water molecule and the consequent greater binding of protons (or alternatively lower affinity for the hydroxyl ion). In addition to this, there is probably a stabilization of the monohydroxy form by hydrogen bonding which can occur only when two water molecules (or hydroxylkyl groups) are present.

It is further noted that an important tendency in the Cu(II) chelates which prevents hydroxy chelate formation is the formation of a relatively stable 2:1 chelate compound. Thus, while the 1:1 Cu(II)-ethylenediamine chelate is quite stable and exhibits normal hydrolytic tendencies, the formation of the corresponding monohydroxy chelate above *p*H 7.0 is prevented by the disproportionation reaction

$$2CuA(OH) \longrightarrow CuA_2 + Cu(OH)_2$$

Thus the formation of the 2:1 Cu(II) chelate compound is accompanied by precipitation of half of the copper as the hydroxide. This reaction is favored by the formation of a highly stable 2:1 chelate compound, with the result that the disproportionation reaction of the type given above results in a favorable free energy decrease. Such reactions are prevented in the hydroxyethylethylenediamines by higher stability of the 1:1 chelate as the result of participation of the weak ethanol donors in chelate formation. Disproportionation reactions are also prevented in the N-alkylated ethylenediamines through lowering of the stability of the 2:1 chelate compound as the result of steric repulsions between the alkyl groups.

On the basis of the behavior of the Cu(II) chelates listed in Table I, therefore, the factors favoring the formation of soluble hydroxy chelates are: 1, the formation of a sufficiently stable bidentate chelate to prevent precipitation of the Cu(II) as hydroxide; 2, high stability of the 1:1 chelate over the corresponding compound in which the ratio of ligand to metal ion is 2:1; 3, the absence of more than two strongly coördinating donor groups on the ligand.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTH CAROLINA]

Diacyl Peroxide Reactions. II. The Reaction of δ-Phenylvaleryl Peroxide with Carbon Tetrachloride

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A quantitative study has been made of the products of the thermal decomposition of δ-phenylvaleryl peroxide in carbon tetrachloride over a more than six hundred-fold variation in peroxide concentration and at two temperatures. The product yields are almost independent of concentration and of temperature. It is reasonably certain that induced decomposition of the peroxide is insignificant at concentrations below 0.02 *M* and of only very minor importance even at about 0.6 *M*. It appears that more than 55% of the radicals derived from the peroxide undergo geminate reaction. The results show that under certain conditions aliphatic diacyl peroxides can be used as reliable sources of free alkyl radicals in solution.

The present paper describes a detailed study of the products of the thermal decomposition of δ-phenylvaleryl peroxide in carbon tetrachloride. It is a continuation of work described in the first paper in the series,[2] and is part of a research program directed toward a study of elementary free radical processes in solution.

The decomposition of δ-phenylvaleryl peroxide in carbon tetrachloride was carried out over a range of concentrations from about 0.001 *M* to about 0.6 *M*, a more than 600-fold variation. Two temperatures were used, 55 and 77°. At the higher temperature the analyses of products accounted for 98 ± 1% of the phenylbutyl groups and for 97.5 ± 0.3% of the carboxyl groups. The solvent fragment balance was not quite so good in that the number of CCl_3 groups found in hexachloroethane did not usually agree very well with the number of Cl groups found in 4-phenyl-1-chlorobutane. It is possible that hexachloroethane was lost in the removal of the last traces of the solvent. Enough experiments were carried out to permit a valid estimate of the accuracy and reliability of the results. The details are presented in Tables I and II; a brief examination of the products of the decomposition of the peroxide in the absence of solvent is summarized in Table III.

Except for minor differences, the results are similar to, but more precise than, those reported in the previous paper.[2] One difference is that the phosgene previously reported as a reaction product has been reduced to a negligible factor by a more effective removal of oxygen in the runs at 77° (reported in Table I). The phosgene apparently arises from reaction of trichloromethyl radicals with oxygen.

Phosgene was evolved in small amounts from the 55° runs during distillation of the carbon tetrachloride through the fractionating column. Since free phosgene previously had been removed by sweeping the reaction mixture with nitrogen, it must be surmised that some unstable product was liberating the phosgene. The trichloromethyl ester of δ-phenylvaleric acid is possibly the phosgene precursor. Its decomposition would also yield δ-phenylvaleryl chloride. The increased amount of δ-phenylvaleric acid found in these runs could be accounted for by this hypothesis. However, another potential phosgene source is hexachlorodimethyl peroxide from reaction of trichloromethyl radicals

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(2) D. F. DeTar and C. Weis, THIS JOURNAL, **78**, 4296 (1956).

