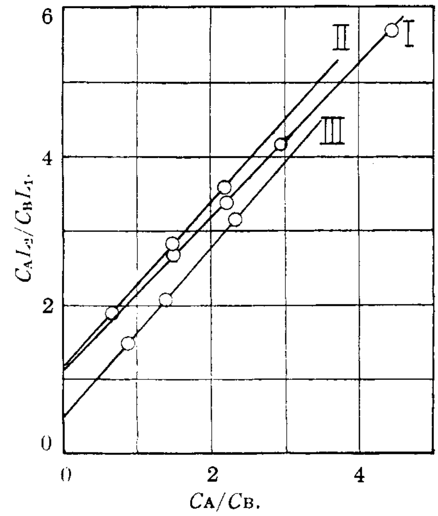

Fig. 4.

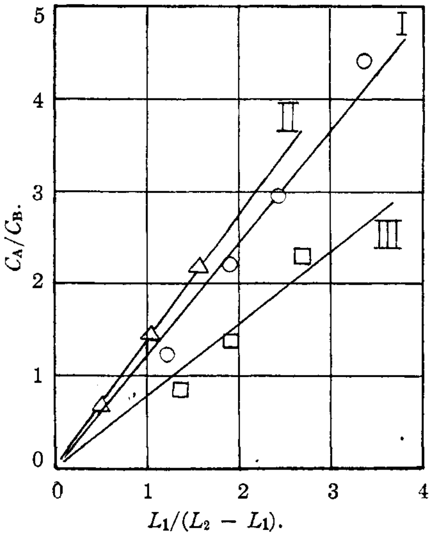

Fig. 5.

lines result but with slopes deviating slightly from the expected value one, being 1.03, 1.11, and 1.16 for I, II, III, respectively. The intercepts give values of p for the different systems:. 1.12, 1.17, 0.48 for I, II, III.

For purposes of analytical work, equation (17) is a more convenient rearrangement of (16)

$$\frac{C_A}{C_B} = p\left(\frac{V_1}{V_2 - V_1}\right) \qquad (17)$$

Figure 5 shows the plot of C_A/C_B *versus* $V_1/(V_2 - V_1)$ or its equivalent, $L_1/(L_2 - L_1)$. Case III does not follow a straight line, through the origin probably because of the large slope in Fig. 4. Values of p calculated from the slopes in Fig. 5 are found to be higher (1.21, 1.39, 0.78 for I, II, III) than those obtained as intercepts in Fig. 4. For analyses a plot such as Fig. 5 would be useful especially if a calibration curve on a set of knowns is first constructed.

Summary

The method of frontal analysis has been extended and applied to the problem of analyzing various mixtures of ethers and sulfides.

EVANSTON, ILLINOIS RECEIVED SEPTEMBER 10, 1949

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

The Decomposition of Benzoyl Peroxide in the Presence of Iodine. I. Aromatic Solvents[1]

BY GEORGE S. HAMMOND

The mechanism of the decomposition of benzoyl peroxide has been studied extensively during the last twenty-five years.[2] The complexity of the process is indicated by the extreme variation in the rate of decomposition in different solvents and at different concentrations in the same solvent.[3] Nozaki and Bartlett have discussed the kinetics in detail and show that the variation in rate may be largely attributed to the ability of radicals, formed either in the primary process or by the reactions of the primary products with solvent, to attack peroxide and destroy it in a chain reaction.

In a solvent in which nearly all of the peroxide is destroyed by this induced reaction it is an easy matter to formulate the propagation reactions from a knowledge of the products formed. This has been done by Cass[4] for decomposition in ether. It is more difficult to account for the products in solvents such as benzene in which both the spontaneous and chain reactions are important. It is of interest to attempt a more complete elucidation of the mechanism in these instances because diacyl peroxides as a class constitute one of the best sources of reactive free radicals at relatively low temperatures.[5] In particular it is important to know whether or not the radical R· is produced in the decomposition of $(RCO_2)_2$ by the loss of carbon dioxide either in the primary process or by

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(1) We gratefully acknowledge the finanical support of this research by the Office of Naval Research.

(2) For references to the older literature, see McClure, Robertson, and Cuthbertson, *Can. J. Research*, **20B**, 103 (1942).

(3) (a) Brown, THIS JOURNAL, **62**, 2657 (1940); (b) Nozaki and Bartlett, *ibid.*, **68**, 1686 (1946); (c) **69**, 2299 (1947).

(4) Cass, *ibid.*, **68**, 1976 (1946).

(5) For example see Kharasch, *et al.*, *J. Org. Chem.*, **14**, 91 (1949), and earlier papers in the series.

the spontaneous decarboxylation of acyloxy radicals. By comparing the relative reactivities of the radicals produced in the decomposition of diacetyl peroxide with those involved in the polymerization of various olefins, Edwards and Mayo[6] have recently shown that there is some doubt as to the actual existence of free methyl. It is suggested that decarboxylation may occur only at the moment of reaction of the acetate radical with another molecule.

