(2.0 ml, 85 mmol). The mixture was stirred rapidly and a stream of dry nitrogen was allowed to pass over the top of the open tube until most of the ether had evaporated. The tube was then connected to a vacuum line and the pressure was slowly reduced to 0.20 mm for 4 hr. There remained at the end of this treatment 2.0 g (99% yield) of a clear viscous oil, which was diphenyl-*p*-methoxyphenylgermyl hydroperoxide.

Preparation of a Bisgermyl Peroxide. Method IIb.—Diphenyl-*p*-trifluoromethylphenylchlorogermane (2.0 g, 4.8 mmol) was dissolved in a solution of anhydrous ether (200 ml) and hydrogen peroxide (0.289 g, 8.5 mmol). At 25° anhydrous ammonia gas was bubbled under the surface for 2 min, and the mixture stirred for another 5 min. The mixture was then filtered through a medium fritted-glass filter and the solvent removed from the filtrate. There remained a clear viscous oil (6.65 g) which was dissolved in 10 ml of pentane and cooled to $-20°$. The white precipitate which formed (3.70 g, 57% yield), after collection by filtration, had an active oxygen content 2.07%. After two recrystallizations from pentane a material having mp 134–137° was obtained.

The Thermal Decomposition of Organogermanium Peroxides and Hydroperoxides[1]

RALPH L. DANNLEY AND GEORGE C. FARRANT

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

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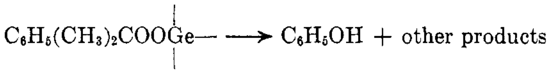
The thermal decomposition reactions of a number of organogermanium peroxides and hydroperoxides were studied to gain information about the mechanism of the cleavage of the peroxidic link when bound to germanium. Bis(triphenylgermyl) peroxide thermally decomposed with first-order kinetics ($E_a = 33.7$ kcal/mol) in hexadecane in the absence of oxygen at 190–210° yielded phenol, diphenylgermanium oxide, triphenylgermanol, but no oxygen. The migratory aptitudes of the phenyl and the *p*-trifluoromethylphenyl groups in the decomposition of bis(diphenyl-*p*-trifluoromethylphenylgermyl) peroxide were about equal, consistent with a free-radical mechanism. The thermal decomposition of triphenylgermyl hydroperoxide (1.0 mmol) in *o*-dichlorobenzene produced oxygen (0.17 mmol), water (0.35 mmol), and triphenylgermanol (0.93 mmol) as the major products, and phenol (0.06 mmol) and diphenylgermanium oxide (0.07 mmol) as the minor products. The effect of solvents, radical initiators, radical inhibitors, and ultraviolet light were consistent with a radical mechanism producing these products. The products of the thermal decomposition of triphenylgermyl hydroperoxides in which one of the phenyl groups was substituted in the *para* position gave a migratory aptitude series (p-$CH_3OC_6H_4$, 1.98; p-CF_3-C_6H_4, 1.36; C_6H_5, 1.00) consistent with a radical mechanism for the formation of phenols in this reaction. Triphenylgermyl hydroperoxide decomposed in *o*-dichlorobenzene at 150–170° in an initially oxygen-free system with zero-order kinetics at 0.01 M concentration ($E_a = 35$ kcal/mol) but followed no simple order at higher concentrations. The thermal decomposition of tricyclohexylgermyl hydroperoxide (1.0 mmol) produced cyclohexene (0.56 mmol), cyclohexanol (0.06 mmol), tricyclohexylgermanol (0.29 mmol), and dicyclohexylgermanium oxide (0.18 mmol).

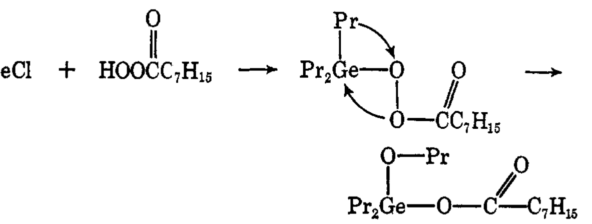
Although there have been several reports[2–4] of the synthesis of organogermanium peroxides, and a disclosure of the synthesis of organogermanium hydroperoxides,[5,6] relatively little is known about the stabilities of these substances or their decomposition products which would permit comparison with the analogous compounds of the other group IVb elements.

Davies[4] suggested a nucleophilic migration of the phenyl group to oxygen to explain his finding that 1-methyl-1-phenylethyl hydroperoxide and germanium tetrachloride gave rise in the course of a few days to phenol and other nonperoxidic products. However, the initial germanium peroxide was not isolated. Davies



$$C_6H_5(CH_3)_2COO\overset{|}{\underset{|}{Ge}}— \longrightarrow C_6H_5OH + \text{other products}$$

also suggested a 1,2 rearrangement to explain his observation that the treatment of alkylgermanium chlorides with peroxy acids gave nonperoxidic products.[4]



Both Davies[4] and Rieche[3] and their coworkers postulated that germanium peroxides undergo some homolytic scission of the peroxide bond because the compounds catalyzed the polymerization of vinyl monomers. However, the extent of the radical *vs.* ionic processes in the decomposition of these compounds has not been established.

