[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

The Decomposition of *sym*-Substituted Benzoyl Peroxides

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A kinetic study of the thermal decomposition of benzoyl peroxide and of fifteen symmetrically substituted peroxides in acetophenone has been made. Under these conditions the rates of decomposition were observed to be first order and generally to be independent of the initial peroxide concentration. It is shown that higher order induced decomposition of the peroxides by a bimolecular radical displacement reaction involving attack by radicals derived from the peroxides is probably negligible and chain decomposition of the peroxides by radicals derived from the solvent acetophenone is held unlikely. The energy and entropy of activation for the decomposition of each peroxide has been estimated, showing that substituents may affect both factors. In attempting a correlation of the effect of meta and para substituents on the rate of decomposition with Hammett's σ values, there is an indication that the homolytic cleavage of symmetrical benzoyl peroxides into free radicals may involve the interaction of two opposing dipoles. The effect of ortho substituents may be correlated with the effects of meta and para substituents.

Although Hammett's equation[2] correlates the effect of meta and para substituents in many polar, non-radical reactions, the first extension of this equation to reactions involving free radicals was made by Walling, Mayo, *et al.*,[3] who correlated the relative rates of addition of the styryl radical to meta- and para-substituted styrenes. Since the thermal decomposition of benzoyl peroxide in solution has been shown to involve an initial cleavage of the peroxide bond forming short lived free radicals,[4-7] and as only scattered observations have been made on the decomposition of substituted benzoyl peroxides[8,9] a systematic study was undertaken to establish a relationship between structure and ease of homolytic cleavage of the peroxide bond.

In addition to a unimolecular spontaneous decomposition it has been demonstrated that benzoyl peroxide decomposes by a parallel bimolecular radical displacement reaction.[4-8] This induced peroxide decomposition has been demonstrated to be effected either by radicals from peroxide or from the solvent. It has also been pointed out that the overall kinetic order of peroxide decomposition may depend on the type of chain termination which predominates.[5,10] Over-all first order kinetics of peroxide decomposition would be obtained only if the induced decomposition of peroxide were carried on by solvent radicals with an exclusive chain termination step of unlike radicals.[5,10]

Among the many investigators who have studied the rate of decomposition of benzoyl peroxide at 80°, in benzene, there seems to be no general agreement either with respect to the kinetic order of the induced reaction, or the rate constant of the spontaneous unimolecular decomposition.[4,6,11] Thus, it was apparent that employing analytical estimations similar to those used by previous authors for arriving at the unimolecular decomposition rate constant of benzoyl peroxide would give relative first order rate constants which would depend upon the particular method employed. Consequently, a reaction medium was used in which induced peroxide decomposition was eliminated, or at least held to a minimum.

In selecting a solvent for the rate studies, two important requirements must be fulfilled: (1) the solvent must show a high solvent capacity for the various substituted peroxides and, (2) the decomposition of the peroxides should exhibit little, if any, induced decomposition. Acetophenone, in general, was found to fulfill these two requirements.

The decomposition of benzoyl peroxide and symmetrically substituted benzoyl peroxides in acetophenone at 80° and other temperatures were observed to be first order. Figure 1 is a plot of the first order rate constant for the decomposition of some meta- and para-substituted benzoyl peroxides in acetophenone at 80° as a function of initial peroxide concentration. In Table I are listed the ob-

