[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, WESTERN DIVISION, THE DOW CHEMICAL CO.]

Oxidation of Aromatic Acids

WARREN W. KAEDING

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A method has been found for oxidizing aromatic carboxylic acids to phenols and carbon dioxide with cupric compounds. The hydroxyl group enters the ring at a position adjacent to the departing carboxyl group. It has been proposed that the reaction proceeds by the thermal decomposition of the cupric salt of the aromatic carboxylic acid.

The stepwise oxidation of the methyl group in toluene to produce benzyl alcohol, then benzaldehyde, and finally benzoic acid is well-known.[1] A large number of oxidizing agents have been used under a variety of conditions. Reaction conditions have been found for the next step in the sequence—the complete oxidation of the methyl group to give phenol and carbon dioxide. Cupric salts appear to be specific oxidizing agents for this reaction. Ettling[2] and Stenhouse,[3] independently, heated cupric benzoate in a retort and isolated a neutral material which they called "benzil." This material was primarily phenyl benzoate contaminated with diphenyl ether. A few years later List and Limpricht[4] studied this product and obtained phenol by treatment with alcoholic potassium hydroxide. Similar experiments were performed more recently where, in addition to phenyl benzoate (8% yield), copper salicylate (14%) and phenol itself (1–10%) were isolated.[5]

Many of these early experiments have been repeated. Phenol and phenyl benzoate were identified as products; however, the high temperatures required for reaction resulted in very extensive decomposition to tars and carbon dioxide.

When benzoic acid was heated with a cupric salt in a homogeneous aqueous solution, phenol was produced and tar formation was virtually eliminated. The results are summarized in Table I.

Equation 1 appears to describe the course of the reaction. The relative molar amounts of reactants used up and products formed are given along with the equation. These values were obtained from an average of five runs shown in Table I. As phenol is a very reactive compound, it is reasonable to assume that some of it was oxidized in the sealed bomb at the relatively high temperatures used. This could readily account for the low phenol and high copper metal values observed experimentally.

$$\begin{array}{llll} & \text{BzOH} + \text{CuSO}_4 + \text{H}_2\text{O} \longrightarrow & & \\ \text{Moles} & 100 \qquad\quad 118 & & \\ & \qquad \text{C}_6\text{H}_5\text{OH} + \text{CO}_2 + \text{Cu} + \text{H}_2\text{SO}_4 & (1) & \\ & \qquad\quad 85 \qquad\quad 90 \quad\; 112 & & \end{array}$$

When cupric chloride was used as the oxidizing agent in a similar manner, cuprous chloride was the exclusive reduction product. An increase in temperature was required to obtain an apparent degree of reaction comparable with cupric sulfate. The results appear in Table I.

By analogy with the cupric sulfate runs, the net reaction is shown by Equation 2. The numerical values were obtained from an average of the runs listed in Table I in a manner similar to that described previously. The amount of phenol obtained in this series, however, was very low. This could not be explained by decomposition to tar. The weight of carbon dioxide indicated that a much larger amount of phenol should have been present. An analysis of the phenolic fraction revealed the presence of chlorine. An independent experiment was performed where phenol and cupric chloride were heated in aqueous solution. The reaction, shown in Equation 3, occurred with virtually quantitative yields.[6]

$$\begin{array}{llll} & \text{BzOH} + 2\,\text{CuCl}_2 + \text{H}_2\text{O} \longrightarrow & & \\ \text{Moles} & 100 \qquad\quad 310 & & \\ & \qquad \text{C}_6\text{H}_5\text{OH} + 2\text{CuCl} + \text{CO}_2 + 2\text{HCl} & (2) & \\ & \qquad\quad 18 \qquad\quad 306 \qquad 97 \qquad 214 & & \end{array}$$

A similar result has been observed when acetone was heated with cupric chloride.[7]

$$\text{C}_6\text{H}_5\text{OH} + 2\,\text{CuCl}_2 + \text{H}_2\text{O} \xrightarrow{180^\circ} o,p\text{-ClC}_6\text{H}_4\text{OH} + 2\,\text{CuCl} + \text{HCl} \quad (3)$$

