are employed in the calculations, the solutions are sufficiently dilute to make this error of minor significance. It is estimated that stability constant values determined as herein described are accurate within 0.2 log K unit.

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[CONTRIBUTION NO. 838 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Structure and Behavior of Organic Analytical Reagents. II. Stability of Chelates of *o*-Aminophenol and of *o*-Aminobenzenethiol[1]

BY ROBERT G. CHARLES AND HENRY FREISER

The acid dissociation constants of *o*-aminophenol and *o*-aminobenzenethiol and the stability constants of the chelates of these reagents with some common divalent metals have been determined by potentiometric titration techniques. The chelates of *o*-aminophenol are less stable than those of *o*-aminobenzenethiol, despite the greater acidity of the latter reagent. This is attributed to the probably greater covalent character of the metal–sulfur bond than that of metal–oxygen bond. While the order of stability of metal chelates in *o*-aminophenol and *o*-aminobenzenethiol is similar to that observed in beta-diketones and salicylaldehydes, there are some significant differences. The reactions of the *o*-aminophenol and *o*-aminobenzenethiol with metals have been observed and tabulated.

Quite a few organic analytical reagents such as the α-amino acids, 8-hydroxyquinoline and quinaldic acid possess the reactive grouping, N–C–C–OH, capable of forming five-membered ringed chelate compounds with metals. For this reason, work on *o*-aminophenol as a model compound was undertaken. It was also desired to investigate the stabilities of Schiff bases of *o*-aminophenol and various aldehydes as compounds more closely analogous to 8-hydroxyquinoline, but unfortunately these compounds reverted almost immediately in solution to the original aminophenol and aldehyde. A comparison of the stabilities of the aminophenol complexes with those of aminobenzenethiol was undertaken in order to evaluate the effect of the substitution of sulfur for the more electronegative oxygen atom.

Experimental

Materials.—The purification of the dioxane and the preparation and standardization of metal perchlorate solutions and of standard sodium hydroxide and perchloric acid has been previously described.[1]

Eastman Kodak Co. practical grade *o*-aminophenol was decolorized with activated charcoal and recrystallized several times from water. It was found necessary to maintain an atmosphere of nitrogen over the hot phenol solution to prevent its oxidation, m.p. 175–176°. *o*-Aminobenzenethiol, provided in generous quantity by the American Cyanamid Co., was purified by fractional distillation under reduced pressure, b.p. 87.5–91.0°, at *ca* 1 mm. Since this compound is very sensitive to atmospheric oxidation, it was distilled shortly before use and kept in a frozen condition under a nitrogen atmosphere until used. Solutions of most of the common metallic ions containing 10 mg. metal per ml. were prepared from reagent grade salts. These were used only in the qualitative tests with the phenol and thiol.

Apparatus.—The apparatus is that previously described.[1]

Titration Procedure.—While the titration procedure used here has been described,[1] a modification employed in the aminobenzenethiol runs is noteworthy. In order to minimize handling and exposure to atmospheric oxygen, the approximate amount of the compound was introduced directly into the titration vessel without weighing. This amount was determined from the titration curve.

Results.—The results of representative titrations of metals with the two compounds are given in Table I along with their acid dissociation constants. It was found that chelate formation with aminophenol in ten fold ratio to metal ion occurred in the same pH region in which metal hydrolysis took place[1] (with the exception of copper). Since no precipitation was observed during these titrations, calculations of formation constants were carried out. Values of constants obtained from these calculations were different from those obtained from titrations in which the aminophenol was present in 100-fold excess in order to lower the pH range of chelate formation. A comparison of these values, presented in Table II, serves to illustrate the danger of accepting as valid, titration data obtained when pH of chelate formation is in the range in which metal ions hydrolyze appreciably.

The chelate formation constants of copper, nickel and cobalt *o*-aminobenzenethiolates could not be obtained from the titration data; because of their insolubility in the solvent these chelates precipitated early in the titration (see Fig. 1). As considerable fractions of the titrations in the case of zinc and lead proceeded in the absence of precipitation, it was

