[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Acid Catalysis and the Mechanism of Decomposition of Bis-phenylacetyl Peroxide[1]

BY PAUL D. BARTLETT AND JOHN E. LEFFLER

Bis-phenylacetyl peroxide (I) decomposes slightly faster at 0° than benzoyl peroxide does at 70°. We investigated it originally in the hope that it might prove a useful initiator for low-temperature polymerization, and to learn the reason for its great instability.

Products of Decomposition.—Bis-phenylacetyl peroxide was decomposed in toluene, in carbon tetrachloride and in *o*-chlorotoluene. The kinetic experiments were done in toluene, as were most of the examinations of products. The products found, in order of importance, were carbon dioxide, dibenzyl, phenylacetic acid and benzyl phenylacetate. Although in toluene some products containing the benzyl group must have arisen from attack of free phenylacetoxyl radicals upon the solvent, there were no corresponding chlorine-containing products found when the peroxide was decomposed in *o*-chlorotoluene. The isolation of products was not quantitative. Some of the results are shown in Table I.

TABLE I

PRODUCTS ISOLATED FROM DECOMPOSITION OF BIS-PHENYLACETYL PEROXIDE

Initial peroxide mole/liter	Solvent	Substance added	% of peroxide accounted for as Dibenzyl	Phenylacetic acid	Benzyl phenyl acetate	Benzyl iodide	Benzaldehyde	Total % accounted for
0.088	Toluene	None	47	31	22	...	..	69^a
.131	Toluene	Oxygen	..	15.1	33	...	53	86^a
.336	CCl_4	None	12	1.0	24	...	..	37
.21	CCl_4	Iodine[2]	23	..	5.7	3.8	..	32.5

[a] Calculated with the assumption that the phenylacetic acid formation gave rise to benzyl radicals from the solvent.

Except for the lack of products clearly arising from interaction with the solvent, the results are similar enough to those in the case of benzoyl peroxide to suggest a similar mechanism, involving initial decomposition into phenylacetate radicals, their decarboxylation to benzyl radicals, and combination of these with one another. The appearance of benzaldehyde instead of dibenzyl in the presence of oxygen would also be consistent with the interception of benzyl or phenylacetoxyl radicals efficiently by oxygen.

Decomposition in Styrene.—The phenylacetyl peroxide from 5.2 g. of phenylacetyl chloride, dissolved at 0° in 50 cc. of styrene, yielded 3 cc. of viscous residue insoluble in methanol after evaporation of the styrene. Calculations from the data of Cohen[3] show that the yield of polystyrene would be only 4.7 g. with 100% efficiency in the generation of free radicals by the peroxide at 0°. This is a result of the extent to which the kinetic chain length in styrene polymerization decreases with lowering of the temperature. Because the amount of polymer produced is so small relative to the amount of peroxide used, and because of the difficulty of separating the products of peroxide decomposition, this experiment yields no definite conclusions as to the extent of production of free radicals from this peroxide.

Fieser Alkylation with Bis-phenylacetyl Peroxide.—Lawsone (2-hydroxy-1,4-naphthoquinone) was converted in 17% yield into 3-benzyl-2-hydroxynaphthoquinone,[4] m. p. 177–178.6°, by bis-phenylacetyl peroxide in glacial acetic acid at the freezing point.

Kinetics of Decomposition.—The decomposition of bis-phenylacetyl peroxide in toluene in any run appears to be closely of the first order (Fig. 1) but the unimolecular rate constant is a linear function of the square root of the initial peroxide concentration (Fig. 2). This curious behavior was traced to an accelerating effect of one of the reaction products, of which only phenylacetic acid, when added separately, proved to be a catalyst for the decomposition. Thus the peroxide decomposition involves, as in the case of benzoyl peroxide,[5] simultaneous first and three-halves order reactions, the decline in rate with time being roughly counteracted by an autocatalysis. Nevertheless, as Fig. 2 shows, the three-halves order part of the rate, presumably representing radical-induced decomposition, is not great enough to account for the high rate of reaction, the apparently spontaneous part being still enormously faster than for simple acyl peroxides. Likewise, no inhibitor has been found which will substantially reduce the rate of decomposition, oxygen, styrene, trinitrobenzene, anthracene and acenaphthene having been tried. Acenaphthene, far from being an inhibitor, increased the rate of decomposition and suppressed the formation of phenylacetic acid, so that in the

---

(1) From a thesis presented by John E. Leffler for the degree of Ph.D. at Harvard University, 1948; presented in part at a symposium of the Division of Physical and Inorganic Chemistry at the Atlantic City Meeting of the American Chemical Society, September, 1949.

(2) P. D. Bartlett and H. Kwart, THIS JOURNAL, **72**, 1050 (1950).

