[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Reaction of Organic Anions with Basic Thorium Chloride Hydrosols. Reversal of Charge with Salts of the Hydroxy Acids and with Nitric Acid

BY ARTHUR W. THOMAS AND CHESTER B. KREMER

A previous investigation[1] dealing with the effect of neutral salt solutions upon thorium oxychloride hydrosols has established an order of reactivity for twelve anions in respect to their ability to displace hydroxo groups from the micellar complex, the increase in *p*H of the hydrosol upon addition of the salt solutions serving as a measure of this displacement. It was found that, as in the case of other "oxide" hydrosols, this action of different anions varied widely; citrate and oxalate being very potent, while chloride and nitrate had but slight effect. Since displacement of hydroxo groups from the complex may be considered to constitute chemical combination of the displacer with the central metallic atom, the reactivity of these anions should be determined by the number and position of combining groups present in each. For the purpose of investigating the influence of chain length and number of carboxyl groups, the potassium salts of the aliphatic monocarboxylic series from formate to valerate, inclusive, and the potassium salts of the aliphatic dicarboxylic series from oxalate to pimelate, inclusive, were studied.

Preparation of the Hydrosols.—The hydrosols used in this investigation were prepared either by the peptization of hydrous thorium dioxide with dilute hydrochloric acid (Sols D, E, F) or by the addition of ammonia to thorium chloride solutions until a permanent turbidity was produced (Sols A and B). All sols were dialyzed against distilled water for varying lengths of time. The micelles of the sols thus prepared were charged positively. These five hydrosols, of which A, B and F were turbid and D and E cloudy in appearance, are described in Table I.

TABLE I

COMPOSITION OF HYDROSOLS

Sol	Thorium, milliequiv. per liter	Chloride, milliequiv. per liter	Eq. Th/Eq. Cl	*p*H[a]
A	51.8	7.3	7	4.02
B	62.8	11.6	5	4.06
D	37.3	3.9	10	3.89
E	63.9	5.7	11	3.97
F	100.9	13.1	8	4.16

[a] *p*H values are those obtained immediately at the completion of dialysis.

Reactions with Salt Solutions.—By means of a technique previously described[1] the *p*H increasing effect of various salts was measured. The results with the potassium monocarboxylates for Sols A and D (typical of all) are given in Table II. It is seen that the difference in reactivity between these homologous anions is slight. This is as expected, since their combination in the complex is controlled by the same factor, *i. e.*, the single carboxyl group.

TABLE II

*p*H INCREASING EFFECT OF POTASSIUM MONOCARBOXYLATES UPON BASIC THORIUM CHLORIDE HYDROSOLS

Final concn. of salt (N)	Formate	Acetate	Propionate	Butyrate	Valerate
		Sol A			
0.0000	3.3	3.3	3.3	3.3	
.0025	3.9	4.4	4.5	4.4	
.0050	4.6	5.2	5.3	5.2	
.0100	5.3	5.6	5.6	5.6	
.0150	5.6	5.8	5.8	5.9	
.0250	5.9	5.9	6.0	6.0	
.0500	6.2	6.2	6.2	6.1	
		Sol D			
0.0000	3.9	3.9	3.9	3.9	3.9
.0025	5.2	5.6	5.6	5.5	5.6
.0050	5.7	6.0	6.1	6.0	6.1
.0075	5.9	6.2	6.2	6.1	6.3
.0150	6.3	6.5	6.4	6.3	6.5
.0250	6.4	6.6	6.5	6.4	6.5
.0500	6.6	6.8	6.6	6.4	6.5

The results with the potassium dicarboxylates are shown for Sol A (typical of all) in Fig. 1. Oxalate is the most reactive of the dicarboxylic anions tried. Malonate is easily seen to be somewhat more reactive than succinate; glutarate, adipate and pimelate are practically the same in reactivity and only slightly less active than succinate. It seems apparent that from glutarate upward in the homologous series the carboxyl groups are too far away to have any effect upon each other and these higher members act more like the monocarboxylates. It also follows from these results that the closer the carboxyl groups are to each other, in the lower members of this series, the more reactive they are as complex formers.

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(1) A. W. Thomas and C. B. Kremer, THIS JOURNAL, **57**, 1821 (1935).

