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(30) The trapping of triptyloxy by phosphite during photolysis of triptyl-*tert*-butyl peroxide[20] is not necessarily related to the production of free triptyloxy radicals, since the reaction may proceed *via* a peroxide–phosphite exciplex, reminiscent of the transition state in the well-known thermal reaction between phosphites and peroxides.[31] Trapping of triptyloxy derived from triptyl alcohol as a free alkoxy radical is less ambiguous.

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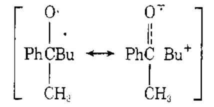

$$\left[\mathrm{Ph}\overset{\overset{\displaystyle O\cdot}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\mathrm{Bu} \longleftrightarrow \mathrm{Ph}\overset{\overset{\displaystyle O^{\cdot-}}{\|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\ \mathrm{Bu}^+\right]$$

However, we were unable to alter the course of fragmentation in basic solvents such as ammonia and tetrahydrofuran to observe the spectrum of acetophenone ketyl.

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Organic Peroxides. X. Kinetics of Decomposition of Some Acyl-*p*-nitrobenzoyl Peroxides Containing Neophyl Groups

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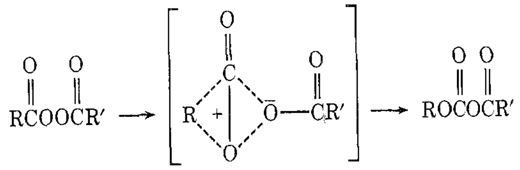
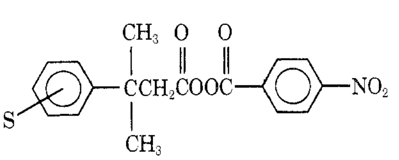
The kinetics of the thermal decompositions of a series of mixed β-(S-phenyl)isovaleryl *p*-nitrobenzoyl peroxides (S = *p*-NO_2, *m*-Br, *p*-Cl, H, *p*-CH_3, and *p*-OCH_3) in cyclohexane and in ethylbenzene were determined iodometrically in the temperature range 60–85° and at concentrations in the 0.002–0.02 *M* range. (Evidence is presented which shows that these peroxides initially form the carboxy-inversion compounds in good yield.) At these low concentrations, the kinetics (in both solvents) were found to be accurately first order, except in decompositions of the peroxide for which S = *p*-NO_2, in which case the first-order plots were curved so as to suggest a first plus higher order induced decomposition. The mathematical method used to correct for induced decomposition is presented. For the data obtained on the decompositions of five compounds at 75° in cyclohexane, an excellent correlation is obtained between log k_d and Hammett σ's, when the corrected value of k_d for the peroxide for which S = *p*-NO_2 is used, giving $\rho = -0.76 \pm 0.02$ ($r = 0.999$). However, for the data obtained at five temperatures in ethylbenzene, log k_d correlates better with σ^+ ($r > 0.992$) than with σ (*r* values near 0.97 at all five temperatures). The ρ values for the σ^+ correlations are −0.89, −0.85, −0.81, −0.77, and −0.74, respectively, at 60, 65, 70, 75, and 80°. The activation parameters obtained for the decompositions of these peroxides show good isokinetic behavior, with β = 214°. The rate constants obtained in ethylbenzene were extrapolated to 120° for comparison with rate constants obtained at that temperature on the decompositions of the corresponding *tert*-butyl peroxy esters by Rüchardt and Hecht. Although a log–log plot of the (extrapolated) peroxide and perester rate constants is not linear, a good correlation is obtained when log $[k_{\mathrm{peroxide}}/k_{\mathrm{perester}}]$ is plotted against σ. The value of $(\rho_{\mathrm{peroxide}} - \rho_{\mathrm{perester}})$ obtained from this correlation (−0.61) indicates more sensitivity to substituents in the peroxide than in the perester series. Although this shows that the peroxide decompositions have more polar character than the decompositions of the peresters, the kinetics data presented here do not clearly delineate between identical and different transition states for the homolytic and carboxy-inversion product forming reactions of the β-phenylisovaleryl *p*-nitrobenzoyl peroxides.

The formation of carboxy-inversion compounds in decompositions of diacyl peroxides has been the subject of a number of investigations during the past two decades.[3] Although some of the details involved in the mechanism are still under discussion,[3o-s] it is generally recognized that the peroxide proceeds to a polar transition state which proceeds to give inversion compound.



In a recent paper from this laboratory which dealt with a series of isobutyrylaroyl peroxides,[3o] in which the aroate groups become anionoid in the polar intermediate, the rate constants obtained (determined spectrophotometrically by the excess stable radical method) were found to give excellent Hammett plots with ρ values of +0.94 (±0.04), +0.89 (±0.01), 0.90 (±0.01), and +0.87 (±0.14), respectively, at 50, 55, 60, and 65°.

In this paper, we present the results of a rather extensive study of the kinetics of decomposition of peroxides of type 1.



Type 1 peroxides

	S
1a	*p*-OCH_3
1b	*p*-CH_3
1c	H
1d	*p*-Cl
1e	*m*-Br
1f	*p*-NO_2

Since it was known that electron-withdrawing groups in the anionoid portion encourage inversion compound formation, it was decided to use *p*-nitrobenzoyl as one of the peroxide substituents. The decision to use ring-substituted β-phenylisovaleryl groups as the cationoid groups was based on the different effects of ring substituents (in neophyl groups) upon the rates of certain reactions. Thus, electron-releasing groups retard the rates of rearrangement of neophyl free radicals,[2b] although they enhance (slightly) the rates of thermal decomposition of the peresters from which they were derived.[2a] At the same time, electron-releasing ring substituents greatly enhance the rates of solvolysis of neophyl brosylates in acetic acid.[4] It was therefore felt that the neophyl system would offer certain advantages in comparing the carboxy-inversion reaction to purely free radical and ionic processes.

Results

First, it should be explained that, although a number of attempts were made initially to perform kinetics–efficiency experiments using excess BDPA,[3o] difficulty was encountered in obtaining reproducibility in experiments.[5] The results of two pairs of such experiments which did seem to behave properly are probably worth mentioning. Thus, for a pair of decompositions of **1c** (S = H) at 75° in benzene, monitored at 860 nm (ϵ 1289), the following data were obtained: $10^4\ k_d$ (sec^{-1}) = 4.77 and 5.05; efficiencies, f = 0.169 and 0.156. A similar pair of runs conducted with BDPA and **1c** (S = H) at 65°, monitored at 490 nm (ϵ 23,700), gave $10^4\ k_d$ (sec^{-1}) = 1.48 and 1.46; f = 0.056 and 0.062. While we cannot explain the large disparity in the efficiencies obtained at the two different temperatures (and at different wavelengths), the rates obtained are in fair agreement with those obtained iodometrically in cyclohexane and in ethylbenzene, when the differences in polarizabilities of the solvents are properly considered.[6] These experiments tend to help establish that type 1 peroxides are in fact initiators of low free radical efficiency, and that inversion-compound formation can be a major reaction pathway.