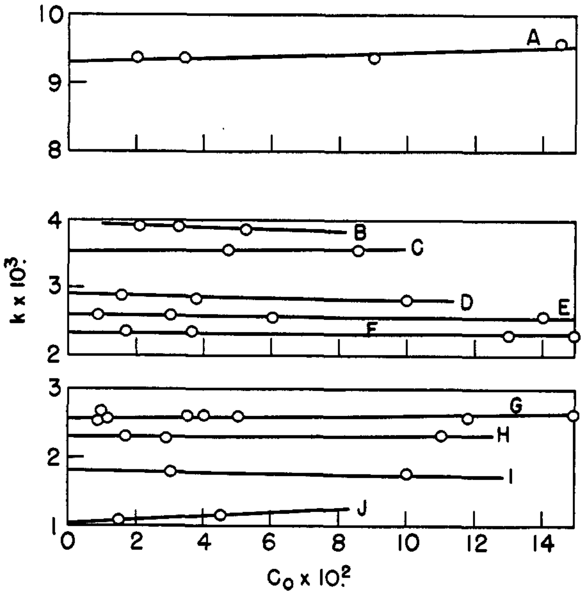

Fig. 1.—k_1, the decomposition rate constant of various peroxides in acetophenone at 80° as a function of C_0, the initial peroxide concentration: A, bis-(*p*-methoxybenzoyl) peroxide; B, bis-(*m*-methoxybenzoyl) peroxide; C, bis-(*p*-methylbenzoyl) peroxide; D, bis-(*m*-methylbenzoyl) peroxide; E, benzoyl peroxide; F, bis-(*p*-chlorobenzoyl) peroxide; G, bis-(*p*-nitrobenzoyl) peroxide; H, bis-(*m*-nitrobenzoyl) peroxide; I, bis-(*m*-chlorobenzoyl) peroxide; J, bis-(3,5-dinitrobenzoyl) peroxide.

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[1] This paper is an abstract of part of the doctoral dissertation presented by A. J. Buselli to the Graduate Faculty of Cornell University in September, 1950.

[2] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, p. 186.

[3] C. Walling, E. R. Briggs, K. B. Wolfstirn and F. R. Mayo, THIS JOURNAL, **70**, 1537 (1948).

[4] K. Nozaki and P. D. Bartlett, *ibid.*, **68**, 1686 (1946).

[5] P. D. Bartlett and K. Nozaki, *ibid.*, **69**, 2299 (1947).

[6] B. Barnett and W. E. Vaughan, *J. Phys. Chem.*, **51**, 926 (1947).

[7] W. E. Cass, THIS JOURNAL, **68**, 1976 (1946).

[8] D. J. Brown, *ibid.*, **70**, 1208 (1948).

[9] L. E. Reddington, *J. Polymer Sci.*, **3**, 503 (1948).

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

[11] D. J. Brown, *ibid.*, **62**, 2657 (1940).

served first order rate constants for some ortho-, meta- and para-substituted benzoyl peroxides at various other temperatures.

Table I

First Order Rate Constants for the Decomposition of Peroxides in Acetophenone at Different Temperatures and Concentrations

Substituted benzoyl peroxide	Temp., °C.	Init. concn. mole/liter	$k_1 \times 10^3$, min.$^{-1}$	Init. concn. mole/liter	$k_1 \times 10^3$ min.$^{-1}$
Bis-(*m*-chloro-	98.07	0.070	14.2	0.031	14.4
Bis-(*m*-methoxy-	72.64	.116	1.71	.033	1.69
Bis-(*m*-methyl-	88.53	.109	7.92	.033	8.05
Bis-(*m*-methyl-	94.92	.056	17.3	.016	17.1
Bis-(*p*-methyl-	94.92	.054	21.6	.015	22.0
Bis-(*o*-methoxy-	58.55	.044	10.45	.095	10.2
Bis-(*o*-methoxy-	50.08	.029	3.64	.080	3.55
Bis-(*o*-nitro-	69.95	.015	8.55	.055	8.25
Bis-(*o*-phenoxy-	76.52	.017	20.50	.033	20.35
Bis-(*o*-phenoxy-	57.53	.019	1.87	.033	1.87
Bis-(*o*-chloro-	80.0	.024	23.1	.094	23.6
Bis-(*o*-methyl-	79.13	.028	16.8	.099	17.0
Bis-(*o*-methyl-	62.01	.037	1.87	.110	1.82

The data given in Fig. 1 and Table I indicate that no appreciable concentration effects were observed for the first order decomposition rate constants of substituted benzoyl peroxides in acetophenone. This excludes all but one course of chain decomposition: namely, the case where peroxide molecules are attacked by solvent radicals and the main chain termination step involves exclusively the recombination of solvent radicals with peroxide radicals. However, this type of chain decomposition may also be ruled out for several reasons. A low rate of decomposition has been observed in acetophenone compared with other solvents in which induced decomposition has been established.[4-8] Further, the rates observed for substituted peroxides are comparable to those found by Clarke, *et al.*, in inhibited experiments using 3,4-dichlorostyrene–dioxane solvent medium.[12,13] This is shown in Table II. Finally, preliminary studies with "inhibitors" or "radical traps" show no appreciable lowering of rates in those peroxides studied. Thus, in the decomposition of 0.05 *M* benzoyl peroxide in acetophenone and 0.2 *M* acetanilide no appreciable lowering of the rate of decomposition was observed. Similarly the rate of decomposition of 0.05 *M* solutions of bis-(*m*-chlorobenzoyl), bis-(*m*-methoxybenzoyl) and bis-(*m*-nitrobenzoyl) peroxides in acetophenone in the presence of 0.2 *M* methyl methacrylate was not significantly altered. It was observed, however, that the first order rate constant for bis-(*p*-cyanobenzoyl) peroxide at 0.015 *M* initial concentration in acetophenone and 0.25 *M* methyl methacrylate was 14.5% lower than the constant obtained in the absence of methyl methacrylate. This lowering which seems to be peculiar to bis-(*p*-cyanobenzoyl) peroxide may be due to the low concentration of peroxide necessitated by its low solubility. A similar peculiarity was noted by Clarke using very low concentrations of benzoyl peroxide in benzene with methyl methacrylate as an inhibitor.[12]