Comparative Action of Isomeric Salts.—It follows from the experiments cited that anions containing the same number of combining groups in the same relative position (or separated sufficiently so as to be without effect upon one another) should exhibit essentially the same reactivity with basic thorium chloride hydrosols; but if the relative positions of the combining groups differ, then the reactivity differs and the one with the combining groups in closest proximity should be the more reactive. A study of the following isomeric salts offered an opportunity to test the above statement: (1) isomers in the monocarboxylic series—potassium butyrate and isobutyrate, potassium valerate and isovalerate; (2) optical isomers—the potassium salts of the inactive tartaric and malic acids and the salts of *d*-tartaric and *l*-malic acids; (3) *cis–trans* isomers—potassium maleinate and potassium fumarate.

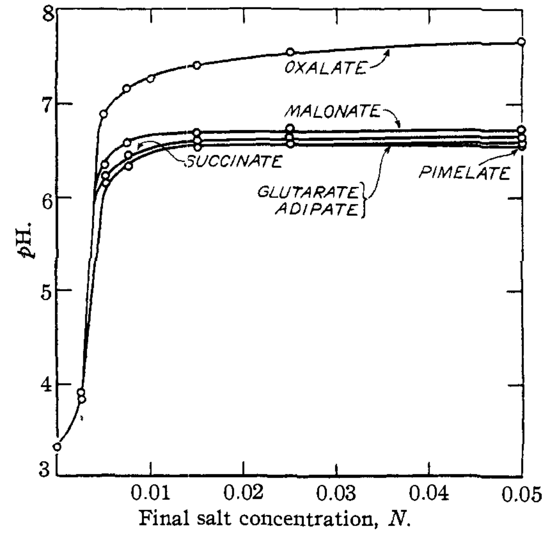

Fig. 1.—Effect of potassium salts of dicarboxylic acids upon the *p*H value of a basic thorium chloride hydrosol.

The ability of the monocarboxylic isomeric salts to raise the *p*H value of the sols was found to be identical throughout the concentrations used. The same was true for optical isomers. The fact that no measurable difference in effects between butyrate–isobutyrate and valerate–isovalerate existed, was not expected since the variation between each pair is restricted to that end of the molecule which does not enter into combination with the metal atoms of the micellar complex.

With the *cis–trans* isomers, however, potassium maleinate proved to be more effective than potassium fumarate. The results obtained with these two isomers upon two of the hydrosols (typical of all) are depicted in Fig. 2. It is interesting to note in this connection that in the crystalloidal chemistry of certain metals, the *cis* acid, citraconic, is a more active complex former than the *trans* acid, mesaconic.[2] Likewise, when the combining groups are hydroxylic rather than carboxylic, the *cis* diols are more active than the *trans* diols.[3]

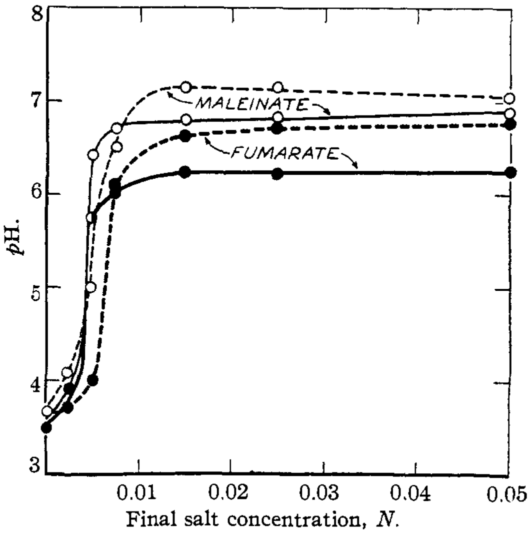

Fig. 2.—Effect of potassium maleinate and fumarate upon *p*H values of basic thorium chloride hydrosols: – – – –, Sol F; ————, Sol E.

Action of Hydroxy Organic Anions.—When certain salts, such as potassium citrate, tartrate, malate, glycolate, lactate and mucate were added to basic thorium chloride hydrosols, small amounts produced precipitation followed by redispersion upon further addition of the electrolyte. Electrophoresis experiments upon the redispersed solution showed that the charge on the micelles (originally positive) had become negative. Other organic anions, not containing hydroxy groups, did not cause charge reversal with the exception of malonate which showed a slight tendency at higher concentrations which may be explained by the existence of the enol form.

