hours were needed for reaction. Four and nine-tenths grams (48%) of *sym*-dichlorotetraphenylethane, m.p. 184–185°, was obtained (lit.,[25] m.p. 185°).

Reduction of 1,1,3-Triphenylindene.—One gram of 1,1,3-triphenylindene was dissolved in 50 ml. of distilled *n*-amyl alcohol.[8] Two grams of sodium metal was cut in small cubes and slowly added to the refluxing solution. After all the sodium had reacted, 5 ml. of water was added and the mixture chilled in an ice bath. The cream-colored precipitate was filtered and crystallized twice from 4:1 ethanol–benzene. Seven-tenths of a gram (70%) of 1,1,3-triphenylindane, m.p. 111–112°, was obtained.

Oxidation of 1,1,3-Triphenylindene.—One gram of 1,1,3-triphenylindene was oxidized with 1 g. of chromium trioxide in 25 ml. of acetic acid following the procedure used for oxidation of 1,1,3-triphenylindane. Crystals of *o*-dibenzoylbenzene were obtained, m.p. 145–146°.

Rearrangement of 1,1,3-Triphenylindene to 1,2,3-Triphenylindene.—Two grams of 1,1,3-triphenylindene was placed in a test tube, a thermometer inserted into the mixture, and the mixture heated at 350° for 2 hr. When cool the solid mass was recrystallized twice from 4:1 ethanol–benzene. 1,2,3-Triphenylindene (80%), m.p. 130–132°, was obtained. A mixed melting point with an authentic sample melted at 131–132°.

Reaction of Chlorodiphenylmethane, 1,1-Diphenylethylene, and *n*-Butyllithium.[26]—Chlorodiphenylmethane (20 g.) and 1,1-diphenylethylene (18.0 g.) were placed in a 100-ml. flask fitted with a thermometer, dropping funnel, condenser, stirrer, and nitrogen purge system. The motor was started and 40 ml. of *n*-butyllithium was slowly added, keeping the temperature between 25–35°. After addition, 20 ml. of water was added, the two-phase solution was separated and the organic layer dried over sodium sulfate. The dried products were separated by chromatography. The 3:1 petroleum ether–benzene fractions, after recrystallization from 4:1 ethanol–benzene, contained 1.7 g. (5%) of 1,1,3,3-tetraphenylpropene, m.p. 126–127°. A mixed melting point with an authentic sample melted at 126–126.5°. Careful chromatography of two reaction mixtures failed to reveal any cyclopropane derivative.

Acknowledgment.—Support of this work by a grant (P-058) from the Robert A. Welch Foundation is hereby gratefully acknowledged.

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[25] H. Staudinger, K. Clar, and E. Czako, *Ber.*, **44**, 1644 (1911).

[26] *n*-Butyllithium (19.8% weight in *n*-heptane) from Lithium Corporation of America, Inc.

Iodo Substituents and the Decomposition of Diacyl Peroxides. IV.[1]
Bis(β-iodopropionyl) Peroxide

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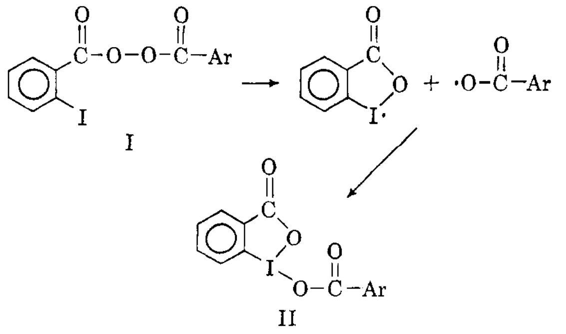
Received July 23, 1962

The decomposition of bis(β-iodopropionyl) peroxide owes its comparatively rapid rate to the presence of the β-iodo substituents. The products of the reaction are β-iodoethyl β-iodopropionate, iodine, ethylene, and carbon dioxide. Evidence is presented for a trivalent iodine compound and a carbonic ester anhydride as transient intermediates. A tentative mechanism is proposed for the reaction.

In *o*-iodo substituted benzoyl peroxides[1a,b] the *o*-iodo substituent accelerates the decomposition of the peroxide by what is probably a free radical analog of the neighboring group effect well known in ionic reactions. Thus the decomposition of *o*-iodobenzoyl peroxide (I) leads to the formation of radicals capable of initiating vinyl polymerization and ultimately to the rearrangement product (II).



