

for 2 hr. at 70°, and after cooling, was hydrolyzed by pouring cautiously onto chipped ice. The lower organic layer was separated, washed once with cold 10% aqueous sodium bicarbonate solution, and again with cold water. The crude reaction mixture (38 g.) was dried with calcium sulfate and magnesium sulfate. By v.l.p.c. this liquid fraction was shown to consist of 8 g. (90%) of 1,2-dichloro-1,2,2-trifluoroethyl fluorosulfate, $\text{CF}_2\text{ClCFClOSO}_2\text{F}$, and 30 g. of unreacted iodide. The conversion to fluorosulfate would clearly be increased considerably at higher reaction temperatures. An analytical sample of $\text{CF}_2\text{ClCFClOSO}_2\text{F}$ was separated chromatographically from the $\text{CF}_2\text{ClCFClI}$ contaminants using a Perkin-Elmer "B" column at 75°. The characteristic v.l.p.c. elution time ratio t_R/t_{CCl_4} is 0.48 for $\text{CF}_2\text{ClCFClOSO}_2\text{F}$ as compared to 2.9 for $\text{CF}_2\text{ClCFClI}$.² Pure $\text{CF}_2\text{ClCFClOSO}_2\text{F}$ is a colorless liquid, b.p. 89°, n_D^{20} 1.3468. The vapor infrared spectrum of the fluorosulfate has a strong band at 6.71 μ characteristic of the $-\text{OSO}_2\text{F}$ group. The principal infrared spectrum maxima for $\text{CF}_2\text{ClCFClOSO}_2\text{F}$ (vapor) are at 6.71vs, 7.98vs, 8.42vs, 8.74vs, 9.18vs, 9.71vs, 10.64s, 11.45sh, 11.77vs, 12.0ssh, 14.1msh and 14.45s μ .

Anal. Calcd. for $\text{C}_2\text{Cl}_2\text{F}_4\text{O}_3\text{S}$: C, 9.6; Cl, 28.3; F, 30.3; S, 12.8. Found: C, 9.8; Cl, 28.2; F, 30.3; S, 12.6.

Ammonolysis of 1,2-Dichloro-1,2,2-trifluoroethyl Fluorosulfate.—Anhydrous ammonia was passed for 15 minutes into a solution of 0.2 g. (0.0008 mole) of $\text{CF}_2\text{ClCFClOSO}_2\text{F}$ in 10 ml. of 1,1,2-trichlorotrifluoroethane cooled at 0°. The reaction mixture was filtered to remove ammonium salts and the filtrate was evaporated. There remained a small amount of white crystals, m.p. 76–77°, from which, after recrystallization from methylene chloride, there was obtained 0.1 g. (97%) of the amide $\text{CF}_2\text{ClCONH}_2$. The infrared spectrum of this amide matched that of $\text{CF}_2\text{ClCONH}_2$ prepared by ammonolysis of $\text{CF}_2\text{ClCOOC}_2\text{H}_5$, and the melting point of the known chlorodifluoroacetamide was not depressed on admixture with the amide derived from the fluorosulfate.

Reaction of $\text{C}_2\text{F}_5\text{CF}(\text{CF}_3)(\text{CH}_2\text{CF}_2)_2\text{I}$ with Fluorosulfonic Acid.—To 40 g. (0.4 mole) of fluorosulfonic acid stirred at 40° was added drop by drop during 15 minutes 10 g. (0.211 mole) of $\text{C}_2\text{F}_5\text{CF}(\text{CF}_3)(\text{CH}_2\text{CF}_2)_2\text{I}$ and stirring was continued

at 40° for 1.25 hr. longer. Crystalline iodine and SO_2 were formed during the reaction. After cooling, the reaction mixture was hydrolyzed by cautiously pouring onto chipped ice. The lower organic layer was separated, washed once with cold 10% aqueous sodium bicarbonate solution and again with water. The crude liquid reaction products (9.5 g.) were dried with calcium sulfate and magnesium sulfate and distilled in a small Vigreux unit. There was obtained 7 g. (75%) of the fluorosulfate $\text{C}_2\text{F}_5\text{CF}(\text{CF}_3)(\text{CH}_2\text{CF}_2)_2\text{OSO}_2\text{F}$, middle cut b.p. 114° at 100 mm. The liquid infrared spectrum of this fluorosulfate has a strong absorption band at 6.75 μ characteristic of the $-\text{OSO}_2\text{F}$ group.

Anal. Calcd. for $\text{C}_8\text{H}_4\text{F}_{14}\text{O}_3\text{S}$: C, 21.5; H, 0.90. Found: C, 21.1; H, 0.90.

A small amount of $\text{C}_2\text{F}_5\text{CF}(\text{CF}_3)\text{CH}_2\text{CF}_2\text{CH}_2\text{COF}$ was detected by v.l.p.c. and infrared spectroscopy.