It seems probable that phenol was formed by the same mechanism in both cases. With cupric chloride, subsequent reactions occurred to give chlorophenols. As the scheme of analysis was based on the titration with bromine to form tribromo-

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[1] (a) M. Weiler, *Ber.*, **33**, 464 (1900). (b) D. M. Newitt and J. H. Burgoyne, *Proc. Roy. Soc.* (*London*), **A153**, 448 (1936); *Chem. Abstr.*, **30**, 2555^9. (c) S. Tonomura, *Bull. Inst. Phys. Chem. Research* (*Tokyo*), **21**, 774 (1942); *Chem. Abstr.*, **41**, 5465g. (d) R. D. Abell, *J. Chem. Soc.*, 1379 (1951).

[2] Ettling, *Ann.*, **53**, 77 (1845).

[3] J. Stenhouse, *Ann.*, **53**, 91 (1845).

[4] K. List and H. Limpricht, *Ann.*, **90**, 190 (1854).

[5] (a) C. R. Kinney and D. P. Langlois, *J. Am. Chem. Soc.*, **53**, 2191 (1931). (b) W. Moser, *Helv. Chem. Acta*, **14**, 971 (1931). (c) E. M. Bamdas and M. M. Shemyakin, *Zhr. Obshchei Khim.* (*J. Gen. Chem.*), **18**, 324 (1948); *Chem. Abstr.*, **43**, 125A (1949). (d) S. J. Kanewskaya and M. M. Schemjakin, *Ber.*, **69B**, 2152 (1936). (e) R. D. Barnard and R. H. Meyer, U. S. Pat. **2,852,567**.

[6] W. W. Kaeding, R. O. Lindblom, U. S. Pat. **2,805,263**.

[7] S. C. Dickerman, K. Wise, and A. K. Ingberman, *J. Org. Chem.*, **21**, 380 (1956).

TABLE I

REACTION OF CUPRIC SALTS WITH BENZOIC ACID[a]

BzOH[b]	Cupric Salt[b]	H_2SO_4[b]	Temp.	Time Heated, Hr.	CO_2	C_6H_5OH	Cu Metal	Anion	Recovered BzOH	Recovered Cu^{+2}
10.66[c]	5.20[d]	—	240	1.5	1.31	1.24	1.69	5.13[e]	9.20	3.48
±0.37	± 0.03				± .30	± .09	± .11	± .05	± .05	± .14
4.10	12.1[d]	1.83	260	2.0	3.77	1.64	4.86	—	1.19	7.12
3.99	11.9[d]	5.49	260	2.0	3.00	1.42	4.12	—	1.71	7.94
4.22	12.0[d]	9.15	260	2.0	2.26	1.17	3.02	—	2.60	9.10
4.07	12.0[d]	34.8	300	2.0	4.94	1.12	4.78	—	1.34	7.02
3.95	12.0[d]	174	300	2.0	4.39	0.43	1.10	—	1.54	10.8
8.26	9.55[f]	—	280	2.0	2.09	0.517	8.42[g]	6.42[h]	5.29	1.00
8.26	13.30[f]	—	280	2.0	3.45	0.514	11.6[g]	7.52[h]	4.85	1.68
8.03	9.93[f]	—	280	2.0	3.00	0.660	8.79[g]	6.19[h]	5.02	1.04
8.60	9.55[f]	8.05[i]	280	2.0	2.48	0.09	7.82[g]	—	4.83	2.16
7.95	9.55[f]	24.15[i]	280	2.0	2.34	0.02	4.98[g]	—	4.86	4.01

[a] 25 ml. of water solvent used for each run. All amounts expressed in mmoles. [b] Starting materials. [c] Average of five runs [d] Copper sulfate. [e] $SO_4^{=}$. [f] Cupric chloride. [g] Cuprous chloride. [h] Hydrochloric acid. [i] Potassium chloride.

phenol, positions occupied by chlorine would result in a low calculated yield.