Similar effects have not been reported in aliphatic diacyl peroxides, although bis(2-iodophenylacetyl) peroxide has been investigated.[1c] The absence of acceleration by *o*-iodine in the decomposition of the latter peroxide has no implications for aliphatic peroxides in general, however, since the competing decomposition mechanisms of the parent compound, bis(phenylacetyl) peroxide, are extremely fast.[3]

Therefore, we decided to investigate the effect of introducing β-iodo substituents on the rate and mechanism of decomposition of dipropionyl peroxide. The parent peroxide decomposes at a moderate rate typical of its homologous series, and the mechanism appears to be a straightforward radical one with no unusual features.[4]

Results and Discussion

The β-iodo substituent in bis(β-iodopropionyl) peroxide does alter the reaction mechanism, but to one somewhat more complicated than had been

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[1] For previous papers in this series see: (a) J. E. Leffler, R. D. Faulkner, and C. C. Petropoulos, *J. Am. Chem. Soc.*, **80**, 5435 (1958). (b) W. Honsberg and J. E. Leffler, *J. Org. Chem.*, **26**, 733 (1961). (c) J. E. Leffler and A. F. Wilson, *ibid.*, **25**, 424 (1960).

[2] This research was supported in part by the National Science Foundation.

[3] P. D. Bartlett and J. E. Leffler, *J. Am. Chem. Soc.*, **72**, 3030 (1950).

[4] J. Smid, A. Rembaum, and M. Szwarc, *ibid.*, **78**, 3315 (1956).

TABLE I

DECOMPOSITION PRODUCTS AND YIELDS[a]

In Benzene

Initial peroxide molarity	Iodine	Moles of product per mole of peroxide: β-iodoethyl β-iodopropionate	β-iodopropionic acid	Ethylene[b]	Carbon dioxide[b,c]
0.201	0.14	0.55	0.01	0.29	0.84
0.0225	0.32	0.83	0.06	0.42	0.88
0.114	0.22[d]	0.42[e]	0.02	0.41	0.86
0.068	...	...	...	32.6%[f]	65.8%[f]
0.0614 under air	0.24	0.53	0.02	...	...

In Cyclohexene[g]

Initial peroxide molarity	Moles of product per mole of peroxide: β-iodopropionic acid	Ethylene[b]	Carbon dioxide[b,c]
0.017	...	0.07	0.26
0.064	...	0.0	0.21
0.072	...	0.05	0.05
0.086	0.63	0.05	0.28
0.041 under air	0.30	...	...

[a] At 62.5° and degassed unless otherwise noted. [b] Burrell analysis. For the equilibrium of addition of iodine to ethylene, see M. J. Polissar, *J. Am. Chem. Soc.*, **52**, 956 (1930). [c] *Initial* carbon dioxide, not counting later evolution during decomposition of ester precursor on work-up. [d] For runs of high initial peroxide concentration, $-\Delta[I_2]/\Delta$ [peroxide] is always greater at the beginning of the run. For a run similar to this one it was 0.35 initially. [e] Not counting 0.31 of ester precursor, *i.e.*, still-residue converted to ester on further heating. [f] % Composition of the gas, by mass spectrographic analysis, courtesy of the Experimental Station, E. I. du Pont Co. A trace of *n*-butane also was found. [g] Cyclohexene absorbs iodine.

anticipated. The rate is enhanced over that of the parent peroxide by a factor of about 17; the enthalpy and entropy of activation are reduced to values suggestive of a cyclic or concerted process; and there appear to be two transient intermediates.

Stable Products of the Reaction.—The products stable enough to be isolable at the end of the decomposition in *benzene* are iodine, ethylene, carbon dioxide, β-iodoethyl β-iodopropionate, and small amounts of β-iodopropionic acid. In *cyclohexene* solution, the stable products are unidentified esters, carbon dioxide, ethylene, and β-iodopropionic acid. The yield of carbon dioxide is only about one-quarter, and the yield of ethylene about one-seventh, of that obtained in benzene. The yield of β-iodopropionic acid, on the other hand, is about twenty times that obtained in benzene. Iodine is not detectable as a product in cyclohexene, because it is absorbed by the solvent. Details of the yields and reaction conditions are given in Table I.

Kinetics and Rate of the Reaction.—The decomposition of bis(β-iodopropionyl) peroxide in benzene is about seventeen times as fast as the decomposition of propionyl or butyryl peroxides,[4] at 65°. The energy of activation is about 26 kcal./mole, and the entropy of activation about +3 cal./mole deg., as compared to 31 kcal./mole and +10 cal./mole deg. for propionyl peroxide.