Since the potassium salts of hydroxy acids produced negatively charged micelles when added to basic thorium chloride sols, it was thought probable that negatively charged hydrosols could be produced by action upon hydrous thoria. Hy-

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(2) E. Ferrell, J. M. Ridgion and H. L. Riley, *J. Chem. Soc.*, 1440 (1934).

(3) J. Böeseken, *Bull. soc. chim.*, **53**, 1332 (1933).

drous thoria was prepared by precipitation from thorium chloride with ammonia and was washed free of chloride by distilled water with the aid of a centrifuge. Portions of the purified hydrate were then placed in 250-cc. "Non-Sol" bottles, 200 cc. of 0.1 *N* salt solution added and the mixture rotated at 7 r. p. m. at 25 ± 0.2° for forty-eight hours. At the end of that period the mixture was centrifuged (1200 r. p. m., 42 cm. radius) for one hour and the charge on the dispersed material determined in an electrophoresis "U" tube. The salts used, potassium, citrate, tartrate, glycolate, mucate and malate, all produced turbid dispersions containing negatively charged micelles.

Action of Concentrated Acids.—It was noted, upon the addition of 12 molar nitric acid to a thorium oxychloride sol, that the latter was first precipitated; then on further addition of the acid, the precipitate redispersed forming a solution as turbid as the original sol. When water was then added to this turbid solution, reprecipitation occurred and on adding a small excess of water, a solution resembling the original sol in turbidity, was produced. Addition of concentrated nitric acid again first produced a precipitate, then a turbid liquid; and water again reversed the procedure as described above.

The sol produced on addition of excess concentrated nitric acid existed at room temperature for only ten or fifteen minutes, when it changed to a clear crystalloidal solution. The sol produced by adding excess water to the acid sol was much more stable, dispersing to a clear solution after standing a few hours at room temperature. Electrophoresis experiments showed that the acid sol micelles were negatively charged; while the micelles of the sol obtained upon addition of excess water to the acid sol, were positively charged.

The following explanation is advanced for what has been described. Nitrate ion has but slight tendency to be coördinatively bound to the central atom. Increasing the concentration, however, will cause such a weak "penetrator" to enter the micelle, but it will only remain in the complex if a high concentration of nitrate ion be maintained. Thus when concentrated nitric acid is added to the sol, the increasing concentration of nitrate ion forces some of this anion into the micelle, replacing aquo groups mainly, while the hydrogen ion converts hydroxo groups in the complex to aquo groups. Replacement of water molecules by nitrate ions results in a diminution of charge on the cation, leading eventually to precipitation. Upon further addition of acid, continued penetration of the nitrate ion takes place and the charge on the micelle becomes negative. After this has happened, addition of water decreases the concentration of nitrate ion present. Nitrate ion therefore moves out of the complex and is replaced by water molecules. This continues upon further dilution and is accompanied by a decrease in negative charge on the micelle until once again the vicinity of zero charge is reached and precipitation occurs. Excess water causes further replacement of nitrate by water molecules and now the charge on the particles becomes positive and the precipitate redisperses.

While the above is happening, deolation is also occurring owing to the high hydrogen-ion activity of the solution. Continued deolation leads to the crystalloidal state. Stiasny[4] working with the crystalloidal chromium complexes, has pointed out that order of tenacity with which certain anions are held to the metal atom and the resulting deolating effect is $SO_4 > Cl > NO_3$. In the case of hydrous alumina[5] and with basic zirconium chloride hydrosols[6] it has also been shown that deolation occurs more readily when the aluminum oxide is treated with acids or the zirconium sol with salts containing strongly coördinative binding anions. The increased attraction of the metal atom for these anions apparently lessens the strength with which it holds the ol groups and deolation by acid is thereby facilitated. The metal atom in this case has little attraction for nitrate and therefore the ol bonds are considerably stronger than if chloride or sulfate were in the complex. It should therefore be expected, with acids of comparable strength as to hydrogen ion, that the order for deolation and subsequent formation of the crystalloidal state should be $H_2SO_4 > HCl > HNO_3$. That this is true for basic thorium sols has been demonstrated qualitatively. The deolating reaction described above with 12 *M* nitric acid, required from ten to fifteen minutes for completion.[7] When 12 molar hydrochloric acid was used, precipitation occurred and further addition of this acid caused redispersion as in the case of nitric acid but deolation to the crystalloidal state was much

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[4] E. Stiasny, "Gerbereichemie," Verlag Theodor Steinkopff, Dresden-Blasewitz, Germany, 1931, p. 351.

