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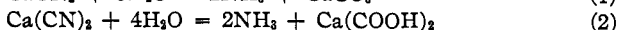
CALCIUM OXALATE FROM CALCIUM CYANAMIDE

BY GEORGE BARSKY AND G. H. BUCHANAN

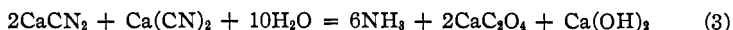
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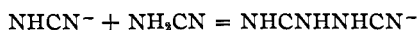
The hydrolysis of calcium cyanamide to ammonia and calcium carbonate is a well-known industrial chemical reaction. The hydrolysis of alkali and alkaline earth cyanides to ammonia and salts of formic acid is also familiar. The reactions, expressed in their simplest form, are shown in the equations



The present paper describes a new reaction, namely, that when a mixture of cyanamide and cyanide is subjected to alkaline hydrolysis there is formed in addition to carbonate and formate, a substantial amount of oxalate, the reaction being expressed by the equation



In a previous communication¹ the present authors discussed the reaction in which cyanamide is converted to dicyandiamide. It was there shown that, confirming the conclusions² of Grube and Krüger,² this polymerization is a reaction between cyanamide ions and cyanamide molecules and that, consequently, the rate of the reaction is a function of the hydrogen-ion concentration. It was shown that theoretical considerations require that this rate be at a maximum at P_{H} 9.6, and this calculated value for the optimum hydrogen-ion concentration was confirmed by experiment. The dicyandiamide-forming reaction is represented by the equation



Turning to the behavior of the second component of the reaction mixture, namely, hydrocyanic acid, we have another compound whose polymerization is known to be influenced by hydrogen-ion concentration. Although no quantitative data on the subject are available, it is known that solutions of hydrocyanic acid which have been slightly acidified are stable almost indefinitely. Solutions made strongly alkaline, *i. e.*, solutions of sodium cyanide containing no free hydrogen cyanide, are also stable. On the other hand, solutions of hydrocyanic acid made faintly alkaline polymerize rapidly, depositing brown flocks of the so-called azulmic compounds. We have at present under way an investigation of the polymerization of hydrocyanic acid in aqueous solution which is expected to show that this polymerization, like the polymerization of cyanamide, is also essentially a reaction between ion and molecule.

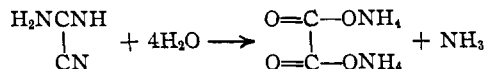
¹ Buchanan and Barsky, *THIS JOURNAL*, 52, 195 (1930).

² Grube and Krüger, *Z. physik. Chem.*, 85, 65 (1913).

That a reaction of the same type takes place between cyanamide and cyanide is shown in the present paper. This reaction may perhaps be represented by the equation



This hypothetical intermediate was not isolated; it hydrolyzes readily to form ammonium oxalate according to the equation



The existence of the intermediate is shown by the fact that mixtures of cyanamide and cyanide allowed to react at 50° in the absence of lime salts must be boiled with hydrochloric acid before precipitating the oxalate if concordant results are to be obtained. When the boiling is omitted, irregular, low results are obtained.

The reaction described may be considered to be a sort of mixed polymerization. Just as cyanamide, given the proper conditions of hydrogen-ion concentration, reacts with itself to give dicyandiamide, and hydrocyanic acid reacts to give the brown azulmic bodies, so can cyanamide and hydrocyanic acid react with each other, this reaction also being influenced by the hydrogen-ion concentration of the solution in which it takes place.

Experimental Part

During the course of experimental work on the autoclaving of the crude calcium cyanide made by fusion of crude calcium cyanamide and salt, it was observed that, in addition to calcium formate, traces of calcium oxalate were always produced. When pure cyanides were autoclaved, no oxalate was obtained. During the attempt to run down the source of this oxalate it was recalled that the crude calcium cyanide contained small amounts of cyanamide; it was then discovered that the autoclaving of mixtures of calcium cyanide and calcium cyanamide greatly increased the production of oxalate. No oxalate is produced when calcium cyanamide is autoclaved alone.

