plex formed, it is seen that the two alternative mechanisms proposed by previous investigators are essentially one and the same. The association complex between Sarin and the metal chelate has two tautomeric forms, which are no doubt in rapid equilibrium. It is apparent that it makes no difference which of these forms is produced initially or which is present in the higher concentration.

The reason for the previous suggestions of two alternative mechanisms was due to the fact that the relative concentrations of two of the metal chelate precursors of VIIa and VIIb, CuL^{2+} and $Cu[OH]L^{+}$, can be determined in these and many other similar systems, coupled with the assumption that the rate determining step was considered to be the nucleophilic attack of the hydroxyl ion in the phosphorus atom, with simultaneous displacement of the fluoride ion. The concept of unimolecular dissociation of fluoride, with or without help from the metal ion or chelate, however, resolves the supposed dichotomy in the mechanism of this reaction.

A similar interpretation may be given to the catalytic effect of the dihydroxo chelate, as is illustrated in Plate II.

Here again, it is seen that, if the dissociation of fluoride ion is rate-determining, it is impossible to distinguish between related pre-equilibrium species which differ only in the positions of hydroxyl groups. In this case, the precursor of the activated complex does not exist in more than one tautomeric form, since it does not contain bound hydrogen ions.

The mechanisms proposed above are also in agreement with other factors known to influence the activity of the Cu(II) chelate as a catalyst. Notable among these are the requirements that the charge of the complex be as positive as possible and that a maximum of two coordination sites of the copper(II) ion be occupied by the ligand. Both of the requirements would act so as to increase the binding of the fluoride ion by the metal of the metal chelate compound, in the formation of the transition state.

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

The Effect of Coördination on the Reactivity of Aromatic Ligands. III. Halogenation of Some 8-Hydroxyquinoline Chelates

BY KEITH D. MAGUIRE AND MARK M. JONES[1]

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Halogenation of 8-hydroxyquinoline chelates of Cr(III), Co(III), Fe(III), Cu(II) and Al(III) results in the same products as are obtained in the halogenation of the free ligand; though the relative amounts of the various haloderivatives may vary somewhat. Under no circumstance has any change in orientation of the entering substituent been observed. A survey of the results available on the reactions of coördinated aromatic ligands shows that the coördination act *per se*, in isolation from other complicating factors. has only a very slight effect on the gross pattern of aromatic reactivity exhibited in the free ligand.

In earlier studies in this series,[2,3] it was shown that the behavior of coördinated aromatic amines toward halogenation showed a surprising resemblance to that shown by the free ligand. The present study was undertaken to provide (1) information on the effect of the central metal ion on the reactivity and (2) data on a ligand capable of forming very stable chelates, 8-hydroxyquinoline. One of the reasons for selection of this ligand was the fact that its reactions have been studied in great detail and those of interest in the present study are well characterized.[4,5] It is important to emphasize that an added advantage of working with this ligand is the considerable stability of the metal chelates involved. This allows the isolation and characterization of the reaction products at each stage in the form of a metal complex. In some cases this stability was so great that isolation and characterization of the halogenated ligand was not possible. In these cases the reaction product was characterized by synthesis via an alternate sequence of reactions.

Experimental[6]

All infrared spectra were taken on a Perkin-Elmer model 137 recording spectrophotometer using a sodium chloride prism. All the spectra of the solid materials were obtained as pressed potassium bromide disks.

Preparation of 8-Hydroxyquinoline Chelates.—These chelates were prepared by the usual methods available in the literature[4] or by slight modifications of the analytical procedures employed for the gravimetric determination of these metal ions with 8-hydroxyquinoline.

The Cr(III) chelate was prepared on a large scale using a proceedure based upon an analytical method due to E. Taylor-Austin.[7]

The Co(III) chelate was prepared by reaction of a solution tris-(carbonato)-cobaltate(III) ion with 8-hydroxyquinoline. The cobalt intermediate was prepared using the procedure due to G. A. Barbieri[8a] and M. Mori, *et al.*[8b]

This compound is a green amorphous solid contrary to an earlier report which describes it as forming lustrous black crystals.[9]

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(1) To whom correspondence concerning this paper should be addressed.

(2) J. C. Taft and M. M. Jones, *J. Am. Chem. Soc.*, **82**, 4196 (1960).

(3) R. L. Jetton and M. M. Jones, *Inorg. Chem.*, in press.