Perret and Perrot[7] have reported the results of a study of the products of a number of reactions of benzoyl peroxide in the presence of iodine. They found that relatively little carbon dioxide was produced in the presence of unsaturated hydrocarbons. With olefins high yields of the corresponding dibenzoates were obtained and with aromatic compounds the principal products were benzoic acid and the aryl benzoate esters. The authors indicated that benzoyl hypoiodite might be an intermediate but did not clarify their views as to how it might be produced. The relatively high yields of products in which the benzoate function remained intact showed that very little decarboxylation occurred in the primary process. However, since it is known that peroxide decomposition by a mechanism not involving radicals is catalyzed by acids,[8,9] it seemed possible to us that the entire course of the reaction was altered by the inclusion of iodine. This view was further justified by the work of Gelissen and Hermans[10] and Reynhart[11] who obtained phenyl benzoate and benzoic acid by treating benzoyl peroxide in benzene with aluminum chloride or ferric chloride. If iodine does not bring about decomposition by a polar mechanism the elucidation of the details of the radical reaction should be somewhat simplified. Because of their high reactivity toward iodine, radicals arising from the abstraction of hydrogen from carbon atoms by the benzoate radical, and perhaps benzoate itself, should be prevented from attacking peroxide. Therefore, the induced decomposition should be inhibited with consequent elimination of any products formed exclusively in this reaction.

In order to establish the identity of the primary process in the presence of iodine, we have followed the rate of peroxide decomposition in solutions containing varying amounts of iodine. We have also determined the effect of iodine concentration on the fate of the peroxide fragments and the extent to which iodine itself becomes permanently involved in reaction products.

Experimental

Benzoyl peroxide was purified by dissolving in chloroform, filtering and pouring the solution into Skelly A. The fine white crystals were collected by suction filtration and dried *in vacuo*.

Iodine, Merck reagent grade, was used without further purification.

Benzene and chlorobenzene were the best commercial grades redistilled once.

Kinetic Runs.—Weighed amounts of peroxide and iodine were dissolved in benzene. Five-ml. aliquots were added to constricted tubes and degassed by freezing to Dry Ice temperature and evacuating to 2 mm. The tubes were then sealed off and heated in a thermostat at 79.0 ± 0.05°. The samples were removed at intervals and 2-ml. aliquots were analyzed for iodine, peroxide and in some cases for acid. The iodine was quantitatively reduced by titrating with standard 0.1 *N* aqueous thiosulfate with swirling. No fading of the end-point due to oxidation of iodide by peroxide was observed under these conditions. The peroxide was reduced by adding 25–30 ml. of glacial acetic acid, 2 ml. of saturated aqueous potassium iodide and Dry Ice to either the mixture from iodine titration or to a fresh aliquot. The iodine produced was titrated with thiosulfate using its own color as an indicator. When acid was determined a 2-ml. aliquot after iodine determination was flushed with nitrogen in an erlenmeyer flask for five minutes and titrated with 0.1 *N* alcoholic potassium hydroxide.

Runs for Product Analysis at Varying Initial Iodine Concentrations.—Two solutions were prepared containing the same concentration of peroxide. The desired amount of iodine was included in one of the solutions. A series of 10-ml. samples were made up in constricted tubes by adding various amounts of the two solutions by means of volumetric pipets. The tubes were degassed, sealed and heated 33–45 hours. Two-ml. samples were analyzed for iodine and acid as described above. A 5-ml. sample was freed of iodine by the dropwise addition of an indeterminate concentrated solution of thiosulfate. The sample was then washed twice with water and flushed with nitrogen until the benzene was evaporated. The benzoic acid remaining in the sample was titrated with the potassium hydroxide solution and 25 ml. excess of the alcoholic alkali was added. The sample was then refluxed for two hours under a condenser which had been flushed with nitrogen and was protected by a soda lime tube. The excess base was then back titrated rapidly with 0.1 *N* aqueous hydrochloric acid. Brom thymol blue was used as the indicator in both titrations. The amount of peroxide remaining in solution was calculated using the rate constant 0.093 hr.$^{-1}$. The saponification analyses were corrected for hydrolysis of this peroxide. The amount of base consumed by the cold solution after washing with water was lower than that expected from the results of the first determination indicating that an appreciable amount of acid has been extracted during the washing to remove iodine.

A 2-ml. aliquot of a sample from one of the above runs in which all the iodine was consumed during the heating period was shaken with distilled water. The extract remained clear after the addition of aqueous silver nitrate indicating that no easily hydrolyzed iodide was produced in the reaction.