TABLE II

FIRST-ORDER RATE CONSTANTS IN BENZENE, DEGASSED[a]

Initial peroxide concn., mole/l.	$k_{10} \times 10^4$ sec.$^{-1}$
.024	2.39
.056	2.43[b]
.071	2.42
.088	2.18
.088	2.30[c]
.093	2.66[d]
.117	2.25

[a] At 62.5°. [b] Styrene added. [c] Protected from light. [d] In the presence of 0.776 *M* acrylonitrile.

The first-order rate constant for the decomposition of bis(β-iodopropionyl) peroxide in *degassed* benzene solution (Table II) is (2.36 ± .07) × 10^{-4} sec.$^{-1}$ at 62.5°. This value is not sensitive to changes in the initial peroxide concentration from 0.0239 to 0.117 *M*, or to the exposure or nonexposure to the ordinary illumination of the laboratory. The lack of higher order terms in the rate expression can be attributed to the well known radical-trapping effect of the iodine formed in the reaction.[5]

The decomposition in benzene *in the presence of air*, on the other hand, is a reaction of mixed first and higher order. Within a run, the rate is approximately first order (Fig. 1), but the apparent first-order rate constant increases with increasing initial peroxide concentration (Table III and Fig. 2). The rate constant obtained by extrapolation to zero concentration appears to be about 15% less than that from the degassed benzene runs and is about the same as that obtained in air-exposed runs to which a substantial amount of iodine has been added at the beginning of the reaction.

Apparently there is some induced decomposition, approximately first order and relatively unimportant,[6] even in the absence of oxygen. In the presence of oxygen, the original radicals are converted

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[5] (a) D. F. DeTar and R. C. Lamb, *J. Am. Chem. Soc.*, **81**, 122 (1959); (b) H. J. Shiner and D. M. Hoffman, *ibid.*, **83**, 2782 (1961).

[6] First-order induced decomposition is possible if attack on the peroxide is exclusively by solvent-derived radicals and if chain-breaking is due to the reaction of peroxide-derived radicals with iodine or with solvent-derived radicals. *Cf.* C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *ibid.*, **72**, 5426 (1950).

Table III

First-order Rate Constants in Benzene in the Presence of Air[a]

Initial peroxide, concn., mole/l.	$k_{10} \times 10^4$, sec.$^{-1}$	Additive, mole/l.
0.029	2.40	
.053	2.69	
.060	2.61	
.071	2.81	
.085	0.692[b]	
.091	0.0201[c]	
.147	3.10[d]	
.153	3.25	
.245	3.26	
.029	2.02	I_2, 0.025
.077	1.88	I_2, .052
.079	2.09	I_2, .046
.122	2.29	I_2, .092
.024	1.95	Styrene, 0.209
.047	2.46	Styrene, .407
.076	2.88	Styrene, .581
.106	2.92	Styrene, .646

[a] At 62.5° unless otherwise noted. In case of curvature the initial k_1 is given. [b] At 52.0°. [c] At 25.0°. [d] Protected from light.

to new radicals more effective at attacking the peroxide, and an important higher order term appears in the rate expression. Iodine in high concentration is able to intercept all uncaged radicals and prevent induced decomposition even in the presence of oxygen.

Effect of Vinyl Monomers, Diphenylpicrylhydrazyl and Galvinoxyl.—In an attempt to get further evidence bearing on radical versus nonradical mechanisms for the decomposition, we carried out experiments in the presence of vinyl monomers and the radical traps diphenylpicrylhydrazyl[7] and galvinoxyl.[8] These experiments were inconclusive. Iodine is a well known inhibitor of vinyl polymerization,[9] so our failure to obtain any polymer is not unexpected. In an effort to overcome this difficulty we used a mixture of styrene with vinyl butyl ether, the latter as a scavenger for the iodine. This experiment also failed to give polymer.

Iodine also interferes with radical trapping by diphenylpicrylhydrazyl (DPPH). When bis(β-iodopropionyl) peroxide is allowed to decompose in undegassed benzene at room temperature in the dark in the presence of DPPH, no fading of the DPPH is found. If uncaged radicals are produced, they are perhaps trapped by the iodine liberated in the reaction rather than by the DPPH. It was noted by Fraenkel and Bartlett[9a] that iodine is removed by styryl radicals fifteen times as fast as DPPH.