Table I

Products of the Thermal Decomposition of δ-Phenylvaleryl Peroxide in Carbon Tetrachloride at 77°[a]

Run no.	4	7	2	3	5	6	9	8	10	Std. dev.[b]	Av.[c]
Reactants											
Peroxide, mmoles	5.65	11.37	11.42	22.8	22.4	23.1	8.62	11.3	11.3		
CCl_4, liters	5.00	5.00	5.00	5.00	1.92	1.00	0.100	0.050	0.015		
Peroxide mole ratio ($\times 10^4$)	1.09	2.20	2.22	4.42	11.3	22.4	83.5	219	730		
Products											
CO_2	1.69	1.680	1.684	1.678	1.686	1.644	1.616	1.614	1.564	0.017(5)[d]	1.677 ± 0.007[d]
C_2Cl_6	0.28	0.41	0.42	0.28	0.26	0.22	0.15	0.097	0.061		
$C_6H_5(CH_2)_4Cl$	.86	.83	.79	.90	.92	.86	.77	.76	.79	.05 (11)[e]	0.86 ± .02[d]
$C_6H_5(CH_2)_4COO(CH_2)_4C_6H_5$	.193	.198	.202	.195	.184	.195	.186	.197	.198	.006(8)[f]	.194 ± .002[f]
$C_6H_5(CH_2)_8C_6H_5$	.26	.32	.27	.24	.24	.21	.22	.22	.23	.03 (16)[g]	.246 ± .01[f]
$C_6H_5(CH_2)_2CHClCH_2CCl_3$	.12	.15	.16	.13	.13	.14	.17	.16	.17	.016(15)[h]	.148 ± .005[f]
$C_6H_5(CH_2)_4COOH$	.06	.06	.06	.06	.10	.10	.14	.17	.20	.03 (11)[e]	.073 ± .012[d]
Total CO_2 groups accounted for, %	97.1	97.1	97.5	96.5	98.3	96.9	97.0	99.0	98.2	0.8 (8)[f]	97.5 ± 0.3[f]
Total $C_6H_5(CH_2)_4$ groups accounted for, %	98	104	98	98	100	96	94	96	101	3 (16)[g]	98 ± 1[f]

[a] Entries are moles of product per mole of peroxide. The run numbers indicate the order of the runs. [b] Standard deviation of individual entries; the number in parentheses is the degrees of freedom. [c] Error estimate is standard deviation of the average. [d] Based on runs 2–7, incl. [e] Based on runs 2–7, 11, 13–18. [f] Based on runs 2–10. [g] Based on all runs, 2–19. [h] Based on runs 2–10, 11, 13–19.

Table II

Products of the Thermal Decomposition of δ-Phenylvaleryl Peroxide in Carbon Tetrachloride at 55°[a]

Run no.	12[b]	19	11	17	16	18	14	15	13	Std. dev.[c]	Av.[d]
Reactants											
Peroxide, mmoles	5.45	5.76	11.46	11.46	22.6	22.4	22.4	22.6	22.4		
CCl_4, liters	5.00	5.00	5.00	5.00	5.00	5.00	2.00	2.00	1.00		
Peroxide mole ratio ($\times 10^4$)	1.06	1.12	2.22	2.22	4.38	4.34	10.8	10.9	21.6		
Products											
CO_2	1.68	1.70	1.73	1.66	1.66	1.67	1.61	1.66	1.59	0.04 (8)[e]	1.66 ± 0.013[e]
C_2Cl_6	0.11	0.09	0.13	0.13	0.18	0.19	0.14	0.14	0.14		
$C_6H_5(CH_2)_4Cl$	.44	.40	.64	.66	.78	.79	.74	.74	.76	.05 (11)[f]	0.73 ± .02[g]
$C_6H_5(CH_2)_4COO(CH_2)_4C_6H_5$	.224	.187	.216	.208	.202	.182	.176	.177	.175	.019(8)[e]	.194 ± .006[e]
$C_6H_5(CH_2)_8C_6H_5$	.22	.24	.28	.22	.21	.22	.20	.20	.18	.03 (16)[h]	.22 ± .01[e]
$C_6H_5(CH_2)_2CHClCH_2CCl_3$	.05	.13	.12	.14	.14	.14	.11	.12	.14	.016(15)[i]	.131 ± .006[j]
$C_6H_5(CH_2)_4COOH$	.48	.46	.22	.22	.20	.14	.23	.24	.24	.03 (11)[f]	.21 ± .01[g]
Total CO_2 groups accounted for, %	120	117	109	105	103	100	101	104	99	3 (6)[g]	103 ± 1[g]
Total $C_6H_5(CH_2)_4$ groups accounted for, %	94	93	99	94	97	94	91	93	92	3 (16)[h]	94 ± 1[e]