(3) S. G. Cohen, *ibid.*, **67**, 18 (1945).

(4) L. F. Fieser, *ibid.*, **48**, 3211 (1925).

(5) K. Nozaki and P. D. Bartlett, *ibid.*, **68**, 1686 (1946).

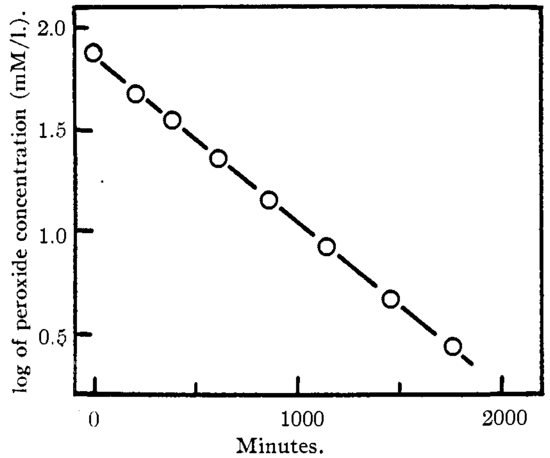


Fig. 1.—Decomposition of bis-phenylacetyl peroxide in toluene at 0°.

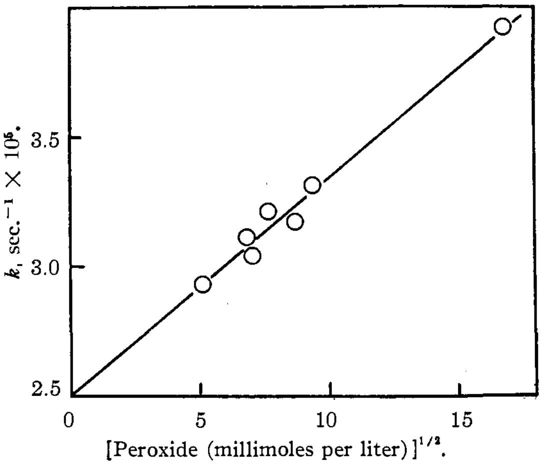


Fig. 2.—Apparent unimolecular rate constant for decomposition of bis-phenylacetyl peroxide in toluene at 0° at different initial peroxide concentrations.

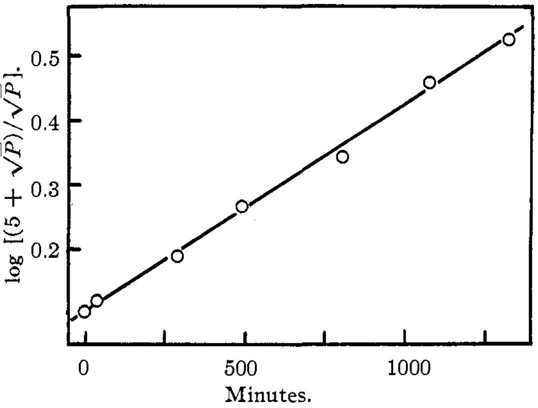


Fig. 3.—Decomposition of bis-phenylacetyl peroxide in toluene at 0° in the presence of 0.14 *M* acenaphthene.

presence of this agent alone the autocatalysis was eliminated and the fit of the data to the equation[5] for simultaneous first- and three-halves order reaction could be established (Fig. 3). The first-order part of this rate has a constant equal to that estimated from the extrapolation of Fig. 2, within 1%. This effect of acenaphthene can be accounted for if the hydrocarbon is supposed to be a powerful chain-transfer agent, reacting with benzyl radicals to yield 7-acenaphthyl radicals which, though stabilized by resonance, have the ability to attack bis-phenylacetyl peroxide in such a way as to induce its decarboxylative decomposition.

From the intercept of the line of Fig. 2 the unimolecular rate constant at infinite dilution at 0° in the absence of oxygen is found to be 2.50 × 10^{-5} sec.$^{-1}$. By a similar method the rate constant at 18° is found to be 3.34 × 10^{-4} sec.$^{-1}$. From these two figures the activation energy is calculated to be 23 kcal./mole. The corresponding figure for benzoyl peroxide is 29 kcal./mole. The rate constant k_i for induced decomposition is 2.66 × 10^{-5} l.$^{1/2}$ moles$^{-1/2}$ sec.$^{-1}$ at 0° and 2.13 × 10^{-4} l.$^{1/2}$ moles$^{-1/2}$ sec.$^{-1}$ at 18°, corresponding to an activation energy for induced decomposition of 18 kcal./mole.

