[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE SCHOOL OF APPLIED SCIENCE]

Effect of Temperature and Solvent upon the Fate of Carboxyl Groups in the Decomposition of Benzoyl Peroxide

BY PAUL F. HARTMAN,[1] HENRY G. SELLERS[1] AND DAVID TURNBULL

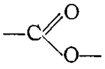
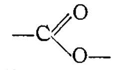
Introduction

In 1937 Hey and Waters[2] advanced arguments to show that the known facts concerning the decomposition of benzoyl peroxide in solvents were consistent with the hypothesis that the reaction took place by a free radical mechanism and that there were difficulties in explaining these facts by the various RH schemes previously proposed. Since that time this viewpoint has been accepted by many investigators but there has been considerable disagreement on the steps involved in the free radical mechanism. It appeared that data on the rate of decomposition of benzyol peroxide in representative hydrocarbons accompanied by quantitative data on the fate of the carboxyl groups should help to clarify this problem. It was the purpose of this investigation to obtain such data.

Recently Nozaki and Bartlett[3] published their investigations on the rate of decomposition of benzoyl peroxide in a large number of organic solvents. Their results offered further support for a free radical mechanism and indicated that a substantial component of the decomposition was induced by free radicals formed in the primary step or by subsequent interaction with the solvent. They found that the rate of peroxide decomposition could be represented by the equation

$$-\mathrm{d}C/\mathrm{d}t = k_1C + k_iC^{3/2} \qquad \text{(A)}$$

where C is the peroxide concentration, k_1C is the component of the rate due to the primary step, and $k_iC^{3/2}$ is the component induced by free radicals. However, they did not report any data on the decomposition products.

While there have been numerous investigations of the products of benzoyl peroxide decomposition in solvents, the fate of the  $-\mathrm{C}{\overset{\displaystyle /\!\!/ \mathrm{O}}{\underset{\displaystyle \backslash \mathrm{O}-}{}}}$ groupings generally has not been accounted for quantitatively. In most of the earlier studies relatively concentrated solutions of peroxide were used so that the reactions resulting in the formation of compounds derived from the  $-\mathrm{C}{\overset{\displaystyle /\!\!/ \mathrm{O}}{\underset{\displaystyle \backslash \mathrm{O}-}{}}}$ grouping must have been complex. Since Bartlett and Altschul[4] have found that the molar ratio of carbon dioxide formed to peroxide decomposed, R_c, is affected by the presence of oxygen it is evidently desirable to carry out the reaction in the absence of oxygen. This precaution was not generally followed in much of the earlier work.

Recently there have been some investigations on the effect of peroxide concentration and temperature on R_c in comparatively dilute benzene solutions. Brown[5] has found that R_c at 80° is considerably greater for an initially 0.1 molar solution than for one initially 0.8 molar. McClure, Robertson and Cuthbertson[6] reported that the evolution of carbon dioxide is approximately a first order reaction with respect to benzoyl peroxide in solutions initially 0.1 molar. They also found that R_c increased markedly with increasing temperature, ranging from 1.07 at 66° to 1.48 at 78°. It appears, however, that they[6] did not exclude air from their system.

Experimental

Materials.—Eastman Kodak Co. benzoyl peroxide was purified according to the procedure of Gattermann.[7] All of the hydrocarbons were fractionated through a 36-inch packed column and redistilled over sodium immediately before use. Cyclohexane and methylcyclohexane were obtained from Eastman Kodak Co., *n*-octane from Connecticut Hard Rubber Company, benzene from J. T. Baker, while *t*-butylbenzene was synthesized by the Friedel–Crafts reaction from Eastman chemicals. Refractive indices of all of the hydrocarbons used agreed with values recorded in the literature within experimental error.

Temperature Control and Measurement.—Temperature was maintained constant to within ±0.015° by means of a mercury thermoregulator in an oil-bath surrounded by an outer oil-bath maintained at a temperature 2–3° below the inner bath. Beckmann thermometers were used which had been standardized against a platinum resistance thermometer calibrated by the Bureau of Standards.

Analysis.—Peroxides were analyzed essentially by the method recommended by Liebhafsky and Sharkey.[8] Acid concentration was determined by titration with alcoholic potassium hydroxide. After completing the titration for acid an excess of base was added and the solution refluxed for one hour. Before refluxing, the solution was flushed well with carbon dioxide-free nitrogen and the necessary precautions for protecting the sample from carbon dioxide were taken during the refluxing. After refluxing, the residual base was titrated with standard acid. During this titration, carbon dioxide-free nitrogen was passed through the mixture continuously. Brom thymol blue was used as indicator in both acid and ester determination.

