Purification of the surfactant has been described.[9] Sodium salts were used for the buffers.

Kinetics. The formation of *o*-nitrophenoxide ion at 25.0 °C was followed at 405 nm, using a Gilford spectrometer for the slower reactions and a Durrum stopped flow spectrometer for the faster reactions. The pH of the buffered solutions was measured in the absence of surfactant. The first-order rate constants, k_ψ, are in reciprocal seconds.

Results and Discussion

The variation of k_ψ with CTABr is shown in Figure 1. In 0.01 M NaOH and no CTABr $k_\psi = 1.35\ s^{-1}$,[13] consistent with the value of 1.74 s^{-1} in 1 M KCl at 30 °C.[1] The substrate, 1, is completely deprotonated in 0.01 M NaOH,[1] and CTABr inhibits spontaneous decomposition of the carbanion (2), with a limiting value of $k_\psi = 0.4\ s^{-1}$ at [CTABr] > 0.02 M (Figure 1).

Reaction at pH ≤8 is catalyzed by CTABr (Figure 1), and for reaction at pH 7 and 8 we observe plateau values of k_ψ which are very similar to the limiting rate constant in CTABr and 0.01 M NaOH, showing that the substrate in micelles of CTABr is almost completely deprotonated even at a nominal pH value of 7. The relatively small differences in the limiting values of k_ψ (Figure 1) could be due to the different salt effects of the buffers.[14] In addition, proton equilibria in aqueous micelles are affected by added anions, even at the same nominal pH.[5]

For experiments at pH 6–8 the rate increase with increasing [CTABr] simply means that the equilibrium is shifted in favor of carbanion 2, which should bind very strongly to the cationic micelle (cf. ref 5d, 15, and 16. We did not reach a limiting rate constant even at high [CTABr] at pH 6. This result is understandable because 1 probably does not bind very strongly to cationic micelles. (The α-CN group should make 1 less hydrophobic than *p*-nitrophenyl acetate, which does not bind strongly to CTABr.[4])

We cannot compare our results with 1 directly with those of Tagaki and co-workers[2] because of differences in the pK_a values and hydrophobicities of the substrates, but the direction and magnitude of the micellar effect depends on the extent of deprotonation of the substrate. For example, the rate enhancement by CTABr is by factors of approximately 6- and 25-fold at pH 8 and 7, respectively, but at pH 6, where we do not reach a limiting rate constant in CTABr, the factor is at least 100-fold (Figure 1). Comparison of micellar effects at only one pH value is therefore not very informative.

The small micellar inhibition of the spontaneous decomposition of the carbonion (2) is consistent with the polarity of the micellar surface being similar to, but slightly lower than, that of water. For example, spectral shifts are consistent with the micelle surface having an effective dielectric constant of ca. 40.[17] Menger has suggested that water penetrates the micellar surface,[18] and, consistently, rate and equilibium constants for some water additions are similar to those in water.[19] The spontaneous decomposition of the carbanion (2) involves dispersion of charge from the carbanionic center to the forming *o*-nitrophenoxide ion and is apparently not very sensitive to the medium.

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Registry No. 1, 22065-72-1; 2, 78480-13-4; CTABr, 57-09-0.

(13) In 0.05 and 0.1 M NaOH k_ψ = 1.34 and 1.32 s^{-1}, respectively.
(14) Deprotonation of 1 is an equilibrium reaction with no buffer catalysis.[1]
(15) Bunton, C. A.; Sepulveda, L. *J. Phys. Chem.* **1979**, *83*, 680.
(16) Martinek, K.; Yatsimirski, A. K.; Levashov, A. V.; Berezin, I. V. In "Micellization, Solubilization and Microemulsions"; Mittal, K. L., Ed.; Plenum Press: New York, 1977; Vol. 2, p 489.
(17) Mukerjee, P. In "Solution Chemistry of Surfactants"; Mittal, K. L., Ed.; Plenum Press: New York, 1979; Vol. 1, p 153. Cordes, E. H.; Gitler, C. *Prog. Bioorg. Chem.* **1973**, *2*, 1.
(18) Menger, F. M. *Acc. Chem. Res.* **1979**, *12*, 111.
(19) Bunton, C. A.; Huang, S. K. *J. Org. Chem.* **1972**, *37*, 1790. Perez de Albrizzio, J.; Cordes, E. H. *J. Colloid Interface Sci.* **1979**, *68*, 292.

