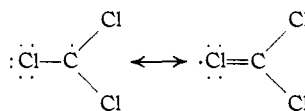


that of peracetate and 2 kcal. below trimethyl- and trichloroperacetate. The unfavorable entropy of activation in phenylperacetate is reasonable on grounds already discussed¹²; there are conformations of the reacting ester which are unfavorable for producing the stabilized benzyl radical itself, but this is not true of the cleavage of the trimethyl- or trichloroperacetate. It remains to be explained why so much less of the stabilization energy of benzyl than of *t*-butyl or trichloromethyl appears to be available at the transition state.

The contrast in behavior between trichloro- and trifluoroperacetate has been commented upon previously.¹³ The failure of $\text{CF}_3\cdot$ to be formed under conditions where $\text{CCl}_3\cdot$ is favored emphasizes that

(12) Reference 2, p. 1402; ref. 3, pp. 286–288.

the stabilization of the latter radical must depend upon interactions peculiar to elements beyond the first row of the periodic table.



The type of interaction shown puts nine electrons in the valence shell of chlorine, which would not be possible for a fluorine atom.

Acknowledgment.—We thank the National Science Foundation for a fellowship to one of us, and for support of this work.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Peresters. IV. Substituent Effects upon the Concerted Decomposition of *t*-Butyl Phenylperacetates¹

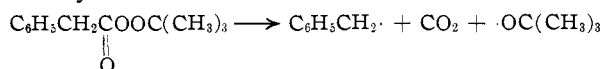
BY PAUL D. BARTLETT AND CHRISTOPH RÜCHARDT^{1c}

RECEIVED AUGUST 18, 1959

The thermal decomposition of *t*-butyl phenylperacetate yields benzyl and *t*-butoxy radicals as primary products. The decomposition rates of this ester and its *p*- and *m*-methoxy, *p*-methyl, *p*- and *m*-chloro, and *p*-nitro derivatives have been measured at a series of temperatures by infrared spectrophotometry and at 56° by the use of iodine in toluene as scavenger. The reaction is entirely homolytic in character and the rate constants fit the Hammett equation with the use of σ^+ rather than σ , the observed value of ρ varying from -1.04 at 100° to -1.20 at 56°. The "efficiency" of radical production by the *p*-methoxy ester measured by iodine in toluene varies from 44 to 72% with changes in iodine concentration and in temperature.

Introduction

It has been observed^{1b} that the benzyl radical possesses sufficient stability to cause the decomposition of *t*-butyl phenylperacetate to take place with concerted rupture of an O—O and a C—C bond producing carbon dioxide and the benzyl and *t*-butoxy radicals.



From the general behavior of a number of diverse peresters, it has been suggested² that the rate and activation enthalpy of the concerted decomposition is determined essentially by the stabilization energy of the carbon radical generated. In some previous instances^{3–5} the cleavage of substituted benzoyl peroxides and *t*-butyl perbenzoates into free radicals has been found to obey the Hammett equation, responding to electron withdrawing and releasing character of the substituent groups in the opposite manner to the ionization constants of the benzoic acids (*i.e.*, with ρ being negative). The explanation which has been offered for this behavior³ is an electrostatic one based upon the

strengthening or weakening of the O—O bond in the perester itself by a systematic variation in the residual charge upon one or both of the oxygens. Such a mechanism, if it operated in the *t*-butyl phenylperacetates, should operate more weakly because of the greater remoteness of the substituent from the O—O bond. On the other hand, if the effect of substituents were exclusively on the resonance energy of the benzyl radical, the Hammett equation might not be followed at all. To investigate this point, we have determined the rates of decomposition of the unsubstituted and six *p*- or *m*-substituted *t*-butyl phenylperacetates.

Results and Discussion

The Rates.—The kinetic results are shown in Table I. The first-order rate constant of *t*-butyl *p*-methoxyphenylperacetate varies by 28% over a tenfold range of concentration, suggesting some induced decomposition at a concentration of 0.5 *M*. For comparisons of the substituted peresters, concentrations in chlorobenzene were used of the order of 0.05 *M* and temperatures, depending upon the perester, from 56 to 100°. There is a clear rate-enhancing effect of the methyl and methoxy groups and a rate-depressing effect of the chloro and nitro substituents. As in the recently reported case of *t*-butyl *N*-phenylperoxycarbamates,⁵ the logarithm of the rate constant is a better linear function of σ^{+6} than of σ (see Fig. 1).

Significance of the Hammett Relation.—The only huge difference between the σ and σ^+ scales

(1) (a) Presented at the 16th National Organic Symposium, Seattle, Wash., June 17, 1959; (b) part III, P. D. Bartlett and D. M. Simons, *THIS JOURNAL*, **82**, 1753 (1960); (c) Chemical Institute, University of Munich.

(2) P. D. Bartlett and R. R. Hiatt, *THIS JOURNAL*, **80**, 1398 (1958).

(3) C. G. Swain, W. H. Stockmayer and J. T. Clarke, *ibid.*, **72**, 5426 (1950).

(4) A. T. Blomquist and I. A. Bernstein, *ibid.*, **73**, 5546 (1951).

(5) Compare also E. L. O'Brien, F. M. Beringer and R. B. Mesrobian, *ibid.*, **81**, 1506 (1959).

(6) H. C. Brown and Y. Okamoto, *ibid.*, **79**, 1913 (1957).

