The adsorption curves of iodide, sulfate and phosphate on clay or carbon were not at all similar to removal curves obtained by filtration or centrifugation. On the basis of this evidence and the failure of soluble cations to show definite radiocolloidal properties, it is concluded that adsorption of ions upon impurities does not appear to be the primary factor in radiocolloid formation.

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Fluoroölefins. III. 1,1-Difluorobutadiene and 1-Fluoro-1-chlorobutadiene[1]

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Although 1,1,1-trichloroethane reacts readily with hydrogen fluoride to give corresponding fluorine substituted products,[2] practically no information is available about the fluorination of similar compounds in the butane group. One reason for this lack of information has been the difficulty in obtaining compounds having the trichloromethyl group; however, this situation has now been improved due to the discovery by Kharasch[3] that bromotrichloromethane reacts readily with terminal olefins to give good yields of 1,1,1-trichloro-3-bromoalkanes. Because of the availability of 1,1,1,4-tetrachloro-3-bromobutane, obtained by the reaction of bromotrichloromethane with allyl chloride, and because the fluorinated derivatives should lead to olefins and dienes of interest, a study was made of its fluorination.

TABLE I

FLUORO COMPOUNDS OBTAINED FROM 3-BROMO-1,1,1,4-TETRACHLOROBUTANE

Compound	B.p., °C.	P, mm.	T, °C.	n_D	d_4	MRD Calcd.	MRD Found	Ag eq.[a] Calcd.	Ag eq.[a] Found	Chlorine, % Calcd.	Chlorine, % Found
$CFCl_2CH_2CHBrCH_2Cl$	77.4	10	26	1.4916	1.784	42.9	41.8	64.6	65.1		
$CF_2ClCH_2CHBrCH_2Cl$	52.4	10	25	1.4551	1.731	37.97	37.93	80.3	80.0		
$CF_2ClCH_2CHFCH_2Cl$	118.4–118.5	760	27	1.3881	1.428	30.12	30.17	[b]			
$CF_3CH_2CHBrCH_2Cl$	135.0–135.5	760	25	1.4156	1.698	32.92	33.10	112.3	114.9		
$CFCl_2CH_2CH{=}CH_2$	88.0	760	27	1.4104	1.188	29.85	30.00			49.6	49.6
$CF_2ClCH_2CH{=}CH_2$	49.2	760	25	1.3550	1.103	24.88	24.95			2.08	28.3
$CFCl{=}CHCH{=}CH_2$	53.4	760	25	1.4267	1.066	24.51	25.50			33.4	33.8
$CF_2{=}CHCH{=}CH_2$	3.5–4.0	760									

[a] Silver equivalent which is defined as the molecular weight divided by the number of halogen atoms other than fluorine. [b] *Anal.* Calcd. for $C_4H_5F_3Cl_2$: C, 26.57; H, 3.18. Found: C, 26.71; H, 2.83. [c] *Anal.* Calcd. for $C_4H_4F_2$: mol. wt., 90.1. Found: mol. wt., 91.5.

In an effort to effect replacement of the chlorine atoms of the trichloromethyl group, an investigation was made of the effectiveness of several of the more commonly used fluorinating agents such as antimony trifluoride or antimony trifluorodichloride, and hydrogen fluoride alone and with mercuric oxide.

Of the reagents studied, only the combination of antimony trifluoride and trifluorodichloride was found to give satisfactory results and even in this case variations in the conditions employed exerted a pronounced effect upon the relative amounts of the fluorobutanes. In one run, in which antimony trifluoride (1.7 moles) and antimony trifluorodichloride (1.3 moles) were allowed to react with 1,1,1,4-tetrachloro-3-bromobutane at 40–50°, a 51% yield of 1,1-difluoro-1,4-dichloro-3-bromobutane was obtained. When the reaction was carried out at a higher temperature or by using a larger proportion of antimony pentahalide, the amount of 1,1-difluoro compound was decreased and more highly fluorinated material was obtained. For example, at 60° and using antimony trifluoride (0.4 mole) and antimony trifluorodichloride (0.6 mole) only a 17% yield of 1,1-difluoro-1,4-dichloro-3-bromobutane was obtained but 1,1,3-trifluoro-1,4-dichlorobutane was separated in a 20% yield. The properties of the various derivatives which were obtained are given in Table I.