(4) R. G. Hollingshead, "Oxine and its Derivatives," Butterworth's Scientific Pubs., London, 1956 four vols.

(5) J. P. Phillips, *Chem. Revs.*, **56**, 271 (1956).

(6) At the suggestion of the referees much of the experimental data has been summarized in tables. Complete details are available in the thesis of K. D. Maguire, Vanderbilt University, June 1962.

(7) E. Taylor-Austin, *Analyst*, **63**, 710 (1938).

(8) (a) G. A. Barbieri, *Atti Acc. Lincei Rend.* [6], **7**, 747 (1928). (b) M. Mori, M. Shibata, E. Kyuno and T. Adachi, *Bull. Chem. Soc. Japan*, **29**, 883, 887 (1957); M. Mori, M. Shibata, E. Kyuno and Y. O. Kuba, *ibid.*, **31**, 291, 940 (1958).

TABLE I

HALOGENATION OF 8-HYDROXYQUINOLINE CHELATES OF Fe(III) AND Cr(III)

Bromination (2 equiv. of bromine/mole of coördinated ligand)

Starting material	Product	Yield, %	Analysis			Characterization
Fe(III) chelate	Fe(III)[b] 5,7-dibromo chelate	82[a]	$Fe(C_9H_4ONBr_2)_3$	Calcd. Found	Br, 49.86 Br, 49.88	Infrared spectrum identical to that of pure Fe(III) 5,7-dibromo chelate[d]
Cr(III) chelate	Cr(III)[b] 5,7-dibromo chelate	83[a]	$Cr(C_9H_4ONB_2)_3$	Calcd. Found	Br, 50.05 Br, 49.90	Infrared spectrum identical to that of pure Cr(III) 5,7-dibromo chelate[d]
Chlorination (2 eq. of chlorine/mole of coördinated ligand)						
Fe(III) chelate	Fe(III) 5,7-dibromo chelate	90[c]				Infrared spectrum indicates ~90% Fe(III) 5,7-dichloro chelate[d,e] in crude product
Cr(III) chelate	Cr(III) 5,7-dichloro chelate	90[c]				Infrared spectrum indicates ~90% Cr(III) 5,7-dichloro chelate[d,e] in crude product

[a] Yields of purified material, based upon tris-(5,7-dihalo-8-hydroxyquinoline)-M(III) chelate—yield of crude materials approx. 95%. [b] Fe(III)-5,7-dibromo chelate, etc., indicates tris-(5,7-dibromo-8-hydroxyquinolinato)-iron(III). [c] Yields based on infrared spectra and are approximate values for crude reaction product. [d] Pure 5,7-dihalo chelate prepared from dihalo ligand and appropriate metal ion. [e] Based on comparison of crude reaction product spectrum with spectrum of pure 5,7-dihalo chelate. Spectral comparison shows approx. 5% unreacted material and approx. 5% trichlorinated material in the crude reaction product.

Analyses:

Tris-(8-hydroxyquinolinato)-aluminum(III) (Al(III) chelate). Calcd. for $Al(C_9H_6ON)_3$: Al, 11.10. Found: Al, 11.18.

Tris-(8-hydroxyquinolinato)-cobalt(III) (Co(III) chelate) Calcd. for $Co(C_9H_6ON)_3$: Co, 12.00. Found: Co., 11.9.

Bis-(8-hydroxyquinolinato)-copper(II) (Cu(II) chelate). Calcd. for $Cu(C_9H_6ON)_2$: Cu, 18.06. Found: Cu, 17.56.

Tris-(8-hydroxyquinolinato)-iron(III) (Fe(III) chelate). Calcd. for $Fe(C_9H_6ON)_3$: Fe, 11.41. Found: Fe, 11.45.

Tris-(8-hydroxyquinolinato)-chromium(III)(Cr(III) chelate). Calcd. for $Cr(C_9H_6ON)_3$: Cr, 10.72. Found: Cr, 10.82.

Preparation of Chelates of 5,7-Dibromo-8-hydroxyquinoline, and 5,7-Dichloro-8-hydroxyquinoline.—The above proceedures were modified only to the extent that a 1% (w./v.) solution of the 5,7-dibromo or 5,7-dichloro ligand in glacial acetic acid was used for the precipitations. Inasmuch as these materials are used in the gravimetric analysis of the metals concerned, they were used as obtained.

Dibromination of the Chelates.—Bromination of the Cu(II), Co(III), Cr(III) and Fe(III) chelates were carried out under conditions identical to those given in the following detailed example for the Al(III) chelate.