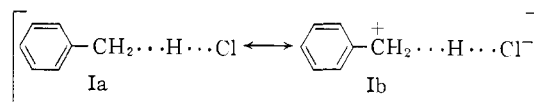
TABLE I
RATES OF DECOMPOSITION OF PERESTERS IN
CHLOROBENZENE, FOLLOWED BY INFRARED

X	Initial concn., M	T, °C.	k, sec. ⁻¹ × 10 ⁴	ΔH*	ΔS*
H	0.0574	79.55	1.05	27.9	2.0
	.0592	90.66	3.53		
	.0614	100.50	10.03		
<i>m</i> -CH ₃ O	.0512	79.55	0.99	29.2	5.3
	.0563	90.66	3.45		
	.0532	100.50	10.51		
<i>p</i> -CH ₃ O	.0567	56.0	0.454		
	.0584	56.0	.460		
	.0438	60.32	.99	25.2	0.0
	.237	60.32	1.12		
	.0500	70.23	3.06		
	.260	70.55	3.46		
	.0539	79.75	8.65		
<i>p</i> -CH ₃	.0556	70.40	0.867	26.5	-0.3
	.0562	79.55	2.37		
	.0560	90.66	7.95		
<i>m</i> -Cl	.0510	79.55	0.405	29.4	4.3
	.0480	90.66	1.44		
	.0588	100.50	4.38		
<i>p</i> -Cl	.0529	79.55	0.844	28.0	2.0
	.0522	90.66	2.95		
	.0546	100.50	8.19		
<i>p</i> -NO ₂	.0554	79.55	0.25	29.8	4.4
	.0558	90.66	0.89		
	.0529	100.50	2.83		

here is that between the values of σ (-0.268) and σ^+ (-0.778) for the *p*-methoxy group, but the differences for *p*-CH₃ and *p*-Cl are also significant. The applicability of the " σ^+ " value shows that the fragment being stabilized by the methoxy and methyl substituents is not a phenylacetate but a benzyl group, for it is only in delocalization of a positive charge into the benzene ring that the *p*-methoxy group shows such a powerful effect. If this be granted, it follows almost certainly that the effect operates upon the stretched and relatively polarizable transition state and is not a simple electrostatic destabilization of the ground state.

In a number of cases⁷⁻¹⁰ polar substituent effects have been discerned in reactions in which a free radical attacks a molecule. The transition state has been pictured as a resonance hybrid deriving some stabilization from charge redistributions which are aided or opposed by the substituent. Thus, in the attack of a chlorine atom upon toluene the transition state may be pictured as

- (7) F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).
 (8) R. van Helden and E. C. Kooyman, *Rec. trav. chim.*, **73**, 269 (1954).
 (9) G. A. Russell, *THIS JOURNAL*, **78**, 1047 (1956); *J. Org. Chem.*, **23**, 1407 (1958).
 (10) C. Walling and B. Miller, *THIS JOURNAL*, **79**, 4181 (1957).



The transfer of an electron in the direction shown is obviously more favored by the character of the chlorine atom than the transfer in the opposite direction would be. According to our plotting of the data⁹ the relative rates of chlorination of substituted toluenes are correlated with σ^+ rather than with σ .

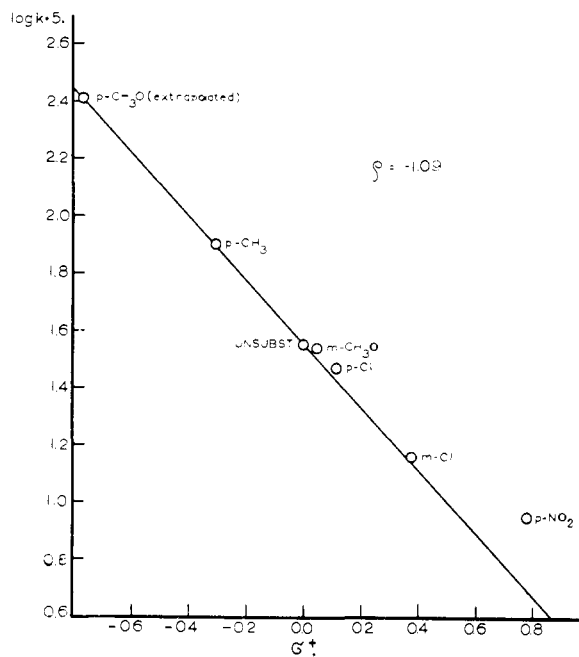
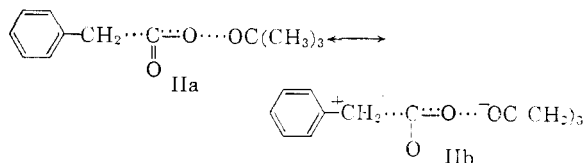


Fig. 1.—Thermal decomposition of $\text{X-C}_6\text{H}_4\text{-CH}_2\text{-COO-OC(CH}_3\text{)}_3$ in chlorobenzene at 90.66° (observed by infrared).

The present case differs from such chain-propagating reactions in that the perester molecule dissociates producing two free radicals. The transition state can be a resonance hybrid between ionic and radical structures only if the spins of the two incipient radicals remain coupled. This must in general be the case during thermal dissociation of a covalent bond into radicals, in contrast to photochemical dissociation where the first excited state may easily drop to a triplet before the actual dissociation begins. If the activated complex for thermal dissociation remains a singlet, then *t*-butyl phenylperacetates will dissociate through a transition state such as IIa-b.