Ammonolysis of $\text{C}_2\text{F}_5\text{CF}(\text{CF}_3)(\text{CH}_2\text{CF}_2)_2\text{OSO}_2\text{F}$.—Anhydrous ammonia was passed for 15 minutes into a solution of 2 g. (0.00449 mole) of $\text{C}_2\text{F}_5\text{CF}(\text{CF}_3)(\text{CH}_2\text{CF}_2)_2\text{OSO}_2\text{F}$ in 10 ml. of anhydrous ethyl ether cooled at 0°. The reaction mixture was filtered to remove ammonium salt and the filtrate was evaporated. There remained 0.15 g. (98%) of an oil shown to be almost entirely pure $\text{C}_2\text{F}_5\text{CF}(\text{CF}_3)\text{CH}_2\text{CF}_2\text{CONH}_2$ by the infrared spectrum. By distillation in a small Vigreux unit there was obtained a fraction of the pure amide, b.p. 85–86° at ca. 0.1 mm., for which there were absorption maxima in the infrared spectrum at 5.93 μ (carbonyl stretching vibration), 3.0 and 3.2 μ (NH stretching vibration) and 6.2 μ (probably NH bending). The spectrum had the general characteristic similarities expected for homologs to the spectrum of $\text{C}_2\text{F}_5\text{CF}(\text{CF}_3)(\text{CH}_2\text{CF}_2)_2\text{CH}_2\text{CONH}_2$ previously made by ammonolysis of the corresponding chlorosulfate.¹

Anal. Calcd. for $\text{C}_8\text{H}_5\text{F}_{11}\text{ON}$: C, 28.16; H, 1.77; N, 4.10. Found: C, 28.02; H, 1.78; N, 3.95.

Acknowledgment.—We wish to thank Dr. A. H. Fainberg for the vapor liquid partition chromatographic and infrared spectroscopic work and Mr. Howard Francis and co-workers for the elemental analyses.

[CONTRIBUTION FROM THE CALIFORNIA RESEARCH CORPORATION, RICHMOND, CALIF.]

Oxidative Decarboxylation of Aromatic Acids to Isomeric Aryloxy Derivatives

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A convenient and highly selective method has been found for converting aromatic carboxylic acids to isomeric phenyl esters of the starting acids. Several new esters were prepared. Corresponding phenols are obtained by simple hydrolysis. A possible mechanism is proposed. Alternate paths are suggested to explain the other products observed when the reaction is allowed to proceed uncontrolled.

Introduction

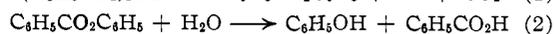
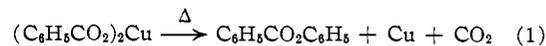
The pyrolysis of copper benzoate, described as early as 1845,¹ was the subject of several old papers.² Dry distillation reportedly gave a mixture of products, including benzene, biphenyl, phenol, diphenyl ether, benzoic acid, salicylic acid and phenyl benzoate. The subject remained dormant until relatively recently when a series of patents was issued. These showed that this reaction can be made highly specific to the formation of phenyl benzoate³ and/or phenol.^{3,4} They also demon-

strated that it can be applied to substituted aromatic carboxylic acids to obtain substituted phenyl esters and phenols.

The present paper is intended to present the experimental work undertaken in exploring the scope of this new reaction and to discuss some of the probable mechanisms involved.

Results

The over-all reactions are illustrated by eq. 1 and 2. They are effected in the temperature range



of 200–350° in a period of one to six hours by merely heating the cupric salt alone or in a solvent such as

Patent 2,727,926, filed January 8, 1954; (c) R. D. Barnard and R. H. Meyer, U. S. Patent 2,852,567, filed January 8, 1954.

(1) Dr. Ettl, *Ann.*, **53**, 77 (1845).

(2) (a) J. Stenhouse, *ibid.*, **53**, 91 (1845); (b) K. List and H. Limpricht, *ibid.*, **90**, 190 (1854); (c) R. Fittig, *ibid.*, **125**, 328 (1863); (d) W. Hoffmeister, *ibid.*, **159**, 197, 204 (1871).

(3) (a) W. G. Toland, U. S. Patent 2,762,838, filed March 16, 1951; (b) W. G. Toland, U. S. Patent 2,766,294, filed May 19, 1952.

(4) (a) M. B. Pearlman, U. S. Patent 2,727,924, filed January 8, 1954; (b) W. W. Kaeding, R. O. Lindblom and R. G. Temple, U. S.