It was the purpose of the present investigation to determine whether the symmetrical peroxides and the hydroperoxides of germanium undergo homolysis or heterolysis of the peroxidic link and to determine the kinetics and products of the thermal decomposition.

Results and Discussion

Thermal Decomposition of Bis(triarylgermyl) Peroxides.—The thermal decomposition of bis(triphenylgermyl) peroxide in hexadecane or *o*-dichlorobenzene occurs *via* a first-order process with an activation energy of 33.7 ± 1.5 kcal/mol[7] (Table I). The products of

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(1) (a) Supported by the U.S. Army Research Office (Durham) through Grant No. DA-ARO(D)-31-124-G720. (b) Taken in part from the dissertation of G. C. Farrant submitted in Jan. 1968 to the Graduate School of Case Western Reserve University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (c) Presented in part at the first Central Regional Meeting of the American Chemical Society, Akron, Ohio, May 10, 1968.

(2) A. Rieche and J. Dahlmann, *Angew. Chem.*, **71**, 169 (1959).

(3) A. Rieche and J. Dahlmann, *Ann.*, **675**, 19 (1964).

(4) A. G. Davies and C. D. Hall, *J. Chem. Soc.*, 3835 (1959).

(5) R. L. Dannley and G. Farrant, *J. Amer. Chem. Soc.*, **88**, 637 (1966).

(6) R. L. Dannley and G. Farrant, *J. Org. Chem.*, **34**, 2428 (1969).

(7) A referee has pointed out that the calculated value of log A is *ca.* 12, which is considerably lower than the corresponding values of 15–16 [(a) R. Hiatt and K. C. Irwin, *J. Org. Chem.*, **33**, 1436 (1968)] for many carbon peroxide decomposition. However, peroxides of elements other than carbon do yield similar low values for their first-order thermal decompositions. Thus log A is 10.1–10.8 for silicon hydroperoxides [(b) R. L. Dannley and G. Jalics, *ibid.*, **30**, 3848 (1965)], 11.4 for bisdiphenylphosphinic peroxide [(c) R. L. Dannley and K. R. Kabre, *J. Amer. Chem. Soc.*, **87**, 4805 (1965)], and 12.2 for trimethyltin hydroperoxide in dilute solution [(d) R. L. Dannley and W. A. Aue, *ibid.*, **30**, 3845 (1965)]. The mechanisms of all these reactions are not clearly established but they are first order with respect to peroxide and there is some evidence for free-radical intermediates.

TABLE I

KINETIC DATA FOR THE THERMAL DECOMPOSITION OF BIS(TRIPHENYLGERMYL) PEROXIDE (0.01 *M*)

Solvent	Temp., °C	$k \times 10^5$, sec^{-1}	Half-life, min
Hexadecane[a]	210	34.5	34
	210	34.0	35
	200	15.9	73
	190	7.40	156
	190	7.20	159
	178.5	5.15	365
	150	0.252[b]	4570[b]
o-Dichlorobenzene	150	0.242	4750
	150	0.231	5020

[a] E_a = 33.7 × 1.5 kcal/mol. [b] Extrapolated from the plot of log *k vs.* 1/*T*.

decomposition of the peroxide in *o*-dichlorobenzene solution were determined. No oxygen was evolved when the reaction was run in a closed system with an initially oxygen-free system. The initial germanium-containing products were not directly identified; instead the mixture of decomposition products was treated with anhydrous hydrogen chloride to convert them into the volatile chlorides which were analyzed by glpc.

$$\underset{1.0}{(C_6H_5)_3GeOOGe(C_6H_5)_3} \xrightarrow{\Delta}$$

$$(\quad) \xrightarrow{HCl} \underset{0.27}{C_6H_5OH} + \underset{0.43}{(C_6H_5)_2GeCl_2} + \underset{1.44}{(C_6H_5)_3GeCl}$$

The acid treatment was particularly necessary for the analysis of the diphenylgermanium moieties, since these germanium oxides exist in several modifications which are difficult to separate. It is apparent from the product analysis that the reaction proceeds by two pathways, one yielding phenol and diphenylgermanium moieties, the second giving triphenylgermanol or one of its derivatives. It has been shown that the analytical procedure does not cleave the carbon–germanium bond in this system. Therefore the diphenylgermanium moieties are accurately measured and the corresponding phenol yield is low, probably owing to partial oxidation by unreacted peroxide during the course of the reaction.

The thermal decomposition of bis(diphenyl-*p*-trifluoromethylphenylgermyl) peroxide in *o*-dichlorobenzene showed that the migratory aptitudes of the trifluoromethylphenyl and phenyl groups are roughly equal ($CF_3C_6H_4/C_6H_5$ = 1.25 from the phenol analysis and 0.75 from the germanium chloride analysis).

