

TABLE III
 ABSORPTION MAXIMA IN ULTRAVIOLET SPECTRA OF 2-SUBSTITUTED 8-METHOXYQUINOLINES^a

2-Substituent	m μ (1)	m μ (2)	m μ (3)	m μ (4)
A. In cyclohexane				
CH ₃ —		242(4.62)		296(3.53)
C ₆ H ₅ — ^b		266		318
<i>o</i> -CH ₃ C ₆ H ₄ —		261(4.56)		306(3.75)
<i>m</i> -CH ₃ C ₆ H ₄ —		268-269(4.69)		316-319(3.87)
<i>p</i> -CH ₃ C ₆ H ₄ —		271(4.71)		322(3.93)
<i>p</i> -ClC ₆ H ₄ —		271(4.79)		320(4.04)
C ₆ H ₅ CH=CH—		288-289(4.57)		341(4.30)
		298(4.57)		
B. In 0.1 N hydrochloric acid				
CH ₃ —		254(4.70)	318(3.54)	345(3.26)
C ₆ H ₅ —	250(4.23)	282(4.61)	337(4.23)	
<i>o</i> -CH ₃ C ₆ H ₄ —	253(4.52)	280(4.26)	331(3.97)	
<i>m</i> -CH ₃ C ₆ H ₄ —	251(4.20)	284(4.53)	340(4.18)	
<i>p</i> -CH ₃ C ₆ H ₄ —	252(4.36)	289(4.48)	344(4.28)	
<i>p</i> -ClC ₆ H ₄ —	252-253(4.26)	288(4.53)	340(4.23)	
C ₆ H ₅ CH=CH—	246(3.87)	308(4.48)	372(4.53)	
	264-266(3.93)			

maximum "4" in a number of the compounds in acid solution.

Support for the hypothesis that metal chelate rings are quite similar in character to the rings formed by hydrogen bridges in the original chelate forming reagent⁹ is illustrated by the close resemblance of the sodium and copper salts of the 8-quinolinols to the unsubstituted compounds in neutral solvents (Tables I and II). The only significant difference is a considerable bathochromic shift in passing from the reagent to the sodium salt to the copper chelate, as would be anticipated from the increasingly complex structure of the hydrogen, sodium and copper ions.

(9) Calvin and Wilson, *THIS JOURNAL*, **67**, 2003 (1945).

Except for a general small hypsochromic shift the spectra of the 8-methoxyquinolines in neutral and acid solvents are virtually identical with the 8-hydroxy analogs.

Summary

The ultraviolet absorption spectra of a group of 2-substituted 8-quinolinols and their 8-methoxy derivatives have been determined in various types of solvents and some tentative associations of structure and spectra made. Evidence for steric inhibition of chelate formation by 2-substituents was not obtained.

BLOOMINGTON, INDIANA

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Reactions of Atoms and Free Radicals in Solution. XXIV. The Reactions of Acetyl Peroxide with Chloro- and Dichloroalkanes¹

BY M. S. KHARASCH AND G. BUCHI

Objectives of the Present Study.—Earlier studies in this Laboratory have indicated that hydrocarbons and halogenated hydrocarbons vary widely in the facility with which they yield hydrogen or halogen atoms to free methyl radicals, forming methane or a methyl halide and a derivative free radical. In a given molecule one (or one of several equivalent) atoms is usually much more susceptible to methyl-radical abstraction than are the others; in such cases it is possible to specify in advance the derived free radical that will result preferentially or exclusively from methyl-radical attack.

On the basis of previous observations it is possible to state that, as points of methyl-radical attack, tertiary hydrogen atoms take preference over secondary hydrogen atoms, which in turn take pref-

erence over primary hydrogen atoms. It has already been shown that methyl radicals abstract preferentially the hydrogen atom of chloroform, one of the bromine atoms of bromoform and the bromine atom of bromotrichloromethane. On this basis, however, no general statement regarding the relative labilities of hydrogen and halogen atoms is justifiable, nor can confident prediction be made as to which of two like but dissimilarly located halogen atoms will prove the more susceptible to methyl-radical attack. One of the objectives of the present study was to cast additional light on these points.

It is further known from previous observation that derived free radicals (formed by the attack of methyl radicals on hydrocarbons or halogenated hydrocarbons) vary widely in their tendencies to (1) react with other components of the reaction system, or (2) react with each other by (a) disproportiona-

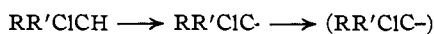
(1) The authors wish to acknowledge the generous support of the Firestone Tire and Rubber Company which made this research possible.

tion or (b) dimerization. Generally speaking, the more reactive (which is to say, the more "electronegative"²) free radicals react with some other component of the reaction system before they have an opportunity to react with each other. Of the less reactive free radicals, those structurally incapable of disproportionation, of course, dimerize. Concerning the remainder one may only hazard the hypothesis that, when no decisive steric effects intervene, the thermodynamically favored of the two processes (disproportionation or dimerization) will prevail. In view of present uncertainties inherent in the estimation of bond energies, further empirical data on this point are desirable. Another major objective of the present study was to acquire such data.

Method of Operation.—The method of the present study consisted in the thermal decomposition of acetyl peroxide in an excess (5–10 equivalents) of chloro- or dichloroalkane, and the quantitative separation and identification of the components of the final reaction mixture. The compounds chosen for investigation were *n*-butyl, *s*-butyl, *s*-heptyl, *t*-amyl, ethylene, propylene, tetramethylene and pentamethylene chlorides. The reaction summaries are given in Figs. 1 to 8.

Preferred Points of Methyl-Radical Attack.—From the relative amounts of methane and methyl chloride liberated in the reactions (see Figs. 1 to 8) it is evident that in all the compounds investigated one of the hydrogen atoms is preferred over a chlorine atom as the point of attack of the methyl radical. In all cases the yield of methane exceeded one mole per mole of acetyl peroxide decomposed. In some cases methyl chloride was not detectable; in no case did it much exceed in amount one-tenth mole per mole of peroxide decomposed.

Only three of the compounds investigated (*s*-butyl, *s*-heptyl and propylene chlorides) had a tertiary hydrogen atom. As might be expected, identification of the respective "dimers" as 3,4-dichloro-3,4-dimethylhexane, 6,7-dichloro-6,7-dichloro-6,7-dimethyldodecane and 1,2,3,4-tetrachloro-3,4-dimethylbutane indicated the tertiary hydrogen atom as the preferred point of attack.



In *t*-amyl chloride there are only two similarly located secondary hydrogen atoms, which may be characterized as being of the RCH_2R' type. In ethylene chloride there are four similarly located secondary hydrogen atoms, which may be described as belonging to the RCH_2Cl type. As might be expected, the respective "dimers" identified (2,5-dichloro-2,3,4,5-tetramethylhexane and 1,2,3,4-tetrachlorobutane) indicate that in each case one of the secondary hydrogen atoms is the preferred point of attack.

Tetramethylene and pentamethylene chlorides, however, both have secondary hydrogen atoms of both types. The respective "dimers" identified (1,4,5,8-tetrachlorooctane and 1,5,6,10-tetrachlorodecane) indicate that, as points of methyl-radical

(2) For a discussion of the relative "electronegativities" of organic radicals see: Kharasch and Reinmuth, *J. Chem. Education*, **5**, 404 (1928); **8**, 1703 (1931); Kharasch, Reimuth and Mayo, *ibid.*, **11**, 82 (1934); **13**, 7 (1936).

attack, secondary hydrogen atoms of the type RCH_2Cl are preferred over those of the type RCH_2R' (when R and R' are alkyl or chloroalkyl radicals).

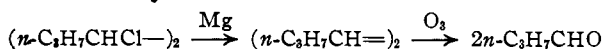
Concerning the relative susceptibilities of dissimilarly located chlorine atoms to methyl-radical attack the evidence is perhaps less clearcut, because (1) the amount of chlorine attack in all cases studied is relatively small, and (2) no attempt was made to equate the concentrations of primary, secondary and tertiary chlorine atoms in the various reaction mixtures. Nevertheless, the facts that the *n*-butyl chloride reaction mixture yielded about one-tenth mole of methyl chloride per mole of acetyl peroxide decomposed and that no methyl chloride could be isolated from the *t*-amyl chloride reaction mixture suggest that the order of preference in methyl-radical attack upon chlorine is primary > tertiary. It may be pointed out, moreover, the primary chlorine atoms of *n*-butyl chloride compete with secondary hydrogen atoms of a type (RCH_2Cl) preferred over that of the competitive secondary hydrogen atoms of *t*-amyl chloride (RCH_2R'). The data of the present study scarcely suffice to determine whether secondary chlorine atoms are more or less preferred than primary chlorine atoms; there is no doubt that they are preferred over tertiary chlorine atoms.

Superficially it might appear surprising that the order of lability for chlorine atoms is the reverse of that for hydrogen atoms; however, consideration of the differing natures of carbon-to-chlorine and carbon-to-hydrogen bonds suffices to resolve the apparent anomaly. The carbon-to-hydrogen bond in methane (*i.e.*, the bond between a methyl radical and a hydrogen atom) is usually regarded as essentially non-polar. Actually this bond has a slight polarity, with the methyl radical at the negative end of the dipole. Any decrease in the electronegativity of the methyl radical through substitution weakens the radical-to-hydrogen bond and diminishes the slight polarity it originally had. The carbon-to-chlorine bond, on the other hand, is generally recognized as definitely polar, with chlorine at the negative end of the dipole. Any decrease in the strength of the bond occasioned by a decrease in the electronegativity of the carbon radical is more than compensated by an increase in the polarity of the bond and consequent increase in the contribution to bond strength made by its partial ionic character. Thus although a tertiary chlorine atom is more labile in reactions involving ionic bond scission than a primary chlorine atom, the reverse is true in reactions involving homopolar bond scission.

Identification of "Dimers"

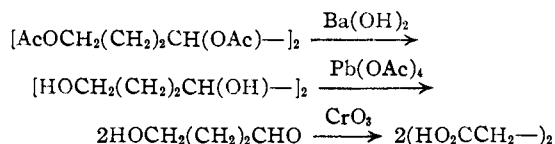
The degradation reactions leading to the identification of the various dimers, described in more detail in the experimental part, may be briefly outlined as follows.

