

nucleophile) nor of the nucleophilicity of the oxyanion which has been correlated with its electrode potential.²² (ii) Many observations bear out the rule that attack on peroxides by an oxygen function has little likelihood of occurrence; rather peroxides are susceptible to attack only by highly polarizable nucleophiles^{23, 24} which does not correspond to the order in Table VII.

The most plausible and consistent basis for explaining the rapid equilibration of many oxyanions with their peroxy conjugates in H₂O₂ solution is given by mechanism A, a direct Walden inversion type displacement *via* HOO⁻. The unusual nature of this mechanism with oxyanions is attributable to the phenominal properties of hydroperoxy anion, HOO⁻, as a nucleophile.²⁵ Thus, while phosphate shows almost no exchange activity toward an ordinarily strong nucleophile like hydroxide ion²¹ our results indicate the substitution reaction with hydroperoxy

(22) J. O. Edwards, *J. Am. Chem. Soc.*, **76**, 1540 (1954).

(23) G. Levey, D. R. Campbell, J. O. Edwards, and J. Maclachlan, *ibid.*, **79**, 1797 (1957).

(24) J. O. Edwards, *ibid.*, **78**, 1819 (1956).

(25) See, for examples: (a) W. P. Jencks and J. Carriuolo, *ibid.*, **82**, 1778 (1960); (b) K. B. Wiberg, *ibid.*, **77**, 2519 (1955); (c) D. L. Ball and J. O. Edwards, *ibid.*, **78**, 1125 (1956); (d) H. O. House and R. S. Ro, *ibid.*, **80**, 2428 (1958); (e) H. E. Zimmerman, L. Singer, and B. S. Thyagarajan, *ibid.*, **81**, 108 (1959); (f) R. G. Pearson and D. N. Edgingrow, *ibid.*, **84**, 4607 (1962); (g) J. Epstein, M. M. Demek, and D. H. Rosenblatt, *J. Org. Chem.*, **21**, 796 (1956).

anion is exceedingly rapid. Again, while the rate of reaction of good nucleophilic agents like amines²⁶ with carbonate increases only weakly and erratically with the amine basicity,⁸ hydrogen peroxide in basic solution appears to give us almost instantaneous conversion to percarbonate; under these conditions acid catalysis appears to be dispensible and, in fact, inhibitive since acid serves to produce uncompensated reduction in the concentration of active nucleophile.

Finally, the extremely rapid reaction of alkaline borate with hydrogen peroxide, documented in the results and discussions above, must be understood on the basis of the great susceptibility of the electrophilic boron (central) atom to nucleophilic attack. Even with hydroxide ion the extremely facile exchange of ligands in the coordination sphere of the B(OH)₄⁻ ion has received comment. The formation of a diperoxyborate and the corresponding diperoxycarbonate formation can be regarded as indication of the ease of displacement of OH⁻ by the stronger nucleophile HOO⁻ accommodating a repetition of the substitution reaction which resulted in their respective monoperoxy species.

Acknowledgment. One of us (H. K.) gratefully acknowledges the support of this program by the National Science Foundation *via* Grant NSF-G6037.

(26) C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, **75**, 141 (1953)

Organic Reactions Under High Pressure. IX. Some Observations on the Decomposition of Diacyl Peroxides¹

Cheves Walling, Howard N. Moulden, James H. Waters, and Robert C. Neuman²

Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. Received October 12, 1964

The rapid decomposition of benzoyl peroxide in acetophenone at high pressures has been shown to be due to adiabatic freezing of solvent, not to a fast induced decomposition as previously reported. However, in a nonfreezing solvent (CHCl₃) a small acceleration in rate is observed above 3000 kg./cm.², presumably due to induced decomposition. The products of decomposition at 6700 kg./cm.² are also consistent with an induced decomposition, proceeding, at this pressure, largely through benzoyloxy radicals. The decomposition of trans-4-t-butylcyclohexanecarbonyl peroxide is slightly pressure accelerated, $\Delta V^ = -4$ cc./mole. This result is consistent with a carboxyl inversion reaction to trans-4-t-butylcyclohexyl trans-4-t-butylcyclohexanecarbonyl carbonate as the rate-determining step in the chief decomposition path, and this intermediate has been detected on the basis of its infrared spectrum and reactions.*

The thermal decomposition of diacyl peroxides³ may occur by three well recognized paths: homolytic scission

(1) Support of this work by grants from the Petroleum Research Fund of the American Chemical Society and from the National Science Foundation is gratefully acknowledged.

