been emphasized in the literature. It is simple to associate m.p. alternation in the present compounds with the diffraction pattern alternation, specifically with long spacing alternation, *i.e.*, the vertical chains of odd acids and the tilted chains of even acids. But there remains the somewhat deeper question of what, in the geometry of the crystallized molecule, lies behind the differences in tilt (it being assumed that alternation is a phenomenon of the solid state in this case as in the case of homologous series).

In considering separately the cases for vertical and tilted chains, it appears to the authors that alternation is not predictable for vertical structures from what we now know, but that it is predictable for tilted structures. That is, a tilted structure for an individual even octadecenoic acid, presumably one of a series of similarly tilted structures, would be expected to show alternation with odd acid structures whether the latter were vertical (as in the present case), differently tilted or even very similarly tilted.

In Fig. 2a there is illustrated a possible alinement of vertical odd and even chains for a pair of alkenoic (*i.e.*, *trans*-octenoic) acids comparable to the *trans*-octadecenoic acids of this paper. There is a certain amount of lateral shifting of elements of the chains which is different in the two cases. This might give rise to measurable alternation, but it is conceivable that it would not, and it appears probable that any alternation would be small. In the different but nevertheless related case of homologous series, Malkin[9] has shown that the lateral shifting involving methyl groups is not associated with measurable alternation in properties associated with vertical structures.

In the absence of relevant experimental data, the case for alternation in vertical *trans*-octadecenoic structures cannot be settled. However, it appears possible to demonstrate a definite basis for alternation with tilted chains. In Fig. 2b it can be seen that the inter-relationship of double bonds, hence of CH groups, in the odd tilted structure is different from that in the even structure. Just this sort of geometric difference should give rise to stability differences, hence alternation of properties for odd and even compounds. It must be that the spacial configuration of tilted odd chains is somehow so unfavorable as to give way to a vertical structure.

The *trans*-octadecenoic forms show no great similarity to stearic acid forms. The perpendicular odd form has no counterpart among stearic forms[4] although in short spacing type it resembles the B and C forms of stearic in the prominence of 4.2 and 3.8 Å. spacings. The tilted even form shows some similarity to the A form of stearic in both short[10] and long spacings.

Acknowledgment.—The authors express their appreciation to those of this Laboratory who have contributed to the experimental work.

[9] T. Malkin, *Nature*, **127**, 126 (1931).

[10] E. S. Lutton, to be reported.

CINCINNATI 17, OHIO RECEIVED DECEMBER 15, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TASMANIA]

Urea–Formaldehyde Kinetic Studies. I. Variation in Urea Solutions

BY LLOYD E. SMYTHE

Previous work on urea–formaldehyde kinetic studies[1,3] indicated variations in the reaction rate and in *p*H upon blending solutions of urea and formaldehyde. This appeared to be connected with variations in the urea solutions and suggested a study of the stability of aqueous urea solutions with keeping and the effect of various urea solutions on the initial urea–formaldehyde reaction. It was found that solutions of urea at room temperature attain equilibrium with small amounts of ammonium carbonate and ammonium cyanate. While traces of such compounds do not affect the general nature of the reaction they have a retarding effect on reaction rate. Reaction rates are given for various urea solutions and the initial reaction is further examined in the light of experiments carried out in relation to the nature of urea and formaldehyde in aqueous solution. It is suggested that the initial bimolecular reaction is between that portion of the 8 M urea solution (40–50%) which exists in an activated form as an anion and that this reacts with the formaldehyde in the dehydrated form. The subsequent and slower bimolecular reaction then takes place as indicated previously[1] with the additional concept of dehydration of the remaining ethylene glycol.[2] Work carried out so far indicates that some 40–50% of urea in aqueous 8 M solutions exists as an anion available for rapid reaction.