In the presence of oxygen the rate of decomposition of the peroxide was increased by 4–20%. The dibenzyl observed in the oxygen-free runs was replaced by an equivalent amount of benzaldehyde. There was also formed a small amount of a stable substance which registered as a peroxide in the iodometric titrations, and which might have been dibenzyl peroxide, benzyl hydroperoxide, 1,2-diphenylethyl hydroperoxide, or some perbenzoic acid produced from the benzaldehyde.

Trinitrobenzene, found by Nozaki and Bartlett[5] to be an inhibitor for the induced decomposition of benzoyl peroxide, has an effect similar to that of oxygen on the decomposition of phenylacetyl peroxide. There is slight acceleration and the formation of a stable substance yielding a final peroxide titer. This observation suggests the formation of a nitronic ester[6] by reaction of some of the free radicals present with the trinitrobenzene. Evidence has been found in other work favoring such an attack of radicals upon aromatic nitro compounds in the course of inhibition of polymerization.[7]

The decomposition of bis-phenylacetyl peroxide in the presence of benzoyl peroxide, from 0.004 to 0.042 molar, showed the same behavior as in the absence of the benzoyl peroxide. That benzyl radicals do not induce the decomposition of benzoyl peroxide is not surprising in view of the inhibitory power of styrene toward such induced decomposition.[8]

From these experiments bearing on the possible radical character of the decomposition we conclude that the dibenzyl is formed by way of benzyl

[6] F. Arndt and J. D. Rose, *J. Chem. Soc.*, 1 (1935).

[7] G. S. Hammond, Thesis, Harvard University, 1947.

[8] J. T. Clarke, Thesis, Massachusetts Institute of Technology, 1948.

free radicals which are formed in the primary decomposition process, but that this does not account for all of the decomposition of the peroxide. The results reported next show that there is also an entirely different mechanism for the decomposition of this compound.

Acid Catalysis in the Decomposition of Bis-phenylacetyl Peroxide.—The rate of decomposition of the peroxide is a linear function of the concentration of phenylacetic acid (Fig. 4).

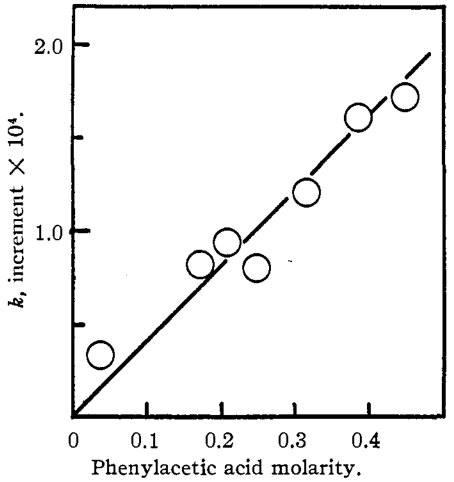


Fig. 4.—Decomposition of bis-phenylacetyl peroxide in toluene at 18°, catalyzed by phenylacetic acid.

The catalytic constant for phenylacetic acid, estimated from data such as those of Fig. 4, is 6.0×10^{-5} l./mole sec. at 0° and 4.0×10^{-4} l./mole-sec. at 18°, corresponding to an activation energy of 16.6 kcal./mole. An examination of other acids in similar fashion showed that each acid is able to catalyze the decomposition of bis-phenylacetyl peroxide at a rate which is related to the ionization constant of the acid. Figure 5 shows a "Brønsted plot" of the logarithm of the catalytic constant against the logarithm of the ionization constant of the acid in water; there is a linear relation similar to those observed in several examples of general acid catalysis.[9] Table II lists the catalytic constants for the several acids investigated.

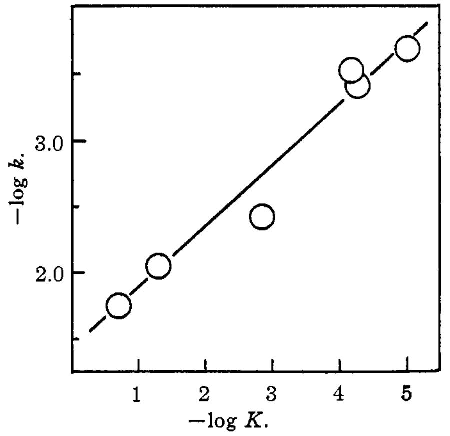


Fig. 5.—Relationship between ionization constants K of acids and catalytic constants k for the decomposition of bis-phenylacetyl peroxide in toluene at 18°.