Aromatic Amines from Carboxylic Acids and Ammonia. A Homogeneous Catalytic Process

Gregory G. Arzoumanidis*[1] and Frank C. Rauch

Stamford Research Laboratories, American Cyanamid Company, Stamford, Connecticut 06904

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A homogeneous metal-catalyzed synthesis of aniline from benzoic acid and ammonia (amination reaction) has been described in a short communication[2] and a U.S. patent.[3] In this paper we present details from the amination of a variety of aromatic acids and we discuss the mechanism of the reaction.

A new industrial aniline process may be based on two reaction steps: (1) decarboxylative amination of benzoic acid with concomitant reduction of Cu(II) to Cu(I) and (2) reoxidation of the ammoniacal solutions of Cu(I) with atmospheric oxygen.

$$2Cu(OOCPh)_2{\cdot}NH_3 \rightarrow PhNH_2 + CO_2 + 2CuOOCPh + PhCOONH_4$$

$$2CuOOCPh + 2PhCOONH_4 + {}^1/_2O_2 \rightarrow 2Cu(OOCPh)_2{\cdot}NH_3 + H_2O$$

$$PhCOONH_4 + {}^1/_2O_2 \rightarrow PhNH_2 + CO_2 + H_2O$$

Inclusion of oxygen in the first step for an in situ oxidation of Cu(I) does not result in catalytic yields of aniline. The aniline-yielding reaction is closely related to the Cu(II)-catalyzed oxidation of benzoic acid to phenol.[4] It must be stated at the outset (vide infra) that production of aniline directly from phenol was shown not to occur under the conditions of the amination reaction.

Results

Aniline from Benzoic Acid. Benzoic acid was heated with CuO or copper benzoate at 190–230 °C under ammonia pressure in an autoclave. Aniline was produced in 70% yield, based on the reduction of Cu(II) to Cu(I). Byproducts were phenol, 7%, and diphenylamine, 8%. Benzamide was also produced through dehydration of ammonium benzoate. The amination reaction is very rapid above 200 °C. Temperatures above 230 °C result in the direct decarboxylation of benzoic acid to benzene and

(1) Amoco Research Center, P.O. Box 400, Amoco Chemicals Corporation, Naperville, IL 60566.
(2) G. G. Arzoumanidis and F. C. Rauch, *J. Chem. Soc., Chem. Commun.*, 666 (1973).
(3) U.S. Patent 3 812 137.
(4) (a) W. W. Kaeding, *J. Org. Chem.* **26**, 3144 (1961); (b) W. W. Kaeding and G. R. Collins, *ibid.*, **30**, 3750 (1965); (c) W. W. Kaeding, H. O. Kerlinger, and G. R. Collins, *ibid.*, **30**, 3750 (1965); (d) W. W. Kaeding and A. T. Shirglin, *ibid.*, **27**, 3551 (1962); (e) W. W. Kaeding, *ibid.*, **27**, 3551 (1962); (f) W. G. Toland, *J. Am. Chem. Soc.*, **83**, 2507 (1961); (g) W. W. Kaeding, *J. Org. Chem.*, **29**, 2556 (1964).

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further dehydration of benzamide to benzonitrile. At the optimum temperature of about 220 °C the reaction is essentially complete within 15–30 min. Accurate rate data could not be obtained from the batch autoclave conditions because of the heat-up periods required (see Experimental Section).

Alkyl-Substituted Aromatic Amines. Comparable results were obtained from the amination of alkyl-substituted benzoic acids. Thus, the decarboxylative amination of *m*-toluic acid and 3,4-dimethylbenzoic acid proceeded smoothly at 220 °C. Direct decarboxylation was almost negligible in both cases and the yield of amines was 50% and 44%, respectively. The isomer distribution provides a strong evidence for an ortho attack. *m*-Toluic acid gave 85% *p*- and 15% *o*-toluidine. 3,4-Dimethylbenzoic acid resulted in 98% 3,4-dimethyl- and 2% 2,3-dimethylaniline.

Chloroanilines. Attempts to synthesize chloroanilines from chlorobenzoic acids yielded predominantly the product of direct decarboxylation, i.e., chlorobenzene. Chloroaniline could not be obtained from *o*-chlorobenzoic acid. The meta isomer, however, did yield small amounts of *p*-chloroaniline.