A previous paper[1] gave kinetic data for the reaction between urea and formaldehyde in aqueous solution. While the observations presented in this paper have been subsequently confirmed and extended by Crowe and Lynch[2] and Bettelheim and Cedwall,[3] the latter authors pointed out that under their conditions changes of *p*H during the reaction are either constant or show little decrease for 1:1 mole ratios using 4.36 M solutions of urea and formaldehyde. This contrasted with the sudden drop in *p*H to 4.95 followed by a gradual rise to *p*H 6.5, upon mixing equal volumes of an 8 M urea solution (*p*H 8.66) with 8 M formaldehyde solution (*p*H 7.0).[1]

Bettelheim and Cedwall in their investigation of *p*H values immediately after blending, adjusted the solutions to the experimentally required conditions with 1 N sodium hydroxide or sulfuric acid and also by adding to the urea, small amounts of ammonia or ammonium salt. By the latter procedure, a lowering of *p*H after blending, to about 5 was obtained but as the reaction progressed the *p*H dropped further.

It seemed desirable, while carrying out a program of investigation of the kinetics of the formation of substituted diamides of carbonic acid, to study the

[1] Smythe, *J. Phys. Colloid Chem.*, **51**, 369 (1947).

[2] Crowe and Lynch, THIS JOURNAL, **70**, 3795 (1948); **71**, 3731 (1949); **72**, 3622 (1950).

[3] Bettelheim and Cedwall, *Svensk Kem. Tid.*, **60**, 208 (1948).

stability of aqueous urea solutions with keeping and the effect of various urea solutions on the initial urea–formaldehyde reaction. Such a study is presented here.

Experimental

Much of the apparatus, chemicals and general technique used in this study has been described.[1] The various grades of urea used were as follows: A, urea B.P. (May and Baker); B, urea (B.D.H. Laboratory Reagent); C, technical Urea (Beetle–Elliott); D, recrystallized urea (May and Baker B.P. urea recrystallized from alcohol; heavy metals, occluded ammonia, ammonium cyanate and ammonium carbonate absent). It was not found possible to purify the urea (D above) by recrystallization from water. Usual methods of purification[4,5] followed by a final recrystallization from absolute alcohol gave a satisfactory product.

The above grades of urea when dried at 105–110° for one hour and made into 8 *M* solutions with distilled water (*p*H 6.13) and freshly boiled and cooled distilled water (*p*H 6.92) gave the following initial *p*H values.

Grade	*p*H Ordinary	Boiled
A	10.67	10.23
B	10.95	10.59
C	9.77	9.52
D	7.15	7.25

These solutions all gave negative tests for carbonate (with barium hydroxide) and cyanate (with silver nitrate and copper sulfate–pyridine tests). By potentiometric titration with 0.05 *N* hydrochloric acid to *p*H 7.0, the alkalinity of solutions A, B and C calculated as free ammonia, corresponded to approximately 0.01% by volume. Solution D may be regarded as a pure solution of urea.

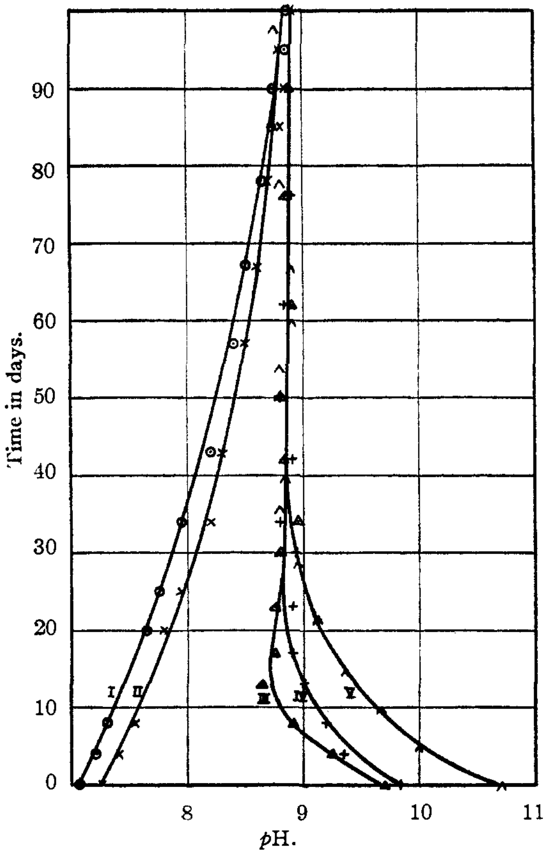

Fig. 1.—Change in *p*H of various urea solutions with time for five of eleven experiments carried out, all of which showed the same general trend. Curves IV and V have not been continued beyond 30–40 days owing to proximity of points for curves III, IV and V. In each case 100 ml. of 8 *M* urea solution was placed in a stoppered flask alone, or with 10 ml. of toluene in the case of sterile solutions. 8 *M* solutions: ⊙, D urea with toluene (I); ×, D urea alone (II); ▲, C urea with toluene (III); +, C urea alone (IV); Λ, A urea alone (V). Note: 100–200 days for all solutions *p*H 8.7–8.9.