TABLE I
RESULTS OF EXPERIMENTS

Mixture, run no.		Weight used in grams	Grams Ca(COOH) ₂ ·H ₂ O in cake
1	Crude calcium cyanide	25.0	0.025
2	Calcium cyanamide	31.5	None
3	Crude calcium cyanide	25.0	9.12
	Calcium cyanamide	31.5	
4	Crude calcium cyanide	25.0	3.91
	Dicyandiamide	10.4	
5	Sodium cyanide (97%)	12.6	3.66
	Dicyandiamide	10.4	

In the first experiments the solids were stirred up in 150 g. of water and the mixture was autoclaved for two hours at 75 pounds' steam pressure. The mixture was then filtered and the cakes analyzed for oxalate.

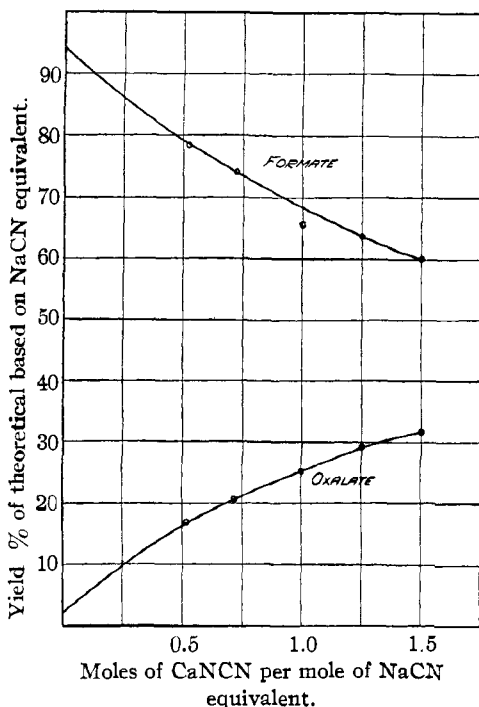


Fig. 1.—Effect of mole ratio on yield.

and the yields of oxalate from cyanide are calculated on the assumption of reaction according to Equation 3. The data are also shown graphically in Fig. 1.

The crude calcium cyanide used contained approximately 48.5% $\text{Ca}(\text{CN})_2$; the calcium cyanamide, 59.6% CaCN_2 .

The total yield of oxalate and formate is less than 100% in all cases,

TABLE II

EXPERIMENTAL DATA

Crude $\text{Ca}(\text{CN})_2$, g.	Calcium cyanamide, g.	H_2O , cc.	Molar ratio $\text{CaNCN}/\text{NaCN}^a$	$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ formed		$\text{Ca}(\text{COOH})_2$ formed		Yield, total, %
				G.	Yield on NaCN, %	G.	Yield on NaCN, %	
25.0	15.8	150	0.52	6.08	16.8	12.7	78.5	95.3
25.0	23.6	150	0.72	7.41	20.5	12.0	74.2	94.7
25.0	31.5	150	1.00	9.12	25.0	11.5	65.6	90.6
25.0	39.4	150	1.25	10.55	29.2	10.3	63.7	92.9
25.0	47.3	150	1.48	11.33	31.3	9.7	60.1	91.4

^a For convenience we use % NaCN equivalent instead of % $\text{Ca}(\text{CN})_2$.

In the case of mixture No. 5 where no lime was present, calcium chloride was added to precipitate the oxalate.

It is seen that dicyandiamide as well as cyanamide yields oxalate when autoclaved with a cyanide.

Continuing the experiments with crude calcium cyanide and calcium cyanamide, various mixtures of the reactants were autoclaved. The experimental procedure consisted in mixing the solids with water and autoclaving for two hours at 75 pounds' steam pressure. Upon removal from the autoclave the mixtures were filtered and calcium oxalate was determined in the filter cakes.

The results are given in Table II, where the amounts of oxalate found are reported

partly if not entirely because of loss of hydrocyanic acid by volatilization and by azulmic formation. The oxalate yield cannot be accounted for if we assume it is derived from cyanide alone or from formate alone. The increasing yield of oxalate with increasing amounts of cyanamide added is additional proof that cyanamide takes part in the reaction.

Effect of Hydrogen-Ion Concentration.—The data show that the oxalate yield based on cyanide increases as the amount of calcium cyanamide used is increased. The reasons for this are apparent if the previous work on the polymerization of cyanamide is recalled. The P_H of a filtered solution of the reaction mixture is 9.8, which is very near the optimum P_H for dicyandiamide formation. In other words, we are dealing with competing reactions, one involving dicyandiamide formation and the other the formation of the complex which eventually decomposes to form oxalate. The experiments given in Table I show that the oxalate yields from cyanide and dicyandiamide are low.