Batch Reaction in Benzene.—A solution containing 20.6 g. of iodine and 20 g. of peroxide in 245 ml. of benzene was prepared. Two 1-ml. aliquots were titrated for iodine and two for total iodine plus peroxide. The titrations indicated that the sample contained 0.078 mole of iodine and 0.078 mole of peroxide. The solution was washed into a flask with a constricted neck with 10 ml. of benzene, degassed, sealed and heated at 79° for 33 hr. It is calculated that 0.074 mole of peroxide was decomposed. After cooling to room temperature two 1-ml. aliquots were titrated for iodine showing that 0.025 mole had been consumed and two 5-ml. aliquots were titrated for acid indicating that 0.0908 mole (61% yield based on theoretical 0.148 mole from 0.074 mole peroxide decomposed) of acid was produced. The remainder of the solution was removed from the flask, which was washed with 10 ml. benzene and was treated with the minimum amount of concentrated aqueous thiosulfate required to remove the iodine.

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(6) Edwards and Mayo, THIS JOURNAL, **70**, 1265 (1950).

(7) Perret and Perrot, *Helv. Chim. Acta*, **28**, 558 (1945).

(8) Leffler and Bartlett, paper delivered at American Chemical Society Meeting at Atlantic City, September, 1949.

(9) Leffler, THIS JOURNAL, **72**, 67 (1950).

(10) Gelissen and Hermans, *Ber.*, **58**, 479 (1925).

(11) Reynhart, *Rec. trav. chim.*, **46**, 54 (1927).

The benzene layer was extracted with 25% aqueous sodium hydroxide. The extraction was actually carried out as a titration to phenolphthalein end-point. Sufficient water was added to dissolve the sodium benzoate. The aqueous solution was acidified with concentrated hydrochloric acid to the red thymol blue end-point. After cooling the solid was filtered off and washed with water. The aqueous filtrate was 154 cc. and began to deposit crystals when allowed to evaporate at room temperature so it was nearly saturated. The acid was air dried, 9.17 g., m. p. 121.5–122.5°.[12] The total yield of acid isolated plus 0.32 g. to saturate the filtrate was 0.078 mole, which is equal to a 0.083 mole (56%) in the original batch before sampling. The benzene solution was dried over calcium chloride, filtered and the drying agent was washed with 25 ml. of benzene. Three 10-ml. aliquots were removed and saponified. The average result showed 0.0013 equivalent of base consumed. Correcting for peroxide and samples removed, this is equal to 0.0302 mole of ester (20%) in the original sample. The remaining solution, which, except for mechanical losses, was equivalent to 83% of the original charge, was distilled through a 44-plate semimicro column at atmospheric pressure. The benzene was removed at 79.2–79.8°, and several fractions were then collected (Table I).

TABLE I

Boiling range, °C.	Weight, g.	$n^{20}D$	Remarks
78.9–79.8	1.25	1.5009	Pink color
80–184.2	0.42	1.5377	
184.2–185.2	4.59	1.6128	

The last fraction is considered to be essentially pure iodobenzene and is equal to 0.026 mole in the original mixture. This is a minimum figure since the still residue and the middle fraction both contained iodobenzene. The dark residue weighed 8.5 g. and deposited crystals when scratched. It was sampled while still liquid. A 1.90-g. sample was diluted to 25.0 ml. with benzene. A 5-ml. aliquot of this solution consumed 1.61 $\times$ 10^{-4} mole of base, showing that some decomposition to acidic substances had occurred during distillation. Saponification indicated that the total residue contained 5.8 g. (24%) of phenyl benzoate if it was the only ester present. The remaining 6.6 g. of residue was dissolved in hot methanol and treated with Norite but deposited a dark oil on cooling. The supernatant liquid was decanted and gave 0.34 g., m. p. 64–67°, of white solid on evaporation of the methanol. The dark oil was distilled at 2 mm. and 2.58 g. of pale yellow solid was collected at about 130°, m. p. 58–63°. The two fractions were combined and recrystallized from methanol, giving 2.43 g., m. p. 66–69°, mixed with phenyl benzoate, 66.5–69.5°; corrected yield of nearly pure ester by isolation, 15%.

Batch Reaction in Chlorobenzene.—Twenty grams of iodine was added to about 250 ml. of chlorobenzene and warmed to effect solution. On cooling to room temperature a small amount of iodine crystallized from the solution. Twenty grams of benzoyl peroxide was washed into the flask with 10 ml. of solvent. After the peroxide had dissolved, the solution was filtered, degassed, sealed off and heated at 79° for 48 hours. The solution was cooled to room temperature and a trace of solid was filtered off. The volume of the filtrate was 264 ml. This solution was analyzed and prepared for distillation as in the benzene run. Titration showed that 0.005 mole of peroxide and 0.029 mole of iodine remained in the solution and indicated a yield of 69% benzoic acid. Solid acid equivalent to 65% yield was isolated. Saponification indicated a 15% yield of ester. The volume of solution distilled was 204 ml. Taking account of benzene used in transfers and samples removed, but not of the partial molal volume of the acid and iodine removed from the original solution, this was equivalent to 71% of the original product. Distillation through the 44-plate column gave the results in Table II.

TABLE II

Fraction	Boiling range, °C.	Pressure, mm.	Amount	Remarks
1	39–40	25	178 ml.	
2	40–82	25	0.64 g.	Nearly all below 41°
3	82–84	25	3.22 g.	
4	84–114	25	One drop	
5	114–?^{a}	25	11.87 g.	
6	120–160	2	2.67 g.	Nearly all 150–160°

^{a} Head temperature started to fall while column was unattended. The pot was then cooled, the pressure reduced and distillation continued.

