

[CONTRIBUTION FROM THE FLUORINE RESEARCH CENTER, UNIVERSITY OF FLORIDA]

## Halogen-Silver Complexes of the Fluorocarbon Carboxylic Acids

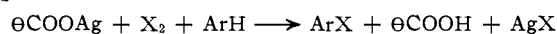
BY G. H. CRAWFORD AND J. H. SIMONS

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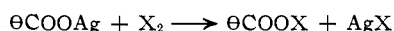
Substances of the general formula  $(C_nF_{2n+1}COO)_2AgI$  have been isolated as products of the reaction of the silver salts of the fluorocarbon carboxylic acids with iodine in fluorocarbon or fluorocarbon derivative (designated in abbreviated form "forbionic") solvents at room temperature. The preparation, 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.<sup>1-5</sup> The reaction may be represented as follows:  $\theta COOAg + X_2 \rightarrow \theta X + AgX + CO_2$  where  $\theta$  is a fluorocarbon radical and X is a halogen atom.

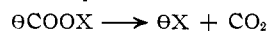
It has been demonstrated that when the above starting materials are combined in an aromatic solvent, such as toluene, ring halogenation occurs.<sup>6-8</sup> The over-all reaction may be represented as



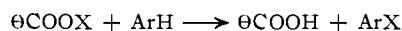
It has been suggested<sup>7-9</sup> that the initial step in both of the above reactions is



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



and



respectively.

The above intermediate has never been isolated from reaction mixtures of (S) and (X). Haszeldine and co-workers<sup>8-10</sup> 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,  $(RCOO)_2AgX$ <sup>11-20</sup>; the carboxy halide,

$RCOOX$ <sup>21-24</sup>; and the halogen triacyl,  $(RCOO)_3X$ .<sup>25,26</sup> 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 forbionic complex. This paper is concerned with the isolation and determination of empirical formula of the forbionic 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  $100^\circ$  *in vacuo*.

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

The forbionic solvents employed were a mixture of  $C_6$  fluorocarbons, a mixture of  $C_3$  fluorocarbons, tributyl 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  $Na_2S_2O_8$ , 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  $180^\circ$  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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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 <sub>3</sub> COOAg               | 28.0   | I <sub>2</sub>  | 16.0   | 126.00 | #3 250 cc. | 3 hr.         | 25-27      | 0.993                 | Complete           |
|     | .....                               | Same   | I <sub>2</sub>  | 0.20   | 1.57   | Same       | 2 hr.         | 25-26      | 1.007                 | Incomplete         |
| 2   | C <sub>2</sub> F <sub>5</sub> COOAg | 5.0772 | I <sub>2</sub>  | 2.3148 | 18.23  | #3 30 cc.  | 2 hr.         | 25-26      | 1.153                 | Incomplete         |
|     | C <sub>2</sub> F <sub>5</sub> COOAg | 0.8081 | ..              | Same   | ....   | Same       | 10 min.       | 25-26      | 0.995                 | Complete           |
| 3   | CF <sub>3</sub> COOAg               | 4.6033 | Br <sub>2</sub> | 1.8668 | 23.36  | #1 25 cc.  | 6 hr.         | 24-26      | 1.121                 | Incomplete         |
|     | CF <sub>3</sub> COOAg               | 0.5675 | ..              | Same   | ....   | #1 25 cc.  | 18 hr.        | 24-26      | 0.998                 | Complete           |
| 4   | C <sub>2</sub> F <sub>5</sub> COOAg | 25.54  | I <sub>2</sub>  | 10.858 | 85.6   | #3 150 cc. | 15 hr.        | 23-25      | 1.07                  | Incomplete         |
|     | C <sub>2</sub> F <sub>5</sub> COOAg | 2.00   | ..              | Same   | ....   | Same       | 15 min.       | 23-25      | 0.999                 | Complete           |
| 5   | C <sub>4</sub> F <sub>9</sub> COOAg | 42.00  | I <sub>2</sub>  | 17.00  | 133.9  | #2 220 cc. | 24 hr.        | 24-26      | 1.33                  | Incomplete         |
|     | C <sub>4</sub> F <sub>9</sub> COOAg | 15.80  | ..              | Same   | ....   | Same       | 3 hr.         | 24-26      | 0.969                 | Complete           |
| 6   | CF <sub>3</sub> COOAg               | 8.6418 | Br <sub>2</sub> | 3.7293 | 46.67  | #3 150 cc. | 6 hr.         | 24-26      | 1.193                 | Incomplete         |
|     | CF <sub>3</sub> COOAg               | 1.933  | ..              | 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<sup>a</sup>