The higher alkalinity of the laboratory grades of urea (A and B) as compared with the technical urea (C) may have been due to partial hydrolysis during the recrystallization process employed by the manufacturer.

Walker and Hambly[6] showed that urea solution when kept at 100° was converted to the extent of 5% into ammonium cyanate. Werner[7] has stated: "... (1) urea in neutral, in acid or in alkaline solution does not undergo reversion to ammonium cyanate until the temperature at which it commences to dissociate is reached; (2) urea in sterile solution (*e.g.*, saturated with toluene) when tested after several months remains neutral (to phenol red) and gives negative tests for carbonate and cyanate; (3) urea in plain distilled water will give after 14 days positive tests for carbonate and cyanate and at the end of six months the solution contains ammonium carbonate but no ammonium cyanate. This decomposition was unquestionably brought about through the agency of urease by microörganisms which had developed in the solution."

Evidence so far obtained, however, indicates that there is an equilibrium between urea, ammonium cyanate and ammonium carbonate after a certain period in aqueous solution at room temperature (av. 18.5°) in both sterile and ordinary solutions with which no special precautions had been taken. The percentage of ammonium cyanate and ammonium carbonate together appears to be approximately 0.03% or

$$\text{Urea } (99.97\%) \rightleftharpoons \underbrace{\text{amm. carbonate} + \text{amm. cyanate}}_{(0.03\%)}$$ [8]

It will be seen that both sterile and ordinary urea solutions prepared from urea not specially purified, attain equilibrium after approximately 30 days. In the case of specially purified urea solutions equilibrium is not attained until after approximately 90 days and cyanate and carbonate are not readily detected until 30 days. After periods 30 and 90 days, depending upon the solution concerned, the proportion of ammonium cyanate and ammonium carbonate is approximately 0.03% for all solutions. Slight fluctuations in *p*H (±0.2 *p*H) at the equilibrium condition were observed to be due to aeration upon removing the stoppers. The original samples are being retained under the same conditions and have so far shown no change after 220 days. It is probable that if the sterile solutions were left freely exposed to the atmosphere equilibrium would be maintained and the concentration of urea would gradually decrease by loss of ammonia. In the case of ordinary urea solutions freely exposed, urease would effect hydrolysis but the conditions (*p*H 8.8 and 18.5°) would not be optimum.

The course of the urea–formaldehyde reaction at temperatures of 20, 30 and 40° was next studied under the following conditions. I. Freshly prepared pure 8 *M* urea solution in ordinary distilled water; *p*H of solution 7.15. 8 *M* formaldehyde solution free from methanol[1] and adjusted to *p*H 7.0 ± 0.05. II. Pure 8 *M* urea solution (*p*H 8.85) which has been allowed to stand 90 days in a stoppered bottle. Formaldehyde solution as in I. III. Freshly prepared pure 8 *M* urea solution in ordinary distilled water with 0.02% added ammonium carbonate plus 0.01% added ammonium cyanate; *p*H solution 8.97. Formaldehyde solution as in I. IV. Freshly prepared 8 *M* urea (Beetle–Elliott Technical Grade) solution (*p*H 9.62) in ordinary distilled water. Formaldehyde solution as in I. The urea solution in this case contained no cyanate or carbonate but alkalinity to the extent of 0.03% ammonia.

Results are summarized in Table I. Experimental details and technique are detailed in a previous paper.[1]

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[4] Bub, U. S. Patent 1,659,190, Feb. 14, 1928.

[5] Divinski and Rodzevich, *Khim. Farm. Prom.*, **20**, No. 2 (1934).

[6] Walker and Hambly, *J. Chem. Soc.*, **67**, 748 (1895).

[7] Werner, "The Chemistry of Urea," Longmans Green and Co., New York. N. Y., 1923.