Substituents in the benzyl group will stabilize IIb by a combination of electrostatic and resonance

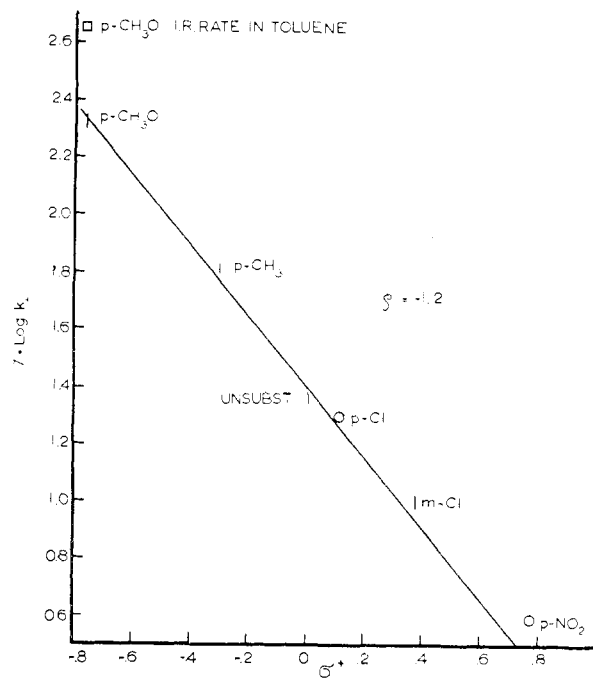


Fig. 2.—Rate of free radical formation from X-C6H4-CH2COOOC(CH3)3 in toluene at 56.0° (counting with iodine).

effects closely resembling that in the α -dimethylbenzyl ion on which the σ^+ scale is based.⁶

Modes of decomposition previously observed for peroxy compounds include simple radical fission, rearrangement by ionic mechanisms, cyclic internal decomposition and concerted decomposition into radical fragments. A process not yet identified would be a concerted decomposition in the extreme sense of structure IIb, proceeding all the way to the benzyl and tertiary butoxide ions.

Experiments with Scavengers.—As a test of this possibility, the reaction rates of the members of this series have been followed, not only by observation of the infrared absorption, but also by observing the disappearance of radical scavengers in solutions of the peresters. The most extensive measurements of this sort were made at 56° in toluene solution with iodine as a radical interceptor.¹¹ The results are shown in Table II and the rates are plotted according to the Hammett equation in Fig. 2. These results show the same parallel between logarithm of rate constant and σ^+ when the process measured is disappearance of iodine color as when it is disappearance of the perester group. The value of ρ in Fig. 2 is -1.20 .

Hammond, Sen and Boozer¹¹ have considered in detail the efficiency of radical production by initiators and the efficiency of radical interception by scavengers. On the basis of quantitative agreement between iodine and inhibited autoxidation where these were used as radical counting methods, and of product studies, these authors conclude that the percentage efficiency characteristic of iodine as a scavenger with azobis-isobutyronitrile represents

(11) G. S. Hammond, J. N. Sen and C. E. Boozer, *THIS JOURNAL*, **77**, 3244 (1955).

TABLE II
RATES OF DECOMPOSITION OF PERESTERS AT 56.0° FOLLOWED BY RADICAL INTERCEPTION WITH IODINE

X	% of run zero order	Perester concn., M	Iodine, M $\times 10^4$	Solvent	$k \times 10^4$, sec. ⁻¹
H	7	0.0875	7.2	Chlorobenzene	0.0162
H	56	.413	7.2	Chlorobenzene	.0158
H	54	.0950	9.05	Chlorobenzene + (C ₆ H ₅) ₃ CH	.0116
H	61	.0865	7.95	Anisole	.0226
H	73	.0755	7.06	Cumene	.0116
H	100	.101	9.08	Toluene	.0238
H	100	.0895	7.23	Toluene	.0218
H	86	.0890	7.22	Toluene	.0216
H	100	.0853	8.10	Toluene	.0219
<i>p</i> -CH ₃ O	100	.0518	9.10	Toluene	.220
<i>p</i> -CH ₃ O	69	.0484	9.10	Toluene	.202
<i>p</i> -CH ₃ O	86	.0704	7.22	Toluene	.206
<i>p</i> -CH ₃ O	82	.0669	7.22	Toluene	.215
<i>p</i> -CH ₃ O	94	.0709	7.22	Toluene	.218
<i>p</i> -CH ₃	100	.0850	9.10	Toluene	.0640
<i>p</i> -CH ₃	100	.0912	9.10	Toluene	.0662
<i>m</i> -Cl	100	.0831	7.5	Toluene	.0105
<i>m</i> -Cl	77	.0742	7.22	Toluene	.0094
<i>p</i> -Cl	63	.0790	9.02	Toluene	.0196
<i>p</i> -NO ₂	76	.0728	7.22	Toluene	.00415
<i>p</i> -NO ₂	53	.00738	7.9	Toluene	.112 ^a

^a At 79.55°.

the fraction of the radicals which become free of the solvent cage under these conditions. The results in Table II show that this conclusion cannot be extended to *t*-butyl phenylperacetate or *p*-methoxyphenylperacetate. With iodine in the solvents chlorobenzene, anisole, cumene and toluene there is a range of twofold in the indicated rates of radical formation. Toluene was by far the most constant solvent for this purpose and was generally adopted when iodine was used as a scavenger. Table III shows some experiments comparing the efficiency of iodine in toluene as an interceptor for the radicals from di-*t*-butyl peroxide, AIBN, *t*-butyl peroxyoxalate and *t*-butyl *p*-methoxyphenylperacetate. The scavenger efficiencies vary from 48% or less with *t*-butyl peroxyoxalate at 25°, and with the *p*-methoxyphenylperacetate at 56°, to a counting rate at 100° for di-*t*-butyl peroxide which is apparently identical with the rate extrapolated from the higher temperature measurements of Raley, Rust and Vaughan. This case is an interesting one in that there may be no mode of product formation between two *t*-butoxy radicals which is of low enough activation energy to occur within the solvent cage.

There is an apparent trend toward higher efficiencies at higher temperatures and higher scavenger concentrations.