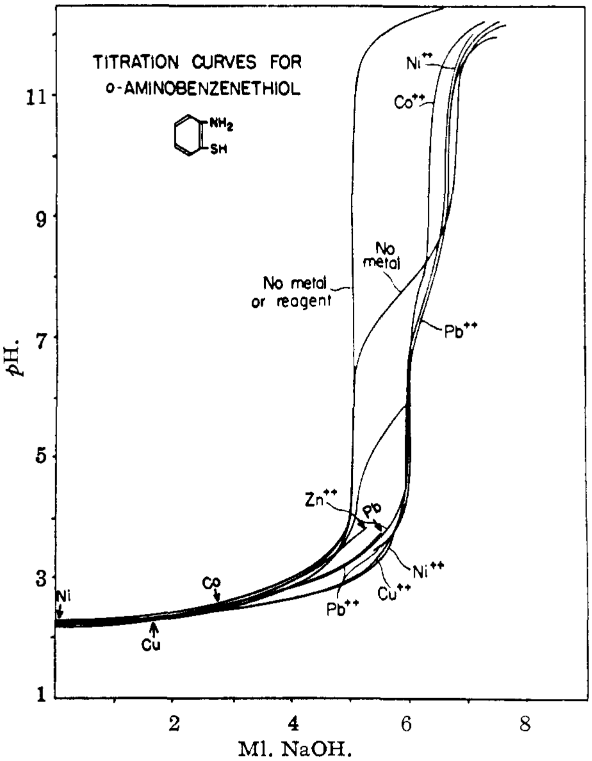

Fig. 1.—Arrow at point of appearance of ppt.

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(1) For paper I see THIS JOURNAL, **74**, 1383 (1952).

TABLE I

TITRATION OF SOLUTIONS OF METAL PERCHLORATES AND *o*-AMINOPHENOL OR *o*-AMINOBENZENETHIOL IN 50% DIOXANE–WATER SOLUTIONS WITH SODIUM HYDROXIDE (0.09312 M) AT 25°

NaOH, ml.	pH	$\bar{n}$[a]	pR[b]
Copper(II) 4.388×10^{-4} mole aminophenol (4-fold excess)			
50.0 ml. 0.009756 M $HClO_4$ 5.01 ml. 0.01057 M $Cu(ClO_4)_2$ 55.0 ml. dioxane			
5.00	4.75	0.41	9.33
5.10	4.81	.48	9.26
5.20	4.88	.55	9.19
5.30	4.93	.66	9 15
5.40	5.01	.74	9.07
5.50	5.09	.84	8.99
5.60	5.18	.94	8.90
Zinc(II) 9.998×10^{-3} mole aminophenol (10-fold excess)			
50.0 ml. 0.009756 M $HClO_4$ 5.01 ml. 0.009352 M $Zn(ClO_4)_2$ 55.0 ml. dioxane			
5.40	7.10	0.33	6.56
5.50	7.29	.53	6.37
5.60	7.41	.72	6.26
5.70	7.55	.92	6.12
5.80	7.68	1.12	6.00
5.90	7.80	1.31	5.88
6.00	7.94	1.51	5.75
6.10	8.19	1.71	5.50
6.20	8.83	1.88	4.87
Zinc(II) 9.164×10^{-3} mole aminophenol (100-fold excess)			
50.0 ml. 0.009656 M $HClO_4$ 5.01 ml. 0.009352 M $Zn(ClO_4)_2$ 55.0 ml. dioxane			
5.20	6.66	0.33	5.98
5.50	6.99	.78	5.70
5.70	7.30	1.11	5.39
5.90	7.69	1.46	5.00
6.00	7.96	1.62	4.73
Nickel(II) 9.164×10^{-3} mole aminophenol (100-fold excess)			
50.0 ml. 0.009656 M $HClO_4$ 5.01 ml. 0.009850 M $Ni(ClO_4)_2$ 55.0 ml. dioxane			
4.90	6.31	0.02	6.37
5.20	6.52	.41	6.17
5.50	6.86	.78	5.83
5.70	7.21	1.07	5.48
6.00	7.91	1.55	4.79
Cobalt(II) 9.164×10^{-3} mole aminophenol (100-fold excess)			
50.0 ml. 0.009656 M $HClO_4$ 5.01 ml. 0.009241 M $Co(ClO_4)_2$ 55.0 ml. dioxane			
5.00	6.52	0.03	6.17
5.20	6.72	.29	5.97
5.40	6.98	.59	5.71
5.60	7.30	.90	5.39
5.80	7.78	1.27	5.00
6.00	8.19	1.60	4.50
Lead(II) 9.164×10^{-3} mole aminophenol (100-fold excess)			
50.0 ml. 0.009656 M $HClO_4$ 5.01 ml. 0.009794 M $Pb(ClO_4)_2$ 55.0 ml. dioxane			
5.00	6.32	0.24	6.37
5.30	6.59	.55	6.10
5.40	6.71	.66	5.98
5.60	7.15	.90	5.54
5.90	8.21	1.31	4.48
Lead(II) 1.678×10^{-4} mole *o*-aminobenzenethiol			
50.0 ml. 0.01034 M $HClO_4$ 5.01 ml. 0.01013 M $Pb(ClO_4)_2$ 55.0 ml. dioxane			
4.30	3.00	0.82	7.87
4.50	3.08	.84	7.80
4.70	3.14	.99	7.77
4.90	3.25	1.02	7.66
5.10	3.38	1.08	7.55
5.30	3.52	1.22	7.44
5.50	3.80	1.28	7.17
Zinc(II) 1.678×10^{-4} mole *o*-aminobenzenethiol			
50.0 ml. 0.01034 M $HClO_4$ 5.01 ml. 0.009352 M $Zn(ClO_4)_2$ 55.0 ml. dioxane			
4.20	3.08	0.24	7.70
4.40	3.18	.25	7.60
4.60	3.30	.28	7.49
4.80	3.42	.42	7.39
5.00	3.58	.57	7.26
5.20	3.70	.84	7.17

