the ligands $As[CH_2CH_2CH_2As(CH_3)_2]_3$ and $P[CH_2CH_2CH_2As(CH_3)_2]_3$ should not differ so markedly.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
VANDERBILT UNIVERSITY, NASHVILLE 5, TENNESSEE

The Effect of Coordination on the Reactivity of Aromatic Ligands. X. Electrophilic Reactions of Bis(8-hydroxyquinolinato)copper(II)

BY NARESH K. CHAWLA AND MARK M. JONES

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Bis(8-hydroxyquinolinato)copper(II) has been found to undergo a large number of electrophilic substitution reactions. Benzoylation, sulfonation, nitration, thiocyanation, mercuration, and condensation with formaldehyde can be effected readily on the complex. Iodination can be effected, but only in poor yields, while acetylation failed. A kinetic study of the mercuration of 8-hydroxyquinoline and its copper(II) complex has been carried out in glacial acetic acid. The rate of mercuration varies in the order copper complex $\gg$ 8-hydroxyquinoline. The rate of mercuration of the copper complex is significantly changed by the addition of either copper(II) acetate or 8-hydroxyquinoline. An improved method of preparing 8-hydroxyquinoline-5-sulfonic acid has been developed.

The studies reported in earlier papers in this series[1] were limited to a relatively small fraction of the possible electrophilic substitution reactions which are possible with complexes of aromatic ligands. The present work was undertaken to extend these studies to a number of other substitution reactions and to determine which of these are suitable for more detailed kinetic studies. The reactions were carried out on bis(8-hydroxyquinolinato)copper(II) because previous work[1] had shown that it possessed sufficient stability to survive most of the reactions of this sort without loss of copper, yet could be decomposed into ligand and copper sulfide. The specific reactions examined were (1) benzoylation with benzoyl chloride in the presence of anhydrous aluminum chloride, (2) sulfonation, (3) nitration, (4) iodination, (5) thiocyanation, (6) mercuration, (7) acid-catalyzed condensation with formaldehyde, and (8) acetylation. Of these, mercuration showed itself amenable to kinetic studies. As a consequence, kinetic studies were carried out on the mercuration of the copper(II) and zinc(II) complexes as well as the free ligand, all in the solvent glacial acetic acid.

Experimental

Bis(8-hydroxyquinolinato)copper(II) and Other Materials Used.—The copper complex was prepared as described previously.[1] The 8-hydroxyquinoline used was Eastman White Label, and the other chemicals used were of reagent or ACS grade wherever possible. The glacial acetic acid used in the kinetic studies was from a lot which assayed 100% acetic acid and was used without further purification.

Benzoylation.—The copper chelate (17.5 g., 0.05 mole) was suspended in dry carbon disulfide (300 ml.) in a three-neck flask fitted with a reflux condenser and a mechanical stirrer, and the mixture was cooled to 0–5° by means of an ice bath. To this, a solution of benzoyl chloride (14 g., 0.10 mole) in carbon disulfide was added over a period of 30–40 min. Anhydrous aluminum chloride (26 g., 0.19 mole) was added over a period of about 1 hr. during which time the temperature of the reaction mixture was not allowed to rise above 5°. This was refluxed for 36 hr., and the slurry was then transferred to a beaker; the carbon disulfide was removed by evaporation. The beaker was then placed in ice, cooled to 0–5°, and concentrated hydrochloric acid (150 ml.) was added dropwise, with stirring, over a period of 60–80 min. The product was filtered and the residue was saturated with hydrogen sulfide. This was continued over a period of 6 hr., until the copper was completely precipitated as copper sulfide, which was removed by filtration. The filtrate was extracted with ether and the ether extract was washed with water until the wash water was no longer acidic. This was then dried over anhydrous calcium chloride and filtered; the filtrate was allowed to evaporate. Recrystallization from ethanol or ether gave a product, m.p. 107–111°, which was not increased upon further recrystallization. The infrared spectrum in a KBr disk indicated the presence of a carbonyl group.

This product was sublimed under vacuum to obtain a pure white product, 5-benzoyl-8-hydroxyquinoline, m.p. 118.5–119.5° (lit.[2] 118–119°). *Anal.* Calcd. for $C_{16}H_{10}NO_2 \cdot H_2O$: C, 67.8; H, 4.6. Found: C, 67.5; H, 4.9.