Table II

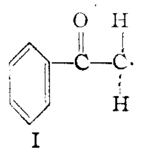
Extrapolated Rate Constants of Substituted Benzoyl Peroxides at 80°

Substituted benzoyl peroxide	$k \times 10^3$ min.$^{-1}$ In acetophenone	In dioxane and[13] 0.2 *M* 3,4-dichlorostyrene
Bis-(*p*-methoxy-	9.32	7.06
Bis-(*m*-methoxy-	3.94	3.45
Bis-(*p*-methyl-	3.55	3.68
Bis-(*m*-methyl-	2.92	2.64
Unsubstituted	2.60	2.52
Bis-(*p*-chloro-	2.30	2.17
Bis-(*m*-chloro-	1.73	1.52
Bis-(*p*-cyano-	1.46	1.22

From the above observations it may be concluded that peroxide decomposition by an induced mechanism is probably negligible under the conditions employed in this investigation. This should be so if one considers the probable role of acetophenone solvent in light of recent theories concerning the nature of bimolecular radical displacement reactions.

Walling, *et al.*,[3] in their studies on the copolymerization of meta- and para-substituted styrenes with methyl methacrylate and unsubstituted styrene, furnished additional evidence that in bimolecular radical reactions, stabilization of the transition state by polar resonance structures, ionic type, involving transfer of an electron from one reactant to another, may be of dominant influence in such reactions, regardless of whether they are of the initiation, propagation, chain transfer or termination type. Recently, Mayo and Walling[14] have extended this idea to radical reactions in general, and point out that the rapid chain decomposition of benzoyl peroxide by ethers involves a chain of two alternating radical displacement reactions, involving in each case interaction of electron rich and electron poor centers.

Radicals from the spontaneous decomposition of benzoyl peroxide may chain transfer with acetophenone solvent molecules by attacking either the benzene ring or the side-chain methyl group. In either case solvent radicals are formed which may be resonance stabilized. Thus, if the methyl group is the site of chain transfer, the resulting radical may be resonance stabilized by structures such as I and II. If the ring is the site of chain transfer, as is the case in the decomposition of benzoyl peroxide in nitrobenzene,[15] the resulting radical can be resonance stabilized by such resonance structures as III–VI.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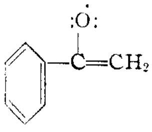
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If in bimolecular radical displacement reactions, the stabilization of the transition state by actual electron transfer to give polar resonance structures

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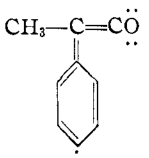
[12] J. T. Clarke, Ph.D. Thesis, Massachusetts Institute of Technology, 1949.

[13] C. G. Swain, W. H. Stockmayer and J. T. Clarke, This Journal, **72**, 5426 (1950).

[14] F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 269 (1950).

