

Organic Peroxides. VIII.³ Kinetics and Free-Radical Efficiencies in the Thermal Decompositions of Some Mixed Isobutyryl-Substituted Benzoyl Peroxides¹⁻³

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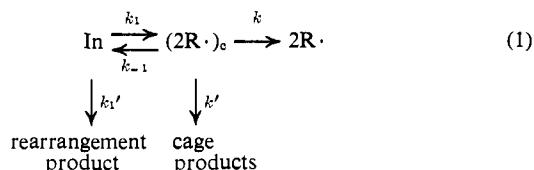
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Abstract: Kinetics–efficiency experiments were performed on a series of isobutyryl-substituted benzoyl peroxides in which the substituents were *p*-OCH₃, *p*-C(CH₃)₃, *p*-CH₃, H, *p*-F, *p*-Cl, *m*-Cl, and *p*-NO₂, using excess BDPA (Koelsch's radical) as the scavenger in cyclohexane, and some iodometric kinetics experiments were performed on the same peroxides. The log *k_d* values obtained at three temperatures, 50, 55, and 60°, give linear Hammett plots. The ρ values lie between +0.94 and +0.90 in this temperature range; thus the substituent effect is opposite to that observed for diaryl peroxides. The free-radical efficiencies (*f* values) decrease from 0.16 for the *p*-OCH₃ peroxide to 0.01 for the *p*-NO₂. The *f* values decrease more rapidly with increasing electron-withdrawing power of the substituent than *k_d*'s increase; the result is that the specific rates of formation of scavengeable free radicals (*2k_df*) decrease as the electron-withdrawing power of the substituent increases. As the over-all rates increase (and the rates of scavengeable radical production decrease), there is an increased yield of inversion product. A possible interpretation of these facts is discussed.

In 1962, Lamb, Rogers, Dean, and Voigt suggested a method for the determination, simultaneously, of both the first-order rate constant and efficiency of radical production in the decomposition of free-radical initiators, by the use of the excess stable radical technique.^{3a}

Since that time, the procedure has proved to be most useful in studies of decompositions of peroxides.^{3a,c-g} Nelson and Bartlett have utilized the procedure in a highly definitive study of the decomposition of azocumene.⁵

For diacyl peroxides, it is convenient to assume that the radical-generating scheme can be represented as eq 1



and that, in the excess stable radical experiments described here, the free radicals so generated are scavenged by the stable radical according to eq 2.



In eq 1, the rearrangement product is the familiar inversion compound which is formed in many diacyl peroxide decompositions,⁶ and the internal return reaction (which occurs at a specific rate *k₋₁*) is included because of recent work of Martin and coworkers.⁷

The integrated rate equation given by eq 3 can be derived from eq 1 and 2. In eq 3, *k_d* is the over-all first-

$$\ln(D - D_\infty) = -k_d t + \ln(2fI_0\epsilon) \quad (3)$$

order rate constant for the decomposition of the initiator, *2f* = number of free radicals produced per molecule of initiator which decomposes, and *D* and *ε* are the optical density and extinction coefficient, respectively, of the scavenger radical, *Z*.

The identities of *k_d* and *f* in terms of the rate constants in eq 1, which are dependent upon the relative importance of rearrangement and internal return, are presented in Table I.

Table I. Definitions of *k_d* and *f* in Equation 3 Derived from Equations 1 and 2^a

Condition	<i>k_d</i>	<i>f</i>
No internal return; no rearrangement	<i>k₁</i>	<i>e_o</i>
Internal return; no rearrangement	<i>k₁(1 - φ)</i>	<i>e_o</i>
No internal return; rearrangement	<i>k₁ + k_{1'}</i>	<i>(e_o)(e_H)</i>
Internal return; rearrangement	<i>k₁(1 - φ) + k_{1'}</i>	<i>(e_o)(e_H)'</i>

^a Abbreviations used: φ = *k₋₁*/(*k₋₁* + *k* + *k'*), the fraction of caged radical pairs which undergo internal return to peroxide; *e_o* = *k*/(*k* + *k'*); *e_H* = *k₁*/(*k₁* + *k_{1'}*); *e_H'* = *k₁*(1 - φ)/(*k₁* + *k_{1'}*). Both *e_H* and *e_H'* are the fraction of the decomposition which is homolytic.