The difficulties encountered in spectrophotometric kinetics experiments using BDPA led to the adoption of iodometric titration as our kinetic method. In the absence of an inhibitor (such as BDPA), radical-induced decomposition of the peroxide becomes possible,[7] and low peroxide concentrations (0.001–0.02 M) were used to minimize this phenomenon as much as possible.

The initial iodometric kinetics experiments were performed using cyclohexane as solvent, in the hope that the rate constants obtained using a nonpolar solvent of low polarizability would be more sensitive to substituents than would these obtained in a polarizable solvent. Although this anticipation was not later realized, the cyclohexane experiments gave data that fit the first-order law with precision, except for the decomposition of **1f** (S = *p*-NO_2), for which the first-order plot exhibited a barely discernible rate diminution at long times. (The method of treating this rate behavior mathematically is discussed subsequently.) The rate constants obtained from decompositions in cyclohexane which fit the first-order law are presented in Table I. That for **1f** (S = *p*-NO_2), which was corrected by a method discussed subsequently, is presented in Table II.

Having performed a few experiments in cyclohexane, it began to appear that a similarity of behavior was emerging between the rate constants obtained for type 1 peroxides at 75°, and the rate constants which were obtained previously by Rüchardt and Hecht on the decompositions of the corresponding *tert*-butyl peroxy esters in ethylbenzene at 120°.[2a] However, because of the disparity in conditions under which the rates in these two series were obtained, the decision was made to perform experiments on type 1 peroxides in ethylbenzene. The data obtained for all kinetics runs performed for all type 1 peroxides except for **1f** (S = *p*-NO_2) were found to fit the first-order law with precision. The results obtained by adjustment to the first-order law for decompositions of **1a–e** (S = *p*-OCH_3, *p*-CH_3, H, *p*-Cl, *m*-Br) in ethylbenzene are presented in Table I, along with the activation parameters deduced therefrom. Also listed in Table I are some rate constants extrapolated to temperatures other than those at which they were experimentally determined which are utilized in the plots presented in the discussion.

The rate data obtained on the decompositions of **1f** (S = *p*-NO_2) in ethylbenzene deviated seriously from first-order behavior; *i.e.*, first-order plots show rate diminutions at long times. This suggests adherence to the rate expression eq 1,

$$-d(P)/dt = k_d(P) + k_i(P)^x \qquad (1)$$

the integral of which is eq 2,

$$\ln\left[(P)^{1-x} + \alpha\right] = -(1 - x)k_d t + \ln\left[(P)_0^{1-x} + \alpha\right] \qquad (2)$$

in which $\alpha = k_i/k_d$; and, since the "first-order" rate constant diminishes with time, $x > 1$.

In going from a first-order to a first plus higher order reaction, the number of disposable parameters increases from two to four. It does not appear possible to obtain explicit solutions to the four constants [x, α, k_d, and $(P)_0$] in eq 2 by the least-squares method, and it is necessary to make estimates by computer. The computer search is made somewhat less laborious if eq 2 is expanded by one

Table I
Iodometric Kinetics Experiments on Type 1 Peroxides[a,b]

Peroxide	$(P)_0$	10^5 ($k_d \pm \sigma$), sec^{-1}	Temp, °C	ΔH^*, kcal, and ΔS^*, eu
		Solvent: Cyclohexane		
1a (S = *p*-OCH_3)	0.0022	19.90 ± 0.63	75	
1c (S = H)	0.0138	21.80 ± 0.15	80	
1c	0.0157	11.80 ± 0.08	75	$\Delta H^* = 30.05 \pm 0.04$
1c	0.0137	5.96 ± 0.03	70	$\Delta S^* = 9.5$
1c	0.0148	3.16 ± 0.03	65	
1d (S = *p*-Cl)	0.0043	7.78 ± 0.06	75	
1e (*m*-Br)	0.0176	6.34 ± 0.05	75	
		Solvent: Ethylbenzene		
1a (S = *p*-OCH_3)		(4783.)[a]	120	
1a		(145.24)	80	
1a	0.00663	88.33 ± 0.35	75	
1a	0.0058	53.07 ± 0.16	70	$\Delta H^* = 23.37 \pm 0.08$
1a	0.0058	31.82 ± 0.03	65	$\Delta S^* = -5.67$
1a	0.0058	18.26 ± 0.21	60	
1b (S = *p*-CH_3)		(3013.)	120	
1b		(65.89)	80	
1b	0.0219	38.11 ± 0.30	75	
1b	0.0122	22.01 ± 0.24	70	$\Delta H^* = 25.63 \pm 0.11$
1b	0.0122	12.54 ± 0.11	65	$\Delta S^* = -0.83$
1b	0.0798	6.79 ± 0.06	60	
1c (S = H)		(2659.)	120	
1c		(45.34)	80	
1c	0.0030	25.68 ± 0.13	75	
1c	0.0028	13.93 ± 0.03	70	$\Delta H^* = 27.35 \pm 0.22$
1c	0.0025	7.59 ± 0.01	65	$\Delta S^* = 3.28$
1c	0.0020	4.10 ± 0.01	60	
1d (S = *p*-Cl)		(1509.)	120	
1d	0.0192	26.79 ± 0.17	80	
1d	0.0186	14.90 ± 0.10	75	$\Delta H^* = 27.10 \pm 0.04$
1d	0.0198	8.38 ± 0.04	70	$\Delta S^* = 1.54$
1d	0.0201	4.58 ± 0.06	65	
1d		(2.44)	60	
1e (S = *m*-Br)		(1310.)	120	
1e	0.0093	21.21 ± 0.20	80	
1e	0.0021	12.01 ± 0.06	75	$\Delta H^* = 27.64 \pm 0.28$
1e	0.0079	6.65 ± 0.09	70	$\Delta S^* = 2.63$
1e	0.0088	3.51 ± 0.05	65	
1e		(1.87)	60	

[a] Rate constants reported in this table for which standard deviations (σ) are given were obtained by adjustment of rate data to the first-order law; parenthesized rate constants were obtained by extrapolation from other temperatures using activation parameters given. [b] $(P)_0$ = initial molar concentration of peroxide.

of the subsequently discussed methods. The expansion of eq 2 by MacLaurin's series leads to the expression of ln (P) as a power series in *t*, *i.e.*, to eq 3,

$$\ln (P) = \sum_{1}^{n} b_n t^{n-1} \tag{3}$$

in which the b_n values can be related back to the original disposable constants, x, α, k_d, and $(P)_0$.