[a] $\bar{n}$ is the average number of chelate molecules per metal ion. [b] pR is the negative logarithm of the reagent anion concentration

ACID DISSOCIATION CONSTANTS IN 50% DIOXANE AT 25°

	pK_{NH^+}	pK_{OH}
o-Aminophenol	3.75	11.57
o-Aminobenzenethiol	<2	7.90

TABLE II

CHELATE FORMATION CONSTANTS IN 50% DIOXANE AT 25°

	log K_1	log K_2	log K_{av}
o-Aminophenol (ten-fold excess)[a]			
Copper(II)	9.25	8.47	8.86
Lead(II)	7.18	5.38	6.28
Nickel(II)	6.62	4.79	5.70
Zinc(II)	6.39	5.77	6.08
Cobalt(II)	5.86	4.57	5.21
o-Aminophenol (hundred-fold excess)			
Lead(II)	6.29	4.05	5.17
Nickel(II)	6.10	4.87	5.57
Zinc(II)	5.99	4.96	5.48
Cobalt(II)	5.81	4.69	5.26
o-Aminobenzenethiol			
Lead(II)	8.41	6.96	7.69
Zinc(II)	7.33	6.77	7.05

[a] 4-fold excess used for copper(II).

possible to calculate formation constants for the aminobenzenethiolates of these two metals.

Reaction of *o*-Aminophenol with Metals.—Upon the addition of a 1% alcoholic *o*-aminophenol solution to solutions of the various metallic cations the following reactions were observed: with Cu(II) a green coloration, with Fe(III) a blood red color still perceptible at a concentration of 2×10^{-5} M Fe(III), with Hg(II), an amber color deepening with time (possible oxidation of the phenol), and with Ag(I) a silver mirror. When the solutions containing the *o*-aminophenol and the metallic cations were made alkaline with sodium hydroxide the following precipitation reactions were noted: greenish-gray with copper(II), reddish-orange with nickel(II), green with cobalt(II), dark red-brown with iron(III), gray with bismuth(III), gray-black with mercury-(II) (probably metallic mercury), white precipitates (indistinguishable from blanks) with aluminum(III), magnesium(II), zinc, manganese(II), lead(II) and cadmium(II). The alkaline earth ions and chromium(III) also gave tests similar to their blanks.

Reaction of *o*-Aminobenzenethiol with Metals.—The following metals in sodium acetate–acetic acid medium gave well-defined precipitation reactions with *o*-aminobenzenethiol: copper(II), greenish-yellow; nickel(II), green; cobalt(II), reddish-brown; bismuth(III), bright orange; zinc(II), white; mercury(II), yellowish-white; silver(I), yellowish-white; cadmium(II), white; iron(III), yellow. No reaction was observed under these conditions with aluminum(III), manganese(II), chromium(III), magnesium(II), or the alkaline earth ions. The bismuth salt was rather soluble in chloroform. The other precipitates formed were only slightly soluble in chloroform. *o*-Aminobenzenethiol may be a useful reagent for bismuth.