TABLE II

CATALYTIC CONSTANTS FOR DECOMPOSITION OF BIS-PHENYLACETYL PEROXIDE BY ACIDS IN TOLUENE AT 18°

Acid	k_A (l./mole-sec. × 10^4)	Acid	k_A (l./mole sec. × 10^4)
Pivalic	2.1	Chloroacetic	38
Benzoic	3.0	Dichloroacetic	89
Phenylacetic	4.0	Trichloroacetic	178

The values of these constants are such that in the presence of 0.01 M trichloroacetic acid the decomposition is about 80% by the acid-catalyzed mechanism. The acid-catalyzed decomposition is of the first order with respect to peroxide throughout and shows no evidence of the fractional-order decomposition characteristic of the radical mechanism.

Acid Catalysis in the Decomposition of Benzoyl Peroxide.—For comparison, experiments were conducted on the decomposition of benzoyl peroxide in the presence of acids. The rates in benzene at 70° without acid, and in the presence of acetic, dichloroacetic and trichloroacetic acids increased perceptibly in that order, but 0.3 M trichloroacetic acid increased the rate of decomposition less than 50% over the rate in pure benzene, whereas with bis-phenylacetyl peroxide the increase would have been about 120-fold. In acetic acid as solvent, 0.179 M sulfuric acid increased the rate of decomposition of benzoyl peroxide only about 25%, but lowered the apparent order of the reaction markedly. Aluminum chloride has been previously observed[10,11] to catalyze the decomposition of benzoyl peroxide at 0° in benzene or chloroform.

Conclusions.—The failure of carbon tetrachloride to undergo observable attack by benzyl radicals[12] seems out of accord with the behavior of this chain transfer agent in the polymerization of styrene.[13] The explanation, as far as our experiments are concerned, is probably to be found in the very low temperature of these experiments compared to those at which carbon tetrachloride appears as an efficient chain transfer agent. The chain transfer reaction, with an activation energy of 10–15 kcal./mole,[14] will decline in importance relatively to radical interaction ($E = \sim 5$ kcal.),[15] on lowering the temperature from 100 to 0°. If the decomposition

---

[9] See L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 222.

[10] A. F. Reynhart, *Rec. trav. chim.*, **46**, 54, 72 (1927).

[11] H. Gelissen and P. H. Hermans, *Ber.*, **58**, 479 (1925).

[12] M. S. Kharasch, S. S. Kane and H. C. Brown, THIS JOURNAL, **64**, 1622 (1942).

[13] F. R. Mayo, *ibid.*, **65**, 2327 (1943).

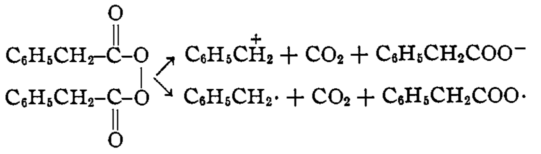
[14] *Ibid.*, p. 2328.

[15] M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, *ibid.*, **71** 2616 (1949).

of phenylacetyl peroxide is investigated at higher temperatures the increased concentration of radicals will also favor termination over transfer.

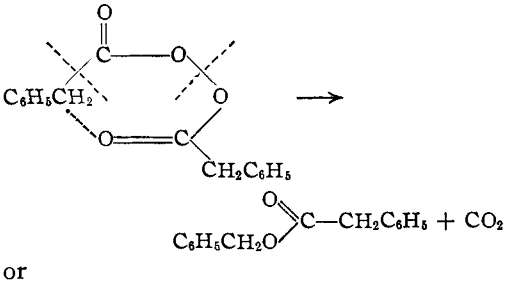
We conclude that the order of the decomposition of bis-phenylacetyl peroxide and the effect of radical interceptors and chain transfer agents upon the nature of the products are best explained on the basis of a normal decomposition by way of free radicals. The susceptibility of the reaction to general acid catalysis indicates that there is available for this reaction a polar mechanism which is favored by electron-accepting reagents. Such polar mechanisms for decomposition and rearrangement of peroxidic compounds are now becoming well recognized.[16,17,18] In an unsymmetrically substituted benzoyl peroxide it has been shown[18] that the radical mechanism or the ionic mechanism can be made to predominate by a change of solvent as well as by the use of catalysts, as here.

In both the radical and ionic mechanisms it is difficult to account for the rapidity of decomposition of bis-phenylacetyl peroxide except by supposing that the cleavage of a C–C bond as well as of an O–O bond is involved in the rate-determining step. Such cleavage might occur with the actual formation of a free benzyl radical or phenylcarbonium ion



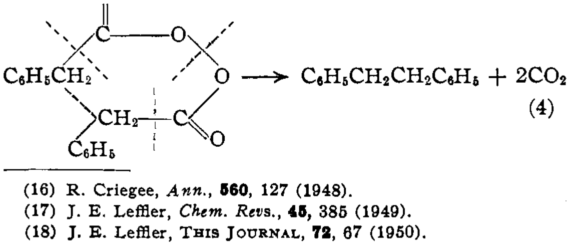
$$C_6H_5CH_2-\overset{O}{\overset{\|}{C}}-O \nearrow C_6H_5\overset{+}{C}H_2 + CO_2 + C_6H_5CH_2COO^- \quad (1)$$
$$C_6H_5CH_2-\underset{O}{\underset{\|}{C}}-O \searrow C_6H_5CH_2\cdot + CO_2 + C_6H_5CH_2COO\cdot \quad (2)$$

or in synchronism with the formation of a new benzyl compound as depicted in equations 3 and 4. In either case some energy, either of resonance in an intermediate fragment or of formation of a new bond, would be available to aid in the formation of the transition state.