Although the b_n values can be obtained by standard computer programs, and the extension of eq 3 through four terms suffices to give estimates of the original constants, it was found that eq 3 does not converge as rapidly as a function which is derived as follows. First, eq 2 is rearranged to eq 4,

$$(P) = [Ce^{-ak_dt} - \alpha]^{1/a} \tag{4}$$

where $C = (P)_0{}^a + \alpha$ and $a = 1 - x$. Equation 4 is then expanded by the binomial theorem to give a relation of the form of eq 5

$$(P) = A_1e^{B_1t} + A_2e^{B_2t} + A_3e^{B_3t} + \ldots \tag{5}$$

in which the following relations hold

$$\begin{aligned} A_1 &= C^{1/a} & B_2 &= -(1 - a)k_d \\ B_1 &= -k_d & A_3 &= (1 - a)\alpha^2[C^{(1/a)-2}]/2a^2 \\ A_2 &= -\alpha[C^{(1/a)-1}]/a & B_3 &= -(1 - 2a)k_d \end{aligned}$$

from which one can calculate

$$\alpha = A_2[1 + (B_2/B_1)]/A^{B_2/B_1}$$
$$(P)_0 = [A^{1+(B_2/B_1)} - \alpha]^{B_1/(B_1+B_2)}$$

The coefficients (A_n and B_n) were established by using a subroutine based on the Marguard algorithm for a least-squares fit of a nonlinear curve to bivariant data.[8] The subroutine was designed to sweep values of $a = 1 - x = 1 + (B_2/B_1)$ through the range $-0.3 > a > -1$.

Considering the small amount of induced decomposition involved in the decompositions of 1f (S = *p*-NO_2), it is not surprising that a definite, constant value of x (*i.e.*, a) was not obtained in the four different runs reported in Table II. The effect of this treatment was to lower the value of k_d (from those obtained when the rate data were adjusted to the first-order law) by less than 20% in each case.

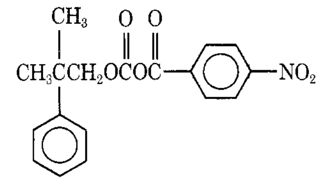
The evidence obtained through product studies to support the contention that type 1 peroxides form inversion

Table II
Iodometric Kinetics Experiments on Peroxide 1f (S = *p*-NO$_2$)[a,b]

Peroxide	(P)$_0$	$10^5 k_d$, sec^{-1}	a	α	Temp, °C	ΔH^*, kcal, and ΔS^*, eu
		Solvent: Cyclohexane				
1f (*p*-NO$_2$)	0.0029	3.12	−0.625	3.74	75	
		Solvent: Ethylbenzene				
1f		(854.9)			120	
1f	0.0220	17.56	−0.510	1.70	85	$\Delta H^* = 30.22 \pm 0.37$ $\Delta S^* = 8.32$
1f	0.0189	9.74	−0.657	5.72	80	
1f	0.0219	5.06	−0.963	22.36	75	
1f		(2.64)			70	
1f		(1.35)			65	
1f		(0.67)			60	

[a] The unparenthesized rate constants were obtained by adjustment of rate data to eq 5; the parenthesized rate constants were obtained by extrapolation of entries 3–5. [b] (P)$_0$ = initial molar concentration of peroxide; $a = 1 - x$; $\alpha = k_i/k_d$ (see eq 1–5).

compounds is rather indirect. Thus, the attempted synthesis of the inversion compound to be expected from **1c** (S = H), *i.e.*, *p*-nitrobenzoyl 2-methyl-2-phenyl-1-propyl carbonate (**2**), from neophyl chloroformate and *p*-nitrobenzoic acid in the presence of triethylamine did not result in a pure compound. Rather, an oil was obtained from which there separated, upon sitting, white crystals which were identified as *p*-nitrobenzoic anhydride (**3**). When a sample of the oil was allowed to stand for 35 days, *p*-nitrobenzoic anhydride precipitated for the first 15 days, then began to redissolve. After 20 days or so, another compound began to precipitate which was later identified as neophyl *p*-nitrobenzoate (**4**). (The isolation of **4** is an indication that the neophyl group does not rearrange during the formation of the inversion product.) The decomposition modes of **2** given above are precisely those which have been described by Tarbell and Longosz[9a,b] and by Windholtz[9c] for mixed carbonic carboxylic anhydrides.



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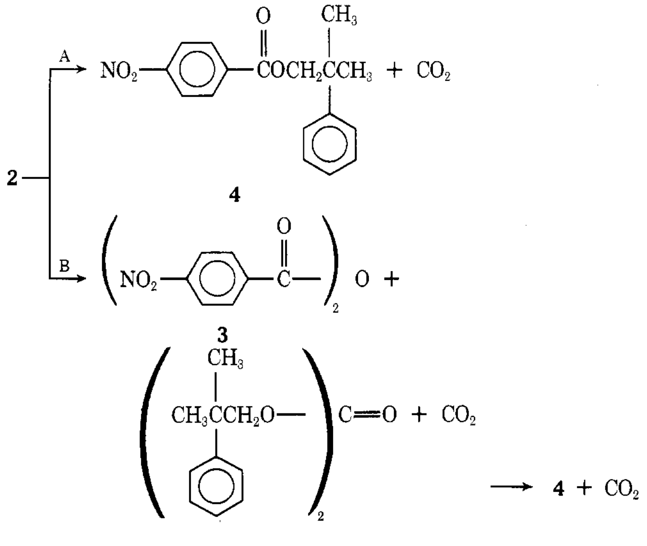


Now when a 0.2 *M* solution of peroxide **1c** (S = H) in cyclohexane was decomposed completely (24 hr) at 75° in an evacuated tube, and the solvent and other volatile products were subsequently removed at the pump, there remained an oil whose infrared spectrum was almost identical with that of the oil obtained in the attempted synthesis of **2** described above. More particularly, there are at least 20 coincidental infrared bands in the two spectra, of which ten are the strongest bands in the spectra. Furthermore, solid samples of **1c** (S = H) were found to decompose slowly in the neat solid state to form a product which was found to be difficultly soluble in ether, and was likewise identified as *p*-nitrobenzoic anhydride (**3**).

