−4.33 p.p.m. The individual members of the triplet showed some fine structure.

The fluorine spectrum of the methyl-2,2,3,3,3-pentafluoropropyl ether consists of a CF_3 peak with a chemical shift of 7.6 p.p.m. and a triplet from the CF_2 group with a chemical shift of 47.2 p.p.m. The triplet arises due to the coupling with the adjacent CH_2 group. The coupling constant is 13 c.p.s. The coupling between the CF_3 group and the CF_2 group was not measured. The proton spectrum consists of a triplet from the CH_2 group with a chemical shift of −3.55 p.p.m. and a singlet from the OCH_3 group with a chemical shift of −3.15 p.p.m.

2,2,3,3,3-Pentafluoropropoxy Acetic Acid.—2,2,3,3,3-Pentafluoro-1-propanol (100 g.) containing 5% water, and chloroacetic acid (70 g.) were heated to 90° and 40% aqueous sodium hydroxide (250 cc.) was added in 2 hr. The charge was heated to 110° for 7 hr. and then acidified with 36% hydrochloric acid (110 cc.). The oil which precipitated was dissolved in aqueous ammonia and reprecipitated (65 g., containing 27.8% F and 0.4% Cl). The distillation was of interest because 20 g. of water distilled first from this water-immiscible oil before the 2,2,3,3,3-pentafluoropropoxyacetic acid (35 g.) distilled at 93°/9 mm.

Anal. Calcd. for $C_5H_5F_5O_3$: C, 28.8; H, 2.4; F, 45.6. Found: C, 29.0; H, 2.35; F, 45.0.

Condensation of Tetrafluoroethylene with Fluoromethyl 2,2,-3,3,3-Pentafluoropropyl Ether.—A charge of fluoromethyl 2,2,3,-3,3-pentafluoropropyl ether (60 g.), hydrogen fluoride (120 g.), and tetrafluoroethylene (50 g.) was heated to 50° for 12 hr.

The reaction mass was poured on ice, the oil which separated (37 g.) was washed acid free, dried, and distilled. Bis(2,2,3,3,3-pentafluoropropyl) ether (10 g.) was obtained, distilling at 92°.

Anal. Calcd. for $C_6H_4F_{10}O$: C, 25.5; H, 1.4; F, 67.4; mol. wt., 282. Found: C, 25.7; H, 1.6; F, 66.9; mol. wt., 292.

Condensation of 1,1-Difluoroethylene with Fluoromethyl 2,2,-3,3,3-Pentafluoropropyl Ether.—Fluoromethyl 2,2,3,3,3-pentafluoropropyl ether (206 g.) was dropped into well agitated hydrogen fluoride over a period of 90 min. at 4–7° and 1,1-difluoroethylene (90 g.) was bubbled through the reaction mass during that time. A colorless oil (165 g.) was obtained when the reaction mass was poured on ice and steam distilled. Upon fractionation of 130 g. of this product, fluoromethyl 2,2,3,3,3-pentafluoropropyl ether (16 g.), b.p. 60°, and 2,2,3,3,3-pentafluoropropanol (9 g.), b.p. 78–80°, were obtained first. The product distilling from 107–109° (22 g.) consisted (based on a nuclear magnetic resonance analysis) of 75% of 2,2,3,3,3-pentafluoropropyl 3,3,3-trifluoropropyl ether and 25% bis(3,3,3-trifluoropropyl) ether.

Anal. Calcd. for $C_6H_6F_8O$: C, 29.8; H, 2.44; F, 61.8; mol. wt., 246. Found: C, 30.4; H, 2.90; F, 60.8; mol. wt., 238.

Bis(3,3,3-trifluoropropyl) ether (13 g.) distilling at 114° was the final fraction. The distillation residue (14 g.) was not investigated.