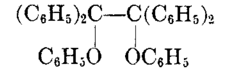
$$\underset{1.0}{[CF_3C_6H_4(C_6H_5)_2GeO]_2} \xrightarrow{160°} \xrightarrow{HCl} \begin{array}{l} \underset{0.089}{CF_3C_6H_4OH} + \underset{0.13}{(C_6H_5)_2GeCl_2} \\ \underset{0.14}{C_6H_5OH} + \underset{0.34}{CF_3C_6H_4C_6H_5GeCl_2} \\ \underset{1.44}{CF_3C_6H_4(C_6H_5)_2GeCl} \end{array}$$

Migratory aptitudes for free-radical migrations have not been well established but a nitrophenyl/phenyl ratio of 4.0–4.4:1 was obtained for both the homolytic decomposition of diphenyl-*p*-nitrophenylmethyl hydroperoxide[8] and the oxidation of diphenyl-*p*-nitrophenylcarbinol with lead tetraacetate.[9,10] The nitro group is expected to give greater resonance stabilization than a trifluoromethyl group. Therefore the migratory aptitude here observed is consistent with a homolytic process but not with an ionic rearrangement to a positively charged site, for which it would be expected that the phenyl group would migrate in preference to the trifluoromethylphenyl group by several orders of magnitude.

A possible mechanism for the reaction involves the homolysis of the peroxide bond and rearrangement of the resultant radical. The rearrangement must be fairly slow since the major product of the reaction is a

$$Ar_3GeOOGeAr_3 \longrightarrow 2Ar_3GeO\cdot$$
$$Ar_3GeO \longrightarrow Ar_2ArOGe\cdot$$
$$Ar_2ArOGe\cdot + Ar_3GeO \longrightarrow Ar_2ArOGeOGeAr_3$$

triphenylgermyl moiety. The lack of any coupled product containing a germanium to germanium bond is in marked contrast to the decomposition of trityl peroxide in which the main product isolated was 1,1,2,2-tetraphenyl-1,2-diphenoxyethane.[11] This result indi-



$$\underset{C_6H_5O}{(C_6H_5)_2C}—\underset{OC_6H_5}{C(C_6H_5)_2}$$

cates that the rearranged triphenylgermyloxy radicals do not accumulate in concentrations high enough to produce coupled products, and that these radicals are not stabilized by delocalization of the unpaired electron to the same degree that the corresponding carbon radicals are.

Thermal Decomposition of Triarylgermyl Hydroperoxides.—The products of the thermal decomposition of triphenylgermyl hydroperoxide under a variety of conditions are shown in Table II. Although these quantitative results were obtained by glpc after hydrogen chloride treatment of the reaction mixture, in preliminary experiments both phenol and triphenylgermanium oxide were isolated in pure form. The oxide probably arose from condensation of two molecules of the germanol, since triphenylgermanol undergoes this reaction under the conditions used for the decomposition of the hydroperoxide.

$$2(C_6H_5)_3GeOH \longrightarrow (C_6H_5)_3GeOGe(C_6H_5)_3 + H_2O$$

Although a 95% recovery of the germanium was usually obtained, only 34% of the original oxygen content of the peroxide was accounted for in the identified products. The reaction mixtures were dark, probably owing to unidentified oxidation products which are responsible for the poor oxygen balance.

The products identified indicate that two competing reactions occurred. The hydroperoxide primarily underwent reduction but some (5–10%) rearrangement also was observed. The principle reaction, forming oxygen and a triphenylgermyl moiety, must be free radical in nature for the product ratios (Table II) were not appreciably affected by a major change in the polarity of the solvent, the oxygen yield is increased by addition of a radical initiator and decreased by a radical inhibitor, and the decomposition is accelerated by ultraviolet light. In addition, the small by-product

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[8] P. D. Bartlett and J. Cotman, *J. Amer. Chem. Soc.*, **72**, 3095 (1950).

[9] W. H. Starnes Jr., *ibid.*, **89**, 3368 (1967).

[10] W. H. Starnes Jr., *ibid.*, **90**, 5807 (1968).

[11] H. Wieland, *Ber.*, **44**, 2553 (1911).

TABLE II

PRODUCTS OF THE DECOMPOSITION OF TRIPHENYLGERYML HYDROPEROXIDE (1.0 mol)

Solvent	Added conditions	$(C_6H_5)_3$-GeOOH concn, *M*	Temp, °C	Amt, mol			
				O_2	$(C_6H_5)_3GeCl$	$(C_6H_5)_2GeCl_2$	C_6H_5OH
o-$C_6H_4Cl_2$[a,b]	None	0.05	160	0.13 ± 0.05	0.93 ± 0.02	0.06 ± 0.02	0.07 ± 0.02
$C_6H_5NO_2$[a,c]	None	0.05	160	0.17 ± 0.03	0.90 ± 0.02	0.05 ± 0.01	0.01 ± 0.01
o-$C_6H_4Cl_2$[d]	ABIN[e]	0.05	120	0.33	0.95	0.04	0.06
$CH_3CO_2C_2H_5$[d]	Uv light	0.005	77	*f*	0.93	0.05	0.06
o-$C_6H_4Cl_2$[d]	DPPH[g]	0.95	150	0.08	0.99	<0.005	<0.005

[a] Three separate decomposition solutions were analyzed, and the results averaged. [b] Water (0.34) yield was determined in only one run. [c] Nitrophenols were also obtained: *o*, 0.0022; *m*, 0.0027; *p*, 0.0074. [d] Only one decomposition solution analyzed. [e] Azobisisobutyronitrile concentration 0.005 *M*. [f] Not determined. [g] 2,2-Diphenyl-1-picrylhydrazyl concentration 0.005 *M*.

yields of nitrophenols obtained when nitrobenzene is used as a solvent correspond in isomer distribution (*ortho* 18%, *meta* 22%, *para* 60%) to the values reported for the hydroxylation of this substrate with Fenton's reagent[12] (*ortho* 25–30%, *meta* 20–25%, *para* 50–55%).