In a control experiment with benzoyl peroxide, we found that DPPH fades at about the rate expected from the predicted decomposition rate of benzyl peroxide at 25° in the dark. In the light the DPPH-benzoyl peroxide reaction mixture faded somewhat more rapidly than in the dark.[10]

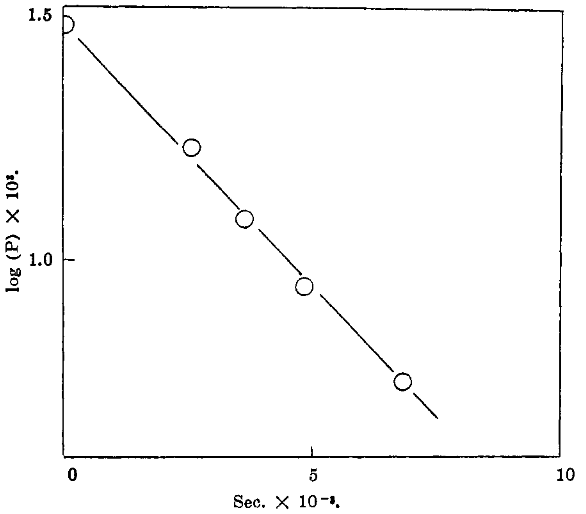

Fig. 1.—Decomposition of $(I\text{-}CH_2CH_2COO)_2$ in benzene at 62.5°, air present, $(P)_0$ = 0.0294 *M*.

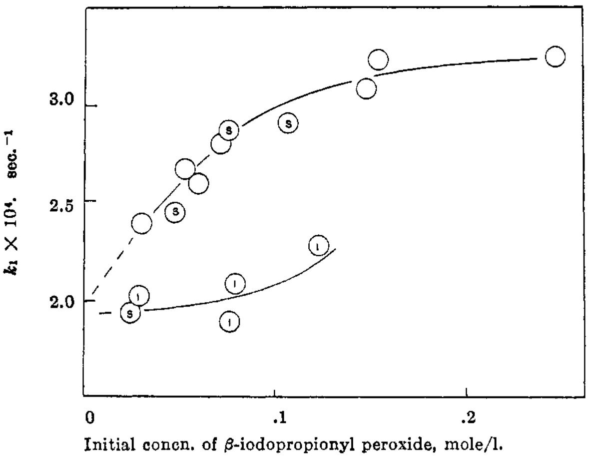

Fig. 2.—○, air; Ⓘ, air plus I_2; Ⓢ, air plus styrene.

A solution, 0.105 *M* in benzoyl peroxide, 0.02 *M* in *iodine*, and 2.2 × 10^{-4} *M* in DPPH, did not fade at all, even in the light.

Effect of Acids, Salts, and Polar Solvents.—The most likely alternative to a free radical mechanism for the decomposition of a diacyl peroxide is an ion-pair mechanism, but the rates of peroxide decompositions going by such mechanisms are quite sensitive to the polarity of the solvent and to the presence even of weak acid catalysts. An example is the decomposition of *p*-methoxy-*p'*-nitrobenzoyl peroxide.[11] Therefore, we undertook a study of the effect of polar media on the rate of the present reaction. The medium effects (Table IV) are small, and acceleration by added acids is

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[7] P. D. Bartlett and H. Kwart, *J. Am. Chem. Soc.*, **72**, 1051 (1950).

[8] G. M. Coppinger, *ibid.*, **79**, 501 (1957); P. D. Bartlett and T. Funahashi, *ibid.*, in press.

[9] (a) G. Fraenkel and P. D. Bartlett, *ibid.*, **81**, 5582 (1959); (b) D. S. Trifan and P. D. Bartlett, *ibid.*, **81**, 5573 (1959).

[10] Light also caused some fading of both DPPH and galvinoxyl with bis(β-iodopropionyl) peroxide in benzene at 25°, although neither faded appreciably with this peroxide in the dark. The rates of fading in light corresponded roughly to 10% of the decomposition rate of the peroxide as measured by titration at 25° (Table III).

[11] J. E. Leffler, *J. Am. Chem. Soc.*, **27**, 67 (1960).