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(3) (a) R. C. Lamb, F. F. Rogers, G. C. Dean, and F. W. Voigt, *J. Am. Chem. Soc.*, **84**, 2635 (1962); (b) R. C. Lamb, P. W. Ayers, and M. K. Toney, *ibid.*, **85**, 3483 (1963); (c) R. C. Lamb and J. G. Pacifici, *ibid.*, **86**, 914 (1964); (d) R. C. Lamb, J. G. Pacifici, and P. W. Ayers, *ibid.*, **87**, 3928 (1965); (e) R. C. Lamb, J. G. Pacifici, and L. P. Spadafino, *J. Org. Chem.*, **30**, 3102 (1965); (f) R. C. Lamb, J. G. Pacifici, and P. W. Ayers, *ibid.*, **30**, 3099 (1965); (g) R. C. Lamb, L. P. Spadafino, R. G. Webb, E. B. Smith, W. E. McNew, and J. G. Pacifici, *ibid.*, **31**, 147 (1966).

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(5) S. F. Nelson and P. D. Bartlett, *J. Am. Chem. Soc.*, **88**, 143 (1966).

(6) (a) J. E. Leffler, *ibid.*, **72**, 67 (1950); (b) D. B. Denney, *ibid.*, **78**, 590 (1956); (c) J. E. Leffler and C. C. Petropoulos, *ibid.*, **79**, 3068 (1957); (d) D. B. Denney and D. G. Denney, *ibid.*, **79**, 4806 (1957); (e) F. D. Greene, H. D. Stein, C. Chu, and F. M. Vane, *ibid.*, **86**, 2080 (1964); (f) C. Walling, H. N. Moulden, J. H. Waters, and R. C. Neuman, *ibid.*, **87**, 518 (1965); (g) J. E. Leffler and J. S. West, *J. Org. Chem.*, **27**, 4191 (1962); (h) P. D. Bartlett and F. D. Greene, *J. Am. Chem. Soc.*, **76**, 1088 (1954); (i) D. Z. Denney, T. M. Valega, and D. B. Denney, *ibid.*, **86**, 46 (1964).

(7) J. C. Martin, J. W. Taylor, and E. H. Drew, *ibid.*, **89**, 129 (1967); (b) J. W. Taylor and J. C. Martin, *ibid.*, **88**, 3650 (1966).

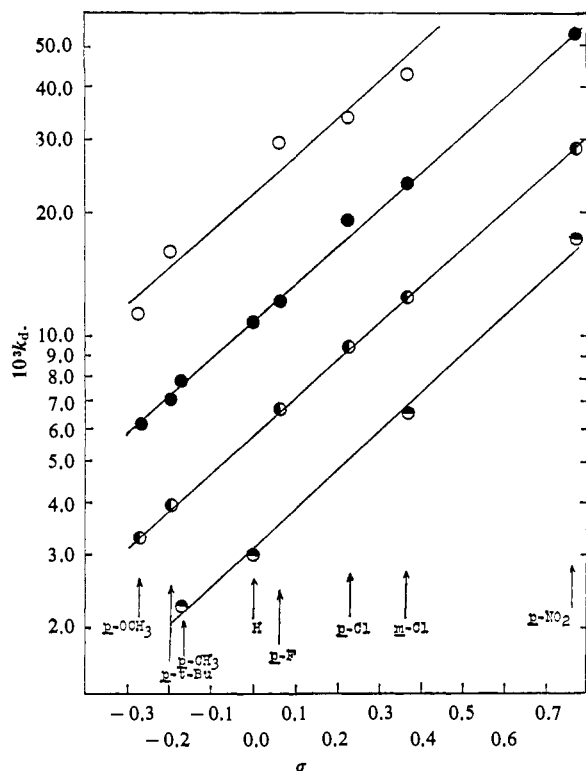
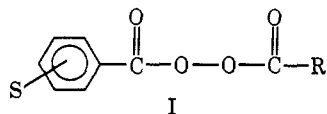


Figure 1. Plot of $\log(10^3 k_d)$ vs. σ . Decompositions of isobutryl-substituted benzoyl peroxides at four temperatures: \bullet , 50°; \circ , 55°; \bullet , 60°; \circ , 65°.

