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Thermal and Photochemical Decomposition of Silver Carboxylates

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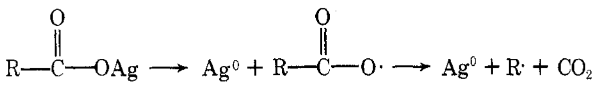
Silver salts of carboxylic acids decompose at 200–350 °C to silver, carbon dioxide, and radicals. Silver benzoate at 276 °C gives polyphenyls containing two to five benzene rings, as well as benzene, benzoic acid, and 3,4-benzocoumarin. Arylation of benzophenone was effected by silver benzoate at 300 °C, along with formation of biphenyl and benzophenone dimer. An intimate mixture of silver isonicotinate and silver benzoate at 275 °C gave coupling products of phenyl and pyridyl radicals with themselves and with each other. Silver trifluoroacetate decomposes thermally above 260 °C or irradiated with ultraviolet light in solution at 25 °C, to silver, carbon dioxide, and trifluoromethyl radicals. As silver trifluoroacetate, unlike most silver salts, is relatively soluble in organic solvents, it may be used as a convenient source of trifluoromethyl radicals. With benzene at 325 °C it gave 38 mol % of benzotrifluoride; 57 mol % of benzotrifluoride resulted from the photochemical reaction. Benzonitrile gave a good yield of the three isomeric trifluoromethyl benzonitriles, mainly ortho. With 4-benzoylpyridine at 300 °C silver trifluoroacetate gave derivatives formed predominantly by addition of trifluoromethyl radicals to the benzene ring. Silver salts of polycarboxylic acids decompose at 200–425 °C to silver, carbon dioxide, and products apparently formed from polyradicals. Silver isophthalate, pyrolyzed under nitrogen at 375 °C and cooled under hydrogen, gives silver imbedded in a black, carbonlike polymer that ignites at 25 °C when exposed to air. Different silver salts give a wide variety of different shapes upon being pyrolyzed. Heteroatoms are retained; silver pyridine-3,5-dicarboxylate at 310 °C yielded carbon dioxide, silver, and black polymer with the theoretical amount of nitrogen. Considerable control of pore-size distribution and surface area for silver imbedded in carbonlike polymers has been achieved by pyrolyzing the appropriate silver polycarboxylate. Silver carboxylates represent a new class of stable radical precursors of great variety, ready availability, and easy preparation.

As organic chemistry developed in the middle and late 19th century, silver salts of carboxylic acids were among the first derivatives prepared, primarily because they were easy to make and to purify. Surprisingly, except for a few scattered references in the literature dealing with explosives,[1] the behavior of silver carboxylates at elevated temperatures has been wholly ignored.

We have discovered that silver carboxylates decompose, when heated, according to the scheme



$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}OAg} \longrightarrow \mathrm{Ag^0} + \mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}O\cdot} \longrightarrow \mathrm{Ag^0} + \mathrm{R\cdot} + \mathrm{CO_2}$$

As an example, 45.8 g (200 mmol) of silver benzoate (276 °C dec), heated in a Pyrex tube under a stream of nitrogen to 280 °C for 1 min, gave the products shown in Table I. The gas evolved, together with benzoic acid and benzocoumarin, accounted for 196 mmol (98%) of CO_2; the products listed in Table I accounted for 197.4 mmol (98.7%) of phenyl radicals.

Silver benzoate was pyrolyzed under a variety of conditions: diluted with twice its weight of silica; in a bomb under 300 psi autogenous pressure; and in a pellet formed under 10 000 psi. In all cases the identical products were formed and in about the same proportions.