Reactions with Phenylenedicarboxylic Acids. Amination of dicarboxylic acids, e.g., phthalic acid, was initially considered as a potentially attractive route to phenylenediamines. However, phthalic acid, its anhydride, and terephthalic acid yielded aniline instead of the diamines. Apparently partial decarboxylation of the starting material takes place before significant amination occurs, although some decarboxylation of the intermediate aminobenzoic acid may also take place. The low yield of aniline in these reactions may be attributable to an unfavorable benzoic acid/CuO ratio. Indeed, not all of the dicarboxylic acid decomposes to benzoic acid. A substantial part of the starting material is converted to the diamide–imide derivatives and benzamide. Direct decarboxylation of the phenylenedicarboxylic acids in the presence of copper ions begins at about 150 °C. Similar results are obtained when phthalic acids react with CuO and H_2O. Phenol is the principal product and no evidence is found for dihydroxy benzenes.[5]

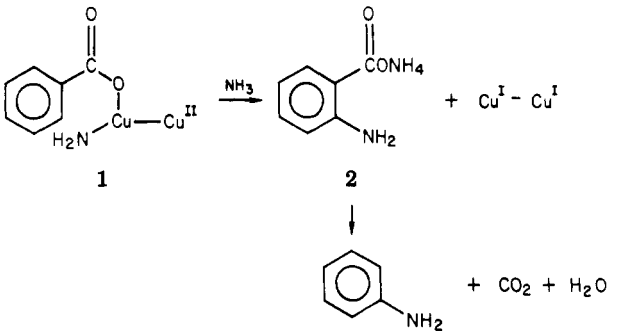
Aminoanthraquinones. The formation of these derivatives was investigated because of their importance as dye intermediates. 2-Aminoanthraquinone was obtained in 5% yield as a product of the amination of anthraquinone-2-carboxylic acid. The one-isomer was produced in only trace amounts. Direct decarboxylation to anthraquinone was the principal reaction.

Discussion

There are a number of similarities between the decarboxylative amination and the decarboxylative hydroxylation (oxidation) reactions.[4] These include: stoichiometry, rates of reaction, substitutional selectivity, and a side reaction of direct decarboxylation. There are also a few differences as deduced by the types of products isolated from each reaction. For the oxidation, Kaeding[4c] distinguishes three categories: (a) the phenol reaction, (b) the salicylic reaction, and (c) the ester reaction. The phenol reaction, yielding either phenol or phenyl benzoate, is favored in protic solvents such as water or benzoic acid. The formation of salicylic acid is favored in aprotic aliphatic hydrocarbon solvents. In the ester reaction an aromatic aprotic solvent, e.g., toluene, participates to give the corresponding aryl ester of benzoic acid, e.g., tolyl benzoate.

(5) U.S. Patent 2727924.

Scheme I. Mechanism of the Amination Reaction



None of these products, with the exception of phenol, nor their corresponding amino analogues, e.g., anthranilic acid, have been observed in the aniline reaction. Diphenylamine is a notable byproduct of the aniline reaction without any corresponding analogue in the oxidation reaction (e.g., diphenyl ether). The route by which phenol is produced in the amination reactions, even when water is deliberately excluded, is probably through ammonolysis of phenyl benzoate. It should be pointed out that once the phenyl–oxygen bond is formed, it cannot be cleaved by NH_3 under the experimental conditions employed in this work. Thus, not even a trace of aniline was detected on heating phenol, CuO, and NH_3 at 230 °C for 4 h; phenol was recovered quantitatively. These findings support the hypothesis of a primary nucleophilic attack of an amino group on the aromatic ring, within the coordination sphere of the metal. Indeed, ammonia forms a variety of coordination coupounds and/or addition complexes with copper benzoate, $Cu(OOCPh)_2 \cdot nNH_3$ (n = 2–8). The complexes decompose thermally in a stepwise fashion, until at 180 °C the last complex of the series (n = 2) decomposes at atmospheric pressure to ammonia and free $Cu(OOCPh)_2$.[6]

Copper benzoate exists in several crystalline modifications.[7-9] There is a large number of adducts of copper carboxylates with the stoichiometry $Cu(RCOO)_2 \cdot X$, where X is a donor molecule. Most of these show anomalously low magnetic moments and are found to be dimeric. A basic copper benzoate having the formula PhCOOCuOH has also been prepared[4d] by partial hydrolysis of the normal salt. The structure of PhCOOCuOH has not been determined. Pyrolysis of the normal salts under anhydrous conditions yields the phenyl esters,[4f] whereas pyrolysis of the basic salt yields salicylic acid,[4d] presumably via a cyclic intermediate.

