

clear colorless oil, b.p. 50–52° (0.2 mm.) (5.0 g., 16%). Pinacol (3.5 g., 19%) was also recovered.

The Carbonylation of Triethylborane in Pentaerythritol.—The bomb was charged with pentaerythritol (39.0 g., 0.287 mole), ethanol (100 ml.) and triethylborane (60.0 g., 0.612 mole). The temperature was maintained at 50° for 30 minutes at a maximum carbon monoxide pressure of 670 atm. The temperature was then maintained at 150° for 2 hours at a maximum pressure of 890 atm. The bomb was cooled and washed with ether, and the resulting solution was concentrated. The solid residue was recrystallized twice from ethanol to give the spiro bicyclic pentaerythritol ester of triethylcarbonylboronic acid as white plates, m.p. 76–76.8° (49.3 g., 49%).

The Peroxide Oxidation of the Ethylene Glycol Ester of Triethylcarbonylboronic Acid.—A mixture of the ethylene glycol ester of triethylcarbonylboronic acid (70.1 g.), 6*N* aqueous sodium hydroxide (84 ml., 30% excess) and 30% hydrogen peroxide (66 ml., 60% excess)⁶ was refluxed for 2 hours, cooled, and extracted with ether. The combined ether layers were dried, concentrated, and distilled to give triethylcarbinol as a clear colorless liquid, b.p. 140–142° (39.1 g., 82%).

(6) The hydrogen peroxide should be added dropwise to a mixture of the boron compound and aqueous sodium hydroxide. The temperature should be kept below 50° during the addition, then the well stirred mixture brought slowly to reflux.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, EMORY UNIVERSITY, ATLANTA 22, GA.]

Kinetics of Autoxidation of Trialkylphosphines

BY M. B. FLOYD¹ AND C. E. BOOZER²

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The kinetics of the autoxidation of tributylphosphines in *o*-dichlorobenzene have been studied by oxygen consumption measurements. The data indicate that the reaction involves the concurrent autoxidation of intermediate phosphinite esters. Tributyl phosphite was found to undergo autoxidation at a rate slower than that of tributylphosphine by a factor of at least 1.5. The data reveal that the reaction requires free radical initiation, which in this study was supplied by azobisisobutyronitrile. The autoxidation is a relatively long chain process with a very small activation energy.

Introduction

A recent investigation by Buckler has elucidated many of the important features of trialkylphosphine autoxidation.³ For example, tributylphosphine in hexane was oxidized by air to a mixture of products identified as tributylphosphine oxide (42%), butyl dibutylphosphonate (49%), dibutyl butylphosphinate (6%) and tributyl phosphate (3%). A mechanism for the reaction was suggested on the basis of a detailed study of the products resulting from different reaction conditions. We wish to report the results of a kinetic study of the azobisisobutyronitrile (AIBN) initiated autoxidation of tributylphosphine, tributyl phosphite and triphenylphosphine in *o*-dichlorobenzene. Our data are compatible with the previously suggested mechanism and in addition provide some other facts regarding the reaction.

Results

Three experiments at 50.6° with *o*-dichlorobenzene as solvent showed that the total oxygen uptake for tributylphosphine was constantly 1.55 gram atoms of oxygen per mole of phosphine to within less than 0.5%. Isolation of the products corresponding to these conditions disclosed that two major products, tributylphosphine oxide and butyl dibutylphosphonate, are formed, in agreement with the work of Buckler.³ The kinetics of this autoxidation were studied at temperatures between 38.0° and 60.0° by following oxygen consumption with time. The solvent used in this study, *o*-dichlorobenzene, was chosen because its low vapor pressure and its relatively inert behavior toward autoxidation reactions make it suitable for kinetic studies of this type. The action of AIBN as a reliable free radical initiator is well known.⁴ The effect on the rate of initial substrate concentration, initiator concentration, oxygen pressure and the concentration of two inhibitors was studied. The dependency of the pseudo-first-order rate constant at 50.6° on initiator concentration is shown in Fig. 1. Two features of the reaction are immediately apparent from this plot. The zero

intercept suggests that the reaction requires radical initiation. In practice such initiation could be provided by the presence of trace amounts of impurities, leading to the well documented observation that trialkylphosphines are spontaneously oxidized by air. The second feature is the first-order dependence on the added initiator, which is usually found in radical chain processes involving unimolecular termination.⁵

Variation of oxygen pressure above the reaction solutions showed a curious effect. In the region from 740 mm. to about 200 mm., the observed pseudo-first-order rate constant was inversely proportional to the pressure. This effect is demonstrated in Table I, where the rate constant is shown to be constant with the constant ratio $[AIBN]/P_{O_2}$.