Benzene and benzoic acid are the products of hydrogen abstraction by phenyl and benzoyloxy radicals, respectively.[2] Biphenyl and higher polyphenyls may form by phenylation of silver benzoate and subsequent decomposition; ortho phenylation gives 3,4-benzocoumarin. Some biphenyl may result from dimerization of phenyl radicals trapped in a solid matrix, although dimerization is not favored in liquid or gas phase reactions of phenyl radicals.[3]

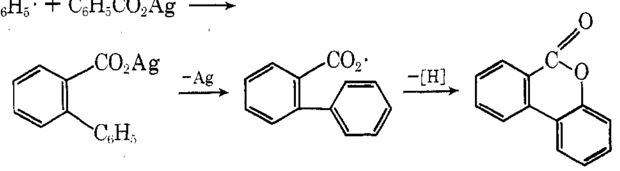
$$\mathrm{C_6H_5CO_2Ag} \xrightarrow{-\mathrm{Ag}} \mathrm{C_6H_5CO_2\cdot} \xrightarrow{[\mathrm{H}]} \mathrm{C_6H_5CO_2H}$$

$$\mathrm{C_6H_5CO_2\cdot} \xrightarrow{-\mathrm{CO_2}} \mathrm{C_6H_5\cdot} \xrightarrow{[\mathrm{H}]} \mathrm{C_6H_6}$$

$$\mathrm{C_6H_5\cdot} + \mathrm{C_6H_5CO_2Ag} \xrightarrow{-[\mathrm{H}]}$$

$$\mathrm{C_6H_5C_6H_4CO_2Ag} \xrightarrow{-\mathrm{CO_2},\ -\mathrm{Ag}} \mathrm{C_6H_5C_6H_4\cdot} \xrightarrow{[\mathrm{H}]} \mathrm{C_6H_5C_6H_5}$$

$$\mathrm{C_6H_5\cdot} + \mathrm{C_6H_5CO_2Ag} \xrightarrow{-[\mathrm{H}]}$$



Silver salts of substituted benzoic acids behave similarly to silver benzoate. Silver *p*-fluorobenzoate and silver pentafluorobenzoate, each decomposed at 300 °C under nitrogen, gave the products shown in Tables II and III, respectively.

Among the heterocyclic compounds, silver thiophene-2-carboxylate at 275 °C gave thiophene and bithiophene in a weight ratio of 3:1. Silver salts of pyridinecarboxylic acids at 280–320 °C gave bipyridyls and terpyridyls with varying amounts of pyridine, as shown in Table IV. Hydrogen abstraction by radicals from thermal decomposition of silver salts, a minor reaction in the aromatic series, becomes more pronounced in some heterocyclic radicals, and is the major reaction of aliphatic radicals.

Although silver arenecarboxylates have little, if any, solubility in most organic solvents, arylation could be effected in high-boiling liquids. A mixture of benzophenone and silver benzoate, 2:1 molar, stirred and refluxed for 30 min, gave phenylbenzophenone and diphenylbenzophenone, as well as some biphenyl and benzophenone dimer.

Mixtures of silver salts give products derived from mixed, as well as like, radicals. Equimolar amounts of silver benzoate and silver isonicotinate, milled together and heated to 275 °C under nitrogen, gave the major products shown in Table V. There were formed additionally benzocoumarin and the mono- and dipyridyl analogues of benzocoumarin in concentrations of 2.2, 2.6, and 0.7 respectively, on the same scale.

Table I. **Products from Silver Benzoate at 280 °C**

Product	mmol[a]	Product	mmol[a]
CO_2	189.9	Terphenyl	12.4
Benzene	10	Quaterphenyl	3
Benzoic acid	1.5	Quinquephenyl	0.5
Biphenyl	61.5	Silver	200
3,4-Benzocoumarin	5.6		

[a] Analysis by gas chromatography and low voltage (7.5 eV nominal) mass spectrometry.