A 0.2-g. portion of sample 3 was treated with chlorine and gave 0.12 g. of yellow solid m. p. 111–114° (dec.) after washing with carbon tetrachloride.[13] An analogous fraction from another run, which is not reported in detail, was nitrated by the procedure of Cheronis and Entrikin[14] and gave a 25% yield of the p-nitro derivative melting 170–173° after one recrystallization from glacial acetic acid. Fraction 5 was semi-solid and was filtered after cooling in the ice box. The white crystals were washed repeatedly with 2 ml. of methanol, 7.02 g., m. p. 53–54° (p-ClC$_6$H$_4$I). More of this isomer was collected by combining the wash solution and mother liquor, allowing the methanol to evaporate, freezing again and drying the crystals with filter paper, 0.23 g., m. p. 52–53°. Portions of Fraction 6 did not crystallize on treatment with Skelly B or methanol. After standing a week the crude sample deposited 11 mg. of brown crystals, soften 150°, m. p. 200–215°. A 1.60-g. portion was chromatographed on alumina. Elution with 50% Skelly B-benzene gave 0.11 g. of p-ClC$_6$H$_4$I, m. p. 52–53.5°, and 0.10 g. of semisolid product. Elution with acetone gave a few mg. melting at 53–55°. Elution with methanol gave an amorphous yellow solid, m. p. 60–90°. Before elution with acetone the column was washed with large volumes of benzene and 50% benzene–ether but no products were obtained. It is certain that any biphenyls would have appeared in one of the first fractions. The still residue was taken up in hot methanol and filtered. On cooling 0.631 g. of tan crystals, m. p. 68–78°, was obtained. On saponification 0.185 g. of this solid consumed base equivalent to 0.167 g. of $C_6H_5COOC_6H_4Cl$. The solution was made strongly alkaline and filtered, giving only a trace of insoluble brown powder. The alkaline solution was acidified and 55 mg. of brown crystals, m. p. 108–113°, mixed with benzoic acid 108–120°, was collected. Sublimation gave white needles, m. p. 120.5–122°. The acid filtrate was treated with bromine water giving 0.30 g. of white solid, m. p. 68–75°, mixed with 4-chloro-2,6-dibromophenol (m. p. 92–92.5°) 72–87°, one recrystallization from aqueous methanol gave 0.11 g., m. p. 76–84°, m. m. p. 80–86°. The methanol solution from which the ester was obtained was saponified and treated as above, giving 0.69 g. of bromophenol, m. p. 77–90°. The ester fraction from an earlier run was recrystallized twice from excess methanol and yielded a small amount of p-$C_6H_5COOC_6H_4Cl$, m. p. 88–89°.

Accuracy.—The analyses for iodine and acid were reproducible and agreed to within ±0.2% with calculated values when weighed samples were dissolved in benzene and titrated. Due to the aqueous phase introduced in the iodine titrations it was necessary to add a relatively large volume of glacial acetic acid to maintain homogeneity of the solution during the reduction of the peroxide. It was

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(12) All melting points are uncorrected and were determined with a Fischer–Johns micro block.

(13) Dr. Louis Soffer of these laboratories has found the molecular compound, $C_6H_5I \cdot Cl_2$ to be a convenient derivative for iodobenzene. The solid is found to decompose in the range 110–114° when freshly prepared. The material deteriorates rapidly on standing.

(14) Cheronis and Entrikin, "Semimicro Qualitative Analysis," Thomas Y. Crowell Co., New York, N. Y., 1947, p. 285.

then necessary to add inconveniently large volumes of water in order to use starch as an indicator. Therefore the iodine color itself was used. The end-point was accurate to ±0.05 ml. of 0.1 *N* thiosulfate. In the analysis of the final solutions in the kinetic runs this represents an error of as much as ±20%. Controls showed that the saponification of phenyl benzoate in benzene with excess 0.1 *N* alcoholic alkali was accurate to ±5%. When values of ester were low the uncertainty was increased by the uncertainty in correcting observed results for small amounts of residual benzoyl peroxide. Our value for the pseudo first order rate constant in 0.2 *M* solution without iodine agrees closely with that reported by Hartmann, Sellers and Turnbull[15] when corrected for the one degree difference in temperature using 33 kilocalories[3a] as the activation energy. This constant is somewhat lower than that reported by Nozaki and Bartlett. The rate in the presence of inhibitor is also slightly lower than their calculated values for the "true" unimolecular rate but the agreement is probably satisfactory.

Results.—The values of k_1, the unimolecular rate constant for peroxide decomposition, which are summarized in column 3 of Table III show no significant variation over a seven-fold range of initial ratios of peroxide to iodine concentrations. Furthermore, the rate of decomposition in a very dilute solution of peroxide in benzene with no added inhibitor agrees well with the inhibited rates. We feel justified in concluding that the "true" unimolecular rate constant at 79° is 0.093 ± 0.002 reciprocal hour in benzene.[16] It is furthermore apparent that a reaction between peroxide and iodine is not rate controlling.