In the present work, peroxides of type I in which



R = isopropyl, and the substituents S are given in Table II, were subjected to kinetics-efficiency experiments of the type just described, using cyclohexane as solvent and BDPA (Koelsch's radical)⁸ as the scavenger. Iodometric kinetics experiments and product studies were also performed on some of these peroxides (Tables III and IV).

The experiments described here were suggested by the work of Denney and Sherman,⁹ who showed that peroxides of type I, S = *m*-Cl, and R = primary, secondary and tertiary alkyl groups, decompose to give products which, upon saponification, give good yields of alcohols. The authors interpreted these results in terms of the familiar rearrangement of the peroxides to the corresponding inversion compounds, Ar-CO-O-CO-O-R. Since the yields of the alcohols were quite high (50–70%), Denney and Sherman called attention to the utility of the reaction in the synthesis of alcohols, R-OH, from the next higher acids, RC(=O)OH.

Results

The results of the spectrophotometric kinetics-efficiency experiments using excess¹⁰ BDPA⁸ and peroxide

(8) (a) C. F. Koelsch, *J. Am. Chem. Soc.*, **79**, 4439 (1957); (b) S. L. Solar and R. M. Lindquist, *ibid.*, **82**, 4285 (1960); (c) R. Kuhn and F. A. Neugebauer, *Monatsh.*, **95**, 3 (1964).

(9) D. B. Denney and N. Sherman, *J. Org. Chem.*, **30**, 3760 (1965).

(10) A stoichiometric excess, i.e., $(Z \cdot)_0 > 2f(P)_0$. Because of low efficiencies, a molar excess of peroxide was used in each experiment.

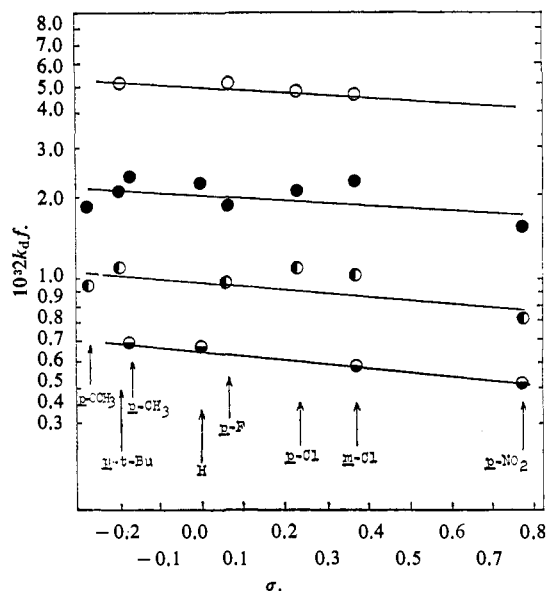


Figure 2. Plot of $\log(10^3 2k_d f)$ vs. σ . Decompositions of isobutryl-substituted benzoyl peroxides at four temperatures: \bullet , 50°; \circ , 55°; \bullet , 60°; \circ , 65°.

in cyclohexane solutions are presented in Table II. The results of some iodometric kinetics runs on somewhat more concentrated cyclohexane solutions of some of the same peroxides are presented in Table III.

The values of k_d determined from eq 3 at temperatures of 50, 55, and 60° give excellent Hammett plots, and those for 65° give a fair correlation (see Figure 1). The values of ρ for these temperatures, respectively, are $+0.94 (\pm 0.04)$, $+0.89 (\pm 0.01)$, $+0.90 (\pm 0.01)$, and $+0.87 (\pm 0.14)$. Therefore, the substituent effects on the over-all rates of decompositions of peroxides of type I are opposite to those observed for bis(aryl) peroxides.^{11,12}

Since " k_d " is the over-all first-order rate constant of the decomposition, f is so defined that $2k_d f$ is the specific rate constant for scavengeable radical formation. Hammett plots of $\log(2k_d f)$ are presented in Figure 2. Since f decreases more rapidly than k_d increases along the series, there are slight *negative* slopes to these plots; the ρ values for these plots are $-0.17 (\pm 0.01)$, $-0.13 (\pm 0.06)$, $-0.10 (\pm 0.07)$, and $-0.066 (\pm 0.03)$ for 50, 55, 60, and 65°, respectively. Therefore the effect of substituents on the specific rate of scavengeable radical production is *opposite* to that observed for the over-all rate constants for decomposition of the peroxides.

