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Halogen–Silver Complexes of the Fluorocarbon Carboxylic Acids

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Substances of the general formula $(C_nF_{2n+1}COO)_2AgI$ have been isolated as products of the reaction of the silver salts of the fluorocarbon carboxylic acids with iodine in fluorocarbon or fluorocarbon derivative (designated in abbreviated form "forbonic") solvents at room temperature. The preparation, identification and some of the reactions of these substances are described.

A number of investigators have employed the reaction between the silver salts of the fluorocarbon carboxylic acids (S) and the halogens at elevated temperatures in the synthesis of fluorocarbon halides.[1–5] The reaction may be represented as follows: $\Theta COOAg + X_2 \rightarrow \Theta X + AgX + CO_2$ where Θ is a fluorocarbon radical and X is a halogen atom.

It has been demonstrated that when the above starting materials are combined in an aromatic solvent, such as toluene, ring halogenation occurs.[6–8] The over-all reaction may be represented as

$$\Theta COOAg + X_2 + ArH \longrightarrow ArX + \Theta COOH + AgX$$

It has been suggested[7–9] that the initial step in both of the above reactions is

$$\Theta COOAg + X_2 \longrightarrow \Theta COOX + AgX$$

giving rise to a hypothetical intermediate "fluorocarbon carboxy halide" which reacts to complete the above reactions by the routes

$$\Theta COOX \longrightarrow \Theta X + CO_2$$

and

$$\Theta COOX + ArH \longrightarrow \Theta COOH + ArX$$

respectively.

The above intermediate has never been isolated from reaction mixtures of (S) and (X). Haszeldine and co-workers[8–10] in a series of papers relating to this reaction, postulate a number of mechanisms involving the assumed $\Theta COOX$ intermediate and suggest that in mixture of (S) and (X) in solution, an equilibrium between $\Theta COOX$ and a substance of the formula $(\Theta COO)_2AgX$ exists. Earlier investigations, involving analogous reactions of the organic carboxylic acid salts, reveal considerable disagreement as to the nature of the intermediately formed substances. Various investigators have presented evidence for the existence of three distinct types of intermediates, *i.e.*, the "Simonini" complex, $(RCOO)_2AgX$[11–20]; the carboxy halide, $RCOOX$[21–24]; and the halogen triacyl, $(RCOO)_3X$.[25,26] In these substances, RCOOAg has combined with halogen in 1:1, 1:2 and 3:4 equivalent ratios, respectively.

Even if an organic complex were identified and proven, it would be hazardous to assign a similar structure to a forbonic complex. This paper is concerned with the isolation and determination of empirical formula of the forbonic complex.

Materials Used.—The silver salts of the fluorocarbon carboxylic acids (S) were prepared by refluxing the acid with excess Ag_2O and water, followed by filtration and removal of water. The salts were purified and dried by recrystallization from absolute ether followed by 24-hour heating at 100° *in vacuo*.

Iodine and bromine (X) were purified by resublimation through P_2O_5 and stored in weighed and tared sealed glass vials.

The forbonic solvents employed were a mixture of C_5 fluorocarbons, a mixture of C_9 fluorocarbons, tributforyl nitride and an eight carbon cyclic fluorocarbon oxide, hereafter designated 1, 2, 3 and 4, respectively. These substances were washed with anhydrous ether, refluxed with KOH, refluxed with CF_3COOAg and I_2, treated with $Na_2S_2O_3$, dried over $CaCl_2$, fractionated and stored over P_2O_5 in sealed Pyrex tubes.

Apparatus.—The reactor was a piece of apparatus fitted with stopcocks and ground joints but sufficiently leak proof to stand evacuation. It consisted of a graduated cylindrical reaction vessel with a flat bottom on which rested a glass enclosed bar of iron. The latter could be rotated by an external magnet to provide stirring. At the top of the reaction vessel was a ground stopper. Joined to the side wall near the top were connections for vacuum, manometers, dry air, an auxiliary gas volume and a buret. Near the bottom of the reaction vessel, but sufficiently above it to enable the liquid to be withdrawn without disturbing the settled precipitate, was a connection carrying a stopcock. It was lightly plugged with glass wool to filter entrained solids. This connection led to a filter weighing bottle, which contained a sintered glass filter near the bottom. It was cylindrical in shape and had male-end-ground-joints both for the entrance and exit. The entrance was at the top. The exit came from the bottom but was bent 180° so as to come parallel with the entrance tube. This design enabled the filter-weighing bottle to be chilled by surrounding it with a vacuum jacketed container of coolant. The exit of this bottle led to traps, manometers, source of vacuum, etc.