(3)

or



(4)

Experimental

Preparation of Phenylacetyl Chloride.—Phenylacetyl chloride was made by the method of Vanino and Thiele[19] and also from Eastman Kodak Co. white label phenylacetic acid and thionyl chloride. Phenylacetic acid (50 g.) was dissolved in 177 g. of thionyl chloride. The mixture was allowed to stand overnight, the excess thionyl chloride removed at atmospheric pressure, and the residue distilled *in vacuo*. The yield of material boiling at about 58° (1 mm.) was 50 g.

Preparation of Phenylacetyl Peroxide.—The method used was similar to that of Vanino and Thiele.[19] To 5.2 g. (3.36×10^{-2} mole) of cold phenylacetyl chloride was added 2.4 cc. of concentrated Becco or 7.5 cc. of Superoxol (30%) hydrogen peroxide, followed by 7.0 g. (17×10^{-2} mole) of sodium hydroxide dissolved in about 50 cc. of water and cooled to the freezing point. The mixture was shaken for several minutes near but below 0°, then extracted with the cold solvent to be used in the run. To facilitate separation of the layers an additional 20 cc. of ice-water was added. Brief cooling of the peroxide solution in a Dry Ice-bath removed the bulk of the water as ice from which the peroxide solution was decanted. Prolonged cooling to Dry Ice temperature caused crystallization of the peroxide, which was very difficult to filter. It was therefore purified by crystallization in a test-tube jacketed by a Dry Ice–alcohol mixture. The peroxide was centrifuged to the bottom of the jacketed tube and the mother liquor decanted. The process was repeated with fresh solvent.

Toluene.—Samples of toluene from several commercial sources were found to contain an impurity, not readily removed by distillation, which yielded a turbidity on cooling. This impurity is not water. The toluene used in these experiments was therefore made from available sodium *p*-toluenesulfonate by hydrolysis with sulfuric acid and water. It was washed with alkali, dried and distilled through a column.

General Procedure in Kinetic Runs under Nitrogen.—The solution of peroxide was placed in a cold round-bottomed flask fitted with an adapter having a vertical tube wide enough to permit entry of a pipet, and a side tube. The side tube was connected to the nitrogen line and the vertical tube to the vacuum line. The flask was cooled in a Dry Ice–alcohol mixture, swept with nitrogen, and evacuated to about 0.5 mm. Then nitrogen was admitted. The flushing was repeated several times. Nitrogen was finally admitted and the pressure allowed to rise above 1 atmosphere. The connection from the vacuum line was removed from the vertical tube and replaced with a small capillary which permitted the escape of a stream of nitrogen. The flask was then removed from the cooling bath and placed in the thermostat.

Nitrogen.—A brand of nitrogen claimed to contain less than 0.001% oxygen and a trace of hydrogen was passed through a copper pipe full of fine copper wire and electrically heated to a dull red glow. The gas was then passed through beds of calcium chloride, Ascarite and Dehydrite.

The Analytical Method.—A 3-cc. aliquot was withdrawn from the thermostatted flask in a pipet precooled well below the temperature of the run. It was drained (ten seconds) into a 125-cc. Erlenmeyer flask containing 11–12 cc. of acetic acid, 1 cc. of freshly prepared, saturated potassium iodide solution and a lump of Dry Ice. The Dry Ice was placed in the flask before the potassium iodide. The flask was loosely stoppered, swirled, and allowed to stand for at least ten minutes. Next, a fragment of Dry Ice and 50 cc. of water were added and the liberated iodine titrated with an appropriate standard solution of thiosulfate to a starch end-point. A blank correction was applied. The isopropyl alcohol method of Kokatnur and Jelling[20] was tried and rejected. It gave higher values than did the acetic acid method. In high

---

[16] R. Criegee, *Ann.*, **560**, 127 (1948).

[17] J. E. Leffler, *Chem. Revs.*, **45**, 385 (1949).

[18] J. E. Leffler, THIS JOURNAL, **72**, 67 (1950).