(2) National Science Foundation Postdoctoral Fellow, 1962-1963.

(3) For general discussion *cf.* C. Walling, "Free Radicals in Solution,"

of the O-O bond, induced decomposition *via* radical chain processes, and rearrangement⁴ to give a carbonic anhydride or (perhaps directly) an ester and carbon dioxide. The effect of pressure on the rate of peroxide decomposition provides a useful tool for distinguishing between these paths, because the effect of pressure on each can be predicted rather unequivocally. Homolytic scission as a bond-breaking process converting one molecule into two should plainly be pressure retarded. Induced decomposition involves some sequence of radical displacements or additions and such steps (and the over-all chains) are, in general, pressure accelerated.⁵ Rearrangement, if it involves a cyclic transition state as is usually assumed, should also show a small pressure acceleration.⁶ This paper describes

John Wiley and Sons, Inc., New York, N. Y., 1957; A. G. Davies, "Organic Peroxides," Butterworth and Co. (Publishers) Ltd., London, 1961.

(4) F. D. Greene, H. P. Stein, C. C. Chu, and F. M. Vane, *J. Am. Chem. Soc.*, **86**, 2080 (1964), and references cited therein.

(5) *Cf.*, for example, C. Walling and J. Pellon, *ibid.*, **79**, 4776, 4782 (1957).

(6) Cope and Claisen rearrangements, for example, are pressure accelerated: C. Walling and M. Naiman, *ibid.*, **84**, 2628 (1962). A possible exception is in rearrangements involving tightly bridged structures where steric requirements require unusual bond stretching: C. Walling and H. Schugar, *ibid.*, **85**, 607 (1963).

some studies carried out over the past few years in these laboratories which illustrate the application of these ideas to the decomposition of benzoyl peroxide and *trans*-4-*t*-butylcyclohexanecarbonyl peroxide and provide further confirmation to currently accepted ideas as to their reactions.

Benzoyl Peroxide. Since the work of Nozaki and Bartlett⁷ it has been recognized that the thermal decomposition of benzoyl peroxide involves a simple homolytic scission on which may be superimposed an induced chain process. This chain reaction varies considerably in kinetic form and may involve radical attack on solvent either as a chain propagating step (as in ethers) or as a radical trapping process (as in styrene). The effect of pressure on the decomposition of benzoyl peroxide in CCl₄ at 70° has been investigated by Nicholson and Norrish⁸ (up to pressures of 3000 kg./cm.²) who analyzed their results in terms of a pressure-retarded, first-order homolytic scission and a ³/₂ order induced decomposition which was pressure accelerated. Activation volumes Δ*V** amounted to 8.7 and -15 cc./mole, respectively.⁹ Walling and Pellon¹⁰ studied the reaction in acetophenone as solvent at pressures up to 6500 kg./cm.². At 1500 kg./cm.² decomposition was retarded, Δ*V** = 4.8 cc./mole, but at 6500 kg./cm.² decomposition became very rapid and apparently of high kinetic order since first-order plots were strongly concave upwards.