This material was also prepared from benzoyl chloride, 8-hydroxyquinoline, and aluminum chloride, using the procedure given by Matsumura. The melting point and infrared spectrum (KBr disk) were identical with those of the compound prepared from the complex. A mixture melting point of the two products was not depressed.

The yields of 5-benzoyl-8-hydroxyquinoline from the copper complex were 36% when carbon disulfide was used as the solvent and 34% when nitrobenzene was used in parallel experiments.

Sulfonation.—The copper complex (10 g., 0.028 mole) was gradually treated with seven times its weight of concentrated sulfuric acid at 0–10°. The mixture was kept 3–4 hr. at room temperature and was then poured over crushed ice. The resulting solid was collected on a filter, washed with cold water, and finally

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(1) K. D. Maguire and M. M. Jones, *J. Am. Chem. Soc.*, **84**, 2316(1962); *ibid.*, **85**, 154 (1963).

(2) K. Matsumura, *ibid.*, **52**, 4433 (1930).

recrystallized from 5% hydrochloric acid. Colorless needles separated, m.p. 323–324° (lit.[3] 322–323°). The yield was 10.5 g., 82% of theory for 8-hydroxyquinoline-5-sulfonic acid. An infrared spectrum (KBr disk) exhibited the characteristic absorption peaks of the sulfonic acid group. *Anal.* Calcd. for $C_9H_7O_4NS \cdot 2H_2O$: C, 41.3; H, 4.21; S, 12.26. Found: C, 41.7; H, 3.99; S, 12.97.

The reaction of 8-hydroxyquinoline with concentrated sulfuric acid was also examined under similar conditions. Only the starting material was recovered. Treatment with fuming (4% SO_3) sulfuric acid for 24 hr. at 8° gives 8-hydroxyquinoline-5-sulfonic acid.[3] Samples prepared in this manner were used for comparative purposes in the characterization of the product obtained from the sulfonation of the complex.

Because of the great apparent difference in the reactivities of the complexed and free 8-hydroxyquinoline in this case, it was decided to determine if the ligand underwent sulfonation with hot sulfuric acid. It was found that it did and that such a reaction could be used as a method of preparation for this compound which was much simpler than that recommended in standard works.[4]

8-Hydroxyquinoline-5-sulfonic Acid.—8-Hydroxyquinoline (10 g., 0.069 mole, Eastman White Label) was added to 50 ml. of concentrated (ACS reagent grade) sulfuric acid and the two were thoroughly mixed to produce a slurry. This mixture was then heated on a steam bath for 1 hr. Before the end of this time, all of the solid in the reaction mixture dissolved. After 1 hr., the entire reaction mixture was poured over ice (150 g.) and allowed to stand for 10–15 min. The light yellow precipitate which formed was collected on a filter and washed with water. The solid (25.5 g.) contains a great deal of water and must be dried at 120° to obtain the anhydrous crude product. The crude wet product can be recrystallized satisfactorily. It was dissolved by stirring with hot (80–100°) 5% hydrochloric acid (500 ml.). This was filtered hot and then cooled in an ice bath, at which point pale yellow needles separated. These were collected on a funnel, washed with water, and dried at 120° for 24 hr. or more to obtain the anhydrous product. The yield of purified anhydrous product obtained in this way was 13.1–13.6 g. (84–88% of theory), and this material had a m.p. of 324° (lit.[3,4] 322–324°). *Anal.* Calcd. for $C_9H_7NO_4S$: C, 48.00; H, 3.11; N, 6.22; S, 14.44. Found: C, 47.85; H, 3.12; N, 6.17; S, 14.18.

Nitration.—Nitric acid (250 ml. of 40%) was cooled to 0 to 10° and stirred. To this, the copper complex (10 g., 0.028 mole) was added slowly over a period of 2 hr. The temperature was not allowed to rise above 10°. The reaction mixture was then allowed to stir overnight. At the end of this time the solid present was collected on a filter and washed with water and ethanol (200 ml.). This residue gave no test for copper. It was subsequently refluxed with glacial acetic acid (200 ml.) to remove any mononitrated 8-hydroxyquinoline, washed with water, and then refluxed with ethanol (200 ml.) and finally collected on a filter and dried at 110° for 4 hr. The greenish yellow solid obtained in this manner could not be recrystallized from any of a large number of solvents which were tried (benzene, toluene, ether, ethanol, chloroform, carbon tetrachloride, dimethylformamide, and dimethyl sulfoxide). The solid gave a positive test for a nitro group,[5] and its infrared spectrum (KBr disk) showed characteristic nitro group absorption at 1350 and 1550 cm.$^{-1}$. The product was found to decompose at 327°. Decomposition temperatures reported for 5,7-dinitro-8-hydroxyquinoline in the literature[6] are 276, 318, 320, and 325°. The yield was 6.2 g., 46.4% of theory. *Anal.* Calcd. for $C_9H_5N_3O_5$: C, 45.96; H, 2.13; N, 17.87. Found: C, 46.13; H, 2.23; N, 17.91.

