metric apparatus, were used in the comparisons of Table II. The permanganate solution was standardized against sodium oxalate. The reduction procedure with sulfur dioxide was essentially that described by Hillebrand and Lundell[5] and Campbell and Woodhams.[6] In the determinations via the silver reductor the solutions contained 1 *M* hydrochloric acid, they were poured through the reductor at a rate of 30 cc./minute, and the reductor was washed with four 25-cc. portions of 1 *M* hydrochloric acid. Since Fryling and Tooley[7] demonstrated by specific tests that significant amounts of hydrogen peroxide are produced when hydrochloric acid solutions containing dissolved oxygen are passed through the silver reductor, air was removed from the reductor, ammonium vanadate solutions, and wash solutions, with hydrogen. The reduced solutions were diluted with an equal volume of water and 0.2 mole (*ca.* 0.08 mole excess) of sodium acetate was added to buffer the solution at a *p*H of about 4.5. The solutions were then allowed to stand in contact with air for fifteen minutes to insure reoxidation to the +4 state of the small amount of +3 vanadium present. Finally 2 cc. of saturated manganous sulfate solution was added, and the solutions were heated to about 80° and titrated with permanganate to a visual end-point.

In five other determinations with the silver reductor, 25-cc. portions of the same ammonium vanadate solution used in the experiments of Table II were reduced without removing air from the solutions. The results averaged 1.3% higher than those in Table II (corresponding to an average excess consumption of 0.24 cc. of 0.1 *N* permanganate), thus confirming the conclusions of Fryling and Tooley[7] that considerable amounts of hydrogen peroxide are formed in the silver reductor and that air must be excluded in accurate work. The excess consumption of permanganate in these experiments is several times larger than that found by Fryling and Tooley[7] in the determination of iron, which indicates that the reaction $O_2 + 2Ag + 2H^+ + 2Cl^- = H_2O_2 + 2AgCl$ is catalyzed by the simultaneous reduction of +5 vanadium. It is interesting to note that these results are in harmony with the polarographic characteristics of oxygen.[8]

Summary

In spite of the fact that the equilibrium constant of the reaction $VO^{++} + Ag + 2H^+ + Cl^- = V^{+++} + AgCl + H_2O$ is 87.9, this reaction takes place so slowly at room temperature that only very slight amounts of +3 vanadium are formed when solutions of +5 vanadium in 0.2 to 2 *M* hydrochloric acid are passed through the silver reductor at a temperature of 25° or lower. Within wide limits, the rate of flow of the solution and the dimensions of the silver column are without effect, but large amounts of +3 vanadium are formed when the hydrochloric acid concentration is increased above 2 *M* and/or when the temperature is increased above 25°.

Experiments in which air-free solutions of +5 and +4 vanadium were shaken with powdered silver demonstrated that many hours are required for the attainment of equilibrium in the foregoing reaction; the equilibrium concentration of +3 vanadium agrees with the value predicted from the standard potentials of the vanadyl–vanadic and silver–silver chloride half-reactions.

The conditions required for an accurate determination of vanadium with the silver reductor *via* reduction to the +4 state and titration with permanganate have been defined.

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(6) E. D. Campbell and E. L. Woodhams, THIS JOURNAL, **30**, 1233 (1908).

(7) C. F. Fryling and F. V. Tooley, *ibid.*, **58**, 826 (1936).

(8) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 307.

CAMBRIDGE, MASSACHUSETTS RECEIVED OCTOBER 9, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Contrast in the Dimerization of Polychloro- and Polyfluoro-ethylene

