REACTIONS OF THE HALOGENS WITH THE SILVER SALTS OF CARBOXYLIC ACIDS

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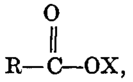
The nature of the product of reaction between silver salt and halogen is dependent upon five factors: (*a*) the nature of the silver salt; (*b*) the ratio of silver salt to halogen; (*c*) the temperature of reaction; (*d*) the presence or absence of other reactive materials; and (*e*) the effect of the solvent. Reaction between equivalent quantities of the silver salt of a carboxylic acid and halogen in an inert solvent produces a complex intermediate, which may be thermally decomposed to give the ester of the corresponding acid and the next lower alcohol. In benzene solutions of olefinic substances this complex intermediate reacts to give the dicarboxylate. Reaction between one equivalent of a silver salt of a carboxylic acid and one mole of halogen produces an active intermediate of the formula  $R-\overset{\overset{O}{\|}}{C}-OX$, in which the halogen apparently has positive character. This substance adds rapidly to olefins, is decomposed thermally to give, by decarboxylation, the corresponding halides, and may be stabilized by coördination of the positive halogen (provided it is iodine) with pyridine.

Descriptions of reactions of the halogens with silver salts of carboxylic acids have appeared periodically in the chemical literature for many years. Peligot (20), as early as 1836, described a reaction between silver benzoate and bromine in which *m*-bromobenzoic acid was isolated. A critical survey of the literature of this subject shows that the nature of the product of reaction between silver salt and halogen is dependent upon five factors: (*a*) nature of the silver salt; (*b*) ratio of silver salt to halogen; (*c*) temperature of reaction; (*d*) presence or absence of other reactive materials; and (*e*) effect of solvent.

The reactions fit definite patterns only when the ratio of equivalents of silver salt to halogen is 1:2 or 1:1. Therefore, cases involving ratios other than these are excluded from this report.

I. REACTIONS INVOLVING EQUIVALENT QUANTITIES OF SILVER SALT AND HALOGEN (SEE TABLE 1)

A. The action of salts of monocarboxylic acids

Work first performed by Simonini (30) and substantiated by other investigators (12, 22, 25, 32) shows that equivalent quantities of iodine and silver salts of monocarboxylic acids react at moderate temperatures to give an active complex intermediate which can be isolated.

$$2RCOOAg + I_2 \xrightarrow[\text{or benzene}]{\text{ether}} (RCOO)_2AgI + AgI$$

TABLE 1

Summary of specific reactions for equivalent quantities of silver salt and halogen

SILVER SALT OF ACID	HALOGEN	REMARKS	ORGANIC PRODUCTS	REFERENCES	YIELD
Acetic acid	Iodine	Solid state; *ca.* 100°C.	Methyl acetate and acetic acid	(2, 11, 29)	50–70 per cent of ester
Acetic acid	Iodine	Petroleum ether as solvent	Complex intermediate	(30, 32)	
Phenylacetic acid	Iodine	Solid state; *ca.* 80°C.	Benzyl phenylacetate and phenylacetic acid	(32)	68 per cent of ester
Triphenylacetic acid	Iodine	Benzene as solvent; 80°C.	Triphenylmethyl ester of triphenylacetic acid	(32)	Quantitative
Caproic acid	Iodine	Solid state; *ca.* 100°C.	Chiefly amyl caproate	(29, 32)	70 per cent
Caproic acid	Iodine	Petroleum ether as solvent	Complex intermediate	(30)	
Palmitic acid	Iodine	Solid state; *ca.* 100°C.	Pentadecyl palmitate	(8, 19)	
Stearic acid	Iodine	Solid state; *ca.* 100°C.	Heptadecyl stearate	(8, 11)	
Lacceric acid	Iodine	Solid state; *ca.* 100°C.	Myricyl laccerate	(9)	
Benzoic acid	Iodine	Ethyl ether or benzene as solvent	Complex intermediate	(12, 22, 32)	
Benzoic acid	Iodine	Decomposition of complex; 150–190°C.	Iodobenzene, benzoic acid, and phenyl benzoate	(32)	Small amount of ester
Glutaric acid	Iodine	Solid state; *ca.* 90°C.	γ-Butyrolactone and glutaric anhydride	(32, 33)	30 per cent of lactone
Adipic acid	Iodine	Solid state; *ca.* 90°C.	δ-Valerolactone and adipic acid	(32)	Low yield of lactone
β,β-Dimethylglutaric acid	Iodine	Solid state; *ca.* 90°C.	β,β-Dimethyl-γ-butyrolactone and β,β-dimethylglutaric anhydride	(33)	40 per cent of lactone
α-Ethylglutaric acid	Iodine	Solid state; *ca.* 90°C.	γ-Caprolactone	(33)	
α,α′-Diethylglutaric acid	Iodine	Solid state; *ca.* 90°C.	α-Ethyl-γ-caprolactone	(33)	
1,1-Cyclohexanediacetic acid	Iodine	Solid state; *ca.* 90°C.	Lactone of 1,1-cyclohexanediacetic acid	(34)	
4-Methyl-1,1-cyclohexanediacetic acid	Iodine	Solid state; *ca.* 100°C.	Lactone of 4-methylcyclohexane-1,1-diacetic acid	(10)	16 per cent