Although the spectrophotometric data fit eq 3 with excellent precision through high conversion, and the rate constants thus determined give excellent Hammett plots at three temperatures, plots of $\log(k_d/T)$ vs. $1/T$ show considerable scatter. The only two peroxides for which such plots are linear are Id (H) and If (*m*-Cl). The corresponding activation parameters are as follows: (a) for Id (H), $\Delta H^* = 26.9 \pm 0.1$ kcal, $\Delta S^* = +4.9 \pm 0.4$ eu; for If (*m*-Cl), $\Delta H^* = 26.6 \pm 0.1$ kcal, $\Delta S^* = +5.6 \pm 0.4$ eu.

Quantitative estimates of the yields of the inversion product, the carboxylic acid (the aroic acid), and the

(11) C. G. Swain, W. T. Stockmayer, and J. T. Clarke, *J. Am. Chem. Soc.*, **72**, 5426 (1950).

(12) A. T. Blomquist and A. J. Buselli, *ibid.*, **73**, 3883 (1951).

Table II. Kinetics-Efficiency Experiments on Decompositions of Mixed Isobutyryl-Substituted Benzoyl Peroxides in Cyclohexane Using BDPA as the Radical Scavenger^{a,b}

Peroxide	10 ³ Z ₀	10 ⁶ P ₀	No. of points	10 ³ (k _d ± 3σ), sec ⁻¹	t _{1/2} , min	f	T, °C
Ia (p-OCH ₃)	4.20	7.93	13	32.08 (±0.41)	36.0	0.166	70
Ia	4.20	7.93	10	18.76 (±0.44)	61.6	0.157	65
Ia	4.20	7.93	9	10.24 (±0.18)	112.8	0.151	60
Ia	4.20	7.93	8	5.456 (±0.202)	211.8	0.145	55
Ib (p-t-Bu)	4.83	14.5	15	50.16 (±0.51)	23.0	0.167	70
Ib	4.83	14.5	13	26.63 (±0.55)	43.4	0.159	65
Ib	4.83	14.5	15	11.71 (±0.21)	98.7	0.150	60
Ib	4.83	14.5	13	6.543 (±0.354)	177	0.140	55
Ic (p-CH ₃)	4.03	12.6	13	13.00 (±0.25)	89	0.153	60
Ic	4.04	4.21	18	3.720 (±0.065)	311	0.133	50
Id (H)	4.06	10.0	16	60.67 (±0.99)	19.0	0.141	70
Id	4.06	10.0	15	18.23 (±0.18)	63.4	0.105	60
Id	4.06	10.0	11	4.965 (±0.190)	232	0.0952	50
Ie (p-F)	4.81	10.3	10	96.03 (±2.28)	12.0	0.101	70
Ie	4.81	10.3	15	48.93 (±0.99)	23.6	0.0864	65
Ie	4.81	10.3	12	20.38 (±0.74)	56.7	0.0766	60
Ie	4.81	10.3	15	11.17 (±0.28)	103.7	0.0720	55
If (p-Cl)	4.10	28.0	15	56.38 (±0.60)	20.5	0.0711	65
If	4.10	28.0	23	32.34 (±0.26)	35.7	0.0628	60
If	4.10	28.0	18	31.93 (±0.38)	36.2	0.0610	60
If	4.10	28.0	15	16.51 (±0.18)	70.0	0.0559	55
Ig (m-Cl)	4.04	20.0	15	71.71 (±1.50)	16.1	0.0544	65
Ig	4.04	20.0	16	39.19 (±0.87)	29.5	0.0488	60
Ig	4.12	28.3	16	20.63 (±0.36)	56.0	0.0415	55
Ig	4.12	28.3	16	10.91 (±0.16)	106	0.0366	50
Ih (p-NO ₂)	4.95	112	13	89.21 (±1.67)	13.0	0.0142	60
Ih	4.95	112	9	47.25 (±0.086)	24.5	0.0124	55
Ih	4.95	112	10	28.895 (±0.065)	40.0	0.0120	50
Ih	4.95	112	6	13.362 (±0.054)	86.5	0.0120	45
Ih	4.95	112	12	8.100 (±0.017)	143	0.0109	40