| (S)                                 | A. Preparation |       |                 |        | B. Analysis |         |                 |                     |                       |                              |                              |      |
|-------------------------------------|----------------|-------|-----------------|--------|-------------|---------|-----------------|---------------------|-----------------------|------------------------------|------------------------------|------|
|                                     | G.             | Meq.  | X               | G.     | Meq.        | Solvent | Mean temp., °C. | Reaction time, min. | Total oxidizing power | Recovered acid               | Recovered Ag                 |      |
|                                     |                |       |                 |        |             |         |                 |                     | Meq.                  | % of theory based on Orig. X | % of theory based on Orig. X |      |
| CF <sub>3</sub> COOAg               | 1.098          | 4.97  | I <sub>2</sub>  | 0.6305 | 4.96        | ØF #2   | 11              | 90                  | 4.1168                | 83.00                        | 4.92                         | 98.9 |
| C <sub>2</sub> F <sub>5</sub> COOAg | 2.558          | 9.44  | I <sub>2</sub>  | 1.1086 | 8.73        | ØF #3   | 20              | 300                 | 7.9459                | 91.02                        | 8.36                         | 103  |
| C <sub>2</sub> F <sub>5</sub> COOAg | 2.7140         | 8.45  | I <sub>2</sub>  | 1.0259 | 8.08        | ØF #3   | 15              | 480                 | 7.6461                | 94.5                         |                              |      |
| C <sub>2</sub> F <sub>5</sub> COOAg | 4.8305         | 13.0  | I <sub>2</sub>  | 1.5945 | 12.55       | ØF #3   | 30              | 600                 | 12.0355               | 95.1                         |                              |      |
| C <sub>4</sub> F <sub>9</sub> COOAg | 2.3930         | 5.66  | I <sub>2</sub>  | 0.6908 | 5.439       | ØF #3   | 30              | 27                  | 4.9798                | 91.5                         |                              |      |
| C <sub>4</sub> F <sub>9</sub> COOAg | 3.2500         | 7.71  | I <sub>2</sub>  | 0.9105 | 7.17        | ØF #3   | 37              | 360                 |                       |                              | 7.68                         | 107  |
| CF <sub>3</sub> COOAg               | 1.6452         | 7.444 | Br <sub>2</sub> | 0.5916 | 7.404       | ØF #2   | 40              | 25                  | 5.6810                | 76.7                         |                              |      |
| CF <sub>3</sub> COOAg               | 10.5751        | 47.84 | Br <sub>2</sub> | 3.7293 | 46.67       | ØF #3   | 150             | 26                  |                       |                              | 45.44                        | 97.3 |
|                                     |                |       |                 |        |             |         |                 |                     |                       |                              | (distilled)                  |      |
| C <sub>2</sub> F <sub>5</sub> COOAg | 1.9888         | 6.195 | I <sub>2</sub>  | 0.7313 | 5.782       | ØF #4   | 75              | 25                  |                       |                              |                              |      |
| C <sub>2</sub> F <sub>5</sub> COOAg | 1.8218         | 5.675 | I <sub>2</sub>  | 0.6975 | 5.492       | ØF #4   | 75              | 26                  |                       |                              |                              |      |
|                                     |                |       |                 |        |             |         |                 |                     |                       |                              | 5.55                         | 96.0 |
|                                     |                |       |                 |        |             |         |                 |                     |                       |                              | (distilled)                  | 107  |
|                                     |                |       |                 |        |             |         |                 |                     |                       |                              | 5.52                         | 97.3 |
|                                     |                |       |                 |        |             |         |                 |                     |                       |                              | (distilled)                  | 102  |
|                                     |                |       |                 |        |             |         |                 |                     |                       |                              | 6.18                         | 99.6 |
|                                     |                |       |                 |        |             |         |                 |                     |                       |                              | 5.61                         | 102  |
|                                     |                |       |                 |        |             |         |                 |                     |                       |                              | 7.45                         | 96.6 |
|                                     |                |       |                 |        |             |         |                 |                     |                       |                              | 7.13                         | 95.7 |