1. *n*-Butyl chloride "dimer"

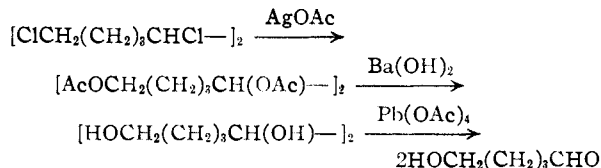


2. Tetramethylene chloride "dimer"

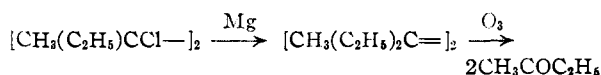




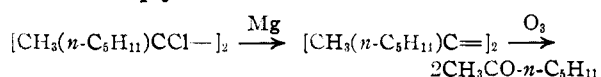
3. Pentamethylene chloride "dimer"



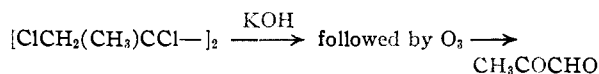
4. *s*-Butyl chloride "dimer"



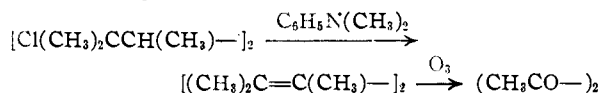
5. *s*-Heptyl chloride "dimer"



6. Propylene chloride "dimer"

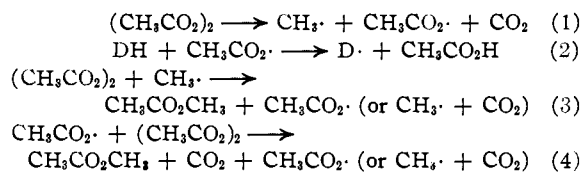


7. *t*-Amyl chloride "dimer"



Products other than "Dimers"

In all experiments performed the usual products of thermal decomposition of acetyl peroxide (namely, carbon dioxide, acetic acid and methyl acetate) were isolated. The authors believe that these are most credibly attributable to the reactions³

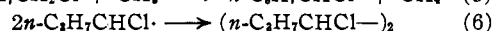
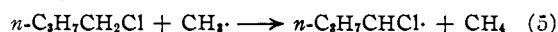


in which the symbol DH signifies a hydrogen donor.

***n*-Butyl Chloride.**—The products formed when acetyl peroxide is decomposed in *n*-butyl chloride are indicated in Fig. 1. Assuming that the tar consists chiefly of condensation products of *n*-butyl chloride, products equivalent to 0.87 mole of the chloride for each mole of peroxide decomposed are thus accounted for.

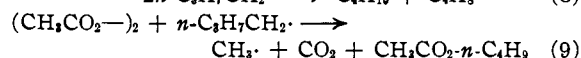
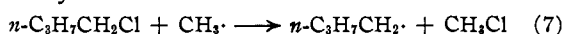
The difficulty of quantitative isolation of numerous products from relatively small reaction batches need scarcely be pointed out. In attempting to strike material balances about all that may be expected is that theoretically equatable quantities shall prove to be of the same order of magnitude.

The "dimer" and some of the methane are, of course, attributable to the reactions

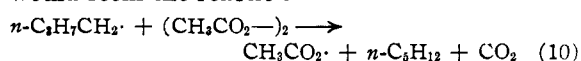


In view of the fact that the "dimer" has two tertiary hydrogen atoms, it should be even more susceptible to methyl-radical attack than *n*-butyl chloride, which has only secondary and primary hydrogen atoms. Such attack would, of course, lead to the formation of higher "polymers." This is assumed to be the principal source of "tar."

Methyl chloride, butane, part of the butenes and *n*-butyl acetate are attributable to the reactions



As a source of *n*-pentane, the reaction $\text{CH}_3\cdot + n\text{-C}_3\text{H}_7\text{CH}_2\cdot \rightarrow n\text{-C}_5\text{H}_{12}$ may be rejected on the grounds that (a) the highly reactive methyl radicals could scarcely be expected to have a long enough life to encounter *n*-butyl radicals in sufficient number, and (b) that reaction between methyl and *n*-butyl radicals would be much more likely to take the course: $\text{CH}_3\cdot + n\text{-C}_3\text{H}_7\text{CH}_2\cdot \rightarrow \text{CH}_4 + \text{C}_4\text{H}_8$. The authors have also considered the reaction $n\text{-C}_3\text{H}_7\text{CH}_2\text{Cl} + \text{CH}_3\cdot \rightarrow \text{Cl}\cdot + n\text{-C}_5\text{H}_{12}$, but, on the whole, regard it as improbable. More credible would seem the reaction



By way of material balance, 0.11 mole of methyl chloride (a figure probably too low by reason of cold-trap loss) may be compared with an aggregate of 0.19 mole of butane, butenes, butyl acetate and pentane. The agreement, of course, is not perfect, but the quantities are of the same order of magnitude.

The 1,2-dichlorobutane probably arises from a relatively small amount of methyl-radical attack on secondary hydrogen atoms of the less preferred type.

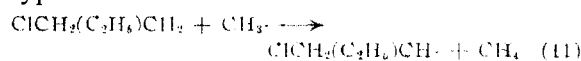
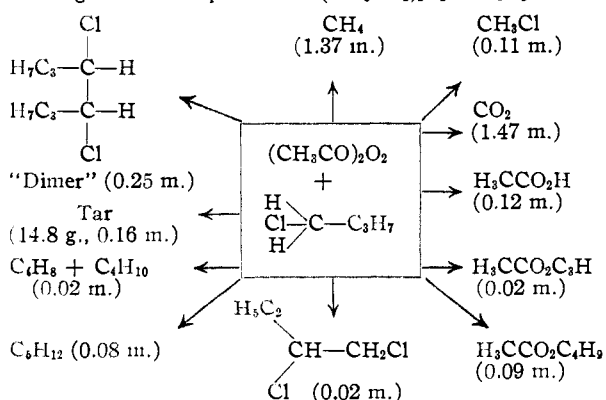
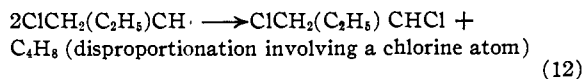


Fig. 1.—Decomposition of $(\text{CH}_3\text{CO}_2)_2\text{O}_2$ in $\text{C}_4\text{H}_9\text{Cl}$.

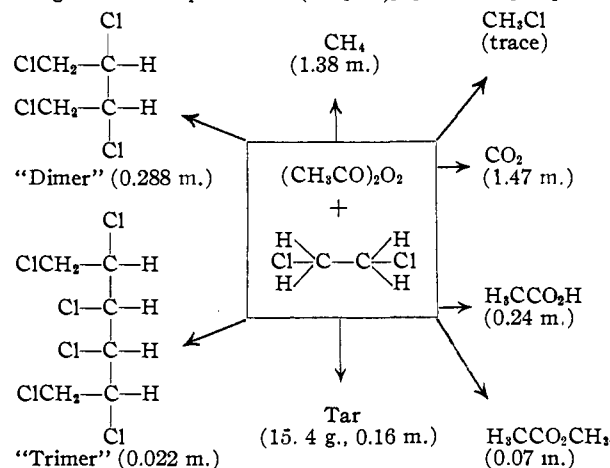


(3) Recently, Fry, Tolbert and Calvin (Brookhaven Conference Report, January, 1950) question the mechanisms of formation of methyl acetate as here outlined since, when acetyl peroxide is decomposed in acetic acid containing C^{14} in the methyl group, the methyl acetate contains C^{14} in both of the methyl groups of the methyl acetate. It is submitted, however, that the "exchange studies" of these authors, namely, that acetic acid does not react with acetyl peroxide at 50° (while of importance) does not preclude interaction at $85\text{--}95^\circ$, nor what is probably more important that exchanges may occur between a free acetoxy radical and the labeled acetic acid molecule to give a labeled free acetoxy radical. The conclusion of the above authors that methyl acetate cannot be formed in the manner proposed by us appears to be unjustified by the evidence presented by them.



Ethylene Chloride.—In addition to the "dimer" (0.29 mole), about 0.02 mole of "trimer" (1,2,3,4,5,6-hexachloroethane) was isolated. Other data are summarized in Fig. 2.

Fig. 2.—Decomposition of $(\text{CH}_3\text{CO})_2\text{O}_2$ in $\text{ClCH}_2\text{CH}_2\text{Cl}$.



Tetramethylene and Pentamethylene Chlorides.—From these reaction mixtures (in addition to the usual peroxide decomposition products) only the respective "dimers" and tar were isolated. The respective material balances (Figs. 3 and 4) suggest that any other products must have been formed in negligible quantities.

Fig. 3.—Decomposition of $(\text{CH}_3\text{CO})_2\text{O}_2$ in $\text{ClCH}_2(\text{CH}_2)_2\text{CH}_2\text{Cl}$.

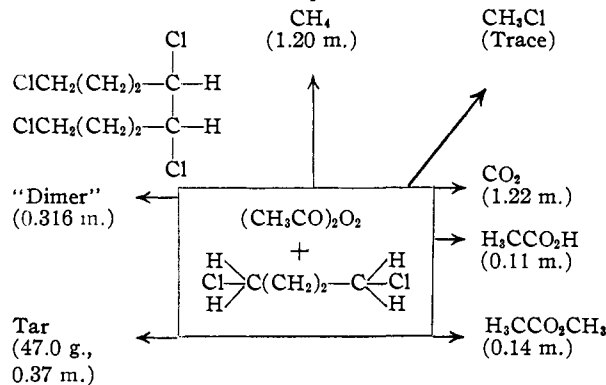


Fig. 4.—Decomposition of $(\text{CH}_3\text{CO})_2\text{O}_2$ in $\text{ClCH}_2(\text{CH}_2)_3\text{CH}_2\text{Cl}$.

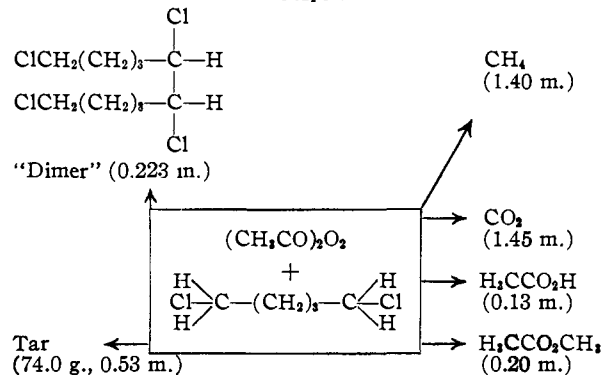


Fig. 5.—Decomposition of $(\text{CH}_3\text{CO})_2\text{O}_2$ in $\text{C}_2\text{H}_5\text{CHClCH}_3$.