Discussion

The rates of decomposition of type 1 peroxides are consistently more rapid in the polarizable solvent, ethylbenzene, than in the solvent of low polarizability, cyclohexane, and as has been pointed out,[6] this is to be expected for peroxides which form the carboxy-inversion product. It is also not surprising that, for the decomposition of **1c** (S = H), the ΔH^* is lower and ΔS^* more negative in the solvent (ethylbenzene) in which the rates are faster (see Table I).

The activation parameters obtained for decompositions of type 1 peroxides in ethylbenzene show quite good isokinetic behavior (see Figure 1) except for the fact that the

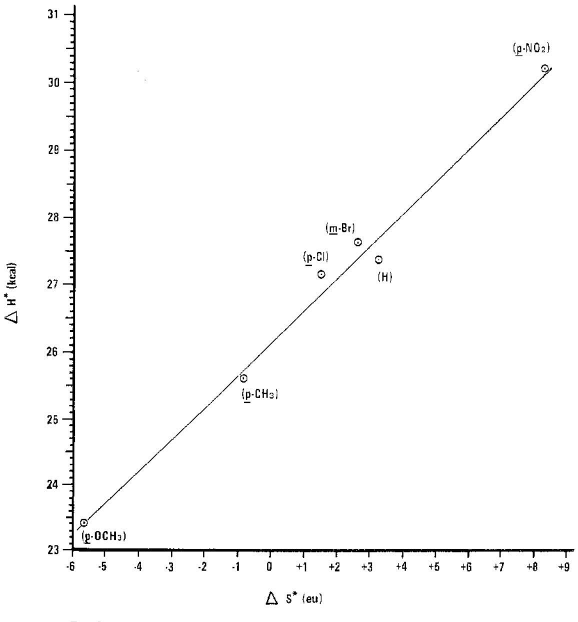


Figure 1. Isokinetic plot for decompositions of type 1 peroxides in ethylbenzene.

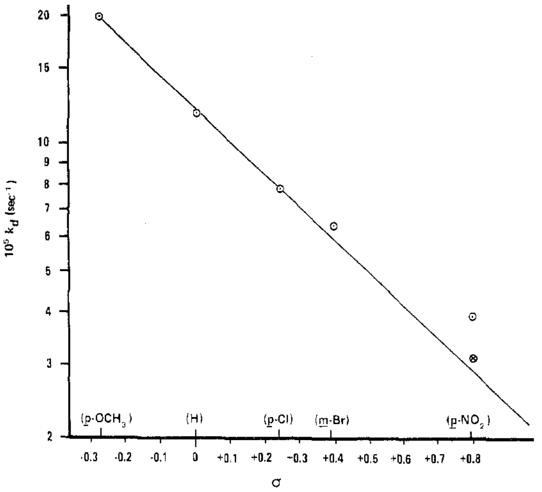


Figure 2. Semilog plot of 10^5 k_d *vs.* Hammett σ's for decompositions of type 1 peroxides in cyclohexane at 75°: ⊙, k_d obtained from correlation of rate data with first-order law; ⊗, k_d obtained by adjustment of data to eq 5.

points for **1d** (S = p-Cl) and **1e** (S = m-Br) fall to the left of **1c** (S = H) on the plot, whereas they would be expected to fall to the right. Nevertheless, the correlation coefficient for the plot in Figure 1 is 0.995, and the slope defines the isokinetic temperature as 487 ± 25°K, or 214 ± 25°. Thus, the temperatures at which the kinetics experiments were performed on type 1 peroxides were more than 100° removed from the isokinetic temperature.[10]

The rate constants for the decompositions of **1a** and **1c–f** (S = p-OCH$_3$, H, p-Cl, m-Br, and p-NO$_2$) in cyclohexane at 75° give an excellent plot *vs.* Hammet σ's if a correction is made for induced decomposition in the decomposition of **1f** (S = p-NO$_2$)[11] (see Figure 2). The ρ value obtained for this correlation is -0.76 ± 0.02 (r = 0.999). At the same time, the rate constants obtained for decompositions of type 1 peroxides in ethylbenzene (Figure 3) do not give good Hammett correlations, because the rate constants for **1a** (S = p-OCH$_3$) are too high. Actually, if the high k_d values for **1a** (S = p-OCH$_3$) are ignored, better correlations are obtained with σ, but when all data are included, better correlations are obtained with σ^+.[12] The ρ values and correlation coefficients for the σ^+ correlations at the five temperatures are as follows: $\rho = -0.89 \pm 0.05$ (r = 0.994) at 60°; $\rho = -0.85 \pm 0.04$ (r = 0.994) at 65°; $\rho = -0.81 \pm 0.05$ (r = 0.994) at 70°; $\rho = -0.78 \pm 0.05$ (r = 0.992) at 75°; and $\rho = -0.74 \pm 0.04$ (r = 0.993) at 80°.

The behavior of the first-order rate constants for type 1 peroxide decompositions in ethylbenzene *vis-à-vis* σ and σ^+ as described above can be more clearly illustrated in terms of the Yukawa–Tsuno equation,[13] *i.e.*, eq 6.

$$\log k = \log k_0 + \rho[\sigma + R(\sigma^+ - \sigma)] = \log k_0 + \rho(1 - R)\sigma + \rho R\sigma^+ \quad (6)$$

The rate constants in Tables I and II were used to calculate values of ρ and R from eq 6. In addition, activation parameters presented in the same tables were used to calculate (extrapolated) rate constants at 100 and 120°, and the latter, in turn, were used to calculate ρ and R values from eq 6 for those temperatures. The results of these calculations were presented in Table III, and plotted in Figure 4.

