

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

**The Direction of Addition of Carbon Tetrachloride to  $\text{CFCl}=\text{CF}_2$  under Polar Conditions<sup>1</sup>**

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In the presence of aluminum chloride, carbon tetrachloride adds to  $\text{CFCl}=\text{CF}_2$  to give the predictable  $\text{CCl}_3-\text{CFCl}-\text{CF}_2\text{Cl}$  and its disproportionation products,  $\text{C}_3\text{F}_4\text{Cl}_4$  and  $\text{C}_3\text{F}_2\text{Cl}_6$ . A report that the opposite direction of addition prevails, with formation of  $\text{CFCl}_2-\text{CF}_2-\text{CCl}_3$ , is shown to be an incorrect interpretation of incomplete evidence.

Under polar conditions,  $\text{CFCl}=\text{CF}_2$  accepts a reagent  $\text{A}^+\text{B}^-$  to yield  $\text{ACFCI}-\text{CF}_2\text{B}$ , exclusively. Hydrogen bromide gives  $\text{HCFCl}-\text{CF}_2\text{Br}$ <sup>2</sup> and alcohols give  $\text{HCFCl}-\text{CF}_2\text{OR}$ .<sup>3</sup> Since the same direction of addition prevails in both electrophilic and nucleophilic attacks, it could be expected that addition of carbon tetrachloride in the presence of aluminum chloride would yield  $\text{CCl}_3-\text{CFCl}-\text{CF}_2\text{Cl}$ . A report<sup>4</sup> that a reversed direction had been observed, with formation of  $\text{CCl}_2\text{F}-\text{CF}_2-\text{CCl}_3$  was therefore regarded as unconvincing, and on reinvestigation was proved incorrect.

When  $\text{CFCl}=\text{CF}_2$  in an excess of carbon tetrachloride is shaken with a small amount of aluminum chloride at about 50°, a slow addition may take place, but more frequently a reaction begins which accelerates very rapidly to raise the temperature to about 200° and is completed in a few minutes. This reaction is mostly a polymerization of the olefin, but about 0.20 of it is addition of the carbon tetrachloride. The major part of the addition product is a trifluoride,  $\text{C}_3\text{F}_3\text{Cl}_5$ , with varying amounts of its disproportionation products,  $\text{C}_3\text{F}_4\text{Cl}_4$  and  $\text{C}_3\text{F}_2\text{Cl}_6$ ; the latter are obviously not primary addition products and, moreover, the trifluoride is not of necessity the primary product either, because it contains varying amounts of crystalline  $\text{CCl}_3-\text{CCl}_2-\text{CF}_3$ , a rearranged product. As this particular isomer is the only high melting one (+109°), it is easily frozen out and collected and it supplies a rough measurement of the extent of rearrangement.

When the addition was rerun at 35° in a large excess of carbon tetrachloride and without sudden heat evolution, the trifluoride fraction no longer showed the presence of the rearranged  $\text{CCl}_3-\text{CCl}_2-\text{CF}_3$  and it froze between -20 and -30°, an indication that it was unlikely to be  $\text{CCl}_2\text{F}-\text{CF}_2-\text{CCl}_3$ , an isomer known not to freeze in Dry Ice.<sup>5</sup>

The literature conclusion<sup>4</sup> that addition is so directed as to make  $\text{CCl}_2\text{F}-\text{CF}_2-\text{CCl}_3$  is based on two counts: (1) that the observed physical properties do not agree with our published constants<sup>5</sup> for  $\text{CCl}_3-\text{CFCl}-\text{CF}_2\text{Cl}$  and (2) that no reaction occurs with zinc, therefore proving that the middle group is a  $\text{CF}_2$  group. The first count is answered by the observation that partly rearranged mixtures were being handled. The second count is now answered by successfully carrying out the zinc reaction with removal of two chlorine atoms and formation, without loss of fluorine, of an olefin  $\text{C}_3\text{F}_3\text{Cl}_3$ , the

oxidation of which gave only one product, monochlorodifluoroacetic acid. These experiments prove that the original addition compound did not carry two fluorine atoms on the central carbon, but did carry two fluorine atoms on the end carbon.

The disagreement in experimental results seems due to the fact that, in boiling ethanol, the zinc dehalogenation is so exceedingly slow that it may give the impression of not proceeding at all. However, when it is performed at 100° in dioxane, it proceeds normally, with formation of zinc chloride and  $\text{C}_3\text{F}_3\text{Cl}_3$ , exclusively.