BY ALBERT L. HENNE AND ROBERT P. RUH

Halogenated derivatives of ethylene are easily polymerized, and several of them give commercial products, for example, $CH_2{=}CHCl$, $CH_2{=}CCl_2$, $CF_2{=}CF_2$. The mechanism of polymerization is mostly postulated, and on insufficient experimental data. We have prepared and examined the dimers of $CHCl{=}CCl_2$, $CClF{=}CF_2$ and $CCl_2{=}CF_2$. None of these dimerizations occurs at random. The first one is a "head to tail" type of polymerization leading to an open chain olefinic dimer; "head to head" type of polymerization does not occur; "head to tail" leads to $CHCl_2CCl_2CH{=}CCl_2$, and "tail to head" leads to $CHCl{=}CClCHClCCl_3$; both formulas are allylic halides, capable of a second form $CHCl_2CCl{=}CHCCl_3$, identical in both cases; the dimer is therefore represented as an allylic equilibrium of chlorinated butenes: $CHCl_2CCl_2CH{=}CCl_2 \rightleftarrows CHCl_2CCl{=}CHCCl_3 \rightleftarrows CHCl{=}CClCHClCCl_3$. In contrast, the fluorinated olefins undergo a *cyclic* dimerization leading to *only one* of the isomers which would result from random polymerization; specifically, $CClF{=}CF_2$ gives $\overline{\mathrm{CClFCClFCF_2C}}\mathrm{F_2}$; and $CCl_2{=}CF_2$ gives $\overline{\mathrm{CCl_2CCl_2CF_2C}}\mathrm{F_2}$; in contrast with the general fragility of cyclobutane cycles, these fluorinated cyclic dimers have proved exceedingly stable.

Proof of Structure

The dimers were first analyzed, then tested for unsaturation by means of permanganate oxidation and behavior toward chlorine. From these tests, the dimer of $CHCl{=}CCl_2$ (81.0% chlorine) is a chain olefin, while the dimers of $CFCl{=}CF_2$ (30.4% chlorine) and of $CCl_2{=}CF_2$ (53.4% chlorine) are saturated cyclic compounds.

$CHCl{=}CCl_2$ Dimer.—On the assumption that dimerization proceeds by addition of a chlorine atom and the remaining free radical to a double bond, the dimer $C_4H_2Cl_6$ could be A_1, B_1, C_1 or D_1. If, however, one considers also the much less probable assumption that dimerization involves an atom of hydrogen and the remaining free radical, two more formulas, E_1 and F_1, become possible.

The dimer $C_4H_2Cl_6$ accepts very readily one molecule of chlorine, to become $C_4H_2Cl_8$, A_2 to F_2.

$$CHCl_2CCl_2CH{=}CCl_2 \quad A_1 \longrightarrow CHCl_2CCl_2CHClCCl_3 \quad A_2$$
$$CHCl_2CCl_2CCl{=}CHCl \quad B_1 \longrightarrow CHCl_2CCl_2CCl_2CHCl_2 \quad B_2$$
$$CCl_3CHClCH{=}CCl_2 \quad C_1 \longrightarrow CCl_3CHClCHClCCl_3 \quad C_2$$
$$CCl_3CHClCCl{=}CHCl \quad D_1 \longrightarrow CCl_3CHClCCl_2CHCl_2 \quad D_2$$
$$CH_2ClCCl_2CCl{=}CCl_2 \quad E_1 \longrightarrow CH_2ClCCl_2CCl_2CCl_3 \quad E_2$$
$$CHCl_2CHClCCl{=}CCl_2 \quad F_1 \longrightarrow CHCl_2CHClCCl_2CCl_3 \quad F_2$$

A_2 and D_2 are identical; the symbol A will hereunder represent both "head to tail" (A) and "tail to head" (D) in the original dimer.

The chlorinated dimer, $C_4H_2Cl_8$, is very sensitive to aqueous potassium hydroxide under the influence of which it quantitatively loses two molecules of hydrogen chloride, to become 1,3-perchlorobutadiene, a known compound. This experiment eliminates E_2 and F_2 from consideration and justifies the view that dimerization involves chlorine rather than hydrogen atoms.

When subjected to fluorination[1] with mercuric oxide and hydrogen fluoride the chlorinated dimer gives two reaction products, $C_4H_2Cl_7F$ and $C_4H_2Cl_6F_2$; the fluorination does not proceed further. From the known ease of fluorination[2] of the various groups, one can predict the probable formulas, A_3, B_3 and C_3.

$$A_2 \longrightarrow CHCl_2CCl_2CHClCClF_2 \quad A_3$$
$$B_2 \longrightarrow CHCl_2CF_2CCl_2CHCl_2 \quad B_3$$
$$C_2 \longrightarrow CCl_2FCHClCHClCCl_2F \quad C_3$$

When the difluoride was chlorinated in sunlight in an effort to convert it to $C_4F_2Cl_6$, decomposition occurred into two fragments which were identified as C_2Cl_6 and CCl_3CClF_2, m. p. 40°. Since both fluorine atoms are found on the same carbon, C_3 is eliminated.