[a] Entries are moles of product per mole of peroxide. [b] Order in which the runs were worked up. [c] Standard deviation of individual entries; the number in parentheses is the degrees of freedom. [d] Error estimate is standard deviation of the average. [e] Based on runs 11–19. [f] Based on runs 2–7, 11, 13–18. [g] Based on runs 11, 13–18. [h] Based on all runs, 2–19. [i] Based on runs 2–10, 11, 13–19. [j] Based on runs 11, 13–19.

TABLE III

PRODUCTS OF THE THERMAL DECOMPOSITION OF PURE δ-PHENYLVALERYL PEROXIDE WITHOUT SOLVENT AT 65°[a]

Run	20	21
Peroxide, mmoles	19.67	18.92
Products		
CO_2	1.27	1.26
$C_6H_5(CH_2)_3CH_3$	0.30	0.28
$C_6H_5(CH_2)_2CH{=}CH_2$	.02	.32
$C_6H_5(CH_2)_8C_6H_5$	.23	.21
$C_6H_5(CH_2)_4COO(CH_2)_4C_6H_5$	.173	.175
$C_6H_5(CH_2)_4COOH$	.27	.53
Tetralin	.20	.27
Total CO_2 groups accounted for, %	85	98
Total $C_6H_5(CH_2)_4$ groups accounted for, %	88	108

[a] Entries are moles of product per mole of peroxide. The exothermic reaction goes out of control at higher temperatures.

with oxygen. In either event the amount involved was small.

The analysis of products formed in the absence of solvent was carried out as previously described for the benzene runs. It was not considered worthwhile to spend the time needed to perfect the analytical techniques for these runs; the error limits are somewhat larger than reported in Tables I and II, those for 1-phenylbutane, for 4-phenyl-1-butene and for tetralin may be fairly large.

The most striking feature of the results is the insensitivity of the product yields to the peroxide concentration and to the reaction temperature. The constancy is so pronounced that it is feasible to summarize many of the data in the form of averages as is done in the final columns of the tables. The deviations from the averages are generally only a few per cent. relative.

These results are strong evidence for the absence of induced decomposition, the usual types of which would lead to the ester, δ-phenylbutyl δ-phenylvalerate, or to the dimer, 1,8-diphenyloctane.[3] Since the yields of these particular products are invariant even for the reaction in absence of solvent, they cannot be produced by an induced chain mechanism. Products that might be expected from induced decomposition of the peroxide by trichloromethyl radicals are $RCCl_3$ or $RCOOCl_3$, in which R is a phenylbutyl group. However, no appreciable amount of these products was present, certainly not enough to account for more than a very few per cent. of induced decomposition. Furthermore kinetic studies[4] show that the reaction is quite accurately first order, and that the rate of disappearance of the peroxide is insensitive to oxygen.[5] The increase in initial rate with increase in peroxide concentrations can be accommodated by an estimated 5% of induced decomposition at an initial peroxide concentration of 0.1 *M*. These results all show that little induced decomposition takes place with δ-phenylvaleryl peroxide at low concentrations in carbon tetrachloride. It is thus possible in considering the reaction mechanism to eliminate the very large number of elementary steps that involve free radical attack on the peroxide.

The reaction products can be accounted for by means of the following series of elementary reactions, and there is some evidence to indicate that nearly all of these steps are occurring.