Iodination.—Bis(8-hydroxyquinolinato)copper(II) (10 g., 0.028 mole) was shaken with iodine (20 g., 0.127 mole) in chloroform (200 ml.) at 0 to 10°. This mixture was stirred overnight at room temperature and the chloroform was evaporated to obtain a gummy product. Attempts to crystallize this material failed and it did not melt at elevated temperatures. It was stirred with 800 ml. of hydrochloric acid (50%) for 2 hr. and then saturated with hydrogen sulfide to remove copper. The precipitate which formed was filtered and the filtrate tested for complete removal of copper. The filtrate was heated on a steam bath to remove hydrogen sulfide. It was then cooled and neutralized with sodium bicarbonate. The green solid which was obtained at this point was extracted with hot ethanol and the residue recrystallized from glacial acetic acid. This resulted in greenish yellow crystals of 5,7-diiodo-8-hydroxyquinoline, m.p. 200–208° dec. (lit.[3] 195–210° dec.). The yield was 1.5 g. or 6.6% of theory. *Anal.* Calcd. for $C_9H_5NOI_2$: C, 27.20; H, 1.26; I, 64.00. Found: C, 28.59; H, 1.47; I, 64.46.

The alcoholic extract obtained above was concentrated and gave a solid product, m.p. 126–132° (lit.[3] 127–128°). The yield of this material was 1 g. (6.5% of theory).

Thiocyanation.—Potassium thiocyanate (11.65 g., 0.120 mole) was stirred with carbon tetrachloride (250 ml.) and bromine (9.50 g., 0.59 mole) was added to this over a period of 40 min., during which time the reaction flask was immersed in ice. Approximately 0.06 mole of thiocyanogen was produced. Bis(8-hydroxyquinolinato)copper(II) (10.6 g., 0.03 mole) was added with stirring and cooling so that the temperature was maintained below 10°. This slurry was stirred overnight at room temperature, filtered, and both filtrate and residue were evaporated to dryness. A sticky product, 10 g., was obtained. It was stirred in concentrated hydrochloric acid for 1 hr. to break it up; the suspension was diluted with an equal volume of water and then saturated with hydrogen sulfide. The precipitated copper sulfide was filtered and the filtrate tested to ensure that all of the copper had been precipitated. The hydrogen sulfide was boiled off, the solution allowed to cool, and the acid then neutralized with sodium bicarbonate. At this point a yellow precipitate appeared which, when collected on a filter and dried, weighed 5 g. It could not be recrystallized from ordinary organic solvents. It was redissolved in concentrated hydrochloric acid which was then neutralized gradually with dilute aqueous ammonia. This gave 4.5 g. of a solid; m.p. 198–204° (lit.[7] 134 and 143°). Its infrared spectrum (KBr disk) exhibited strong absorption at 2200 cm.$^{-1}$ due to the thiocyano group. Its analysis corresponded to a mixture of 70% mono- and 30% dithiocyano-8-hydroxyquinoline. *Anal.* Calcd. for $C_{10}H_6N_2OS$: C, 59.38; H, 2.99; S, 15.86. Calcd. for $C_{11}H_5N_3OS_2$: C, 50.94; H, 1.94; S, 24.73. Found: C, 57.39; H, 3.43; S, 18.80.