TABLE I

AUTOXIDATION OF TRIBUTYLPHOSPHINE		
[AIBN]/ P_{O_2} = constant = 8.44×10^{-6} mole/l. \times mm., $T = 49.0^\circ$, $[(C_4H_9)_3P]_0 = 4.00 \times 10^{-2}$		
[AIBN] $\times 10^2$	P_{O_2} ^a	$k \times 10^4$, sec. ⁻¹
6.25	740	5.51
5.00	592	5.18
3.75	444	5.25
2.50	296	4.96

^a All pressures reported are corrected for vapor pressure of solvent.

The reaction is first order in tributylphosphine. At 50.6° with $[AIBN] = 9.08 \times 10^{-3}$ and initial concentrations of substrate ranging from 3.65×10^{-2} to 16.4×10^{-2} molar, eight runs disclosed that the pseudo-first-order rate constant showed no variable trends. With the oxygen pressure equal to 740 mm., this constant was 1.38×10^{-4} sec.⁻¹. The mean deviation was less than 10% of this constant.

The results of these experiments may be summarized by a kinetic equation in the form

$$-\frac{dO_2}{dt} = \frac{k[AIBN][(C_4H_9)_3P]}{P_{O_2}}$$

It should be mentioned that all kinetic runs were made under conditions which ensured that the reaction was kinetically controlled rather than diffusion controlled, throughout the entire duration of the experiment.

(5) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 418.

(1) From the M.S. Thesis of M. B. Floyd, 1961.

(2) Alfred P. Sloan Foundation Fellow.

(3) S. A. Buckler, *J. Am. Chem. Soc.*, **84**, 3093 (1962).

(4) (a) F. M. Lewis and M. S. Matheson, *ibid.*, **71**, 747 (1949); (b) C. G. Overberger, M. T. O'Shaughnessy and M. Shalit, *ibid.*, **71**, 2661 (1949); (c) M. Talot-Erben and S. Bywater, *ibid.*, **77**, 3712 (1955).

If in the early stages the rate of oxygen consumption was limited by the rate of diffusion into solution rather than by the true chemical rate, an anomalously high rate was found in the later stages of kinetic control. This observation is in keeping with the fact that the rate was found to be inversely proportional to oxygen pressure.

In the temperature range from 38.0 to 60.0° no induction period was observed with AIBN initiation. On the contrary, the rate of oxygen consumption in the initial stages was more rapid than in the latter. The oxygen consumption data were plotted according to the method of Guggenheim,⁶ and the slope of the line drawn through points corresponding to the latter stages of the reaction was used in calculating pseudo-first-order rate constants. The points in this region described a straight line out to at least 90% reaction.

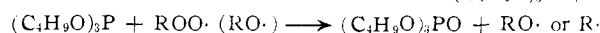
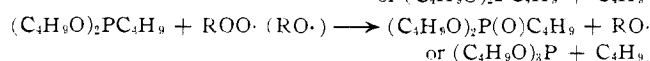
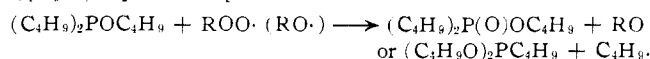
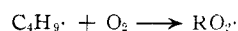
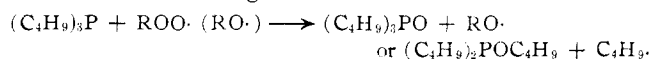
In a manner similar to the above, the kinetics of the reaction of tributyl phosphite with oxygen were studied. Walling and Rabinowitz have noted that triethyl phosphite is capable of undergoing a radical chain process with oxygen, yielding triethyl phosphate.⁷ In our experiments tributyl phosphite showed the expected stoichiometry since it consumed one gram atom of oxygen per mole of phosphite to within less than 5%. This reaction was also found to be first order in substrate and in AIBN. The rate of tributylphosphine oxidation was faster than the corresponding phosphite by a factor of about 1.5, as shown in Table II.

TABLE II
HYPOTHETICAL RATE CONSTANTS
[AIBN] = 1.0, p_{O_2} = 740 mm.

T , °C.	$k \times 10^4$, sec. ⁻¹	T , °C.	$k \times 10^4$, sec. ⁻¹
Tributylphosphine		Triphenylphosphine	
38.0	1.63	60.0	16.8
49.0	9.20	70.0	62.3
50.6	14.7	Tributyl phosphite	
60.0	57.2	70.0	100
70.0	153 ^a		

^a Extrapolated value.