Reaction of Hexafluoropropylene with Formaldehyde.—Paraformaldehyde (30 g.), hydrogen fluoride (200 g.), and hexafluoropropylene (160 g.) were heated to 160° for 8 hr. (maximum pressure 140 atm.). After dilution on ice, steam distillation and fractionation 2,3,3,3-tetrafluoro-2-trifluoromethyl-1-propanol (28 g.) was obtained as the anhydrous product, b.p. 94.5°. Its identity was established by infrared and nuclear magnetic resonance analysis. The unchanged hexafluoropropylene contained carbon monoxide and hydrogen.

Reaction of 1,1-Difluoroethylene with Formaldehyde.—Paraformaldehyde (120 g., 4 moles) was dissolved in hydrogen fluoride (560 g.) and 1,1-difluoroethylene was passed into the solution at 0–10°. It was completely absorbed for 45 min. and gas (1,1,1-trifluoroethane) started to pass through the reaction when 271 g. of 1,1-difluoroethylene (4.2 moles) had been used. The reaction mass was poured on ice (3000 g.), and the oil which precipitated was steam distilled, dried over sodium sulfate and fractionated. Bis(3,3,3-trifluoropropyl) ether (200 g.), b.p. 114°, was obtained. A distillation residue (63 g.) could not be distilled without decomposition.

Anal. Calcd. for $C_6H_8F_6O$: C, 34.28; H, 3.81; F, 54.3; mol. wt., 210. Found: C, 34.1; H, 3.9; F, 54.2; mol. wt., 212.

A vapor phase chromatographic analysis showed the absence of impurities.

Reaction of Fluoroethylene with Formaldehyde.—Fluoroethylene (160 g.) was added to a Dry Ice and acetone-cooled solution of paraformaldehyde (30 g.) in hydrogen fluoride (200 g.). Because of a valve failure the addition took place in less than 1 min., causing the temperature to rise to 100°. Upon dilution on ice, steam distillation, and fractionation bis(3,3-difluoropropyl) ether (37 g.), b.p. 147°, was obtained.

Anal. Calcd. for $C_6H_{10}F_4O$: C, 41.3; H, 5.74; F, 43.7. Found: C, 41.6; H, 5.8; F, 43.0.

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The Addition of Fluorine to Halogenated Olefins by Means of Metal Fluorides

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The selective addition of fluorine to the double bond of olefins by means of vapor phase reaction with cobalt trifluoride at 20–125° has been found to be quite general for stable halogenated olefins. Chloroethylene, *cis*-1,2-dichloroethylene, trichloroethylene, 1,1-difluoroethylene, 2-bromo-1,1,1-trifluoropropene, and 2-fluoropropene produced the respective vicinal difluoro derivatives in fair yields. In addition, compounds produced by the displacement of hydrogen or halogen by fluorine were obtained in lesser amounts, dependent upon the temperature of the reaction. The presence of an inert gas diluent and contact time were also important variables in the process. Silver difluoride, cerium tetrafluoride, and manganese trifluoride also added fluorine selectively to 1,1-difluoroethylene and *trans*-1,2-dichloroethylene.

The ability of some of the high valence metallic fluorides, notably cobaltic fluoride, silver difluoride, manganese trifluoride, cerium tetrafluoride, and lead tetrafluoride to fluorinate organic compounds is well known and has been extensively utilized to synthesize perfluorinated compounds. The various reactions of this class of fluorides has been excellently reviewed by Stacey and Tatlow.[1]

In general, these high valence metallic fluorides undergo three types of reaction.

(1) Replacement of hydrogen

$$-\overset{|}{\underset{|}{C}}H + 2MF_x \longrightarrow -\overset{|}{\underset{|}{C}}F + HF + 2MF_{x-1}$$

(2) Replacement of halogen

$$2-\overset{|}{\underset{|}{C}}X + 2MF_x \longrightarrow 2-\overset{|}{\underset{|}{C}}F + X_2 + 2MF_{x-1}$$

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[1] M. Stacey and J. C. Tatlow, "Advances in Fluorine Chemistry," Vol. 1, M. Stacey, J. C. Tatlow, and A. G. Sharpe, ed., Academic Press, Inc., New York, N. Y., 1960, p. 166.