Table II. **Products from Silver *p*-Fluorobenzoate at 300 °C**

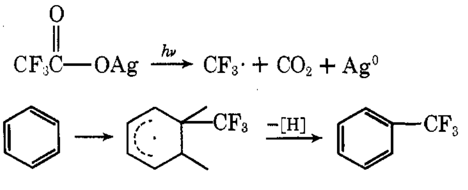
Product[a]	Concn[b]	Product[a]	Concn[b]
Fluorobenzene	2.1	Trifluoroterphenyl	13.8
Difluorobiphenyl	27.4	Fluorophenylfluorobenzocoumarin	9.0
Fluorobenzocoumarin	13.8	Fluorophenyldifluorobenzocoumarin	4.7
Difluorobenzocoumarin	22.9	Tetrafluoroquaterphenyl	4.0

[a] Isomers are included. [b] Percent of total ions in the low-voltage mass spectrum.

Silver trifluoroacetate differs from most silver salts in being relatively soluble in organic solvents. Silver trifluoroacetate decomposes when heated above 260 °C or irradiated with ultraviolet light in solution at 25 °C to give silver, carbon dioxide, and trifluoromethyl radical, and thus may be used as a convenient source of this radical.

For example, a solution of 4.4 g (20 mmol) of silver trifluoroacetate in 600 ml of benzene was added dropwise to a vertical Vycor tube containing Vycor chips at 325 °C; contact time was 5 s. The benzene condensate, analyzed by gas chromatography, contained 7.6 mmol of benzotrifluoride, a yield of 38 mol %.

The same solution was rotated in a 1-l. quartz flask 2 in. from a 500-W Hanovia high-pressure mercury lamp for 6 h at 25 °C. Irradiation was interrupted every hour to remove with nitric acid the silver mirror that deposited on the inner surface of the flask. The filtered benzene solution contained 11.4 mmol (57 mol % yield) of benzotrifluoride, formed evidently by these reactions:



$$CF_3\overset{\overset{O}{\|}}{C}—OAg \xrightarrow{h\nu} CF_3\cdot + CO_2 + Ag^0$$

A mixture of 50 mmol of silver trifluoroacetate and 150 mmol of chlorobenzene was heated in a bomb at 300 °C for 5 min. Chlorobenzotrifluoride isomers, 5.9 mol % yield, consisted of 83% ortho and 17% para; no *m*-chlorobenzotrifluoride was detected. The accuracy of the analysis was somewhat impaired by interference from other components of the mixture. Nonetheless, trifluoromethylation evidently is mainly ortho, as has been found for other radical additions to aromatic compounds such as arylation of chlorobenzene by phenyl radicals.[4]

A better yield of products was obtained from benzonitrile. A mixture of 100 mmol of benzonitrile and 50 mmol of silver trifluoroacetate in a bomb at 300 °C for 10 min gave a 70 mol % yield of trifluoromethylbenzonitrile of isomer composition 50.7% ortho, 14.1% meta, and 35.2% para. The three isomers gave qualitatively similar mass spectra, the most pronounced difference occurring at *M/z* 170, corresponding to $(M - H)^+$. Intensity at *M/z* 170 relative to that of the molecular ion, the most abundant ion in each of the spectra, is 28% for the meta isomer and 22% for the ortho and para. The difference may well be a reflection of the fact that only the meta isomer contains a ring hydrogen not deactivated by one or both electron-withdrawing substituents.

The products other than trifluoromethylbenzonitrile consisted mainly of bis(trifluoromethyl)benzonitrile, with

Table III. **Products from Silver Pentafluorobenzoate at 300 °C**

Product	Concn[a]
Perfluorobiphenyl	86
Perfluoroterphenyl	10
Perfluoroquaterphenyl	4

[a] Percent of total ions in the low-voltage mass spectrum.

Table IV. **Products from Silver Pyridinecarboxylates at 280–320 °C**

Pyridinecarboxylate isomer	2-	3-	4-
Product[a]		Concn[b]	
Pyridine	53.2	46.0	2.4
Bipyridyl	36.6	36.7	80.9
Terpyridyl	8.6	14.8	14.2
Quaterpyridyl	1.6	2.5	2.3

[a] Isomers are included. [b] Percent of total ions in the low-voltage mass spectrum.