It can now be concluded that no abnormal addition occurs. Even the rearranged and the disproportionated compounds do not have a  $\text{CF}_2$  group in the middle; this is in agreement with Miller's observations<sup>6</sup> on  $\text{CF}_2\text{Cl}-\text{CFCl}_2$ , that aluminum chloride causes preferential elimination or displacement of the lone fluorine in  $-\text{CFCl}_2$ , and does not affect the  $-\text{CF}_2\text{Cl}$  group at moderate or low temperature.

The addition of carbon tetrachloride to  $\text{CFCl}=\text{CF}_2$  in the presence of aluminum chloride thus proceeds in the same direction as that previously observed for a free radical addition.<sup>7</sup>

**Experimental**

**Uncontrolled Additions.**—Six moles (924 g.) of carbon tetrachloride, 2 moles (232 g.) of  $\text{CFCl}=\text{CF}_2$  and 50 g. of  $\text{AlCl}_3$  were placed in a 2-liter steel vessel strapped in the heating jacket of a rocking device. The heating was set for 50°; after one hour, a sudden rise of temperature and pressure was noted. The vessel was removed from the jacket and allowed to cool to room temperature; its pressure fell to zero. The material was poured over cracked ice containing some hydrochloric acid, steamed, dried and distilled. The steaming left a polymerized residue of 153 g. After removing 667 g. of carbon tetrachloride, the distillation gave 107 g. of intermediate, b.p. 80–110°; 91 g. (0.36 mole) of  $\text{C}_3\text{F}_4\text{Cl}_4$ , b.p. 110–114°; 44 g. of intermediate, b.p. 114–148°; 41 g. (0.15 mole) of  $\text{C}_3\text{F}_3\text{Cl}_5$ , b.p. 148–155°, which crystallized in the condenser; and 101 g. (0.35 mole) of  $\text{C}_3\text{F}_2\text{Cl}_6$ .

A second run of the same size was strapped on the shaker, but without heating jacket. After shaking at room temperature for 1.5 hours, and observing no temperature or pressure change, heat was applied with a bunsen burner until a temperature of 50° was reached. Since both the temperature and the pressure fell slowly after this, heat was again applied after 40 minutes; shortly after, the temperature rose suddenly to 160° and the pressure reached eight atmospheres; after one hour of shaking, the temperature was back to 30° and the pressure was zero. This run was worked up as above, and gave similar results, specifically 0.28 mole of  $\text{C}_3\text{F}_4\text{Cl}_4$ , 0.19 mole of solid  $\text{C}_3\text{F}_3\text{Cl}_5$  and 0.35 mole of residual  $\text{C}_3\text{F}_2\text{Cl}_6$ .

**Controlled Additions.**—In subsequent series, the ratio of carbon tetrachloride to olefin was nearly doubled, and the temperature was maintained at 35°. Slow addition took place in 16 to 24 hours. After removal of 180 g. of polymer and the excess of carbon tetrachloride, a typical run gave 80 g. of intermediate, b.p. 80–110°; 62 g. (0.24 mole) of  $\text{C}_3\text{F}_4\text{Cl}_4$ ; 25 g. of intermediate, b.p. 114–148°; 32 g. (0.12

(1) Presented as paper 29, Abstracts of 119th Meeting A. C. S., page 79M, Cleveland, Ohio, April, 1951.

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(3) Henne, Smook and Pelley, *ibid.*, **72**, 4756 (1950).

(4) Coffman, Cramer and Rigby, *ibid.*, **71**, 979 (1949).

(5) Henne and Ladd, *ibid.*, **60**, 2491 (1938).

(6) Miller, *ibid.*, **62**, 993 (1940); *ibid.*, **72**, 705 (1950).

(7) Henne and Kraus, *ibid.*, **73**, 1791 (1951).

mole) of  $C_3F_5Cl_3$ , liquid at room temperature; and 49 g. of residual material computed as 0.17 mole of  $C_3F_5Cl_3$ .

**Zinc Dehalogenations.**—A 20-g. portion of tetrafluoride was placed in a steel vessel with three times its volume of absolute ethanol and 10% excess of granular zinc. This bomb was rocked for 12 hours at a temperature of 100°. The material was poured into water and decanted; the aqueous layer was diluted to 500 cc. and a 50-cc. aliquot was titrated with silver nitrate, indicating the presence of 0.0154 g. atom of chloride which corresponded well with the observed zinc consumption of 0.077 g. atom. A qualitative test for fluoride ion was negative. About 0.6 g. of the original paraffin was recovered and, after purification, 10 g. of olefin  $C_3F_4Cl_2$ , b.p. 42–48°,  $n_D^{20}$  1.3490, and 2 g. of tar were collected; possible amount of olefin would have been 14 g.