We have now investigated this high-pressure region further and have found that the rapid decomposition is essentially an experimental artifact. Slow application of pressure greatly reduced the decomposition rate, while periodic release and reapplication of pressure maintained rapid decomposition until the peroxide was exhausted. Acetophenone freezes at 20° at atmospheric pressure, and it became evident that, at 6500 kg./cm.², its freezing point lies considerably above 80°.¹¹ Accordingly, on compression it freezes and the release of its latent heat of fusion raises the temperature to the point where peroxide decomposition is greatly accelerated. Carbon tetrachloride freezes at 76° at 3000 kg./cm.²,¹² and attempted kinetic experiments at 80° at 6300 kg./cm.² showed precisely the same sort of results as we had obtained with acetophenone. Some typical reaction plots showing the magnitude of the effects are shown in Figure 1. Accordingly, we turned to chloroform, which only freezes at 84° at 10,000 kg./cm.²,¹² for further studies at higher pressures. Typical decomposition plots are shown in Figure 2. There appears to be a slight decrease in rate at 760 kg./cm.², but at higher pressures decomposition rates increase to greater than their atmospheric pressure value. Although attempts to analyze the data in terms of first-order and higher reactions did not yield any unequivocal separation, the general form of the results are certainly consistent with a fast induced process

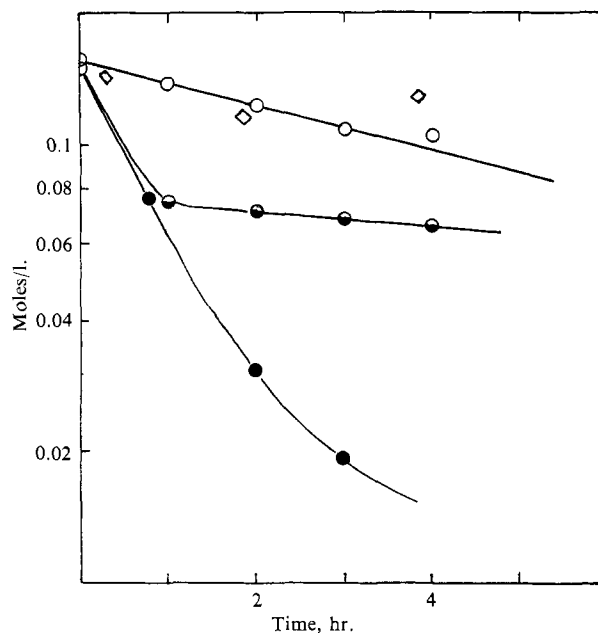
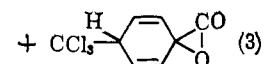
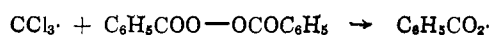
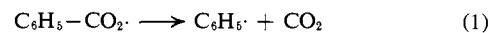


Figure 1. Effect of adiabatic freezing on the decomposition of benzoyl peroxide at 80° in CCl₄. Open circles, 1 kg./cm.²; half-open circles, 4300 kg./cm.²; filled circles, 4300 kg./cm.², repeated application of pressure; diamonds, 4300 kg./cm.², very slow application of pressure.

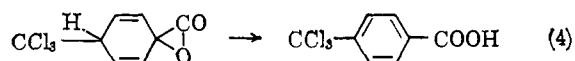
taking over the decomposition at higher pressures, even though the magnitude of the phenomenon is smaller than that reported earlier.¹⁰

An examination of the reaction products of decomposition in CHCl₃ gave results which are consistent with a predominant chain decomposition at high pressure and throw some light on its nature.

Elsewhere¹³ we have suggested that the induced decomposition of benzoyl peroxide in aliphatic hydrocarbons and chlorinated solvents occurs largely *via* a chain which for CHCl₃ might involve the propagating steps



and the rearrangement



Inspection of Table I indicates that at atmospheric pressure, while reaction 1 occurs readily, induced decomposition is relatively unimportant at this concentration (0.5 *M*) of peroxide; the yield of terephthalic acid is only 20%, and 67% of the radicals produced are accounted for as C₂Cl₆, an obvious chain termination product. At 6700 kg./cm.² the decarboxylation reaction is suppressed, since much less benzene is produced, and the decrease in C₂Cl₆ is consistent with an increase in induced decomposition. However, the small increase in terephthalic acid indicates that the chain reaction is now taking a different course. Investigation of the residue suggests that decomposition here is occurring

(13) C. Walling and E. S. Savas, *J. Am. Chem. Soc.*, **82**, 1738 (1960).

(7) K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.*, **68**, 1686 (1946).