Determination of Stoichiometry of the Reaction.—The procedure for conducting controlled reactions of (S) and (X) and measuring the stoichiometry of these reactions without danger of side reactions with contaminants was as follows.

The reactor was vacuum dried. A sample of (S) weighed

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on the analytical balance was placed in the graduated reactor vessel, and the reactor alternately evacuated and flushed with dry air to remove any moisture acquired by (S) during weighing and transfer.

The low solubility of (X) in the forbonic solvents employed rendered the titrations of (S) with standard solutions of (X) impractical; hence the following procedure. A vial containing (X) amounting to a slight excess over a 1:1 equivalent ratio with (S) above was dropped into the reaction vessel through the top while maintaining a stream of dry air from the system. Breakage of the vial could be assured by shooting it in with a "slingshot" arrangement attached to the tube rim.

Solvent was admitted from the buret, magnetic stirring started, and a reasonable time allowed for the reaction to go to completion. Enough (S) was added to bring the (S) content to equivalence with (X). This rapidly removed the color of excess (X) which was invariably present at this point. Experimental data showing the proportions in which (S) and (X) were found to combine appear in Table I.

Reaction mixtures containing exactly equivalent amounts of (S) and I_2 were titrated with a solution of I_2 in the forbonic solvent. A blank containing only AgI and solvent was titrated with the same solution. The colors observed

TABLE I

THE STOICHIOMETRY OF THE REACTION OF SILVER SALTS OF FLUOROCARBON CARBOXYLIC ACIDS WITH IODINE OR BROMINE IN FORBONIC SOLVENTS

	(S)	G.	Meq.	X	G.	Meq.	Solvent	Reaction time	Temp., °C.	(S)/(X), equiv. ratio	Extent of reaction
1	CF_3COOAg	28.0	126.7	I_2	16.0	126.00	#3 250 cc.	3 hr.	25-27	0.993	Complete
	....	Same	....	I_2	0.20	1.57	Same	2 hr.	25–26	1.007	Incomplete
2	C_3F_7COOAg	5.0772	15.81	I_2	2.3148	18.23	#3 30 cc.	2 hr.	25–26	1.153	Incomplete
	C_3F_7COOAg	0.8081	2.52	..	Same	....	Same	10 min.	25–26	0.995	Complete
3	CF_3COOAg	4.6033	20.83	Br_2	1.8668	23.36	#1 25 cc.	6 hr.	24–26	1.121	Incomplete
	CF_3COOAg	0.5675	2.57	..	Same	....	#1 25 cc.	18 hr.	24–26	0.998	Complete
4	C_3F_7COOAg	25.54	79.5	I_2	10.858	85.6	#3 150 cc.	15 hr.	23–25	1.07	Incomplete
	C_3F_7COOAg	2.00	6.2	..	Same	....	Same	15 min.	23–25	0.999	Complete
5	$C_5F_{11}COOAg$	42.00	99.8	I_2	17.00	133.9	#2 220 cc.	24 hr.	24 26	1.33	Incomplete
	$C_5F_{11}COOAg$	15.80	37.5	..	Same	....	Same	3 hr.	24–26	0.969	Complete
6	CF_3COOAg	8.6418	39.10	Br_2	3.7293	46.67	#3 150 cc.	6 hr.	24–26	1.193	Incomplete
	CF_3COOAg	1.933	8.74	..	Same	....	Same	6 hr.	24–26	0.975	Complete

NOTE: In the second part of each of the six experiments shown, an additional amount of the indicated reactant was added to the reaction mixture.