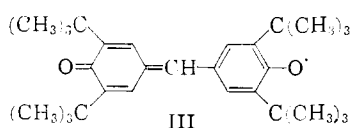
Such variability in the results means that iodine, though efficient in intercepting radicals from AIBN, is unreliable for phenylperacetates. In trying other scavengers we found that diphenylpicryl-

TABLE III
DECOMPOSITION RATES OF INITIATORS, MEASURED WITH IODINE IN TOLUENE

Initiator	$M \times 10^4$	$M \times 10^4$	$T, ^\circ\text{C.}$	$k \times 10^7$	% of rate by i.r. or titration	% of run zero order	% of run Ref.
<i>t</i> -Bu ₂ O ₂	577	6.7	100.5	7.56	..	67	^a
<i>t</i> -Bu ₂ O ₂	576	6.82	100.5	6.97	..	41	^a
AIBN	312	8.26	56.0	42	77	91	^b
<i>t</i> -Bu ₂ C ₂ O ₆	148	11.4	25	100	48	72	^c
<i>p</i> -CH ₃ OC ₇ H ₇ CO ₂ <i>t</i> -Bu	480-710	7.2-9.1	56.0	202-220	44-48	69-100	^d
<i>p</i> -CH ₃ OC ₇ H ₇ CO ₂ <i>t</i> -Bu	3.9	7.56	70	59	^e
<i>p</i> -CH ₃ OC ₇ H ₇ CO ₂ <i>t</i> -Bu	3.9	7.56	70	59	^e
<i>p</i> -CH ₃ OC ₇ H ₇ CO ₂ <i>t</i> -Bu	10.25	14.9	70	64	^e

^a This rate constant is not significantly off the line if the logarithms of the published rate constants for *t*-Bu₂O₂ decomposition in cumene are plotted against $1/T$ [J. H. Raley, F. F. Rust and W. E. Vaughan, *THIS JOURNAL*, **70**, 1336 (1948)].
^b Taking k_{56}^0 as 5.53×10^{-6} by interpolation according to J. P. Hook and A. V. Tobolsky, *ibid.*, **80**, 779 (1958). ^c $k = 2.1 \times 10^{-6}$ (D. Darwish, unpublished work in this Laboratory). ^d Extremes of 5 kinetic runs from Table II. ^e Product study runs; total iodine consumption determined after heating in sealed tube for more than 10 half-lives.

hydrazyl was entirely unsatisfactory, giving curves of optical density *vs.* time which were more nearly of second than of zero order. Better adapted to this problem was the hindered oxygen radical III,¹² (known in this Laboratory for convenience as "galvinoxyl"). The concentration of this deep



blue radical can be followed over a range from 10^{-5} to 10^{-2} *M* by use of the intense absorption at $410 \text{ m}\mu$ (ϵ 24,000) or of the weaker absorption at $530 \text{ m}\mu$ (ϵ 560). Results of the use of this scavenger will be reported elsewhere.

Tables II and III include indications of the extent to which the disappearance of the scavenger followed a zero-order course. In a few cases an induction period was observed, possibly due to faulty degassing, but in most cases the "% zero order" entry in the table indicates the percentage of the scavenger which had disappeared when the curve of optical density *vs.* time first departed from linearity. Experiments using iodine in toluene generally gave strikingly constant rates of disappearance which were maintained as long as measurable light absorption was occurring. Some runs showed a retardation before this point, and these included the ones in chlorobenzene, which gave quite low fractions of the spectrometric rate constant.

The rates of iodine disappearance in chlorobenzene were smaller and the kinetics less clean than in toluene. A possible explanation is that toluene, by donating hydrogen rapidly to the *t*-butoxy radical, replaces it by the benzyl radical which reacts with iodine to yield a stable product, benzyl iodide. This course for the reaction is confirmed by product studies (see below). Cumene was tried as a solvent with the idea that its greater activity as a hydrogen-atom donor might make it cooperate still better in the radical interception by iodine. In cumene the measured rate constant was $1.16 \times 10^{-6} \text{ sec.}^{-1}$ compared with 2.22 in toluene. Linear over 73% of its course, the iodine disappearance in this solvent was the only one to show

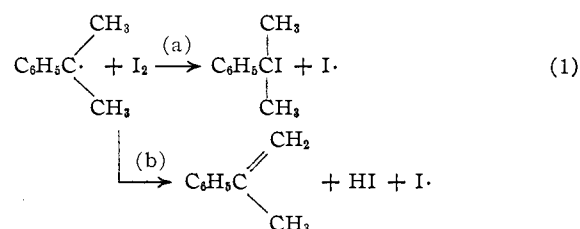
(12) Galvin M. Coppinger, *THIS JOURNAL*, **79**, 501 (1957).

TABLE IV
PRODUCTS FROM DECOMPOSITION OF *t*-BUTYL PHENYLPER-
ACETATE IN TOLUENE AT 95° IN PRESENCE OF IODINE

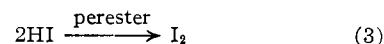
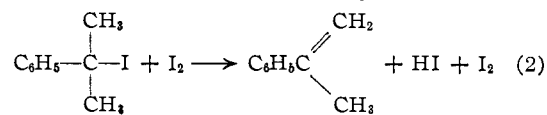
Experiment	1	2 ^{1a}	3 ^{1a}
Millimoles perester taken	2.413	4.93	4.64
Millimoles iodine taken	1.881	6.29	8.98
Millimoles iodine consumed	1.641	3.55	3.38
Products			
Moles formed per mole perester			
Carbon dioxide	0.956	0.962	0.953
<i>t</i> -Butyl alcohol	.672	.664	.668
Acetone	.075	.046	.043
Benzyl iodide	1.40	1.37	1.38
Benzyl <i>t</i> -butyl ether	0.12 ^a	0.214 ^c	0.223 ^c
	0.165 ^b		
Unidentified carbonyl compound (infrared peak at 5.86μ)		0.043 ^d	0.046 ^d

^a By infrared, after destruction of benzyl iodide. ^b By comparing infrared spectrum with that of synthetic mixture of benzyl iodide and benzyl *t*-butyl ether. ^c Separated by vapor phase chromatography. ^d Based on arbitrary mol. wt. of 150.

an *acceleration* toward the end of the reaction. Comparison of the cumyl and benzyl radicals suggests one way in which the former might divert iodine by means of a reaction cycle competing with the formation of α -iodocumene



or possibly, by electrophilic catalysis



The reaction of product to form iodine would, of course, lower the observed rate (still zero order) of iodine disappearance, depending upon the ratio k_a/k_b if only (1) and (3) operated, or upon the

(13) We are indebted to Dr. G. J. Karabatsos for experiments 2 and 3 in Table IV.

product $k_2(I_2)$ if step 2 were taking place. In the latter case an increased rate of over-all iodine disappearance toward the end of the reaction would be expected.