The data in Table II also support a free-radical mechanism for the rearrangement process. Thus the amount of rearrangement is unaffected by the polarity of the solvent, ultraviolet light, or the presence of a radical initiator. Confirmation of the homolytic classification was obtained from the relative migratory aptitudes observed in the thermal decomposition of substituted triphenylgermyl hydroperoxides (Table III).

TABLE III

PRODUCTS FOR THE THERMAL DECOMPOSITION OF *para*-SUBSTITUTED TRIPHENYLGERMYL HYDROPEROXIDES (1 mol) [p-$XC_6H_4(C_6H_5)_2GeOOH$][c]

Product	Amt, mol	
	X = CF_3[a]	X = CH_3O[b]
O_2	0.18 ± 0.060	0.12 ± 0.03
C_6H_5OH	0.038 ± 0.010	0.034 ± 0.005
XC_6H_4OH	0.025 ± 0.010	0.035 ± p.005
$(C_6H_5)_2GeCl_2$	0.033 ± 0.010	0.33 ± 0.12[c]
$XC_6H_4C_6H_5GeCl_2$	0.046 ± 0.010	0.051 ± 0.002[c]
$XC_6H_4(C_6H_5)_2GeCl$	0.88 ± 0.030	0.61 ± 0.010[c]

[a] Results are the average analyses of three separate runs. [b] Results are the average analyses of two separate runs. [c] Hydrogen chloride treatment cleaved some of the anisyl groups from the germanium products. Therefore the diphenyldichlorogermane analysis is too high, and the methoxyphenylgermanium chlorides too low. [c] Registry no.: X = CF_3, 19987-82-7; X = CH_3O, 19987-83-8.

From the yields of phenols, the migratory aptitudes are, for *p*-anisyl, 1.9 ± 0.1; *p*-trifluoromethylphenyl, 1.3 ± 0.4; and phenyl, 1.0. With diphenyl-*p*-trifluoromethylphenylgermyl hydroperoxide, the diarylgermyl dichloride analysis could be used to confirm the migratory aptitude (1.4 ± 0.2), but a similar check could not be obtained with diphenyl-*p*-methoxyphenylgermyl hydroperoxide, since some of the anisyl groups are cleaved from the germanium-containing products by the hydrogen chloride treatment.[6]

The low migratory aptitudes obtained for substituted phenyl groups with widely different electronic requirements are characteristic of a homolytic rearrangement process. The anisyl–phenyl ratio slightly greater than 1 is comparable with the values of 1.1–3.5 for anisyl migrations in the free-radical oxidation of diphenyl-*p*-methoxyphenylcarbinol with lead tetraacetate[9,10] and the values of 0.35–1.2 reported for anisyl migrations in carbon radicals.[13–15] In contrast, in ionic reactions such as the acid-catalyzed decomposition of diphenyl-*p*-methoxyphenylmethyl hydroperoxide[16] or the rearrangement of the corresponding perbenzoate,[17] exclusive anisyl migration occurs.

The observations above are consistent with the mechanism given in eq 1–5. The reaction is initiated

$$Ar_3GeOOH \longrightarrow Ar_3GeO\cdot + \cdot OH \qquad (1)$$

$$Ar_3GeOOH + R\cdot \longrightarrow RH + Ar_3GeOO\cdot \qquad (2)$$

$$2Ar_3GeOO\cdot \longrightarrow 2Ar_3GeO\cdot + O_2 \qquad (3)$$

$$Ar_3GeO\cdot \longrightarrow Ar_2\dot{G}eOAr \qquad (4)$$

$$Ar_2\dot{G}eOAr + Ar_3GeO\cdot \longrightarrow Ar_2ArOGeOGeAr_3 \qquad (5)$$

(eq 1) thermally or photolytically by dissociation into the triarylgermyloxy and hydroxy radicals. Oxygen is produced through an induced decomposition (eq 2) by any of the radicals generated to give the triarylgermylperoxy radical which, from its analogy to alkylperoxy radicals,[18–22] should yield oxygen and triarylgermyloxy radicals (eq 3) or bis(triarylgermyl)peroxide. The bisperoxide cannot be an important intermediate in any proposed mechanism since triphenylgermyl peroxide decomposes some 14 times slower than triphenylgermyl hydroperoxide in *o*-dichlorobenzene. However, the peroxide formation in low yields cannot be discounted at this time.

The rearrangement (eq 4) must be slow relative to the other reactions of the triarylgermyloxy radicals for only 5–10% of this reaction occurs. It cannot be a cage process because it is eliminated by the addition of small quantities (10%) of 2,2-diphenyl-1-picrylhydrazyl. Although the original product of rearrangement was not isolated, it may have the structure depicted in eq 5 for such a compound is stable in the silicon series.[23]

Kinetics of the Thermal Decomposition of Triphenylgermyl Hydroperoxide.—Reproducible kinetic data for the thermal decomposition of triphenylgermyl hydroperoxide were difficult to obtain. However, by using carefully purified material (mp 137.5–139°) the reproducible values given in Table IV were obtained.