[19] L. Vanino and E. Thiele, *Ber.*, **29**, 1727 (1896).

[20] V. R. Kokatnur and M. Jelling, THIS JOURNAL, **63**, 1432 (1941).

concentrations of isopropyl alcohol, at least, this was due to the slowness of the reaction between iodine and thiosulfate. It was found that trinitrobenzene did not affect the blank.

Temperature Control.—The runs at 0° were immersed in a slush of shaved ice and water. Those at 18° were carried out in a thermostat of conventional design which was constant in temperature within less than ±0.01°.

Timing.—Zero time was taken as the time of immersion for the runs at 0°, the time of reaching 18° for the runs at 18°.

Styrene Polymerization.—In a preliminary experiment, the phenylacetyl peroxide from 5.2 g. of the acid chloride was added (with a minimum of toluene mother liquor) to 50 cc. of freshly vacuum-distilled styrene. The mixture was degassed at −70°, then allowed to stand under pure nitrogen at 0° overnight. The mixture remained fluid. On removal of the excess styrene *in vacuo* at room temperature, 3 cc. of a viscous oil remained. This was completely soluble in ether but largely insoluble in methyl alcohol. In Run 20 a solution of phenylacetyl peroxide in toluene was added to 40.2 g. of freshly distilled styrene, total volume 63 cc., and treated in the usual manner of a kinetic run at 0°. After standing under nitrogen overnight, the excess solvent was removed *in vacuo*. The very viscous oil remaining weighed 2.5 g.

Benzoyl Peroxide.—Eastman Kodak Co. (white label) benzoyl peroxide was purified by precipitation from chloroform with methyl alcohol, m. p. 103–103.8° (microscope).

The Acid-Catalyzed Decomposition.—The best commercial grades of acid were used. Pivalic acid was kindly supplied by Dr. William F. Sager. The dichloroacetic acid was redistilled, b. p. 193–195°.

In the early experiments with phenylacetic acid, the acid was present while the run was reaching the bath temperature. This technique was not satisfactory with trichloroacetic acid, however. In Runs 50 and 51, using this technique, the first sample, taken shortly after the run reached the bath temperature, contained only about 10% of the expected amount of phenylacetyl peroxide. The figures are given below.

Run 50 Time, min.	mM./l.	Run 51 Time, min.	mM./l.
1.6	4.5	3.6	9.4
13.1	0.1	14.6	2.2
(0.37 molar Cl_3CCOOH)		24.6	0.8
		(0.14 molar Cl_3CCOOH)	

The residues from Runs 50 and 51 were combined, washed with sodium carbonate, dried and separated by chromatography on alumina. There was only one fraction, an oil which distilled at 0.6 mm. in a short-path apparatus. The distillate, $n^{20}D$ 1.5700, 0.113 g., was refluxed with excess 10% sodium hydroxide for twenty minutes. The water layer was acidified and extracted with benzene. The benzene was dried over a very small amount of magnesium sulfate and evaporated. There was no residue. The neutral layer weighed 0.068 g.

In later runs with phenylacetyl peroxide and added acid, the acid was added only after the run had reached the bath temperature, and the moment of addition was taken as zero time.

The acid-catalyzed and the control runs with benzoyl peroxide were done in degassed ampoules, one for each point. Since the effect of acid on benzoyl peroxide is less pronounced, the error introduced by having the acid in the ampoule while the bath temperature was reached is unimportant.

Benzoyl Peroxide in Concentrated Sulfuric Acid.—To 11.1 g. of concentrated sulfuric acid was cautiously added 1.0 g. of benzoyl peroxide. The resulting warm, green solution was poured on ice and a precipitate of 0.6 g. of benzoic acid, m. p. 113–116° (microscope), was collected. The crude benzoic acid was identified by a mixed melting point.

Phenylacetyl Peroxide in *o*-Chlorotoluene.—The peroxide from 5.2 g. of phenylacetyl chloride was extracted with about 50 cc. of *o*-chlorotoluene and allowed to decompose in an atmosphere of carbon dioxide at 0°. The usual products, dibenzyl, phenylacetic acid and benzyl phenylacetate, were formed. The first two were identified by mixed melting points and the ester by saponification to phenylacetic acid and benzyl alcohol, the latter identified as its α-naphthylurethan, m. p. 129–133°. No products ascribable to the solvent were observed.