TABLE I
 COPPER-CATALYZED OXIDATION OF AROMATIC ACIDS

	1	2	3	4	5	6	7	8	9	10	11
Aromatic acid, mole	Benzoic	Benzoic	Benzoic	<i>o</i> -Toluic	<i>o</i> -Toluic	<i>m</i> -Toluic	<i>m</i> -Toluic	<i>p</i> -Toluic	<i>p</i> - <i>t</i> -Bu- benzoic	<i>p</i> - <i>t</i> -Bu- benzoic	Salicylic
	0.5	1.0	1.0	0.84	0.25	0.5	2.2	0.5	0.56	0.8	0.25
Copper compd., mole	CuO	Cu	CuO	Cu (<i>o</i> -tolu- ate) ₂	CuO	CuO	Cu	CuO	CuO	CuO	CuO
	0.25	0.1	0.015	0.42	0.005	0.25	0.047	0.25	0.25	0.02	0.1
Oxidizing agent	Cu ⁺⁺	Air	O ₂	Cu ⁺⁺	Air	Cu ⁺⁺	O ₂	Cu ⁺⁺	Cu ⁺⁺	Air	Cu ⁺⁺
Rate in cc./min.	..	250	190	..	200	..	234	250	..
Temp., °C.	260-296	252	246	250-270	248-285	260-288	270-275	248-293	288	260	204-315
Reacn. time, min.	330	180	40	180	155	540	150	1000	480	105	360
CO ₂ evolved, mole	0.269	0.575	0.75	0.265	0.212	0.253
H ₂ O evolved, mole	0.222	0.28	0.15	0.278	0.67	0.250	0.212	0.39	0.050
Ester formed, mole	0.155	0.163	0.074	0.154	0.57	0.065	0.1
Phenol by hydrol., mole	Phenol	Phenol	<i>m</i> -Cresol	<i>m</i> -Cresol	50-50 <i>o</i> - <i>p</i> -cresol	50-50 <i>o</i> - <i>p</i> -cresol	<i>m</i> -Cresol	<i>m</i> - <i>t</i> -Bu- phenol	<i>m</i> - <i>t</i> -Bu- phenol	Phenol
	0.125	0.098	0.06	0.033	0.48	0.201	0.17
Acid recovd., mole	0.193	0.365	0.892	0.934	0.10	1.47	0.035	0.113	0.500
Conv., mole %	61.4 ^b	63.5 ^a	10.8 ^b	44.7 ^b	80.0 ^a	33.2 ^a	93.0 ^a	75.5 ^a	37.5 ^b
Yield, %	40.8 ^b	51.4 ^c	90.7 ^b	8.0 ^b	77.1 ^a	66.3 ^a	23.7 ^a	57.6 ^a	67.0 ^b

^a To ester; ester not hydrolyzed in these experiments. Yield represents recovered ester. ^b To isolated phenol.

excess carboxylic acid, inert hydrocarbon or water under pressure. Phenyl esters are favored in non-aqueous systems, while the phenols are formed in aqueous media or by the introduction of water vapor into the reaction medium. The esters can, of course, be hydrolyzed readily to phenols. When reactions 1 and 2 are effected together in an aqueous solution, decarboxylation to benzene is favored, probably due to the ready availability of protons. This technique is therefore less preferable to the relatively anhydrous systems, even though some phenol is formed.

When properly applied, this reaction has excellent preparative value. Only cupric salts show sufficient specificity to be practical, although many other metal salts were screened. Among aromatic carboxylic acids, yields of phenyl esters and phenols as high as 90% of theoretical can be obtained. Cupric salts of aliphatic acids react differently, undergoing instead simple decarboxylation and non-specific oxidations.

A remarkable feature of this work was the discovery that isomerization is inherent in the reaction. The new phenolic group occupies a position *ortho* to the carboxyl group initially present but lost during reaction. Thus, for example, both *o*- and *p*-substituted benzoic acids yield *m*-substituted phenols, while *m*-substituted acids give an approximately 50-50 mixture of *o*- and *p*-substituted phenols. This is illustrated in the formation of *m*-cresyl *p*-toluate (or *m*-cresol) from *p*-toluic acid, and *m*-*t*-butylphenyl *p*-*t*-butylbenzoate (or *m*-*t*-butylphenol) from *p*-*t*-butylbenzoic acid, and the formation of an approximately 50-50 mixture of *o*- and *p*-cresyl *m*-toluates (or *o*- and *p*-cresols) from *m*-toluic acids. Table I illustrates some typical results.

Furthermore, it was found that if oxygen is introduced during the reaction, only catalytic quantities of copper are required and the same products result (eq. 2a and Table I). This is distinguishable from eq. 1



by the formation of water. If this water is not removed from the reaction zone as formed, hydroly-

sis of the ester occurs, with liberation of phenol. During such oxidations, hydrolysis can be favored or repressed by control of the partial pressure of water in the system.

The use of oxygen and catalytic quantities of copper in benzoic acid appears capable of giving not only better mixing but faster reactions than pure copper benzoate alone. In general, the highest yields are attained at lower conversions. Over-oxidation becomes more pronounced as the products increase in concentration with respect to unreacted carboxylic acids. Any oxidizable substituents tend to decrease yields. The toluic acids give poorer yields than benzoic acid. A further decrease in yield would be expected from compounds containing longer alkyl groups with the greatest decrease from those with secondary groups. On the other hand, the *t*-butyl and methyl groups have similar stabilities under comparable conditions, as shown in Table I, runs 7 and 10. Oxidizable *o*-substituents are particularly susceptible to attack as demonstrated by the low yields obtained from *o*-toluic acid. Other substituents such as halogen might be expected to be relatively unaffected. Electron-withdrawing groups, such as nitro, carboxyl, sulfonyl, acyl and aroyl, while relatively stable toward oxidation, would be expected to induce decarboxylation as a side reaction in many cases. This is borne out by the formation of phenol in preference to dihydric phenols from all three phthalic acids.⁵ However, the reaction should have relatively broad utility and offers a means of preparing phenolic isomers otherwise difficult to obtain.

Experimental

Reagents.—Benzoic acid, Baker C.P.; toluic acids by cobalt-catalyzed air oxidation of corresponding 95+ % purity xylene isomers, distilled; *p*-*t*-butylbenzoic acid, Shell Chemical.