A similar zinc treatment was applied to the difluoride  $C_3F_2Cl_4$ , to show the formation of 0.15 g. equivalent of chloride corresponding to the 0.077 g. atom of zinc consumed. A qualitative test for  $F^-$  proved negative. The olefin was dark and tar-like and was not treated further.

The trifluoride, when treated with zinc and alcohol at 100° gave a high boiling polymerized material. When the solvent was shifted to dioxane, satisfactory results were obtained at 100°; at higher temperature the dioxane is affected by the generated zinc chloride and becomes tarry. It is more convenient to carry the reaction under a dephlegmator and slowly distil a mixture of olefin and dioxane; this gave about half olefin,  $C_3F_5Cl_3$ , and half unreacted paraffin to be retreated. The chloride ion titration corresponds to the

zinc consumption, and a fluoride ion test proves negative.

**Oxidation of the Olefins.**— $C_3F_5Cl_3$  was oxidized with basic permanganate by our previously described procedure.<sup>8</sup> The reaction mixture was continuously extracted with ether, and the ether extract was distilled until a temperature of 105° was passed, to ensure the removal of any possible  $CF_3CO_2H + H_2O$  azeotrope. Alcohol, benzene and a few drops of sulfuric acid were added to the residue. Distillation through a dephlegmator was then performed until the boiling point of the alcohol/benzene binary azeotrope (68.2°) was reached; this procedure collected as distillate the azeotropes of water, benzene, alcohol and all of the ester. The distillate was washed with water to remove the alcohol; the benzenic solution of the ester was then subjected to a stream of dry ammonia. After distilling off most of the benzene, the amide crystallized out, with a m.p. of 78°. A known sample of  $CF_2ClCO_2H$  was then transformed into its amide by the same procedure, and a m.p. of 78° was observed. A mixed m.p. gave 77.5°. The m.p. would have been 126° if the sample had been a monofluoride,  $CFCl_2CONH_2$ , instead of the difluorinated compound. The yield of purified amide from crude olefin was 62%.

$C_3F_4Cl_2$  was similarly treated and gave, in similar yield, only  $CF_2ClCONH_2$ , m.p. 78°, mixed m.p. 77.5°. A search for possible  $CF_3CO_2H$  in the oxidation products proved negative.

(8) Henne and Trott, *THIS JOURNAL*, **69**, 1820 (1947).

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## Electrostatic Interactions in Aliphatic Dicarboxylic Acids and the Kirkwood–Westheimer Theory<sup>1</sup>

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Dissociation constants of some of the saturated aliphatic dicarboxylic acids from four carbon atoms to fourteen carbon atoms have been determined at 25.0° in 20 wt. per cent. methanol–water solution by the method of Speakman. These experimental results and also the available constants for water as solvent are analyzed in terms of the theory of Kirkwood and Westheimer. It is found that the theory gives quite satisfactory agreement with the experimental results.

### Introduction

The purpose of this work is to provide a further test of the Kirkwood–Westheimer theory<sup>3</sup> of the electrostatic influence of substituents on dissociation constants. Aside from its applications to physical and organic chemistry, the theory has important biological implications in its relation to the behavior of amino acids, proteins and polyelectrolytes in solution.

Since publication of the original work<sup>3</sup> a number of applications and discussions of the subject have appeared.<sup>4–13</sup> In particular, Westheimer and Kirk-

wood<sup>13</sup> have given an extensive review of the successes and limitations of the theory. One aspect of their treatment not tested in much detail by Westheimer and Kirkwood,<sup>3,13</sup> or by Wynne-Jones and Rushbrooke,<sup>12</sup> pertains to the predicted effective dielectric constant in a series of long ellipsoidal molecules, for example the aliphatic dicarboxylic acids. Dissociation constants of these acids are available in the literature<sup>14</sup> up to  $C = 9$  ( $C =$  number of carbon atoms in the molecule), with water as solvent. Decreasing solubility is the limiting factor in extending these measurements to larger values of  $C$ . In this paper we report measurements to  $C = 14$ , made possible by use of 20% (by weight) methyl alcohol as solvent. As will be seen below, the Kirkwood–Westheimer theory is in satisfactory agreement with both sets of experimental dissociation constants.

### Experimental

**Method.**—If the ratio of the successive thermodynamic dissociation constants  $K_1$  and  $K_2$  of a dicarboxylic acid is of the order  $10^3$  or greater, then it is sometimes possible to obtain quite accurate values for the dissociation constants by

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