An examination of the results of a large number of runs made utilizing cupric sulfate as the oxidizing agent revealed that less than 50% of the cupric ion was reduced to the metal in *every* case. On one occasion, the characteristic precipitate of metallic copper was absent immediately after reaction. During manipulation prior to workup, copper metal suddenly began to plate out on the benzoic acid crystals. This indicated the presence of a metastable cuprous form which disproportionated to the metal and cupric ion.

The presence of appreciable amounts of cuprous sulfate in aqueous solution contradicts observations made which demonstrated that it rapidly decomposed in the presence of moisture.[8] However, the formation of cuprous sulfate is favored by an increase in temperature.[9] Perhaps at 250° a considerable amount of cuprous sulfate may have been stable in aqueous solution. The presence of certain organic reaction products may have stabilized the cuprous form as the temperature was lowered.

When cupric sulfate and benzoic acid were heated in various organic solvents such as benzene, toluene, nitrobenzene, or benzoic acid, the salt did not dissolve and a reaction did not occur. Soluble cupric benzoate on the other hand, was completely reduced to cuprous benzoate. A careful analysis of the products indicated the net reaction shown by Equation 4. Benzoic acid was especially desirable as a solvent because its high boiling point permitted the reaction to proceed at room pressure. When air was bubbled through the solution, the cupric salt was rapidly regenerated as shown in Equation 5, permitting one to convert large amounts of benzoic acid to products. The simultaneous introduction of steam resulted in the direct production of phenol either by the hydrolysis of phenyl benzoate or by the prevention of its formation during the primary decomposition of cupric benzoate. A convenient method has thus become available to convert carboxylic acids to phenols and carbon dioxide in good yields as summarized by Equation 7. The results utilizing a variety of acids are shown in Table II.

$$2\,Cu(OBz)_2 \longrightarrow C_6H_5COOC_6H_5 + 2\,CuOBz + CO_2 \qquad (4)$$

$$2\,CuOBz + 2\,BzOH + {}^1/{}_2O_2 \longrightarrow 2\,Cu(OBz)_2 + H_2O \qquad (5)$$

$$C_6H_5COOC_6H_5 + H_2O \longrightarrow C_6H_5OH + BzOH \qquad (6)$$

$$BzOH + {}^1/{}_2O_2 \longrightarrow C_6H_5OH + CO_2 \qquad (7)$$

The steric course of the reaction strongly suggests a stable and well oriented configuration between the acid and the cupric atom. A cyclic intermediate involving a nucleophilic attack by an oxygen atom at the position adjacent to the carboxyl group is proposed (Equation 8).

Here cupric benzoate is represented as a dimer. The broken line indicates that the two copper atoms are relatively close to each other. Recent work on the structure of cupric acetate has indicated that molecules are arranged in pairs with the two copper atoms only slightly farther apart than the arrangement found in metallic copper.[10] Furthermore, there is evidence that the dimeric structure is preserved in solution.[10c]

If this condition applies to cupric benzoate in benzoic acid solution, the concerted reduction of a pair of cupric ions to the cuprous form would provide the two electrons required for the oxidation of benzoic acid. Kinetic studies now in progress have indicated that this reaction is second order with respect to the concentration of cupric benzoate.

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(8) E. Heinerth, *A. Elektrochem.*, **37**, 61 (1931).

(9) F. Foerster and F. Blankenberg, *Ber.*, **39**, 4428 (1906).

(10) (a) B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956). (b) R. C. Herron and R. C. Piuls, *J. Chem. Soc.*, 3948 (1956). (c) D. P. Graddon, *Nature*, **186**, 715 (1960).