[15] H. Scheifle, M.S. Thesis, Cornell University, 1950.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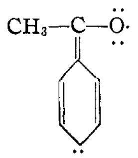
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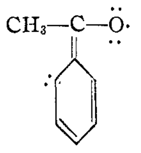
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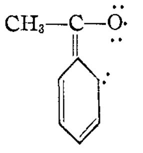
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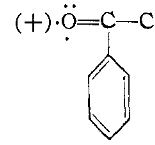
be the dominating factor in the variation of rate with structure, then any radical displacement reaction involving a radical from benzoyl peroxide and an acetophenone molecule should be facilitated if such a stabilization is possible. This may involve electron transfer from acetophenone to the benzoyl radical to give a stable benzoate ion and an oxonium ion radical capable of resonance stabilization by such structures as VII–IX. However, since the total acid formed in the decomposition of benzoyl peroxide in acetophenone at 80° was found to be approximately 17% of the theoretical maximum, the above process may not be of major importance. It has been observed in this investigation that 65 ± 2% of the carbonyl groups of a 0.16 *M* solution of benzoyl peroxide decomposing in acetophenone at 80° can be accounted for as carbon dioxide. This would seem to indicate that if radicals from the spontaneous decomposition entered into a chain transfer process with solvent, a substantial part of this process would be carried on by phenyl radicals. Such a model would seem to demand that in an electron transfer process the phenyl radical be the electron donor since the carbonyl group of acetophenone would be expected to be an electron acceptor. The transition state may then be resonance stabilized by three identical carbonium ion structures. The acetophenone may be represented in the same transition state as a stable enolate ion whose resonance hybrid partakes of properties represented by such structures as X–XII.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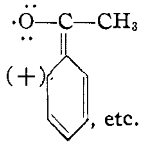
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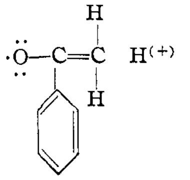
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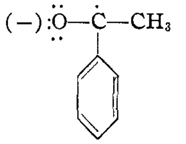
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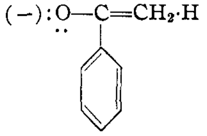
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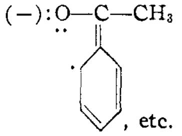
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With acetophenone as a solvent, any radical derived therefrom would not be expected to possess significant electron donor properties for two principal reasons; (1) the radicals themselves have resonance stabilization increasing the activation energy in any bimolecular displacement reaction, and (2) the radicals contain a carbonyl group. Any reasonable polar resonance structure which might be written for such radicals exhibiting donor properties in the transition state, since the peroxide molecule would be expected to be an electron acceptor, would involve resonance structures with an oxonium ion having only six electrons in its valence orbital. Consequently, first order induced decomposition of peroxide molecules, that is, attack by acetophenone radicals, should not be favored and is probably negligible.

Discussion of Results.—Figure 2 shows a plot of log k/k_0 *vs.* 2σ, where k_0 and k are the first order constants of benzoyl peroxide and substituted peroxides, respectively, at infinite dilution and σ is the usual Hammett substituent sigma value. The function 2σ has been used here since in the Hammett significance of a σ value, symmetrical substitution of a like substituent in the ring of each benzoyl group would increase or decrease the electron density of the reaction center, the peroxide bond, by a factor of two as compared to the effect of a substituent in but one of the rings.

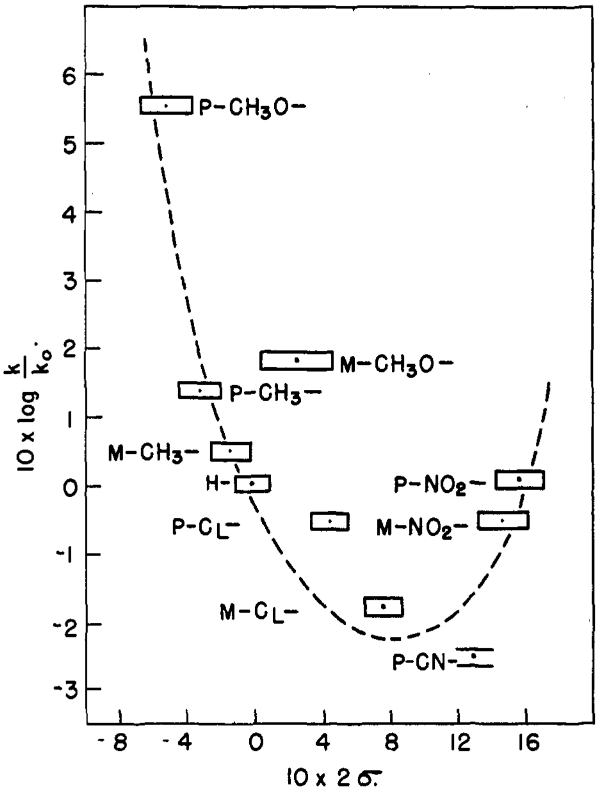

Fig. 2.—log k/k_0 as a function of σ, where k is the decomposition rate constant of the substituted benzoyl peroxide and k_0 that of unsubstituted benzoyl peroxide, both extrapolated to zero concentration, and σ represents Hammett's sigma values. The height of the rectangles represents a standard error of 3% in k, while the width represents the probable error in σ as tabulated by Hammett.[2] [The σ value for the *p*-cyano substituent was calculated from log K/K_0 for *p*-cyanobenzoic acid, *cf.* M. Kilpatrick and R. D. Eanes, THIS JOURNAL, **65**, 589 (1943).]