<sup>a</sup> The assumption upon which the % of theory in the above table is calculated is that the complex has the formula (OCOO)<sub>2</sub>AgX.

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<sub>2</sub> were titrated with a solution of I<sub>2</sub> in the forbonic solvent. A blank containing only AgI and solvent was titrated with the same solution. The colors observed

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)<br>(O) or (A)  |                   |
|---|--------------------------------------|-----------------------|----------------------------|---------------------|--|--------------------|-------------------|
| 1 | CF <sub>3</sub> COOAg                | 0.8347 g. (3.76 meq.) | 10                         | 0.00993             | Insufficient material in soln. for measurement |                    |                   |
|   |                                      |                       | 20                         | 0.01986             |  |                    |                   |
|   |                                      | I <sub>2</sub>        | 0.4245 g. (3.34 meq.)      | 10                  |  | 0.00993            |                   |
|   | θF #2                                | 65 cc.                | Residue                    |                     |  |                    |                   |
|   |                                      |                       | total                      | 3.2141              | 3.729  | 1.17               |                   |
| 2 | C <sub>3</sub> F <sub>7</sub> COOAg  | 1.0600 g. (3.30 meq.) | 10                         |                     | 0.3009   | 0.491 <sup>a</sup> |                   |
|   |                                      |                       | 10                         | 0.2976              |  | .489 <sup>a</sup>  |                   |
|   |                                      | I <sub>2</sub>        | 0.4114 g. (3.23 meq.)      | 10                  | .2857  |                    | .524 <sup>a</sup> |
|   |                                      |                       | 10                         | .2877               |  | .522 <sup>a</sup>  |                   |
|   |                                      | θF #3                 | 65 cc.                     | 10                  | .2858  |                    | .502 <sup>a</sup> |
|   |                                      |                       |                            | Residue             | 1.2598   |                    | 2.6869            |
|   |                                      | total                 | 2.2726                     |                     | 3.3224   | 1.46               |                   |
| 3 | C <sub>6</sub> F <sub>11</sub> COOAg | 1.71 g. (4.06 meq.)   | 10                         | 0.0516              |  | 0.438 <sup>a</sup> |                   |
|   |                                      |                       | 10                         | 0.0506              |  | 0.475 <sup>a</sup> |                   |
|   |                                      | I <sub>2</sub>        | 0.4740 g. (3.372 meq.)     | 10                  |  | 0.0528             |                   |
|   |                                      |                       | 10                         |                     | 0.0528   |                    |                   |
|   |                                      | θF #3                 | 65 cc.                     | Residue             | 3.3067   |                    | 3.7296            |
|   |                                      | 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 <sub>2</sub> F <sub>6</sub> COOAg | 0.9868 g. (3.641 meq.) | 5                      | 0.3050              |       |
|   |                                     |                        | 5                      | .2910               |       |
|   |                                     | I <sub>2</sub>         | 0.4471 g. (3.250 meq.) | 5                   | .2950 |
|   |                                     |                        | Residue                | 2.6170              | 1008  |
|   | θF #4                               | 65 cc.                 | total                  | 3.5080              |       |
| 5 | C <sub>2</sub> F <sub>6</sub> COOAg | 1.4121 g. (5.211 meq.) | 10                     | 0.4010              |       |
|   |                                     |                        | 10                     | .2650               |       |
|   |                                     | Br <sub>2</sub>        | 0.3987 g. (4.987 meq.) | 10                  | .1830 |
|   |                                     |                        | 10                     | .1400               |       |
|   |                                     |                        | 10                     | .1010               |       |
|   |                                     |                        | 10                     | .0050               |       |
|   | θF #4                               | 120 cc.                | Residue                | 3.5350              |       |
|   |                                     | total                  | 4.6300                 |                     |       |