Mercuration.—The copper complex (5 g., 0.014 mole) was dissolved in 1 l. of glacial acetic acid and a solution of mercuric acetate (4.46 g., 0.014 mole) in glacial acetic acid (100 ml.) was added. On standing, a green precipitate appeared which gradually increased in amount. After standing overnight, the precipitate was collected on a filter, washed with water, and then dried in a vacuum desiccator. The green product, which could not be recrystallized from any common solvents (ethanol, benzene, toluene, carbon tetrachloride, chloroform, dimethylformamide, or dimethyl sulfoxide) weighed 5.8 g. The product was the copper complex of 8-hydroxyquinoline in which three mercuriacetate groups are present. Presumably, one of the chelate rings bears a single –HgOAc group while the other ring bears two. *Anal.* Calcd. for $CuC_{24}H_{18}N_2O_8Hg_3$: C, 25.55; H, 1.60. Found: C, 25.62; H, 1.80.

Acetylation.—The copper complex (17.5 g., 0.05 mole) was suspended in dry nitrobenzene (200 ml.) in a three-neck flask fitted with a reflux condenser and a mechanical stirrer, and the

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[3] K. Matsumura, *J. Am. Chem Soc.*, **49**, 810 (1927).

[4] (a) F. J. Welcher, "Organic Analytical Reagents," Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1947, p. 333; (b) R. G. W. Hollingshead, "Oxine and Its Derivatives," Vol. III, Butterworths Scientific Publications, London, 1956, p. 822, contain the literature on this compound.

[5] R. L. Shriner and R. C. Fuson, "The Identification of Organic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1947, p. 171.

[6] (a) R. Schmitt and F. Engelmann, *Ber.*, **20**, 2690, 2693 (1887); (b) G. M. Bennett and J. F. Grove, *J. Chem. Soc.*, 378 (1945); (c) Z. Skrowaczewska, *Roczniki Chem.*, **22**, 154 (1948); (d) R. P. Dikshoorn, *Rec. trav. chim.*, **48**, 557 (1929).

[7] Q. Fernando, J. F. Emery, and J. P. Phillips, *J. Am. Chem. Soc.*, **75**, 1983 (1953).

mixture was cooled to 0–5° by means of an ice bath. Acetyl chloride (7.10 ml., 0.1 mole) was added to this vigorously stirred suspension over a period of 40 min. Anhydrous aluminum chloride (26 g., 0.2 mole) was added in small portions over a period of 1 hr. The slurry was refluxed for 30 hr., the solvent was distilled under vacuum, and the crude tarry product was transferred to a beaker. This product was cooled in ice, treated with 250 ml. of concentrated hydrochloric acid, stirred for about 1 hr., and collected on a filter. The residue was treated with concentrated hydrochloric acid and saturated with hydrogen sulfide by the addition of sodium sulfide, and the copper sulfide which formed was filtered under suction. The filtrate was tested for the complete removal of copper. The hydrogen sulfide was boiled out of the solution which was then cooled and neutralized. At this point only unreacted 8-hydroxyquinoline separated. The use of carbon disulfide as a solvent or an increase in the time of reflux did not result in any improvement in yield or product. Increasing the amount of acetyl chloride to four moles per mole of copper complex and working up the product in the usual way gave a tarry product which defied characterization.

Condensation with Formaldehyde.—The copper complex (5 g., 0.014 mole) was mixed with 37% aqueous formaldehyde (20 g.) and a few drops of dilute hydrochloric acid. The mixture was stirred at room temperature for about 6 hr. and then evaporated to dryness to obtain a green compound (5 g.), m.p. 300–305°. This material was insoluble in alcohol, acetone, benzene, and chloroform. It had an infrared absorption spectrum with a strong absorption at 1450 cm.$^{-1}$, due to the $-CH_2-$ grouping, and also absorption in the region 600 to 900 cm.$^{-1}$ attributable to $\geqslant$C–H rocking. Neither of these was present in the spectrum of the starting material. The copper complex was stirred with concentrated hydrochloric acid, and this mixture was saturated with hydrogen sulfide. The copper sulfide which precipitated at this point was removed by filtration and the filtrate neutralized with sodium bicarbonate. At this point a fluffy, light green precipitate was obtained. It melted at 65–66° and had an infrared spectrum in which the absorption at 1450 cm.$^{-1}$ was not as prominent as it was in the complexed material. The condensation of formaldehyde with 8-hydroxyquinoline was carried out in a similar manner. The product obtained melted at 68–70°. Its infrared spectrum was almost identical with that of the material obtained from the copper complex. *Anal.* Calcd. for $C_{19}H_{14}O_2N_2 \cdot 1.5H_2O$: C, 69.30; H, 5.16. Found: C, 70.01; H, 5.07.