Treating the difluoride with aqueous potassium hydroxide caused the removal of only one molecule of hydrogen chloride, and the quantitative formation of an olefin $C_4HF_2Cl_5$. From previous studies[2] formulas A_4 and B_4 can be predicted, neither of which permits the removal of a second hydrogen chloride, in agreement with the experimental fact.

$$A_3 \longrightarrow CHCl_2CCl{=}CClCClF_2 \quad A_4$$
$$B_3 \longrightarrow CHCl_2CF_2CCl{=}CCl_2 \quad B_4$$

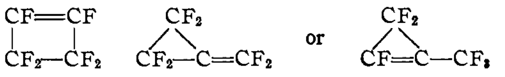
In quartz, with sunlight illumination, addition of chlorine to the double bond proceeded easily, without evidence of substitution. The resulting $C_4HF_2Cl_7$ should be A_5 or B_5.

$$A_4 \longrightarrow CHCl_2CCl_2CCl_2CClF_2 \quad A_5$$
$$B_4 \longrightarrow CHCl_2CF_2CCl_2CCl_3 \quad B_5$$

A treatment with aqueous sodium hydroxide removed one mole of HCl, and quantitatively transformed $C_4HF_2Cl_7$ into $C_4F_2Cl_6$. This experiment eliminates B_5, which could lose only hydrogen fluoride and leaves for consideration A_5 which can be transformed into $CCl_2{=}CClCCl_2CClF_2$. To check this conclusion, chlorine was added to the double bond, to give $CCl_3CCl_2CCl_2CClF_2$, b. p. 161° at 25 mm., m. p. 41.9 to 42.4°. This is a new compound (% Cl found 76.5, calcd. 76.8), which differs from the only other isomer[3] containing both fluorine atoms on the same carbon, *viz.*, $CCl_3CF_2CCl_2CCl_3$ b. p. 98° at 3 mm., m. p. 8.42°.

The original dimer is therefore $CHCl_2CCl_2CH{=}CCl_2$ or $CCl_3CHClCCl{=}CHCl$ or both. But since both are allylic halides, the dimer is really a mixture of three allylic isomers: $CHCl_2CCl_2CH{=}CCl_2 \rightleftarrows CHCl_2CCl{=}CHCCl_3 \rightleftarrows CHCl{=}CClCHClCCl_3$. The inclusion of the middle isomer does not modify the preceding reasoning, because chlorine addition leads to a paraffin identical with A_2 and D_2. The conclusion is therefore that "head to head" or "tail to tail" dimerization does not occur, but only the "head to tail."

$CClF{=}CF_2$ Dimer.—The possible formulas are restricted to a cyclobutane ring, or else a cyclopropane with a side chain. The dimer $C_4F_6Cl_2$, under the influence of zinc[4] in alcohol loses quantitatively two atoms of chlorine and yields C_4F_6, which can be represented by only three formulas.



Permanganate oxidation yields a diacid $C_4F_4O_4H_2$, which can come only from the cyclobutene ring and must therefore be perfluorosuccinic acid, $HO_2CCF_2CF_2CO_2H$. The original dimer is therefore $\overline{CClFCClFCF_2CF_2}$ uncontaminated with its isomer $\overline{CClFCF_2CClFCF_2}$. The cyclic dimerization

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[1] Henne, THIS JOURNAL, **60**, 1569 (1938).

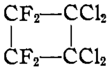
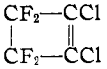
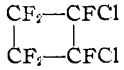
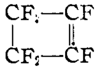
[2] Henne in "Organic Reactions," Vol. 2, John Wiley and Sons, New York, N. Y., 1944.

[3] Henne and Hinkamp, THIS JOURNAL, **67**, 1094 (1945).

[4] Henne and Zimmerschied, *ibid.*, **69**, 281 (1947).