This fact serves to explain the initial rapidity of oxygen consumption in the phosphine autoxidation. At first, the only trivalent phosphorus compound undergoing autoxidation is the phosphine itself. According to the work of Buckler,³ phosphinite esters are intermediates in this reaction and are also susceptible to autoxidation. Therefore, in the later stages of a given oxidation of tributylphosphine the following reactions are occurring



The first two of these reactions occur to the greatest extent, resulting in the major products tributylphosphine oxide and butyl dibutylphosphonate. Our rate constant for tributylphosphine autoxidation corresponds to the situation described by the above reactions. Since this constant is about 1.5 times as fast as that for the phosphite alone, it may be inferred that the relative reactivity of the trivalent compounds toward alkoxy or peroxy radicals decreases in the order $(C_4H_9)_3P > (C_4H_9)_2POC_4H_9 > (C_4H_9O)_2PC_4H_9 > (C_4H_9O)_3P$. Due to problems involving equilibration of

(6) E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

(7) C. Walling and R. Rabinowitz, *J. Am. Chem. Soc.*, **81**, 1243 (1959).

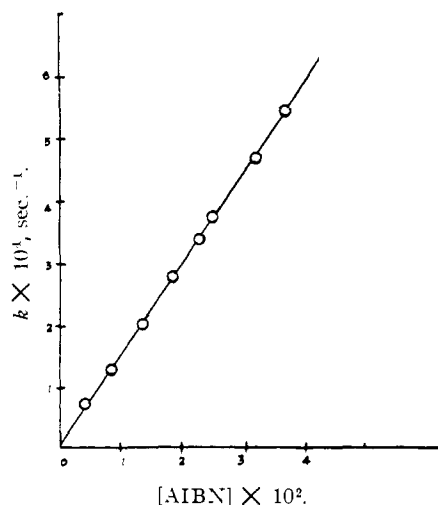
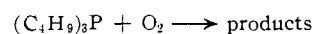


Fig. 1.—Rate of AIBN initiated autoxidation of tributylphosphine; $T = 50.6^\circ$, $p_{O_2} = 740$ mm.

the kinetic apparatus, it was not possible to obtain reliable values for a rate constant corresponding to time zero in the phosphine autoxidation. This would be the true rate constant for the reaction



Our empirical rate constants for the autoxidation of tributylphosphine, therefore, necessarily represent a composite of the constants for several species. If the linearity of our kinetic plots in the later stages of the reaction is an indication of a static ratio of concentrations of the trivalent phosphorus species, then a quasi steady state situation may be said to apply.

The data presented in Table II summarize the effect of temperature on the rate of reaction of all of the compounds studied. The rate constants depicted in this table are for the hypothetical situation where [AIBN] is unity, obtained by calculating the slope of rate constant *vs.* [AIBN] plots similar to Fig. 1. These data were used to determine the activation energies for the autoxidation of tributyl- and triphenylphosphine. The latter compound was studied with a procedure identical with that described above for the sake of comparison. The results are summarized in Table III.

TABLE III
RATE OF AIBN INITIATED AUTOXIDATION OF TRIPHENYLPHOSPHINE AT $T = 60.0^\circ$

$[(C_6H_5)_3P]_0$ $\times 10^3$, moles/l.	[AIBN] $\times 10^2$, moles/l.	p_{O_2}	$k \times 10^4$, sec. ⁻¹
8.05	5.00	740	6.78
4.83	5.00	740	8.50
3.22	5.00	740	10.6
1.61	5.00	740	11.8
4.83	6.25	740	9.43
4.83	5.00	740	8.50
4.83	4.38	740	7.23
4.83	3.75	740	6.12
4.83	2.50	740	4.22
4.83	1.88	740	3.18
3.22	5.00	740	10.6
3.22	5.00	650	11.4
3.22	5.00	580	12.0
3.22	5.00	520	11.9

An Arrhenius plot was made for tributylphosphine. The observed activation energy calculated from this is 29.8 kcal./mole. Using a value of 30.5 kcal./mole for the activation energy of AIBN decomposition in *o*-dichlorobenzene,⁸ and the relation

(8) C. E. Boozer, unpublished results.

$$E_p = E_{obs} - \frac{1}{W}(E_i - E_t)$$

an activation energy very close to zero is found for the chain propagation steps⁹; E_t is the activation energy for chain termination and W is the order of the termination process with respect to radical species. Here it is fairly safe to assume that E_t is virtually zero, and the first-order dependency of rate on initiator concentration suggests that W is unity.

Several kinetic runs were made employing known free radical inhibitors, either chloranil or 2,6-di-*t*-butyl-*p*-cresol with the usual reaction charge. Neither of these inhibitors was very effective in halting the reaction. For example, the presence of 2,6-di-*t*-butyl-*p*-cresol to the extent of 10 mole per cent of tributylphosphine only retarded the rate, with no discernible inhibition period. In concentrations of inhibitor between 1 and 10% of the phosphine concentration, the observed rate constant was inversely proportional to the square root of the inhibitor concentration. Chloranil, surprisingly, exhibited a similar effect, as shown in Fig. 2.

