product. These findings are what would be expected when a salt like VI is dissolved in a solvent such as chloroform.

Analogous mechanisms can be written for the decomposition of other peroxy compounds by trisubstituted phosphines. Of particular interest is the mode of decomposition of the intermediate ions or ion-pairs formed in these reactions, and experiments designed to shed further light on these processes are in progress.

Experimental[7]

Benzoyl Peroxide-carbonyl-O^{18} (I) and Triphenylphosphine.—Benzoyl peroxide-carbonyl-O^{18}, 2.70 g. (0.011 mole), was dissolved in 500 ml. of warm pentane; to this solution there was added a solution of 2.90 g. (0.011 mole) of triphenylphosphine in 150 ml. of pentane. After standing for one hour, the solution was concentrated on a steam-bath to 150 ml. The triphenylphosphine oxide was removed by filtration and the solution was evaporated to give an oil which crystallized on cooling and scratching. The solid was crystallized from petroleum ether (60–90°) to give 1.05 g. (42%) of benzoic anhydride (II), m.p. 41–42°. The crude triphenylphosphine oxide was crystallized from benzene–petroleum ether (60–90°) to afford 2.10 g. (69%), m.p. 154–155°.

Benzoic Anhydride (II) and Ammonia.—To 20 ml. of liquid ammonia there was added 0.41 g. (0.00181 mole) of labeled II. The mixture was swirled until all of the anhydride had dissolved, and then the ammonia was allowed to evaporate. The residue was treated with 5 ml. of 10% sodium bicarbonate solution. The resulting mixture was extracted with three 5-ml. portions of chloroform. The chloroform extracts were dried over magnesium sulfate. Evaporation of the solvent *in vacuo* afforded 0.18 g. (84%) of benzamide, m.p. 127–129°. Recrystallization from methanol–water yielded 0.14 g. of benzamide, m.p. 129.5–130°.

The basic extracts were acidified and extracted with two 10-ml. portions of ether. The ether was dried over magnesium sulfate and then evaporated to yield 0.18 g. (84%) of benzoic acid, m.p. 112–115°. Recrystallization from hexane afforded 0.15 g., m.p. 121–122°.

Benzoyl Peroxide and Triphenylphosphine in the Presence of *p*-Nitrobenzoate Ion.—To a solution of 1.21 g. (0.0050 mole) of benzoyl peroxide and 1.13 g. (0.0050 mole) of trimethylammonium *p*-nitrobenzoate in 30 ml. of chloroform, which had been dried over calcium chloride, there was added 1.50 g. (0.0057 mole) of triphenylphosphine. The solution became warm, *ca.* 50°. After standing for 5 min., it was poured into 20 ml. of 5% sodium bicarbonate solution. The chloroform solution was washed with 10 ml. of water and dried over magnesium sulfate. The chloroform was evaporated to afford 2.63 g. of an oily solid. Infrared analysis of this material showed a peak at 1531 cm.$^{-1}$, which is characteristic of the nitro group. The rest of the spectrum was in agreement with that expected for a mixture of anhydrides and triphenylphosphine oxide.

Anal. Found: N, 1.04.

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[6] In an early experiment, II was treated with aniline in ether to give benzanilide and benzoic acid. Analysis of these compounds indicated that all of the oxygens of II were equally labeled. Since such a distribution is mechanistically infeasible, an unsymmetrically labeled benzoic anhydride was prepared by an independent method. Treatment of this anhydride with aniline in ether again yielded products which, upon analysis, indicated that all of the oxygens were equivalent. Treatment with liquid ammonia yielded products which analyzed correctly for the predicted distribution of oxygen-18 in the anhydride. Clearly the reaction of the anhydride with aniline is following a different course than the reaction with ammonia. For a further discussion of these observations see an article by D. B. Denney and M. A. Greenbaum, THIS JOURNAL, **78**, 877 (1956).

[7] Analyses by W. Manser, Zurich, Switzerland.