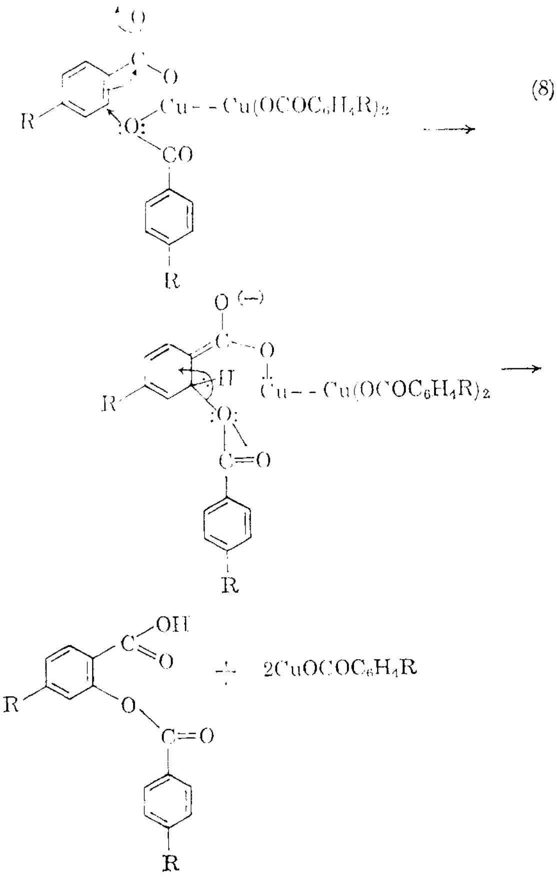
TABLE II

Oxidation of Various Substituted Benzoic Acids

Acid	Solvent	Temp. Heated	Products Isolated
o-Toluic	*o*-Toluic acid	200	*m*-Cresol, phthalide
o-Toluic	Water[a]	250	*m*-Cresol, phthalide
m-Toluic	*m*-Toluic acid	250	*o*-Cresol, *p*-cresol
m-Toluic	Water[a]	275	*o*-Cresol, *p*-cresol
p-Toluic	*p*-Toluic acid	250	*m*-Cresol
p-Toluic	Water[a]	270	*m*-Cresol
p-*t*-Butylbenzoic	*p*-*t*-Butylbenzoic acid	250	*m*-*t*-Butylphenol
p-Nitrobenzoic	*p*-nitrobenzoic acid	250	*m*-Nitrophenol
Salicylic	Salicylic acid	200	Phenol
p-Hydroxylbenzoic	Water	240	Phenol, resorcinol
p-Anisic	*p*-Anisic acid	270	Methyl anisate, anisole, *m*-methoxyphenol, phenol
o-Chlorobenzoic	*o*-Chlorobenzoic acid	250	Phenol, *m*-chlorophenol, chlorobenzene
p-Chlorobenzoic	Water	265	Chlorobenzene, dichlorobenzenes, *m*-chlorophenol, phenol
1-Naphthoic	Water[b]	225	2-Naphthol
2-Naphthoic	Water[b]	240	2-Naphthol
3-Pyridinecarboxylic	Water[b]	240	2-Hydroxypyridine

[a] M. B. Pearlman—private communications. [b] M. B. Pearlman, U. S. Pat. 2,764,587.

The location of the R-group in the para position illustrates how a *meta* substituted phenol could be obtained by subsequent hydrolysis and decarboxylation. The products obtained from *ortho* and *meta* substituted starting benzoic acids are also consistent with this mechanism.



(8)

ortho and *p*-chlorobenzoic acids gave a variety of products in addition to the *m*-chlorophenol predicted by the proposed mechanism. Important side reactions occurred involving an interaction between the copper and chlorine atoms to ultimately produce cuprous chloride. The number and variety of products indicate a complex reaction.

Migration of the methyl group in anisic acid to produce methyl anisate appeared to be an important side reaction. The resulting *p*-hydroxybenzoic acid as well as the starting acid itself probably underwent a simple decarboxylation reaction to give phenol and anisole.

It was of special interest to observe that only 2-naphthol was identified as a reaction product starting with 2-naphthoic acid. The 3-position appears to be a much more reactive site than the other adjacent 1-position.