Phenylacetyl Peroxide in Carbon Tetrachloride.—The peroxide (maximum, 16.8 millimoles) from 5.2 g. of the acid chloride was extracted with 50 cc. of cold carbon tetrachloride, a middle cut from distillation through a forty-plate column, b. p. 77°. The extract was washed once with cold water and let stand with a lump of Dry Ice in a flask which was then kept closed with a capillary for thirty-eight hours at 0°. Acid and hydrolyzable chlorine were estimated by shaking a portion of the solution with an equal volume of 10% sodium bicarbonate solution for four minutes. The results indicated 0.09 milligram-atom of chlorine and 0.165 millimole of phenylacetic acid in the carbon tetrachloride left after the decomposition. By chromatographic separation of the carbon tetrachloride solution there was isolated about 2 millimoles of dibenzyl and 4 millimoles of benzyl phenylacetate. Benzyl chloride might have been present in small amount without being detected by this treatment.

Phenylacetyl Peroxide and Iodine in Carbon Tetrachloride.—To 62.5 cc. of 0.21 molar solution (13.1 millimoles) of phenylacetyl peroxide in carbon tetrachloride (an 83% yield from 5.2 g. of the acid chloride) was added 2.1 g. of iodine. A piece of Dry Ice was added and the flask closed with a capillary and let stand at 0° for forty-five hours. The solution was then washed with sodium bisulfite, dried over magnesium sulfate, concentrated, and distilled in a short-path apparatus at 2 mm. pressure. By repeated distillations there were isolated 0.22 g. of crude benzyl iodide (1.01 millimoles, 3.8%), 0.17 g. of benzyl phenylacetate (0.75 millimole, 5.7%), and 0.55 g. of crude dibenzyl (3.01 millimoles, 23%). The crude benzyl iodide was identified by its melting point (a slush at 15°) and by hydrolysis to iodide ion collected as silver iodide (88% yield) and benzyl alcohol (α-naphthylurethan, m. p. 126–130°); it is a strong lachrymator. The dibenzyl was identified by a mixed melting point, the ester by hydrolysis and the melting points of phenylacetic acid and benzyl α-naphthylurethan. A similar run in which chromatography on magnesium sulfate was used to isolate the products gave similar results.

Products from Phenylacetyl Peroxide in Toluene, Run 5.—The initial peroxide concentration was 0.0885 molar. From 41 cc. of the residual solution there was isolated by chromatography on magnesium sulfate 0.311 g. (crude) (1.71 millimoles, 47%) of dibenzyl melting after crystallization from ligroin, at 49–50°, not depressed by an authentic sample, and 0.308 g. (2.26 millimoles, 31%) of crude phenylacetic acid, m. p. 71–75°, 75–77° after one crystallization from ligroin, not depressed.

Products from Phenylacetyl Peroxide in Toluene in the Presence of Oxygen.—The residual liquor from an experiment, 31 cc., containing originally 4.06 millimoles of peroxide, gave by chromatography on magnesium sulfate 0.168 g. of phenylacetic acid (1.23 millimoles, 15.1%) and 0.306 g. of benzyl phenylacetate (1.35 millimoles, 33%), identified as above. There was also obtained 0.456 g. of benzaldehyde (3.73 millimoles, 46%), identified as its 2,4-dinitrophenylhydrazone.

The residual solution from another representative run did not lose its titer on exposure to silver or to platinized asbestos, but did lose it on boiling at atmospheric pressure.

In another experiment in which the peroxide solution was exposed to the air, the initial titer was 0.200 molar, the stable titer, 0.037 molar. From 2 cc. of this solution there was made 0.58 g. of benzaldehyde 2,4-dinitrophenylhydrazone. No reaction with α-naphthyl isocyanate could be detected.

The solution left after Run 49, in which a toluene solution of phenylacetyl peroxide was decomposed in the presence of oxygen at 18°, had a stable peroxide content of 5.65 mM/l.; the initial concentration was 46.0 mM/l. When a portion of the residual solution (5.65 mM/l.) was shaken with 10% sodium hydroxide, the peroxide content was reduced to 2.32 mM/l. The concentration of the residual solution after standing one more day was 4.88 mM/l. To 3 cc. of the latter solution in 10 cc. of acetic acid was added a solution of lead tetraacetate in acetic acid equivalent to 5.51 cc. of 0.01009 N thiosulfate. If all the peroxide were of the type not attacked by lead tetraacetate, the titer should have been 2.90 plus 5.51 cc. Actually the titer was, after letting the solution stand half an hour and treating with sodium acetate–potassium iodide solution, 4.90 cc. This suggests that only about 61% of the peroxide is hydroperoxide, in fair agreement with the proportion destroyed by alkali, 59.5%.

Carbon Dioxide Evolution.—The carbon dioxide was swept through an Ascarite tube by a stream of pure nitrogen until the tube attained a constant weight. Toluene and water vapor were kept out by a Dry Ice and alcohol trap.