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(12) H. H. Loebel, G. Stein, and J. Weiss, *J. Chem. Soc.*, 2079 (1949).

(13) C. Rüchart, *Ber.*, **94**, 2609 (1961).

(14) C. Rüchart and H. Trautwein, *ibid.*, **96**, 160 (1963).

(15) C. Rüchart and J. C. Hect, *ibid.*, **98**, 2471 (1965).

(16) W. Dilthey, F. Quint, and H. Dierichs, *J. Prakt. Chem.*, **151**, 25 (1938).

(17) I. J. Levine, Ph.D. Dissertation, University of Kansas, 1960, *Dissertation Abstr.*, **21**, 2478 (1961).

(18) G. A. Russell, *J. Amer. Chem. Soc.*, **79**, 3871 (1957).

(19) P. D. Bartlett and T. G. Traylor, *ibid.*, **85**, 240 (1963).

(20) H. S. Blanchard, *ibid.*, **81**, 4548 (1959).

(21) J. R. Thomas, *ibid.*, **87**, 3935 (1965).

(22) P. D. Bartlett and G. Guaraloi, *ibid.*, **89**, 4799 (1967).

(23) G. Jalics, Ph.D. Dissertation, Western Reserve University, 1964.

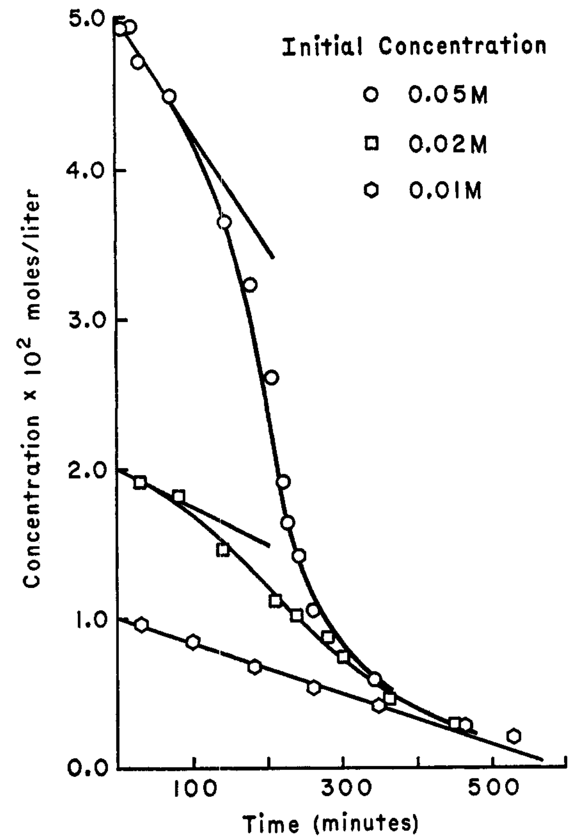


Figure 1.—Plot of concentration *vs.* time for the thermal decomposition of triphenylgermyl hydroperoxide in *o*-dichlorobenzene at 160.0°.

TABLE IV
KINETIC DATA FOR THE DECOMPOSITION OF TRIPHENYLGERMYL HYDROPEROXIDE IN *o*-DICHLOROBENZENE

Temp, °C	Concn, M	$K_0 \times 10^7$, mol/sec	Half-life, min	Remarks
170^a	0.01	7.0	111	
170^a	0.01	6.9	120	
160^a	0.01	2.88	290	
160^a	0.01	2.83	295	
150^a	0.01	1.11	750	
150^a	0.01	1.07	770	
150	0.05	5.0	317	Initial rate
150	0.01	1.2	650	Run in Teflon bottle
150	0.01	1.29	600	Glass wool added
160	0.02	5.5	240	Initial rate
160	0.05	13.9	210	Initial rate
160	0.01	1.67	490	0.1 mmol of $(C_6H_5)_3GeOH$ added
160	0.01	2.80	297	Reaction carried out under air atmosphere

[a] These values were used to calculate the E_a (3.50 ± 0.3 kcal/mol).

The hydroperoxide decomposed in *o*-dichlorobenzene in a very complex manner (not a simple first-order process as originally reported[5]) dependent upon the initial hydroperoxide concentration (Figure 1). At concentrations of 0.01 M or less, a zero-order plot was obtained with an activation energy of 35.5 ± 1.0 kcal/mol (Figure 2). At higher concentrations the order changed over the course of the reaction. However the initial portion (5–10%) of the reaction followed first-order kinetics, since the plot of the log of the initial rate *vs.* log of the initial concentration gives a straight line with slope +1.06 (Figure 3). The initial first-order rate and the succeeding complex order are consistent with the initial homolysis of the peroxide link followed by induced decomposition, as proposed.