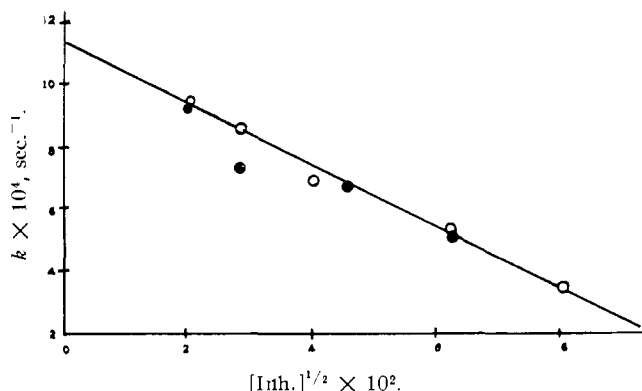


Fig. 2.—Action of inhibitors on autoxidation rate of tributylphosphine; $[AIBN] = 2.00 \times 10^{-2}$, $T = 60.0^\circ$; O, for 2,6-di-*t*-butyl-*p*-cresol; ●, for chloranil.

The autoxidation of tributylphosphine has been shown to proceed more slowly in aromatic solvents than in aliphatic solvents.³ However, even in the solvent *o*-dichlorobenzene used in this study the chain length is fairly large. At 50.6° using a solution 0.165 molar in tributylphosphine and 9.08×10^{-3} molar in AIBN an observed rate constant of 1.40×10^{-4} sec.⁻¹ was obtained. An approximate chain length under these conditions may be written as

(9) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 244.

$$= k_{obs} [(C_4H_9)_3P]_0 / 2ak_i [AIBN]$$

According to decomposition studies of AIBN carried out in this Laboratory the rate constant k_i at 50.6° is 3.2×10^{-6} sec.⁻¹.⁸ The efficiency a may be taken as 0.6.¹⁰ This gives a chain length of between 10^2 and 10^3 . Therefore the autoxidation of trivalent organophosphorus compounds in solution is quite facile in comparison to autoxidation of most other substrates including hydrocarbons which have been the subject of much study.

Experimental

Materials.—Tributylphosphine from Metal and Thermit was distilled through a spinning band column. A center cut, b.p. 75° (2 mm.), was used in kinetic runs. The compound was stored in a flask suitable for withdrawing small samples under nitrogen. Triphenylphosphine from Metal and Thermit was recrystallized from 95% ethanol and dried in a vacuum desiccator over Drierite; m.p. $81-81.5^\circ$. For the purpose of kinetic runs a solution of the phosphine in *o*-dichlorobenzene was prepared and stored under nitrogen. Suitable volumes of this solution were withdrawn for each run. Azobisisobutyronitrile (AIBN) from K. and K. Laboratories was recrystallized from benzene; m.p. $104-106^\circ$. For the purpose of the kinetic runs small quantities of a 0.250 *M* solution in *o*-dichlorobenzene were prepared at intervals. Such solutions were stored at room temperature and were discarded if the duration of storage exceeded two weeks. Eastman practical grade tributyl phosphite was distilled through the spinning band column (b.p. $117-119^\circ$ 7 mm.) and stored under nitrogen. Eastman best grade of *o*-dichlorobenzene was dried and stored over silica gel. U.S.P. oxygen was passed through Drierite for kinetic runs.

Kinetic Runs.—The kinetics of oxygen uptake were studied in an apparatus similar to that described by Bolland.¹¹ Reactions were run at constant pressure. Pressure changes in the system were detected by a photoelectric device using a Clairex CL-3 photocell mounted near a manometer which was installed between reaction vessel and a thermostated reference pressure. With the photoelectric relay closed, an electrolysis cell containing oxalic acid generated sufficient CO_2 to force the oil level in a calibrated buret to rise until the system was restored to the reference pressure. The cycle was repeated about twice a minute. A rheostat in series with the power line supplying the cell aided in controlling the rate of CO_2 evolution. The thermostated buret just described was calibrated to 0.05 cc. Readings are considered accurate to ± 0.01 cc. The thermostated reaction vessels were jacketed distillation receivers of about 25-cc. capacity. A magnetic stirrer was used for agitation of the reaction mixtures. The temperature of the thermostat was controlled to $\pm 0.05^\circ$.

Reagents were handled with hypodermic syringes. After placing solvent and substrate in the reaction vessel, the system was alternatively evacuated and filled with oxygen three times. Thermostated water was then routed through the jacket of the vessel. After 5 minutes initiator solution was introduced. This addition was defined as time zero. About 5 minutes elapsed before reliable buret readings could be obtained. Control experiments with the apparatus were performed to ensure that oxygen consumption from the reaction under study was the only factor responsible for movement of oil in the buret. The total volume of solutions used was 10 cc.

(10) G. S. Hammond, J. N. Sen and C. E. Boozer, *J. Am. Chem. Soc.*, **77**, 3244 (1955).

(11) J. L. Bolland, *Proc. Roy. Soc. (London)*, **A186**, 218 (1948).