(8) A. E. Nicholson and R. G. W. Norrish, *Discussions Faraday Soc.*, **22**, 97 (1956).

(9) Calculated from their data at 1 and 1000 kg./cm.². The rate constant for the ³/₂ order process is however a composite quantity and both numbers are surprisingly large.

(10) C. Walling and J. Pellon, *J. Am. Chem. Soc.*, **79**, 4686 (1957).

(11) Although we have not determined any phase diagram, if a sample of acetophenone is held at 80° and 6500 kg./cm.² for 1 hr. and the pressure released quickly, still-frozen acetophenone is found in the reaction vessel on opening.

(12) P. G. Bridgeman, *Phys. Rev.*, **3**, 153 (1914).

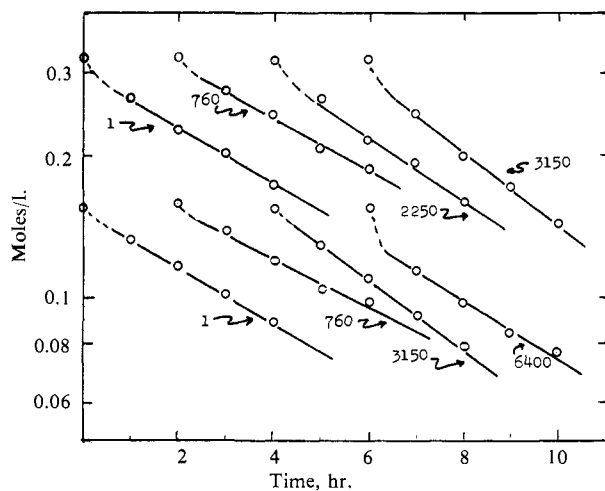


Figure 2. Effect of pressure on decomposition of benzoyl peroxide at 80° in CHCl₃. Scales have been displaced sideways to separate experiments, and initial points not considered in drawing lines because of uncertainty in zero time.

largely by attack of benzoyloxy radicals on peroxide, since refluxing the residue with methanol and sulfuric acid converted it largely to methyl benzoate together with dimethyl terephthalate and small quantities of several other unidentified materials. If such complicated crossovers in mechanism are occurring, our failure to obtain a detailed kinetic analysis is hardly surprising, and the large compensating ΔV^* values reported by Nicholson and Norrish⁸ are somewhat suspect.

Table I. Decomposition Products of Benzoyl Peroxide^a

Product	1 kg./cm. ²	6700 kg./cm. ²
Benzene	1.41	0.45
C ₂ Cl ₆	0.67	0.03
C ₆ H ₅ COOC ₆ H ₅	0.01	0.03
C ₆ H ₄ (COOH) ₂ ^b	0.21	0.25
Peroxide accounted for (%)	81	38
Residue (%) ^c		25

^a 0.4–0.5 M in CHCl₃ at 70° (moles/mole of peroxide). ^b Terephthalic acid from hydrolysis of *p*-trichloromethylbenzoic acid. ^c Wt. % of original peroxide.

trans-4-*t*-Butylcyclohexanecarbonyl Peroxide. The thermal decompositions of α -branched aliphatic diacyl peroxides are noteworthy in producing relatively high yields of ester products with retention of stereochemistry in both acid and alcohol moieties.^{3,4} The question whether these products arise from recombination of acyloxy and alkyl radicals (perhaps within the original solvent cage) or *via* a rearrangement has been a long-standing question in peroxide chemistry which, as noted in our introduction, can be answered by a study of the pressure coefficient of decomposition since recombination must be preceded by a pressure-retarded bond scission. *trans*-4-*t*-Butylcyclohexanecarbonyl peroxide appeared to provide a particularly striking case for study since Lau and Hart¹⁴ have reported that in *sym*-tetrabromoethane it decomposes to the *trans*-*trans* ester in 90% yield. Because of its high freezing point, tetrabromo-

(14) H. H. Lau and H. Hart, *J. Am. Chem. Soc.*, **81**, 4897 (1959).