TABLE II

PREPARATION AND ANALYSIS OF REACTION MIXTURES OF SILVER SALTS OF FLUOROCARBON CARBOXYLIC ACIDS AND IODINE OR BROMINE[a]

A. Preparation										B. Analysis							
										Total oxidizing power		Recovered acid	% of theory based on		Recovered Ag	% of theory based on	
(S)	G.	Meq.	X	G.	Meq.	Solvent	Cc.	Mean temp., °C.	Reaction time, min.	Meq.	% of theory	Meq.	Orig. X	Orig. Ag	Meq.	Orig. X	Orig. Ag
CF_3COOAg	1.098	4.97	I_2	0.6305	4.96	ΘF #2	11	25	90	4.1168	83.00				4.92	98.9	98.8
C_2F_5COOAg	2.558	9.44	I_2	1.1086	8.73	ΘF #3	20	24	300	7.9459	91.02						
C_3F_7COOAg	2.7140	8.45	I_2	1.0259	8.08	ΘF #3	15	26	480	7.6461	94.5				8.36	103	98.9
C_4F_9COOAg	4.8305	13.0	I_2	1.5945	12.55	ΘF #3	30	25	600	12.0355	95.1						
$C_5F_{11}COOAg$	2.3930	5.66	I_2	0.6908	5.439	ΘF #3	30	27	840	4.9798	91.5						
$C_5F_{11}COOAg$	3.2500	7.71	I_2	0.9105	7.17	ΘF #3	37	26	360			7.68	107	99.6	7.45	104	96.6
CF_3COOAg	1.6452	7.444	Br_2	0.5916	7.404	ΘF #2	40	25	480	5.6810	76.7				7.13	96.4	95.7
CF_3COOAg	10.5751	47.84	Br_2	3.7293	46.67	ΘF #3	150	26	480			45.44 (distilled)	97.3	95.0			
C_3F_7COOAg	1.9888	6.195	I_2	0.7343	5.782	ΘF #4	75	25	300			5.55 (distilled)	96.0	89.6	6.18	107	99.6
C_7F_7COOAg	1.8218	5.675	I_2	0.6975	5.492	ΘF #4	75	26	300			5.52	100	97.3	5.61	102	98.9

[a] The assumption upon which the % of theory in the above table is calculated is that the complex has the formula $(\Theta COO)_2AgX$.

TABLE III

ANALYSIS OF THE COMPLEXES IN SOLUTION IN FORBONIC SOLVENTS

A. Relationship between acid number, oxidizing power and removable silver

	Contents of the reaction mixtures		Sample, cc.	Oxidizing power (meq.) (O)	Acid no. (meq.) (A)	Recoverable Ag (meq.) (R)	(R) / (O) or (A)
1	CF_3COOAg	0.8347 g. (3.76 meq.)	10	0.00993	Insufficient material in soln. for measurement		
			20	0.01986			
	I_2	0.4245 g. (3.34 meq.)	10	0.00993			
			Residue	3.1744		3.729	1.17
	θF #2	65 cc.	total	3.2141		3.729+	1.16+
2	C_3F_7COOAg	1.0600 g. (3.30 meq.)	10		0.3009	0.1477	0.491[a]
			10	0.2976		.1454	.489[a]
	I_2	0.4114 g. (3.23 meq.)	10	.2857		.1498	.524[a]
			10	.2877		.1487	.522[a]
	θF #3	65 cc.	10	.2858		.1436	.502[a]
			Residue	1.2598		2.6869	2.13
			total	2.2726		3.3224	1.46
3	$C_5F_{11}COOAg$	1.71 g. (4.06 meq.)	10	0.0516		0.0226	0.438[a]
			10	0.0506		0.0240	0.475[a]
	I_2	0.4740 g. (3.372 meq.)	10		0.0528		
			10		0.0528		
	θF #3	65 cc.	Residue	3.3067		3.7296	1.128
			total	3.5460		3.9374	1.109