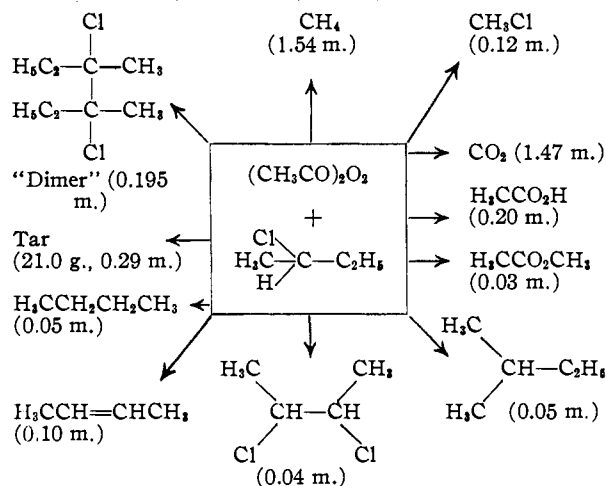


Fig. 6.—Decomposition of $(\text{CH}_3\text{CO})_2\text{O}_2$ in $\text{C}_8\text{H}_{11}\text{CHClCH}_3$.

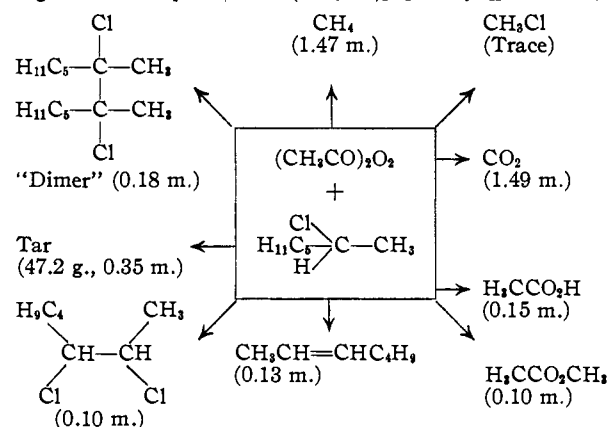
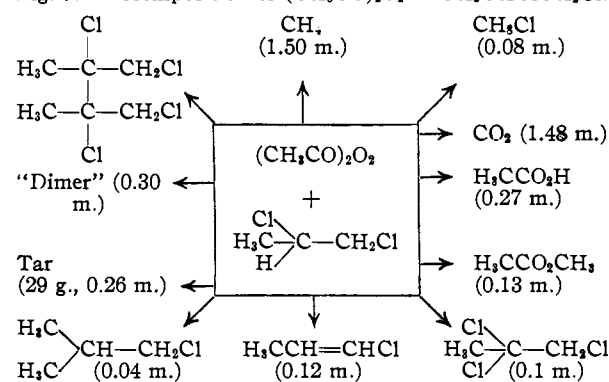
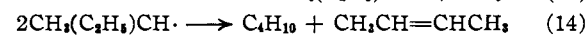
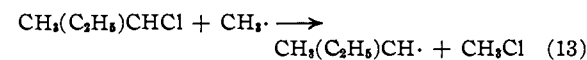


Fig. 7.—Decomposition of $(\text{CH}_3\text{CO})_2\text{O}_2$ in $\text{CH}_3\text{CHClCH}_2\text{CH}_2\text{Cl}$.

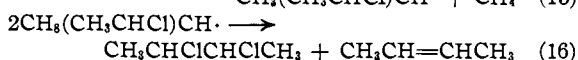
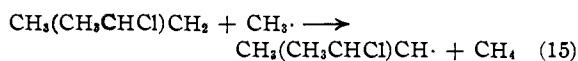


s-Butyl Chloride.—In addition to the "dimer" and other expected products, the formation of butane, 2 butenes, 2,3-dichlorobutane and isopentane is of considerable theoretical interest.

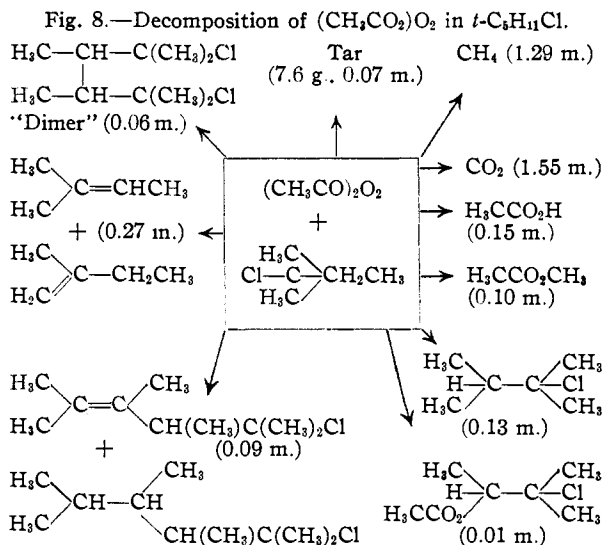
The formation of butane and butenes is attributed to the reactions



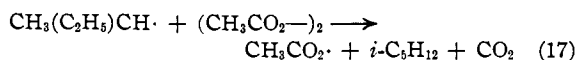
The formation of 2,3-dichlorobutane is attributed to an hitherto unreported type of disproportionation involving a chlorine atom



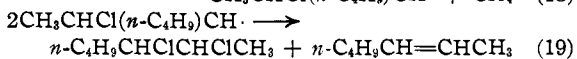
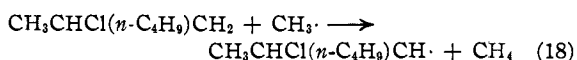
2-Butenes are formed simultaneously with butane and 2,3-dichlorobutane. The balance, 0.10 mole of the former against an aggregate of 0.09 mole of the latter two, is better than could be expected in view of the experimental errors involved.



The formation of isopentane is attributed to the reaction



***s*-Heptyl Chloride.**—In addition to the "dimer" and other expected products, the formation of 2-heptenes (0.13 mole) and 2,3-dichloroheptane (0.10 mole) is of considerable interest. These latter products are assumed to be formed as a result of a disproportionation reaction involving chlorine atoms

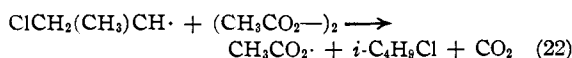
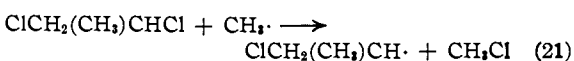


Propylene Chloride.—In addition to the "dimer" and other expected products, the formation of 1-chloropropene (0.12 mole), 1,2,2-trichloropropane (0.10 mole), and isobutyl chloride (0.04 mole) is of interest.

The 1-chloropropene and 1,2,2-trichloropropane are attributed to a disproportionation reaction of the free radical involving a chlorine atom (similar to the disproportionation of a free *n*-butyl radical to butane and 2-butene, which involves a hydrogen atom), or disproportionation of $\text{ClCH}_2(\text{CH}_2)\text{CCl}$ and $(\text{CH}_3\text{CHCl})\text{CHCl}$ free radicals.



The formation of isobutyl chloride is attributed to the reaction

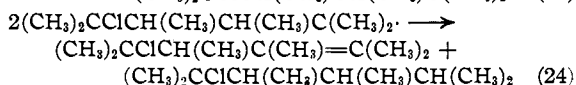
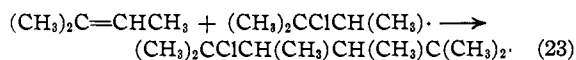


***t*-Amyl Chloride.**—Under the experimental conditions imposed *t*-amyl chloride apparently undergoes some dehydrochlorination, for hydrogen chloride was detected among the effluent gases and 2-methyl-1-butene and 2-methyl-2-butene (aggregating 0.27 mole) were isolated from the reaction mixture.

3-Chloro-3-methyl-2-butyl acetate (*ca.* 0.01 mole) is attributed to a reaction similar to that proposed to account for *n*-butyl acetate (equation 9).

2-Chloro-2,3-dimethylbutane is attributed to reactions similar to those proposed to account for *n*-pentane (equation 10), isopentane (equation 17) and isobutyl chloride (equation 22).

2,3,4,5-Tetramethyl-5-chloro-2-hexene and the corresponding saturated chloride, to the aggregate of 0.09 mole, were also isolated. They are attributed to the reactions



Behavior of Derived Free Radicals

On *a priori* grounds it would be estimated that free radicals of the type $\text{RCCI} \cdot$ (in which R is alkyl) are less electronegative² than the corresponding radicals of the type $\text{RCH}_2 \cdot$, and should therefore prove generally less reactive. The results of the present study appear to confirm this estimate. For example, in the *n*-butyl chloride experiment *n*-butyl acetate was obtained in isolable quantity (equation 9), but 1-chloro-*n*-butyl acetate could not be detected.

The tendency toward disproportionation depends both upon the reactivity of the free radical (with respect to its ability to abstract a hydrogen or other atom from a donor) and its ability to serve as a donor of a hydrogen or other atom. The results of the present study suggest that the former property is the decisive one. For example, there is no reason to suppose that a *n*-butyl radical should prove an appreciably better hydrogen donor than a 1-chloro-*n*-butyl radical. It is well known that *n*-butyl radicals readily undergo disproportionation. In the present study disproportionation products of *n*-butyl radicals were isolated, but no products attributable to disproportionation of 1-chloro-*n*-butyl radicals could be detected; the dimer, however, was obtained in good yield.

The estimate that free radicals of the type $\text{RR}'\text{CCl} \cdot$ (in which R and R' are alkyl) should be less electronegative and therefore generally less reactive than the corresponding radicals of the type $\text{RR}'\text{CH} \cdot$ also appears to be confirmed by the results of the present study. Although disproportionation products of the $\text{CH}_3(\text{C}_2\text{H}_5)\text{CH} \cdot$ and $\text{ClCH}_2(\text{CH}_2)\text{CH} \cdot$ radicals were isolated, all radicals of the type $\text{RR}'\text{CCl} \cdot$ underwent dimerization in preference to disproportionation.

Dimerization is, of course, the natural fate of all free radicals of sufficiently low reactivity and consequently relatively long life. Even such ex-

tremely unreactive and consequently long-lived free radicals as the triphenylmethyl dimerize without difficulty.

Of considerable theoretical moment insofar as the theory of halogenation of alkyl halides is concerned is the tendency of free radicals of the type $\text{ClCH}_2\text{RCH}\cdot$ to undergo a disproportionation involving a transfer of a chlorine atom (equations 19 and 20) instead of a hydrogen atom. We hope to discuss this point in somewhat greater detail in a report describing the results obtained in a study of halogenation of a number of alkyl halides.