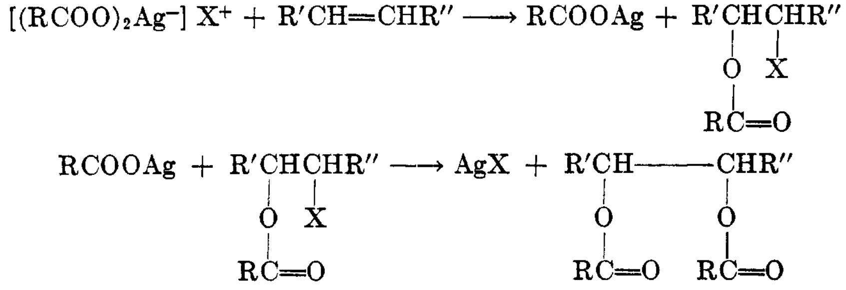
cis-Hexahydrohomophthalic acid	Iodine	Solid state; *ca.* 90°C.	*cis*-Hexahydrophthalide and *cis*-hexahydrohomophthalic acid	(34)	
trans-Hexahydrohomophthalic acid	Iodine	Solid state; *ca.* 90°C.	*cis*-Hexahydrophthalide and *trans*-hexahydrohomophthalic acid	(34)	
cis-Hexahydroisophthalic acid	Iodine	Solid state; *ca.* 90°C.	Lactone of *cis*-hexahydroisophthalic acid	(34)	
Camphoric acid	Iodine	Solid state; *ca.* 90°C.	Anhydride of camphoric acid	(34)	
Phthalic acid	Iodine	Solid state; *ca.* 130°C.	Phthalic anhydride	(32)	84 per cent
Glycolic acid	Iodine	Solid state	Formaldehyde and glycolic acid	(32)	
Lactic acid	Iodine	Benzene as solvent; room temperature	Acetaldehyde and lactic acid	(32)	
Mandelic acid	Iodine	Benzene as solvent; room temperature	Benzaldehyde and mandelic acid	(32)	60 per cent of aldehyde
Benzilic acid	Iodine	Room temperature	Complex intermediate	(32)	
Benzilic acid	Iodine	Decomposition of complex; 55–60°C.	Benzophenone and benzilic acid	(32)	42 per cent of acid
Acetic acid	Iodine	Benzene solution of 1-pentene	1,2-Pentanediol diacetate	(23)	Good
Acetic acid	Iodine	Benzene solution of unsymmetrical diphenylethylene	Glycol diacetate of unsymmetrical diphenylethylene	(23)	Good
Benzoic acid	Iodine	Benzene solution of ethylene	1,2-Ethanediol dibenzoate	(23)	Good
Benzoic acid	Iodine	Benzene solution of propylene	1,2-Propanediol dibenzoate	(23)	Good
Benzoic acid	Iodine	Benzene solution of 1-pentene	1,2-Pentanediol dibenzoate	(23)	Good
Benzoic acid	Iodine	Benzene solution of 1-hexadecene; hydrolysis of product	1,2-Hexadecanediol	(18)	33 per cent
Benzoic acid	Iodine	Benzene solution of 1-eicosene; hydrolysis of product	1,2-Eicosanediol	(18)	70 per cent
Benzoic acid	Iodine	Benzene solution of 1-octadecene; hydrolysis of product	1,2-Octadecanediol	(18)	73 per cent
Benzoic acid	Chlorine, bromine, or iodine	Carbon tetrachloride solution of olefinic compounds; no further details	Isolation of the benzoates of the corresponding halo alcohols	(25, 28)	
Benzoic acid	Iodine	Benzene solution of styrene	Glycol dibenzoate of styrene	(23)	Good