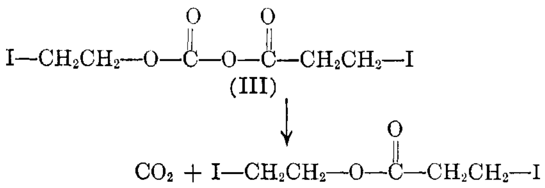
TABLE IV
MEDIUM EFFECTS[a]

Initial peroxide concn., mole/l.	Medium	$k_{10} \times 10^4$, sec.$^{-1}$
0.082	Benzene with .118 M CH_3COOH	2.64
.036	Benzene with .116 M Cl_3CCOOH	3.13
.041	Benzene with .190 M Cl_3CCOOH	4.81
.045	Benzene with .251 M Cl_3CCOOH	7.12
.057	Benzene with .139 M Cl_3CCOOH	5.22
.104	$CHCl_3$	2.4
.0189	*n*-Butyl vinyl ether	2.47
.0400	95% Ethanol	4.0
.0625	Cyclohexene	2.7
.0325	Acetone	2.19[b]
.0335	Acetone with 0.33 M $LiClO_4$	2.71[b]

[a] At 62.5° and with air present unless otherwise noted. [b] At 56°.

observed only for a very strong acid in quite high concentration. These results are entirely compatible with a free radical reaction having a moderate degree of polar character in the transition state, but are extremely unlikely for an ion-pair mechanism.

Evidence for Metastable Intermediates.—The β-iodoethyl β-iodopropionate appears to be formed from a metastable ester precursor, probably compound III, which we have been able to isolate only in crude form.



$$\mathrm{I{-}CH_2CH_2{-}O{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}CH_2CH_2{-}I}$$

(III)

$$\downarrow$$

$$\mathrm{CO_2 + I{-}CH_2CH_2{-}O{-}\overset{O}{\overset{\|}{C}}{-}CH_2CH_2{-}I}$$

Similar unstable ester precursors have been observed in the decomposition of 4-methoxy-3′,5′-dinitrobenzoyl and ditriptoyl peroxides.[12,13] A stable carboxy-inversion product, or carbonic ester anhydride, has been isolated in pure form from the decomposition products of 4-methoxy-4′-nitrobenzoyl peroxide.[11] The decomposition of carbonic ester anhydrides has been studied by Tarbell and co-workers, who report two modes of decomposition, one leading to carbon dioxide and ester, the other to carbon dioxide, dialkyl carbonate, and acid anhydride.[14]

The evidence for the presence of III in the reaction mixture is the occasional isolation of an oil with an infrared spectrum like that of typical carbonic ester anhydrides. On attempted molecular distillation this oil loses carbon dioxide and gives β-iodoethyl β-iodopropionate. During the peroxide decomposition in benzene, carbonic ester anhydride bands appear at 1800–1830 cm.$^{-1}$ and at 1740–1750 cm.$^{-1}$. The first of these is at about the same place as one of the peroxide bands but increases in intensity as the peroxide decomposes. Its final intensity is again decreased due to partial decomposition to the ester. The second band coincides with one of the ester bands and reaches a constant intensity during the first few half-lives.

There is also evidence suggestive of yet another metastable intermediate, a substance which has a carbonyl band at about 1720 cm.$^{-1}$ and which is titrated like free iodine in our analyses of aliquots for kinetics. By about 0.5 half-lives of the peroxide in benzene the 1720 cm.$^{-1}$ band is visible along with the 1750 cm.$^{-1}$ band as a shoulder on the main peroxide absorption band at 1790 cm.$^{-1}$. By 1.2 half-lives, both shoulders are better resolved from the waning peroxide band and are seen as a doublet at 1750 and 1720 cm.$^{-1}$. After 28 half-lives, the 1720 cm.$^{-1}$ band has vanished, and only the 1750 cm.$^{-1}$ ester and ester-precursor band remains. The other evidence for the second metastable intermediate is the apparent iodine material balance. Initial free iodine yields determined by the slope $-\Delta[I_2]/\Delta[\text{peroxide}]$ are always considerably greater than the final iodine yield. In fact, they are almost equal to the final yield of ethylene and push the iodine material balance well over 100%. If part of the material titrating like free iodine is actually another metastable precursor of the ester, its iodine would be counted twice, once as "free iodine" and again as covalently bound iodine. A possible structure for the suspected intermediate is IV, a trivalent iodine compound whose trivalent iodine atom is attached to saturated carbon. Although trivalent iodine compounds in which the iodine is attached to aromatic or unsaturated carbon atoms are well known and fairly stable, corresponding saturated compounds decompose at low temperatures and have been isolated only in a very few instances.[15]

A Tentative Mechanism.—The high rate and low enthalpy and entropy of activation for the decomposition of this peroxide indicate an initial step involving some sort of concerted reaction. The evidence for induced decomposition, together with the smallness of the medium effects, suggests that the initial step is a radical decomposition, *via* a transition state of moderate polar character. On the other hand, the free radical nature of the reaction is still in doubt in view of the inconclusive results of the radical trapping experiments.