In experiments where a manometric method was used to determine carbon dioxide the fragile tip of a sealed reactor containing the decomposition products was broken under pressure tubing attached to an evacuated line containing a manometer. Before this operation the reactor had

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[1] Taken from theses submitted by Paul F. Hartman (present address: U. S. Rubber Company, Passaic, New Jersey) in partial fulfilment of the requirements of the Ph.D. degree and by Henry G. Sellers (present address: Southern Research Institute, Birmingham, Alabama) in partial fulfilment of the requirements of the M. S. degree.

[2] Hey and Waters, *Chem. Rev.*, **21**, 169 (1937).

[3] Nozaki and Bartlett, THIS JOURNAL, **68**, 1686 (1946).

[4] Bartlett and Altschul, *ibid.*, **67**, 812 (1945).

[5] Brown, *ibid.*, **62**, 2657 (1940).

[6] McClure, Robertson and Cuthbertson, *Can. J. Research*, **20B**, 103 (1942).

[7] Gattermann and Wieland, "Laboratory Methods of Organic Chemistry," Macmillan Company, 1932.

[8] Liebhafsky and Sharkey, THIS JOURNAL, **62**, 190 (1940).

been cooled from reaction temperature and brought to equilibrium in a temperature bath maintained at 25.0 ± 0.1°. From the manometer drop, "dead space," reactor volume, vapor pressure of benzene, and solubility of carbon dioxide in benzene[9] it was possible to calculate the quantity of carbon dioxide formed. In this connection it may be remarked that in using reactors having a volume of 70 cc. and containing 25 cc. of solution the amount of dissolved carbon dioxide was very significant. In most of the carbon dioxide analyses a gravimetric method was used. For these determinations reactors were constructed having inlet (extending into the solution) and outlet tubes so that they could be attached to an analytical train which was assembled in the following order: nitrogen source, mercury valve, ascarite tube, drying tube, reactor, cold trap (Dry Ice–naphtha), drying tube, ascarite absorber, drying tube, and sodium hydroxide trap. After breaking both tips on the reactor under the rubber tubes to which it was attached nitrogen was passed through the system for two hours. From the gain in weight of the ascarite absorber corrected for the blank (about 0.5%) the number of moles of carbon dioxide was calculated.

Procedure.—A specified amount of peroxide solution was added to a reactor which was then evacuated and sealed off. During evacuation the reactor was cooled by a Dry Ice–chloroform bath. For rate determination experiments about 12 reactors were sealed and placed in the bath for various periods of time.

Results

Rate of Peroxide Decomposition.—In these experiments, which were done before the results of (3) were available, the starting peroxide concentrations were made as small as seemed consistent with accurate analytical determinations (0.01 to 0.05 molar) in order to minimize the importance of any component of the decomposition which might be induced by radicals. In all five of the hydrocarbons a first order relation for the decomposition was approximated but in cyclohexane, methylcyclohexane, and benzene solutions definite departures from a first order relation were observed. While these departures indicated that a part of the decomposition followed an order greater than unity the results were not extended over a sufficient concentration range to establish what this order was. Data reported in ref. 3 for three of the solvents used in this investigation show that the proportion of the decomposition induced by radicals is still very significant for peroxide concentrations of 0.01 mole/liter and less.

In Table I the half-life values of the slopes of curves obtained by plotting $\log_e C$ against t for the decomposition in the five solvents at 80° are tabulated. These values are compared with those calculated from (3) for solvents common to both investigations and the agreement is fairly satisfactory. It may be noted that considerable discrepancies exist in the values of $d \ln C/dt$ reported in earlier investigations for the decomposition of the peroxide in benzene at 80.0°. Thus for a peroxide concentration of 0.025 $d \ln C/dt$ was calculated to be 0.0016 (min.$^{-1}$) from (5), 0.0021 from the results of Kamenskaya and Medvedev,[10] and 0.0029 from (6).