TABLE 1—*Concluded*

SILVER SALT OF ACID	HALOGEN	REMARKS	ORGANIC PRODUCTS	REFERENCES	YIELD
Benzoic acid	Iodine	Benzene solution of unsymmetrical diphenylethylene	Glycol dibenzoate of unsymmetrical diphenylethylene	(23)	Good
Benzoic acid	Iodine	Benzene solution of stilbene	Glycol dibenzoate of stilbene	(23)	Good
Benzoic acid	Iodine	In presence of allylbenzene; hydrolysis of product	3-Phenyl-1,2-propanediol	(12)	Good
Benzoic acid	Iodine	Benzene solution of $RCH{=}CHCH_2OCOC_6H_5$; no further details	Dibenzoate of corresponding glycol	(22)	70 per cent
Benzoic acid	Iodine	Benzene solution of $RCH{=}CHOCOC_6H_5$; no further details	Dibenzoate of corresponding glycol	(22)	35 per cent
Benzoic acid	Iodine	Benzene solution containing excess butadiene; hydrolysis of products	80 per cent of 1,2-dihydroxy-3-butene and 4 per cent of 1,4-dihydroxy-2-butene	(26)	←
Benzoic acid	Iodine	Benzene solution of acetylene	Iodo- and diiodo-acetylenes	(24)	
Benzoic acid	Chlorine, bromine, or iodine	Benzene solution of 1-heptyne	Corresponding haloheptyne	(28)	Good
Benzoic acid	Iodine	Benzene solution of phenylacetylene	1-Iodo-2-phenylacetylene	(24)	

Upon hydrolysis the complex yields the parent acid, silver iodide, and silver iodate, indicating that the iodine in the complex has positive character and has undergone an autoöxidation-reduction. Thermal decomposition of the intermediate gives, as the main product, the ester of the corresponding acid and the next lower alcohol. The ester, along with some free acid, is also formed at elevated temperatures in solid-state reactions between equivalent quantities of halogen.

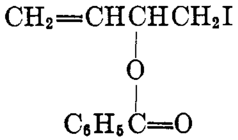
Prévost (22) first demonstrated that in the presence of benzene solutions of olefinic substances, the complex intermediate, described above, reacts to give the dicarboxylate, which upon hydrolysis yields the corresponding glycol in good yield. With olefinic materials capable of *cis–trans* isomerism, the *trans* addition predominates (23). According to Prévost (25, 27), the reaction proceeds in two steps:



$$[(RCOO)_2Ag^-]\,X^+ + R'CH{=}CHR'' \longrightarrow RCOOAg + R'\underset{\substack{|\\ O\\ |\\ RC=O}}{C}H\underset{\substack{|\\ X}}{C}HR''$$

$$RCOOAg + R'\underset{\substack{|\\ O\\ |\\ RC=O}}{C}H\underset{\substack{|\\ X}}{C}HR'' \longrightarrow AgX + R'\underset{\substack{|\\ O\\ |\\ RC=O}}{C}H\text{———}\underset{\substack{|\\ O\\ |\\ RC=O}}{C}HR''$$

When carbon tetrachloride is used as solvent (25, 28) the halogen esters can be isolated, since the second phase of the reaction takes place very slowly in this medium. It is interesting to note that the complex $[(C_6H_5COO)_2Ag]^-I^+$ reacts slowly with excess butadiene to form a syrup which upon hydrolysis gives an 80 per cent yield of 1,2-dihydroxy-3-butene (26). This reaction also proceeds by the mechanism given above, since the intermediate,



$$CH_2{=}CH\underset{\substack{|\\ O\\ |\\ C_6H_5C=O}}{C}HCH_2I$$

can be isolated.