If the assumption is made, in accordance with the stoichiometry of the reaction, that this mixture contains 0.19 g. of triphenylphosphine and 1.39 g. of triphenylphosphine oxide, then the residue, 1.05 g. contains 2.6% nitrogen. If it is then further assumed that this residue is a mixture of benzoic and benzoic *p*-nitrobenzoic anhydrides, then of this mixture 1.2 mole is benzoic anhydride and 1.0 mole is benzoic *p*-nitrobenzoic anhydride.

Benzoic Anhydride and Triphenylphosphine in the Presence of *p*-Nitrobenzoate.—To a mixture of 0.50 g. of triphenylphosphine and 1.13 g. (0.005 mole) of benzoic anhydride in 30 ml. of dry chloroform at a temperature of 50°, there was added 1.13 g. (0.005 mole) of trimethylammonium *p*-nitrobenzoate. The solution was allowed to stand for 5 min. and then poured into 20 ml. of 5% sodium bicarbonate solution. The chloroform was further extracted with 10 ml. of water and then dried over magnesium sulfate. The chloroform was evaporated to yield 1.60 g. of material which partially crystallized. Infrared analysis showed a small peak at 1531 cm.$^{-1}$.

Anal. Found: N, 0.19.

If we assume that of the 1.60 g. recovered 0.50 g. is triphenylphosphine then the remaining 1.10 g. contains 0.28% nitrogen, which using the reasoning applied above, indicates that the mixture contains 21 moles of benzoic anhydride to 1 mole of benzoic *p*-nitrobenzoic anhydride.

Benzoyl Peroxide and *p*-Nitrobenzoate Ion.—A solution of 1.21 g. (0.005 mole) of benzoyl peroxide and 1.13 g. (0.005 mole) of trimethylammonium *p*-nitrobenzoate in 30 ml. of chloroform was allowed to stand for two hours. The mixture was then extracted with two 10-ml. portions of 10% sodium bicarbonate solution followed by 10 ml. of water. The chloroform solution was dried over magnesium sulfate and the solvent was removed *in vacuo*. Infrared analysis of the resulting white solid showed the absence of the nitro group band at 1531 cm.$^{-1}$. The material was crystallized from chloroform–methanol to yield 0.95 g. (78%) of benzoyl peroxide, m.p. 103.5–104°.

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[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, TEXTILE FIBERS DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO., INC.]

Preparation and Pyrolyses of Some Organophosphonates

BY LUTHER A. R. HALL AND C. WAYNE STEPHENS

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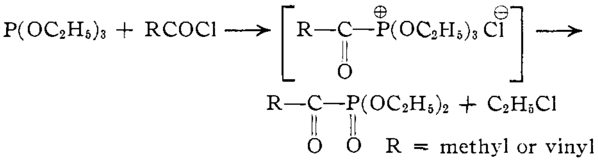
Acyl phosphonates were prepared by the reaction of acyl halides and a trialkyl phosphite. Unexpected molecular weight observations on the products as well as an infrared study of by-products of the preparative reaction are discussed. The pyrolyses of diethyl 1-cyano-1-hydroxyethylphosphonate and 1,1-bis-(diethylphosphono)-ethyl acetate lead to excellent yields of acrylonitrile and acetic acid, respectively.

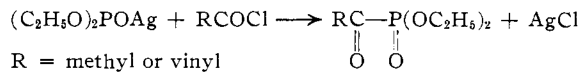
The reaction of acetyl chloride with triethyl phosphite in the Arbuzov reaction to yield diethyl acetylphosphonate has been reported along with the preparation of a cyanohydrin derivative.[1] It was desired to extend the Arbuzov reaction, which can be employed to prepare either alkyl- or acylphosphonates, to the preparation of unsaturated alkyl- or acylphosphonates.