Products of Perester Decomposition in Presence of Iodine.—Table IV shows the results of three experiments in which the reaction products were accounted for. There is a small but clear increase in the radical count under conditions of product isolation (iodine excess) compared with that under kinetic conditions (100-fold excess of initiator). The presence in the product of 1.40 moles of benzyl iodide per mole of perester shows that in this experiment 70% of the possible radicals either were originally benzyl radicals or produced them by reaction with the solvent. As would be predicted under these circumstances, the *t*-butoxy radical is fixed as *t*-butyl alcohol to the extent of 90%. The 95.6% evolution of carbon dioxide is consistent with the overwhelmingly concerted nature of this decomposition. Because of an overlapping of the infrared absorptions of benzyl iodide and benzyl *t*-butyl ether, an estimate of the amount of the latter present in the reaction residue from the first experiment was made both before and after destroying the benzyl iodide. The amount apparently present before the destruction of benzyl iodide represented 16.5% of the maximum amount possible. The amount after destruction of benzyl iodide was estimated as 12%. In the other two experiments the amounts of the products, including benzyl *t*-butyl ether, were determined by vapor phase chromatography, the ether amounting to 21.4 and 22.3%. Benzyl *t*-butyl ether is the only known product of this reaction which could arise by radical coupling within the solvent cage. Had we been dependent upon the kinetic experiments with iodine scavenger, we should have estimated the cage effect at about 40%. If we used the iodine consumption in the product study, we should say that the cage effect amounted to 32%. By actual determination of the cage reaction product, however, we get down to a cage effect of not over 23%.

The Nature of the Substituent Effects.—The Mayo-Walling view of ionic resonance in the transition state, as adapted here to the process of homolytic dissociation, raises the question whether a combination of polar substitution and medium effects might shift the dissociation to an ionic mechanism in which benzyl cation and *t*-butoxide anion would be the direct products. Such a change of mechanism has been observed in unsymmetrically substituted benzoyl peroxides.^{14,15} If it appeared here it would be most probable in *t*-butyl *p*-methoxyphenylperacetate. The first-order rate constants for decomposition of this ester in cyclohexane, nitrobenzene and ethanol at 70.4° are in the ratio¹⁶ 1:3.6:3.8 in the presence of 0.1 *M* styrene to inhibit chain decomposition in the non-aromatic solvents. This is considerably below the factors of 7.8 and 94 between nitrobenzene and benzene observed^{14,15} for two benzoyl peroxides which are changing to an ionic mechanism. Espe-

cially convincing is the essential identity of the dependence of rate on structure whether the rate is followed by observing the decrease in perester concentration or by observing rate of generation of radicals (Figs. 1 and 2). Whatever might happen with a higher degree of substitution, our present substituent effects lie entirely within the homolytic dissociation mechanism.

The existence of this purely ionic influence on a purely radical reaction calls for a re-examination of the general view which we have expressed^{2,17} that the ability of a perester to undergo the type of concerted decomposition in question depends primarily upon the resonance energy of the carbon radical which splits from the carboxyl group. The evidence includes the similarity in rate of concerted homolytic cleavage of *t*-butyl trimethylperacetate and trichloroperacetate, and the great difference between the latter and its fluorine analog.^{1b,2} It might be thought that at least the *p*-nitro group would be capable of aiding the resonance stabilization of the benzyl radical. Actually, the *p*-nitro group does deviate positively from the Hammett plot, both for the *t*-butyl phenylperacetates and for the analogous *t*-butyl peroxy-*N*-phenylcarbamates recently reported,⁵ although its over-all effect is one of depression of the rate. We have not made a sufficient study of *t*-butyl *p*-nitroperbenzoate to exclude a small amount of Criegee rearrangement like that of *t*-butyl benzenepersulfonates.¹⁸ In this connection, it is of interest that the scavenger method (Fig. 2) shows a smaller positive deviation of *p*-nitro from the Hammett plot than does the over-all rate measurement by infrared. In the total list of peresters we are dealing with large radical stabilizations, up to 25–30 kcal., and changes in enthalpy of activation amounting to 16 kcal. These effects are the most important. By comparison, *meta* and *para* substitution produces only small changes, and evidently these are predominantly through providing favorable ionic contributions to the transition state.

Experimental

Preparation of Peresters. *p*-Nitrophenylacetyl Chloride.—*p*-Nitrophenylacetic acid (54 g., 0.3 mole), m.p. 155.4–155.8°, white label grade from Matheson, Coleman and Bell, was warmed slowly with 49 g. of thionyl chloride (0.4 mole) and held at 70° in an oil-bath for half an hour. After all the acid had dissolved, the thionyl chloride was taken off under vacuum and the residue was recrystallized from benzene-cyclohexane; yield 43 g. (0.23 mole, 77%), m.p. 45.8–46.8°, lit.¹⁹ 45–46°.

t-Butyl *p*-Nitrophenylperacetate.—*p*-Nitrophenylacetyl chloride (6.0 g., 0.030 mole) and 6.0 g. of *t*-butyl hydroperoxide were dissolved in a mixture of 110 ml. of benzene and 60 ml. of cyclohexane and cooled in an ice-bath to 0–5°. A solution of 2.6 g. (0.033 mole) of dried pyridine in 50 ml. of cyclohexane was added slowly with stirring while maintaining the temperature below 5°. The mixture was stirred for 0.5 hour after completion of the pyridine addition. The precipitate of pyridinium chloride was filtered off, and the solution was washed successively with 10% sulfuric acid, water, 10% sodium bicarbonate and water. After drying with anhydrous magnesium sulfate, most of the solvent was removed under vacuum at room temperature. When crystallization began, a little benzene was added to redissolve the crystals, and a small amount of yellow impurity was re-

(14) J. E. Leffler, *THIS JOURNAL*, **72**, 67 (1956).