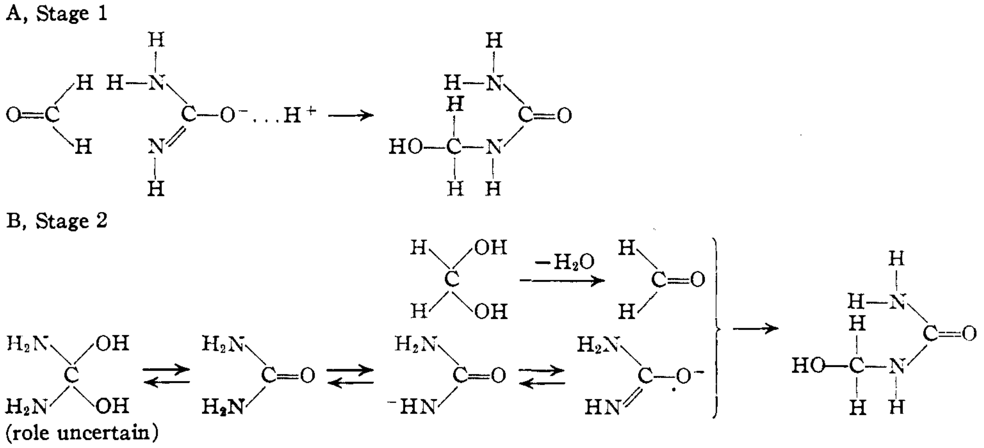
[8] Determination with Leeds and Northrup Model 7663 *p*H meter accuracy ±0.05 *p*H.

TABLE I

Temp., °C. ±0.1°)	Conditions	Initial pH 0 sec.	Final pH after ( ) sec.	CH_2O used 1st. 300 sec., %	$k \times 10^{-5}$ liter/gram mol./sec.[a]	Yield monomethylolurea after 8 hours, %
20	I	7.05	6.20(19,200)	40	5.0(19,200)	91
30	I	7.10	6.31(12,000)	43	10.5(12,000)	95
40	I	7.08	6.05(15,600)	45	21.6(15,600)	95
20	II	5.15	6.38(22,500)	36	2.6(15,600)	91
30	II	5.02	6.20(15,600)	39	5.4(15,600)	93
40	II	5.05	6.58(15,600)	41	11.2(15,600)	93
20	III	5.20	6.40(15,600)	39	2.8(15,600)	92
30	III	5.15	6.52(12,000)	41	5.8(12,000)	93
40	III	5.16	6.70(12,000)	46	12.1(12,000)	94
20	IV	5.65	6.70(15,600)	37	5.0(15,600)	91
30	IV	5.52	6.80(15,600)	39	10.4(15,600)	94
40	IV	5.60	6.90(12,000)	40	22.1(12,000)	94

[a] Disregarding 1st 300 sec., k equals average for no. of seconds in brackets minus 300.

An examination of the data in Table I reveals the following. (a) Experiments under conditions I and IV give similar values for k_1 thus showing that the alkalinity of the technical grade urea does not cause any divergence from reaction rate as compared with pure urea. (b) Experiments under conditions II and III give comparable values for k at the three temperatures but only approximately one-half of the values obtained for conditions I and IV. This is of interest in relation to the role of ammonium cyanate and ammonium carbonate. The presence of these compounds under the conditions studied retards the reaction rate, irrespective of the lower initial pH values. It is probable however that with other molecular ratios such as 1:2, the ammonium carbonate or ammonium cyanate in higher concentrations would lead to the formation of higher condensed systems in which the methylol ureas would be only transitory stages and not readily isolated in a pure state. It is now clear that the urea solutions used in previous experiments[1] and which were made up and allowed to stand before use, contained approximately 0.03% of ammonium carbonate and ammonium cyanate together. The presence of these compounds while influencing reaction rate does not affect the order of the reaction, the initial rapid reaction during the first 300 seconds, the almost exclusive yield of monomethylol urea and other general characteristics of the reaction such as energy of activation. (c) No evidence of the reversibility of the reaction was found. When formaldehyde is detected in small amounts in the reaction mixtures after 24 hours or more it results from the polymerization of monomethylol urea and the elimination of formaldehyde resulting in the formation of polymeric substances. This apparently does not hold for very dilute solutions.[2]