TABLE I

REACTIONS OF COBALT TRIFLUORIDE WITH OLEFINS

Olefin	Temp., °C.	Flow rate, g./min.	N_2 rate, ml./min. approx.	Product	Yield, % of crude product	Yield, %
$CH_2{=}CHCl$	38 ± 5	1.0	670	$CH_2F{-}CHClF$	43	28
				$CH_2F{-}CHF_2$	17	13
$CHCl{=}CHCl$ (*cis*)	35 ± 15	1.1	500[a]	$CHClF{-}CHClF$	79	53
				$CHClF{-}CHF_2$	20	12
$CH_2{=}CCl_2$	35 ± 15	1.0	800	$CHClF{-}CClF_2$	6	2
				$CHClF{-}CCl_2F$	30	11
				$CCl_2F{-}CCl_2F$	14	4
				$CHCl_2{-}CCl_2F$	7	2
$CHCl{=}CCl_2$	25 ± 7	0.53	500[a]	$CHClF{-}CCl_2F$	72	31
				$CHClF{-}CClF_2$	9	4
$CH_2{=}CF_2$	125	2.2	None	$CF_3{-}CH_2F$	69	54 (81%)[b]
				$CF_3{-}CHF_2$	19	15
$CF_3CBr{=}CH_2$	75	1.1	500[a]	$CF_3{-}CBrF{-}CH_2F$	36	28
				$CF_3{-}CBrF{-}CHF_2$	53	38
$CH_3CF{=}CH_2$	65 ± 15	1.4	600	$CH_3{-}CF_2{-}CH_2F$	31	31
				$CH_2F{-}CF_2{-}CH_2F$[c]	52	44
$CF_2{=}CHBr$	35 ± 15		None	$CF_3{-}CHBrF$	64	60
				$CF_3{-}CHF_2$	4	...

[a] Nitrogen saturated with olefin. [b] Yields as high as 81% were obtained on larger scale runs. [c] Contains some $CH_3{-}CF_2{-}CHF_2$.

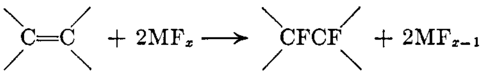
TABLE II

NEW FLUORINATION PRODUCTS

Compound	B.p., °C.	n^T_D	Carbon, %		Hydrogen, %		Halogen, %	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
$CH_2F{-}CHClF$	35.0	1.3416^{20}	23.9	23.6	3.01	3.09	35.3 (Cl)	34.6
$CF_3CBrFCH_2F$	49.0	1.3265^{22}	16.9	16.9	0.95	1.00	37.5 (Br)	37.4
$CF_3CBrFCHF_2$	35.7	1.3078^{22}	15.6	15.6	.44	0.50	34.6 (Br)	34.0
$CH_3CF_2CH_2F$	18.7	...	36.7	35.9	...	...	58.1 (F)	58.4
$CH_2FCF_2CH_2F$[a]	27.0	...	31.0	31.1	...	...	65.5 (F)	65.9

[a] Contains some $CH_3CF_2CHF_2$.

(3) Addition of fluorine to double bonds



$$>C{=}C< + 2MF_x \longrightarrow >CFCF< + 2MF_{x-1}$$

At high temperatures, all three of these reaction types may occur as illustrated by the reaction.[2]

$$C_7H_2Cl_3F_9 \xrightarrow[300-350°]{CoF_3} C_7F_{16} + C_7ClF_{15} + C_7Cl_2F_{14} + C_7Cl_3F_{13}$$

The displacement of chlorine atoms, however, is inhibited at lower temperatures and it is possible to limit the reaction to the double bond addition and hydrogen displacement processes.[3]

$$C_7HCl_3F_6 \xrightarrow[150-225°]{CoF_3} C_7Cl_3F_{11}$$

Iodine is normally displaced by fluorine under these conditions[4,5] and Stacey and Tatlow state that "two examples suggest that bromine falls in the usual intermediate position; it can be retained to an appreciable extent being eliminated more readily than chlorine, but less readily than hydrogen."