TABLE I

REACTION RATES AND THEIR APPARENT ENERGY OF ACTIVATION, E, FOR THE DECOMPOSITION OF BENZOYL PEROXIDE IN VARIOUS HYDROCARBONS AT 80.0°

Solvent	Concentration = C (moles/liter)	$d \ln C/dt$ (min.$^{-1}$) This investigation	Nozaki and Bartlett	E (kcal./mole)
Benzene	0.0050	0.00199	0.00219	
Benzene	.025	.00218	.00240	29.9
t-Butylbenzene	.012	.00268	.00303	30.4
Cyclohexane	.012	.00620	.00607	28.2
Methylcyclohexane	.012	.00359		30.7
n-Octane	.0080	.00226		29.0

Also tabulated in Table I are apparent energies of activation [see (3)] for the decomposition in the five solvents calculated from the half life values of $d \ln C/dt$ at two temperatures for each solvent.

Rate of Formation of Carbon Dioxide.—It has been reported[6] that the formation of carbon dioxide from the decomposition of benzoyl peroxide in benzene is first order with respect to the peroxide. Since the results of this investigation on R_c were in disagreement with those of ref. 6, it seemed advisable to repeat this study. To test for a first order reaction $\log (x_f - x)$, where x = moles of carbon dioxide evolved per liter at time, t, and $x_f = x$ at $t = \infty$, was plotted against t. A linear relation between these variables was approximated at both of the temperatures investigated, 79.60 and 89.60°. However, these results do not rule out the possibility that a part of the carbon dioxide is evolved in the radical induced decomposition. Slopes of these curves at the half-life concentrations differed by an average of 1.7%, with a maximum deviation of 3%, from the slopes of the relations between $\log C$ and time found by iodimetric titration. Figure 1 compares the fraction of the two reactions, x/x_f and $(C_0 - C)/C_0$, which had taken place at various times for an experiment conducted at 89.60°.

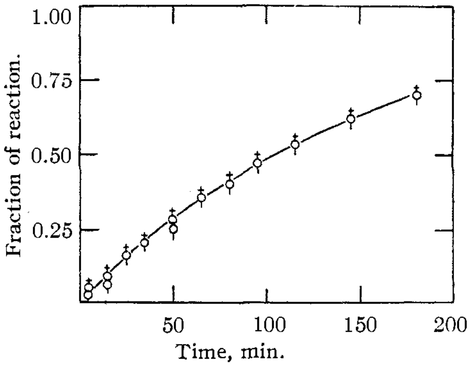

Fig. 1.—Comparison between fraction of original peroxide decomposed $(C_0 - C)/C_0$, with fraction of final amount of carbon dioxide formed, x/x_f, at various times for a benzoyl peroxide solution, initially 0.0459 molar, in benzene at 89.6°. Key: ♂, $(C_0 - C)/C_0$; ♀, x/x_f.

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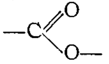
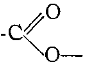
[9] "International Critical Tables," Vol. III, p. 265.

[10] Kamenskaya and Medvedev, *Acta Physicochim., U. S. S. R.*, **13**, 565 (1940).

TABLE II

RATIOS OF THE NUMBER OF MOLES OF CO_2, ACID OR ESTER FORMED PER MOLE OF BENZOYL PEROXIDE DECOMPOSED IN HYDROCARBONS AT VARIOUS TEMPERATURES

Solvent	Temp., C.	C_0	R_c Manometric method	R_c Gravimetric method	R_a	R_e	$R_c + R_a + R_e$
Benzene	69.60	0.045		1.61 ± 0.01	0.230 ± 0.01	0.148 ± 0.01	1.99 ± 0.02
	79.60	.045	1.61 ± 0.03	1.66 ± .00	.218 ± .01	.122 ± .01	2.00 ± .02
	89.60	.045	1.66 ± .03	1.66 ± .01	.206 ± .01	.112 ± .01	1.98 ± .02
t-Butylbenzene	80.00	.024		1.55 ± .01	.42 ± .015	.03 ± .00	2.00 ± .03
	87.00	.024		1.56 ± .02	.42 ± .00	.03 ± .00	2.01 ± .02
Cyclohexane	69.60	.024		0.927 ± .012	1.06 ± .01	.00	1.99 ± .02
	79.60	.024		.966 ± .015	1.06 ± .01	.00	2.03 ± .03
Methylcyclohexane	73.00	.024		.98 ± .00	0.93 ± .01	.05 ± .01	1.96 ± .02
	80.00	.024		1.05 ± .01	.83 ± .00	.09 ± .015	1.97 ± .03
n-Octane	79.60	.015		1.390 ± .003	.614 ± .01	.00	2.00 ± .01
	89.60	.015		1.409 ± .003	.600 ± .01	.00	2.01 ± .01