Summary

Bis-phenylacetyl peroxide like benzoyl peroxide decomposes with mixed first order and three-halves order kinetics. It is an inefficient initiator of the polymerization of styrene at 0°, at which temperature the peroxide decomposes slightly faster than benzoyl peroxide does at 70°. Despite evidence that free radicals are involved in the decomposition, this reaction is subject to general acid catalysis, the efficiency of an acid catalyst being parallel to its acid strength. It is concluded that bis-phenylacetyl peroxide can decompose according to conditions by both free radical and ionic mechanisms and that a carbon–carbon bond as well as an oxygen–oxygen bond must be broken in the rate-determining step.

CAMBRIDGE 38, MASS. RECEIVED SEPTEMBER 6, 1949

[CONTRIBUTION FROM THE ARGONNE NATIONAL LABORATORY]

The Capillary Rise, Contact Angle and Surface Tension of Potassium

BY LLOYD A. QUARTERMAN AND WILLIAM L. PRIMAK

The surface tension of potassium was first measured by Quincke[1] using a drop weight method in an atmosphere of carbon dioxide. He reported 37 mg./mm. This was recalculated by G. Meyer[2] who obtained the result 411 dynes/cm. The authors recalculated Quincke's results using modern values for the density of potassium[3] and the drop weight corrections given by Harkins and Brown[4] and obtained 500–580 dynes/cm. The Harkins–Brown correction is a little uncertain since Quincke did not completely describe the shape of his drops; but the correction, being always positive, would cause the corrected value to be larger than the value originally reported. If these values are correct, a large capillary rise (or depression) might be expected because the density of potassium is so low. This is not found to be the case.

(a) The Surface Tension Apparatus.—A short mercury thread was run down several lengths of Pyrex capillary and observed with a microscope equipped with a micrometer disk eyepiece. From one section whose radius was found constant to 1%, a short piece was selected. The length of a long mercury thread was then measured with a comparator at three positions along this capillary tube, and the mercury weighed. The radius was computed to be 0.0380 cm. with an extreme deviation of 0.5% among the three results. The value agreed with a direct measurement of the cut end of the capillary using a microscope with a micrometer disk eyepiece calibrated against a stage micrometer. The cross section was found to be circular within the precision of the latter measurement (3%). The capillary was sealed to a 35 mm. o. d. tube (about 32 mm. i. d.) to form the apparatus G of Fig. 1, similar to the apparatus described by Richards and Coombs.[5]

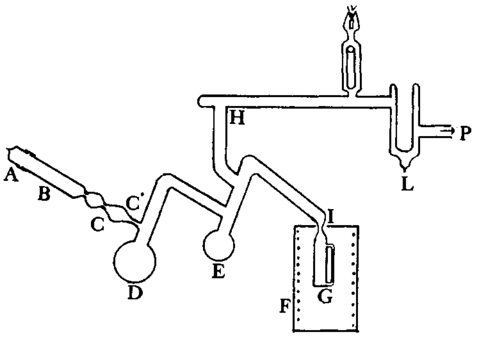


Fig. 1.—Arrangement for filling the surface tension apparatus: L, liquid air trap; P, mercury pump.

(b) Preparation of Potassium.—A quantity of commercial C. P. potassium weighing about 150 g. was cleansed of oil by washing in petroleum ether. It was introduced into the tubulation B of the apparatus drawn in Fig. 1, and was dried by passing a stream of purified helium over it while gently warming the glass. The cap A was waxed on, and the apparatus evacuated. The potassium was melted and permitted to flow through the constrictions C and C′ into the 250 ml. flask D, leaving behind a crust of oxide. The tubulation was then sealed off at the constriction C′, and the potassium was refluxed in high vacuum in the flask D. Some potassium was driven into the manifold H to remove volatile impurities and to act as a getter. After refluxing for one hour, about half of the potassium was distilled into the flask E (125 ml.) which had been flamed during the refluxing operation. During the period of refluxing and distillation (some three hours), the surface tension apparatus G was baked out in an oven maintained between 450 and 520°. The glass was colored slightly brown (additive type color centers) as a result of this treatment. About 40 ml. of potassium was now distilled into the surface tension apparatus, and the apparatus sealed off the line at the constriction I. This sample was not analyzed, but another sample prepared in the same way was analyzed. Two assays by the perchlorate method gave the results 99.9_6 and 99.8_2 weight per

---

[1] Quincke, *Ann. Physik* (*Poggendorff*), **135**, 621 (1868).

[2] Landolt-Börnstein, "Physikalisch-Chemische Tabellen," 5th ed., p. 200.

[3] "International Critical Tables," Vol. II, p. 463.

[4] Harkins and Brown, THIS JOURNAL, **41**, 519 (1919).

[5] Richards and Coombs, *ibid.*, **37**, 1670 (1915).