Carboxy inversion, concerted decomposition into atomic iodine, ethylene, and carbon dioxide, and a neighboring group or cyclic mechanism involving the iodo substituent could all conceivably account for the acceleration and low entropy of activation. However, the observation that the reaction in cyclohexene, *which goes at about the same rate as the reaction in benzene*, gives greatly reduced

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(12) J. E. Leffler and C. C. Petropoulos, *J. Am. Chem. Soc.*, **79**, 3068 (1957).

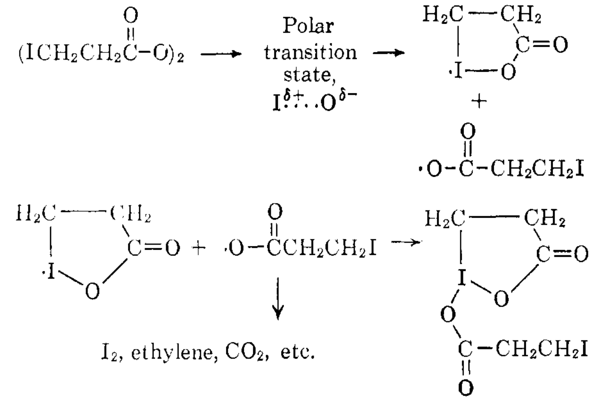
(13) P. D. Bartlett and F. D. Greene, *ibid.*, **76**, 1088 (1954).

(14) E. J. Longosz and D. S. Tarbell, *J. Org. Chem.* **26**, 2161 (1961); D. S. Tarbell and N. A. Leister, *ibid.*, **23**, 1149 (1958).

(15) C. Willgerodt, "Die Organischen Verbindungen mit Mehrwertigem Jod," Ferdinand Enke Verlag, Stuttgart, 1914.

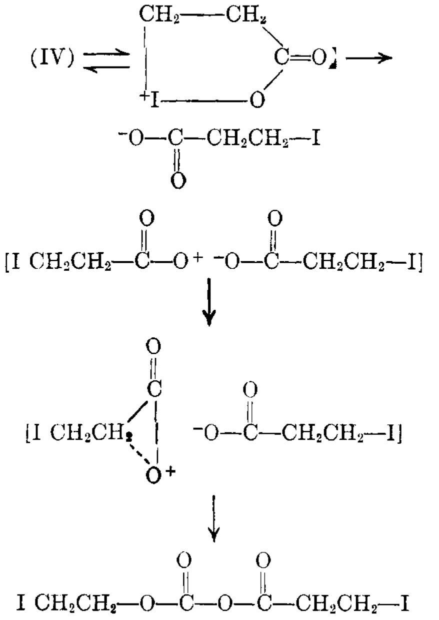
carbon dioxide and ethylene yields, eliminates the first two reactions as the initial rate-determining step.

There remains a mechanism analogous to the iodo-assisted decomposition of I but leading to a metastable trivalent iodine compound IV rather than to an isolable product. For the sake of concreteness, we will write the intermediates as free radicals.



IV

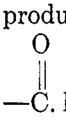
Compound IV is not isolated but decomposes by unknown mechanisms to give the observed reaction products. The carboxy conversion product III might come from an ion-pair decomposition of IV.

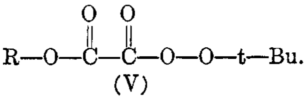


(III)

This hypothesis is supported by the observation that the yields of material titrating like free iodine are lower in the more polar solvents. If IV decomposes by an ionic reaction, less of it should accumulate in such solvents.