A, Stage 1

B, Stage 2

As in previous experiments[1] it was not found possible to follow the reaction during the first 300 seconds and in this connection figures for the percentage of formaldehyde used during this period are of interest. The value of 36–46% for temperatures of 20–40° is also supported by previous experiments.[1] This is in marked contrast to values calculated from the data of Bettelheim and Cedwall.[3] They found that for 4.36 M solutions in 1:1 mole ratio at 40° between 16–19.3% of formaldehyde was used in the first 500 seconds. By extrapolation of values in their graph, this approximates to 12–15% of available formaldehyde used in the first 300 seconds. Present work[9] indicates that 36–50% of the formaldehyde is utilized in the first 300 seconds and the discrepancy must remain unclarified for the time being.

The almost instantaneous utilization of formaldehyde is interesting in the light of current theories regarding the behavior of urea and formaldehyde in aqueous solution. Blair[10] has suggested that in aqueous solution hydrated forms of urea may exist. Similarly work has shown that formaldehyde exists in the methylene glycol form in aqueous solution[11] to the extent of approximately 98% for molar solutions and 49% for 8 M solutions at 20°. With dilute solutions the rate of reaction between urea and formaldehyde[2] has been shown to be dependent both upon the rate of dehydration of formaldehyde and rate of anion formation of urea.[1,2] From available evidence it does not appear that hydration of urea plays an important role at concentrations of 0.003–8 M.[1,2,3]

Under the conditions studied the initial reaction (Stage I) could be explained if approximately

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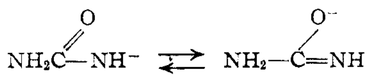
[9] Other details (including those for higher temperatures) will be given in Part II of these studies.

[10] Blair, THIS JOURNAL, 48, 87 (1926).

[11] Walker, "Formaldehyde," A. C. S. Monograph 98 (1944).

40–50% of the urea in 8 *M* urea solutions existed in an activated form as the anion



and that this reacts rapidly with the formaldehyde *not* in the methylene glycol form. The subsequent slow bimolecular reaction (Stage 2) then takes place as indicated previously[1] with the additional concept of dehydration of the remaining methylene glycol as after Crowe and Lynch.[2]

HOBART, TASMANIA, AUSTRALIA RECEIVED OCTOBER 4, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Thermodynamics of Fluorine–Chlorine Exchange Reactions. The Systems NaF–$NaCl$, BaF_2–$BaCl_2$, NiF_2–$NiCl_2$ and $PbClF$–$PbCl_2$[1]

BY GEORGE C. HOOD AND MARK M. WOYSKI

This investigation was undertaken to study the thermodynamics of reactions of the type: $HF(g) + MCl(s) \rightleftarrows HCl(g) + MF(s)$. The information was desired in order to evaluate the thermodynamic fluorinating ability of several metal fluorides and to obtain data which may give reliable values for the free energies of formation of these metal fluorides.

The thermodynamic fluorinating abilities of NaF, BaF_2, NiF_2 and $PbClF$ were determined by a dynamic equilibrium method. These data along with information available in the literature were employed to set up a thermochemical scale of reactivity for certain halogen exchange reactions. It was determined that the fluorination of lead chloride by anhydrous hydrogen fluoride yields lead chlorofluoride as a product rather than lead fluoride. An approximate value for the heat of formation of lead chlorofluoride was obtained.

Experimental

Equilibria in reactions $HF(g) + MCl(s) = HCl(g) + MF(s)$ were determined by a dynamic method. Anhydrous hydrogen fluoride diluted with nitrogen was passed over the solid metal chloride kept at a constant temperature and the composition of the effluent gas mixture determined. The equilibria were approached from the other direction by passing anhydrous hydrogen chloride over the metal fluorides. X-Ray procedures were employed to determine whether solid solutions formed and to check on the crystalline state of the solid substances.

Preparation and Purity of the Materials. Hydrogen Fluoride.—Harshaw Chemical Co., anhydrous, hydrogen fluoride was used without special purification. Part of the contents of a six pound cylinder were allowed to escape in order to reduce the concentration of volatile impurities.

Hydrogen Chloride.—Harshaw Chemical Co. anhydrous hydrogen chloride was used without special purification except for the removal of condensable material in a trap cooled in a Dry Ice–acetone-bath.