It has been previously indicated that the halogen in the complex intermediate has positive character. Further proof of this is shown by the fact that it reacts with the alkynes, acetylene and phenylacetylene, by substitution rather than addition to give the corresponding haloalkynes (24).

B. The action of salts of dicarboxylic acids

Birnbaum and Gaier (3) first studied the reaction between equivalent quantities of the silver salts of some dicarboxylic acids and iodine. When silver oxalate is heated with iodine the only products obtained are carbon dioxide and silver iodide; salts of malonic, succinic, malic, tartaric, fumaric, and maleic acids yield the corresponding acids or anhydrides, carbon monoxide, carbon dioxide, and silver iodide. The reactions proceed vigorously, in the absence of air, below 200°C. Wieland and Fischer (32) reported results on the same compounds which differ slightly from those given above.

Wieland and Fischer and other investigators (10, 32, 33, 34) demonstrated that with silver salts of dicarboxylic acids capable of forming lactones, the chief products are the lactone and the acid or acid anhydride. For example, silver glutarate and iodine react to yield, besides silver iodide, γ-butyrolactone and glutaric anhydride.

C. The action of salts of α-hydroxy acids

As a general rule, salts of α-hydroxy acids react with equivalent quantities of iodine to give, as organic products, the free acid and the next lower aldehyde (13, 32). In this connection, it is interesting that only in the case of silver benzilate was an intermediate complex of the type discovered by Simonini (30) isolated (32). Apparently, the temperatures for formation and decomposition of most of the complexes of this type are very close together.

II. REACTIONS INVOLVING ONE EQUIVALENT OF SILVER SALT WITH TWO OF HALOGEN (SEE TABLE 2)

A. The degradation of the reaction product

When 1 equivalent of a silver salt of a carboxylic acid is treated with 1 mole of halogen in the cold, there is apparently formed a product of the composition RCOOX(1, 5), the nature of which will be discussed later in this report. Several investigators have studied the decomposition of this substance, RCOOX, where the halogen is either chlorine or bromine. In every case, there is formed by decarboxylation, the corresponding halo compound, RX, in excellent yield.

$$RCOOAg + X_2 \longrightarrow RCOOX + AgX$$

$$RCOOX \xrightarrow{\text{heat}} RX + CO_2$$

The salts of substituted acids react in a similar manner, giving always compounds poorer by one carbon atom.

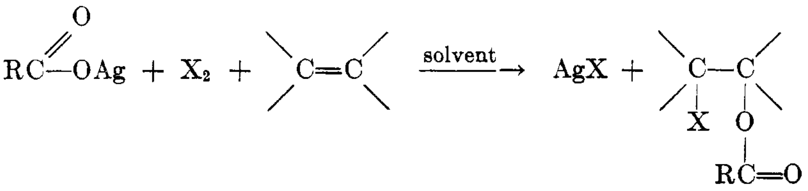
With a few exceptions, the compounds investigated have been salts of fatty acids or substituted fatty acids. Bockemüller and Hoffmann (5) have shown that bromine reacts with silver benzoate in boiling carbon tetrachloride to give an 80 per cent yield of bromobenzene. On the other hand, Lüttringhaus and Schaede (17) claim that with silver salts of aromatic carboxylic acids the degradation is unsatisfactory. The types of reactions carried out have been summarized (16). In each case the salts of the acid were used.

1. Alkyl halides are obtained from fatty acids.
2. α-Hydroxy acids give hydrogen halide compounds of the aldehydes.
3. From hydroxy acids in which the hydroxyl group is not in the alpha position, the hydroxyalkyl halides are formed.