Decomposition Products.—Quantitative analyses for products derived from  $-C(=O)O-$ groupings were made on samples in which the decomposition of peroxide was permitted to go to completion. All analyses for each product were run in duplicate on two or more separate samples contained in independent reactors for each solvent at two or more temperatures. Table II gives the average result and the mean deviations for the various analyses. C_0 represents the initial concentration of peroxide (this was known to at least three significant figures for every individual sample), while R_c, R_a and R_e represent the ratio of the number of moles of carbon dioxide, acid or ester formed, respectively, per mole of peroxide decomposed. It is evident that within experimental error, the  $-C(=O)O-$ groupings are accounted for quantitatively by the carbon dioxide, acid, and ester analyses. This result constitutes a good independent check on the consistency of the data.

It is noteworthy that the temperature coefficients of R_c are very small for all five solvents. This is in sharp disagreement with the results reported[6] for the decomposition in benzene. For example, at 69.60° the value of R_c interpolated from the results of ref. 6 is 1.18. This disagreement may be due to the failure in the earlier investigation[6] to eliminate oxygen from the system or to correct for carbon dioxide dissolved in the solution.

It is apparent from the results that R_c, R_a and R_e vary in a significant manner for different solvents. Appreciable values of R_e were observed for only the aromatic solvents. R_c was greatest for the aromatic solvents and least for the cycloparaffins.

In all of the solvents the fraction of peroxide decomposing to give ester was rather small. Approximate minimum values of R_e may be evaluated from the results of ref. 3 for three of the solvents on the basis of the assumption that one molecule of ester is formed for every molecule of peroxide decomposed by radicals.[3] Values of R_e at 80° calculated in this way for the initial concentrations listed in Table II are: benzene, 0.15; cyclohexane, 0.34; *t*-butylbenzene, 0.32. For cyclohexane and *t*-butylbenzene these values are much larger than those actually observed. Unless very unstable esters which hydrolyze easily are formed, this indicates that for these solvents ester is not an important product of the induced decomposition.

Discussion

It is possible to calculate the rate of formation of carbon dioxide, acid or ester on the basis of any simple radical mechanism assumed for the decomposition. From these reaction rates the instantaneous values of the ratios R_c, R_a and R_e, which shall be referred to as r_c, r_a and r_e, may also be calculated. Experimental values for these quantities and their variation with time and peroxide concentration should be of considerable value in deciding between various possible reaction mechanisms.

Where chain transfer to the solvent takes place a simple mechanism may be formulated in the following way

$$(PhCOO)_2 \xrightarrow{k_1} 2PhCOO^{\cdot} \qquad (B)$$

$$PhCOO^{\cdot} + RH \xrightarrow{k_2} PhH + CO_2 + R^{\cdot} \qquad (C)$$

$$PhCOO^{\cdot} + RH \xrightarrow{k_3} PhCOOH + R^{\cdot} \qquad (D)$$

$$R^{\cdot} + (PhCOO)_2 \xrightarrow{k_4} PhCOOR + PhCOO^{\cdot} \qquad (E)$$

$$R^{\cdot} + R^{\cdot} \xrightarrow{k_5} R{-}R \qquad (F)$$

Concentrations of free radicals are calculated by the usual steady state approximation. Instantaneous ratios of products formed to peroxide decomposed are defined by equations of the type

$$r_c = -d[CO_2]/dt/dC/dt = -d[CO_2]/dC \qquad (G)$$

Equations analogous to (G) give r_a and r_e. For convenience $k_4\sqrt{2k_1/k_5}$ is defined as k_i in conformity with the notation of (3).

With these assumptions and definitions expressions for the rates of peroxide decomposition; rates of formation of carbon dioxide, acid and ester; and r_c, r_a and r_e have been derived and tabulated in Table III. Column 3 of the table gives the value of each of these quantities when $C \rightarrow 0$, while column 4 shows whether r increases (+) or decreases (−) as C increases.