(15) J. E. Leffler and C. C. Petropoulos, *ibid.*, **79**, 3068 (1957).

(16) K. H. Lee, unpublished work.

(17) P. D. Bartlett, *Experientia Suppl.*, **VII**, 275 (1957).

(18) P. D. Bartlett and B. T. Storey, *THIS JOURNAL*, **80**, 4954 (1958).

(19) H. P. Ward and E. F. Jenkins, *J. Org. Chem.*, **10**, 371 (1945).

moved on a 5'' Florisil column. After concentration of the benzene solution under diminished pressure and addition of an equal amount of cyclohexane, the perester crystallized in almost colorless leaflets, m.p. 53.2–53.4° on standing in the refrigerator, yield 2.3 g. (30%). The infrared spectrum contained no extraneous bands, the carbonyl peak appearing at 5.58 μ .

Anal. Calcd. for $C_{12}H_{16}O_5N$: C, 56.91; H, 5.97; N, 5.53. Found: C, 56.68; H, 5.85; N, 5.54.

***m*-Methoxyphenylacetyl Chloride.**—*m*-Methoxyphenylacetic acid (technical grade from the Winthrop Laboratories, New York) was recrystallized from water using charcoal to decolorize the solution. A second recrystallization brought the melting point to 71.0–71.2° (lit.²⁰ 68°). The infrared spectrum indicated no impurities or isomers to be present. The acid (20 g., 0.12 mole) was transformed to the acid chloride as described above for the *p*-nitro acid with thionyl chloride. The acid chloride was purified by vacuum distillation, boiling at 126–128° (15 mm.). The yield was 19 g. (85%).

***t*-Butyl *m*-Methoxyphenylperacetate.**—The perester was prepared in the same manner as described below for the *p*-methoxy isomer. On evaporation of the pentane solution of the perester, an oil was obtained which crystallized only at Dry Ice–acetone-bath temperature. From 7.4 g. of acid chloride (2.040 mole) and 7.0 g. of *t*-butyl hydroperoxide, there was isolated 8.4 g. (88%) of oily material, which was purified by passage in pentane through a short Florisil column. The infrared spectrum showed no extraneous bands and had the carbonyl peak at 5.59 μ .

Anal. Calcd. for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.66; H, 7.65.

***p*-Methoxyphenylacetyl Chloride.**—*p*-Methoxyphenylacetic acid (Matheson, Coleman material melting at 86–87° lit.²¹ 85–87°) was converted into the acid chloride in the manner described above except that the temperature used was 50° and the time 45 min. The yield from 33 g. (0.20 mole) of acid was 29 g. (0.16 mole) of acid chloride boiling at 127–128° under 9 mm. pressure (79% yield).

***t*-Butyl *p*-Methoxyphenylperacetate.**—*p*-Methoxyphenylacetyl chloride (7.4 g., 0.04 mole) and *t*-butyl hydroperoxide (7.0 g., 0.078 mole) in 150 ml. of pentane at 0° was slowly treated with 3.5 g. (0.045 mole) of pyridine in 50 ml. of pentane. There was precipitation of pyridinium chloride and, later in the reaction, some perester. When the addition was complete, the mixture was stirred for a further 15 min. The pentane solution was filtered, washed with ice-cold 10% sulfuric acid, water, 10% sodium bicarbonate, and water and dried over magnesium sulfate. The precipitate was treated with 200 ml. of pentane and 50 ml. of 10% sulfuric acid. The pentane layer was separated and treated as described above. The combined pentane solutions were filtered from the drying agent and the solvents removed under diminished pressure at 0°. When crystallization started, the solution was cooled to –20°. White, shiny leaflets separated in a yield of 6.1 g. A further crop of 1.5 g. was obtained from the concentrated mother liquor. The melting point, 38.6–38.9°, was not raised by recrystallization from pentane. The yield was 80%. The carbonyl peak in the infrared spectrum appeared at 5.61 μ .

Anal. Calcd. for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.69; H, 8.10.

***t*-Butyl Phenylperacetate.**—*t*-Butyl phenylperacetate was prepared as described by Bartlett and Simons.¹ The oily product, obtained in 60% yield, was purified by passing through a column of Florisil.

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.20; H, 7.74. Found: C, 69.17; H, 7.44.

***m*-Chlorophenylacetic Acid.**—*m*-Chlorophenylacetonitrile (50 g., 0.33 mole) from the Aldrich Chemical Co. was heated under reflux for one hour with 50 ml. of acetic acid together with equal volumes of concentrated sulfuric acid and water. The crude acid obtained by pouring the cold reaction mixture on ice was filtered and dissolved in a dilute solution of sodium carbonate. After several extractions with ether, the solution was acidified with sulfuric acid and the acid pre-

cipitated, filtered, and dried. The yield was 31 g. (61%) of crude product. After recrystallization from cyclohexane, 28 g. of pure acid was obtained, m.p. 78.6–78.8° (lit.²² 76°).