Copper Salt Pyrolyses. Non-aqueous.—For those runs in which copper salts were decomposed without addition of oxygen, the reagents as shown in Table I were intimately mixed in a 200-cc. round-bottomed Pyrex flask equipped with a water separator and reflux condenser fitted with a measuring buret for evolved gases. About 15 cc. of xylene was added to aid removal of water as formed without sub-

(5) M. B. Pearlman, U. S. Patent 2,727,924, filed January 8, 1954.

TABLE II
 PROPERTIES OF NEW PHENOLIC ESTERS

Compound	Source, acid	B.p., °C.	M.p., °C.	S.E. ^a	Calcd., mol. wt.	n _D ²⁰	d ₄ ²⁰	Carbon, %		Hydrogen, %	
								Calcd.	Found	Calcd.	Found
<i>m</i> -Cresyl <i>o</i> -toluate	<i>o</i> -Toluic	181–182 ^b	Liquid	233.5	226.2	1.5688	1.1056	79.15		6.24	
								79.62	79.19	6.18	6.31
<i>o</i> -Cresyl <i>m</i> -toluate	<i>m</i> -Toluic	180 ^b	Liquid	220.0	226.2	1.5615	1.0820	79.17		6.17	
<i>p</i> -Cresyl <i>m</i> -toluate								79.62	79.29	6.18	6.18
<i>m</i> -Cresyl <i>p</i> -toluate	<i>p</i> -Toluic	190 ^b	64.8–66	230.2	226.2	79.45		6.35	
<i>m-t</i> -Butylphenyl <i>p-t</i> -butylbenzoate								79.62	79.60	6.18	6.28
<i>m-t</i> -Butylphenyl <i>p-t</i> -butylbenzoate	<i>p-t</i> -Butylbenzoic	196 ^c	40–41.4	311.5	310.4	1.5426	1.0135	81.25	81.43	8.60	8.60
								81.57	81.57	8.38	8.42

^a Saponification equivalent. ^b At 10 mm. pressure. ^c At 2 mm. pressure.

limation of aromatic acid. The flask was heated by an electric mantle, and the temperatures were measured with a thermometer immersed in the molten reactants. Poor heat transfer in these partially solid mixtures hindered accurate thermometry. Magnetic stirring bars were used in some runs but were not always effective. After completion of reaction as shown by cessation of gas and water evolution, products were diluted with xylene to facilitate handling and filtered to remove copper metal as a finely divided powder. Carboxylic acids were extracted with aqueous sodium bicarbonate from which they were recovered by acidification and identified by neutralization equivalent after washing and drying. Phenols then were extracted with aqueous 5% sodium hydroxide. Only traces were found in unhydrolyzed reaction products. Neutral products then were distilled through an 18-inch helices-packed glass column under vacuum. The ester fractions were recrystallized from ethanol. Fractions of ester were hydrolyzed with water alone or with 1–5% sulfuric acid at 250° in Carius tubes or with alcoholic sodium hydroxide under 2 hours of reflux. Infrared spectra of the phenyl esters served to identify phenyl benzoate specifically, but only the ester group could be verified in the products from substituted acids. Saponification equivalents and elemental analyses proved their identity. Table II gives the properties of the esters. After hydrolysis, the resultant phenol isomers were identified by melting and boiling points, infrared spectra and bromide-bromate titrations where applicable. Carbon dioxide was determined by mass spectral analysis. The principal impurity was CO, usually in small amounts. Recovered acid was identified by melting point and neutralization equivalent. Water liberated during the heating of the copper salt always had the odor of phenol which after analysis was included in the total phenol obtained by hydrolysis.

The infrared spectra of the phenols were obtained using a Perkin-Elmer Infracord spectrophotometer. Solutions of 10% concentration were made up in carbon disulfide solvent. For the cresol isomers, the standard spectra from API Project No. 44, Serial No. 1433, 1434 and 1435, were used for comparison. The peaks as listed were used for identification: *o*-cresol, 13.365 μ ; *m*-cresol, 12.90 μ ; and *p*-cresol, 12.229 μ . In all three cases, there were no measurable amounts of isomers other than those indicated in Table I. In the case of *m-t*-butylphenol, comparison was made with independently synthesized samples of *o*- and *p*-isomers, and spectra compared on the basis of peaks at 13.42 and 12.05 μ , respectively. There were no detectable peaks in either region, but strong peaks at 12.80 and 14.29 μ , typical for *m*-substitution. Strong peaks at 7.33 and 7.19 μ confirmed the *t*-butyl group.

To determine the course of the cuprous salt reaction, a mixture of 71.5 g. (0.5 mole) of Cu₂O and 178.0 g. (1.0 mole) of *p-t*-butylbenzoic acid was heated to 225° in the same equipment as above. No gas evolution was observed. A total of 7.6 cc. of water was collected overhead. Upon raising the temperature to 265–270°, gas evolution began and a total of 0.73 mole of CO₂ was collected in 12.5 hours, a much slower reaction than with the cupric salts. In addition, a total of 43.8 g. (0.33 mole) of *t*-butylbenzene was collected in the overhead and from distillation of the products under vacuum. A major reaction is decarboxylation.