The substitution reaction proceeded normally to give the various products containing fluorine on the first carbon atom. One compound, $CF_2ClCH_2CHFCH_2Cl$, was isolated in which the bromine atom of the original 1,1,1,4-tetrachloro-3-bromobutane was replaced by fluorine. It seems likely that a simple replacement did not occur but rather that $CF_2ClCH{=}CHCH_2Cl$ was formed and this olefin reacted with hydrogen fluoride, which is nearly always a by-product in reactions of this type. The structure of the compound was established on the basis of its failure to react with zinc under conditions where chlorine atoms on adjacent carbon atoms are known to react.

Although 1,1-difluoro-1,4-dichloro-3-bromobutane may presumably be converted to 1,1-difluorobutadiene by either of two routes

$$\begin{tikzcd}
CF_2ClCH_2CHBrCH_2Cl \arrow[r, "Zn"] \arrow[d, "KOH"] & CF_2ClCH_2CH{=}CH_2 \arrow[d, "KOH"] \\
CF_2ClCH{=}CHCH_2Cl \arrow[r] & CF_2{=}CHCH{=}CH_2
\end{tikzcd}$$

the method employed here went through the butene-1 because the product from reaction with potassium hydroxide would be low boiling, and, therefore, the chance for side reactions in this step would be minimized.

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(1) Preceding papers in this series are: Paul Tarrant and Henry C. Brown, THIS JOURNAL, **73**, 1781, 5831 (1951).

(2) E. T. McBee, H. B. Hass, W. A. Bittenbender, W. E. Weesner, W. G. Toland, W. R. Hausch and L. W. Frost, *Ind. Eng. Chem.*, **39**, 409 (1947).

(3) M. S. Kharasch, Otto Reinmuth and W. H. Urry, THIS JOURNAL, **69**, 1105 (1947).

1,1-Difluorobutadiene polymerized on standing to a rubber-like material. Maleic anhydride did not form an adduct with 1,1-difluorobutadiene.

Experimental

Fluorination of 3-Bromo-1,1,1,4-tetrachlorobutane.—Powdered antimony trifluoride (3 moles) was placed in a flask equipped with stirrer and reflux condenser. A stream of chlorine was introduced near the bottom of the flask until 90 g. (1.3 moles) had been absorbed. The flask was then carefully cooled in an ice-bath to give a thin film of $SbF_3 \cdot SbF_3Cl_2$ which could be broken up and dispersed throughout the organic compound to be fluorinated. After the addition of $CCl_3CH_2CHBrCH_2Cl$ (550 g., 2 moles), vigorous stirring was begun and the mixture allowed to warm to 40–50° where it was maintained for three hours.

The reaction mixture was made slightly basic with potassium carbonate and steam distilled to give 356 g. of organic product. Fractionation through a 40-cm. column packed with protruded packing gave 16.5 g. (4.5% conversion) of $CF_2ClCH_2CHFCH_2Cl$, b.p. 38–50° (27 mm.), 274 g. (51% conversion) of $CF_2ClCH_2CHBrCH_2Cl$, b.p. 52–57° (11 mm.), and 32 g. (6.2% conversion of $CFCl_2CH_2CHBrCH_2Cl$, b.p. 75–85° (11 mm.).

By carrying out the reaction with antimony fluoride (1 mole), chlorine (0.6 mole) and $CCl_3CH_2CHBrCH_2Cl$ (0.5 mole) at a maximum temperature of 62°, a larger amount (20%) of $CF_2ClCH_2CHFCH_2Cl$ was obtained with a decrease (17%) in the amount of $CF_2ClCH_2CHBrCH_2Cl$ formed.

Several experiments were carried out and the products combined and purified to give the compounds listed in Table I.

1,1-Dichloro-1-fluorobutene-3 and 1-Chloro-1,1-difluorobutene-3.—One mole of $CCl_2FCH_2CHBrCH_2Cl$ was added to a vigorously stirred slurry of zinc dust (1.3 moles) in methanol (380 ml.) maintained at the reflux temperature. The reaction was carried out in three hours. The mixture was steam distilled and the water-insoluble layer separated, dried and fractionated to give 58 g. of $CFCl_2CH_2CH{=}CH_2$, b.p. 84–92°.

By essentially the same procedure, $CF_2ClCH_2CHBrCH_2Cl$ (0.93 mole), zinc dust (1.54 moles) and isopropyl alcohol (110 ml.) gave a 79% yield of $CF_2ClCH_2CH{=}CH_2$, b.p. 47–53°.