Kinetic Studies.—The rates of mercuration of the copper complex, 8-hydroxyquinoline itself, and bis(8-hydroxyquinolinato)zinc(II) were determined in glacial acetic acid. The mercurating agent used was reagent grade mercury(II) acetate, and the samples were thermostated to within ±0.1° of the reported temperature. The solutions of the substrate and the mercuric acetate were kept separately in the constant temperature bath for about 20 min. to equilibrate. They were then mixed in such a ratio that 1 mole of mercuric acetate was provided for each mole of coordinated 8-hydroxyquinoline. The samples were then thoroughly shaken, placed in a glass-stoppered flask, and immersed in the constant temperature bath. Samples were taken at intervals and pipetted into a beaker surrounded by ice to quench the reaction. A few ml. of dilute nitric acid and a few ml. of saturated ferric alum indicator solution were added, and the sample was then titrated to a pink end point with a standard solution of potassium thiocyanate. The reactions were followed to the extent of about 75% completion in the case of the complex. The much slower ligand reaction was followed to the extent of 25 to 50% completion.

The composition of the mercuration product under the conditions of the kinetic studies was established by isolation and analysis of the product. Bis(8-hydroxyquinolinato)copper(II) (3.5154 g. or 0.010 mole) was dissolved in glacial acetic acid (500 ml.) and mixed with a solution of mercuric acetate (1.5931 g. or 0.005 mole) in glacial acetic acid (100 ml.). This solution was kept overnight at room temperature, by the end of which time a precipitate had appeared. It was collected on a filter and dried under vacuum to give residue A (0.80 g.). The filtrate was diluted with 600 g. of ice and the precipitate which subsequently formed was also collected on a filter and dried under vacuum to give residue B (0.5 g.). Neither of these could be recrystallized from any of a number of solvents. *Anal.* Calcd. for $CuHg_3C_{24}H_{18}O_8N_2$: C, 25.55; H, 1.60; N, 2.48. Calcd. for $CuHg_2C_{22}H_{16}O_6N_2$: C, 30.39; H, 1.84; N, 3.22. Found for residue A: C, 31.60; H, 2.30; N, 2.90. Found for residue B: C, 31.87; H, 2.30; N, 3.18.

These analyses indicate that the initial product contains two mercuriacetate groups and this assumption was used in the reduction of the rate data.

Results

The products obtained in the various reactions carried out on bis(8-hydroxyquinolinato)copper(II) are collected in Table I.

TABLE I

REACTION PRODUCTS

Reaction	Product orientation
Benzoylation	5-Benzoyl group introduced
Sulfonation	5-Sulfonic acid group introduced
Nitration	Nitro groups introduced at 5- and 7-positions
Iodination	5-Iodo group introduced
Thiocyanation	5-Thiocyano group introduced
Mercuration	Mercuriacetate groups presumably introduced at 5- and 7-positions
Acetylation	No apparent reaction
Formaldehyde condensation	Bridging –CH– group, probably 5-position

The kinetic studies were carried out on the copper complex, the free ligand, and solutions of the copper complex containing added species. For the copper complex itself, reasonably satisfactory second-order kinetics was found, the rate being proportional to both the concentration of mercuric acetate and that of the coordinated ligand. This result, that the mercuration is second order in both substrate and the attacking mercury species, is in complete accord with kinetic studies on the mercuration of aromatic compounds which are second-order reactions.[8] The results obtained in a typical run are summarized in Table II.

TABLE II

MERCURATION OF BIS(8-HYDROXYQUINOLINATO)COPPER(II) AT 30° IN GLACIAL ACETIC ACID[a]

Time, sec.	ml. of 0.01 M KSCN required for 10-ml. sample	Concn. of unreacted $Hg(OAc)_2$, M	k_2, l. mole^{-1} sec.$^{-1}$
462	17.80	0.00890	0.070
1914	9.10	0.00455	0.073
2532	7.45	0.00373	0.074
2940	6.30	0.00315	0.081
3450	5.95	0.00298	0.074
		Av.	0.074 ± 0.002

[a] The initial solution was prepared by mixing 50 ml. of 0.012622 M bis(8-hydroxyquinolinato)copper(II) with 50 ml. of 0.02524 M mercuric acetate. Ten-ml. samples were removed for analysis.

The results for various temperatures and concentrations of added species are collected in Table III.