***m*-Chlorophenylacetyl Chloride.**—The acid was transformed in the usual manner with thionyl chloride into the acid chloride. From 25 g. of acid, 23 g. (72%) of acid chloride was obtained boiling at 121° under 17 mm. pressure.

***t*-Butyl *m*-Chlorophenylperacetate.**—The perester was obtained from 5 g. of acid chloride (0.027 mole) and 4 g. of *t*-butyl hydroperoxide in pentane as described for the *m*-methoxy derivative. After purification on a Florisil column, 3.8 g. (58%) of a perester was obtained with an infrared spectrum free of extraneous bands.

Anal. Calcd. for $C_{12}H_{15}O_3Cl$: C, 59.38; H, 6.23. Found: C, 59.70; H, 6.51.

***p*-Chlorophenylacetyl Chloride.**—*p*-Chlorophenylacetonitrile (100 g., 0.66 mole) from the Eastman Kodak Co. was saponified as described for the *m*-chloro isomer. The purification procedure was similar except that water was used as a solvent for recrystallizing the acid, which was obtained in a yield of 46 g. (0.3 mole, 45%), m.p. 106–106.6°. From the treatment of 30 g. of acid (0.19 mole) with 30 g. of thionyl chloride in the usual manner, 28 g. of *p*-chlorophenylacetyl chloride (0.14 mole, 74%) was obtained, b.p. 119° (14 mm.).

***t*-Butyl *p*-Chlorophenylperacetate.**—The acid chloride (5.0 g., 0.027 mole) and 4 g. of *t*-butyl hydroperoxide with 2.5 g. of pyridine in pentane, treated as described for the *m*-methoxy derivative, yielded 3.5 g. (0.0145 mole, 54%) of perester as an oily product. Purification was achieved on a Florisil column. The infrared spectrum showed no extraneous bands, the carbonyl maximum being at 5.61 μ .

Anal. Calcd. for $C_{12}H_{15}O_3Cl$: C, 59.38; H, 6.23. Found: C, 59.37; H, 6.25.

***p*-Tolylacetyl Chloride.**—*p*-Tolylacetic acid (kindly donated by the New York Quinine and Chemical Works) was recrystallized from water, melting at 90.8–91.3°. A preparation of the acid chloride by refluxing with thionyl chloride in the usual manner yielded from 30 g. (0.2 mole) of the acid, 24 g. (71%) of pure *p*-tolylacetyl chloride, b.p. 108–111° (20 mm.).

***t*-Butyl *p*-Tolylperacetate.**—The *t*-butyl perester was prepared from the acid chloride in the usual manner in 70% yield as an oily product. The infrared spectrum showed no extraneous bands, the carbonyl maximum appearing at 5.61 μ .

Anal. Calcd. for $C_{13}H_{18}O_3$: C, 69.81; H, 8.13. Found: C, 70.24; H, 8.16.

t-Butylhydroperoxide was purified as previously described.²

Pyridine (reagent grade from Merck and Co.) was dried over barium oxide for 10 days and fractionated in a 40 cm. column. The main fraction with a boiling range of 0.5° was collected and stored over potassium hydroxide.

Chlorobenzene was shaken 6 times with concentrated sulfuric acid until the acid no longer became colored. After washing with water, 10% sodium bicarbonate solution and water, it was dried for 12 hours over calcium chloride. The chlorobenzene was filtered and fractionally distilled from phosphorus pentoxide through a 40 cm. column. The fraction used had a boiling range of 0.2°.

The carbon tetrachloride for the characterizing infrared spectra was reagent grade from Merck and Co.

Toluene from Merck and Co. was shaken several times with concentrated sulfuric acid and washed with water, bicarbonate and water. After drying over calcium chloride, it was fractionated in a 30-cm. column with a reflux ratio of 10:1; the middle fraction boiling within 1° was collected.

Anisole from the Eastman Kodak Co. was washed with 2 *N* sodium hydroxide, water and sulfuric acid containing ferrous sulfate, water, and was dried over calcium chloride. It was fractionated with a 30-cm. helix-packed column with a reflux ratio of 10:1; the middle fraction boiling within 1° was collected.

Azobisisobutyronitrile from the Eastman Kodak Co. was recrystallized twice from ether before use.

Di-*t*-butyl peroxide from the Union Bay State Co. was redistilled, b.p. 36.3° at 56 mm.

Di-*t*-butyl peroxalate and diphenylpicrylhydrazyl were kindly provided by Dr. D. Darwish.

(20) S. N. Chakravarti, R. D. Haworth and W. H. Perkin, *J. Chem. Soc.*, 2270 (1927).

(21) J. C. Cain, J. L. Simonsen and C. Smith, *ibid.*, 103, 1036 (1913).

(22) J. Kenner and F. Morton, *ibid.*, 679 (1934).

Galvinoxyl was kindly provided by Dr. G. M. Coppinger. **Benzyl iodide** was prepared by the procedure of Norris,²³ and purified by the procedure of Sibbett and Noyes.²⁴

Benzyl *t*-butyl ether was prepared by the method of Milas²⁵ except that potassium *t*-butoxide instead of sodium *t*-butoxide was used. The reaction time in excess *t*-butyl alcohol was reduced from two months at room temperature to 10 hours at 80°.