^a Abbreviations used: Z₀ and P₀ = initial concentrations of BDPA and peroxide, respectively; k_d = observed first-order rate constant; f = free-radical efficiency (2f = no. of radicals formed per mole of peroxide). BDPA = 1,3-bis(diphenylene)-2-phenylallyl, or Koelsch's radical. ^b Rates and efficiencies determined spectrophotometrically, using the 490-mμ band of BDPA.

Table III. Iodometric Kinetics Experiments on Decompositions of Mixed Isobutyryl-Substituted Benzoyl Peroxides in Cyclohexane^a

Peroxide	10 ³ P ₀	No. of points	10 ³ (k _d ± 3σ), sec ⁻¹	t _{1/2} , min	T, °C
Ib (p-t-Bu)	6.4	5	17.98 (±0.09)	64	60
Ic (p-CH ₃)	1.9	6	47.72 (±1.35)	24.2	70
Ic	2.8	6	13.05 (±0.56)	89	60
Ic	2.8	6	3.619 (±0.103)	319	50
Ic	1.9	6	0.961 (±0.034)	1202	40
Id (H)	2.7	6	68.72 (±3.10)	16.8	70
Id	2.6	6	19.24 (±1.04)	60.0	60
Id	2.6	6	5.398 (±0.197)	214	50
Id	0.51	4	1.454 (±0.113)	795	40
Ie (p-F)	2.5	6	25.63 (±2.01)	45	60
If (p-Cl)	3.5	6	10.29 (±1.17)	112	50
Ig (m-Cl)	3.7	6	43.78 (±2.29)	26.4	60
Ig	3.7	6	13.62 (±0.43)	85	50
Ig	3.7	6	3.486 (±0.173)	331	40

^a See footnote a in Table II.

Table IV. Product Studies on Decompositions of Type I Peroxides^{a,b}

Peroxide	P ₀	Inversn prod	Ar-COOH	Ar-COO-CH(CH ₃) ₂
Ib (S = p-t-C ₄ H ₉)	0.064	0.55 ^c	0.36 ^c	0.06
Ic (S = p-CH ₃)	0.080	0.61 ^d	0.24 ^c	0.07
Id (S = H)	0.031	0.65 ^d	0.32 ^c	0.03
If (S = p-Cl)	0.070	0.68 ^c	0.30 ^e	0.01
Ih (S = p-NO ₂)	0.043	0.75 ^c	0.20 ^e	(<0.01)

^a Yields are reported in moles of product per mole of peroxide decomposed. P₀ = initial molar concentration of peroxide. ^b Solvents used: cyclohexane for Ib, c, d, and f; chloroform for Ih. Decomposition temperature for all experiments, 60°. ^c Determined by ir analysis. ^d Determined by barium hydroxide titration of sample which had been degassed after decomposition. ^e Determined by isolation.

ester, Ar-COOCH(CH₃)₂ for decompositions of five peroxides of type I at 60° are presented in Table IV.

The inversion products formed in these decompositions are stable under the conditions used in our product studies. For example, it has been shown by Windholtz that isopropyl benzoyl carbonate, the inversion product formed in the decomposition of the unsubstituted isobutyryl benzoyl peroxide (Id), decomposes (neat liquid) only at temperatures of 160–170°. ¹³ We observed that, in decompositions of type I peroxides, all the ester was formed during the decomposition of the peroxide; no additional ester was formed after all the peroxide had decomposed. Therefore, all the ester came from the decomposition of the peroxide. A similar observation has been made concerning the ester formation in the decomposition of the peroxide of type I (S = p-Br, R = benzyl) by Greene, Stein, Chu, and Vane,^{6c} who suggested that ester is probably formed by cage recombination of aryloxy and alkyl radicals.