Bromination of tris-(8-Hydroxyquinolinato)-aluminum-(III).—The aluminum chelate (4.6 g., 0.01 mole) was dissolved in 100 ml. of chloroform and the mixture cooled to 0° in an ice bath. The solution was stirred vigorously while a solution of bromine (10.1 g.) in chloroform (100 ml.) was added. This quantity of bromine is approximately 5% in excess of the amount required to dibrominate the ligands, and it was added over a period of 90 minutes. A yellow precipitate was obtained which was filtered off. The solid product was washed thoroughly with ice cold chloroform and then dried at 100°. The yield of crude product was 12.4 g. This material was purified by solution in aqueous tetrahydrofuran (10% water) and reprecipitated by the addition of water. A yield of 73% of the purified bromination product was obtained, based upon the dibrominated aluminum(III) chelate.

The recovery and isolation of the free ligand required the disruption of the complex and the removal of the aluminum. The purified brominated complex (1.54 g.) was dissolved in dimethylformamide (50 ml.) by heating to boiling and acetic acid (5 ml.) was added. Aluminum phosphate was precipitated by the addition of a saturated aqueous solution of sodium dihydrogen phosphate (5 ml.). The precipitated aluminum phosphate was removed by filtering the solution while it was still hot; cooling the solution yielded 1.2 g. of pale yellow needles, m.p. 200–201°. A pure white product was obtained by recrystallization from benzene or ethanol or by vacuum sublimation at 175° and 0.5 mm. All these products have a m.p. 200–201°. Calcd. for 5,7-dibromo-8-hydroxyquinoline: C, 35.67; H, 1.66; N, 4.62; Br, 52.76. Found: C, 35.44, H, 1.84; N, 4.52; Br, 52.66. Heilbron[10] gives a m.p. of 196° as does Beilstein. The infrared absorption spectrum in a KBr disk was identical with the spectrum of a pure specimen of 5,7-dibromo-8-hydroxyquinoline and also with the spectrum recorded on file card No. 1319 in the National Research Council National Bureau of Standards collection.

Dichlorination of the Chelates.—Chlorination of the Al(III), Cr(III) and Fe(III) chelates was carried out using quantities and conditions identical to those given for the following detailed example for the Cu(II) chelate. Parallel chlorination experiments were run on the free ligand to provide strictly comparable data.

Dichlorination of Bis-(8-hydroxyquinolinato)-copper(II).—The chelate (3.5 g. 0.01 mole) was suspended in 250 ml. of dry carbon tetrachloride, and the mixture was maintained at 0° by means of an ice bath. The suspension was treated with 4 equivalents of chlorine (*i.e.* two equivalents per mole of coordinated 8-hydroxyquinoline). The chlorine gas was condensed in a graduated trap at the temperature of an acetone–Dry Ice mixture and 1.8 ml. of this liquid was allowed to volatilize slowly and pass under its own pressure into the reaction mixture. The chlorine addition was accomplished over a period of 40 minutes. The product was a green solid which was suspended in the carbon tetrachloride; it was collected on a filter and washed well with carbon tetrachloride. It was purified by solution in hot aqueous tetrahydrofuran, filtration and reprecipitation by pouring into cold water. This solid was collected on a filter and washed with water until free of chloride ion. The yield of the purified material was 90% of theory, based on bis-(5,7-dichloro-8-hydroxyquinolinato)-copper(II).

The isolation and identification of the halogenated ligand was accomplished as follows. The chlorinated product (2 g.) was dissolved in dilute (1:1) aqueous hydrochloric acid (50 ml.) with the aid of warming. To this solution was added water (100 ml.) and a slight excess of an aqueous solution of thioacetamide to precipitate the copper as copper sulfide. The mixture was left on the steam-bath for a further 30 minutes and then ammonium acetate (15 g.) and dilute aqueous ammonia were added until the *p*H was 1. The precipitated copper sulfide was filtered off and the yellow filtrate obtained yielded a pale yellow precipitate when neutralized with sodium bicarbonate. This precipitate was collected on a filter and washed well with water. Purification was effected by vacuum sublimation at 150° and 0.5 mm. followed by recrystallization from benzene. The product consisted of white needles, m.p. 180–181°. A mixed melting point with pure 5,7-dichloro-8-hydroxyquinoline was 180–181°. The literature values[4] range from 178° to 183°.