<sup>a</sup> If the complex in solution has the formula (C<sub>3</sub>F<sub>7</sub>COO)<sub>2</sub>AgI [or (C<sub>6</sub>F<sub>11</sub>COO)<sub>2</sub>AgI] 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<sub>2</sub> per molecule. Titrations of this kind were performed with similar results with (S) being CF<sub>3</sub>COOAg, C<sub>2</sub>F<sub>6</sub>COOAg, C<sub>3</sub>F<sub>7</sub>COOAg, C<sub>4</sub>F<sub>9</sub>COOAg and C<sub>6</sub>F<sub>11</sub>COOAg. A small amount of I<sub>2</sub> 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<sub>3</sub>. 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 (θCOO)<sub>2</sub>AgBr and (θCOO)<sub>2</sub>AgI 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<sub>2</sub>F<sub>6</sub>COO)<sub>2</sub>AgBr and (C<sub>2</sub>F<sub>6</sub>COO)<sub>2</sub>AgI are compared.

TABLE IV  
 PREPARATION, ISOLATION AND ANALYSIS OF THE SOLID COMPLEXES

| (S)                                  | Preparation |       |                   |       |               | Meq. oxidizing power |        | Analysis <sup>a</sup> |                    |        | Meq. AgI |                    |        |        |                    |
|--------------------------------------|-------------|-------|-------------------|-------|---------------|----------------------|--------|-----------------------|--------------------|--------|----------|--------------------|--------|--------|--------------------|
|                                      | G.          | Meq.  | I <sub>2</sub> g. | Meq.  | Sol-vent, cc. | Wt. of ppt., g.      | Found  | Theor.                | Found theor. × 100 | Found  | Theor.   | Found theor. × 100 | Found  | Theor. | Found theor. × 100 |
| CF <sub>3</sub> COOAg                | 1.5308      | 6.926 | 0.8778            | 6.912 | #1<br>50      | 0.1757               | 0.6490 | 0.7622                | 85                 |        |          |                    | 0.3937 | 0.3811 | 103                |
| C <sub>2</sub> F <sub>5</sub> COOAg  | 1.4233      | 5.253 | 0.6471            | 5.095 | #1<br>65      | .2560                |        |                       |                    | 0.8659 | 0.9126   | 95                 | .4613  | .4563  | 101                |
| C <sub>3</sub> F <sub>7</sub> COOAg  | 2.9342      | 9.140 | 1.1378            | 8.959 | #1<br>50      | .2125                | .6220  | .6420                 | 97                 |        |          |                    | .3198  | .3210  | 100                |
| C <sub>4</sub> F <sub>9</sub> COOAg  | 2.5466      | 6.864 | 0.8674            | 6.829 | #1<br>65      | .1989                |        |                       |                    | .5001  | .5230    | 95.5               | .2600  | .2635  | 100                |
| C <sub>6</sub> F <sub>11</sub> COOAg | 3.2135      | 7.633 | 0.9390            | 7.394 | #1<br>65      | .2360                | .5320  | .5466                 | 97.5               |        |          |                    | .2730  | .2733  | 100                |

<sup>a</sup> The theoretical values are calculated on the basis of the formula of complex being (OCOO)<sub>2</sub>AgI.

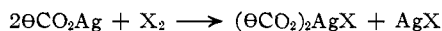
**Isolation and Identification of the Solid Complexes.**—The complexes were prepared as before, employing solvent 1. The filter weighing bottle was chilled in Dry Ice-acetone. After the precipitate had settled, the stopcock between the reactor and weighing bottle was opened and the solution allowed to 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<sub>3</sub> 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<sub>3</sub> 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 (OCOO)<sub>2</sub>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 OCOOX were not detected either as isolatable materials or in equilibrium with (OCOO)<sub>2</sub>AgX.

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<sup>27</sup> and Menefee and Cady<sup>28</sup> 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,<sup>29</sup> 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 oxygen 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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