Discussion

Except for the first and penultimate entries in Table III, from which it can be seen that the iodometrically determined rate constants differ from those determined spectrophotometrically by 50 and 30%, respectively, there is generally fair agreement between the rate constants determined by the two methods. In all other cases, the rate constants determined by the two methods differ by 20% or less, and in all cases, the rates determined iodometrically are greater than those determined spectrophotometrically. Since the initial peroxide concentrations in the iodometric runs were greater than

(13) T. B. Windholtz, *J. Org. Chem.*, **25**, 1703 (1960).

those used in spectrophotometric runs by factors of 100–1000, it is reasonable to assume that some of the disparity between the iodometrically and spectrophotometrically determined rate constants can be ascribed to radical-induced decomposition in the iodometric runs.¹⁴ In any event, the differences in the rates determined spectrophotometrically and iodometrically cannot be ascribed to cage reactions. The over-all first-order rate constant is obtained as the slope of eq 3. The slope is not a product of the rate constant and the efficiency; the efficiency appears only in the intercept.

Except for the annoying differences between the rates determined by the two methods, the data which are recorded in the Results form a fairly consistent picture of decompositions of type I peroxides. One may summarize the information by stating that, in proceeding across the series of peroxides in order of increasing values of Hammett substituent constants, the following changes are observed: (a) the over-all first-order rate constants (k_d values), and the yields of inversion product, increase; and (b) the rate constants for scavengable radical production ($2k_d f$ values), and yields of ester (although low), decrease.

The decompositions of type I peroxides clearly involve two important types of reaction, the formation of inversion product and homolysis. The assumption that the two are separate processes is in agreement with previous observations that the formation of the inversion product is catalyzed by protic^{6a,c} and Lewis⁶ⁱ acids, and occurs more readily in polar solvents;^{6c} the concept is also in agreement with the observation of stereospecificity^{6e,f} in the formation of inversion product and with the ¹⁸O experiments of Denney and Denney.^{6b,d}

The assumption that the two reactions are separate was used in the derivations of k_d and f given in Table I. For type I peroxides, since inversion products are formed (but it is not known whether there is internal return of acyloxy radicals), either the third or fourth entries in Table I can be chosen as representative of the mechanism. For simplicity, the definitions in the third row are used in the following discussion. If it is assumed that inversion product formation is the only nonhomolytic side reaction, it follows that the yield of inversion product = $1 - e_H$. Yields of inversion product for Ib, c, d, and f can be used to calculate values of e_H . Since $k_1 = k_d e_H$ and $k_1' = k_d(1 - e_H)$, the individual rate constants for homolysis and for rearrangement may be calculated.

Figure 3 shows plots of the logarithms of k_d , k_1' , k_1 , and $2k_d f$ vs. Hammett σ 's for Ib, c, d, and f. The ρ values for these plots are +0.90, +1.00, +0.70, and -0.10, respectively, at 60°.

Therefore the total picture which our data describe may be summarized thusly. The over-all rates of decomposition, the rates of rearrangement, and the gross rates of homolysis all increase with increasing Hammett σ 's, while the rates of scavengable radical production decrease.

The use of inversion product yields for the disentanglement of rate constants is not without objection, because it ignores the induced decomposition which our kinetics data suggest occurs in solutions as concentrated as those used in our product studies. However,

(14) (a) C. Walling and Z. Čekovič, *J. Am. Chem. Soc.*, **89**, 6081 (1967); (b) M. M. Schwartz and J. E. Leffler, *ibid.*, **90**, 1368 (1968).