$$P(OC_2H_5)_3 + RCOCl \longrightarrow \left[R-\underset{\underset{O}{\|}}{C}-\overset{\oplus}{P}(OC_2H_5)_3\overset{\ominus}{Cl} \right] \longrightarrow R-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{P}(OC_2H_5)_2 + C_2H_5Cl$$

R = methyl or vinyl

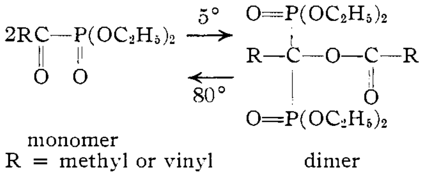
The acylphosphonates possess an active carbonyl group which can undergo many of the normal carbonyl reactions including formation of hydrazones with materials such as 2,4-dinitrophenylhydrazine.[1c] The phosphonates above can also be prepared by the procedure



$$(C_2H_5O)_2POAg + RCOCl \longrightarrow R\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{P}(OC_2H_5)_2 + AgCl$$

R = methyl or vinyl

The α-ketophosphonates prepared exhibited molecular weight properties which indicated that they could exist in an equilibrium between a monomeric and a postulated dimeric form. Other materials such as acetyl cyanide (pyruvonitrile) are known to form dimers easily. In the case of α-ketophosphonates the equilibrium is apparently reversible.

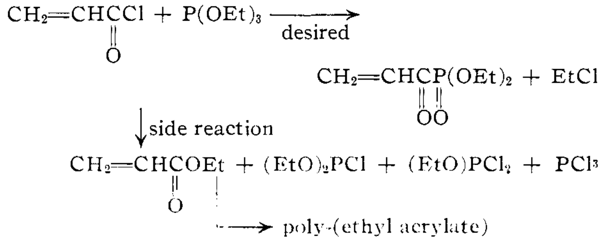


$$2R\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{P}(OC_2H_5)_2 \underset{80^\circ}{\overset{5^\circ}{\rightleftarrows}} R-\overset{O=P(OC_2H_5)_2}{\underset{O=P(OC_2H_5)_2}{C}}-O-\underset{\underset{O}{\|}}{C}-R$$

monomer
R = methyl or vinyl dimer

The molecular weight of these compounds taken by a cryoscopic method in benzene at 5° showed them both to be essentially dimers, while ebullioscopic molecular weights in benzene at 80° indicated them to be all or largely monomeric. It is presumed that at room temperature they exist as some mixture of the two forms. Attempts to dimerize diethyl acetylphosphonate deliberately using alkaline catalyst were unsuccessful, however.

While the preparation of diethyl acrylylphosphonate was relatively straightforward, the same method applied to the formation of diethyl acrylylphosphonate led to a rather large variety of products including the desired one. A possible side reaction that could occur in the reaction of acrylyl chloride and triethyl phosphite is



$$CH_2=CH\underset{\underset{O}{\|}}{C}Cl + P(OEt)_3 \xrightarrow[\text{desired}]{} CH_2=CH\underset{\underset{O}{\|}}{C}\underset{\underset{O}{\|}}{P}(OEt)_2 + EtCl$$

$$\downarrow \text{side reaction}$$

$$CH_2=CH\underset{\underset{O}{\|}}{C}OEt + (EtO)_2PCl + (EtO)PCl_2 + PCl^3$$

$$\longrightarrow \text{poly-(ethyl acrylate)}$$

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[1] (a) M. I. Kabachnik and P. A. Rossiiskaya, *Bull. Acad. Sci. U.R.S.S., Classe Sci. Chim.*, 364 (1945); *C. A.*, **40**, 4688 (1946); (b) M. I. Kabachnik, P. A. Rossiiskaya and E. S. Shepeleva, *ibid.*, 163 (1947); *C. A.*, **42**, 4133 (1948); (c) A. E. Arbuzov and M. M. Azanovskaya, *Doklady Akad. Nauk. S.S.S.R.*, **58**, 1961 (1947); *C. A.*, **46**, 8606 (1952).