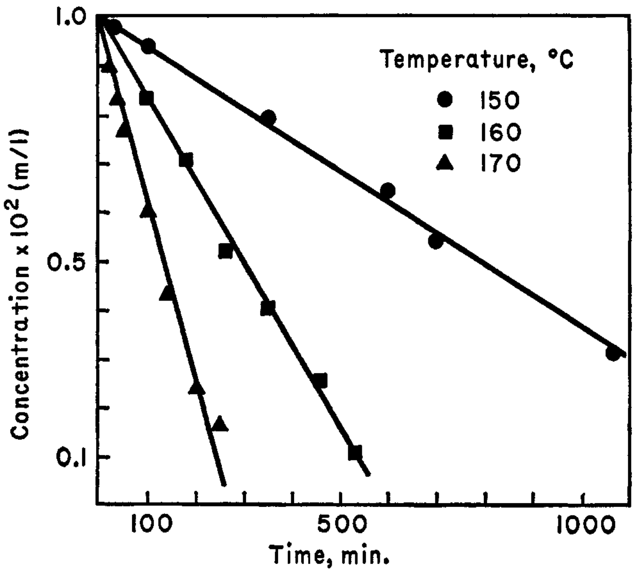


Figure 2.—Plot of concentration *vs.* time for the thermal decomposition of triphenylgermyl hydroperoxide in *o*-dichlorobenzene: initial concentration, 0.01 M.

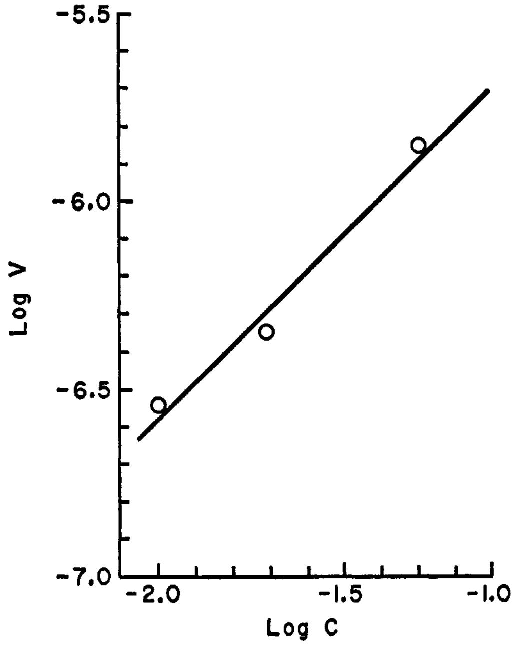
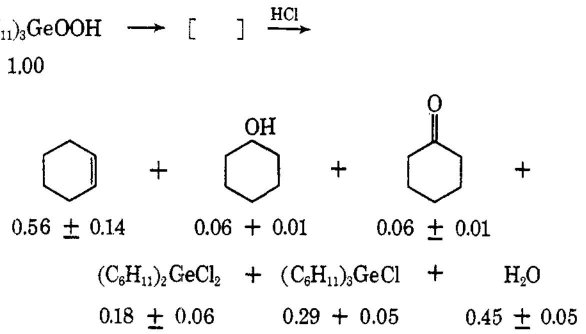


Figure 3.—Plot of log initial rate (V) of hydroperoxide disappearance at 160° *vs.* log initial concentration (C) for the thermal decomposition of triphenylgermyl hydroperoxide in *o*-dichlorobenzene.

The cause of the pseudo-zero-order reaction, however, is not clear. While some zero-order reactions are due to surface reactions it was shown that altering the surface of the vessel by adding glass wool or changing to a Teflon vessel neither appreciably affected the rate nor changed the order. The rate of the reaction was also unaffected by either air or a nitrogen atmosphere (Table IV), but it was found that the addition of 0.1 M triphenylgermanol to the system decreased the rate appreciably (49%). The solvents and the peroxide are of the highest purity obtainable but the presence of trace amounts of impurities which might cause the zero-order rate cannot be discounted.

The germanium compound decomposed at a much slower rate (half-life at 150°, 325 *vs.* 25 min) and with a higher activation energy (35.5 *vs.* 27.0 kcal/mol) than the corresponding silicon compound.[7b] Although this result is surprising, it is in accord with Rieche's[3] qualitative observation that bis(triphenylgermyl) peroxide is more stable than the corresponding bis(triphenylsilicon) peroxide.

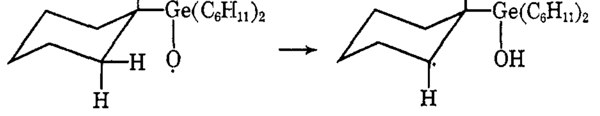
Thermal Decomposition of Tricyclohexylgermyl Hydroperoxide.—The products of the thermal decomposition of tricyclohexylgermyl hydroperoxide in *o*-dichlorobenzene differed widely in nature from the products obtained from the triaryl anologs. As no oxygen was evolved, an induced decomposition yielding a peroxy radical must be excluded. The low recovery of germanium moieties (47%) indicates that some products containing germanium to germanium bonds may have been formed, for such compounds are not converted into volatile halides by the hydrogen chloride treatment. The yield of cyclohexene (56%) is similar to the quantity of germanium moiety unaccounted for (53%), although this may be fortuitous.



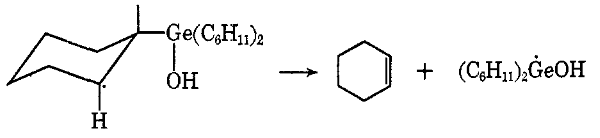
The cyclohexanol, by analogy to the triphenylgermyl hydroperoxide decomposition, should arise from a rearrangement. However, the identical yields of cyclohexanol (6%) and cyclohexanone (6%) suggest a disproportionation by cyclohexyloxy radicals. Also, the combined yield of these two compounds (12%) is too high compared with the maximum phenyl rearrangement yield (7%) for a radical rearrangement. Therefore, these data are insufficient to select between alternate mechanisms.