In aqueous solution, a small concentration of cupric benzoate is proposed by the equilibrium shown in Equation 9. The addition of hydrogen ion initially

$$Cu^{+2} + 2\,HOBz \rightleftharpoons Cu(OBz)_2 + 2H^+ \qquad (9)$$

strongly inhibited the production of phenol, Table I. The presence of chloride ion (Table I) had a similar effect, possibly by competing with benzoic acid for the cupric atom.

EXPERIMENTAL

Benzoic acid, a cupric salt, and water were sealed in heavy walled glass bombs (2.5 × 20 cm.) with a capacity of about 75 ml. Three glass bombs, separated by a metal partition, were placed in the 1-l. metal bomb of a Parr High Pressure Hydrogenation Apparatus, Series 4000, equipped with an automatic timer and temperature control. Water was also placed in the metal bomb to equalize the pressure exerted by the solvent on the glass bomb wall at the ele-

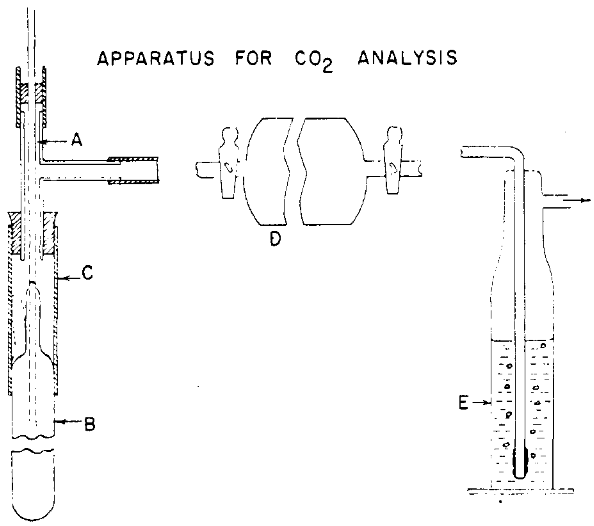


Fig. 1. A = tube for nitrogen; B = glass bomb; C = rubber tubing; D = gas bulb; E = gas absorption bottle

vated temperatures used. Approximately 0.75 to 2 hr. time was required to bring the temperature to the desired level (200–300°).

As carbon dioxide was a product of the reaction, only a relatively small amount of starting material (8–10 mmoles) was used, to avoid the danger of excessive gas pressures in the glass bombs at the end of the run. Before the bomb was opened, it was cooled to 0°. It was then wrapped with a cloth and heavy lead foil, with the stem protruding. The bomb was then opened behind a shield, or in the apparatus for absorbing carbon dioxide. Many runs were made for the purpose of identifying reaction products. In general, the organic products were extracted with ether or methylene chloride and separated from the precipitated copper and the aqueous phase. Benzoic acid was removed by extracting the organic phase with saturated aqueous bicarbonate solution. This was followed by extraction of the phenol with 5% aqueous sodium hydroxide solution. Evaporation of the remaining ether solution gave neutral products of reaction.

Method of analysis for bomb runs. Since only 4–10 mmoles of benzoic acid were used in each individual glass bomb, with the production of 1 mmole or less of phenol, it was impractical to separate and weigh all of the reaction products. A scheme of analysis was developed which made it possible to determine the major reaction products with accuracy. This procedure refers primarily to runs made in aqueous solution with cupric sulfate as the oxidizing agent, however, with certain modifications other copper salts may be treated in a similar manner.

(*a*) *Carbon dioxide.* After the bomb was cooled to ice temperature and the neck scratched, it was placed in the apparatus illustrated in Fig. 1. A slow stream of nitrogen was allowed to flow through the system. The bomb was broken by manipulating the flexible rubber tube (C) which connected the bomb to the closed system. The movable glass tube was lowered into the bomb to sweep the carbon dioxide into the gas absorption bottle. The gas was absorbed by excess standard barium hydroxide solution, back titrated to a phenolphthalein end point with standard acid. To remove the carbon dioxide remaining in the supersaturated aqueous solution, the nitrogen stream was turned off and the gas bulb (D) was evacuated. The stopcock leading to the section where the bomb was attached was carefully opened. A considerable amount of carbon dioxide (up to 20–25% of the total) would bubble out of the solution as the pressure was reduced. The stream of nitrogen was turned on again and the liberated gas was carried to the absorption bottle. In some of the later runs, the carbon dioxide was absorbed with ascarite.