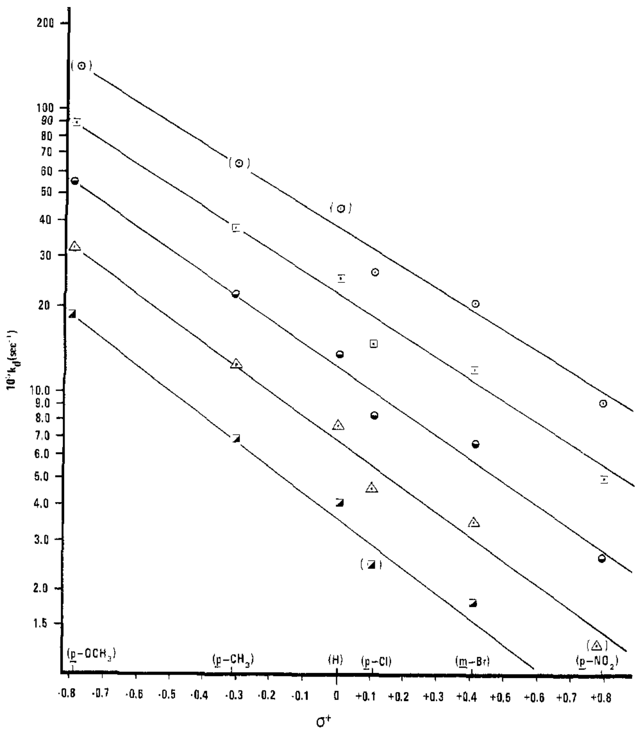


Figure 3. Semilog plot of 10^5 k_d for type 1 peroxides in ethylbenzene *vs.* σ^+ at five temperatures: ⊙, 80°; ◫, 75°; ◒, 70°; ▲, 65°; ◪ 60°. The parenthesized points are extrapolated rate constants (see Tables I and II).

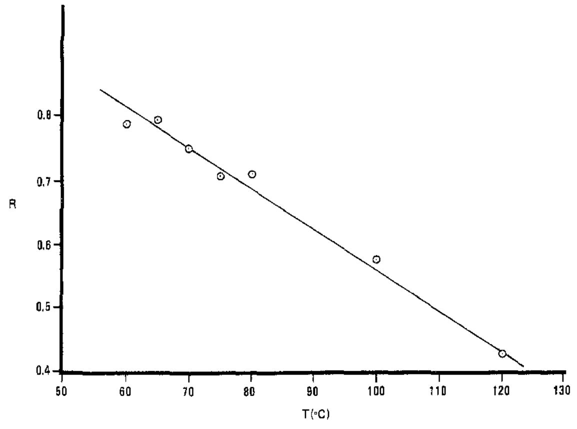


Figure 4. Plot of Yukawa-Tsuno R *vs.* temperature.

The Yukawa–Tsuno equation is designed such that $0 < R < 0.5$ indicates a better correlation with σ than with σ^+, while $0.5 < R < 1$ indicates a better correlation with σ^+. Figure 4 indicates a fairly linear correlation of R with temperature, which suggests that, although our rate data on type 1 peroxides in ethylbenzene give a better correlation with σ^+ at the experimental temperatures (60–80°), at temperatures of 117° and above, better correlations would be obtained with σ.

It is instructive to compare the kinetic behavior of type 1 peroxides with that which has been described by Ru-

Table III[a]
Adjustment of Rate Data for Type 1 Peroxides to the Yukawa–Tsuno Equation $Y = a\sigma + b\sigma^+ + c$

Temp, °C	a	b	c	R	ρ
60	−0.206	−0.755	0.592	0.786	−0.961
65	−0.195	−0.727	0.861	0.788	−0.922
70	−0.218	−0.667	1.122	0.753	−0.885
75	−0.250	−0.609	1.377	0.709	−0.859
80	−0.237	−0.580	1.622	0.710	−0.817
(100)[b]	−0.297	−0.407	2.536	0.578	−0.704
(120)[b]	−0.340	−0.255	3.365	0.428	−0.595

[a] $Y = 5 + \log k$; $a = \rho(1 - R)$; $b = \rho R$; $c = 5 + \log k_0$. [b] Values of constants for 100 and 120° were obtained by adjustment of extrapolated rate constants to the equation.

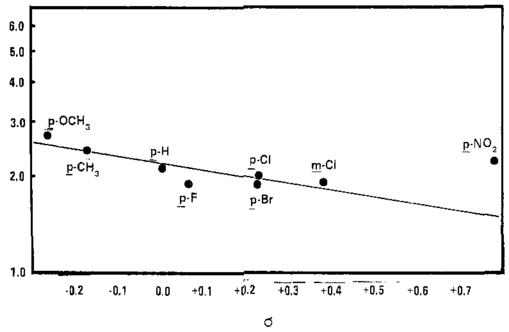


Figure 5. Semilog plot of 10^4 k_d *vs.* Hammett σ's for decompositions of ring-substituted *tert*-butyl β-(S-phenyl)peroxyisovalerates in ethylbenzene at 120° (after Rüchardt and Hecht[2]).

chardt and Hecht[2] for the decompositions of the *tert*-butyl peresters of ring-substituted β-phenylisovaleric acids in ethylbenzene. First, it should be explained that the perester rate constants reported by Rüchardt and Hecht do not correlate well with either σ or σ^+; the plot of log k_d for the peresters *vs.* σ is presented in Figure 5. In view of our experience with type 1 peroxides, however, it would seem reasonable to ascribe the high value of k_d for the p-NO_2-substituted perester to induced decomposition. If the rate constant for the p-NO_2-substituted perester is ignored on this account, the following σ correlation is obtained: $\rho = 0.21 \pm 0.05$ ($r = 0.871$).

Although the rate constants for both the peroxides and the peresters (at 120°) give somewhat better correlations with σ than with σ^+, the log-log correlation between the 120° rate constants for the two series is very poor. However, there is a fairly good correlation between log $[k_{\text{peroxide}}/k_{\text{perester}}]$ *vs.* σ, giving $(\rho_{\text{peroxide}} - \rho_{\text{perester}}) = -0.61 \pm 0.06$ ($r = 0.987$); the plot is presented in Figure 6.

It is necessary at this point to recall that Walling and coworkers[3p] have suggested that the formation of both radical and polar products (including the carboxy-inversion product) proceed from the same polar transition state and intermediate. The Walling mechanism was altered somewhat by Ward, Lawler, and Cooper,[3q] who failed to observe spin polarization in the inversion product formed in the decomposition of bis(isobutyryl) peroxide. Recently, Leffler and More[3r] expressed considerable doubt about the validity of the Walling mechanism, but, failing to discount a common transition state and intermediate (for homolysis and inversion product forming reactions) entirely, suggested somewhat different electronic structures for the intermediate.