4. Polyhydroxy acids with one hydroxyl group in the alpha position yield the hydrogen halide compounds of the hydroxyaldehydes.
5. 1,1-Halogenated hydrocarbons are formed from α-halo fatty acids.
6. From n-fold halogenated fatty acids the $(n + 1)$-fold halogenated hydrocarbons are obtained.
7. Dicarboxylic acids give rise to disubstituted hydrocarbon halides.
8. From ester acids the halogenated fatty acid esters are obtained. In this regard, it is noteworthy that Hunsdiecker, Erlbach, and Vogt (14) have utilized the ω-halo fatty acids, obtained by the degradation of the silver salts of dicarboxylic acid monoesters, to synthesize large-membered lactone rings and ring ketones.
9. α-Keto acids yield the acid halides poorer by one carbon atom.
10. Cycloalkane-monocarboxylic and -polycarboxylic acids yield the corresponding cycloalkyl halides.
11. From α-amino acids the alkylidenimine hydrohalides are obtained.
12. From other amino acids the haloalkylamines are formed.

B. The reaction of the product with some nucleophilic substances

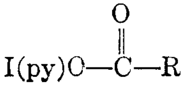
The product of reaction of equimolecular quantities of halogen and silver salt adds to the double bond of olefinic substances to give the corresponding halo esters (1, 5, 31). The general reaction may be expressed by the equation:



$$RC(=O)OAg + X_2 + {>}C{=}C{<} \xrightarrow{\text{solvent}} AgX + {>}C(X)\text{—}C(OCOR){<}$$

According to Birckenbach and coworkers (1), the immediate product of the reaction may be considered to be RCOOX, a mixed-halogen-like material. These investigators showed that the filtrate from the reaction at −80°C. of equimolecular quantities of silver acetate and iodine adds to cyclohexene at room temperature to give the acetate of 2-iodo-1-cyclohexanol. This is undisputed evidence for the presence of CH_3COOI in solution.

That iodine is undoubtedly the positive part of substances of the type RCOOI is shown by the work of Carlsohn (6), who was able to stabilize the positive iodine by coördination with pyridine, to form compounds of the type



$$I(py)O\text{—}C(=O)\text{—}R$$

These compounds liberate iodine from potassium iodide, and in the presence of water undergo an autoöxidation–reduction, forming iodine and pyridinium iodate. Moreover, they immediately attack an acidic solution of phenol

TABLE 2

Summary of specific reactions for equimolecular quantities of silver salt and halogen

SILVER SALT OF ACID	HALOGEN	REMARKS	ORGANIC PRODUCTS	REFERENCES	YIELD
Acetic acid	Bromine	Dry state	Methyl bromide	(16)	80 per cent
Butyric acid	Bromine	Nitrobenzene as solvent	Propyl bromide and butyric acid	(5)	61 per cent of propyl bromide
Lauric acid	Bromine	Carbon tetrachloride as solvent	Undecyl bromide	(16)	75–80 per cent
Palmitic acid	Bromine	Dry state	Pentadecyl bromide	(16)	75–80 per cent
Stearic acid	Chlorine	Dry state; *ca.* 100°C.	Heptadecyl chloride	(16)	Variable
Stearic acid	Bromine	Carbon tetrachloride as solvent	Heptadecyl bromide and stearic acid	(5)	37 per cent
9,10-Dichloroöctadecanoic acid	Bromine	Carbon tetrachloride as solvent	1-Bromo-8,9-dichloroheptadecane	(16)	76 per cent
α-Bromostearic acid	Bromine	Carbon tetrachloride as solvent	1,1-Dibromoheptadecane	(16)	70 per cent
α-Hydroxypalmitic acid	Bromine	Dry state	The hydrobromide of the pentadecyl aldehyde	(16)	
Mandelic acid	Bromine	Ether as solvent	The hydrobromide of benzaldehyde	(16)	Variable
Pyruvic acid	Bromine	Carbon tetrachloride as solvent	Acetyl bromide	(16)	
Benzoic acid	Bromine	Boiling carbon tetrachloride as solvent	Bromobenzene	(5)	80 per cent
Phenylpropiolic acid	Iodine	Boiling benzene as solvent	1-Iodo-2-phenylacetylene	(32)	Good
Adipic acid	Bromine	Boiling carbon tetrachloride as solvent	1,4-Dibromobutane	(5)	10 per cent
Sebacic acid	Bromine	Carbon tetrachloride as solvent	1,8-Dibromoöctane	(16)	62 per cent
Adamantanedicarboxylic acid	Bromine	Carbon tetrachloride; *ca.* 70°C.	1,3-Dibromoadamantane	(21)	
Monomethyl ester of 1,6-hexanedioic acid	Bromine	Carbon tetrachloride as solvent	Methyl ester of 5-bromopentanoic acid	(15)	68 per cent
Monomethyl ester of 1,8-octanedioic acid	Bromine	Carbon tetrachloride as solvent	Methyl ester of 7-bromoheptanoic acid	(15)	70 per cent