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(9) A. Ablov, *Bull. Soc. Chim. France* [4], 53, 234 (1933).

(10) I. Heilbron and H. M. Bunbury, eds., "Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1953.

TABLE II

HALOGENATION OF 8-HYDROXYQUINOLINE CHELATES OF Cu(II) AND Al(III)

A. Infrared spectrum identical with that of pure 5,7-dibromo-8-hydroxyquinoline and published spectrum for same compound on National Research Council—National Bureau of Standards Spectra file card No. 1319.

Complex			Isolated ligand				
Starting material	Product	Yield, %	Separation of metal	M.p., °C.	Analysis		Characterization
			Bromination (2 equiv. of bromine/mole coördinated ligand)				
Cu(II) chelate	Cu(II)[a] 5,7-dibromo chelate	75[b]	Precipitation of copper sulfide	200-201[c,d]	Calcd. for $C_9H_5NOBr_2$	Found	A
					C, 35.67	C, 35.48	
					H, 1.66	H, 1.82	
					N, 4.62	N, 4.56	
					Br, 52.75	Br, 53.15	
Al(III) chelate	Al(III)[a] 5,7-dibromo chelate	73[b]	Precipitation of aluminum phosphate	200–201[c,d]	Calcd. for $C_9H_5NOBr_2$	Found	A
					C, 35.67	C, 35.44	
					H, 1.66	H, 1.84	
					N, 4.62	N, 4.52	
					Br, 52.76	Br, 52.66	
			Free ligand 8-hydroxyquinoline				
8-Hydroxyquinoline	...	90	...	200–201[c,d]	Calcd. for $C_9H_5NOBr_2$	Found	A
					Br, 52.76	Br, 52.61	

[a] Cu(II) 5,7-dibromo chelate, etc., implies bis-(5,7-8-hydroxyquinolinato)-copper(II). [b] Yields of purified material based upon 5,7-dibromo chelate. [c] Corrected. [d] Lit. value, m.p. 197°.

Anal. Calcd. for 5,7-dichloro-8-hydroxyquinoline $C_9H_5NOCl_2$: C, 50.26; H, 2.43; N, 6.51; Cl, 32.97. Found: C, 50.17; H, 2.49; N, 6.67; Cl, 33.25.

As a further check on the identity of the halogenated ligand, its infrared spectrum was obtained. This spectrum was found to be identical with the spectrum of a specimen of 5,7-dichloro-8-hydroxyquinoline prepared by the dichlorination of 8-hydroxyquinoline in carbon tetrachloride[4] and also with the spectrum given on card No. 2500 of the NRC-NBS file for 5,7-dichloro-8-hydroxyquinoline.

Trichlorination of the Al(III) Chelate.—Trichlorination of the Al(III) chelate was accomplished employing similar conditions to those described for the dichlorination but using three equivalents of chlorine per mole of coördinated 8-hydroxyquinoline. Trichlorination of 8-hydroxyquinoline was accomplished by a modification of the procedure of Hebebrand.[11]

Characterization of Halogenation Products of the Fe(III) and Cr(III) Chelates.—These materials are of such an intractable nature that it was not possible to separate the halogenated ligand from the metal. The reaction products were characterized by comparison of their infrared spectra with the spectra of pure materials prepared from the halogenated ligand and the respective metal ion. The results of the halogenations are summarized in Tables I to III.

Discussion

The results of the present work agree qualitatively with previous studies from this Laboratory[2,3] on the halogenation of coördinated aromatic amines. The positions susceptible to electrophilic substitution in 8-hydroxyquinone are the 5 and the 7 positions with the former being somewhat more reactive than the latter. In all the cases examined, regardless of the nature of the central metal or the magnitude of its charge, the product of halogenation was invariably the 5,7-dihalo derivative when two moles of halogen were used per mole of coördinated 8-hydroxyquinoline.

Bromination of the parent ligand is rapid and quantitative[4]; strictly comparable yields are obtained when its complexes are brominated. It may thus be concluded that the effect of coördination upon the reactivity, *in this particular case*, is virtually negligible, since neither the product nor the yield are affected.

A study of the chlorination of 8-hydroxyquinoline has been carried out by Jackson.[12] He was unable to obtain a yield of the dichloro derivative greater than 30% regardless of the solvent employed. In the present study, yields of 80–90% of the 5,7-dichloro derivative were obtained when the complexes were chlorinated. The higher yields may be accounted for when it is noted that the effect of coördination is to hold the ligand in the form of the more reactive phenolate anion while at the same time it protects this group from oxidation by the halogen.