B. Comparison of stabilities of complexes in solution

	Contents of the reaction mixtures		Sample, cc.	Oxidizing power, meq.	Age of sample, min.
4	C_2F_5COOAg	0.9868 g. (3.641 meq.)	5	0.3050	15
			5	.2910	633
	I_2	0.4471 g. (3.250 meq.)	5	.2950	1008
			Residue	2.6170	
	θF #4	65 cc.	total	3.5080	
5	C_2F_5COOAg	1.4121 g. (5.211 meq.)	10	0.4010	10
			10	.2650	130
	Br_2	0.3987 g. (4.987 meq.)	10	.1830	250
			10	.1400	370
	θF #4	120 cc.	10	.1010	490
			10	.0050	1330
			Residue	3.5350	
			total	4.6300	

[a] If the complex in solution has the formula $(C_3F_7COO)_2AgI$ [or $(C_5F_{11}COO)_2AgI$] the theoretical value is 0.500.

NOTE: In obtaining totals for oxidizing power and recoverable silver, appropriate values are substituted for those not determined.

in the two titrations matched for proportional amounts of added solution. This showed that (S) did not react with more than one atom of I_2 per molecule. Titrations of this kind were performed with similar results with (S) being CF_3COOAg, C_2F_5COOAg, C_3F_7COOAg, C_4F_9COOAg and $C_5F_{11}COOAg$. A small amount of I_2 is removed by AgI, probably due to adsorption.

Analysis of the Reaction Mixtures.—The complexes were prepared as before, using equivalent quantities of (S) and (X) in a forbonic solvent.

Total oxidizing power was determined by adding KI solution to the reaction mixture and immediately titrating the liberated iodine with standard thiosulfate. It was found that one equivalent of oxidizing power is available for each equivalent of halogen consumed.

Liberated acid was determined on separate reaction mixtures by treatment with water, followed by titration with standard base to a phenolphthalin end-point. In other cases, a considerable excess of (S) was employed. The iodine solution resulting from the addition of water was distilled into a closed receiver. More water was added and the process repeated until all the free acid was obtained. This acid was then titrated as before.

In the first method above, one equivalent of acid was found for each equivalent of (S) present. In the second case the acid number corresponded to the (X) equivalent consumed. Thus the amount of free acid liberated from the reaction mixture by hydrolysis with water is independent of any (S) present in excess of a 1:1 equivalent ratio.

In several instances the precipitate obtained upon treatment of the reaction mixture with water was separated, washed and vacuum dried. These samples were observed to possess a small amount of oxidizing power and were presumed to contain $AgXO_3$. These precipitates were analyzed according to the cyanide method and were found to be almost pure AgX. Data obtained from the analyses of reaction mixtures appear in Table II.

Analysis of Complex-containing Solutions.—The complexes were prepared as before. The clear supernatant liquids were pipetted from the reactor, while extreme precautions against moisture entering the system were taken, and analyzed for the same quantities measured above. These were obtained as functions of the amount of complex present in solution. The total oxidizing power was found to equal the acid number and the recoverable silver equal to one-half that value. Experimental and analytical data appear in Table III.

The last two experiments in this series were designed to determine the relative stabilities of $(\Theta COO)_2AgBr$ and $(\Theta COO)_2AgI$ in solution. Values of total oxidizing power for samples removed from reaction mixtures at measured time intervals were determined. In Part B of Table III the time variations of this quantity for $(C_2F_5COO)_2AgBr$ and $(C_2F_5COO)_2AgI$ are compared.

TABLE IV

PREPARATION, ISOLATION AND ANALYSIS OF THE SOLID COMPLEXES

Preparation							Analysis[a]								
							Meq. oxidizing power			Meq. acid number			Meq. AgI		
(S)	G.	Meq.	I_2, g.	Meq.	Solvent, cc.	Wt. of ppt., g.	Found	Theor.	$\frac{\text{Found}}{\text{theor.}} \times 100$	Found	Theor.	$\frac{\text{Found}}{\text{theor.}} \times 100$	Found	Theor.	$\frac{\text{Found}}{\text{theor.}} \times 100$
CF_3COOAg	1.5308	6.926	0.8778	6.912	#1 50	0.1757	0.6490	0.7622	85				0.3937	0.3811	103
C_2F_5COOAg	1.4233	5.253	0.6471	5.095	#1 65	.2560				0.8659	0.9126	95	.4613	.4563	101
C_3F_7COOAg	2.9342	9.140	1.1378	8.959	#1 50	.2125	.6220	.6420	97				.3198	.3210	100
C_4F_9COOAg	2.5466	6.864	0.8674	6.829	#1 65	.1989				.5001	.5230	95.5	.2600	.2615	100
$C_5F_{11}COOAg$	3.2135	7.633	0.9390	7.394	#1 65	.2360	.5320	.5466	97.5				.2730	.2733	100

[a] The theoretical values are calculated on the basis of the formula of complex being $(\Theta COO)_2AgI$.