The selective addition of fluorine to the double bond of an olefin containing both hydrogen and halogen atoms has been investigated to a very limited extent. Henne and Waalkes[6] using lead tetrafluoride added fluorine to $CHCl{=}CHCl$ (32%) and $CHCl{=}CCl_2$ (17%) without mention of hydrogen or chlorine substitution. Trichloroethylene was fluorinated with cobaltic fluoride at 50–100° to yield the addition product.[7] Again, no mention was made of chlorine or hydrogen substitution, and no yield data were given. A more detailed study[8] of the fluorination of trichloroethylene with cobaltic fluoride at 120° showed that in addition to the product $CHClFCCl_2F$ (5%), replacement of hydrogen and chlorine and the apparent addition of chlorine across the double bond followed by replacement of some of the chlorine, resulted in the production of eight additional compounds. The fluorination of trichloroethylene with manganese trifluoride at 120 and 220° showed this reagent to be milder than cobaltic fluoride and at 220°, nearly a 40% yield of the addition product was obtained.

The products obtained by passing eight olefins containing both hydrogen and halogen over cobaltic fluoride are summarized in Tables I and II. In each case, except that of 1,1-dichloroethylene, a fair yield of the desired fluorine addition product was obtained along with at least one other more highly fluorinated compound. Since this series of olefins contains many of the representative compounds of the possible halogenated olefin combinations, it may be concluded that, in general, fluorine may be selectively added to volatile,

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(2) E. T. McBee, *et al.*, *Ind. Eng. Chem.*, **39**, 310 (1947).

(3) F. B. Stilmar, W. S. Strune, and R. N. Lulek, U. S. Patent 2,503,077 (April 4, 1950).

(4) R. N. Haszeldine, *J. Chem. Soc.*, 3761 (1953).

(5) M. Hauptschein, M. Braid, and F. E. Lawlor, *J. Am. Chem. Soc.*, **79**, 2549 (1957).

(6) A. L. Henne and T. P. Waalkes, *ibid.*, **67**, 1639 (1945).

(7) A. L. Dittman and J. M. Wrightson, U. S. Patent 2,690,459 (September 28, 1954).

(8) G. Fuller, M. Stacey, J. C. Tatlow, and C. R. Thomas, unpublished results referenced by M. Stacey and J. C. Tatlow, "Advances in Fluorine Chemistry," Vol. 1, M. Stacey, J. C. Tatlow, and A. G. Sharpe, ed. Academic Press, Inc., New York, N. Y., 1960, p. 182.

TABLE III

FLUORINATING ABILITY OF VARIOUS METAL FLUORIDES

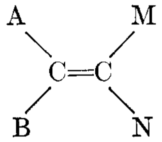
trans-1,2-Dichloroethylene[a]

Metal fluoride	Temp., °C.	Flow rate, g./min.	N_2 rate, ml./min.	$CHClF—CHClF$ Yield, % prod.	Yield, % theory	$CHClF—CClF_2$ Yield, % prod.	Yield, % theory	$CHCl=CHCl$ *cis* % prod.	*trans* % prod.
CoF_3[b]	35 ± 15	1.1	600	79	53	20	12	. . .	. .
MnF_3	250 ± 50	1.3	50	8	4.2	Trace	. .	34	47
AgF_2	35 ± 10	0.2	30	42	20	26	14	Trace	32
CeF_4	115 ± 25	.4	50	33	19	Trace	. .	30	37

1,1-Difluoroethylene

Metal fluoride	Temp.	Flow rate, g./min.	$CF_3—CH_2F$ Yield, % prod.	Yield, % theory	CF_3CHF_2 Yield, % prod.	Yield, % theory	$CH_2=CF_2$ % prod.
CoF_3[b]	125 ± 20	2.2	69	54	19	15	. .
MnF_3	250 ± 20	1.6	6	68	Trace	. .	89
AgF_2	110 ± 70	0.7	58	56	8	6	26
CeF_4	235 ± 25	.4	54	54	17	14	17

[a] Except for reaction with CoF_3 where *cis* isomer was used. [b] Large reactor, others on small reactor.

stable olefins of the type  where A, B, M, and N represent bromine, chlorine, fluorine, hydrogen, trifluoromethyl, or methyl groups. The failure of 1,1-dichloroethylene to produce the addition compound may be attributed to its lack of stability.