The possibility might be raised that during these reactions the ligand splits off from the complex, reacts and is then recoördinated.

It is difficult to visualize how such a mechanism can account for the higher yields obtained in the chlorinations of the coördinated ligands.

In the present case the benzenoid ring is activated by the oxygen atom of the hydroxyl group, and this oxygen atom will maintain the same formal charge in the complex that it has in the free ligand. The positive charge of the central metal ion is sufficiently neutralized upon coördination that it does not cause any significant change in the reactivity of the ligand. It is not easy to explain how coördination can cause little change in the electronic density patterns of the ligands. If these reactions were determined more by the relative polarizability of the positions,[13] such slight changes in reactivity are more readily comprehended.

Although these results may seem unusual at first glance, such evidence as is presently available is in accord with the hypothesis that coördination of an aromatic system *via* a donor atom external to that system (*e.g.* phenols through the oxygen or aromatic amines through the nitrogen) has little qualitative effect on the relative reactivity of the positions of the aromatic system for electrophilic reagents. This idea has been used intermit-

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(11) A. Hebebrand, *Ber.*, **21**, 2977, 2981 (1888).

(12) D. E. Jackson, C.A.D.O. Tech. Rep. N6-ori-71. Chem. Task Order VII Sept. 1, 1950.

(13) P. B. D. De La Mare and J. H. Ridd, "Aromatic Substitution," Butterworths, London, 1959, pages 19–22.

TABLE III

HALOGENATION OF 8-HYDROXYQUINOLINE CHELATES OF Cu(II) AND Al(III)

A. Infrared spectra identical with that of authentic 5,7-dichloro-8-hydroxyquinoline, and with literature spectrum: National Research Council—National Bureau of Standards spectrum No. 2500. All A spectra are identical.
B. All B infrared spectra are identical.

Complex			Isolated ligand				
Starting material	Product	Yield, %	Separation of metal	M.p., °C.[d]	Analysis		Characterization
Dichlorination (2 equiv. of chlorine/mole of coördinated ligand)							
Cu(II) chelate	Cu(II) 5,7-dichloro chelate[a]	90[b]	Precipitation of copper sulfide	180–181[e]	Calcd. for $C_9H_5ONCl_2$ C, 50.26 H, 2.43 N, 6.51 Cl, 32.97	Found C, 50.17 H, 2.49 N, 6.67 Cl, 33.25	A
Al(III) chelate	Al(III) 5,7-dichloro chelate[a]	92[b]	Precipitation of aluminum phosphate	180–181[e]	Calcd. for $C_9H_5ONCl_2$ C, 50.26 H, 2.43 N, 6.51 Cl, 32.97	Found C, 50.32 H, 2.61 N, 6.44 Cl, 32.82	A
8-Hydroxyquinoline	5,7-dichloro-8-hydroxyquinoline	40	...	180–181[e]	Calcd. for $C_9H_5ONCl_2$ C, 50.26 H, 2.43 H, 6.51 Cl, 32.97	Found C, 50.40 H, 2.50 N, 6.32 Cl, 33.00	
Trichlorination (3 equiv. of chlorine/mole of coördinated ligand)							
Al(III) chelate	Al(III) 5,6,7-trichloro chelate[a]	86[c]	Precipitation of aluminum phosphate	219–220[f]	Calcd. for $C_9H_4NOCl_3$ C, 43.5 H, 1.62 N, 5.64 Cl, 42.80	Found C, 43.70 H, 1.72 N, 5.64 Cl, 42.57	B
8-Hydroxy-	5,6,7-trichloro-8-hydroxyquinoline	30		220	Calcd. for $C_9H_4ONCl_3$ C, 43.5 H, 1.62 N, 5.64 Cl, 42.80	Found C, 43.75 H, 1.67 N, 5.70 Cl, 43.0	B

[a] Cu(II) 5,7-dichloro chelate, etc., implies bis-(5,7-dichloro-8-hydroxyquinolinato)-copper(II). [b] Yield of crude material, [c] Yield of crude ligand. [d] M.p. corrected. [e] Literature[4] values 178–183°. [f] Literature value 220°: J. C. Burckhalter, V. C. Stephens, H. C. Scarborough, Jr., N. S. Brinagar and W. H. Edgerton, *J. Am. Chem. Soc.*, **76**, 4902 (1954).