TABLE III

KINETICS OF PEROXIDE DECOMPOSITION IN BENZENE CONTAINING IODINE AT 79.0 ± 0.05°

Initial peroxide, moles/liter	Initial iodine moles/liter	k_1 in hr.$^{-1}$	Average deviation of k_1	Probable error in k_1	dI_2/dP	$dI_2/dP \times [I_2]_0$
0.199	None	0.163	0.008	0.003		
1.15×10^{-3}	None	.091	.016	.008		
0.199	0.0639	.097	.005	.003	0.18	2.8
.099	.0641	.098	.005	.003	.22	3.4
.204	.195	.087	.016	.007	.35	1.8
.100	.197	.093	.010	.003	.38	2.0
.203	.399	.089	.009	.003	.63	1.6
.198	.474	.098	.014	.009	.71	1.5
.216	.450	.092	.020	.008	.75	1.7

While kinetics of peroxide decomposition have been rendered relatively uninvolved by the inclusion of iodine in the system, the rate at which iodine is consumed is a rather complex function of the iodine concentration. The iodine concentration in the various runs is plotted against peroxide in Figs. 1–3. In the runs in which the concentration of iodine is relatively high the relative rate of iodine consumption, dI_2/dP, decreases as the runs progress as would be ex-

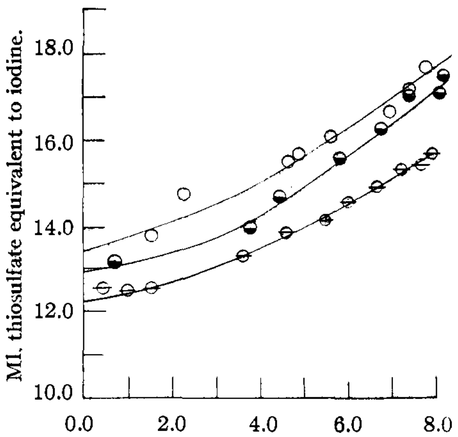

Fig. 1.—Relative rate of iodine uptake: ○, $[P]_0 = 0.198$, $[I_2]_0 = 0.474$; ●, $[P]_0 = 0.216$, $[I_2]_0 = 0.450$; -⊖-, $[P]_0 = 0.203$, $[I_2]_0 = 0.399$.

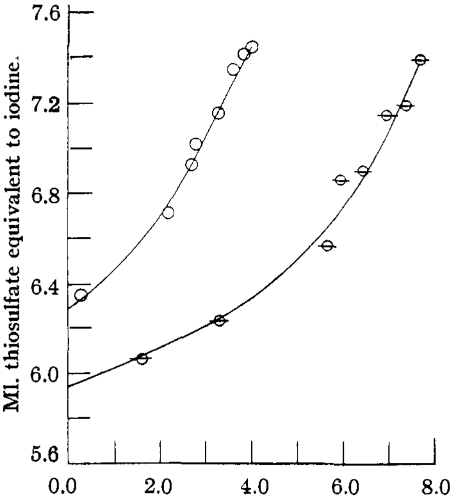

Fig. 2.—Relative rate of iodine uptake: ○, $[P]_0 = 0.100$, $[I_2]_0 = 0.197$; -⊖-, $[P]_0 = 0.204$, $[I_2]_0 = 0.195$.

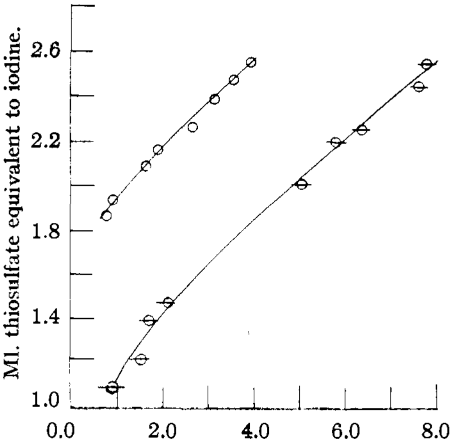

Fig. 3.—Relative rate of iodine uptake: ○, $[P]_0 = 0.099$, $[I_2]_0 = 0.0641$; -⊖-, $[P]_0 = 0.199$, $[I_2]_0 = 0.0639$.

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[15] Hartmann, Sellers and Turnbull, THIS JOURNAL, **69**, 2416 (1947).