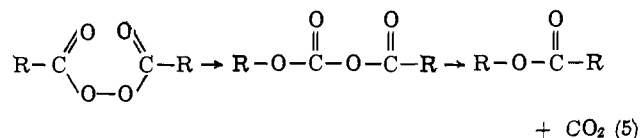
ethane is not a suitable solvent for pressure studies so, after trying several alternatives, including CCl₄ and cumene, *n*-butyl chloride was chosen as most convenient and as yielding reproducible results. Rate constants obtained both in *n*-butyl chloride alone and in the presence of 0.1 M methyl methacrylate (to suppress any interfering chain decomposition) are summarized in Table II. Since methacrylate slightly retards the decomposition a small amount of chain decomposition is indicated, but in both series the decomposition is definitely accelerated, and the change in rate to 1000 kg./cm.² in the presence of methacrylate (the most significant data) corresponds to $\Delta V^* = -4.1$ cc./mole.

Table II. Effect of Pressure on the Decomposition of 0.01 M *trans*-4-*t*-Butylcyclohexanecarbonyl Peroxide in *n*-Butane at 40°

<i>P</i> (kg./cm. ²)	<i>k</i> (sec. ⁻¹ × 10 ⁵)	<i>P</i> (kg./cm. ²)	<i>k</i> (sec. ⁻¹ × 10 ⁵) ^a
1	1.29 ± 0.06	1	1.20 ± 0.06
1	1.21 ± 0.06	1	1.22 ± 0.04
1000	1.67 ± 0.04	1000	1.41 ± 0.09
		1000	1.41 ± 0.08
2000	1.72 ± 0.11	2000	1.50 ± 0.11
		2000	1.61 ± 0.09
3000	1.67 ± 0.21	3000	1.59 ± 0.11

^a Methacrylate present.

Although such a result definitely rules out the radical recombination process as the major path of ester formation, careful examination of the products showed that the "rearrangement" goes at least in large part *via* carboxyl inversion to a carbonic anhydride followed by decarboxylation (eq. 5). Our own identification of the



intermediate is based upon its infrared spectrum and hydrolysis to acid, alcohol, and CO₂, but Greene has recently come to an identical conclusion, confirmed by actual isolation of the anhydride intermediate.⁴

Greene's work and ours on the anhydride intermediate are now certainly more compelling than our pressure measurements in establishing the mechanism of ester formation in the decomposition of this and related peroxides, and indicate that the value of ΔV^* we have obtained must refer to the transition state for the carboxyl inversion process. As such, the small negative value is consistent with the cyclic intramolecular path which would be expected for such a process. Its small absolute value may indicate either that bond breaking and bond forming have proceeded to comparable extents, or that excess bond breaking is balanced by electrostriction of surrounding solvent brought about by increased polarity of the transition state.

Experimental

Materials. Unless noted reagents were commercial materials purified or dried in conventional fashion.

trans-4-*t*-Butylcyclohexanecarbonyl peroxide was prepared from *p*-*t*-butylbenzoic acid by several modifications of the procedure of Lau and Hart,¹⁴ of which

the following was most successful. Reduction of the sodium salt of 17.8 g. of acid to mixed *cis-trans* isomers was carried out in water using Raney Nickel at 3000 p.s.i. and 200° for 24 hr. The mixture was esterified with *n*-butyl alcohol and H₂SO₄ and the esters were equilibrated to a *trans*-rich mixture by refluxing for 24 hr. with 4 g. of potassium *t*-butoxide in 75 ml. of *t*-butyl alcohol. Hydrolysis and crystallization from *n*-hexane gave 6.7 g. (39%) of *trans*-4-*t*-butylcyclohexanecarboxylic acid. This was converted to acid chloride, b.p. 80.5–80.0° (0.9 mm.) with thionyl chloride as described by Lau and Hart. The best conversion to peroxide was obtained by dissolving 12 g. of acid chloride in 20 ml. of ether cooled in an ice bath and adding 10% excess of 90% H₂O₂. The mixture was vigorously stirred and 10% excess NaOH in 4 ml. of water was added dropwise over 20 min. After 6.5 hr. the mixture still smelled of acid chloride, so an additional 0.3 ml. of 90% H₂O₂ and 0.5 g. of NaOH in 2 ml. of water were added and stirring was continued for 90 min. The mixture was next transferred to a precooled separatory funnel with 150 ml. of cold ether and 200 ml. of ice-water; the ether was separated, washed with cold bicarbonate and ice-water, dried over Na₂SO₄ at 0°, and removed *in vacuo* at 0°. The crude peroxide was crystallized from pentane at –25°, filtered, dried, and stored at –25°, purity by titration 98.5%. Best titration results for peroxide (pure or in kinetic runs) were obtained by adding samples to 10 ml. of acetic anhydride and 1 g. of NaI in a flask under CO₂, warming in a water bath at 35–40° for 20 min., adding 20 ml. of water, and titrating with thiosulfate. It was found necessary to add starch indicator 1–2 ml. before the end point, or no blue color appeared.