One other point perhaps needs stressing here, namely, that free radicals may attack both the carbon-to-carbon and the oxygen-to-oxygen bonds in acetyl peroxide. Note for instance the formation of *n*-pentane and *n*-butyl acetate when acetyl peroxide is decomposed in *n*-butyl chloride, and the formation of isobutyl chloride when acetyl peroxide is decomposed in propylene chloride.

Experimental⁴

Reagents.—Acetyl peroxide was prepared as described in previous papers of this series.⁵ *n*-Butyl chloride, Eastman Kodak Co. pure grade, was redistilled through a Vigreux column (b.p. 78.5° (740 mm.), n_{20}^D 1.4021). Eastman Kodak Co. *s*-butyl chloride was redistilled (b.p. 68°, n_{20}^D 1.3970). *s*-Heptyl chloride (Columbia Organic Chemicals Co.) was carefully fractionated; its physical constants agreed with those recorded for 2-chloroheptane⁸ (b.p. 45–46° (20.0 mm.), n_{20}^D 1.4221). *t*-Amyl chloride was prepared from *t*-amyl alcohol by the method described in "Organic Syntheses"⁷ (b.p. 84–86°, n_{20}^D 1.4053). Ethylene chloride, Eastman Kodak Co. technical grade, was distilled through a Vigreux column (b.p. 84°, n_{20}^D 1.4442). Eastman Kodak Co. pure grade propylene chloride was redistilled (b.p. 96°, n_{20}^D 1.4386). Tetramethylene chloride (du Pont) had the following constants: b.p. 155° (740 mm.), n_{20}^D 1.4542. Pentamethylene chloride (du Pont) was redistilled through a Vigreux column (b.p. 178°, n_{20}^D 1.4563).

Procedure.—A solution of acetyl peroxide in aliphatic chloride was added dropwise through a capillary tube with a sub-surface outlet to an excess of chloride contained in a 500-cc. flask heated by an oil-bath. The gaseous and low-boiling products passed through a reflux condenser and then through a train consisting of a cold trap kept at –10° and two traps immersed in a Dry Ice-acetone-bath. To determine the amount of hydrogen chloride and carbon dioxide formed in the reaction uncondensed gases were passed through one U-tube filled with Michler ketone and two U-tubes containing ascarite. The unabsorbed gas was collected in a pneumatic trough.

Decomposition of Acetyl Peroxide in *n*-Butyl Chloride.—Forty-eight grams (0.407 mole) of acetyl peroxide, dissolved in 70 g. (0.757 mole) of *n*-butyl chloride, was added dropwise to 304 g. (3.3 moles) of refluxing *n*-butyl chloride. The addition required 5 hours; after 15 hours there was no further evolution of gas, and the test for peroxides was negative. Carbon dioxide (31.2 g., 0.71 mole) and crude methane (12.5 l., 0.558 mole) were collected in the usual manner. The gas collected in the pneumatic trough had an apparent molecular weight of 16.9 (calcd. for CH_4 , 16.0). The crude methane was condensed in the vacuum line at the temperature of liquid nitrogen and fractionated under reduced pressure at this temperature. The residual gas has a molecular weight of 48.0 (calcd. for CH_3Cl , 50.5), and showed the vapor pressure of methyl chloride contaminated with a small amount of ethane. The amount of methyl chloride was approximately 1.2 g.

Material distilled from the liquid reaction mixture up to

the boiling point of *n*-butyl chloride was combined with the liquid condensed in the cold traps. Distillation of this volatile mixture through a Fenske column packed with glass helices gave the following fractions: fraction 1, –60 to –5°, 1.1 g.; fraction 2, –5 to 10°, 0.4 g.; fraction 3, 30–35°, n_{20}^D 1.3552, 2.3 g.; fraction 4, 55–58°, n_{20}^D 1.3588, 0.6 g.; fraction 5, 73–74°, n_{20}^D 1.3990, 2 g.

Fraction 1, a gas at room temperature, gave a positive Beilstein test for halogen, had an apparent molecular weight of 49.0 (calcd. for CH_3Cl , 50.5), and a vapor pressure of 420 mm. at –40° (recorded⁸ for CH_3Cl , 400 mm. at –40°). The total amount of methyl chloride isolated, therefore, was about 2.3 g. (0.045 mole).

Fraction 2, apparent molecular weight 56.5 (calcd. for C_4H_{10} , 56.0), was butene containing some butane. A bromine addition product was prepared, but the amount was too small to permit separation and identification of isomers.

Fraction 3 had an apparent molecular weight of 70.5, and a vapor pressure of 230 mm. at 2°. It was identified by its physical constants as *n*-pentane (b.p. 36.3°, n_{20}^D 1.3470; mol. wt. 72.0; recorded vapor pressure⁸ 200 mm. at 1.9°).

Tentative identification of fraction 4 as methyl acetate (b.p. 57.1°, n 1.35935) was confirmed by conversion to the hydroxamic acid.⁹

Fraction 5 was recovered *n*-butyl chloride (b.p. 78°, n 1.4015).

The more volatile portion of the main liquid reaction mixture, found to be free of hydrogen chloride, was extracted with water to remove acetic acid. The amount of acid, determined by titration, was 2.9 g. (0.05 mole). The remaining liquid, distilled through a Vigreux column, yielded the following fractions: fraction 6, 74–75°, n_{20}^D 1.4020; fraction 7, 42–47° (24 mm.), n_{20}^D 1.4170, 1.2 g.; fraction 8, 37–42° (10 mm.), n_{20}^D 1.4231, 4.0 g.; dark-brown residue.

Fraction 6 was recovered *n*-butyl chloride.

Fraction 7, b.p. 115° (740 mm.), apparent mol. wt. 126.5, contained some butyl acetate that could not be separated by distillation. The chlorine analysis suggested the presence of 1,1-dichlorobutane (b.p. 113–115°, mol. wt. 127.0).

Fraction 8 gave the usual qualitative ester reactions, and, when treated in pyridine with 3,5-dinitrobenzoyl chloride, yielded *n*-butyl 3,5-dinitrobenzoate, m.p. 62.0–63.5°, identical with an authentic sample. It was thus identified as butyl acetate.

The dark-brown residue remaining from this distillation was transferred to a Claisen flask and distilled at 11 mm.; it yielded the following fractions: fraction 9, 82–90°, n_{20}^D 1.4526, apparent mol. wt. 179, 1.9 g.; fraction 10, 90–95°, n_{20}^D 1.4580, apparent mol. wt. 182, 3.8 g.; fraction 11, 95–97°, n_{20}^D 1.4595, 8.5 g.; fraction 12, 97–97.5°, n_{20}^D 1.4610, apparent mol. wt. 184, 4.4 g.; tarry residue, 6 g. As was subsequently shown by degradation, fractions 9–12 (aggregating 18.6 g.) consisted of 4,5-dichlorooctane, and were undoubtedly mixtures of the *meso* and racemic forms.

Anal. Calcd. for $\text{C}_8\text{H}_{16}\text{Cl}_2$: Cl, 38.7; mol. wt., 183.0. Found: Cl, 38.5; mol. wt., 182.5.

The black, tarry distillation residue was dissolved in ligroin and filtered through a column of activated alumina. The slightly yellowish oil remaining upon removal of the ligroin had an apparent molecular weight of 300.0, and showed slight unsaturation when tested with bromine solution.

Degradation of the *n*-Butyl Chloride "Dimer" (4,5-Dichlorooctane).—To 4.1 g. of the dimer, dissolved in 10 cc. of anhydrous ether, was added 1.5 g. of magnesium turnings, and the mixture refluxed for 5 hours, at the end of which time the ethereal solution was decanted onto powdered Dry Ice. The ethereal solution was extracted with sodium bicarbonate solution, which was then acidified, saturated with ammonium sulfate, and extracted with ether. The ethereal extract was dried over anhydrous sodium sulfate and the solvent removed. The thick, oily residue (100 mg.) could not be induced to crystallize and was not further investigated.

The non-acidic portion of the reaction mixture was dried and distilled, yielding a fraction (1.4 g.) boiling at 121–124° under atmospheric pressure and a small amount of recovered "dimer" (b.p. 85–95° (11 mm.)). The lighter distillate (presumably 4-octene in 79% yield) was dissolved in an-

(4) All melting points were determined in a Thiele apparatus and are uncorrected. Apparent molecular weights of liquid and solid samples were determined by the cryoscopic method in benzene.

(5) Kharasch, McBay and Urry, *J. Org. Chem.*, **10**, 394 (1945).

(6) Sherrill, *This Journal*, **52**, 1985 (1930).

(7) "Organic Syntheses." Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 2nd ed., 1941, p. 144.

(8) Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

(9) Davidson, *J. Chem. Education*, **17**, 81 (1940).

hydrous ethyl acetate and was ozonized for 9 minutes at -80° . The ethyl acetate was removed under reduced pressure and the oily ozonide was decomposed by heating with water for 30 minutes. The water solution had the characteristic odor of *n*-butyraldehyde. When treated with 2,4-dinitrophenylhydrazine, it yielded 3.8 g. (62%) of the 2,4-dinitrophenylhydrazone of *n*-butyraldehyde (m.p. 122–123°). The melting point was not depressed by admixture of the product with an authentic sample. The "dimer" (fractions 9–12), therefore consisted essentially of 4,5-dichlorooctane, contaminated with only very small amounts of materials that react with magnesium to form Grignard reagents or cyclopropane derivatives (see reaction series 1 under identification of "Dimers.")

Decomposition of Acetyl Peroxide in Ethylene Chloride.—Acetyl peroxide (46.0 g., 0.39 mole), dissolved in ethylene chloride (69.0 g., 0.70 mole), was added gradually over a period of 3.5 hours to an excess (240.0 g., 2.42 moles) of the chloride maintained at reflux temperature. Gas evolution was complete in 5 hours. Carbon dioxide (25.1 g., 0.57 mole) and methane (12.0 l., 0.54 mole) were collected, and the methane was identified by molecular-weight determination (calcd. for CH_4 , 16.0; found, 17.2). When warmed to room temperature, about five drops of the cold-trap content distilled into a second cold trap. This material gave a positive Beilstein test for halogen, and had an apparent molecular weight of 45.0. Vapor pressure measurements seemed to indicate a mixture of methyl chloride and ethane. The remainder of the cold-trap content was separated by distillation through a small Fenske column packed with glass helices into two fractions: fraction 1, b.p. 55–57°, 2.1 g. (methyl acetate, identified by conversion to the hydroxamic acid⁹); fraction 2, b.p. 82–84°, n_{D}^{20} 1.4440 (recovered ethylene chloride).