Discussion of Results

It is noteworthy that both zinc and lead, the only metals for which it was possible to determine *o*-aminobenzenethiol chelate formation constants, formed complexes which are significantly more stable than those with aminophenol. The fact that this latter reagent is both stronger as a base and weaker as an acid than the aminobenzenethiol would tend to increase chelate stability, according to Calvin.[2] This is a good indication of the possibility that the strength of the bond of metal with sulfur is greater than that with oxygen because of the lower electronegativity of the sulfur and consequent increase in covalent character of the bond. The chelates formed by *o*-aminophenol are more stable than those of the β-diketones and substituted salicylaldehydes.[2] The difference in chelate stability here may involve the questions of ring size (5 *vs.* 6-membered rings), the amount of unsaturation in the reactive groupings, and steric factors but, nevertheless, is what would be expected since the electronegativity of nitrogen is lower than that of oxygen.

The order of decreasing stability of the complexes of *o*-aminophenol with respect to K_{av} is (Cu, Ni), Zn, Co, Pb. This is in general agreement with the results reported for sodium 5-salicylaldehyde sulfonate[3] and for salicylaldehyde.[4] The most pronounced difference with respect to the latter is the position of lead which is relatively more stable with salicylaldehyde. It should be noted however that this is not the case when the two stability sequences with respect to K_1 are compared. Apparently there is some steric interference associated with the introduction of a second aminophenol anion about the lead atom. From the titration curves of Fig. 1, it is possible to approximate the stability order of the complexes of *o*-aminobenzenethiol. The order found is (Cu, Ni), Pb, Zn, Co with the position of Co not entirely certain. This order is again similar to that found for salicylaldehyde. It is significant that the titration curves obtained for the copper and nickel complexes of *o*-aminobenzenethiol are nearly identical, indicating that the two complexes may be of nearly the same stability. It is hoped that the measurement of the stabilities of chelates of reagents similar to the thiol, *e.g.*, 8-mercaptoquinoline, will reveal more concerning the order of metals found here.

Acknowledgment.—The authors are grateful for a research grant from the Atomic Energy Commission.

[2] M. Calvin and K. W. Wilson, THIS JOURNAL, **67**, 2003 (1945).

[3] M. Calvin and N. C. Melchior, *ibid.*, **70**, 3270 (1948).

[4] L. E. Maley and D. P. Mellor, *Australian J. Sci. Research*, **2**, 92 (1949).

PITTSBURGH 13, PENNA. RECEIVED AUGUST 21, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND PURDUE RESEARCH FOUNDATION, PURDUE UNIVERSITY]

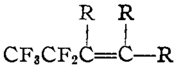
Alcohols and Olefins Containing the Pentafluoroethyl Group[1]

BY E. T. MCBEE, J. F. HIGGINS AND O. R. PIERCE

The reactions of pentafluoropropionaldehyde 3,3,4,4,4-pentafluoro-2-butanone and ethyl pentafluoropropionate with alkylmagnesium halides have been investigated as a means of preparing a series of pentafluoroethyl substituted ethylenes. Normal addition products were obtained as well as materials formed by the reduction of the aldehyde or ketone. Dehydration of the fluorinated alcohols produced was not accomplished with sulfuric acid, hot alumina or pyrolysis of the corresponding xanthate or acetate esters. However, phosphorus pentoxide was successfully employed.

Discussion

The preparation of a series of olefins containing the pentafluoroethyl group was undertaken because of interest in the effect of adjacent groups containing fluorine on the reactions of double bonds. It was planned to synthesize the six possible compounds of the type where R could be hydrogen or a methyl group.



$$CF_3CF_2\overset{R}{\overset{|}{C}}{=}\overset{R}{\overset{|}{C}}{-}R$$

The reaction of pentafluoropropionaldehyde[2] with methyl, ethyl and isopropyl Grignard reagents and subsequent hydrolysis was expected to yield alcohols which on dehydration would give three of the desired olefins. Although methylmagnesium iodide gave the expected addition product, 3,3,4,4,4-pentafluoro-2-butanol, in 85% yield, ethylmagnesium iodide gave only 34% of the addition product, 1,1,1,2,2-pentafluoro-3-pentanol and 55% of the reduction product, pentafluoropropanol. When pentafluoropropionaldehyde was added to isopropylmagnesium iodide only the reduction product,

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[1] This paper represents part of a thesis submitted by J. F. Higgins to the Graduate School, Purdue University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. This work was supported by the Westinghouse Electric Corporation.

[2] D. R. Husted and A. H. Albrecht, 118th Meeting of The American Chemical Society, Chicago, Illinois, September, 1950.