TABLE III

RATES OF FORMATION OF CARBON DIOXIDE, ACID, OR ESTER AND VALUES FOR r_c, r_a AND r_e CALCULATED ON THE BASIS OF THE ASSUMED REACTION MECHANISM

Quantity	General expression	Expression where $C \rightarrow 0$	Change in r with increasing C
$-\mathrm{d}C/\mathrm{d}t$	$k_1C + k_iC^{3/2}$	k_1C	
$\mathrm{d}[\mathrm{CO_2}]/\mathrm{d}t$	$k_2(2k_1C + k_iC^{3/2})/(k_2 + k_3)$	$2k_2k_1C/(k_2 + k_3)$	
$\mathrm{d}[\text{acid}]/\mathrm{d}t$	$k_3(2k_1C + k_iC^{3/2})/(k_2 + k_3)$	$2k_3k_1C/(k_2 + k_3)$	
$\mathrm{d}[\text{ester}]/\mathrm{d}t$	$k_iC^{3/2}$	0	
r_c	$\dfrac{k_2(2k_1 + k_iC^{1/2})}{(k_2 + k_3)(k_1 + k_iC^{1/2})}$	$2k_2/(k_2 + k_3)$	−
r_a	$\dfrac{k_3(2k_1 + k_iC^{1/2})}{(k_2 + k_3)(k_1 + k_iC^{1/2})}$	$2k_3/(k_2 + k_3)$	−
r_e	$k_iC^{1/2}/(k_1 + k_iC^{1/2})$	0	+

Expressions obtained for the rates of formation of carbon dioxide and acid (see Table III) indicate that the reaction order for these processes is similar to that for peroxide decomposition excepting that the first order component is relatively more important.

In dilute peroxide solutions r_c approaches $2k_2/(k_2 + k_3)$ and it may be predicted from this expression that the temperature coefficient of r_c should be small. This seems likely because the energies of activation for reactions C and D above, having rate constants k_2 and k_3, should be quite small and of the same order of magnitude. This is probably the basis for the small temperature variation for R_c found in this investigation.

A further requirement of the mechanism under consideration is that both r_c and r_a should decrease with increasing peroxide concentration. There is some evidence (5) that r_c does increase with peroxide concentration in benzene solutions.

It is likely that the sequence of reactions B through F represents an over-simplification of the actual reaction mechanism for most solvents. Thus when relatively concentrated solution of benzoyl peroxide decompose in aromatic solvents (RH) other than benzene the predominant hydrocarbon which is formed appears to be R–Ph rather than R–R or Ph–Ph (see Hermans[11]). This result is difficult to account for unless it is assumed that hydrogen radicals are formed in intermediate stages of the reaction. No evidence was found in this or earlier investigations that molecular hydrogen was formed in appreciable quantities in the decomposition, so that any hydrogen atoms or molecules which were formed must have disappeared quickly by further reactions.

It has been pointed out that the observed values of R_e for cyclohexane and *t*-butylbenzene are much smaller than the values calculated on the basis of equation (E) for the induced decomposition. It appears, therefore, that some different assumption must be advanced for the radical induced decomposition in these solvents. Two possible assumptions for this which do not lead to ester formation are: (a) hydrogen radicals react with peroxide to form acid and PhCOO· (b) R· radicals react with peroxide as follows

$$\mathrm{R^{\cdot} + (PhCOO)_2 \longrightarrow R{-}Ph + CO_2 + PhCOO^{\cdot}} \quad \text{(G)}$$

Replacement of reaction (E) of the previous mechanism with (G) gives a modified mechanism which requires that r_c increase with increasing peroxide concentration. No data, obtained with air free reactors, showing the effect of peroxide concentration on r_c are available for either of the two solvents under consideration.

From this discussion it may be concluded that important information about the mechanism of peroxide decomposition may be gained from the rates of formation of acid, ester, and carbon dioxide and their variation with peroxide concentration.

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They also thank Dr. C. F. Prutton for his continued interest and helpful suggestions.

Summary

1. Reaction rates and the corresponding apparent energies of activation for the decomposition of benzoyl peroxide in dilute solution of five hydrocarbons have been measured.

2. Ratios of the number of moles of carbon dioxide, acid, or ester formed to moles of peroxide decomposed, R_c, R_a and R_e, respectively, have been measured for the decomposition in all five hydrocarbons at two temperatures.

3. It has been shown that under the experimental conditions chosen the diacyl peroxide grouping decomposes quantitatively to carbon dioxide, acid, and ester.

4. It was found that R_c and R_a had very small temperature coefficients for all of the hydrocarbons.

5. There was considerable variation in the values of R_c, R_a, and R_e with change in solvent.

6. Excepting for benzene solutions, R_a was very much larger than R_e.

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(11) Hermans, *Rec. trav. chim.*, **54**, 760 (1935).