The homolytic mechanism given by eq 6–9 is proposed to account for the formation of cyclohexene and the low recovery of organochlorogermanes. In the carbon system (homolytic addition of an alcohol to an olefin) the equilibrium of eq 8 lies to the left but a germanium–carbon bond is so much weaker (32 kcal Ge–C_6H_5)[24] than a carbon–carbon bond (90 kcal for C–C_6H_5)[25] that eq 8 as written should be energetically favored.

$$(C_6H_{11})_3GeOOH \longrightarrow (C_6H_{11})_3GeO\cdot + \cdot OH \qquad (6)$$



(7)



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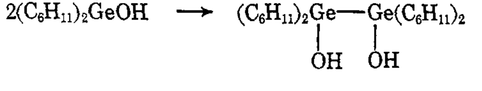
$$2(C_6H_{11})_2\dot{G}eOH \longrightarrow \underset{OH}{(C_6H_{11})_2Ge}—\underset{OH}{Ge(C_6H_{11})_2} \qquad (9)$$

Experimental Section

Triphenylchlorogermane, triphenylbromogermane, diphenyldichlorogermane, tricyclohexylchlorogermane, and germanium tetrachloride were purchased either from Metallomer Laboratories or Alfa Inorganics, and were used without further purification. The germanium peroxides and hydroperoxides as well as the reference organogermanium chlorides, hydroxides, and oxides were prepared according to methods outlined in a previous paper.[6]

Dicyclohexyldichlorogermane ($n^{25}D$ 1.5257) was prepared by adding cyclohexylmagnesium chloride (60 mmol) in ether (250 ml) to an ice-cold solution of germanium tetrachloride in toluene (650 ml) over a period of 2 hr. The mixture was then warmed to room temperature, filtered, and the solvent removed from the filtrate. The residue was distilled at reduced pressure, and the fraction (2.0 g, 21% yield) boiling between 117 and 120° (0.15 mm) was shown to be better than 99% pure by glpc (column D). *Anal.* Calcd for $C_{12}H_{22}GeCl_2$: C, 46.51; H, 7.16; Ge, 23.47. Found: C, 46.61; H, 7.27; Ge, 23.70.

Analytical Procedures.—All glpc analyses were carried out on an Aerograph (Varian Associates) gas chromatograph, Model 1520B, using a thermal conductivity detector. The temperature of the injection port and detector were maintained at 250–270°. The chromatographic columns and conditions used are given in Table V.

The composition of a reaction solution was quantitatively determined using the internal standard technique. Calibration fractors were obtained from standard solutions of the reference chlorides and an appropriate internal standard. Three to five determinations of both the reaction mixture and the standard solution were made for each analysis and the results averaged. Usually the precision was within ±3–5% between any two runs.

Product Analysis of the Thermal Decomposition of the Hydroperoxides and Peroxides.—The hydroperoxide or peroxide (1.00 mmol) and 20.0 ml of the purified solvent were placed in a 25-ml volumetric flask connected to a manifold containing three valves. One valve was attached by means of tygon tubing to a gas buret filled with mercury, another was connected to a tank of dry nitrogen (G.E. Lamp grade), while the third valve could be vented to the atmosphere. The system was purged with nitrogen for 1 hr and the system closed. It was determined from other experiments that the atmosphere contained better than 99.9% nitrogen. The solution was then heated to 150–160° from 12 to 72 hr, depending upon the compound, then cooled to room temperature. After the system came to equilibrium, the pressure, temperature, and volume of gas increase were measured.

To prove that the evolved gas was oxygen, the atmosphere was assayed by withdrawing 0.50–2.0-ml samples *via* a gas-tight syringe and analyzing them on the gas chromatograph (column B). The concentration of oxygen was determined by multiplying the ratio of the area of the oxygen to nitrogen peaks times the volume above the solution. In all instances in which an air-tight syringe was used, good agreement between the concentration of oxygen calculated from the gas increase and that analyzed by glpc was obtained, indicating that the only gaseous product of the reaction was oxygen.

The solution was then assayed for active oxygen, and in all instances better than 99% of the hydroperoxide or peroxide had decomposed. A portion of the solution (5.0 ml) was withdrawn and *m*-chlorophenol added as an internal standard. The solution was treated with anhydrous hydrogen chloride for 5 min and then analyzed for phenols (columns A or E). In some instances the trimethylsilyl derivatives of the phenols were prepared by treating an aliquot (5.0 ml) of the decomposition solution with 5.0 ml of hexamethyldisilazane. A pinch of sand was added together with the internal standard (*m*-dinitrobenzene) and the mixture refluxed for 3 hr. It was shown independently that the procedure quantitatively formed the trimethylsilyl ethers from the phenols present in the reaction mixture. The trimethylsilyl ethers were analyzed

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[24] K. H. Birr, *Z. Anorg. Allg. Chem.*, **315**, 175 (1962).