TABLE IV

REACTIVITIES OF FREE AND COÖRDINATED LIGANDS

Ligand	Reaction	Products from ligand and complexes	Lit.
Phenols and phenol acids	Diazotization	Identical	a–c
m-Toluidine	Chlorination	Identical	d
Nitriles	With aluminum isopropoxide	Identical	e
Aromatic amines	Oxidation to phenazines	Identical	f
Pyridine	Halogenation	Identical	g–h
Pyridine	Sulfonation	Identical	i, j
Tropolone	Bromination	Free ligand gives 3-bromo tropolone, copper complex gives 5 bromo tropolone	k

[a] V. I. Kuznetsov, *J. Gen. Chem.* (*U.S.S.R.*), **20**, 807 (1950); *C. A.*, **45**, 1452f; **26**, 3657 (1956) (C. B. trans.). [b] V. I. Kuznetsov and A. A. Nemodruk, *Sbornik Statei Obshchei Khim.*, **2**, 1378 (1953); *C. A.*, **38**, 10347; *J. Gen. Chem.* (*U.S.S.R.*) Suppl. II, 1378 (1958); **25**, 117 (1955), *C. A.*, **50**, 1698. [c] A. A. Nemodruk, *J. Gen. Chem.* (*U.S.S.R.*), **28**, 1051 (1958) (C. B. trans.). [d] M. Gentschev, I. Pojarliev and D. Kolev, *Compt. rend. Acad. bulgare Sci.*, 12, 307 (1959). [e] H. W. Johnston, *J. Org. Chem.*, **25**, 454 (1960). [f] E. F. G. Herington, "International Conference on Coördination Chemistry," Special Publication of the Chemical Society No. 13, The Chemical Society, London, 1959, p. 129. For the reaction of the free ligand see R. E. Elderfield "Heterocyclic Compounds," John Wiley and Sons, Inc., New York, N. Y., Vol. VI, page 636. [g] German Patent 595,461 (M. A. Kunz, K. Köberle and E. Berthold), *Chem. Zentr.*, **105**, II, 1029 (1934); Swiss Patent 174,893, to Chemische Fabrik von Hayden A. G., *Chem. Zentr.*, **106**, II, 2283 (1935). [h] D. E. Pearson, W. W. Hargrove, J. K. T. Chow and B. R. Suthers, *J. Org. Chem.*, **26**, 789 (1961). [i] H. C. Brown and B. Kanner, *J. Am. Chem. Soc.*, **75**, 3865 (1953). [j] N. Muller and W. J. Wallace, *J. Org. Chem.*, **24**, 1151 (1959). [k] J. W. Cook, A. R. M. Gibb and R. A. Raphael, *J. Chem. Soc.*, 2244 (1951).

tently, and perhaps unconsciously, for many years. An early example may be seen in German patents in which the diazotization and coupling of easily oxidized aromatic systems is carried out on their metal chelates, which are more resistant to oxidation.[14] In these processes the same dye is obtained by diazotization and coupling of either the free ligand or the chelate, but the use of the metal chelate results in a much higher yield. The other

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(14) German Patents 174,905; 175,827; 177,624; 178,304; 188,819 cited in Friedländer, "Forschritte der Teerfarbenfabriken und verwandte Industriezweige," Vol. VIII, 612, 616, 619, 620 (1904)

instances where comparative data are available on the reactivity of free and coördinated aromatic ligands are collected in Table IV. With the exception of tropolone, there are no authenticated instances where coördination changes the reactive position of an aromatic ligand toward electrophilic reagents.

One final important factor must be mentioned. This is the effect of charge on reactivity that arises when a neutral ligand coördinates to a metal ion to produce a charged complex. This effect of charge may be expected to be rather considerable but may also be masked by ion - pair formation which is often extensive with large, highly charged ions.[15] The introduction of a highly charged cation in the neighborhood of a neutral ligand such as would result from complexing is known to result in an appreciable deactivation of the ligand towards certain reagents which probably attack the ligand "positive-end on."[16]

This work has been supported by a grant from the Army Research Office (Durham) for which we wish to express our sincere gratitude.

(15) A. Jensen, F. Basolo and H. M. Neumann, *J. Am. Chem. Soc.*, **80**, 2354 (1958), which also contains citations to earlier work.

(16) R. N. Keller and L. J. Edwards, *ibid.*, **74**, 216 (1952); W. C. Drinkard, H. F. Bauer and J. C. Bailar, Jr., *ibid.*, **82**, 2992 (1960).