Table V. **Products from Silver Benzoate and Silver Nicotinate at 275 °C**

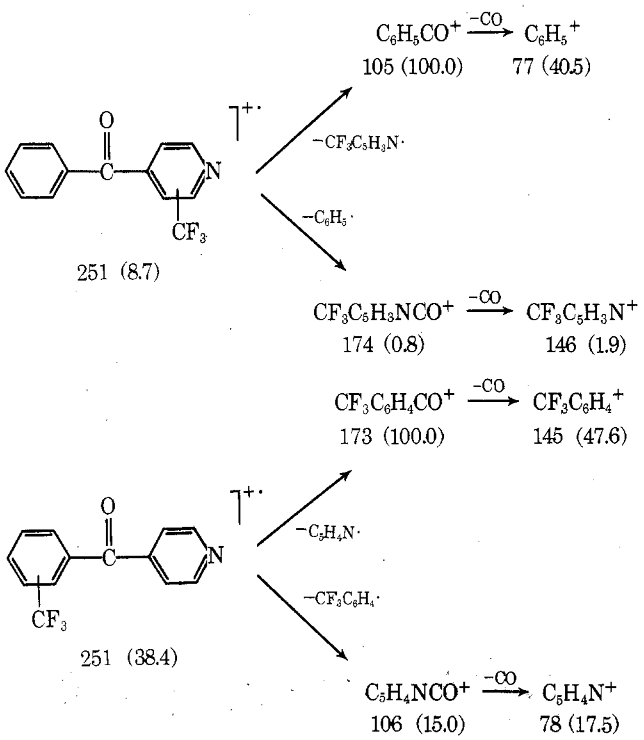
Product[a]	Concn[b]	Product[a]	Concn[b]
Benzoic acid	11.8	Phenylbipyridyl	7.1
Biphenyl	9.6	Terpyridyl	0.9
Phenylpyridine	16.5	Quaterphenyl	2.6
Bipyridyl	4.1	Pyridylterphenyl	3.8
Terphenyl	7.7	Diphenylbipyridyl	2.0
Diphenylpyridine	14.2	Phenylterpyridyl	0.5

[a] Isomers are included. [b] Percent of total ions in the low-voltage mass spectrum.

traces of benzoyl fluoride, biphenyl, and trifluoromethylbiphenyl.

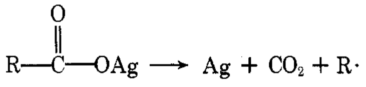
Reagents boiling above 260 °C could be trifluoromethylated at atmospheric pressure. A stirred mixture of 50 mmol of silver trifluoroacetate and 100 mmol of benzophenone at 290 °C for 10 min gave 26 mol % of trifluoromethylbenzophenone isomers. Coumarin and 4-benzoylbiphenyl, under the same conditions, gave 18 and 32 mol %, respectively, of the corresponding trifluoromethyl derivatives. In all these reactions small amounts of bis(trifluoromethyl) derivatives and dehydro dimers of the reagent also formed.

A mixture of 50 mmol each of 4-benzoylpyridine and silver trifluoroacetate, heated at 300 °C for 10 min, yielded 14 mol % trifluoromethylbenzoylpyridine isomers. To find the distribution of trifluoromethyl radicals between the benzene and pyridine rings, we analyzed the products by directly coupled gas chromatography–mass spectrometry. The analysis showed that a considerably greater portion of the product was trifluoromethylphenyl pyridyl ketone than phenyl trifluoromethylpyridyl ketone. The CF_3 radical added to the phenyl group in preference to the pyridyl. The mass spectra of individual gas chromatographic fractions judged to comprise chiefly the ketones shown below indicated decompostion of the molecular ions to RCO^+ and R^+ according to the scheme (initial numbers are masses, those in parentheses are relative intensities):