A less attractive alternative hypothesis is that III comes from the rearrangement of the acyloxy *free radical* rather than the cation, even though previous examples of the carboxy-inversion reaction usually have been coupled with evidence of an ionic mechanism for the decomposition of the peroxide. The transition state for the rearrangement of the acyloxy radical would resemble the alkoxycarbonyl product radical in some respects. Radicals $R-O-\overset{\overset{O}{\|}}{C}\cdot$ have been reported as intermediates in the decomposition of the peroxides V.[16]





$R-O-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-O-O-t-Bu.$

(V)

Experimental

Bis(β-iodopropionyl) Peroxide.—β-Iodopropionic acid was converted into the acid chloride by dissolving it in thionyl chloride (1 cc./g.), allowing it to stand for 1 hr., and removing the excess thionyl chloride by evaporation. The acid chloride from 1 g. of the acid was dissolved in 5 ml. of ether and cooled in an ice bath. To the cold solution was added 0.19 ml. of 90% hydrogen peroxide followed by 0.40 ml. of pyridine, both dropwise and with stirring and continued cooling. The precipitate of bis(β-iodopropionyl) peroxide was washed successively with 1 ml. of ice water, 2 ml. of ethanol, and 5 ml. of *n*-hexane. It was then crystallized from 1 ml. of chloroform by adding 1 ml. of ether and cooling. Yields are about 25%.

Equivalent wt. by the sodium iodide–acetone method: Calcd. 199; found 194, 201, 200, 208. The product melted with decomposition, using rapid heating, at temperatures ranging from 68 to 73°. Melting took place over a 2° range or less and was accompanied by gas and iodine evolution. The infrared spectrum in benzene had the characteristic carbonyl doublet at 5.5 μ (medium), 5.6 μ (strong); the spectrum in this region was identical to that of bis(β-chloropropionyl) peroxide and very similar to those of bis(β-phenoxypropionyl) and bis(β-nitropropionyl) peroxides.[17] All four peroxides also have a strong band in the 9 to 9.3 μ-region.

Reduction of the peroxide with potassium iodide in slightly aqueous acetone gave the equivalent weights quoted above. However, reduction with hydrogen iodide in water at 35° gives β-iodopropionic acid in only about two-thirds of the theoretical yield, the rest of the peroxide apparently forming the ester precursor (see below).

β-Iodoethyl β-iodopropionate.—This compound was prepared in the usual way from the acid and β-iodoethyl alcohol. It was purified by molecular distillation.

Anal. Calcd. for $C_5H_8I_2O_2$: C, 16.95; H, 2.26; I, 71.75; O, 9.04. Found: C, 17.27; H, 2.10, 2.41; I, 71.25, 72.57; O, 8.91, 8.32.

Gas Analyses.—The flask containing the solution of decomposition products under solvent vapor was attached to the gas buret of a Burrell gas analysis apparatus. The gas was transferred to the buret by means of several cycles of freezing, Töpler pumping, and thawing. Carbon dioxide was determined volumetrically by absorption in potassium hydroxide, ethylene by absorption in Burrell Lusorbent solution.

Nonvolatile Products.—β-Iodopropionic acid was isolated by sodium bicarbonate extraction and compared with an authentic sample. Ester was obtained by molecular distillation of the residue remaining after removal of benzene

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[16] P. D. Bartlett, B. A. Gontarev, and H. Sakurai, *J. Am. Chem. Soc.*, **84**, 3101 (1962).

[17] L. J. Story, this laboratory.

from the solution of decomposition products. The solution was first washed with sodium bicarbonate and treated with mercury to remove acid and iodine.

The infrared spectrum of the ester is identical with that of the synthetic β-iodoethyl β-iodopropionate. It was further identified by saponification to β-iodoethanol and β-iodopropionic acid, identified by infrared spectrum and mixed melting point. Before molecular distillation, the infrared spectrum of the nonvolatile products resembled those of model alkyl acyl carbonates.[12] It had bands at 3600 cm.$^{-1}$ (w), 2900 cm.$^{-1}$ (w), 1820 cm.$^{-1}$ (w), 1740 cm.$^{-1}$ (s), 1410 cm.$^{-1}$ (m), 1370 cm.$^{-1}$ (w), 1350 cm.$^{-1}$ (w), 1330 cm.$^{-1}$ (w), 1270 cm.$^{-1}$ (m) (shoulder), 1230 cm.$^{-1}$ (s), 1090 cm.$^{-1}$ (s), 1050 cm.$^{-1}$ (s) (shoulder), 930 cm.$^{-1}$ (w), and 800 cm.$^{-1}$ (w). In one experiment, this ester precursor was observed to evolve gas spontaneously after the solvent had been removed *in vacuo* and while the residue was being allowed to warm up to room temperature. Thereafter it had a spectrum identical to that of the synthetic β-iodoethyl β-iodopropionate. An attempt to repeat this delayed carbon dioxide evolution quantitatively, with absorption of the carbon dioxide in barium hydroxide, gave a yield of barium carbonate of only 7%.