[16] It is of interest that unpublished data obtained in these laboratories indicate that the rate of decomposition in perfluoromethylcyclohexane is significantly lower.

pected if iodine is consumed in a reaction which is higher than zero order in iodine and competitive with some other reaction. However, in the runs in which the initial iodine concentration is lowest (Fig. 3) and in which the largest proportional amount is ultimately consumed, the slope of the curve increases. A similar result was obtained in a series of experiments in which samples containing the same concentration of peroxide but varying amounts of iodine were heated until nearly all of the peroxide was decomposed and the resulting solutions analyzed for products and residual iodine. Figure 4 shows the amount of iodine consumed per mole of peroxide decomposed plotted against initial iodine concentration. In the calculations the initial peroxide content was corrected for the calculated amount of residual peroxide using the average rate constant reported above. This correction was very small in all cases. In the range of initial concentrations of more than 0.2 molar the decrease in iodine consumption is, within experimental error, a linear function of the initial concentration. Below this level the trend is reversed and *more* iodine was consumed in some of the most dilute solutions than in the intermediate cases. The sixth column in Table III gives the values of the initial slopes, dI_2/dP, determined by estimating the tangents to the curves in Figs. 1–3. In the last column these values are divided by the initial iodine concentrations. Because of the uncertainty of determining the tangents it is considered that the data are at least consistent with the view that the reaction which consumes iodine is kinetically one order higher in iodine than the important competing reaction in the more concentrated solutions. It is noteworthy that the relative rate of disappearance of iodine is relatively insensitive to changes in peroxide concentration.

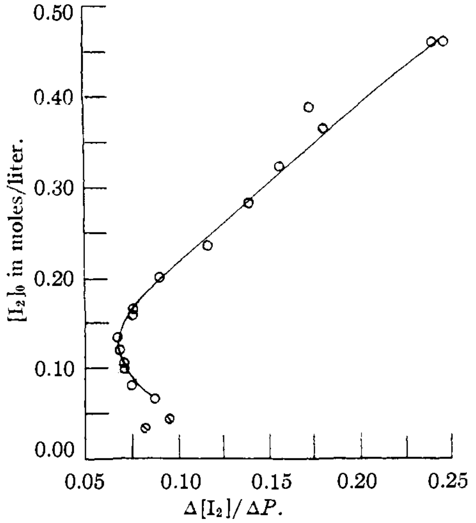

Fig. 4.—Dependence of iodine consumption per mole of peroxide decomposed on initial iodine concentration: initial peroxide = 0.2 *M* in all cases; solutions heated at 79° until nearly all peroxide had decomposed; in samples marked ⊘ the iodine was completely consumed.

In the experiments described last, acid products, other than carbon dioxide, and total ester were determined as well as residual iodine. Isolation of products showed that the acid was exclusively benzoic and that the ester was phenyl benzoate. In benzene solution the only other product formed in significant yield was iodobenzene. The isolation of products was carried out for only one set of concentrations, and it is assumed that no other products become important when concentrations are changed. The analyses show that the relative amounts of ester and acid formed are influenced considerably by the iodine concentration. While the yield of acid increases steadily with increasing iodine concentration, the yield of ester passes through a maximum. However, the sum of the acid plus ester increases rapidly from the values in a solution which does not contain inhibitor to a constant value which is reached at about 0.2 *M* initial iodine concentration. This value represents approximately ninety per cent. of the peroxide decomposed if it is assumed that each molecule of ester is formed from a benzoate radical and a phenyl group derived from the solvent. These data are summarized in Fig. 5.

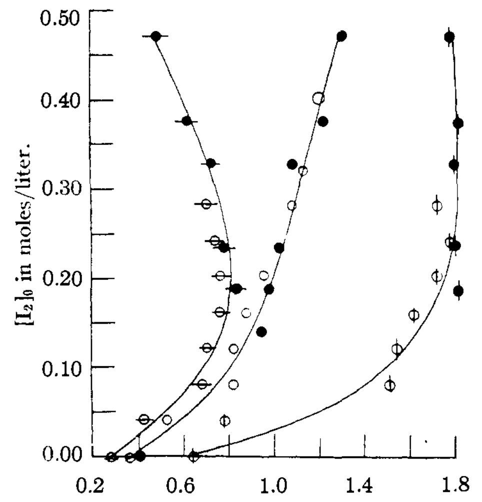

Fig. 5.—Influence of initial iodine concentration on reaction products: open and closed circles represent different runs; -⊖-, ester; O, acid; ⏀, total ester plus acid.

In order to be able to distinguish aryl groups derived from the peroxide from those of the solvent the products of the reaction in chlorobenzene containing iodine were investigated. The yields of ester and acid were determined by titration and the acid was shown to be benzoic and the ester fraction was found to be a mixture which contained some *p*-chlorophenyl benzoate. The iodinated products were isolated semiquantitatively by careful fractional distillation. Table IV summarizes the results from batch runs in both benzene and chlorobenzene.

TABLE IV

DECOMPOSITION IN BENZENE AND CHLOROBENZENE AT 79°

Substance	Moles consumed or produced[a] Benzene	Moles consumed or produced[a] Chlorobenzene
Peroxide	0.074	0.078
Iodine	.025	.047[b]
Benzoic acid	.083	.107
Esters	.032	.104
Iodobenzene	.026[c]	.016
Iodochlorobenzenes		.051

[a] Initial concentrations, $[P] = [I_2] = 0.31$ *M* in both cases. [b] The value is high by a small, undetermined amount due to an uncertainty in the initial iodine concentration. [c] Represents minimum value.