(b) *Unchanged cupric ion and sulfuric acid.* The low pH of the system after reaction (<2) indicated that a strong acid (sulfuric acid, or hydrochloric acid if cupric chloride was used as the oxidizing agent) was a product of the reaction. The bomb contents were then filtered with a sintered glass funnel to remove the solids. The bomb was rinsed with two 5-ml. portions of ice water which were poured over the solids on the filter and immediately drawn through the filter. The combined filtrates were then treated with excess standard sodium hydroxide solution. The cupric ion was precipitated and removed by filtration. The excess base in the clear filtrate was then back titrated with standard acid to the Thymol Blue end point. The washed cupric hydroxide was dissolved in dilute acetic acid and titrated for copper iodometrically to give a value for the unchanged cupric ion. The net amount of sodium hydroxide used after subtracting for that used to precipitate the cupric ion was assumed to be equivalent to the sulfuric acid formed plus a small amount of the water soluble, unchanged benzoic acid. The amount of sulfuric acid was calculated from the unchanged cupric ion as described below. With this value, the amount of soluble benzoic acid was determined.

A second method was also used to determine the sulfuric acid produced. All of the organic material was removed from the aqueous phase by repeated extractions with methylene chloride. The remaining solution was titrated as described above. The net amount of base used, after subtracting for that used to precipitate the copper, was equivalent to the sulfuric acid formed. As analytical results indicated that sulfate ion was unchanged in the reaction, an alternate calculation that was made as a check was: sulfuric acid = initial cupric sulfate − final Cu^+. This assumed that a mole of sulfuric acid was formed for every mole of cupric ion reduced to the metal. A fair check was usually obtained, ±5%.

(c) *Unchanged benzoic acid.* Most of the unchanged benzoic acid remained on the filter as a solid in step (b) above. It was dissolved with two 5-ml. portions of freshly distilled, peroxide-free neutral dioxane, previously used to rinse the bomb and stem. After a subsequent water rinse, the filtrate was titrated to the thymol blue end point with standard sodium hydroxide solution to give a value for the insoluble benzoic acid. The value obtained in step (b) for the soluble acid was added to this to give the total acid.

(d) *Phenol.* The remaining filtrates from steps (b) and (c) were titrated for phenol by means of the well known method utilizing bromine.[11] It was assumed that all bromine used up could be found as tribromophenol. In certain runs, the precipitated material was filtered off and weighed. The amount obtained plus an infrared analysis of the brominated product indicated that the above assumption was correct.

(e) *Copper metal.* The final solid residue on the filter was identified as metallic copper by analysis. It was dissolved with nitric acid and determined quantitatively by standard methods.

(f) *Sulfate ion.* Sulfate ion was determined gravimetrically by precipitation as barium sulfate.

In order to check the accuracy of the method outlined above, a number of synthetic mixtures were made with amounts of material similar to that actually found in a bomb run. With ten mixtures, the errors were as follows:

Phenol ±2%, benzoic acid ±4%, Cu^{++} ±1%, H_2SO_4 ±1%.

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[11] S. Siggia, *Quantitative Organic Analysis via Functional Group*, 2nd ed., Wiley, New York, 1954, p. 162.

The procedure and apparatus for utilizing the carboxylic acid as a solvent in the presence of air and steam have been described.[12]

Acknowledgment. I am indebted to Mr. R. D. Barnard, Mr. R. H. Meyer, Dr. R. W. Meikle, and Mr. A. K. Johnson for many helpful suggestions when this work was initiated.

PITTSBURG, CALIF.