Pressure techniques in kinetic runs were essentially those employed in previous work.^{5,6,10} Peroxide solutions were degassed and transferred under nitrogen to collapsible Teflon reaction vessels, placed in the thermostated pressure apparatus for varying lengths of time, removed, and titrated for peroxide, the cyclohexanecarbonyl peroxide as above and benzoyl peroxide as previously.¹⁰ Benzoyl peroxide runs were carried to approximately 50% reaction. The cyclohexanecarbonyl peroxide runs were carried to 60–90% reaction and gave good first-order plots over the entire range, although with some scatter as indicated by the experimental errors indicated. Each rate constant in Table II was calculated from 5 to 8 points obtained from aliquots of a single solution.

Products from benzoyl peroxide decompositions (Table I) were determined by analysis of solutions which had been allowed to react to completion. Distillation of the chloroform solvent separated the benzene which was determined quantitatively by gas-liquid chromatography (g.l.c.) using a known amount of *n*-butyl bromide as internal standard. The residue was taken up in ether and shaken with NaHCO₃ solution, and the aqueous layer was continuously extracted with ether for 12 hr. Acidification of the aqueous layer yielded terephthalic acid, m.p. >300° (dimethyl ester m.p. 43°), which results from the facile hydrolysis of *p*-trichloromethylbenzoic acid.¹³ The ether extract was evaporated and the resulting residue was placed on an alumina column and eluted with hexane. Hexachloroethane, m.p. 182°, appeared in the first eluate, followed by phenyl benzoate, which was determined quantitatively by g.l.c. using bibenzyl as an internal standard. Continued elution of the high-pressure reaction product with hexane and ethanol gave a dark brown oil. This was heated with methanol–H₂SO₄ to convert acid and ester groups to methyl esters and investigated by g.l.c. Approximately 70% of the volatile products was found to be methyl benzoate. Dimethyl terephthalate was also identified by infrared spectrum, and the chromatogram indicated small quantities of some eight other products.

trans-4-*t*-Butylcyclohexyl *trans*-4-*t*-Butylcyclohexanecarbonyl Carbonate. Evidence for the formation of this intermediate in the decomposition of *trans*-4-*t*-butylcyclohexanecarbonyl peroxide was based upon the following observations.

1. A solution (approximately 6%) of the peroxide was heated in *n*-butyl chloride for 16 hr. (essentially complete decomposition). Examination of the infrared spectrum showed strong peaks at 1801 and 1754 cm.⁻¹ characteristic of an anhydride linkage, and not observed in authentic samples of the corresponding acid and ester.

2. Hydrolysis of the residue from an aliquot of the above reaction mixture with 1% carbonate-free NaOH led to the liberation of carbon dioxide (88% of theory based on barium carbonate precipitation).

3. Acid or base hydrolysis occurred readily to yield *trans*-4-*t*-butylcyclohexanecarboxylic acid (isolated) and *trans*-4-*t*-butylcyclohexanol, detected by infrared spectra. Since the intermediate carbonate has been isolated and identified specifically by Greene, these reactions are not described in greater detail.