The trend shown in Fig. 2 indicates that substitution in the meta and para positions of groups whose electron releasing nature decreases as described by Hammett's σ values effects a decrease in the rate of decomposition of the corresponding peroxides. This suggests that the two carboxyl groups are negative in the sense in which such terms are used in consideration of dipoles, and that substituents alter the stability of substituted peroxides by altering the coulombic repulsive forces between the two carboxyl groups. The fact that the first order rates are generally higher in acetophenone than in 3,4-dichlorostyrene–dioxane solution agrees with such a polar model in the transition state. Acetophenone, with a dielectric constant of 18 at 20° as compared to 2.2 for dioxane, would be expected to have the greater solvent interaction with the partially separated polar fragments of the transition state.

Figure 2 also suggests that under the conditions employed in this investigation, a minimum is reached in the trend, and that the enhanced reactivity of the nitrosubstituted peroxides may be due to a change in dipole direction. On the other hand this may be due solely to some induced decomposition in these peroxides, and not a change in dipole direction. Against this, however, are the facts that these peroxides showed good first order decomposition kinetics with only negligible concentration effects. Compared to Clarke's experiments under "inhibited" conditions, the rates observed here are slower by half, and addition of methyl methacrylate to acetophenone had no significant effect on the decomposition rate of bis-(*m*-nitrobenzoyl) peroxide. As was concluded by Swain, *et al.*,[13] peroxides with strong electron attracting substituents would be most susceptible to induced decomposition. Since the ionization constant of 3,5-dinitrobenzoic acid is considerably greater than that of either meta- or para-nitrobenzoic acid, bis-(3,5-dinitrobenzoyl) peroxide would be expected to have an even larger degree of induced decomposition. However, considering only coulombic repulsive forces of two interacting dipoles, bis-(3,5-dinitrobenzoyl) peroxide should not be less stable than bis-(*p*-nitrobenzoyl) peroxide. Figure 1 shows that the former is the more stable of the two peroxides.

The first order rate constants at various temperatures for the peroxides studied are listed in Table III. The energy of activation was estimated from a plot of log *k* against $1/T$. The corresponding entropy of activation was then calculated at 80° according to the formula from transition state theory.[16] These results indicate that the rate constants may depend on both the energy and entropy of activation, especially with substituents in the ortho position. Although in many cases the differences in E and ΔS for substituents is less than the probable experimental error, there seems to be nevertheless a qualitative relationship between the two properties for both the meta–para series, and the ortho series.[17]

TABLE III

ENERGY AND ENTROPY OF ACTIVATION OF THE THERMAL DECOMPOSITION OF SUBSTITUTED BENZOYL PEROXIDES IN ACETOPHENONE

Substituent	Temp., °C.	$k \times 10^{3a}$ min.$^{-1}$	E, kcal. mole^{-1b}	ΔS, cal. degree^{-1} mole^{-1b}
Bis-(*p*-methoxy)	72.44	4.08	28.7	3.0
	80.00	9.35		
	86.64	21.50		
Bis-(*m*-methoxy)	72.99	1.69	28.9	2.0
	80.0	3.85		
	89.79	11.95		
Bis-(*p*-methyl)	73.36	16.80	29.9	4.3
	80.00	3.55		
	91.13	13.32		
	94.92	21.60		
Bis-(*m*-methyl)	80.00	2.82	30.2	4.7
	88.53	8.13		
	94.92	17.10		
Unsubstituted	70.0	0.691	30.2	4.5
	80.0	2.59		
	94.5	13.8		
Bis-(*p*-chloro)	80.0	2.30	30.4	5.2
	92.38	10.7		
	102.9	33.6		
Bis-(*m*-chloro)	80.0	1.71	30.7	5.3
	91.73	6.93		
	98.07	14.3		
Bis-(*p*-cyano)[a]	80.0	1.46	31.2	6.4
	90.19	5.02		
	97.81	12.6		
Bis-(*m*-nitro)	80.0	2.28	30.2	4.2
	94.87	12.1		
	100.76	23.8		
Bis-(*p*-nitro)	80.0	2.60	30.3	4.8
	89.12	7.78		
	91.92	11.0		
	97.26	19.2		
Bis-(3,5-dinitro)	80.0	1.12	31.2	5.8
	94.64	11.74		
Bis-(*o*-methoxy)	50.08	3.60	27.2	3.8
	58.55	10.48		
	68.08	33.8		
	80.0[c]	129.0		
Bis-(*o*-nitro)	59.26	3.48	28.6	6.9
	65.95	8.30		
	70.67	14.45		
	75.73	27.7		
	80.0[c]	80.6		
Bis-(*o*-phenoxy)[a]	57.53	1.87	29.0	6.0
	65.0	4.91		
	76.52	20.4		
	80.0[c]	30.0		
Bis-(*o*-chloro)	60.43	2.04	29.4	6.7
	70.68	7.22		
	80.0	23.3		
	86.84	54.2		
Bis-(*o*-methyl)	62.01	1.87	30.2	8.7
	70.01	5.41		
	79.13	16.9		
	80.0[c]	18.8		