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[12] W. W. Kaeding, R. O. Lindblom, and R. G. Temple, U. S. Pat. 2,727,926.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CANTERBURY]

Resonance Interactions in Naphthalene Derivatives: Dissociation of Substituted Naphthols and Naphthoic Acids

L. K. CREAMER, A. FISCHER, B. R. MANN, J. PACKER,
R. B. RICHARDS, AND J. VAUGHAN

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In order to compare resonance interactions in 4-X-1-naphthyl derivatives with those in corresponding benzene compounds, the thermodynamic *p*K values, in water at 25°, of a series of substituted 1-naphthols have been measured, together with the value for *p*-hydroxybenzophenone. An explanation has been offered for differences in resonance interaction noted for some electron-withdrawing substituents. The *p*K values, in water at 25°, of a number of substituted 1-naphthoic acids have also been determined and have been compared with those of the corresponding benzoic acids.

In recent publications Wepster and co-workers[1] and Taft and his colleagues[2,3] have shown, using different approaches, that the concept of discrete sigma values (σ^+, σ^-, and σ) is fallacious. Taft *et al.* have demonstrated that reactivity data for a select group of *meta*-substituted phenyl groups are correlated by the Hammett equation with much greater generality and precision than data for other substituted phenyl groups. They designated the mean *sigma* values, for this select group of substituents, as σ^0 values. As there is no direct conjugative interaction between *meta* substituent and side-chain reaction center (and consequently no contribution, by a resonance effect, to the relative rate) such σ^0 values are a measure of the inductive effect of an $X-C_6H_4-$ group, relative to the phenyl group. For *para*-substituted benzene derivatives, conjugation between the substituent and side-chain reaction center will occur to an extent which will vary from one reaction series to another and consequently for these substituents, a range of *sigma* values is required. Taft *et al.* obtained σ^0 values for *para*-substituted phenyl groups from the reactivities of benzyl derivatives. In these compounds resonance between the ring and reaction center is prevented by the interposed methylene group.

We have previously shown[4-6] that the Hammett reaction constant (ρ) for alkaline hydrolysis of substituted ethyl 1-naphthoates in 85% ethanol at 50° (+2.21) is not significantly different from that for the corresponding reaction of ethyl benzoates (+2.32). In ester hydrolysis, (extra) resonance contributions to the relative rates are small and insignificant, except for those *para* substituents with very large resonance (+M) effects.[7] The resonance interaction between such a substituent and the carbonyl group, which is frozen out in the transition state, is inhibited by the cross-conjugated ethoxy group. Thus the experimental result, that the relative reactivities of substituted ethyl 1-naphthoates and benzoates are closely similar, implies that the inductive effect of a substituted 1-naphthyl group (relative to the 1-naphthyl group) is equal to the inductive effect of the correspondingly substituted phenyl group (relative to the unsubstituted phenyl group). As ρ is a measure of the susceptibility of the reaction to the *inductive* effects of substituents, it follows that reaction constants for corresponding benzene and naphthalene reactions will be the same.

In order to determine whether or not resonance interactions in naphthalene derivatives, between a 4-substituent and a conjugated 1-side-chain, are the same as those in the corresponding benzene derivatives, we have measured the dissociation constants of a series of substituted 1-naphthols. The corresponding reaction in the benzene series is known to involve substantial variation in the resonance interaction between *para* −M substituted phenyl groups and side-chain, in going from reactant to product. Thus *para* −M substituted phenyl groups make a resonance contribution to

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[1] H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. Trav. Chim.*, T.78, 815 (1959).

[2] R. W. Taft and I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343 (1959).

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[5] A. Fischer, J. M. Mitchell, G. S. Ogilvie, J. Packer, J. E. Packer, and J. Vaughan, *J. Chem. Soc.*, 1426 (1958).

[6] A. Fischer, H. M. Fountain, and J. Vaughan, *J. Chem. Soc.*, 1310 (1959).

[7] *Cf.* Fig. 1 and Table X of ref. 3.