The more volatile portion of the main liquid reaction mixture was separated by room-temperature distillation at 10 mm. The distillate was extracted with water, and acetic acid (5.5 g.) was determined by titration of the water layer, which was found to contain no more than traces of hydrochloric acid. The sodium sulfate-dried distillate, redistilled through a Vigreux column, yielded fraction 3, b.p. 82.5–84°, n_{D}^{20} 1.4441 (recovered ethylene chloride). The yellow oil remaining from the room-temperature distillation (36.0 g.) was further distilled at reduced pressure, yielding: fraction 4, 40–65° (10 mm.), 5.0 g.; fraction 5, 65–95° (10 mm.) 22.0 g.; fraction 6, 75–84° (0.01 mm.), 2.5 g.; residue (tar), 6.0 g.

Fraction 4, redistilled through a Fenske column at atmospheric pressure, yielded about 1.0 g. of material, b.p. 90–95°, which contained chlorine, and which reacted with hydroxylamine, but was not further investigated.

Fraction 5 underwent partial crystallization upon standing for a few hours. The mixture was triturated with ligroin and was stored at 0° for several days. The solid material (8.5 g.) was separated by filtration and recrystallized from ligroin (m.p. 72.5°). There was no depression in melting point when the material was mixed with an authentic sample of the solid isomer of 1,2,3,4-tetrachlorobutane¹⁰ (mol. wt. calcd. for $\text{C}_4\text{H}_6\text{Cl}_4$: 196.0; found, 195.0).

Ligroin was distilled from the filtrate on the steam-bath, and the remaining liquid was distilled from a Claisen flask at 40 mm. (108–114°, n_{D}^{20} 1.5022,¹¹ 12.5 g.).

Anal. Calcd. for $\text{C}_4\text{H}_6\text{Cl}_4$: Cl, 72.4; mol. wt., 196.0. Found: Cl, 72.1; mol. wt., 194.0.

The material was, therefore, identified as the liquid isomer of 1,2,3,4-tetrachlorobutane.

Fraction 6, tentatively regarded as the "trimer" of ethylene chloride (1,2,3,4,5,6-hexachlorohexane), was distilled from a Hickman flask attached to a vacuum line at ca. 0.001 mm. at an oil-bath temperature of 80–84°.

Anal. Calcd. for $\text{C}_6\text{H}_8\text{Cl}_6$: Cl, 72.7; mol. wt., 292.0. Found: Cl, 72.5; mol. wt., 289.0.

The brown, tarry residue from the original distillation was dissolved in a 2:1 ligroin-benzene mixture and filtered through a column of activated alumina. The yellowish oil remaining upon removal of the solvent had an apparent molecular weight of 342.0.

Decomposition of Acetyl Peroxide in Tetramethylene Chloride.—Acetyl peroxide (40.0 g., 0.34 mole), dissolved in

63.0 g. (0.50 mole) of tetramethylene chloride, was added gradually over a period of 4 hours to an excess (287.0 g., 2.26 moles) of the chloride maintained at 85°. Carbon dioxide (17.7 g., 0.40 mole) and methane (9.0 l., 0.40 mole) were isolated and determined in the usual manner. The cold-trap content was distilled through a small helix-packed column, yielding the following fractions: fraction 1, 20°, 0.1 g.; fraction 2, 55–62°, n_{D}^{20} 1.3589, 3.0 g.; fraction 3, 62–104°, 0.5 g.; fraction 4, 105–155°, 0.2 g.; fraction 5, 155–156°, n_{D}^{20} 1.4539, 3.9 g. The low boiling point and a positive Beilstein test indicate that fraction 1 contains traces of methyl chloride.

Fraction 2 was identified as methyl acetate (b.p. 57.1°, n 1.35935) by preparation from it of acetoxyhydroxamic acid⁹ and methyl 3,5-dinitrobenzoate.

Fractions 3 and 4 were discarded. Fraction 5 consists of recovered tetramethylene chloride.

The more volatile portion of the main reaction mixture was removed under reduced pressure (10 mm.) at about 40°. A water extract of the distillate showed only traces of hydrochloric acid; acetic acid (4.6 g.) was determined by titration with 2 *N* sodium hydroxide solution. The dried, redistilled distillate proved to be essentially recovered tetramethylene chloride, n_{D}^{20} 1.4538. No unsaturated products could be detected with bromine solution. The brown oil that constituted the less volatile portion of the main reaction mixture was distilled from a Claisen flask, 80–108° (0.5 mm.), 27.0 g. Redistillation then yielded the following fractions: fraction 6, 85–88° (0.3 mm.), n_{D}^{20} 1.4900; fraction 7, 88–92° (0.3 mm.), n_{D}^{20} 1.4935, apparent mol. wt. 246, 3.0 g.; fraction 8, 92–96° (0.3 mm.), n_{D}^{20} 1.4940, 15.0 g.; fraction 9, 96° (0.3 mm.), n_{D}^{20} 1.4990, 8.0 g.

Fractions 6–9 are believed to consist essentially of 1,4,5,8-tetrachlorooctanes; the range in boiling points and refractive indices is attributed to varying relative concentrations of the *meso* and racemic forms.

Anal. Calcd. for $\text{C}_8\text{H}_{12}\text{Cl}_4$: Cl, 56.3; mol. wt., 252.0. Found (fraction 8): Cl, 56.2; mol. wt., 247.0.

The dark-brown, resinous residues from the low-pressure distillations (aggregating 16.0 g.) were dissolved in a 2:1 ligroin-benzene mixture and filtered through a column of activated alumina. The yellow oil remaining upon removal of the solvent had an apparent molecular weight of 384.0.

Degradation of the Tetramethylene Chloride "Dimer"

(1,4,5,8-Tetrachlorooctane).—To fraction 9 of the dimer (8.0 g.), dissolved in glacial acetic acid and heated to reflux temperature, was added in five equal portions a total of 35.0 g. of silver acetate. After 72 hours the insoluble silver salts were filtered from the cooled solution and acetic acid was removed under reduced pressure. The residue was taken up in ether and the ether solution extracted with 2 *N* sodium hydroxide solution and then dried over sodium sulfate. After distillation of the ether, the oily residue was refluxed for 12 hours with 50 cc. of a 10% barium hydroxide-methanol mixture. Excess barium hydroxide was then precipitated with carbon dioxide and the mixture cooled to 0° and centrifuged. After removal of the methanol under reduced pressure at room temperature, the residue was taken up in ether, which was then extracted with water. Upon evaporation of the water layer there remained 4.2 g. (68%) of a white amorphous solid (1,4,5,8-tetrahydroxyoctane), which was not further purified.

To the 1,4,5,8-tetrahydroxyoctane (4.2 g.), dissolved in 20 cc. of acetic acid, was added 12.0 g. of lead tetraacetate. After 24 hours the excess reagent was decomposed by the addition of 20 cc. of hot water; lead dioxide was removed by centrifugation. The γ -hydroxybutyraldehyde resulting from the lead tetraacetate oxidation was further oxidized by the addition of 2 g. of chromic acid (CrO_3) to the aqueous acetic acid solution. After 10 hours excess reagent was decomposed by the addition of a few drops of methanol. The solution was then saturated and extracted with ether in a continuous extractor for 24 hours. The ether solution was dried, and ether and acetic acid were removed by distillation. The amorphous residue (succinic acid) was crystallized from water, m.p. 186–187°, 3.5 g. (63% on the basis of tetrahydroxyoctane). Admixture did not depress the melting point of an authentic sample of succinic acid.

The foregoing degradation thus identifies the "dimer" of tetramethylene chloride as 1,4,5,8-tetrachlorooctane (see reaction series 2 under Identification of "Dimers").

(10) Firestone Tire and Rubber Co. sample.

(11) Firestone Tire and Rubber Co. sample of the liquid isomer of 1,2,3,4-tetrachlorobutane, n_{D}^{20} 1.5018.

Decomposition of Acetyl Peroxide in Pentamethylene Chloride.—Acetyl peroxide (35.0 g., 0.30 mole), dissolved in 70 g. (0.50 mole) of pentamethylene chloride was added gradually over a period of 3 hours to excess (139.0 g., 1.98 moles) chloride maintained at 85°; gas evolution ceased within two hours. Carbon dioxide (19.1 g., 0.43 mole), methane (9.3 l., 0.42 mole), methyl acetate (3.5 g., 0.05 mole) and acetic acid (2.3 g., 0.04 mole) were isolated and identified in the usual manner. A trace of methyl chloride was detected, and excess starting chloride was recovered as previously described. The main portion of the liquid reaction mixture (non-volatile at 70° (15 mm.)) was distilled from a Claisen flask, and yielded the following fractions: fraction 1, 89–92° (0.01 mm.), apparent mol. wt. 267.0, 3.0 g.; fraction 2, 92–110° (0.01 mm.), 3.5 g.; fraction 3, 110° (0.01 mm.), n_D^{20} 1.4880, apparent mol. wt. 274.0, 5.0 g.; fraction 4, 110–112° (0.01 mm.), n_D^{20} 1.4922, apparent mol. wt. 276, 7.0 g. All fractions consist essentially of the "dimer" of pentamethylene chloride. The boiling range is attributable to the presence of *meso* and racemic forms.

Anal. Calcd. for $C_{10}H_{18}Cl_4$: Cl, 51.8; mol. wt., 274. Found (fraction 3); Cl, 51.5; mol. wt., 280.

The tarry residue was dissolved in 20 cc. of a 2:1 ligroin-benzene solution and filtered through a column of activated alumina. The yellow oil remaining upon evaporation of the solvent had an apparent molecular weight of 405.0 (calcd. for "trimer," 420.0).