$$(RCOO)_2 \longrightarrow [2RCOO\cdot] \quad (1)$$
$$\longrightarrow [RCOO\cdot + R\cdot] + CO_2 \quad (2)$$
$$\longrightarrow [2R\cdot] + 2CO_2 \quad (3)$$
$$[2R\cdot] \longrightarrow 2R\cdot \quad (4)$$
$$\longrightarrow R{-}R \quad (5)$$
$$\longrightarrow C_6H_5(CH_2)_3CH_3 + C_6H_5(CH_2)_2CH{=}CH_2 \quad (6)$$
$$[RCOO\cdot + R\cdot] \longrightarrow R\cdot + RCOO\cdot \quad (7)$$
$$\longrightarrow RCOOR \quad (8)$$
$$\longrightarrow RCOOH + C_6H_5(CH_2)_2CH{=}CH_2 \quad (9)$$
$$[2RCOO\cdot] \longrightarrow 2RCOO\cdot \quad (10)$$
$$\longrightarrow (RCOO)_2 \quad (11)$$
$$RCOO\cdot \longrightarrow R\cdot + CO_2 \quad (12)$$
$$R\cdot + CCl_4 \longrightarrow RCl + \cdot CCl_3 \quad (13)$$
$$CCl_3\cdot + C_6H_5(CH_2)_2CH{=}CH_2 \longrightarrow C_6H_5(CH_2)_2\underset{\underset{I}{\cdot}}{CH}CH_2CCl_3 \quad (14)$$
$$CCl_4 + I \longrightarrow C_6H_5(CH_2)_2CHClCH_2CCl_3 + CCl_3\cdot \quad (15)$$
$$2CCl_3\cdot \longrightarrow C_2Cl_6 \quad (16)$$

Radicals capable of geminate reaction[6,7] in a solvent "cage" are shown in brackets as indicated in eq. 5, 6, 8, 9 and 11. Equations 4, 7 and 10 represent escape of the radical partners from the "cage," and eq. 12–16 represent reactions of the resulting "free" radicals. The principal evidence for the geminate reactions in this particular case is the absence of $C_6H_5(CH_2)_4CCl_3$, the cross termination product from phenylbutyl radicals and trichloromethyl radicals.[2,7] The geminate products are 1,8-diphenyloctane (eq. 5), δ-phenylbutyl δ-phenylvalerate (eq. 8) and δ-phenylvaleric acid (eq. 9). The 1,1,1,3-tetrachloro-5-phenylpentane is also a geminate product in the sense that all of the 4-phenyl-1-butene (eq. 9) is converted to the tetrachloro compound under the reaction conditions. The non-geminate products are 4-phenyl-1-chlorobutane and hexachloroethane. 1-Phenylbutane is absent.[2] In the 77° runs the yield of δ-phenylvaleric acid is nearly large enough to admit the formation of all of the 4-phenyl-1-butene by eq. 9. There is no excess of the acid, and therefore any δ-phenylvaleryloxy free radicals produced by eq. 7 and 10 must lead to 4-phenyl-1-chlorobutane and carbon dioxide either by eq. 12 and 13 or by formation of an unstable acyl hypochlorite which gives the same products: $RCOO\cdot + CCl_4 \rightarrow RCOOCl + \cdot CCl_3$; $RCOOCl \rightarrow RCl + CO_2$.

As an alternative to the geminate reaction hypothesis it has been suggested[8] that disproportionation products such as olefin and acid (*cf.*, eq. 9) are

(3) *Cf.* W. E. Cass, THIS JOURNAL, **69**, 500 (1947).

(4) D. F. DeTar and R. C. Lamb, unpublished results.

(5) *Cf.* K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946); **69**, 2299 (1947).

(6) R. M. Noyes, *ibid.*, **77**, 2042 (1955). *Cf.* J. C. Roy, R. R. Williams, Jr., and W. H. Hamill, *ibid.*, **76**, 3274 (1954), and J. Frank and E. Rabinowitsch, *Trans. Faraday Soc.*, **30**, 120 (1937).

(7) For other evidence *cf.*, D. F. DeTar and C. Weis, THIS JOURNAL, **79**, 3045 (1957).

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

formed by a rearrangement reaction. Ester may also presumably be formed by rearrangement. If there is only a single product to be explained by a rearrangement reaction, then it is difficult to find a good criterion for distinguishing between a rearrangement process and a geminate radical process. In the present example, however, there are three sets of products to be explained by rearrangement reactions, by geminate radical reactions, or by other as yet not postulated processes. If the ester, the dimer, and the 1,1,1,3-tetrachloro-5-phenylpentane are all ascribed to rearrangement reactions, then this is an example of the possible but remarkable circumstance of a compound undergoing three concurrent rearrangement reactions plus a free radical cleavage all at rather comparable rates. It is still more remarkable to have four such reactions with nearly identical temperature coefficients, yet the yields of the "rearrangement" reactions are indeed temperature independent over a more than 20° range. The geminate radical reaction hypothesis requires fewer coincidences: for reactions as fast as geminate combination, the temperature coefficients should be negligible. To attempt to select one product as arising by a rearrangement reaction and to ascribe the rest of the products to geminate radical reactions is wholly arbitrary. It is for these reasons that the rearrangement reactions have not been included in the mechanistic scheme.