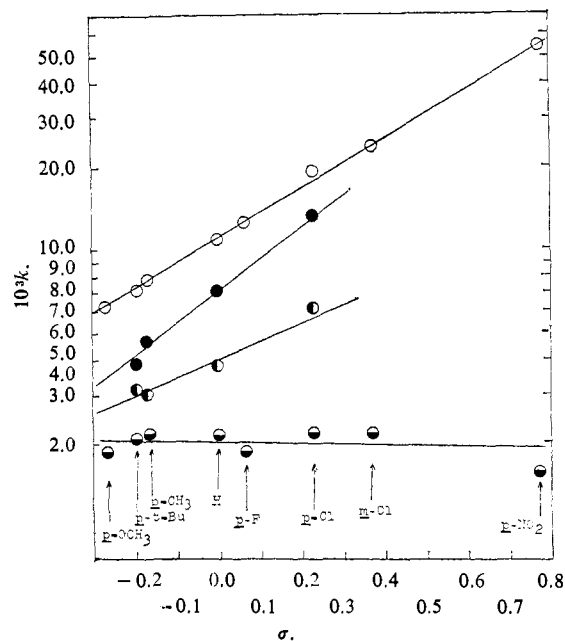


Figure 3. Semilog plot of rate constants vs. Hammett σ 's: \odot , $10^3(2k_d f)$; \bullet , $10^3 k_1 = 10^3 k_d(e_H)$; \circ , $10^3 k_1' = 10^3 k_d(1 - e_H)$; \circ , $10^3 k_d$. All rate constants are in min^{-1} .

the calculations serve to illustrate the complexity of the first-order component of type I peroxide decompositions.

From the point of view of synthesis of alcohols, R-OH, from peroxides of type I, it would appear that considerable control can be asserted upon the reaction rate by proper choice of substituent, without decreasing significantly the yields of products (ester and inversion product) which can be saponified to the alcohol.

Experimental Section¹⁵

BDPA was prepared by the method of Kuhn and Neugebauer.^{8c} The peroxyaric acids, with the exception of *p*-methoxyperbenzoic acid, were prepared by a method described by Silbert, Siegel, and Swern.¹⁶ The *p*-methoxyperbenzoic acid was synthesized by a method described by Leffler and Petropoulos.^{8c}

Esters used in the product study were synthesized by reaction of the acid chloride with isopropyl alcohol. Purification was by vacuum distillation except for isopropyl *p*-nitrobenzoate, which was recrystallized from ethanol. The esters were identified by ir and nmr.

The mixed isobutyryl aroyl peroxides were synthesized and purified by methods described by Denney and Sherman.⁹ Peroxide Ih ($S = p\text{-NO}_2$) was the only peroxide which could be isolated as a solid at room temperature, and as a solid, Ih decomposed rapidly with evolution of carbon dioxide. In general the liquid peroxides could be obtained in purities between 90 and 96%. As soon as the peroxides were isolated, they were placed in a stoppered flask and stored at -70° . The peroxides were identified by ir and nmr. The peroxide carbonyl doublets fell in the range 1770–1850 cm^{-1} in cyclohexane solvent. The nmr spectra (10% in CDCl_3 using TMS reference at 25°) gave the expected proton ratios. The nmr spectra of the peroxides were similar to those of the esters except that, in the peroxide, the multiplet (due to the secondary isopropyl hydrogen) was centered around τ 7.25 while that in the ester was centered around τ 4.80.

(15) Perkin-Elmer Model 137 and Beckman IR-12 infrared spectrophotometers were used, the latter for the quantitative analyses. A Hitachi Perkin-Elmer Model R-20 nmr instrument and a Perkin-Elmer Model 900 gas chromatograph were also used.

(16) L. S. Silbert, E. Siegel, and D. Swern, *J. Org. Chem.*, **27**, 1336 (1962).

Kinetics Runs. The apparatus used for the spectrophotometric runs may be described as follows. A Beckman Model DU-2-visible spectrophotometer, equipped with a Beckman 2180 dual thermospacer set, was also equipped with a specially built aluminum-block cell holder and a thermostated aluminum box cover for the cell compartment. From a constant-temperature bath, propylene glycol was pumped through the thermospacer set, cell block, and cell cover and returned to the bath. The temperature was monitored by the use of a calibrated thermister which was embedded in the bath liquid inside the cell block. Temperature control of $\pm 0.05^\circ$ was usually obtained with this thermostated assembly.