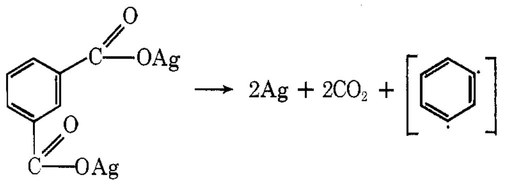
Relative intensities of the various ions show that, in these decompositions to ions and neutral products, the molecules preferentially yield benzoyl and thence phenyl ions rather than pyridoyl and pyridyl, regardless of which group carries the CF_3 substituent. The same preference for primary loss of the pyridyl radical over that of phenyl is observed in the mass spectra of the isomeric unsubstituted benzoylpyridines.[5] The difference suggests a preference for charge localization in the phenyl ring of the molecular ions,[6] in accord with the difference between the ionization potentials of the $C_6H_5CO\cdot$ and $C_5H_3NCO\cdot$ radicals, the former an estimated 0.6 eV lower than the latter (para isomer).[7] The ionization potential difference is increased by CF_3 substitution in the pyridyl ring; it is decreased by CF_3 substitution in the phenyl ring, but not enough to change the algebraic sign. The implied greater electron-releasing ability of the benzoyl radical, in turn, offers a plausible rationale for the addition of the electrophilic $CF_3\cdot$ radical to the phenyl ring in preference to the pyridyl.[8]

As silver salts of monocarboxylic acids decompose at 200–300 °C to metallic silver, carbon dioxide, and free radicals



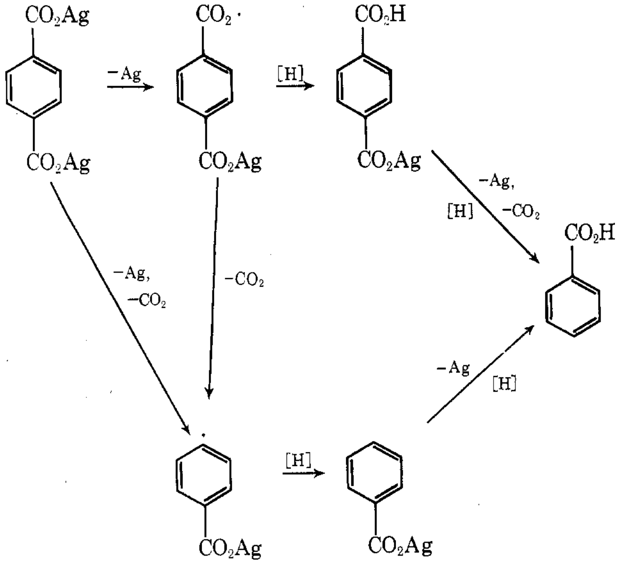
$$R{-}\overset{O}{\overset{\|}{C}}{-}OAg \longrightarrow Ag + CO_2 + R\cdot$$

silver salts of dicarboxylic acids should decompose to give diradicals and products derived from diradicals. To investigate this intriguing possibility we heated silver isophthalate to 375 °C under nitrogen. At this temperature the solid expanded rapidly and voluminously, gave off carbon dioxide, and left a black residue that analyzed 74% Ag, 24% C, and 1.3% H. Calculated for $[2Ag{\cdot}C_6H_4]_n$ from the reaction



Ag, 73.9%; C, 24.7%; H, 1.4%.

Losses of weight of silver polycarboxylates at their decomposition temperatures were determined. In separate experiments, the amounts of carbon dioxide evolved were measured. Results are shown in Table VI. In all cases the thermogravimetric curves had smooth, single inflections, indicating concerted, rather than stepwise, decompositions. Evidence for some stepwise decomposition was obtained by compressing the silver salts at 10 000 psi in a tabletting machine and pyrolyzing the tablet. Silver isophthalate (10 mmol), thus tabletted and pyrolyzed at 375 °C, gave 0.1 g of acetone-soluble products consisting mainly of benzoic acid, biphenyl, terphenyl, and benzocoumarin. Silver terephthalate (30 mmol) gave 0.18 g of acetone-soluble products identical with those from silver isophthalate although differing somewhat in relative amounts. The products from both silver salts are similar to those from pyrolyzed silver benzoate, Table I, and evidently formed by hydrogen abstraction by radical intermediates.