[a] Since concentration effects for all peroxides at some temperatures were negligible, concentration effects at all temperatures were not studied and all rates are for approximately 0.05 M initial peroxide concentration except for bis-(*p*-cyanobenzoyl) peroxide and bis-(*o*-phenoxybenzoyl) peroxide which are at 0.015 and 0.033 M initial peroxide concentration, respectively. [b] The maximum probable error in E is ±0.7 kcal., while the maximum probable error in ΔS is ±1.5 cal. [c] These values of *k* at 80° are the extrapolated values obtained from a plot of log *k* *vs.* $1/T$.

A comparison of the ortho-substituted peroxides with the meta and para isomers (Table III) shows that the ortho-substituted peroxides decompose at a considerably faster rate. This is accounted for in most cases by a lower energy of activation and a

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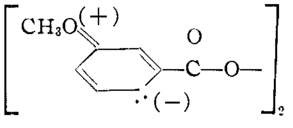
(16) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 199.

(17) C. N. Hinshelwood, "Kinetics of Chemical Change," Oxford University Press, p. 257, 1940.

higher entropy of activation. It is significant that for the isomeric bis-(methylbenzoyl) peroxides the enhanced decomposition rate of the ortho isomeride is due to the entropy factor only. The comparative rate of increase in rate of decomposition effected by a substituent in the ortho position relative to the same substituent in the meta or para positions is proportionately greater with substituents which would be expected to give proportionately higher degrees of charge separation in the ortho position. It is also significant that groups which are capable of charge separation, due to resonance, show the same relative reactivity regardless of the position they occupy in the benzene ring, *i.e.*

$$CH_3O > NO_2 > Cl$$

Although the peroxide molecule can orientate itself in such a manner as to place the ortho substituents several atomic distances from each other, the data indicate that additional field effects between the ortho substituents may be operating. If this can be assumed, then the relationships observed for ortho substituents are correlated with those in the meta and para positions. Thus, an ortho-methoxy substituent not only increases the repulsive forces in the peroxide bond, but also repulsive coulombic forces between the two ortho substituents are possible. A nitro group in the ortho position would involve considerable charge separation but, as observed, in the meta and para positions, the nitro group stabilizes the peroxide bond relative to a methoxyl group in the same position. That an ortho-phenoxy substituent should be less effective in promoting decomposition relative to an ortho-methoxy substituent may be due to steric inhibition of resonance. Any resonance involving the phenoxy group would require the phenyl group to be in the same plane as the benzene ring of the peroxide. In bis-(*o*-phenoxybenzoyl) peroxide scale space models reveal that the phenyl group may be hindered from assuming a coplanar position with the benzoyl group. The fact that bis-(*o*-chlorobenzoyl) peroxide is less stable than bis-(*o*-methylbenzoyl) peroxide indicates that field effects in the ortho position may overcome substituent effects in the peroxide bond. Since resonance with the methoxyl group in bis-(*m*-methoxybenzoyl) peroxide would involve charge separation in the ortho position this may explain the unexpected relatively high reactivity of this peroxide.



Experimental

Materials.—Acetophenone (Paragon) was fractionated at atmospheric pressure, b.p. 202° at 750 mm., and then redistilled under reduced pressure; $n^{18.8}\text{D}$ 1.5342. No peroxides could be detected in this solvent even after standing for several months. Methyl methacrylate (du Pont) was freed from inhibitors by distillation, b.p. 101°. The acetanilide used had a m.p. of 112–114°.