Discussion.—The following equations outline a reaction sequence which is compatible with both our data and previously published results.

$$(C_6H_5CO_2)_2 \longrightarrow 2C_6H_5CO_2\cdot \qquad (1)$$

$$(C_6H_5CO_2)_2 \longrightarrow C_6H_5CO_2\cdot + C_6H_5\cdot + CO_2 \qquad (2)$$

$$C_6H_5CO_2\cdot + I_2 \longrightarrow C_6H_5CO_2I + I\cdot \qquad (3)$$

$$C_6H_5CO_2\cdot + I_2 \longrightarrow C_6H_5I + CO_2 + I\cdot \qquad (4)$$

$$C_6H_5CO_2I - \left\{\begin{array}{ll} \xrightarrow{\hspace{2em}} C_6H_5I + CO_2 & (5) \\ \xrightarrow{ArH,\ I_2} C_6H_5CO_2Ar + HI & (6) \\ \xrightarrow{ArH,\ 2I_2} C_6H_5CO_2H + ArI & (7) \end{array}\right.$$

$$2I\cdot \longrightarrow I_2 \qquad (8)$$

$$C_6H_5CO_2I + HI \longrightarrow C_6H_5CO_2H + I_2 \qquad (9)$$

We believe that in the presence of high concentrations of iodine, benzoate radicals are formed in the primary process and are converted to the unstable benzoyl hypoiodite which reacts rapidly with the aromatic solvent in iodine-catalyzed, non-radical reactions. There must be at least two such reactions, one giving exclusively benzoic acid and the other producing the ester. In order to explain the increase in the yield of acid with increasing iodine concentration it is necessary that the first reaction be kinetically higher order in iodine than the second.[17] While we have no conclusive evidence to bear on the point we believe that iodine is probably also involved in the reaction which produces the ester. Birkenbach and Meisenheimer[18] obtained considerably lower yields of both acid and ester from the decomposition in benzene of the product of the reaction of silver benzoate with iodine. It is likely that the intermediates in the two reactions are the same and that the excess iodine present in our system was responsible for the increased yield of ester and acid. We have also noted an increase in the iodine uptake when it is present in low concentrations. This phenomenon and the concomitant increase in the yield of carbon dioxide may be attributed to the increasing importance of reaction (5), the uncatalyzed decarboxylation of benzoyl hypoiodite. However, it is also possible that at low iodine concentrations other reactions of the benzoate radical, such as hydrogen abstraction from solvent and spontaneous decarboxylation, produce radicals which react with iodine to form stable products. The constant ten per cent. discrepancy between the actual and theoretical yields of carboxylated products at high iodine concentrations must be attributed to reactions (2) and (4). Otherwise the yield of carbon dioxide should approach zero rather than ten per cent. It is not known whether or not reaction (3) is reversible under our conditions. If it is, then it is necessary to assume that decarboxylation occurs in a second primary process, reaction (2).

It is interesting to note that in reaction (7), in which chiefly *p*-iodochlorobenzene was produced in chlorobenzene solution, the orientation is that to be expected in a typical electrophilic substitution. This observation is hardly a proof of a polar mechanism since Walling[19] has pointed out the fact that the contribution of ionic structures to the transition states in radical reactions may frequently give rise to similar relative reactivities in ionic and radical reactions. However, Waters and Hey[20] have recently indicated that, contrary to popular belief, orientation in radical substitution of aromatic systems is a random process.

The occurrence of a reaction such as (7) in which several molecules are involved is reminiscent of the suggestion that the bromination of benzene is kinetically high order with respect to bromine.[21]

We have formulated the intermediate compound as benzoyl hypoiodite for lack of more definite information. If, as is indicated with certain aliphatic analogs,[22] the acyl iodate is stabler it may well be involved as well. Such species could arise from the reaction of the hypoiodite with benzoate radicals. This would not materially affect the above discussion providing such compounds react rapidly with the aromatic solvents in a manner similar to that suggested for the hypoiodite.

Our results could also be interpreted on the hypothesis that benzoate rather than the iodine compound distributes itself according to equations (5–7). This formulation demands that the average lifetime of benzoate radical should not be materially decreased by the addition of iodine. Brown[3a] and Barnett and Vaughan[23] have shown that, in the absence of an inhibitor, the yield of carbon dioxide increases with increasing dilution indicating that if benzoate radicals live long

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[17] It has been pointed out by a referee that hydrogen iodide reacts rapidly with benzoyl peroxide and that it is therefore necessary that the rate of reaction (9) must be very rapid if it is to account for the fate of all hydrogen iodide produced. Because of the unsymmetrical nature of the hypoiodite it seems likely to us that it will actually react much more rapidly than peroxide. If this could be shown to be untrue it would necessitate reformulation of reaction (6).

[18] Birkenbach and Meisenheimer, *Ber.*, **69**, 723 (1936).