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(8) (a) H. C. Brown and M. Dubeck, *J. Am. Chem. Soc.*, **81**, 5608 (1959) **82**, 1939 (1960); (b) C. Perrin and F. H. Westheimer, *ibid.*, **85**, 2774 (1963).;

TABLE III

RATES OF MERCURATION OF 8-HYDROXYQUINOLINE AND ITS COMPLEXES IN GLACIAL ACETIC ACID

Substrate, *M*	Temp., °C.	$Hg(OAc)_2$, *M*	$Cu(OAc)_2$, *M*	Free ligand, *M*	k_2, l. mole^{-1} sec.$^{-1}$
Copper Complex					
0.01275	35.0	0.02550			1.21×10^{-1}
0.006311	35.0	0.01262			1.39×10^{-1}
0.006375	35.0	0.01275			1.35×10^{-1}
0.01262	30.0	0.02524			0.74×10^{-1}
0.01275	30.0	0.02550			0.97×10^{-1}
0.006375	30.0	0.01275			0.70×10^{-1}
0.006375	25.0	0.01275			0.43×10^{-1}
0.012622	25.0	0.02524			0.50×10^{-1}
0.002483	35.0	0.004966	0.00124		3.86×10^{-2}
0.002069	35.0	0.004138	0.002069		3.53×10^{-2}
0.001552	35.0	0.003104	0.003104		1.65×10^{-2}
0.001035	35.0	0.002069	0.00414		1.7×10^{-2}
0.00296	35.0	0.00592		0.0003	8.93×10^{-2}
0.00272	35.0	0.00544		0.0008	8.26×10^{-2}
0.00251	35.0	0.00502		0.0013	4.59×10^{-2}
0.00211	35.0	0.00422		0.0021	3.12×10^{-2}
8-Hydroxyquinoline					
	40.0	0.01262		0.01262	2.03×10^{-2}
	40.0	0.00631		0.00631	2.08×10^{-2}
	35.0	0.01262		0.01262	0.8×10^{-2}
	35.0	0.02524		0.02524	1.3×10^{-2}
	35.0	0.01262		0.01262	9.0×10^{-3}
	35.0	0.01262		0.01262	8.5×10^{-3}
	35.0	0.01262		0.01262	8.7×10^{-3}
	30.0	0.01262		0.01262	7.3×10^{-3}
	30.0	0.01262		0.01262	7.4×10^{-3}
	30.0	0.01262		0.01262	7.4×10^{-3}
	25.0	0.01262		0.01262	5.6×10^{-3}
	25.0	0.01262		0.01262	5.4×10^{-3}
	25.0	0.01262		0.01262	5.5×10^{-3}
Zinc Complex					
0.0155	35.0	0.0310			0.96×10^{-1}

For the copper complex, use of the Arrhenius equation gives an energy of activation of 19 kcal. and a frequency factor of 9.6×10^{12} sec.$^{-1}$ ($\Delta S^* = -6.9$ e.u.). The kinetic behavior of the mercuration of the copper complex in the presence of either added cupric acetate or added 8-hydroxyquinoline is somewhat erratic. The course of such runs indicates that the mercuration reagent is partially destroyed, as the reaction stops before the mercuration reaction is nominally complete. The general pattern of the mercuration process makes it rather unsuitable for detailed kinetic studies involving reasonably active substrates. Multiple mercuration of one substrate molecule can occur prior to the initial mercuration of another. The attacking reagent is also susceptible to inactivation by Lewis bases, such as the acetate ion, because only positively-charged mercury(II) complexes are effective as electrophiles.

The error in the determination of the individual rate constants is rather large, about 8–13%. Part of this is due to the difficulty of observing the end point in the mercury(II) titration, because of the presence of the colored complex. Part is due to the limited solubility of the complex in glacial acetic acid. A more effective medium for such a study would have been an aqueous one, but this was ruled out by the insolubility of the complex in water.

Discussion

The principal result which is confirmed in these studies is that the phenolic ring of coordinated 8-hydroxyquinoline undergoes reaction with typical electrophilic reagents and that this is a *general* phenomenon. In a communication, Bostic, Fernando, and Freiser[9] reported that 8-hydroxyquinoline-5-sulfonic acid could be iodinated but that its complexes could not. Although neither the reaction nor the products were completely characterized by these workers, it is probable that both *do* undergo such a reaction, though the rate constants for the complexes were probably too low to be measured by the experimental methods used. Iodination reactions are frequently very slow and reversible.[10] It is apparent from the kinetic data on mercurations that the copper complex undergoes this reaction much more rapidly than the free ligand itself. The mercuration reaction is subject to many disturbances which affect the nature of the attacking reagent. Thus any added acetate or Lewis base will coordinate to the mercury and interfere with the

(9) C. Bostic, Q. Fernando, and H. Freiser, *Inorg. Chem.*, **2**, 232 (1963).