Isolation and Identification of the Solid Complexes.—The complexes were prepared as before, employing solvent 1. The filter weighing bottle was chilled in Dry Ice–acetone. After the precipitate had settled, the stopcock between the reactor and weighing bottle was opened and the solution allowed to pass into the bottle. Trapped air in the bottle was vented by opening a stopcock provided for this purpose. Any suspended particles were removed by a glass-wool plug in the exit line from the reaction vessel. After sufficient time had been allowed for crystal formation, suction was applied to the exit of the weighing bottle. The solvent was drawn from the filter-weighing bottle, leaving the precipitated complex on the septum. Residual solvent was removed under vacuum. The weighing bottle was removed from the apparatus, plugs inserted in the ends of the ground joints, stopcock grease removed, and the bottle weighed immediately on the analytical balance. The contents of the bottle were immediately titrated, either for acid number or total oxidizing power. Titrations were performed directly in the filter-weighing bottle, using a micro-buret. The precipitated silver residues were then washed free of titrating solution. The samples that had been titrated for available acid were treated with thiosulfate to reduce any $AgIO_3$ to AgI.

Excess standard KCN solution was added and the bottle stoppered and allowed to stand with occasional shaking until all the AgI was dissolved. The solution was washed into an erlenmeyer flask and titrated with standard $AgNO_3$ according to the Deniges method.

Experimental conditions and results appear in Table IV.

Discussion

As can be seen from the foregoing tables, the reaction between the halogen and the silver salt of a fluorocarbon carboxylic acid forms a complex of the formula $(\Theta CO_2)_2AgX$.

$$2\Theta CO_2Ag + X_2 \longrightarrow (\Theta CO_2)_2AgX + AgX$$

Halogen added in excess of that required for the above equation was shown to be uncombined with the silver salt. Hydrogen-containing solvents react with the complex so that purified fluorocarbons or fluorocarbon derivatives, "forbons" for short, enable the complex to be dissolved and thus removed from the silver halide. The iodine complexes thus isolated could be crystallized and identified. This identification must be done rapidly, however, as they undergo decomposition at room temperature in the absence of the forbonic solvent. The bromine complexes decompose rapidly even in solution as is seen in Table IIIB. Before separation of the complex from the silver halide, the mixture is relatively stable at room temperature in the absence of moisture. This is true for either the iodine or bromine containing complexes. The complexes react rapidly with water or with reducing agents such as potassium iodide.

Substances of the formula $\Theta COOX$ were not detected either as isolatable materials or in equilibrium with $(\Theta CO_2)_2AgX$.

The fluorocarbon carboxy iodide was not found in this work. A complex having some of the same chemical reactions was found which is stable in forbonic solutions or in combination with silver iodide. The carboxy bromide was not found and even its complex is unstable at room temperature. Cady and Kellogg[27] and Menefee and Cady[28] found the fluorocarbon carboxy fluorides to be unstable. Thus the assumption of fluorocarbon carboxy halides as intermediates in reactions is not justified.

As the alkforyl radical can be considered a replacement of a fluorine atom in a molecule just as an alkyl radical can be considered a replacement of a hydrogen atom,[29] from the above, one would expect instability for hydrogen free fluorocarbon esters or in fact any esters in which the alkforyl group is attached to the oxgen atom.

This generates some skepticism in regard to the actual existence of the hypothetical organic carboxy halides previously postulated as either stable species or reaction intermediates. The hydrogen content of the alkyl group would certainly prohibit the presence in the same molecule of such a powerful oxidizing group.

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