Aqueous.—A 2.5-l. 316 stainless steel rocking autoclave was charged with 900 cc. of water, 245 g. (2 moles) of benzoic acid and 500 g. (2 moles) of CuSO₄·5H₂O. After heating with shaking at 315° for 1 hour, products were adjusted to

pH 12 with aqueous sodium hydroxide and steam distilled to yield 84.1 g. (1.08 moles) of benzene. The distilled water layer (810 cc.) was found to contain 5.1 g. of phenol. The still residue after filtration to remove 97.6 g. of copper metal (1.53 moles) and copper hydroxide (separated by redissolving in aqueous HCl) was acidified and ether extracted. Distillation of the ether solutions gave 9.2 g. of 90% pure phenol, for a total yield of 13.4 g. Some additional copper was recovered from solution by precipitation with H₂S to give 15 g. of the sulfide (0.16 mole). Evaporation of the residue showed additional copper salts present, which were not determined. No other organic products were found.

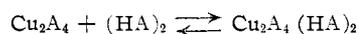
Catalytic Oxidations. Non-aqueous.—The reactions employing air or oxygen as the oxidant were carried out in a glass turbomixer of 200-cc. capacity. This vessel gives vigorous mixing with a Trubore stirrer shaft on which is mounted vertically three sets of four blades. The blades are located opposite vertical indentations in the vessel walls so that a shearing action is achieved, which disperses gases very effectively. An inlet at the base is provided for gases. Nichrome ribbon heaters are wound on the outside glass wall. A side arm near the top leads to a water separator, reflux condenser, a CO₂ adsorber containing aqueous caustic, and a wet test meter. Oxygen or air is measured through a flowmeter.

One procedure with the catalytic system is illustrated by run 3 of Table I. The vessel was charged with 122 g. (1 mole) of benzoic acid, 1.2 g. of copper oxide and about 10 cc. of benzene to aid water separation and then was heated electrically to 246°. Oxygen then was metered in at the base, with agitation, at a rate of 190 cc. per minute for 40 minutes. After the first half-hour, the exit gases contained 21.4% CO₂; and after 40 minutes 50.7% CO₂. Water and some phenol and benzoic acid collected in the water separator. All products were digested overnight with 60 g. of sodium hydroxide dissolved in 500 cc. of water and 50 cc. of ethanol to saponify phenyl benzoate. The ethanol then was removed by distillation, and the aqueous solution was filtered to remove copper and acidified with hydrochloric acid to pH 6 to liberate phenol but not benzoic acid. The phenol was extracted with ether, the ether was evaporated, and the residue was distilled to give 11.1 g. of phenol of 82% purity, the heart cut of which contained 6.1 g. of 95% phenol. The aqueous solution of sodium benzoate was heated to remove ether and acidified to pH 2 with hydrochloric acid to precipitate the benzoic acid, which was filtered, washed, and dried to give a total of 109 g. The conversion of benzoic acid to phenol was 10.8%, with a yield of 90.7%.

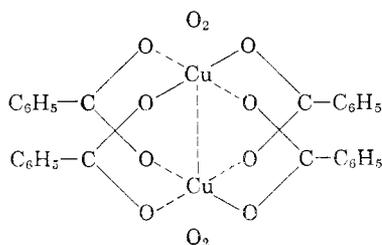
Aqueous.—Equipment was a 4.5-l. autoclave equipped in the same way as for aqueous copper salt pyrolysis studies. It was charged with 1000 cc. of water, 8.0 g. (0.1 mole) of cupric oxide, 245 g. (2.0 moles) of benzoic acid and 46.5 atmospheres of air (approximately 1 mole O₂). Reaction began at about 250°. Heating and shaking were continued for 2 hours at 275°. The products, initially at pH 2, were filtered from 13.8 g. of copper metal and some corrosion products after neutralization. A benzene phase was produced, but no phenyl benzoate was found. From the water and benzene there was recovered 138 g. (1.13 moles) of benzoic acid and 23.4 g. (0.25 mole) of phenol. Since this would represent a 250 mole per cent. yield based upon the copper oxide used, the phenol must have been formed largely through regeneration of cupric salt from the oxygen in the air.

Discussion

The Role of Oxygen and Copper.—The specific point at which participation by molecular oxygen occurs has not been determined but it must be intimately associated with the copper rather than the aromatic acid. It could be visualized as one of these: (a) copper metal is reoxidized to cupric salt in benzoic acid with formation of water; (b) cuprous salt, if an intermediate in the course of reaction 1, is oxidized to a cupric oxybenzoate, such as $(C_6H_5CO_2Cu)_2O$, which may then react with more benzoic acid with formation of water; and (c) cupric salt coordinates with free oxygen as a complex in such a way that copper never need reduce but by simple electron shifts is maintained as cupric salt forming possibly the above type of oxybenzoate intermediate. All three reactions may occur, but there is increasing evidence that (c) may play a dominant part in the catalytic oxidation in the presence of sufficient oxygen. The recent work of Graddon⁶ on the solvated structure of cupric alkanoate solutions shows spectral evidence for solvation by free acid of the type



Oxygen might also "solvate" such structures to give a molecule such as



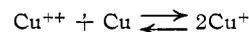
with either one or two oxygen molecules as shown, or a single oxygen molecule bridging the two copper atoms.