TABLE I

PHYSICAL CONSTANTS

Compound	B. p., °C.	Mm.	F. p., °C.	t, °C.	d^t_4	n^tD	MR Found	MR Calcd.
$CHCl_2CCl_2CHClCFCl_2$	123	11	Glass	20	1.7729	1.5230	54.7	54.7
$CHCl_2CCl_2CHClCF_2Cl$	99.3	11	Glass	25	1.7550	1.4905	49.6	49.7
$CHCl_2CCl{=}CClCF_2Cl$	140.9	23	−51	20	1.6830	1.4838	44.9	44.5
$CHCl_2CCl_2CCl_2CF_2Cl$	158	48	Glass	25	1.8476	1.5112	54.5	54.7
$CCl_2{=}CClCCl_2CF_2Cl$	125.8	47	−50.7	25	1.8047	1.5073	49.3	49.3
$CCl_3CCl_2CCl_2CF_2Cl$	161	25	41.9–42.4					
	131.6	762	84.8					
	67.1	61.5	−43.4	25	1.5340	1.3699	28.8	28.8
	59.87		−24	20	1.6441	1.3340	29.2	29.2
	1.13		−60.37					

therefore proceeds by junction of "head to head" and "tail to tail" exclusively.

$CCl_2{=}CF_2$ Dimer.—The dimer $C_4F_4Cl_4$ is quantitatively transformed into $C_4F_4Cl_2$ by zinc in alcohol.[4] The latter, by permanganate oxidation,[4] yields exclusively perfluorosuccinic acid; its formula must therefore be $CCl{=}CClCF_2CF_2$, and the original dimer must be $CCl_2CCl_2CF_2CF_2$, uncontaminated with isomeric $CCl_2CF_2CCl_2CF_2$. The cyclic dimerization proceeded therefore exclusively by "head to head" and "tail to tail" junctions.

Experimental

Dimerization of $CHCl{=}CCl_2$.—This was done by refluxing over benzoyl peroxide in bright illumination.[5] The dimer is also available commercially.

Dimerization of $CCl_2{=}CF_2$.—The olefin (400 g.) was agitated at 200° for twelve hours in a stainless steel bomb. The unchanged monomer (75 g.) was recovered by distilling it off. The residue was dissolved in ether, then distilled to give 313 g. of crystalline dimer, b. p. 131–132°, in about 80–85% yield which is about 80% conversion and 92% net yield.

Dimerization of $CFCl{=}CF_2$.—The olefin (48 g.) was agitated at 200° for eight hours in a stainless steel bomb. Distillation of the reaction mixture gave 28 g. of recovered starting material, and 16 g. of crude dimer, b. p. 47 to 60° (33% conversion, 80% yield).

Summary

Dimerization of $CHCl{=}CCl_2$ leads by a "head to tail" type of polymerization to a chain halogenated butene, the formula of which is demonstrated. In contrast, the dimerization of $CClF{=}CF_2$ and of $CCl_2{=}CF_2$ lead to stable cyclobutane rings $CClFCClFCF_2CF_2$ and $CCl_2CCl_2CF_2CF_2$ respectively; noisomer is present and the cyclization process is exclusively a "head to head," "tail to tail" joining.

COLUMBUS, OHIO RECEIVED SEPTEMBER 9, 1946

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(5) French Patents 814,423 and 840,867; British Patent 417,195.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Fluorinated Acids

BY ALBERT L. HENNE AND W. J. ZIMMERSCHIED

A few fluorinated acids are known, all of which have the fluorine atoms located on the carbon adjacent to the acid group. The pronounced electronegative effect of the fluorinated cluster causes these acids to be very strong. The same exaltation of the acidity has been observed in alcohols bearing a fluorinated group next to the alcohol function. We have now attempted to prepare a series of acids in which the fluorinated group would be located at increasing distances from the acid function, in order to permit a measurement of the electronegative influence in terms of the distances. The present paper reports the synthetic work.

Alpha fluorinated acids ($CH_3CF_2CO_2H$ and $C_2H_5CF_2CO_2H$) were made by the alkaline oxidation procedure[1] reported for the preparation of trifluoroacetic acid.

Beta fluorinated acids could not be made by the same procedure because the alkalinity caused a loss of hydrogen fluoride, to yield $CF_2{=}CHCO_2H$ instead of $CF_3CH_2CO_2H$ and $CH_3CF{=}CHCO_2H$ instead of $CH_3CF_2CH_2CO_2H$. The addition of

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(1) Henne, Alderson and Newman, THIS JOURNAL, 67, 918 (1945).