Procedure for Kinetic Runs.—A weighed sample of perester was dissolved in a known volume of the solvent, usually 25 cc. The solution was distributed into a series of sealed tubes from a manifold in an atmosphere of nitrogen. At successive time intervals, tubes were removed from the constant temperature bath and immersed in a Dry Ice-acetone-bath. The concentration at zero time was taken as that in a tube removed after about 5 minutes in the constant temperature bath. When all the samples from a kinetic run had been chilled, the percentage transmission of each one was measured at the frequency maximum of the perester carbonyl band in the infrared (5.61 μ). The procedure was essentially the same as that used by Bartlett and Hiatt.² The measurements were taken in a concentration range where Beer's law was obeyed as verified by a plot of $\log T_\infty - \log T$ against relative concentration of perester. The kinetic equation used was

$$k_1 t = \ln \frac{P_0}{P} = 2.3 \log \frac{\log T_\infty - \log T_0}{\log T_\infty - \log T}$$

In the experiments using scavengers, known solutions of scavenger and perester in the solvent were introduced separately into the two side arms of a closed apparatus sealed to a Beckman absorption cell and degassed by repeated freezing, evacuating, and warming. Finally the cell was filled with nitrogen and sealed off. After the two solutions had come to temperature in the thermostat, they were mixed at zero time, and the decrease in optical density at the selected wave length was followed in the Beckman DU Spectrophotometer. The kinetic equation used was $k = -\lambda/2(P_0)$ where λ is the slope of the plot of optical density versus time, P_0 is the essentially constant perester concentration and ϵ is the extinction coefficient of the scavenger.

The extinction coefficient of iodine in chlorobenzene at 510 $m\mu$ was determined as 886 ± 11 . Diphenylpicrylhydrazyl and 2,4,6-triphenylphenoxy radical proved to be inefficient scavengers.

Product Analyses. The first experiment was performed in a reaction flask fitted with a side tube in which the solution of iodine in toluene could be separated from the main solution of tertiary butyl phenylperacetate in the flask. There was

(23) J. F. Norris, *Am. Chem. J.*, **38**, 638 (1907).

(24) D. J. Sibbett and R. M. Noyes, *THIS JOURNAL*, **75**, 761 (1953).

(25) N. A. Milas, *ibid.*, **53**, 221 (1931).

also a side arm provided with a **great seal** by which the previously sealed apparatus could be attached to another all-glass closed system. To minimize possible direct attack of iodine upon the perester, small amounts of the iodine solution were periodically introduced into the main flask by tilting the apparatus. In this way a visible iodine color was maintained in the reaction from the start. Both solutions were degassed in the usual manner to remove all oxygen or carbon dioxide. The apparatus then was sealed off under vacuum and immersed in a bath at $95 \pm 3^\circ$ for 7 hours, which is more than ten half lives. At the end of this time, the flask was attached to a vacuum line which then was evacuated. The break seal was broken while the reaction mixture was cooled in liquid nitrogen and the pressure of non-condensable gases was recorded. The system was re-evacuated and the reaction flask was warmed to 0°. The solvent containing tertiary butyl alcohol and ester was then distilled into the first trap of the vacuum line, cooled by Dry Ice-acetone, and the carbon dioxide was trapped by liquid nitrogen in the second trap. When all solvent had distilled over at a temperature below 0°, no pressure rise was observed in the vacuum system. The carbon dioxide trap was isolated from the system and the amount of the gas determined by pressure. The residual iodine was determined spectrophotometrically and by titration. The acetone and tertiary butyl alcohol were determined by measuring the infrared absorption at 5.79 μ and at 10.95 and 8.7 μ , respectively. The last 10 cc. of the toluene solvent removed by distillation was tested by vapor phase chromatography for the presence of ethylbenzene using a 20% silicone oil on Celite column at 90°. The fraction, however, proved to be pure toluene. The infrared spectrum of the non-volatile residue dissolved in 25 cc. of carbon tetrachloride was determined. The benzyl iodide was estimated by the sharp and characteristic band at 8.66 μ . Because benzyl iodide interferes with the bands of the second non-volatile component, benzyl tertiary butyl ether, the benzyl iodide was destroyed by heating the carbon tetrachloride solution with an excess of *n*-butylamine on the steam-bath for 5 minutes and washing the solution with hydrochloric acid, sodium carbonate and water. Traces of iodine were destroyed using a dilute bisulfite solution. Infrared analysis of benzyl tertiary butyl ether was then performed at 8.34 μ .

In the second and third product analyses the volatile products were separated by vapor phase chromatography.¹³

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY, HARVARD UNIVERSITY]

Peresters. V.¹ Di-*t*-butylperoxyoxalate

BY PAUL D. BARTLETT, ERHARD P. BENZING AND RICHARD E. PINCOCK

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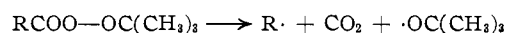
Di-*t*-butylperoxyoxalate, m.p. 50.5–51.5°, decomposes at room temperature in benzene or cumene to yield carbon dioxide (2 moles), *t*-butyl alcohol, acetone and biphenyl (7%) or bicumyl (86%). Ethers produce induced chain decomposition, which in the case of isopropyl ether is fairly rapid at 0°, and leads to isopropyl isopropenyl ether, carbon dioxide and *t*-butyl alcohol. Iodometric titration, hydrolysis and transesterification cleave the molecule with ionic scission of the perester group not initially attacked. The thermal decomposition of di-*t*-butylperoxyoxalate has ΔH^* 25.5 kcal., ΔS^* 5.1 e.u., and a calculated half-life at 60° of 6.8 minutes, placing it among the most reactive peresters previously reported. It is a low-temperature initiator for the polymerization of styrene and of diethylene glycol bis-allyl carbonate (CR 39). The mechanisms of its reactions are briefly discussed. See also Part VI.

Introduction

Previous studies in this Laboratory^{1,2} have established that certain peresters undergo con-

(1) (a) Part IV, P. D. Bartlett and C. Rüchardt, *THIS JOURNAL*, **82**, 1756 (1960); (b) presented before the Organic Division at the 133rd Meeting of the American Chemical Society, San Francisco, Calif., April, 1958.

certed decomposition at a C–C bond together with an O–O bond yielding carbon dioxide and an alkoxy free radical as primary decomposition products



(2) P. D. Bartlett and R. R. Hiatt, *THIS JOURNAL*, **80**, 1398 (1958).