Synthesis of Peroxides.—All peroxides were prepared according to the method Price and Krebs[18] used for bis-(*p*-nitrobenzoyl) peroxide. Approximately 0.2 mole of the appropriate acid chloride dissolved in three times its volume of dry toluene was cooled to 0–5° and added dropwise to a vigorously stirred 10% aqueous solution of sodium peroxide containing 0.13 mole of the peroxide. The peroxide solution contained some crushed ice. Stirring was continued for one hour after the addition of the acid chlorides. Most of the peroxides separated as white crystalline solids at this point and were filtered and washed with cold water. Bis-(*o*-methylbenzoyl) peroxide and bis-(*m*-methylbenzoyl) peroxide were isolated by cooling the toluene solution in a Dry Ice–acetone mixture and filtering while cold. Bis-(*o*-phenoxybenzoyl) peroxide was isolated by removing the toluene under reduced pressure, washing the residual oil with heptane, and finally stirring vigorously with some fresh heptane until the peroxide crystallized.

The peroxides were usually recrystallized by dissolving in hot solvents at the maximum temperatures indicated in Table V, filtering the hot solutions, and cooling rapidly in an ice-bath. The peroxides were collected on sintered glass funnels, washed with dry pentane or Freon and air-dried. No explosions were encountered with the peroxides thus prepared even when allowed to stand at room temperature for several weeks. However, ortho-substituted peroxides, especially bis-(*o*-methoxybenzoyl) peroxide, showed appreciable decomposition on standing at room temperature. Table V lists the peroxides studied together with some pertinent data.

Analytical Methods.—For the quantitative determination of peroxides in organic solvents a modification of the method used by Barnett and Vaughan[19] was found to be the most useful and precise. Aliquots of the sample to be determined (2 to 5 cc.) were pipetted into 125- and 250-cc. glass-stoppered Pyrex flasks and 20 to 35 cc. (depending upon sample size) of reagent grade acetone was added. Small pieces of Dry Ice were then added to remove oxygen, to avoid oxidation of iodide ion by atmospheric oxygen. After warming the flask on a hot-plate, 2 cc. of a saturated solution of sodium iodide in acetone was added from a buret. The contents of the flask were swirled during this addition and for a few seconds afterwards. Quantitative liberation of iodine was complete within a minute, even for the most stable peroxide tested. In some cases the sodium salt of the corresponding acid precipitated as a gelatinous mass. After standing for about a minute the solution was acidified with 10–15 cc. of carbonated water and immediately titrated with 0.01 *N* or 0.005 *N* thiosulfate depending upon the concentration of peroxide in the sample. The end-point is usually sharp and its determination is aided by a white background and strong illumination. Only in instances where strongly colored decomposition products are formed, especially in the case of bis-(*p*-nitrobenzoyl) peroxide, were the end-points difficult to ascertain. A blank was run on each new batch of acetone used and in no case were peroxides found. The procedure was reproducible to within ±0.5% even for the more dilute solutions. In samples of runs containing bis-(*p*-nitrobenzoyl) peroxide of greater than 40–50% decomposition the precision is probably not better than ±1.0%. Under these conditions the iodination of acetone either before or after the addition of acidified water was too slow to cause any difficulties.

Analysis for Total Acid Content.—Samples of the reaction mixture, 2–5 cc., were diluted with 10–15 cc. of acetone and 5 cc. of water. After adding 3 drops of brom thymol blue the sample was titrated immediately with standard aqueous sodium hydroxide. The end-point was taken as a blue-green color persisting for at least 20 seconds. A blank was run on acetone and acetophenone only and the volume of base consumed was subtracted from the total titer. Upon checking this procedure with known concentrations of benzoic acid a reproducibility of ±2% was observed.

Method of Decomposition.—The decompositions were carried out in 50-cc. round-bottomed Pyrex flasks fitted with a 24/40 female ground glass joint and also fitted just below the neck with a small side-arm of 7-mm. Pyrex glass tubing. Over the end of the side-arm was fitted a No. 711 Red Sleeve Serum Stopple from the Faultless Rubber Co., Ashland, Ohio. This was made fast with two turns of copper wire. The peroxide–acetophenone solution was then placed in the flask and a water condenser having 24/40 ground glass joints was attached. To the end of the condenser a three-way stopcock was attached on the one-way

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(18) C. C. Price and E. Krebs, *Org. Syntheses*, **23**, 65 (1943).

(19) B. Barnett and W. E. Vaughan, *J. Phys. Colloid Chem.*, **51**, 929 (1947).