(10) P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution," Butterworths Scientific Publications, London, 1959, p. 110 ff.

substitution process. With only the copper complex present, however, reasonable second-order kinetic data are obtained. The sulfonation reaction also indicates that the complex is much more reactive and that the difference in reactivity is sufficiently great to be of synthetic utility. The copper complex is the most stable complex formed with any divalent metal ion of the first row transition series. It is quite insoluble in most aqueous media including acidic ones. In the case of the sulfonation reaction, the initial attack seems to be on the insoluble complex. This results in the direct sulfonation of the ligand which solubilizes the complex.

The remaining reactions fall into the same general pattern. Acetylation appears to be extremely sluggish, but this is in accord with the fact that the Friedel–Crafts reactions of 8-hydroxyquinoline are normally rather difficult to effect[11]; alkylations, for example, are unknown.

From the temperature variation of the rate constant for mercuration, the energy of activation and the frequency factor were calculated using the Arrhenius equation. These were found to be 19 kcal./mole and 9.6×10^{12} sec.$^{-1}$ ($\Delta S^* = -6.9$ e.u.), respectively, for the copper complex, and 13.6 kcal./mole and 5×10^{7} sec^{-1} ($\Delta S^* = -25$ e.u.) for 8-hydroxyquinoline itself. The frequency factor here is considerably greater for the complex and is responsible for the greater rate in this case, in spite of a higher activation energy. The strict comparison of the free and the complexed ligand in this reaction is hindered by the temperature-dependent ionizations of the free ligand. The activation energy for the complex is fairly close to that reported for simple aromatic systems.[12] For these latter, which include benzene and toluene, the activation energies are about 21 kcal./mole and the frequency factor is close to 10^{10}. The relative order of reactivity of free 8-hydroxyquinoline and its complexes toward mercuration is the same as that found for diazo coupling[1] and bromination,[13] *i.e.*, the protonated species is less reactive than the metal complex. The relative order of aromatic ligands toward *electrophilic* reagents supports the general order of rates given by the sequence: L > ML > HL. Here L can be a phenolate anion, an aromatic amine, pyridine, or any other aromatic ligand. This is also found in the nitration of α,α'-dipyridyl,[14] which proceeds more readily when the α,α'-dipyridyl is complexed to iron(III), cobalt(III), or chromium(III) than when the ligand is protonated on both nitrogens.

While one would expect that the reverse order of reactivity should hold for nucleophilic substitution reactions, only scattered information is available on this point. Nucleophilic reactions of pyridine derivatives are catalyzed by protonation[15] and also by the formation of a coordinate bond to oxygen (*i.e.*, by the formation of pyridine N-oxides).[16] Here the order of reactivity appears to be HL > OL > L.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
VANDERBILT UNIVERSITY, NASHVILLE, TENNESSEE

Coordinate Bond Energies and Inner Orbital Splitting in Some Tervalent Transition Metal Acetylacetonates

BY JAMES L. WOOD AND MARK M. JONES

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The heats of combustion of the tris acetylacetonate complexes of the transition metal ions from scandium(III) through cobalt(III) have been measured in an oxygen bomb calorimeter. The heats of sublimation of these complexes were determined using a static vapor pressure method. Using these data in a suitable thermochemical cycle, the bond energies for the heterolytic cleavage of the metal to ligand bonds were calculated. These heterolytic bond energies vary with the atomic number of the central metal ion in the fashion predicted by crystal field theory. From a knowledge of the spin states of the central ions it is possible to estimate $10Dq$ for some of these complexes from thermochemical data alone. These thermochemical $10Dq$ values are in fair agreement with those obtained by spectroscopic methods.

In previous work in this laboratory coordinate bond energies in a wide variety of complexes have been determined.[1-3] The present work was undertaken to determine the variations in metal to ligand bond energies in a series of closely related complexes. The complexes of the tervalent first row transition metal ions with acetylacetone were selected for this work. These compounds are well characterized. They are known to

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