Degradation of the Pentamethylene Chloride "Dimer" (1,5,6,10-Tetrachlorodecane).—A 7.0-g. sample of the "dimer" was treated with 30.0 g. of silver acetate as described for the tetramethylene chloride "dimer." The resultant tetraacetoxy compound was hydrolyzed with 10% methanolic barium hydroxide. The resultant tetrahydroxy compound (3.5 g., 66.8%) was dissolved in 20 cc. of acetic acid and oxidized with 10.0 g. of lead tetraacetate. After 24 hours excess reagent was decomposed with warm water; lead dioxide was removed by centrifugation and the solution evaporated under reduced pressure at room temperature. The resultant δ -hydroxyvaleraldehyde was taken up in methanol and converted to the 2,4-dinitrophenylhydrazone (6.6 g., 71.0%), which, after recrystallization from methanol, melted at 109.5–110°. The melting point was not depressed by admixture with an authentic sample of the 2,4-dinitrophenylhydrazone of δ -hydroxyvaleraldehyde prepared from dihydropyran by the method of Paul.¹²

Anal. Calcd. for $C_{11}H_{14}N_4O_6$: N, 19.9. Found: N, 19.7.

The "dimer" of pentamethylene chloride is thus identified as 1,5,6,10-tetrachlorodecane (see reaction series 3 under Identification of "Dimers").

Decomposition of Acetyl Peroxide in *s*-Butyl Chloride.—Acetyl peroxide (40.0 g., 0.34 mole), dissolved in 80.0 g. (0.87 mole) of *s*-butyl chloride, was added dropwise over a period of 8 hours to an excess (172.0 g., 1.86 moles) of chloride maintained at reflux temperature. After 20 hours gas evolution had virtually ceased and the reaction was assumed to be complete. Carbon dioxide (22.0 g., 0.50 mole) and methane (11.6 l., 0.52 mole) were isolated in the usual manner. About 500 mg. of methyl chloride and a trace of ethane were separated from the methane fraction. The more volatile portion of the liquid reaction mixture (up to the boiling point of *s*-butyl chloride) was combined with the cold-trap content and the mixture was distilled through a helix-packed Fenske column, yielding the following fractions: fraction 1, –20 to 0°, 1.5 g.; fraction 2, 0–10°, 2.9 g.; fraction 3, 27–31°, 1.1 g.; fraction 4, 55–56.5°, 0.8 g.; fraction 5, 65–67°.

Fraction 1 was essentially methyl chloride; it had an apparent molecular weight of 48.5 (calcd. for CH_3Cl , 50.5) and vapor pressures of 420 mm. (–40°) and 215 mm. (–50°) (recorded⁸ for CH_3Cl , 400 mm. (–38°) and 200 mm. (–51°)). The total amount of methyl chloride isolated was 2.0 g. (0.04 mole).

Fraction 2 had the characteristic odor of the lower aliphatic hydrocarbons. The gas was passed repeatedly through bromine-carbon tetrachloride solution to remove olefins (ca. 70% of the mixture). The saturated hydrocarbon had an apparent molecular weight of 61.0 (calcd. for C_4H_{10} , 58.0) and a vapor pressure of 370 mm. (–15°) (recorded⁸ for *n*-butane, 400 mm. (16.3°)).

The bromide was recovered and distilled from a Hickman flask; b.p. 85° (50 mm.), 163° (740 mm.); n_D^{20} 1.5097. The physical constants indicate a mixture of the *meso* and racemic forms of 2,3-dibromobutane. The original product, therefore, must have been 2-butene.

Fraction 3 was redistilled; b.p. 28–31°, n_D^{20} 1.3542, mol. wt. 68.9, vapor pressure 460 mm. (10°). Literature and calculated values for isopentane: b.p. 27–31°, n_D^{20} 1.3548, mol. wt. 72.0, vapor pressure⁸ 400 mm. (10.5°).

Fraction 4 was identified as methyl acetate.

Fraction 5 was recovered *s*-butyl chloride.

The less volatile portion of the liquid reaction mixture was extracted with water and acetic acid (4.4 g., 0.07 mole) was determined by titration. The remaining reaction mixture was freed of a trace of residual acetyl peroxide by shaking with 20 cc. of a saturated aqueous ferrous sulfate solution acidified with a few drops of sulfuric acid. After drying it was distilled through a Vigreux column, yielding the following fractions: fraction 6, 67–68°, n_D^{20} 1.4220; fraction 7, 95–110° 1.6 g.; dark-brown residue.

Fraction 6 was recovered *s*-butyl chloride.

Fraction 7 was redistilled, most of it passing over at 109–112°; mol. wt. 130.0; n_D^{20} 1.4381. Literature and calculated constants for *DL*-2,3-dichlorobutane: b.p. 112–114°, 115–120°; mol. wt. 127.0; *n* 1.4400.

Anal. Calcd. for $C_4H_8Cl_2$: Cl, 55.8. Found: Cl, 55.8.

Hydrolysis with 60% sulfuric acid yielded no ketonic material; 2,2-dichlorobutane is therefore absent. The dark-brown residue remaining from the preceding distillation was distilled from a Claisen flask yielding the following fractions: fraction 8, 65–70° (10.0 mm.), n_D^{20} 1.4662, 2.5 g.; fraction 9, 70–72° (10.0 mm.), n_D^{20} 1.4672, 8.0 g.; fraction 10, 72–76° (10.0 mm.), n_D^{20} 1.4695 1.5 g.; black tarry residue, 7.0 g.

Fractions 8–10 (12.0 g.) consisted of mixtures of the *meso* and racemic forms of 3,4-dichloro-3,4-dimethylhexane. Fraction 9 was redistilled from a Hickman flask and analyzed.

Anal. Calcd. for $C_8H_{16}Cl_2$: Cl, 38.7; mol. wt., 182.0. Found: Cl, 38.3; mol. wt., 185.0.

The residual black tar was dissolved in ligroin and filtered through a column of activated alumina. The yellow oil remaining after solvent removal had an apparent molecular weight of 271.0.

Degradation of the *s*-Butyl Chloride "Dimer" (3,4-Dichloro-3,4-dimethylhexane).—Four grams of the "dimer" were treated with magnesium turnings in 30 cc. of ether. The procedure followed in the isolation of products was the same as that described for the *n*-butyl chloride dimer. The amount of acidic material isolated subsequent to carbonation did not exceed 100 mg. The olefin (1.9 g., 75.0%) distilled at 112–115° (740 mm.). A 0.9-g. sample, dissolved in 40 cc. of anhydrous ethyl acetate, was ozonized for ten minutes at –80°. Upon hydrolysis of the ozonide and treatment of the product with 2,4-dinitrophenylhydrazine a hydrazone melting at 115–117° was obtained (1.9 g., 49.0%). No depression of melting point resulted from admixture with an authentic sample of the 2,4-dinitrophenylhydrazone of methyl ethyl ketone. The olefin, therefore, is 3,4-dimethyl-3-hexene and the "dimer" is thus identified as 3,4-dichloro-3,4-dimethylhexane (see reaction series 4 under Identification of "Dimers").

Decomposition of Acetyl Peroxide in *s*-Heptyl Chloride.—Acetyl peroxide (34.0 g., 0.29 mole), dissolved in 60.0 g. (0.45 mole) of *s*-heptyl chloride was added dropwise over a period of 5 hours to an excess (214.0 g., 1.59 moles) of the chloride maintained at 85°; decomposition of the peroxide was complete in eight hours. Carbon dioxide (18.9 g., 0.43 mole) and methane (9.5 l., 0.43 mole) were isolated in the usual manner. A small amount (ca. 300 mg.) of a gas having the physical constants of a mixture of ethane and methyl chloride and giving a positive Beilstein test was separated from the methane fraction. The cold-trap content was distilled through a helix-packed Fenske column; fraction 1, 52–55°, n_D^{20} 1.3588, 2.1 g.; fraction 2, 58–80°, 0.3 g.

Fraction 1 was identified as methyl acetate; fraction 2 was not further investigated.

The main portion of the liquid reaction mixture was extracted with water and acetic acid was determined by titration (3.0 g., 0.05 mole). The dried organic layer was distilled from a Claisen flask and the distillate was fraction-

(12) Paul, *Bull. soc. chim.*, [5] 1, 971 (1934).

ated with the aid of a Vigreux column: fraction 3, 90–95°, n_{20}^D 1.4020, 3.6 g.; fraction 4, 86–89° (104 mm.), n_{20}^D 1.4230; fraction 5, 62–64° (12.0 mm.), n_{20}^D 1.4470, 0.7 g.; fraction 6, 65–67° (15.0 mm.), n_{20}^D 1.4470, 0.7 g.; fraction 7, 75–78° (15.0 mm.), n_{20}^D 1.4468.

Fraction 3 revealed unsaturation when tested with bromine solution. The index of refraction suggested a 2-heptene (the literature value for a *cis-trans* mixture of unspecified composition is n_{20}^D 1.4040). A 0.5-g. sample of the material, dissolved in carbon tetrachloride, was ozonized at 0° for 10 minutes. Water (20 cc.) was added, and the mixture was refluxed for 40 minutes. The water layer was separated and treated with a hot saturated aqueous solution of methone. The precipitate, crystallized from ethanol, melted at 138° and upon admixture did not depress the melting point of an authentic sample of the methone derivative of acetaldehyde.

The carbon tetrachloride layer was evaporated and the residue treated with 2,4-dinitrophenylhydrazine. The melting point of the derivative (97–100°) was not depressed upon admixture with an authentic sample of the 2,4-dinitrophenylhydrazone of valeraldehyde. The ozonization products, acetaldehyde and valeraldehyde, establish the presence of 2-heptene in the reaction mixture.

Fraction 4 was recovered *s*-heptyl chloride; the transition fraction 5 was discarded.

Fraction 6, b.p. 75–78° (25 mm.), n_{20}^D 1.4495, apparent mol. wt. 165, is probably a mixture of 1,2-dichloroheptane¹³ and 2,3-dichloroheptane. Hydrolysis yielded no ketonic material; hence 2,2-dichloroheptane is absent.

Fraction 7 was too small for thorough investigation. A positive hydroxamic acid test⁹ makes the presence of *s*-heptyl acetate probable.

The black residue from the preceding distillation was fractionated at low pressure: fraction 8, 45–60° (0.03 mm.), 2.8 g.; fraction 9, 60–66° (0.03 mm.), n_{20}^D 1.4608, mol. wt. 267, 3.0 g.; fraction 10, 66–76° (0.03 mm.), n_{20}^D 1.4670, 9.5 g.; fraction 11, 76–80° (0.03 mm.), n_{20}^D 1.4688, 1.1 g.; black tar, 15.0 g.

Fraction 8, a mixture of unknown composition, was not investigated. As was subsequently established by degradation, fractions 9–11 consist of mixtures of the *meso* and racemic forms of 6,7-dichloro-6,7-dimethyldodecane. Fraction 10 was redistilled and analyzed.