In our proposed mechanism for the amination reaction, Scheme I, we assume the formation of an amide copper benzoate intermediate 1 analogous to PhCOOCuOH. Copper amides, known for several years,[10] have not been investigated as thoroughly as other metal amides.[11] The observed regioselectivity (i.e., the exclusive orthosubstitution, 2) is a strong indication for a cyclic mechanism in the amination reaction as well. Steric and/or electronic effects may favor one ortho position over the other, as

(6) F. Ephraim and E. Rosenberg, *Ber. Dtsch. Chem. Ges.* **51**, 644 (1918).
(7) (a) C. Oldham in "Progress in Inorganic Chemistry", F. A. Cotton, Ed., Interscience, New York, 1968, Vol. 10, p 249; (b) R. J. Doedens in "Progress in Inorganic Chemistry", S. J. Lippard, Ed., Interscience, New York, 1976, Vol. 21, p 209; (c) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 4th ed., Wiley-Interscience, New York, 1980, p 817.
(8) R. D. Gielard, D. M. Harris, and G. Wilkinson, *J. Chem. Soc.*, 2838 (1964).
(9) D. B. W. Yawney, J. A. Moreland, and R. J. Doedens, *J. Am. Chem. Soc.*, **95**, 1164 (1973).
(10) D. Nichols, "Inorganic Chemistry in Liquid Ammonia", Elsevier, New York, 1979, pp 139, 135.
(11) Reference 7c, p 606.

Table I. Amination of Aromatic Acids

acid	mmol	CuO, mmol	NH_3, mmol	H_2O, mmol	reaction temp, °C	reaction time, h	products (% yield)[a]
m-toluic	146.9	37.7	411	166	220	0.5	*p*-toluidine (42.5), *o*-toluidine (7.5), *p*-cresol (3), *o*-cresol (1), aniline (trace), *m*-toluamide[b]
3,4-dimethylbenzoic	133.5	40.2	411	166	220	0.5	3,4-dimethylaniline (43.1), 2,3-dimethylaniline (0.9), 3,4-dimethylphenol (3.5), 3,4-dimethylbenzamide[b]
o-chlorobenzoic	125.5	41.5	470	194	215	0.5	aniline,[b] phenol,[b] diphenylamine[b] (main product)
m-chlorobenzoic[c]	25.5	12.6	117	55	215	0.5	*p*-chloroaniline (2), aniline,[b] diphenylamine[b]
terephthalic	84.6	68.5	587	222	220	0.5	aniline (1.9), phenol (1.2), ammonium benzoate[b] (2.2 mmol), terephthalic diamide[b]
phthalic	123.4	96.8	881	277	205	0.5	aniline (2.4), phenol (trace), diphenylamine (trace), benzamide,[b] phthaldiamide,[b] phthalimide[b]
phthalic anhydride	62.0	247.4	821		215	1.0	aniline, (1.5) benzamide[b]
anthraquinone-2-carboxylic acid	34.9	22.6	411	166	220	0.5	2-aminoanthraquinone (5), 1-aminoanthraquinone (trace), anthraquinone[b] (4.8 mmol), anthraquinone-2-carboxamide[b]

[a] Based on the reduction of Cu(II) to Cu(I). [b] Products from a nonoxidative route. [c] Benzene (225.3 mmol) was used as a solvent.

shown by the amination of substituted benzoic acids and the anthraquinone-2-carboxylic acid. In the latter case, an ortho substitution predominantly in the 3-position of the anthraquinone ring produces 2-aminoanthraquinone after decarboxylation.

Experimental evidence based on product yields (vide infra) supports an overall one-electron reduction of Cu(II). The amination is a two-electron redox process. Consequently, electron transfer to a second Cu(II) atom is required. The electron transfer is facilitated by the well-established Cu–Cu interaction[7] of the copper benzoate dimer.