Silver isophthalate decomposed at 375 °C in air, giving silver imbedded in a black, carbonlike polymer[9] that rapidly ignited and burned, leaving a web of silver metal. The

Table VI. Weight Loss and Carbon Dioxide Evolved from Silver Polycarboxylates upon Pyrolysis

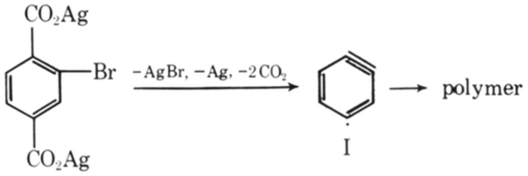
Registry no.	Silver salt	Dec temp, °C	Calcd wt loss as CO_2, %[a]	Found: Wt loss, %	Found: CO_2 evolved, %
29327-92-2	Ag_2 terephthalate	425	23.2	23.6	22.8
57664-97-8	Ag_2 isophthalate	375	23.2	23.5	22.7
57664-98-9	Ag_3 trimellitate	305	24.9	26.2	24.0
57664-99-0	Ag_3 trimesate	325	24.9	25.8	24.4
57665-00-6	Ag_4 pyromellitate	332	25.8	26.8	24.7
57665-01-7	Ag_5 benzenepentacarboxylate	330	26.4	28.0	24.7
19403-20-4	Ag_6 mellitate	280	26.8	*b*	24.0
23417-03-0	Ag_2 naphthalene-2,6-dicarboxylate	430	20.5	20.7	20.1
57665-02-8	Ag_2 pyridine-3,5-dicarboxylate	302	23.2	23.8	23.5
57665-03-9	Ag_2 thiophene-2,5-dicarboxylate	315	22.9	23.8	22.8

[a] Calculated on the basis $R(CO_2Ag)_n \rightarrow R(Ag)_n + nCO_2$. [b] Rapid runaway reaction, which was reproducible. Approximate weight loss, 70%.

polymer first formed may contain radicals that react readily with oxygen; if formed under nitrogen and exposed to air at 80 °C or higher, the polymer ignites readily. Silver isophthalate, pyrolyzed under nitrogen and cooled under hydrogen, gives a product that ignites spontaneously at 25 °C when exposed to air.

The silver polycarboxylates listed in Table VI give a variety of curious shapes when pyrolyzed under nitrogen; pyrolyzed silver trimesate, silver thiophene-2,5-dicarboxylate, silver terephthalate (Ag_2TA), and silver isophthalate (Ag_2IA) are shown in the photomicrographs (Figure 1), all at 50× magnification.

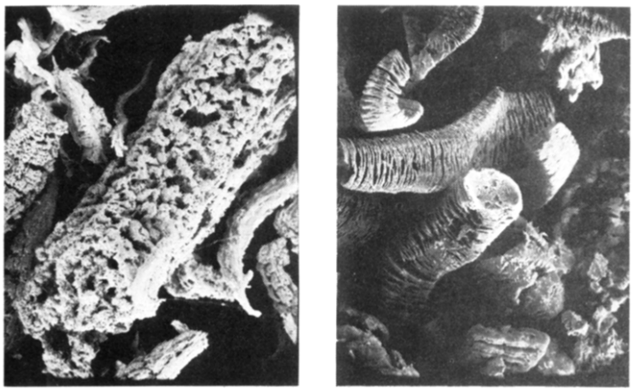
X-Ray photoelectron spectroscopy (ESCA) revealed sharp lines in all pyrolyzed salts for silver absorption at binding energies of 368–369 eV; these were of relatively low intensity, 70–80 Hz, consistent for Ag imbedded in carbonlike polymer, with only a small amount lying on the surface. Two species of silver were shown clearly by broad peaks in the ESCA spectrum for pyrolyzed silver bromoterephthalate, as called for by the equation



The benzynyl free radical I has been suggested previously to explain the products from 4-nitrophthalic anhydride in the gas phase at 600 °C.[10]

A strong nitrogen line at 402.7 eV appeared in both silver pyridine-3,5-dicarboxylate as prepared and the salt pyrolyzed at 310 °C under helium, as evidence that the heteroatom was retained in the carbonlike polymer. Additional evidence came from elemental analysis. Anal. Calcd for $[2Ag\cdot C_5H_3N]_n$: N, 4.8. Found: N, 4.4.