Anal. Calcd. for $C_{14}H_{28}Cl_2$: Cl, 26.6; mol. wt., 267.0. Found: Cl, 26.3; mol. wt., 270.0.

The tarry residue was dissolved in ligroin and filtered through a column of activated alumina. The yellow oil remaining after solvent evaporation had an apparent molecular weight of 455.0.

Degradation of the *s*-Heptyl Chloride "Dimer" (6,7-Dichloro-6,7-dimethyldodecane).—A 3.9-g. sample of the "dimer," dissolved in 20 cc. of ether, was treated with 0.7 g. of magnesium turnings as described for the "dimer" of *n*-butyl chloride. The acidic products resulting from carbonylation of the reaction mixture did not exceed in amount 100 mg.

The neutral product was distilled: b.p. 115–120° (11.0 mm.), 2.0 g. (70%). The residue was recovered "dimer." A portion (1.1 g.) of the olefin, dissolved in 30 cc. of dry ethyl acetate, was ozonized for 11 minutes at –80°. The ketone was isolated in the usual way. The phenylhydrazone was oily; the semicarbazone, after four recrystallizations from methanol, melted at 125–127° (literature¹⁴ value for the melting point of the semicarbazone of 2-heptanone, 127°). The "dimer" is thus shown to consist essentially of the *meso* and racemic forms of 6,7-dichloro-6,7-dimethyldodecane (see reaction series 5 under Identification of "Dimers").

Decomposition of Acetyl Peroxide in Propylene Chloride.—Acetyl peroxide (32.5 g., 0.28 mole), dissolved in 60.0 g. (0.53 mole) of propylene chloride, was added gradually to an excess (97.0 g., 0.86 mole) of the chloride maintained at 80°. Carbon dioxide (17.9 g., 0.41 mole) and methane (9.2 g., 0.41 mole) were isolated in the usual way. Upon warming to room temperature the cold-trap content yielded 1.1 g. (0.02 mole) of methyl chloride. The remaining cold-trap material was further distilled through a helix-packed column, yielding the following fractions: fraction 1, 30–

40°, 2.4 g.; fraction 2, 51–55°, n_{20}^D 1.3587, 2.6 g.; fraction 3, 60–70°, n_{20}^D 1.3958, 1.1 g.

Fraction 1 gave a positive Beilstein test and decolorized bromine-carbon tetrachloride solution. The material was brominated in carbon tetrachloride at –20°. After removal of the solvent the bromination product was distilled from a Hickman flask: b.p. 110° (76 mm.), 177° (740 mm.); n_{20}^D 1.5398; mol. wt., 236.0. The physical constants agree with those recorded for 1-chloro-1,2-dibromopropane; fraction 1, therefore, consists essentially of 1-chloropropene (b.p. 35–36°) as its distillation range suggests.

Fraction 2 had the odor of methyl acetate and this tentative identification was confirmed by preparation of the hydroxamic acid⁹ and of methyl 3,5-dinitrobenzoate.

The refractive index of fraction 3 is in close agreement with that reported for isobutyl chloride (b.p. 68.0°, n 1.3960). For identification the material was refluxed in methanol with sodium 3,5-dinitrobenzoate and thus converted to isobutyl 3,5-dinitrobenzoate, m.p. 84.5–86° (lit. m.p. 86°). The more volatile portion of the main liquid reaction mixture was removed under reduced pressure at 35° and extracted with water. Acetic acid (4.45 g., 0.07 mole) was determined by titration of the water layer. The organic layer was dried and redistilled through a Vigreux column: fraction 4, 94.5–96°, n_{20}^D 1.4385; fraction 5, 74–82° (200 mm.), 5.0 g.

Fraction 4 consists of recovered propylene chloride. Fraction 5 was redistilled b.p. 120–123°, n_{20}^D 1.4610. The boiling point agrees with that reported for 1,1,2-trichloropropane¹⁵; the isomeric 1,2,2-trichloropropane is higher-boiling (135°).¹⁶ On treatment of the compound with hydrochloric acid and 2,4-dinitrophenylhydrazine the osazone of methylglyoxal (CH_3COCHO) was obtained.

Anal. Calcd. for $C_3H_5Cl_3$: Cl, 72.1; mol. wt., 147.0. Found: Cl, 71.9; mol. wt., 143.0.

The less volatile portion of the main liquid reaction mixture was distilled from a Claisen flask: fraction 6, 46–50° (0.03 mm.), n_{20}^D 1.4989, 2.0 g.; fraction 7, 50–54° (0.03 mm.), n_{20}^D 1.5028, 5.0 g.; fraction 8, 54° (0.03 mm.), n_{20}^D 1.5055, 10.0 g.; fraction 9, 54–55°, n_{20}^D 1.5073, 2.0 g.; black tarry residue, 8.0 g.

Fractions 6–9 consist of mixtures of the *meso* and racemic forms of 1,2,3,4-tetrachloro-2,3-dimethylbutane, as was subsequently shown by degradation experiments.

Anal. Calcd. for $C_6H_{10}Cl_4$: Cl, 63.3; mol. wt., 224.0. Found: Cl, 63.0; mol. wt., 229.0.

The tarry residue was dissolved in 2:1 ligroin-benzene solution and filtered through a column of activated alumina. The yellow oil remaining upon solvent removal had an apparent molecular weight of 396.0.

Degradation of the Propylene Chloride "Dimer" (1,2,3,4-Tetrachloro-3,4-dimethylbutane).—A 4.5-g. sample of the "dimer" in 20 cc. of ethanol was refluxed with 2.1 g. (2 equiv.) of potassium hydroxide for 30 minutes. Precipitated potassium chloride was removed by filtration; the filtrate was freed from ethanol and the residue dissolved in 30 cc. of ethyl acetate and filtered through a column of anhydrous sodium sulfate. The solution was diluted with an additional 70 cc. of ethyl acetate and ozonized at –60°. Ethyl acetate was removed under reduced pressure and the residue decomposed by boiling with water for 20 minutes. Ether was added to the mixture, the layers separated and the ether layer extracted repeatedly with small portions of water. The combined aqueous portions yielded a 2,4-dinitrophenylhydrazone which melted at 303–304° in an evacuated tube (5.5 g., 60.0%). Upon admixture with the osazone of methylglyoxal there was no depression in melting point. In one experiment the 2,4-dinitrophenylhydrazone of hydroxyacetone (m.p. 127°) was isolated. In an experiment employing four equivalents of potassium hydroxide for the hydrolysis only the derivative of methylglyoxal was obtained. No ozonization products other than these were detected. The "dimer" is necessarily a 2,3-dimethylbutane, and, therefore, 1,2,3,4-tetrachloro-2,3-dimethylbutane (see reaction series 6 under Identification of "Dimers").

Decomposition of Acetyl Peroxide in *t*-Amyl Chloride.—Acetyl peroxide (46.7 g., 0.40 mole), dissolved in 60.0 g.

(13) Bachmann and Hill, *THIS JOURNAL*, **56**, 2730 (1934), report for 1,2-dichloroheptane n_{20}^D 1.4490.

(14) Michael, *ibid.*, **41**, 417 (1919).

(15) Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 700.

(16) Kharasch and Brown, *THIS JOURNAL*, **61**, 2145 (1939).

(0.51 mole) of *t*-amyl chloride, was added gradually to an excess (277.0 g., 2.60 moles) of the chloride maintained at 85°. Carbon dioxide (26.9 g., 0.61 mole) and methane (14.1 l., 0.51 mole) were isolated in the usual way. The methane contained a trace of methyl chloride, which, however, was not isolated. About 100 mg. of hydrogen chloride was also isolated. The more volatile portion (up to the boiling point of *t*-amyl chloride) of the liquid reaction mixture was removed by distillation and combined with the cold-trap content. The volatile mixture was then distilled through a helix-packed Fenske column: fraction 1, 31–40°, 7.5 g.; fraction 2, 48–57°, n_D^{20} 1.3611, 3.0 g.; fraction 3, 83–85°, n_D^{20} 1.4051.

Fraction 1 was chlorine-free; the boiling range suggested the presence of isoamylene. A 1.5-g. sample, dissolved in carbon tetrachloride (30 cc.), was ozonized at –10°. The effluent gases were washed with water to extract any lower aldehydes formed in the reaction. Addition of a saturated methone solution to the wash-water caused an immediate separation of crystalline material, which, thrice recrystallized from methanol, melted at 187–188°. Admixture with an authentic sample of the methone derivative of formaldehyde did not depress the melting point.

Concentration of the aqueous mother liquor yielded a derivative which, after repeated crystallization, melted at 138–139.5°. There was no depression of melting point upon admixture with an authentic sample of the methane derivative of acetaldehyde. Solvent was removed from the liquid ozonization mixture under reduced pressure and the ozonide was decomposed by boiling with water. After extraction with ether the aqueous solution, upon treatment with 2,4-dinitrophenylhydrazine, yielded a derivative melting at 126°. There was no depression of melting point upon admixture with an authentic sample of the 2,4-dinitrophenylhydrazone of acetone. Three successive water extracts of the ether yielded further quantities of the acetone derivative. From the fifth and sixth water extracts a 2,4-dinitrophenylhydrazone (m.p. 115–116°), identified as that of 2-butanone, was obtained. The ozonization products and the relative quantities in which they are formed, indicate that fraction 1 is a mixture of about one part of 2-methyl-1-butene with about three parts of 2-methyl-2-butene.

Fraction 2 was identified as methyl acetate; fraction 3 is recovered *t*-amyl chloride.

The remaining liquid reaction mixture was partially distilled (up to 40° (10 mm.)), and the distillate was extracted with water. The water extract was titrated for acetic acid (3.5 g., 0.06 mole). The dried distillate was then redistilled through a Vigreux column: fraction 4, 83–86°, n_D^{20} 1.4054; fraction 5, 104–110°, n_D^{20} 1.4332, 1.5 g.; fraction 6, 110–112°, n_D^{20} 1.4380, mol. wt., 119.0, 3.0 g.; fraction 7, 112–113°, n_D^{20} 1.4410.

Fraction 4 consisted of *t*-amyl chloride; fraction 5, obviously a mixture, was discarded.

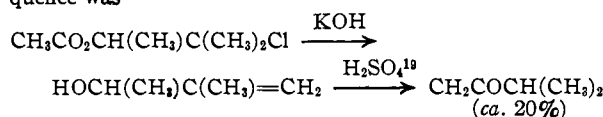
Fraction 6 and 7 have a boiling range close to the boiling point (112° (749 mm.)) reported¹⁷ for 2-chloro-2,3-dimethylbutane. A sample of the combined fractions was treated with bromine-carbon tetrachloride solution and illuminated. Solvent was removed under reduced pressure and the product was crystallized from ligroin (m.p. 171–173°). The recorded¹⁸ melting point of 2,3-dibromo-2,3-dimethylbutane is 173–174°. The yield of the bromination reaction was 82.0%.