Returning now to Figure 6, the difference in behavior of type 1 peroxides and the corresponding peresters as demonstrated in this plot can be interpreted in either of two ways. One of these is to suppose that a common intermediate mechanism holds for type 1 peroxide decompositions. If one adopts this view, then Figure 5 simply demonstrates that there is a significantly greater difference in polarities of the ground and transition states in the decompositions of type 1 peroxides than in decompositions of the corresponding perester.

This view is not without merit. One of the big differences between perester and diacyl peroxide decompositions is that an alkoxy group in perester is such a strongly basic "leaving" group that a transition state polarized in the direction R-COO$^+$ $^-$O-R simply cannot occur; and if it were possible, it is likely that dialkyl carbonates would be formed as rearrangement products. (The well-known Criegee rearrangement[14] requires polarization in the opposite direction, R-COO$^-$ $^+$O-R.) The "leaving" groups in the peroxide and perester series which are being compared in Figure 5 (*i.e.*, the p-nitrobenzoate and *tert*-butoxide anions) differ in basicity by several powers of ten. Thus, it is not unreasonable to assume that the transition state leading to radicals in the type 1 peroxide series is significantly more polar than the radical-producing transition state in the perester series, and it could conceivably lead to an intermediate which also produces inversion product. Along this line, curvature was not discernible in the ln (k_d/T) *vs.* $1/T$ plots over admittedly short (15°) temperature ranges, so that the ΔH^* values reported here for type 1 peroxides have a precision of ±1% or better.

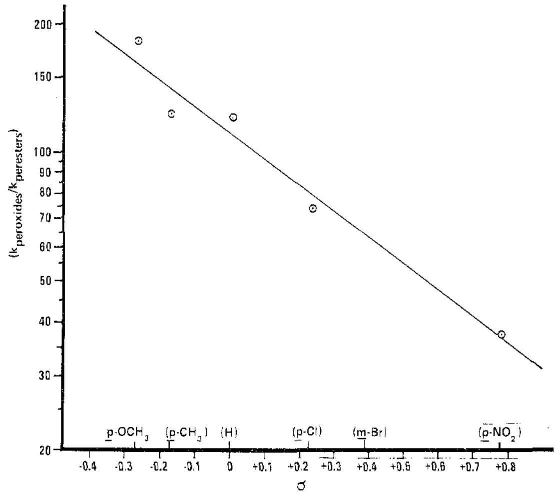


Figure 6. Plot of log $[k_{\text{peroxides}}/k_{\text{peresters}}]$ *vs.* Hammett σ's for type 1 peroxides and the corresponding *tert*-butyl peresters (after Rüchardt and Hecht[2]) in ethylbenzene at 120°.

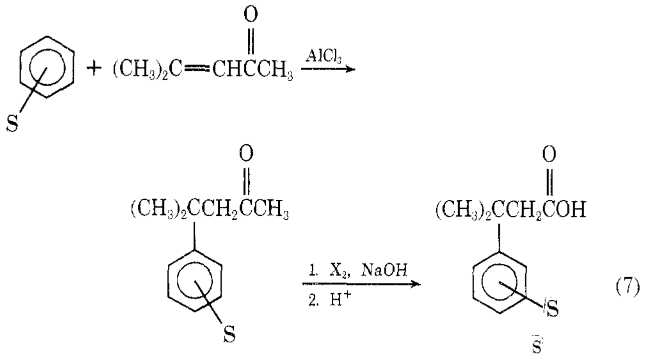
On the other hand, Rüchardt and Hecht showed that the peresters decompose exclusively by one-bond homolytic cleavage of the peroxide linkage, and one could reasonably argue that the plot in Figure 5 means that, when the substituent effect on the homolytic reaction is subtracted, the residual observed slope is to be ascribed to the carboxy-inversion reaction alone. The point is that the rate data presented here for type 1 peroxide decompositions do not clearly favor either the single or the double transition-state postulate, but if either is favored slightly, it is the former.

The substituent effects in type 1 peroxide decompositions, however, should be put in proper perspective. In the first place, the rate constant for the decomposition of **1c** (S = H) in cyclohexane is no more than a factor of three greater than that for bis(acetyl) peroxide.[7h] Secondly, the effect of ring substituents on type 1 peroxide decompositions, ρ (*vs.* σ^+) = −0.74 to −0.89, more nearly approximates that of the corresponding perester decompositions, ρ (*vs.* σ) = −0.21, than that of the solvolyses of the neophyl brosylates,[4] ρ (*vs.* σ^+) = −2.96 (in acetic acid). The data do not suggest a high degree of bond breaking in the -CH_2-C=O bond in the transition state for type 1 peroxide decompositions.

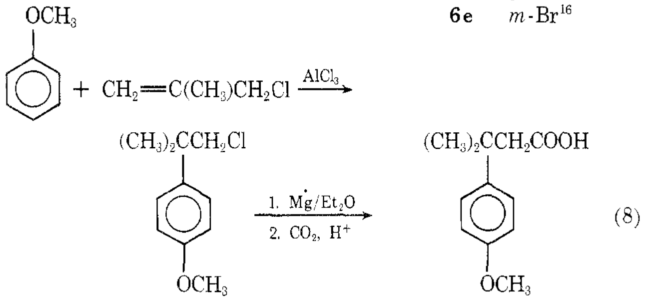
Experimental Section[15]

The ring-substituted β-phenylisovaleric acids were synthesized by two different methods (eq 7[16] and 8).

In general, procedures were followed in the synthesis of the acids which were developed by Hoffman,[17] by Corse and Rohrmann,[18] and by Rüchardt and coworkers.[19] The β-(p-nitrophenyl)-isovaleric acid (**6f**, not shown) was obtained by nitration of the parent acid according to the Corse and Rohrmann procedure.[18] The methyl β-(S-phenyl)isobutyl ketones (eq 7) were transformed to the acid salts both by the sodium hypochlorite method of Newman and Holmes[20] and by the sodium hypobromite method described by Sandler and Karo.[21] The observed melting points of the acids were identical with or within 1° of those which have



S
6b p-CH_3
6c H
6d p-Cl
6e m-Br[16]