A real difference exists in the behavior of cupric as compared with cuprous salts under reaction conditions. Most of the runs in Table I employing cupric copper as the oxidant left no excess acid. In this way, the complete pyrolysis of the cupric salt alone was studied. When an excess of acid was used under otherwise similar conditions, the reaction stopped short of completion, and soluble cuprous salts were found in the products. This reflected in part the better heat transfer possible with such a medium for the reaction, and the probability that higher temperatures than those measured in Table I were reached near the sides of the reaction vessel, aiding the complete decomposition of solventless cupric salts. The course of cuprous salt decomposition therefore was determined separately, by forming and then decomposing cuprous *p-t*-butylbenzoate in an excess of the acid. Only above about 270° did gas evolution begin, and then only slowly, accompanied by decarboxylation to *t*-butylbenzene as a major reaction. This is only a very minor reaction from cupric salts. The cuprous state appears to have considerable stability in the range 200–260°. From these facts, it is

(6) D. P. Graddon, *Nature*, **186**, 715 (1960).

concluded that cuprous salts do not play a major role in the pyrolysis of the corresponding cupric salts.

It is highly likely that cuprous salts are formed at reaction temperature from the equilibrium

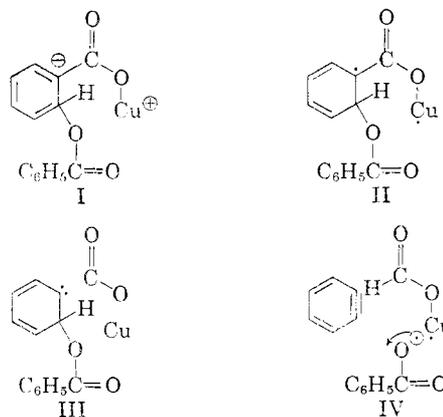


This requires the presence of free copper. Free copper also may play only a small part, if present at all in catalytic oxidations. By entering into this equilibrium, it would give rise to cuprous salts and decarboxylations which are observed not to be significant.

Mechanism.—The fact that *o*-substitution by the entering phenolic oxygen is observed in every case strongly suggests a mechanism involving cyclic intermediates. Intramolecular ring closures involving a single aromatic acid moiety are less feasible than those involving two, as are present in cupric benzoate. A second molecule of acid must somehow be attacking the *o*-position.

Somewhat idealized over-all paths for the non-catalytic cupric carboxylate reactions are suggested in the following scheme. The facts to support them will be discussed.

Assume the conformation A for the cupric carboxylate. This might be compared in spatial arrangement with the stable chelate of copper salicylate. Four mechanisms by which reaction 1 might occur should be considered, one involving heterolytic cleavage of a copper to oxygen bond, or ionization, and three involving homolytic cleavage or free radical formation. The evidence for and against each is given.



I. Heterolytic Cleavage and Nucleophilic Substitution.—As shown in A of Fig. 1, the proximity of an oxygen atom to the position *ortho* to the carboxyl group should permit nucleophilic attack at this position. This attack would be enhanced by the ionization of the copper–oxygen bond. The next step could involve shift of either a hydride ion or a proton. The hydride ion would shift from its *o*-position to displace the carboxylate group. Such hydride displacements have been reviewed recently by Sauer and Huisgen.⁷ A proton shift would occur through an intermediate as shown in I. Polarization of a ring double bond occurs by shift of an electron pair to the carboxyl-containing

(7) J. Sauer and R. Huisgen, *Angew. Chem.*, **72**, No. 9, 294 (1960).

carbon and is followed by shift of the proton to this carbon. This type of nucleophilic displacement is relatively common. Expulsion of the carboxyl with its electron pair is favored by its ability to stabilize as CO_2 with the release of the electron pair shared with copper, reducing the latter to the free metal. Indeed, the strong tendency of the copper to reduce should be a potent driving force in such a concerted mechanism.

II. Homolytic Cleavage.—In this case, a radical rather than an ionic attack by oxygen is involved to give II. With the evidence at hand, it is not possible to determine whether this and succeeding transformations occur in a stepwise or a concerted manner. Oxygen attack at the *o*-position is accompanied or followed by a shift of the hydrogen atom at that position to the ring carbon attached to the carboxyl group. Decarboxylation and aromatization occur with the formation of metallic copper by a series of single electron transfers.

III. Formation of a Carbene.—The preceding radical mechanism could lead to a carbene, III. This path depends upon the timing of the steps involved following the formation of I or II. If decarboxylation occurs before the hydrogen atom shifts, a carbene is formed. This can be followed by the shift of a hydrogen (with or without electrons) and aromatization. The principal drawback to this route is the lack of evidence concerning the relative tendencies of hydrogen and benzoate to undergo the *ortho* shift. Only if it is exclusively a hydrogen shift will the products have the orientations found experimentally.