The total yield of the benzoic acid reaction products derived from an oxidative–decarboxylative route (aniline, phenol, diphenylamine) is approaching 90%, based on an one-electron reduction of Cu(II). A molar ratio of $C_6H_5COONH_4/CuO$ equal to 4 appears to maximize the sum of product yields. Benzamide and benzonitrile are produced via dehydration of ammonium benzoate. These side reactions reduce product yields by decreasing the amount of ammonium benzoate available for the oxidative–decarboxylative reactions, i.e., by shifting the $C_6H_5COONH_4/CuO$ ratio below the optimum level. A gradual reduction of product yields due to the formation of benzamide was demonstrated in the recycle runs (see Experimental Section). Water was added in these runs to retard the formation of benzamide. However, water generally promotes the formation of phenol at the expense of aniline. A molar ratio of ammonia to water in the range of 3.0–3.5, at $C_6H_5COONH_4/CuO$ molar ratio equal to 4 maximizes the aniline yield. Cu(I) in the form of Cu_2O is also active in the amination reaction. The aniline yield with Cu_2O was 35%, i.,e., one-half the yield obtained with CuO. Presumably Cu(I) disproportionates to Cu and Cu(II). The latter affects the amination. Among other metal ions investigated as potential replacements for Cu(II), Pd(II) as palladium benzoate shows a 30% aniline yield. MoO_3 gave only a trace of aniline, whereas Co_2O_3 and Fe_2O_3 were inactive.

Experimental Section

Materials and General Procedures. Reagent grade chemicals were obtained from commercial sources and used without further purification. A 14-cm GC column was used packed with 15% Carbowax 20M on 80/90 mesh Anakrom AS. For the anthraquinone amines only, the GC column was 71 cm packed with 3% OV-17 on 100/200 mesh QC-Q. The isolated products were compared via IR, NMR, and mass spectrometric techniques with authentic samples.

Aniline from Benzoic Acid. Typical Run. A mixture of 3.0 g (37.7 mmol) of CuO, 20.1 g (164.7 mmol) of benzoic acid, and 3.0 g (167 mmol) of water was charged to a 300-mL Hastelloy C autoclave. Ammonia (10 g, 588 mmol) was admitted to the autoclave under pressure. The autoclave was then sealed and heated to 220 °C while being rocked. The heat-up period was 1 h and the temperature was maintained at 220 °C for 30 min. The reaction was then quenched by immersing the autoclave in ice water, and the gases were vented to the atmosphere. The autoclave was opened, and the contents were removed by washing with water. Products were isolated by steam distillation and extraction with ethyl ether of the distillate, under base (extraction of amines) and acid (extraction of phenols). Yields were calculated from an aliquot of the extract by GC using an internal standard. The yield of aniline was 70% (1.23 g, 13.2 mmol), phenol 7% (0.12 g, 1.3 mmol), diphenylamine 8% (0.13 g, 0.76 mmol). In addition, benzamide (1.17 g, 9.7 mmol) and benzoic acid (16.94 g, 138.7 mmol) was recovered.

Reoxidation of Cu(I). Recycle Runs. The oxidation of Cu(I) occurs concurrently with the steam distillation, when carried out under air. The green Cu(I) suspension changes to the characteristic blue Cu(II)–ammonia solution. The autoclave reaction was repeated 10 times. Each time benzoic acid was added prior to the run in amounts mole-equivalent to the products removed. The $[NH_3]:[H_2O]$ ratio during the runs was maintained at about 3. The conversion to products based on the Cu(II) reduction to Cu(I) starts at about 90% and levels off after the third run at about 35%. The average product selectivity at steady state is as follows: aniline, 80%; phenol, 15%; diphenylamine, 5%. The conversion of benzoic acid to the above products is nearly quantitative.

Amination of Other Aromatic Acids. A procedure similar to the above typical run was followed for the decarboxylative amination of other acids. Details are presented in Table I.

Acknowledgment. We thank Dr. Arthur K. Hoffmann for numerous discussions and suggestions, and the American Cyanamid Company for the permission to publish this work.

Registry No. Benzoic acid, 65-85-0; *m*-toluic acid, 99-04-7; 3,4-dimethylbenzoic acid, 619-04-5; *o*-chlorobenzoic acid, 118-91-2; *m*-chlorobenzoic acid, 535-80-8; terephthalic acid, 100-21-0; phthalic acid, 88-99-3; phthalic anhydride, 85-44-9; anthraquinone-2-carboxylic acid, 117-78-2; copper oxide, 1317-38-0; ammonia, 7664-41-7; aniline, 62-53-3; phenol, 108-95-2; diphenylamine, 122-39-4; *p*-toluidine, 106-49-0; *o*-toluidine, 95-53-4; 3,4-dimethylaniline, 95-64-7.