6a

been reported. The nmr spectra (CCl_4, S) exhibit 6 H singlet absorptions in the range of δ 1.40–1.48 for the *gem*-dimethyl groups and 2 H singlet absorptions in the δ 2.53–2.69 range for the methylene groups; **6a** (S = p-OCH_3) shows a 3 H singlet at δ 3.75 for the methoxyl group, and **6b** (S = p-CH_3) shows a singlet methyl absorption at δ 2.35. The aromatic protons exhibit a 4 H multiplet for **6a** (S = p-OCH_3) at δ 7.10, and **6b** at δ 7.20 (S = p-CH_3); a 5 H singlet at δ 7.21 for **6c** (S = H); a 4 H singlet at δ 7.22 for **6d** (S = p-Cl); a 4 H multiplet at δ 7.50 for **6e** (S = m-Br); and a 4 H multiplet for **6f** (S = p-NO_2) at δ 7.91. The ir spectra of the acids exhibit characteristic absorptions in agreement with assigned structures. The corresponding acid chlorides were prepared by treatment of the acids with excess thionyl chloride.[2a] The nmr spectra of the acid chlorides (CCl_4, S) show considerable similarity to those of the acids, except for the fact that the 2 H singlet absorptions for the methylene groups lie in the range δ 3.14–3.29. The mass spectra of four of the acid chlorides are described subsequently.

p-Nitroperoxybenzoic acid was prepared from p-nitrobenzoic acid, hydrogen peroxide, and methanesulfonic acid by the method of Silbert, Siegel, and Swern,[22] except that double quantities of methanesulfonic acid were used, mp 138–139° (lit.[22] mp 138°).

Type 1 peroxides were synthesized by the treatment of p-nitroperoxybenzoic acid with the acid chlorides in the presence of pyridine. Thus, for the synthesis of **1c** (S = H), p-nitroperoxybenzoic acid (3.66 g, 0.02 mol) and β-phenylisovaleryl chloride (3.93 g, 0.02 mol) were dissolved in 100 ml of diethyl ether in a 300-ml three-necked flask equipped with stirrer, alcohol thermometer, and dropping funnel. The solution was cooled quickly to $-20°$ in a Dry Ice–acetone bath, and pyridine (1.58 g, 0.02 mol), dissolved in 25 ml of diethyl ether, was added dropwise over a 15-min period. The mixture was allowed to stir for 5 hr while the flask was immersed in the Dry Ice–acetone bath (during which time the temperature was held below $-30°$), the bath was removed, and the solution was allowed to warm to 10°. The white precipitate was taken into solution by addition of more diethyl ether; the ether solution was transferred to a separatory funnel and washed respectively with 5% hydrochloric acid (3 × 50 ml), water (2 × 50 ml), 5% sodium bicarbonate (3 × 50 ml), and water (2 × 50 ml). The ether solution was dried over anhydrous sodium sulfate and filtered, and the ether was removed at the rotary evaporator. The pale yellow crystals thus obtained were recrystallized from an ether–pentane mixture, yield 4.4 g (65% of theory) of white crystals, mp 63–64°. Iodometric titration indicated a purity of 99.2%. The melting points of the peroxides are as follows: **1a** (S = p-OCH_3), 77–78°; **1b** (S = p-CH_3), 73–74°; **1c** (S = H), 63–64°; **1d** (S = p-Cl), 84–86°; **1e** (S = m-Br), 64–65°; **1f** (S = p-NO_2), 89–91°. The nmr spectra (CCl_4, TMS) exhibit 6 H singlet absorptions in the δ 1.53–1.61 region for the *gem*-dimethyl groups and 2 H singlet absorptions in the δ 2.79–2.92 region for the methylene groups; and all peroxides show a 4 H multiplet for p-nitrobenzoyl centered at δ 8.27. The β-(S-phenyl)isovaleryl groups show the following absorptions for aromatic hydrogens: **1a** (S = p-OCH_3), a 4 H multiplet at δ 7.14; **1b** (S = p-CH_3), a 4 H multiplet at δ 7.23; **1c** (S = H), a 5 H singlet at δ 7.39; **1c** (S = p-Cl), a 4 H singlet at δ 7.34; **1d** (S = m-Br), a 4 H multiplet at δ 7.37; **1f** (S = p-NO_2), a 4 H multiplet at δ 7.90.[23] There are additional 3 H singlet methyl absorptions for **1a** (S = p-OCH_3) and **1b** (S = p-CH_3) at δ 3.80 and 2.33, respectively, for the ring substituents. All of the ir spectra of the peroxides exhibit the following bands: a carbonyl-stretch doublet with one band in the 1795–1808 cm^{-1} (m) region, and another in the 1767–1773 cm^{-1} (s) region; an aryl-nitro band near 1530 cm^{-1}; a band in the 1460 cm^{-1} (s) region due to CH_3- and -CH_2-; a -$CH_2C{=}O$ band near 1410 cm^{-1} (w); a *gem*-dimethyl doublet in the 1390 (w) and 1370 cm^{-1} (m) regions; and an aryl-nitro band near 1350 cm^{-1} (w). Other ir bands also confirmed the assumed structures. Iodometric titration indicated purities above 98% for all the peroxides.

Mass spectra were obtained on the acid chlorides for which S = p-OCH_3, p-CH_3, m-Br, and p-NO_2, and on two type 1 peroxides, **1b** (S = p-CH_3) and **1e** (S = m-Br). The following ions (or their m/e equivalents) were obtained for all of these derivatives: $SC_6H_4C_4H_7^+$, $SC_6H_4C_3H_6^+$, $SC_6H_4CH_2^+$, $C_6H_5C_4H_6^+$, $C_6H_5C_3H_3^+$, $C_6H_5C_3H_2^+$, $C_6H_5CH_2^+$ (or tropylium+), $C_6H_5^+$, and CO^+ (or N_2^+). The peroxide spectra also showed CO_2^+ and $NO_2C_6H_4COOH^+$. The 100% peak for all the acid chlorides corresponded to $SC_6H_4C_3H_6^+$; the 100% peak for the two peroxides, however, was a peak of m/e 131, corresponding to $C_6H_5C_4H_6^+$. The mass spectra of only two of these compounds showed small parent ions: the acid chlorides for which S = p-NO_2 and p-OCH_3.

Neophyl alcohol (2-phenyl-2-methyl-1-propanol) was prepared by oxygenation of neophylmagnesium chloride by the method of Cadogan and Foster,[24] mp of the p-nitrobenzoate 58–59.5°. The nmr spectra of the alcohol and the p-nitrobenzoate agree with the assigned structures.

Neophyl chloroformate was prepared by treating neophyl alcohol with phosgene in the presence of *N,N*-dimethylaniline, using a procedure similar to that described by Dodonov and Waters,[25] bp 82–85° (0.5 mm).