[CONTRIBUTION FROM THE WM. A. NOYES LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS]

Spectrophotometric Evaluation of the Thermodynamic Data for the Formation of the Dimethylbenzamide–Iodine Addition Compound

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The free energy and enthalpy of association of the addition compound formed between dimethylbenzamide and iodine are reported. Values of $-\Delta H = 4.0 \pm 0.2$ kcal./mole and $K = 3.8 \pm 0.1$ l. mole^{-1} at 25° are obtained. Changes in the molar absorptivity of iodine and the complex are observed with changes in temperature in some spectral regions. These changes can lead to an appreciable, systematic error in the enthalpy calculation if neglected. A procedure is indicated for obtaining reliable data on systems where these changes are occurring. Comparison of the heat of formation of the iodine adduct of N,N-dimethylbenzamide with values reported for a series of aliphatic amides and with the σ^* values for these amides indicates that the benzene ring is conjugated with the amide group.

Introduction

In a recent publication[2] a procedure referred to as an enthalpy determination was reported for evaluating heats of formation of weak molecular complexes. In this procedure the differences in absorbance between an iodine solution and a single iodine-base solution are measured as a function of temperature. The equilibrium constant K and molar absorptivity of the complex ϵ_C are determined at 25° by the standard methods.[3,4] The molar absorptivity obtained at 25° is employed for all temperatures, and K at different temperatures is calculated from the absorbance readings. Excellent reproducibility in the ΔH values (to $\pm$ 0.1 kcal.) is obtained at a given wave length. The calculated heat varies only slightly when $\epsilon_C - \epsilon_I$ is varied within the limits of error of its determination as long as it is constant at all temperatures. The calculated equilibrium constant varies considerably with changes in the value of $\epsilon_C - \epsilon_I$ at a given temperature, depending strongly upon the magnitude of K and the concentrations of the reactants. As a result, a slight change in either or both ϵ_C or ϵ_I with temperature will result in an appreciable difference in the actual value for ΔH and the one calculated assuming constant $\epsilon_C - \epsilon_I$.[5]

It is found that at different wave lengths, different values are obtained for ΔH. It is proposed[2] that ϵ_C and ϵ_I change with temperature and both the magnitude and direction of the change is wave length dependent. This proposal is borne out in this article by a careful analysis of the absorption spectra obtained for solutions containing N,N-dimethylbenzamide and iodine.

It should be emphasized that the errors introduced by a changing value of $\epsilon_C - \epsilon_I$ with temperature do not invalidate the use of this procedure for determining ΔH. In the classical procedure,[3,4] errors in the preparation of the individual solutions result in errors in the calculated values of $\epsilon_C - \epsilon_I$ and ΔH which are greater than the errors we discuss. This is verified by the random values reported in the literature for changes of $\epsilon_C - \epsilon_I$ with temperature. Errors of the order of magnitude being discussed ($\pm$ 0.7 kcal./mole at 95% confidence) are normally encountered in the evaluation of ΔH by the classical procedures at certain wave lengths. A procedure is described for carrying out these measurements with a precision of $\pm$ 0.2 kcal./mole.

Experimental

Preparation and Purification of Materials.—Baker and Adamson iodine was resublimed three times and stored in a desiccator over phosphorus pentoxide.

Fischer Spectroanalyzed carbon tetrachloride was employed as solvent in all measurements made.

Dimethylbenzamide was prepared by adding benzoyl-chloride dissolved in ether dropwise and with stirring to an ether solution saturated with dimethylamine at 0°. Following the addition of the acid chloride excess dimethyl-

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(1) General Electric Foundation Predoctoral Fellow, 1961–1962; abstracted in part from the Ph.D. Thesis of Robert L. Carlson, University of Illinois (1962).

(2) R. S. Drago, R. L. Carlson, N. J. Rose and D. A. Wenz, *J. Am. Chem. Soc.*, **83**, 3572 (1961).

(3) N. J. Rose and R. S. Drago, *ibid.*, **81**, 6138 (1959).

(4) J. A. A. Ketelaar, *et al.*, *Rec. trav. Chim.*, **71**, 1104 (1952).

(5) This research is concerned with an evaluation of K from the overlapping iodine and blue shift complex peaks. The difference in molar absorptivity of the complex ϵ_C, and iodine ϵ_I is required. See ref. 3.