1-Chloro-1-fluorobutadiene-1,3.—To a refluxing solution of $CFCl_2CH_2CH{=}CH_2$ (0.4 mole) in ethanol was added dropwise a solution of potassium hydroxide (0.63 mole) in 120 ml. of ethanol. The addition was carried out over a period of 1.5 hours and the mixture was refluxed an additional hour. The product was washed with water, dried and distilled to give 23 g. (53.5%) of 1-chloro-1-fluorobutadiene-1,3, b.p. 52–54.5°.

1,1-Difluorobutadiene.—A solution of potassium hydroxide (2.68 moles) in ethanol (450 g.) was slowly added to $CF_2ClCH_2CH{=}CH_2$ (1.66 moles) in a flask equipped with stirrer, addition funnel and reflux condenser connected to traps cooled in Dry Ice. The heat of the reaction was sufficient to maintain a gentle reflux. Reflux was maintained for one hour after the addition. The product in the cold trap was distilled through a vacuum jacketed column to give 50 g. of $CF_2{=}CHCH{=}CH_2$, b.p. 3.5–5.0°.

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The Association of Acetate with Ammonium and Guanidinium Ions

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It has recently been observed by Walker[1] that amidine salts of carboxylic acids are relatively insoluble. This observation led Walker to suggest that complex formation might occur (even in solution) between amidinium and carboxylate ions. A complex between these ions would be expected to be stabilized by the existence of several possible resonance forms.

If such complex formation were to occur in the particular case of guanidinium ion, it would be of great importance in the chemistry of proteins. All proteins contain guanidinium and carboxylate groups on their side chains, and complex formation between them could play a role in the maintenance of the native protein structure: it could account, for example, for the abnormally large intrinsic ionization constant observed for the carboxyl groups of serum albumin.[2]

Accordingly, the experiments described below were performed to test the extent to which guanidinium ions, as compared to ammonium and potassium ions, affect the activity of acetate ions in solution. The method used was intended to give only the order of magnitude of the interaction, and a more accurate study had been planned if evidence for appreciable interaction had been found. It was found, however, that complex formation between guanidium and acetate ion is only very weak, and probably weaker than that between ammonium and acetate ions. The association constant (K_a) is of the order of 0.5, *i.e.*, less than that for association between the ions of many strong electrolytes (*e.g.*, KNO_3).[3] It is much too weak to cause any appreciable association between guanidinium and carboxylate groups of protein molecules. The association constant would have to be ten times as great to account for the abnormal pK of the carboxyl groups of serum albumin.

Experimental

Reagent grade chemicals were used without further purification. Twenty-five ml. of a solution of 0.0104 M NaOAc and 0.0569 M HOAc was placed in a vessel containing a stirrer and Beckman glass and calomel electrodes, which were connected to a Beckman Model G pH meter. Approximately 3 M KCl was added from a buret in small increments, and the pH measured after each addition. The experiment was repeated using NH_4Cl and $C(NH_2)_3Cl$ in place of KCl, and all three determinations were repeated starting with 25 ml. of a solution of 0.0208 M NaOAc and 0.0561 M HOAc. A constant temperature of 25.0° was maintained. The results are shown in Fig. 1. Volumes were assumed additive in the calculation of concentrations.

In Fig. 2 is shown a plot of $pH + 0.5\sqrt{\mu}$ for the points at lowest ionic strengths. Below $\mu = 0.05$ these points should fall roughly on a horizontal straight line and should extrapolate at $\mu = 0$ to a value of $pK + \log C^{\circ}_{OAc^-}/C^{\circ}_{HOAc}$, where $C^{\circ}_{OAc^-}/C^{\circ}_{HOAc}$ represents the ratio of added acetate and acetic acid concentrations, and pK is $-\log K_a$ for the ionization of acetic acid. Within the probable error of ±0.01 of the pH measurements, the three chlorides are indistinguishable. The best horizontal straight lines through the data give pK values of 4.765 and 4.758, respectively, in good agreement with the value of 4.756, obtained from accurate e.m.f. measurements.[4]

At higher concentrations of the added salts (Fig. 1) the pH in the experiments with ammonium and guanidinium ions falls below the curve obtained with KCl. If no complex formation at all is assumed to take place between po-

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