Surface areas and pore-size distributions for some of the pyrolyzed silver salts in Table VI were determined. These physical characteristics varied widely depending on the silver salt pyrolyzed. The surface area of pyrolyzed silver terephthalate was 0.57 m^2/g; that for silver trimesate, 549 m^2/g. Silver mellitate pyrolyzed under N_2 contained pores from 15 to 600 Å in diameter, uniformly distributed; pyrolyzed silver trimesate under the same conditions had pores 80% of which were 15–20 Å in diameter. Evidently we have achieved considerable control of pore-size distribution and surface area for silver imbedded in carbonlike polymer matrices by pyrolyzing the appropriate silver polycarboxylate.


Ag_3 Trimesate X50 Ag_2 Thiophene-2,5-Dicarboxylate X50

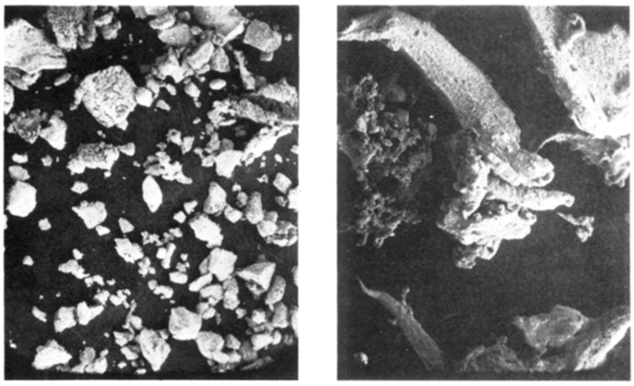

Ag_2 Terephthalate X50 Ag_2 Isophthalate X50

Figure 1.

Experimental Section

Silver salts of the carboxylic acids were prepared by adding the sodium salts in aqueous solution to aqueous silver nitrate in 5% molar excess at 20 °C with rapid stirring. The precipitated silver salts were collected on a filter, washed thoroughly with water, and dried in vacuo at 90 °C.

Thermal decompositions were run in Pyrex or Vycor tubes, heated in a tube furnace with the dry silver salt spread evenly in shallow layers. Weight losses were determined in a Du Pont Model 950 thermogravimetric attachment for the Model 900 thermal analyzer. Surface areas and pore-size distributions were determined by the Digisorb 2500 computerized analyzer (Micromeritics, Norcross, Ga.). Mass spectra were measured on a Du Pont Model 21-

104 instrument using electrical scanning, with normal and low-voltage electron energies set at 70 and 7.5 eV nominal, and with inlet and source temperatures of 350 and 250 °C, respectively. Directly coupled gas chromatography–mass spectrometry utilized a 5 ft × 0.125 in. stainless steel column packed with 10% SE-30 on Chromosorb W, coupled via a jet-orifice separator to a Du Pont Model 21-491 mass spectrometer; electron energy was 70 eV and ion source temperature was 250 °C.

Acknowledgment. The authors are greatly indebted to Drs. A. P. Yu of Amoco Oil Co., J. B. Hall and B. L. Meyers of Standard Oil Co. (Indiana), and C. A. Lucchesi of Northwestern University for much of the data on products from silver polycarboxylates.