IV. The Formation of a Benzyne.—This requires that decarboxylation be accompanied by a hydrogen shift to give a formate. Either cupric benzoate-formate is formed if no copper oxygen bond is broken, or cuprous formate and a benzoate radical. Such a mechanism can be immediately ruled out on the basis of the observed orientation effects when substituents are present on the ring. Exclusive *ortho* attack of benzoate would not be predicted.⁸

The mechanism of choice at this point is the heterolytic path, although the homolytic and carbene routes cannot be eliminated. Heterolytic cleavage offers a simple explanation which not only fits all the observed facts but has many analogies to known systems. Homolytic cleavage requires radicals, which might be determined by electron spin resonance. It implies that the open chain conformations of cupric benzoate would also form radicals. These would not be subject to cage effects and should be expected to manifest themselves by the formation of typical radical chain oxidation products. These are not evident to any large extent. On the other hand, heterolytic cleavage of cupric benzoate in open conformation leads simply to the reversible ionization of the salt.

An alternate reaction path is shown by reaction 4 of Fig. 1. In this case, a 1,4-shift is required to form the carboxylic acid and metallic copper. Either mechanism I or II would permit this, but it could not be done *via* a carbene. The carboxylic acid C could then undergo simple decarboxylation

(8) J. D. Roberts, D. A. Semenov, H. E. Simmons, Jr., and L. A. Carlsmith, *J. Am. Chem. Soc.*, **78**, 601 (1956).

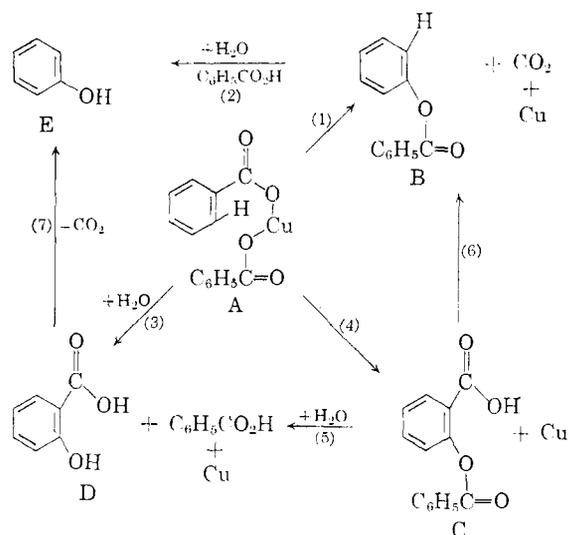


Fig. 1.

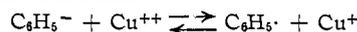
to give phenyl benzoate, reaction 6, a reaction reported by List and Limpricht.¹ However, the free aromatic carboxylic acids are known to be much more stable than their carboxylates. Thus while reaction 4 occurs under certain conditions, phenyl benzoate formation would be more favorable from the initial carboxylate than from the *o*-carboxyphenyl benzoate. The fact that oxygen utilization did not occur without simultaneous evolution of CO_2 argues against the stability of such salicylic acid derivatives (C). Furthermore, the experiment with cuprous *t*-butyl benzoate, which decarboxylated as a major reaction, suggests that this would also occur if the cuprous state were reached during cupric decomposition. Since at this point the new *ortho* bond would have formed, the decarboxylation would lead directly to phenyl benzoate; and no 1,4-shift would be necessary.

If any of these paths involving a cyclic intermediate are valid, an extension of this type reaction should be possible by heating unsymmetrical cupric salts, either organic or organic-inorganic, and introducing other functional groups in the *o*-position. Such reactions are under study.

For the other reactions of Fig. 1 to occur, water must participate. This is certainly possible and indeed was demonstrated, but it would be expected to act either by simple hydrolysis of phenyl benzoate (Reaction 2) or of *o*-carboxyphenyl benzoate (reaction 5). Direct attack upon the copper carboxylate (reaction 3) is more difficult to visualize. It would lead to salicylic acid, more logically expected as the result of two sequential reactions (4 and 5) rather than a single concerted one. It is formed in small yields from copper benzoate pyrolysis.¹ Phenol then could be formed by decarboxylation (7), but the same arguments hold for favoring path 1 and 2 over any involving 7 as were given for path 1 over 4 and 6.

Other reported products such as benzene, biphenyl and diphenyl ether can be accounted for by mechanisms other than those above. Simple decarboxylation of benzoate ion to benzene is favored in aqueous solution (see Experimental) and would be expected wherever ionization is en-

hanced. Biphenyl and diphenyl ether could result from reactions of phenyl radicals. For example, this equilibrium could exist



Waters has suggested similar systems.⁹ Phenyl anion probably is an intermediate in the decarboxylation of carboxylate. However, resultant

(9) W. A. Waters, *Quart. Revs. (London)*, **12**, 277 (1958).

radical reactions could not explain the main reaction product, phenyl benzoate, with selective *ortho* substitution.