[19] Walling, *et al.*, THIS JOURNAL, **70**, 1537 (1948).

[20] Waters and Hey, *Nature*, **162**, 183 (1948).

[21] Robertson, *et al.*, *J. Chem. Soc.*, 100 (1948), and earlier papers in the series; Bruner, *Z. physik. Chem.*, **41**, 513 (1902).

[22] Oldham and Ubbelohde, *J. Chem. Soc.*, 368 (1941).

[23] Barnett and Vaughan, *J. Phys. and Colloid Chem.*, **51**, 926 (1947).

enough in solution they undergo reactions resulting in decarboxylation. This observation also shows that carbon dioxide probably is not produced in the propagation step of the chain reaction. The low yield of carbon dioxide in the presence of iodine points to a relatively short life for this species. An alternative explanation of the source of carbon dioxide in uninhibited experiments would be that it arises from the reaction of solvent radicals with benzoate and that these solvent radicals are removed rapidly by iodine. However, such a reaction would represent a chain terminating step in the induced process and would make the induced reaction first order rather than three halves order with respect to peroxide.[3c]

Matheson[24] has suggested that radicals produced in the primary process may react with each other before leaving the solvent cage. This effect cannot be of great significance in chlorobenzene because the peroxide fragments are accounted for nearly quantitatively in products derived from reactions involving the solvent or iodine. It is still possible that a proximity effect does operate and that termolecular reactions involving two primary fragments and a foreign molecule do occur. This question is being further investigated in these laboratories.

Summary

The decomposition of benzoyl peroxide in benzene and chlorobenzene has been studied kinetically and by product analysis. The rate of peroxide decomposition is constant over a range of iodine concentrations but the relative rate of iodine uptake and the nature of the products depend on the iodine concentration. It is suggested that benzoyl hypoiodite is formed and reacts rapidly with the solvent in non-radical reactions which are catalyzed by iodine. The products of the reaction indicate the "cage effect" is unimportant in benzene solution. A maximum of ten per cent. of the theoretical amount of carbon dioxide is formed in the primary process.

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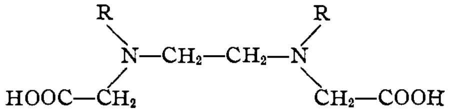
(24) Matheson, *J. Chem. Phys.*, **13**, 584 (1945).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CLARK UNIVERSITY]

The Preparation and Properties of Some N,N'-Dialkylethylenediaminediacetic Acids

BY ALBERT E. FROST, JR.,[1] AND ARTHUR E. MARTELL

The purpose of this investigation was the preparation and study of the properties of a series of N,N'-dialkylethylenediaminediacetic acids, of the general formula



where R represents the *n*-butyl-, cyclohexyl-, *n*-octyl-, *n*-dodecyl- and benzyl-radicals. These symmetrically substituted ethylenediamine derivatives are of practical and theoretical interest since they constitute a new series of complexing agents and bear a structural similarity to the powerful chelating agent, ethylenediaminetetraacetic acid.

The N,N'-dialkylethylenediamines, utilized as intermediates in the synthesis of the N,N'-dialkylethylenediaminediacetic acids, were synthesized by the reaction of excess amine with ethylene dichloride by methods similar to that of Sebrell and Clifford.[2] The diamines were characterized as the dipicrates and the di-(phenylureides). These substances have been recently described.[3]

Condensation of sodium chloroacetate with the appropriate N,N'-dialkylethylenediamine was used for the preparation of N,N'-dibutyl-, N,N'-dioctyl-, N,N'-dibenzyl and N,N'-dicyclohexylethylenediaminediacetic acids, but gave poor yields. The dibutyl and dioctyl derivatives were also prepared by a variation of the method similar to that of Smith, *et al.*[4] Details of this preparation will be published later.[5] The condensation of ethylene dichloride with the respective N-alkylglycine was used as an additional method of preparation for the N,N'-dioctyl- and N,N'-didodecylethylenediaminediacetic acids. Although the yields reported are rather poor, it is felt that considerable improvement would result from a further study of these reactions. In Table I are summarized pertinent data on the products obtained.

The N,N'-dialkylethylenediaminediacetic acids are soluble in polar solvents and insoluble in non-polar solvents. The order of solubility in water is dibutyl- > dicyclohexyl- ≫ dibenzyl- > dioctyl- > didodecyl-. The latter three acids are only slightly soluble in water.

The tendency of the N,N'-dialkylethylenediaminediacetic acids to form complex salts with copper and calcium ions, taken as examples of the transition and alkaline earth metals, was

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(1) This paper is based on a dissertation presented by Albert E. Frost, Jr., to the Faculty of Clark University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1949.

(2) Sebrell and Clifford, U. S. Patent 1,948,317 (Feb. 20, 1934).

(3) Frost, Chaberck and Martell, THIS JOURNAL, **71**, 3842 (1949).

(4) Smith, Bullock, Bersworth and Martell, *J. Org. Chem.*, **14**, 355 (1949).

(5) Martell, Doran and Bersworth, unpublished.