The less volatile portions of the liquid reaction mixture was distilled through a Vigreux column at reduced pressure: fraction 8, 55–58° (15.0 mm.), 0.3 g.; fraction 9, 58–75° (15.0 mm.), 0.8 g.; fraction 10, 79–82° (15.0 mm.), 0.8 g.; fraction 11, 38–44° (0.1 mm.), n_D^{20} 1.4620, 2.8 g.; fraction 12, 44–50° (0.1 mm.), n_D^{20} 1.4670, 3.1 g.; fraction 13, 50–60° (0.1 mm.), n_D^{20} 1.4675, 5.0 g.; tarry residue, 3.0 g.

Fractions 8 and 9 were discarded.

Fraction 10 gave a positive ester test with hydroxylamine and had an apparent molecular weight of 156.0. The material, dissolved in 5 cc. of methanol, was refluxed with 1.5 g. of potassium hydroxide for 2 hours. The solution was then acidified with sulfuric acid and refluxed for another hour, when it was cooled, diluted with water, and extracted with ether. The residue obtained upon evaporation of the ether extract yielded the 2,4-dinitrophenylhydrazone of 3-

methyl-2-butanone (m.p. 117–117.5°). The reaction sequence was

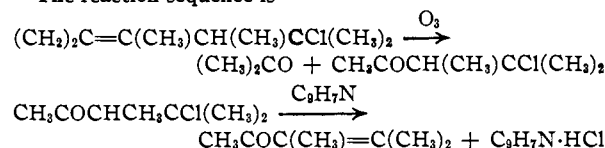


Fractions 11 and 12 gave a positive test for unsaturation with bromine and with tetranitromethane.

Anal. Calcd. for $\text{C}_{10}\text{H}_{19}\text{Cl}$: Cl, 20.3. Found: Cl, 20.5.

A 2.0-g. sample of the combined fractions, dissolved in 55 cc. of ethyl acetate, was ozonized at –60° for 10 minutes. The solvent was evaporated under reduced pressure and the residue boiled with water for 30 minutes. The cooled suspension was extracted with ether. The water layer yielded the 2,4-dinitrophenylhydrazone of acetone (m.p. 126°). The ether layer was dried and the ether evaporated. The residue, a colorless oil, contained chlorine and gave a positive methyl ketone test. It was mixed with 2 g. of quinoline in a small Hickman still and heated to 160°. The colorless, chlorine-free distillate yielded a semicarbazone melting at 185–186°, in agreement with the melting point recorded²⁰ for 2,3-dimethyl-2-penten-4-one (over-all yield 25%).

The reaction sequence is



Fractions 11 and 12, therefore, contained 2,3,4,5-tetramethyl-5-chloro-2-hexene. The corresponding saturated compound was probably present also, but could not be isolated in pure form.

Fraction 13 was saturated toward bromine and probably contained tertiary chlorine, for it reacted readily with alcoholic silver nitrate.

Anal. Calcd. for $\text{C}_{10}\text{H}_{20}\text{Cl}_2$: Cl, 33.6; mol. wt., 211.0. Found: Cl, 34.0; mol. wt., 215.0.

One gram of the material was refluxed for 8 hours with 10 cc. of dimethylaniline; the mixture was poured into water and the suspension extracted with ether. The ether layer was freed of dimethylaniline by washing with dilute hydrochloric acid and was then dried over sodium sulfate. The residue remaining upon evaporation of the ether was dissolved in ethyl acetate and ozonized at –60°. The water-insoluble product, isolated in the usual manner, yielded a dinitrophenylhydrazone melting at 316°, in agreement with the melting point reported for the derivative of biacetyl.

Fraction 13, therefore, consisted essentially of the "dimer" of *t*-amyl chloride, 2,5-dichloro-2,3,4,5-tetramethylhexane (see reaction series 7 under Identification of "Dimers").

The black tarry distillation residue (3.0 g.) was dissolved in ligroin and filtered through a column of activated alumina. The yellow oil remaining after solvent removal had an apparent molecular weight of 328.0.

Acknowledgment.—The authors are deeply indebted to Mr. Hyman Ratner for performing many experiments here described.

Summary

A study has been made of the products resulting from the thermal decomposition of acetyl peroxide in the following aliphatic chlorides: *n*-butyl, ethylene, tetramethylene, pentamethylene, *s*-butyl, *s*-heptyl, propylene and *t*-amyl. From a consideration of the respective reaction products and the relative quantities in which they are formed the following conclusions are drawn.

1. Among points of methyl-radical attack the following order of preference prevails: tertiary hydrogen > secondary hydrogen of the type $\text{RCH}_2\text{-Cl}$ (where R is alkyl) > secondary hydrogen of the

(17) Pawlow, *Ann.*, **196**, 124 (1879).

(18) Bartlett, Condon and Schneider, *THIS JOURNAL*, **66**, 1533 (1944).

(19) Kondakow, *J. Russ. Phys.-Chem. Soc.*, **1**, 290 (1885); *Ber.*, **18** Referate, 660 (1885).

(20) Bardhan, *J. Chem. Soc.*, 2614 (1928).

type $RR'CH_2$ (where R and R' are alkyl) > primary and secondary chlorine > tertiary chlorine and primary hydrogen.

2. Free radicals of the type $RCHCl\cdot$ (in which R is alkyl) are less reactive generally, less susceptible to disproportionation, and more inclined to dimerization than the corresponding free radicals of the type $RCH_2\cdot$.

3. Free radicals of the type $RR'CCl\cdot$ (in which R and R' are alkyl) are less reactive generally, less susceptible to disproportionation, and more inclined to dimerization than the corresponding free radicals of the type $RR'CH\cdot$.

4. A disproportionation reaction involving transfer of chlorine atoms has been described.

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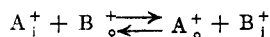
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Gibbs-Donnan Equilibria in Ion Exchange Resin Systems

BY HARRY P. GREGOR

Two phenomena are characteristic of ion exchange reactions. The first is that equivalent amounts of ions are exchanged; the second is that there is usually a selective uptake of one ion species over another. Many theories have been reported to account for these phenomena; there is an excellent review of the older literature by Griessbach.¹

The early attempts to formulate a theory were based on the law of mass action. For the cation exchange process



where the subscripts i and o refer to the exchange body phase and the external solution phases, respectively, the distribution constant K_D was defined as

$$K_D = (B^+/A^+)_i (A^+/B^+)_o \quad (1)$$

The terms in parentheses refer to concentrations. Experimental evidence showed, however, that in the case of univalent ions and in the absence of a chemical reaction K_D was not a constant for given ionic species, but varied for different concentration ratios in the external phase, for different absolute concentrations, and particularly for different ion exchange systems. Marshall and Gupta,² Jenny,³ and Boyd, Schubert and Adamson⁴ ascribed these variations in K_D with different experimental conditions as being entirely due to changes in the ratio of cationic activity coefficients within the exchange body phase, when activities rather than concentrations are used. This hypothesis was not confirmed by direct, independent experiment. The ratio of cationic activity coefficients was calculated only from experimental values of K_D .

Ion exchange was also considered as an adsorption process by Wiegner,⁵ Rothmund and Kornfeld,⁶ and others, who applied the Freundlich isotherm to the adsorption of the exchanging ion; the distribution constant K_D was

$$K_D = (X_B/X_A)_i (C_A^+/C_B^+)_o^p \quad (2)$$

(1) R. Griessbach, "Preparation and Applications of Ion Exchange Absorbents," Verlag Chemie, Berlin, 1939.

(2) C. E. Marshall and R. S. Gupta, *Soc. Chem. Ind.*, **52**, 433 (1933).

(3) H. Jenny, *J. Phys. Chem.*, **40**, 501 (1936).

(4) G. E. Boyd, J. Schubert and A. W. Adamson, *THIS JOURNAL*, **69**, 2818 (1947).

(5) G. Wiegner, *J. Landw.*, **60**, 1111 (1912).

(6) Rothmund and Kornfeld, *Z. anorg. u. allgem. Chem.*, **103**, 129 (1918).

where X refers to the mole fraction of the ion in the exchange body phase, and p is a parameter. Expression (2) fits the data somewhat better than does (1), and is useful as an empirical expression.

Vanselow⁷ treated exchange processes in terms of the formation of a complex between the movable ions and the exchange body. Other authors, notably Marshall and Gupta,² Anderegg and Lutz,⁸ and Mattson and Wiklander⁹ also considered the formation of associated compounds.

Mattson and Wiklander⁹ as well as Bauman and Eichhorn¹⁰ considered this phenomenon as being capable of representation as a Donnan equilibrium between the inner or exchange phase and the external solution. The expressions derived were identical with (1) except that activities were used.

Jenny³ derived expressions for ion exchange processes on the assumption that the exchanging ions oscillated in a volume element associated with each fixed exchange group, and the probability of finding a specific ion in a volume element was calculated statistically. The size of a volume element was assumed to be a function of the nature of the ion, of the surface, and of the surface forces. The final expressions reduced to (1) for univalent ions.

The theories of ion exchange outlined above require the introduction of empirical parameters or the use of parameters which can be defined only in terms of the exchange system itself. The thermodynamic theory of ion exchange outlined in a note by Gregor¹¹ is an attempt to predict the behavior of various ion exchange systems from well-defined physical properties of the system, which properties are measurable apart from the ion exchange process. This theory considers the pressure-volume contributions to the free energy of the process, and here is applied to ion exchange resin systems. Cation exchange resins will be used as samples, although the theory is equally applicable to anion exchange resins.

The Physico-chemical System

Certain studies have indicated the fundamental physico-chemical nature of ion exchange systems. The cation exchange resins are high molecular weight, insoluble polyacids, usually of the sulfonic,

(7) A. P. Vanselow, *Soil Science*, **33**, 95 (1932).

(8) F. O. Anderegg and R. P. Lutz, *ibid.*, **24**, 403 (1927).

(9) S. Mattson and L. Wiklander, *ibid.*, **49**, 109 (1940).

(10) W. C. Bauman and J. Eichhorn, *THIS JOURNAL*, **69**, 2830 (1947).

(11) H. P. Gregor, *ibid.*, **70**, 1293 (1948).