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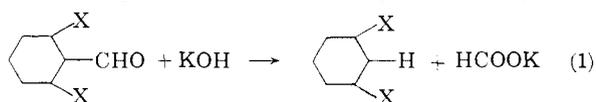
Kinetics and Mechanism of the Alkali Cleavage of 2,6-Dihalobenzaldehydes¹

BY J. F. BUNNETT, J. H. MILES AND K. V. NAHABEDIAN

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Kinetics of the hydroxide ion cleavage of four 2,6-dihalobenzaldehydes to *m*-dihalobenzenes and formate ion have been studied. The dependence on hydroxide ion concentration of the pseudo-first-order rate coefficient, k_{ψ} , is accurately described, at constant ionic strength, by the equation, $k_{\psi} = k_c K_1 [\text{OH}^-]^2 / (1 + K_1 [\text{OH}^-])$, in which K_1 is the equilibrium constant for addition of hydroxide ion to the aldehyde carbonyl group. The reaction is twice as fast in deuterium oxide as in ordinary water. These results give a clear indication of the reaction mechanism, a key feature of which is the intermediacy of a 2,6-dihalophenyl anion. When one or both of the halogens are fluorine, there is a competing reaction involving direct displacement of fluorine by hydroxide ion and forming a 6-halosalicylaldehyde as an isolable product. In the most weakly basic solutions studied, hydroxydefluorination is the main reaction. The rate of the cleavage reaction is relatively insensitive to the identity of the halogen atoms in the positions *ortho* to the aldehyde group.

During the 1930's, Lock² found that 2,6-dihalobenzaldehydes are cleaved by refluxing 50% potassium hydroxide with formation of *m*-dihalobenzenes and potassium formate in quantitative yields.

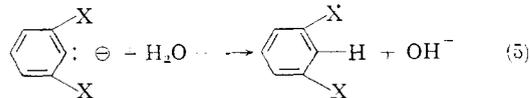
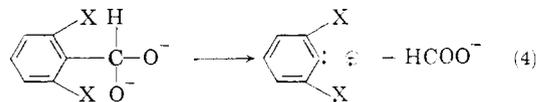
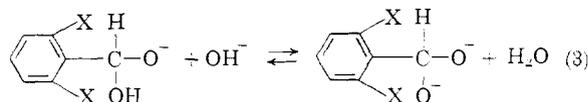
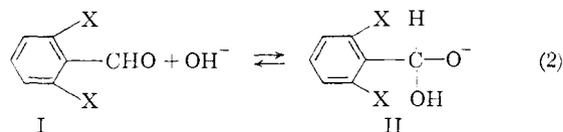


Several examples were described. This was part of a general study by Lock of the action of strong bases on aromatic aldehydes and ketones.²

Cleavage was observed only when both positions *ortho* to the formyl group were occupied by a halogen atom or a nitro group. Otherwise the Cannizzaro reaction occurred. This suggests, but does not prove, that *ortho* halogen substituents have a special accelerating effect on the cleavage reaction. A similar effect appears to operate in the cleavage of *o*-halobenzophenones by potassium amide in liquid ammonia.³

It seemed likely that Lock's aldehyde cleavage belonged to the large family of reactions in which alkaline reagents cleave carbonyl compounds with rupture of carbon-carbon bonds. Scission of chloral hydrate,⁴ β -ketoalkylpyridinium salts,⁵ acetylacetone,⁶ methylacetylacetone,⁶ nitroacetone,⁷ ω -nitroacetophenone⁷ and β -ketodihydrobenzothio-phenone 1-dioxide⁷ have been studied kinetically in detail. To judge from the kinetics, these reactions are closely related in mechanism. Adapting the

general scheme to the case of present interest, one postulates the following mechanism for the alkali cleavage of 2,6-dihalobenzaldehydes



Even if this adaptation is basically correct, several points of uncertainty remain. These include the questions of whether step 3 is necessary, and if so whether all the steps have separate existences as shown. Conceivably steps 3 and 4, or steps 4 and 5, could be concerted.

If the postulated mechanism is correct, substituted phenyl anions are intermediates (step 4). Such anions are also formed transiently in the formation of benzyne by action of bases on halobenzenes⁸⁻¹⁰ and in the decarboxylation of 2,4,6-trinitrobenzoic acid.¹¹ Their chemistry is neverthe-

(1) Financial support by the Office of Ordnance Research, U. S. Army, is gratefully acknowledged.

(2) (a) G. Lock, *Ber.*, **61**, 2234 (1928); (b) **66B**, 1527 (1933); (c) **66B**, 1759 (1933); (d) **68B**, 1505 (1935); (e) **69B**, 2253 (1936).

(3) J. F. Bunnett and B. F. Hrutford, Abstracts, 135th Meeting, American Chemical Society, Boston, Mass., April, 1959, p. 94-O.

(4) C. Gustafson and M. Johanson, *Acta Chem. Scand.*, **2**, 42 (1948).

(5) R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, **70**, 1933 (1948).

(6) R. G. Pearson and E. A. Mayerle, *ibid.*, **73**, 926 (1951).

(7) R. G. Pearson, D. H. Anderson and L. L. Alt, *ibid.*, **77**, 527 (1955).

(8) J. D. Roberts, D. A. Semenov, H. E. Simmons, Jr., and L. A. Carlsmith, *ibid.*, **78**, 601 (1956).

(9) G. E. Hall, R. Piccolini and J. D. Roberts, *ibid.*, **77**, 4540 (1955).

(10) R. Huisgen and J. Sauer, *Angew. Chem.*, **72**, 91 (1960).

(11) F. H. Verhoek, *J. Am. Chem. Soc.*, **61**, 186 (1939).