Monomethyl ester of 1,9-nonanedioic acid	Bromine	Carbon tetrachloride solvent	Methyl ester of 8-bromoöctanoic acid	(15)	70 per cent
Monomethyl ester of 1,10-decanedioic acid	Bromine	Carbon tetrachloride as solvent	Methyl ester of 9-bromononanoic acid	(15)	75 per cent
Monomethyl ester of 1,11-undecanedioic acid	Bromine	Carbon tetrachloride as solvent	Methyl ester of 10-bromodecanoic acid	(15)	71 per cent
Monomethyl ester of 1,13-tridecanedioic acid	Bromine	Carbon tetrachloride as solvent	Methyl ester of 12-bromododecanoic acid	(15)	78 per cent
Monomethyl ester of 1,14-tetradecanedioic acid	Bromine	Carbon tetrachloride as solvent	Methyl ester of 13-bromotridecanoic acid	(15)	71 per cent
Monomethyl ester of 1,15-pentadecanedioic acid	Bromine	Carbon tetrachloride as solvent	Methyl ester of 14-bromotetradecanoic acid	(15)	73 per cent
Monomethyl ester of 1,16-hexadecanedioic acid	Bromine	Carbon tetrachloride as solvent	Methyl ester of 15-bromopentadecanoic acid	(15)	70 per cent
Monomethyl ester of 1,17-heptadecanedioic acid	Bromine	Carbon tetrachloride as solvent	Methyl ester of 16-bromohexadecanoic acid	(15)	70 per cent
Monomethyl ester of 1,18-octadecanedioic acid	Bromine	Carbon tetrachloride as solvent	Methyl ester of 17-bromoheptadecanoic acid	(15)	75 per cent
Acetic acid	Iodine	Ether solution of cyclohexene; room temperature	Acetate of 2-iodo-1-cyclohexanol	(1)	80 per cent
Acetic acid	Chlorine	Carbon tetrachloride solution of allyl chloride	Acetate of 2,3-dichloro-1-propanol	(5)	10 per cent
Propionic acid	Bromine	Chloroform solution of cyclohexene; −25° to −30°C.	Propionate of 2-bromo-1-cyclohexanol	(31)	48 per cent
Benzoic acid	Chlorine	Carbon tetrachloride solution of cyclohexene; −10°C.	Benzoate of 2-chloro-1-cyclohexanol	(31)	15 per cent
Benzoic acid	Bromine	Same as above	Benzoate of 2-bromo-1-cyclohexanol	(31)	42 per cent
Benzoic acid	Iodine	Ether solution of cyclohexene	Benzoate of 2-iodo-1-cyclohexanol	(1)	60 per cent
Phthalic acid	Iodine	Same as above	Di(1-iodocyclohexyl) phthalate	(1)	60 per cent
Benzoic acid	Iodine	Inert solvent containing pyridine	Monopyridine iodine (I) benzoate	(6)	Good
β-Naphthoic acid	Iodine	Same as above	Monopyridine iodine (I) β-naphthoate	(6)	Good
Benzilic acid	Iodine	Same as above	Monopyridine iodine (I) benzilate	(6)	Good

to give iodophenol, a reaction which Cofman (7) has shown can only be carried out by positive univalent iodine.[1]

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[1] When iodine or bromine is attached to a group which is more electronegative than a carboxylic acid residue, it is sufficiently positive (electrophilic) to iodinate or brominate benzene directly. Birckenbach and Goubeau (Ber. **65,** 395 (1932)) have demonstrated that iodine or bromine reacts with silver perchlorate in benzene to give a good yield of iodo- or bromo-benzene. They postulate the existence of $IClO_4$ as an intermediate in the first reaction.