The geminate products account for 59% of the peroxide at 77° and 55% at 55°; these yields are just significantly different at the 95% level in the statistical sense, but the difference is so small that they may be considered to be essentially the same from the chemical point of view. The only important direct free radical product is 4-phenyl-1-chlorobutane. Since induced decomposition reactions do not interfere under the present conditions, these results show that it is possible to find conditions under which aliphatic diacyl peroxides are a reliable source of free alkyl radicals in solution.

In eq. 1–3 it is postulated that the peroxide decomposition occurs by some combination of reactions involving cleavage of one, two or three bonds simultaneously in the initial step. With reasonable assumptions it is possible to account for the products on the hypothesis that reactions 2 and 3 are much faster than reaction 1, but the presence of ester and of acid exclude the occurrence of reaction 3 as the only cleavage. On the other hand if only reaction 1 can occur, then the decarboxylation reaction, eq. 12, must be able to compete with geminate radical reactions in order to give the products. This problem has been discussed previously,[9] but further work is clearly required before a decision is possible.

(9) P. D. Bartlett and F. D. Greene, This Journal, **76**, 1088 (1954); D. F. DeTar and J. C. Howard, *ibid.*, **77**, 4393 (1955).

Experimental

The identification of the reaction products and the experimental procedure for carrying out the reaction has already been described.[2] The present runs were carried out with refinements of detail as in the better removal of oxygen.

In the quantitative determination of products, the solvent was removed using a 12 × 300 mm. column packed with glass helices. The residual 40–60 ml. of solution was then extracted with three 10-ml. portions of ice-cold 2 *N* potassium hydroxide solution, then with water, with dilute hydrochloric acid, and again with water. After drying over sodium sulfate, the carbon tetrachloride was removed through a small column, and the residue was quantitatively transferred to a small Claisen flask. At this point it contained about 5 ml. of CCl_4. In the subsequent distillation the receiver was cooled in Dry Ice, and the system was backed by traps. The oil-bath temperature was raised gradually to just under 130°, and two fractions were collected: distillate (b.p. up to 70° at 3 mm.) and residue. The distillate, containing hexachloroethane and 4-phenyl-1-chlorobutane, was analyzed by an infrared spectrophotometric procedure and the residue was analyzed by a combination utilizing chromatographic separation of the ester and infrared spectrophotometric analysis of the non-ester fraction. The carbon tetrachloride distilled into the traps.

Known mixtures of the reaction products were dissolved in 300 ml. of carbon tetrachloride and subjected to the complete separation and analytical procedure; the results are summarized in Table IV.

Table IV

Test of Isolation and Analytical Procedure on Known Mixtures

	Taken,[a] mg.	Found, mg.	Taken,[b] mg.	Found, mg.
C_2Cl_6	179	180	930	880
$C_6H_5(CH_2)_3CH_3$	0	0	365	394
$C_6H_5(CH_2)_4Cl$	811	859	1520	1410
$C_6H_5(CH_2)_8C_6H_5$	471	460	792	809
$C_6H_5(CH_2)_2CHClCH_2CCl_3$	177	173	446	429
$C_6H_5(CH_2)_4COO(CH_2)_4C_6H_5$	437	456	900	917
$C_6H_5(CH_2)_4COOH$	208	211	210	210

[a] Receiver cooled in Dry Ice, preventing loss of 4-phenyl-1-chlorobutane. [b] Receiver cooled with ordinary ice.

The runs at 55° were carried out in sealed flasks of appropriate capacity. These flasks had a sealed-on head containing a gas inlet tube (sealed off during the runs), a filling tube of 12 mm. tubing, and a break-seal side tube attached to a ball joint. The carbon tetrachloride was refluxed while nitrogen was introduced through a tube extending into the filling tube. The flask was cooled to 40° and the peroxide introduced as a carbon tetrachloride solution. The filling tube was then sealed off so that the flask was completely sealed.

The flasks were placed in an oil-bath constructed from a 55-gal. drum and were maintained at 55.5–55.2° for the first 30 days, 55.2–54.8° for the next 30 days and 54.8–54.6° for the last 18 days. The flasks were then removed. At room temperature the pressure was less than atmospheric. The gas inlet was opened, the flask attached to the aniline bulb–cold trap–Ascarite tube train previously described, and the break-seal opened. A stream of nitrogen was passed through while the mixture was refluxed. Some phosgene was present in these runs. The isolation and analysis of the products was carried out as described.

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