Registry No.—Silver benzoate, 532-31-0; sodium benzoate, 532-32-1; silver *p*-fluorobenzoate, 57665-04-0; sodium *p*-fluorobenzoate, 499-90-1; silver pentafluorobenzoate, 3796-31-4; sodium pentafluorobenzoate, 4830-57-3; silver 2-pyridinecarboxylate, 27876-60-4; sodium 2-pyridinecarboxylate, 57665-05-1; silver 3-pyridinecarboxylate, 57665-06-2; sodium 3-pyridinecarboxylate, 54-86-4; silver 4-pyridinecarboxylate, 57665-07-3; sodium 4-pyridinecarboxylate, 16887-79-9; Na_2 terephthalate, 10028-70-3; Na_2 isophthalate, 10027-33-5; Na_3 trimellitate, 50976-34-6; Na_3 trimesate, 17274-08-7; Na_4 pyromellitate, 148-04-9; Na_5 benzenepentacarboxylate, 145-45-9; Na_6 mellitate, 145-44-8; Na_2 napthalene-2,6-dicarboxylate, 16303-32-5; Na_2 pyridine-3,5-dicarboxylate, 57665-08-4; Na_2 thiophene-2,5-dicarboxylate, 57665-09-5; silver nitrate, 7761-88-8.

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Studies on Catalytic Hydrogenation. I. The Influence on Reaction Rates of the Metal–Carrier Ratio of Solvents and Acidity[1]

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It is shown that in aqueous methanolic and aqueous acetic acid solutions catalytic hydrogenations of a variety of substrates can be conducted at rates independent of hydrogen pressure and substrate concentration. The pressure above which hydrogen availability ceases to be limiting is about 3 atm. Substrate adsorption is a function of the activity (and an inverse function of the solubility) of the substrate in the solvent. Platinum, palladium, and rhodium adsorbed on carbon (charcoal and powdered graphite) were examined. Platinized carbon is highly sensitive to acidity, palladized carbon only in the reduction of C–O functions. Rhodium on carbon is somewhat inhibited by acidity in reductions of benzene and acetophenone and indifferent to acidity in the reduction of cyclohexene. The efficiency of various metal–carrier ratios varies somewhat with the substrate, especially with rhodium. Metallized graphites resemble closely the corresponding metallized charcoals but require 10–20 times as much carrier.

This investigation had a dual purpose: to provide a basis of standard catalyst activity for poisoning studies and to relate the behaviors of metallized charcoals and graphites.[2] For both projects it was necessary to have more knowledge of the reaction kinetics and the effect thereon of the solvent medium.

The kinetics of catalytic hydrogenation of nitro compounds in aqueous alcoholic solutions have been studied by Yao and Emmett[3] and of cycloalkenes in cyclohexane by Hussey and his co-workers.[4] Both groups gave extended discussions of theoretical and experimental kinetics. For the present purpose eq 1

$$\text{rate} = \frac{\text{mmol}}{\text{min}}\,H_2 = Akw\theta_H\theta_S \qquad (1)$$

is proposed as valid when small amounts of catalyst are used. Here A is a constant containing factors dependent on the solubility of hydrogen in the solvent, the viscosity and surface tension of the solvent, and the efficiency of mixing.[5] w and k are the weight of catalyst (in default of the unknown surface area) and the real constant of hydrogenation and θ_H and θ_S are adsorption terms for hydrogen and substrate.[6]

In extended form, the substrate adsorption term

$$\theta_S = \frac{\alpha_s C_s}{\beta + \alpha_s C_s + \alpha_{SH}C_{SH} + \Sigma\alpha_{sv}C_{sv} + \alpha_i C_i}$$

where β is a constant,[7] the C symbols refer to concentrations of substrate, reduced substrate, solvents, and inhibitor, if any, and the α symbols are the appropriate adsorption coefficients. The term $\alpha_{SH}C_{SH}$, if sizable, corresponds to product inhibition, frequently observed with enzymes. It is probably not significant in the present work except in the reduction of nitrobenzene. Consideration of $\alpha_i C_i$ is to be taken up later. In the absence of poison or product inhibition

$$\theta_S = \frac{\alpha_s C_s}{\beta + \alpha_s C_s + \Sigma\alpha_{sv}C_{sv}}$$

and two simple methods of treatment are available.

Yao and Emmett chose to regard the denominator as