TABLE IV

SUBSTITUTED BENZOYL PEROXIDES

Peroxide	M.p., °C., dec.	Recryst. solvent	Yield, %	Purity, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Benzoyl	106–107 Rep. 106–108[a]	$CHCl_3 + CH_3OH$[a]		98.5				
Bis-(*p*-methoxybenzoyl)	128 Rep. 128[b]	Toluene, 80°[b]	65.5	99.2				
Bis-(*p*-nitrobenzoyl)	157–158 Rep. 156[c,d]	Toluene, 80°[c,d]	56	99.0				
Bis-(*p*-chlorobenzoyl)	140 Rep. 139[e]	1:1 benzene–cyclohexane, 80°[e]	70.5	100.0				
Bis-(*m*-nitrobenzoyl)	137 Rep. 137	Benzene, 80°	38.5	98.0				
Bis-(*p*-methylbenzoyl)	136	3:1 benzene–cyclohexane, 80°	70	100.0	71.10	71.4	5.22	5.75
Bis-(*m*-methoxybenzoyl)	82–83	3:1 cyclohexane–benzene, 80°	67	99.2	63.6	63.3	4.73	4.88
Bis-(*m*-chlorobenzoyl)	123	1:1 benzene–cyclohexane, 80°	84	100	54.04	54.10	2.59	2.85
Bis-(*m*-methylbenzoyl)	54	Cyclohexane, 80°	57	99.1	71.10	71.21	5.22	5.99
Bis-(3,5-dinitrobenzoyl)	161–162	Boiling $CHCl_3$, cooled and CH_3OH added	37	100	39.83	39.83	1.42	1.60
Bis-(*o*-chlorobenzoyl)	95	1:1 benzene–cyclohexane	75	99.85	54.04	54.22	2.59	3.04
Bis-(*o*-nitrobenzoyl)	145	Acetophenone, 50°	88.5	99.8	50.6	50.58	2.4	2.61
Bis-(*o*-methylbenzoyl)	52.5–53.5	Ligroin, 60–70°	63	99.5	71.2	71.26	5.2	5.18
Bis-(*o*-methoxybenzoyl)	85–86	Dissolve in ether, add pet. ether	71.1	98.7	63.64	63.58	4.73	4.89
Bis-(*o*-phenoxybenzoyl)	66–67	Dissolve in ether, add pentane[f]	88	97.1	73.29	73.18	4.22	4.38
Bis-(*p*-cyanobenzoyl)	178	Glas. [HOAc, 80°], washed with Freon	35	99.9	65.75	65.66	2.76	2.88

[a] L. Gattermann and H. Wieland, "Laboratory Methods of Organic Chemistry," 24th ed., Macmillan and Co., Ltd., London, 1943, p. 125. [b] L. Vanido and E. Uhlfelder, *Ber.*, **37**, 3624 (1904). [c] G. Braun, "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 431. [d] *Cf.* ref. 19. [e] H. Gelissen and P. H. Hermans, *Ber.*, **58**, 285 (1925). [f] Synthesized by D. F. DeTar and A. Hlynsky, Cornell University.

side through a ground glass joint. One outlet on the two-way side was connected by means of rubber tubing, impregnated with paraffin, to a dibutyl phthalate trap while the second outlet was connected to the one way side of a second three-way stopcock. The two outlets of the latter stopcock were connected to a vacuum pump and to a tank of prepurified nitrogen. After having first flushed the trap with nitrogen, the apparatus was assembled, evacuated, and filled with nitrogen. After four such evacuations and refillings the system was connected to the trap through the first stopcock. The flask containing the sample was then lowered into a constant temperature paraffin oil-bath, accurate to ±0.1° and maintained at a given temperature within a range of ±0.02°. Samples were removed from the flask by inserting a hypodermic syringe through the serum stopple. Samples of the desired size were then transferred to test-tubes and placed in an ice-bath. After allowing the sample to come to room temperature, aliquots were analyzed for peroxide content and the results expressed as C_0/C were plotted against time either on semilogarithmic or coördinate graph paper. The half-life period was estimated graphically and from this the first order rate constant calculated. Decompositions were carried out to the extent of 50–90% with five or more experimental points used to determine the rate constant. Deviations from the best straight line were seldom greater than ±2%. Check runs at the same initial peroxide concentrations very seldom gave rate constants which deviated by as much as 3%, and only with initial peroxide concentrations of less than 0.02 *M* were deviations observed as great as 5%.

The total carbon dioxide evolved was measured volumetrically by a method similar to that described by Barnett and Vaughan.[6] The rate of evolution of carbon dioxide for the decomposition of benzoyl peroxide at 80° was found to be first order having a rate constant of 2.65×10^{-3} min.$^{-1}$ for a 0.18 *M* initial peroxide concentration.

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