Kinetics Runs. Stock solutions of the peroxides were prepared at the concentrations indicated in Tables I and II, and 8-ml aliquots were injected into tared Pyrex vials, each of which had a previously constricted stem leading to a 10/30 ₮ joint. Each vial was weighed, attached to a vacuum manifold, immersed in liquid nitrogen, and carefully degassed. The stem was then sealed under vacuum.

For a given run, six to ten sealed vials were used. These were placed in a thermostated (±0.05°) bath at the same time, and removed at various times, quenched by immersing in a Dry Ice–acetone slurry, and subsequently titrated. For each titration, the contents of the tube were washed into an iodine flask with cold acetone saturated with carbon dioxide. A saturated solution of sodium iodide in acetone (5 ml), likewise kept cold and saturated with carbon dioxide using Dry Ice, was added. The iodine liberated was titrated with standard sodium thiosulfate solution.[26]

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Registry No.—**1a**, 51380-77-9; **1b**, 51380-78-0; **1c**, 51380-79-1; **1d**, 51380-80-4; **1e**, 51380-81-5; **1f**, 51380-82-6; **6a**, 1136-01-2; **6b**, 42288-08-4; **6c**, 1010-48-6; **6d**, 42288-16-4; **6e**, 42288-04-0; **6f**, 42288-06-2; β-(p-methoxyphenyl)isobutyl chloride, 51380-83-7; methyl β-(p-methylphenyl)isobutyl ketone, 10528-65-1; methyl β-phenylisobutyl ketone, 7403-42-1; methyl β-(p-chlorophenyl)isobutyl ketone, 6269-30-3; methyl β-(m-bromophenyl)isobutyl ketone, 51380-84-8; β-(p-methoxyphenyl)isovaleryl chloride, 4094-65-9; β-(p-methylphenyl)isovaleryl chloride, 51380-85-9; β-phenylisovaleryl chloride, 4094-64-8; β-(p-chlorophenyl)isovaleryl chloride, 4094-67-1; β-(m-bromophenyl)isovaleryl chloride, 51380-86-0; β-(p-nitrophenyl)isovaleryl chloride, 51380-87-1; p-nitroperoxybenzoic acid, 943-39-5; neophyl p-nitrobenzoate, 51380-88-2; neophyl chloroformate, 51380-89-3.

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(1) This investigation was supported by a grant from the National Science Foundation, GP-13845. The work was taken for the most part from the M.S. Theses of L. L. Vestal (1972) and G. R. Cipau (1974).

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(5) These results are in keeping with our experiences of the past several years using the excess stable radical method, namely, that it is difficult to obtain reproducible data on initiators that decompose slowly above 60°. The method usually works well for low-temperature initiators.

(6) It has been shown that, for decompositions of bis(isobutyryl) peroxide, a peroxide which forms the inversion compound in good yield, the rate constants obtained in a series of nonpolar solvents of different polarizabilities increase with increasing solvent polarizability, *i.e.*, benzene > toluene = *p*-xylene > carbon tetrachloride > cyclohexane. Therefore, for type 1 peroxides, the sequence benzene > ethylbenzene > cyclohexane is in complete agreement with the previously established series (*cf.* Figure 1 in ref 3n).

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(11) The uncorrected value for $10^5 k_d$ = 3.90 for **1f** (S = *p*-NO_2) in cyclohexane at 75°. The corrected value is presented in Table II.

(12) Thus, when all rate constants are included, the correlation coefficients for the correlations with σ are near 0.97 at all five temperatures. However, if rate constants for **1a** (*p*-OCH_3) are ignored, the *r* values are near 0.997.

(13) *Cf.* J. Shorter, "Correlation Analysis in Organic Chemistry," Oxford University Press, London, 1973, pp 15–16. We have used capital *R* for the Yukawa-Tsuno constant to distinguish it from *r*, which is used in this paper to designate the correlation coefficient.

(14) *Cf.* R. Curci and J. O. Edwards in "Organic Peroxides," Vol. I, D. Swern, Ed., Wiley-Interscience, New York, N. Y., 1970, pp 212–218.

(15) Infrared spectra were obtained using Perkin-Elmer Model 137 and Model 257 spectrophotometers; nmr spectra were obtained using Hitachi Perkin-Elmer Model R-20 and Varian Model A-60 spectrometers; Atlas Model CH-4 and CH-5 mass spectrometers were used to obtain mass spectra.

(16) Rüchardt and Trautwein showed that the acid obtained from bromobenzene by this procedure, mp 109–110°, is actually the meta isomer. The proof consisted of the oxidation of the decarbonylation products of the corresponding aldehyde to *m*-bromobenzoic acid, and by the independent synthesis of β-(*p*-bromophenyl)isovaleric acid, mp 68–69°, from β-(*p*-aminophenyl)isovaleric acid. *Cf.* C. Rüchardt and S. Eichler, *Chem. Ber.*, **95**, 1921 (1962).

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Kinetics and Mechanisms of Reactions of 3-Buten-2-one and Related Compounds in Aqueous Perchloric Acid

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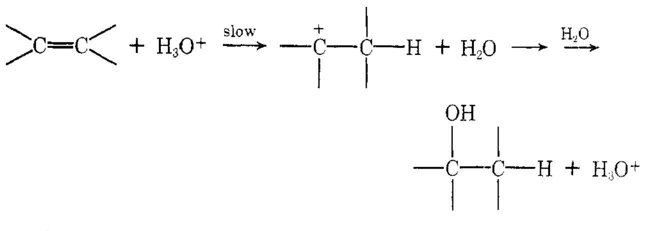
A detailed study of the hydration of homologs of 3-buten-2-one is reported. Rate constants for the hydration and dehydration reactions have been separated and activation parameters, precise solvent isotope effects, and acidity dependences have been measured over a wide range of acidity, 1–10 *M* perchloric acid. These mechanistic criteria are discussed in view of other olefin hydrations.

Hydration of olefins in aqueous acidic media has been studied extensively and the reaction mechanisms for several classes of olefins have been established.[1-5] For simple aliphatic olefins, dienes, and substituted styrenes, the mechanism of hydration has been shown to involve rate-determining proton transfer from hydronium ion to olefinic carbon, followed by addition of water to the carbonium ion thus formed[1-4] (Scheme I).

Scheme I



These reactions are characterized by solvent isotope effects, $k(H_2O)/k(D_2O)$, of 1.4–5 and entropies of activation of −5 to 0 eu. 3-Buten-2-one and its homologs are a special class of olefins having a carbonyl group conjugated with a double bond. Hydration of some α,β-unsaturated ketones has been reported previously.[6-9] The compounds studied