[25] J. S. Roberts and H. A. Skinner, *Trans. Faraday Soc.*, **45**, 339 (1949).

TABLE V

CHROMATOGRAPHIC COLUMNS AND CONDITIONS

Column	Size ft × in.	Material	Packing	Conditions	
				Temp, °C	He flow rate, ml/min
A	8 × 0.25	Copper	10% Carbowax 20M on Chromosorb W	180–210	30–60
B	8 × 0.25	Copper	Molecular Sieve 5A	50	60
C	8 × 0.25	Copper	5% Silicone oil D.C. 710 on Chromosorb G; A/W, DMCS treated, 80–100 mesh	220–230	150–200
D	5 × 0.25	Stainless steel	5% Silicone oil D.C. 710 on Chromosorb; A/W, DMCS treated, 80–100 mesh	220–255	150–300
E	5 × 0.25	Stainless steel	5% FFAP on Chromosorb G; A/W, DMCS treated, 80–100 mesh	195–210	30
F	25 × 0.25	Copper	5% silicone gum rubber on Chromosorb G; A/W, DMCS treated, 80–100 mesh	125	60
G	6 × 0.25	Copper	10% butadiol adipate on Anakrom 70–80 mesh	100	120
H	5 × 0.125	Stainless steel	Poropak Q, 150–170 mesh	100	30
I	10 × 0.25	Stainless steel	5% STAP on Chromsorb W; A/W, DMCS treated, 80–100 mesh	125	100

on columns F and I. Another 5.0-ml aliquot of the decomposition solution was withdrawn, triphenylmethane added as an internal standard, and the mixture treated with hydrogen chloride for 10 min. The resulting solution was then analyzed for organogermanium chlorides (column C or D). Water was determined by adding ethanol as an internal standard to another 5.0-ml portion of the decomposition mixture and analyzing on column H. When tricyclohexylgermyl hydroperoxide was used, cyclohexene, cyclohexanol, and cyclohexanone were analyzed on columns F and G using *p*-xylene as the internal standard.

Isolation of Organogermanium Compounds.—The germanium-containing compounds resulting from the thermal decomposition of the hydroperoxides were isolated by removing the solvent under vacuum and then purified by chromatography through neutral alumina. The eluents were evaporated and the solid residues, recrystallized from appropriate solvents, agreed in physical properties (melting point, ir and nmr spectra) with authentic materials described in a preceding paper.[6] The yields are given in Table VI.

TABLE VI

YIELDS OF GERMANIUM COMPOUNDS ISOLATED FROM THE THERMAL DECOMPOSITION OF ORGANOGERMYL HYDROPEROXIDES

Hydroperoxide	Organogermanium product	Yield[a]
$(C_6H_5)_3GeOOH$	$[(C_6H_5)_3Ge]_2O$	0.30
$CF_3C_6H_4(C_6H_5)_2GeOOH$	$[CF_3C_6H_4(C_6H_5)_2Ge]_2O$	0.25
$CH_3OC_6H_4(C_6H_5)_2GeOOH$	$[CH_3OC_6H_4(C_6H_5)_2Ge]_2O$	0.29
	$CH_3OC_6H_4(C_6H_5)_2GeOH$	0.18
$(C_6H_{11})_3GeOOH$	$(C_6H_{11})_3GeOH$	0.45

[a] The yields (mole/mole of hydroperoxide) described are not optimum but rather the observed yield after several recrystallizations.

General Kinetics Procedure.—A standard solution of the hydroperoxide or peroxide was prepared. Approximately 50 ml of the solution was placed in a Raysorb-coated (Kimax) 100-ml volumetric flask which had two side arms attached to it. The protective coating prevented any extraneous ultraviolet light below 450 mμ from entering the flask. Through one of the side arms was a glass tube which extended into the flask below the surface of the solution. The other side arm was connected to a trap filled with the solvent to prevent any diffusion of air back into the system. The top of the vessel was sealed with a rubber septum and the system was purged with a stream of nitrogen (approximately 200 cc/min). After 30 min, the nitrogen flow was reduced to 10 cc/min and the flask was placed in a thermostated oil bath (±0.1° at 150° and ±0.2° at 210°). A period of 4 min was allowed for the system to come to equilibrium, after which samples of the solution were periodically withdrawn *via* a needle and syringe and discharged into a hot solution of sodium iodide in 20:80 acetic acid–isopropyl alcohol. This mixture was boiled for 5 min and the liberated iodine back-titrated with a standard solution of sodium thiosulfate. When hexadecane was used as the solvent, the syringe had to be filled with nitrogen to prevent oxidation of the solvents by air at these high temperatures. In all the runs, several determinations of a blank were made; this average value was subtracted from the original titer. In no case did the blank ever exceed 0.3 ml of 0.01 *M* thiosulfate. The zero point titers usually consumed 9–10 ml.

The ultraviolet light catalyzed decomposition of triphenylgermyl hydroperoxide in refluxing ethyl acetate was carried out in a quartz flask by a Rayonet reactor using light at 2537 Å. The temperature was maintained by refluxing (77.1°) the mixture.

Registry No.—Dicyclohexyldichlorogermane, 19978-36-0; bis(triphenylgermyl) peroxide, 5695-57-8: triphenylgermyl hydroperoxide, 5274-38-4.