Except for the fact that the absorbance at $490\text{ m}\mu$ due to BDPA was continually monitored, the kinetics runs were accomplished by methods which have been described.^{3a}

Product Analysis. Peroxide vials were prepared in the previously described manner and decomposed for ten half-lives of the peroxide at 60° . Esters were analyzed by vpc methods analogous to those in paper II in this series.^{3b} Columns used were (a) 5% Apiezon L on Chrom GAW DMCS, 3 ft \times $\frac{1}{8}$ in.; (b) 2% QF-1 on Anakrom Abs, 10 ft \times $\frac{1}{8}$ in.; (c) 10% methyl phenyl silicone oil on Chrom WAW HMDS. Column b at a column temperature of 120° and a flow rate of 30 ml/min was found to be the best for speed and reproducibility.

Acids from the decomposition of peroxides If and Ih were insoluble in the reaction mixture and were isolated and identified by melting point and mixture melting point. Acids from the decomposition of Ib, Ic, and Id were estimated by standard ir analysis of the reaction mixture.

Inversion products from peroxides Ib, If, Ih were isolated by decomposing 0.1 g of the respective peroxide in 25 ml of CHCl_3 under reflux for 1 hr. Extraction of the acid from the solution with bicarbonate, drying over anhydrous sodium sulfate, and removal of the solvent in a stream of nitrogen yielded fairly pure inversion product. The inversion product derived from Ih was the only solid, mp $50\text{--}55^\circ$. The only major impurity was ester which was corrected for in making up the standard solutions for determination of the yield of inversion product by ir.

Inversion products from peroxides Ic and Id were estimated by a barium hydroxide titration method which was patterned after a procedure used by Leffler.^{6a}

Acknowledgment. We wish to thank the grant agencies whose support made this work possible.² We are especially indebted to Dr. David C. Lunney, who constructed the thermostated cell compartment for the spectrophotometer.

Photocycloaddition of Thiocarbonyl Compounds to Olefins. The Reaction of Thiobenzophenone with Various Types of Olefins^{1,2}

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Abstract: The mechanism of photocycloaddition of thiobenzophenone to various types of olefins has been studied. Electron-rich olefins react with the n, π^* triplet state of thiobenzophenone yielding either 1,4-dithiane or thietane derivatives depending on the structure of the olefin. Steric effect is an important factor in determining the reaction path. Electron-deficient olefins react with the π, π^* singlet state of thiobenzophenone giving thietane derivatives. The kinetics and product analyses of the reactions show that the reaction with the former type of olefin proceeds *via* a radical mechanism, whereas that with the latter type of olefin takes place by a nucleophilic attack of excited thiobenzophenone on the olefins or through complexes between the olefins and the π, π^* singlet state of thiobenzophenone. In the reactions that produce 1,4-dithiane derivatives, *trans* addition of two molecules of thiobenzophenone is verified. The structure and the configuration of the products have been determined both spectroscopically and chemically.

Thiobenzophenone is a unique compound in view of its absorption spectrum. The band of $n \rightarrow \pi^*$ transition (λ_{max} $609\text{ m}\mu$ (ϵ 180) in cyclohexane³) is completely separated from that of $\pi \rightarrow \pi^*$ transition (λ_{max} $314.5\text{ m}\mu$ (ϵ 15,500) in cyclohexane³). Therefore, by the irradiation with light of a suitable wavelength, it is possible to promote specifically only one of the transitions. Consequently, this compound lends itself easily to photochemical studies. Thiobenzophenone has other advantages over carbonyl compounds in the mechanistic study of the photoreaction with olefins: (i) since the olefins used in this study are transparent to $5890\text{-}\text{\AA}$

light from a sodium lamp,^{2c} there is no direct interaction between incident light and olefin; (ii) the energy of the n, π^* triplet state of thiobenzophenone (40–43 kcal/mol⁴) is too low to be transferred to olefins. Therefore, the reaction of excited olefins need not be considered.

In previous papers,^{2a–c} we have reported that olefins, in the photocycloaddition with thiobenzophenone, can be classified into three categories.

Case I olefins are those olefins which are substituted by electron-releasing groups. The reaction with this type of olefin, on irradiation with 5890 \AA light, proceeds through the n, π^* state of thiobenzophenone, resulting in the formation of 1,4-dithiane derivatives by the addition of two molecules of thiobenzophenone.^{2c,d}

Case II olefins are those olefins which are substituted by electron-withdrawing groups. The reaction with

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