[5] A. W. Thomas and R. D. Vartanian, THIS JOURNAL, **57**, 4 (1935).

[6] A. W. Thomas and H. S. Owens, *ibid.*, **57**, 2131 (1935).

[7] There are individual differences in sols.

more rapid. Dilution with water tended to effect a partial reversal, but this procedure could not be repeated as in the case of nitric acid. When the acid used was 6 molar sulfuric, precipitation resulted, followed by rapid conversion to a clear crystalloidal solution on addition of more acid and no reversibility with water could be effected.

Summary

The reactivity of an organic anion with basic thorium chloride hydrosols depends not only on the number of combining groups present, but on their relative positions, and the closer the combining groups are to each other, the more active is the anion.

Hydroxy organic anions reverse the charge of basic thorium chloride (cationic) micelles producing aniono thoreate micelles. Peptization of hydrous thorium dioxide by the potassium salts of these anions also results in the production of hydrosols containing negatively charged micelles.

Concentrated nitric acid reverses the charge of basic thorium chloride micelles producing short-lived nitrato thoreate micelles.

The order of deolation of basic thorium chloride sols and subsequent formation of the crystalloidal state with concentrated inorganic acids has been found to be sulfuric > hydrochloric > nitric.

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A New Organic Reagent for Cadmium

BY ALFRED W. SCOTT AND ELEANOR G. ADAMS

Introduction

The lack of a specific easily recognizable test for cadmium ion in the presence of cupric ion has given rise to many difficulties, especially in elementary classes in qualitative analysis. Copper is usually converted into the cyanide complex or precipitated as the sulfide. The cyanide separation is dangerous for inexperienced students, and the cadmium sulfide precipitated by the second method is often masked by traces of impurities. This investigation was undertaken in an attempt to prepare a new organic reagent which would be specific for cadmium ion, characterized by a colored precipitate, sensitive to fairly low concentrations of the metallic ion and not too easily affected by interfering ions.

Several new organic compounds containing sulfur were prepared by combining organic radicals which are present in reagents that have been found useful in detecting cadmium ions. These were tested as analytical reagents with nitrate solutions of the cations met in qualitative analysis. The most effective precipitant prepared was 1-(2-quinolyl)-4-allyl thiosemicarbazide. A saturated solution of this reagent in 50% alcohol, in the presence of potassium iodide, gave a yellow precipitate with cadmium ion as dilute as one part in a million. Cadmium was detected in the presence of copper (in the absence of ammonia and sulfate) by the addition of potassium iodide solution, thiosemicarbazide solution, and ammonium hydroxide; cadmium gave a yellow precipitate, while copper gave a blue solution.

Experimental

Materials.—Allyl isothiocyanate, 2-aminoresorcinol hydrochloride (practical), 2-amino-4-nitrophenol, and 2-quinolylhydrazine, all were from Eastman Kodak Company.

$C_3H_5NHCSNHC_6H_3(OH)_2$, **N-Allyl-N′-2,6-dihydroxyphenyl thiourea,** was prepared from equimolar solutions of allyl isothiocyanate and 2-aminoresorcinol hydrochloride in 95% alcohol. The brown needles from alcohol–ether decomposed at 230°. This compound is too insoluble in water for use as a precipitant.

$C_3H_5NHCSNHC_6H_3(OH)(NO_2)$, **N-Allyl-N′-2-hydroxy-5-nitrophenyl thiourea,** was prepared from equimolar solutions of allyl isothiocyanate and 2-amino-4-nitrophenol in ether. The orange-red needles, melting at 122°, are soluble in alcohol, and somewhat soluble in water and in chloroform. The saturated water solution of this reagent added to nitrate solutions of the cations gave precipitates only with cadmium, copper, iron and nickel, the first three being yellow and the last white. The use of a 1% solution of the reagent in alcohol makes the precipitation of cadmium more complete and more sensitive, but care must be taken that excess reagent itself does not precipitate because of its slight solubility in water.

$C_3H_5NHCSNHNHC_9H_6N$, **1-(2-Quinolyl)-4-allyl-thiosemicarbazide,** was prepared from 10 cc. of allyl isothiocyanate and 16 g. of crystalline 2-quinolylhydrazine in ether; yield 20 g. Slow recrystallization from ether gave colorless crystals, melting at 158°, fairly soluble in ether