Several of the compounds obtained were previously unknown. These were identified by their infrared and mass spectrograms and by elemental analysis (Table II). The known compounds were identified by their physical constants and infrared spectra.

The fluorination reactions were, as expected, quite exothermic and had a tendency to react in "hot spots," and the reaction temperature was found to be the most important factor in determining the course of the reaction. The ease of displacement of hydrogen and halogen atoms at higher temperatures placed a fairly low ceiling on the maximum temperature that could be employed. A minimum fluorination temperature was also found in the case of 2-bromo-1,1,1-trifluoropropene, which did not react appreciably at 30°, but reacted completely at 75° with considerable complicating hydrogen displacement. For most olefins the minimum temperature was below room temperature and, therefore, not obtained.

The use of nitrogen as an inert diluent gas was found to have a profound effect on the reaction. Chloroethylene, for example, was smoothly fluorinated in a stream of nitrogen but in its absence reacted violently, and produced large amounts of chlorine and hydrogen fluoride and very little of the desired addition product. The nitrogen carrier gas probably moderated the reaction by inhibiting the formation of "hot spots" and by decreasing the retention time of the organic compound in the reactor.

The yields reported in this study are not necessarily the maximum obtainable, but are, except for $CH_2=CF_2$ and $CF_2=CHBr$, the results of single experiments which were designed to determine whether the olefin could be selectively fluorinated. The yields could probably be increased significantly by a study of the reaction variables; temperature, carrier gases, and contact time.

In contrast with previous data on high temperature fluorination with cobaltic fluoride, it was found that chlorine was more easily displaced than hydrogen under the conditions herein employed. For example, in the cases of chloroethylene, 1,2-dichloroethylene, and trichloroethylene the only identifiable by-products were those representing chlorine displacement. This suggests that the hydrogen displacement reaction may have a much greater temperature dependency than does chlorine displacement. The retention of bromine in preference to hydrogen as observed in the fluorination of 2-bromo-1,1,1-trifluoropropene may be due to a steric factor since bromine is normally more easily displaced than chlorine.

The results obtained from the fluorination of trichloroethylene may be compared with those recently reported by other workers.[8] At 120°, the product comprised less than 5% of the desired addition compound, 1,2-difluoro-1,1,2-trichloroethane, about 4% of the chlorine displacement product, 1,2-dichloro-1,1,2-trifluoroethane, and nearly 26% of the hydrogen displacement product, 1,1,2-trichloro-1,2,2-trifluoroethane. In the present study at 25°, the product was about 72% 1,2-difluoro-1,1,2-trichloroethane and 9% 1,2-dichloro-1,1,2-trifluoroethane; no 1,1,2,-trichloro-1,2,2-trifluoroethane was isolated. These large differences in the ratio of the products obtained dramatize the sensitivity of the reaction to temperature conditions.

Initially, in the fluorination of $CF_2=CHBr$, a small amount of bromine was observed in the collection trap along with a liquid material. However, at the end of fifteen minutes, no additional bromine was formed and the product was colorless.

In addition to cobaltic fluoride, silver difluoride, manganese trifluoride, and cerium tetrafluoride were found to be capable of selectively fluorinating double bonds. The results obtained from the vapor phase reactions of 1,1-difluoroethylene and *trans*-1,2-dichloroethylene with these fluorides are summarized in Table III.

As in the cobalt trifluoride–olefin reactions, these experiments were designed primarily to determine whether the selective fluorination could be effected and the yields are, therefore, not the maximum obtainable. Despite this fact, several general observations seem appropriate. Firstly, the temperature required for the conversions obtained suggested that the fluorinating ability of the salts varies $CoF_3 \sim AgF_2 > CeF_4 > MnF_3$. This order may, however, vary with the olefin employed. Silver difluoride, for example, reacted extremely exothermically with 1,1-difluoroethylene but only sluggishly with 1,2-dichloroethylene, whereas coablt trifluoride reacted smoothly with both these olefins. Manganese trifluoride which reacted with these olefins only with difficulty has been reported to fluorinate trichloroethylene in fair yields at 120° and 220°.[8] This difference in reactivity of manganese trifluoride may have been primarily due to differences in the reaction conditions and reactor design and not necessarily in the olefin reactivity.