Kinetics.—Degassed runs were done in ampoules, each containing slightly more than enough for one analysis. The ampoules and their contents were degassed by the usual freezing and thawing cycles on a vacuum line. After removal from the thermostat, the ampoules were quenched by rapid cooling to room temperature. *Non-degassed* runs were carried out using a single flask fitted with a condenser above the bath level. Aliquots were removed by pipetting and quenched by rapid cooling.

Total peroxide plus free iodine was determined by adding a 1.00-ml. aliquot to 10 ml. of aqueous acetone potassium iodide solution and titrating the resulting iodine solution with sodium thiosulfate. Free iodine was determined by adding a 1.00-ml. aliquot to 10 ml. of acetone and then rapidly titrating the resulting solution with sodium thiosulfate. Control experiments using solutions made by mixing iodine and peroxide solutions of known concentration gave peroxide concentrations with a mean 1.5% error, and iodine concentrations with a mean 2.9% error.

Substituent Effects on Free Radical Formation[1]

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Received July 9, 1962

The ease of attack of a *tert*-butoxy radical on a series of monosubstituted cyclohexanes has been measured, both neat and in benzene. The attacking radicals were formed by the thermal decomposition of *tert*-butyl peroxide, and the measurements made by gas chromatographic analyses of the relative amounts of *tert*-butyl alcohol and acetone formed. Consideration of the results with regard to relative reactivities, solvent effects, Hammett equation relationships, and radical complexing suggests that the inductive effect of the substituent determines the ease of C—H bond breaking.

Previous studies[3] on the rates of hydrogen atom abstraction from various compounds by atoms and radicals yielded data which indicated the reactivities of the hydrogens were affected by resonance, steric, polar, and solvent effects. This investigation was concerned with the effect of substituents upon the reactivities of C—H bonds, in an aliphatic system, toward hydrogen atom abstraction by *tert*-butoxy radicals in solution. It appeared that a good measure of the inductive and resonance effects, with an approximately constant steric effect, could be obtained for a number of monosubstituted cyclohexanes. This could be obtained from a series indicating the ease of hydrogen atom abstraction from the variously substituted cyclohexanes relative to abstraction of a hydrogen atom from cyclohexane. Adopting Russell's[4] postulate that the relative importance of polar and resonance effects in determining the reactivity of C—H bonds may be separated by observations on the magnitude of the solvent effect, the same compounds were caused to react with the *tert*-butoxy radicals in benzene and carbon tetrachloride solvents.

Results

The reactivities of the carbon–hydrogen bonds toward *tert*-butoxy radicals have been determined for a series of substituted cyclohexanes. The *tert*-butoxy radicals were formed by the decomposition of *tert*-butyl peroxide in solutions of the various compounds studied. This decomposition was assumed to proceed in the following manner

$$(CH_3)_3CO{-}OC(CH_3)_3 \xrightarrow{k_1} 2(CH_3)_3CO\cdot$$

$$(CH_3)_3CO\cdot + RH \xrightarrow{k_2} (CH_3)_3CO{-}H + R\cdot$$

$$(CH_3)_3CO\cdot \xrightarrow{k_3} CH_3COCH_3 + CH_3\cdot$$

The ratio of rates may be determined by measuring the amount of *tert*-butyl alcohol and acetone produced. In order to obtain the correct concentration of reactant in moles/liter, measurements were taken on the compounds studied to determine the volume change for each compound from room temperature to 135°, the reaction temperature. From these data and the densities at room temperature, the concentration of each of the compounds at 135° could be calculated. The amount of expansion was found to be approximately 12%

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[1] From the M.S. thesis of E. L. P., University of Connecticut, 1961.

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[3] (a) R. L. Huang and S. Singh, *J. Chem. Soc.*, 891 (1958); (b) G. A. Russell, *J. Org. Chem.*, **23**, 1407 (1958); (c) G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4987 (1958); (d) C. Walling and B. Miller, *ibid.*, **79**, 4181 (1957); (e) G. A. Russell, *J. Org. Chem.*, **24**, 300 (1959); (f) H. C. Brown and A. B. Ash, *J. Am. Chem. Soc.*, **77**, 4019 (1955).

[4] G. A. Russell, *ibid.*, **80**, 4997 (1958).