Nitrogen.—Commercial nitrogen was used directly from the cylinder. The condensable impurities were removed by passage through a trap cooled by liquid air.

Sodium Chloride.—Mallinckrodt analytical reagent sodium chloride was recrystallized once from water in a porcelain dish and then dried at 600° for six hours. A gravimetric analysis for chloride ion by the precipitation of silver chloride gave 60.69 ± 0.04% chloride (theoretical 60.66%).

Barium Chloride.—Anhydrous barium chloride was prepared for use by recrystallizing Merck reagent grade material twice from water in a porcelain dish and drying at 600° for eight hours in a stream of anhydrous hydrogen chloride. Analysis for chloride ion showed 34.06 ± 0.04% chloride (theoretical 34.09%).

Nickel Chloride.—Merck reagent grade nickel chloride was recrystallized from a mixture of hydrochloric acid and water. It was dried at 300° in an atmosphere of anhydrous hydrogen chloride. The salt was then sublimed in a Vycor tube in a stream of anhydrous hydrogen chloride. Analysis for chloride ion showed 54.38 ± 0.04% chloride (theoretical 54.72%).

Lead Chloride.—Mallinckrodt analytical reagent material was recrystallized from a mixture of hydrochloric acid and water in a porcelain dish. It was dried at 400° for six hours. Analysis for chloride ion gave 25.62 ± 0.04% chloride (theoretical 25.49%).

Sodium Fluoride.—Two different samples of sodium fluoride were prepared in different ways in order to determine whether or not the previous history of the sample had any appreciable effect on the measurable equilibrium constant.

Sample A was prepared by recrystallizing Merck reagent grade sodium fluoride twice from water in a platinum dish. The sample was dried at 550° for 12 hours.

Sample B was prepared by decomposing solvated sodium fluoride ($NaF\cdot xHF$) which was produced from Sample A.

Analyses for the fluoride ion by the precipitation of lead chlorofluoride showed for sample A 45.20 ± 0.2% fluoride, and for sample B 45.21 ± 0.2% fluoride (theoretical 45.24%).

Barium Fluoride.—Two different samples of barium fluoride were also prepared. Sample A was prepared by the action of aqueous hydrofluoric acid on barium chloride in a platinum dish. The sample was dried at 600° for six hours. Sample B was prepared by treating anhydrous barium chloride with anhydrous hydrogen fluoride at various temperatures over 250° in a silver tube. Analyses for fluoride ion showed for sample A 21.70 ± 0.2% fluoride and for sample B 21.75 ± 0.2% fluoride (theoretical 21.67%).

Nickel Fluoride.—This material was prepared by the action of anhydrous hydrogen fluoride on anhydrous nickel chloride prepared as previously indicated. The reaction was carried out at various temperatures between 100 and 500° in a fine silver tube. The reaction was not complete and there was some nickel chloride in the sample.

Lead Fluoride.—This salt was prepared by treating Mallinckrodt N.F. VII lead monoxide with aqueous hydrofluoric acid in a platinum dish. The lead fluoride was dried at 550° for six hours. Analysis for fluoride ion showed 15.09 ± 0.2% fluoride (theoretical 15.49%).

Lead Chlorofluoride.—The compound was prepared according to the procedure of Starck.[2] It was dried at 350° for five hours. Gravimetric analysis for chloride ion yielded 13.61 ± 0.04% chloride (theoretical 13.55%).

Apparatus.—The apparatus consisted of two main systems, one for passing hydrogen fluoride through metal chlorides and the other for passing hydrogen chloride through metal fluorides.

To control the rate of flow of hydrogen fluoride a steady stream of nitrogen was saturated with hydrogen fluoride vapor at 0°. The rate of flow of nitrogen was varied by adjusting the pressure across a capillary tube, by means of a bubbler attached at the input side of the flow meter. The retaining fluid was dibutyl phthalate. The nitrogen was dried by passage through a glass wool filter immersed in liquid air and was then bubbled through liquid hydrogen

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[1] From the Ph.D. Dissertation of George C. Hood.

[2] G. Starck, *Z. anorg. allgem. chem.*, **70**, 173 (1911); *C. A.* **5**, 2049 (1911).