The various metal fluorides differed in their tendency to form by-products through hydrogen and halogen displacements as determined by the ratio of the % yields of the product to the by-products obtained from $CF_2{=}CH_2$ and $CHCl{=}CCl_2$ as is shown in Table IV. Compared to cobaltic fluoride, silver difluoride displaced less hydrogen but more chlorine. The propensity of silver difluoride to displace halogen has been previously reported.[1] Cerium tetrafluoride, on the other hand, exhibited about the same tendency to displace hydrogen as did cobaltic fluoride but a decreased tendency to displace chlorine. The poor yields obtained from the manganese trifluoride reactions preclude any evaluation of its hydrogen and halogen atom displacement propensity.

TABLE IV

RATIO OF PRODUCTS OBTAINED

Reactants		Product ratio of % yield
Metal fluoride	Olefin	CH_2FCF_3/CF_3CHF_2
CoF_3	$CH_2{=}CF_2$	3.6
AgF_2	$CH_2{=}CF_2$	9.3
CeF_4	$CH_2{=}CF_2$	3.8
		$CHCl.FCCl_2F$/- $CHClFCClF_2$
CoF_3	$CHCl{=}CCl_2$	4.4
AgF_2	$CHCl{=}CCl_2$	1.4
CeF_4	$CHCl{=}CCl_2$	19/trace

The observed isomerization of *trans*-1,2-dichloroethylene to the *cis* isomer with silver difluoride, manganese trifluoride, and cerium tetrafluoride suggests that the addition reactions may proceed through the reversible formation of a complex in which the carbon–carbon bond is freely rotating. There is not sufficient evidence, however, to allow the postulation of a reaction mechanism.

Experimental

Apparatus.—The reactions involving cobaltic fluoride were carried out in a stirred reactor very similar to that described by Barbour, Barlow, and Tatlow.[9] The reactor consisted of a 3 × 50 in. monel pipe equipped with an electric furnace and a paddle type coaxial stirrer which rotated at 12 to 16 r.p.m. The temperature was measured and controlled by thermocouples placed between the pipe and the furnace and was, therefore, only approximate. The reactor contained about 12 moles of cobaltic fluoride.

The other metallic fluoride fluorinations were performed in a smaller, unstirred reactor constructed from a 1 × 18 in. nickel pipe. This reactor was heated with a 12-in. electric furnace and the temperature was measured and controlled by means of a thermocouple placed in a nickel well which extended down the center of the pipe. Agitation for the reaction was provided by intermittent manual rotation of the nickel pipe. The reactor utilized from 1 to 2 moles of the metal fluoride.

Preparation of Metal Fluorides.—The high valence metallic fluorides were prepared by passing fluorine over the salts heated to 300° until the concentration of fluorine in the effluent gas stream was sufficiently high to ignite cotton linters. The reactor was then purged with nitrogen for several hours or preferably overnight. The pipe was stirred or occasionally rotated throughout the operation. The metal fluorides were regenerated after each fluorination using this same procedure.

General Procedure.—After the temperature of the reactor was adjusted to the desired temperature as shown for each olefin in Tables I and III, the vaporized olefin was passed over the metal fluoride at the nitrogen and olefin flow rates shown in the tables.

The effluent vapors were collected in traps cooled with Dry Ice–acetone or liquid nitrogen. The crude product was then fractionally distilled. The total quantity of olefin fluorinated in a single experiment varied from one to four moles with the large reactor described above and from 0.2 to 0.8 mole with the small reactor thus maintaining a large excess of the high valence metallic fluoride.

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(9) A. K. Barbour, G. B. Barlow, and J. C. Tatlow, *J. Appl. Chem.*, **2**, 127 (1952).