This suggested that the reaction be conducted at a P_H less favorable to dicyandiamide formation and led to an attempt to investigate the effect of hydrogen-ion concentration upon the oxalate forming reaction by following its course in buffered solutions. The technique of these experiments was the same as that employed in our study of the polymerization of cyanamide.¹

The study proved very difficult, particularly in solutions of lower alkalinity than P_H 9. The solutions discolored badly due to azulmic formation and there were large losses of hydrocyanic acid by vaporization. The data obtained are therefore only approximate and are presented with this qualification. The results are shown in Fig. 2. The curve for dicyandiamide is taken from our work on cyanamide.¹ The heavy portions of the oxalate curve represent our best experimental data; the broken portions present the less accurate values.

It is apparent from these data that little can be done toward increasing

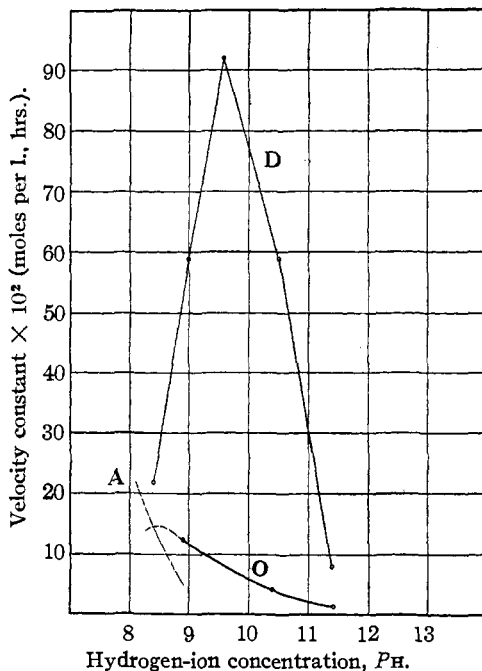


Fig. 2.—Effect of hydrogen-ion concentration. A, azulmic; D, dicyandiamide; O, oxalate; temp., 50° C.

the yield by conducting the experiments at higher or at lower P_H 's than the normal P_H of the reaction mixtures. At higher P_H 's cyanide is stable but dicyandiamide formation is rapid. At lower P_H 's cyanide is lost by azulmic formation. At P_H 's at which oxalate formation is most rapid it is accompanied both by dicyandiamide formation and by azulmic decomposition. The reason is, of course, that the ionization constants of hydrocyanic acid and of cyanamide are so nearly alike that it is impossible to have cyanide ions in the presence of cyanamide molecules without having hydrocyanic acid molecules and cyanamide ions present as well.

That reduction of the P_H is right in theory was also shown by a few experiments in which calcium chloride was added to the reaction mixture. The purpose was to reduce the P_H to a more favorable value by reducing the solubility of calcium hydroxide to which the alkalinity of the solution is due. The results are given in Table III.

TABLE III

25 g. of crude calcium cyanide; 31.5 g. of calcium cyanamide; 150 cc. of water; 2 hours at 75 pounds' pressure

Mixture a	CaCl ₂ in mixture, g.	Dry cake, g.	Calcium oxalate		
			% in cake	G.	Yield calcium on NaCN, %
	0	25.0
1	11.7	48.24	21.33	10.3	28.5
2	35.0	55.13	21.78	12.0	33.1

^a From Table II.

The practical significance of this moderate increase of oxalate yield by the addition of calcium salts is derived from the fact that the solutions obtained by the autoclaving of mixtures of cyanamide and cyanide contain large amounts of formate which is formed from that part of the cyanide which does not react with cyanamide. The return of this solution to a succeeding autoclave charge is practical and was adopted as regular procedure.

Stage Addition of Cyanamide.—The results of some preliminary experiments indicated that small concentrations of cyanamide were more effectively employed in the reaction with cyanide, presumably because less of other products were formed from the cyanamide. That is, the reaction of cyanamide to form dicyandiamide is accelerated by increased concentration to a greater extent than is the formation of oxalate. By keeping the concentration of cyanamide low, that is, by continuous addition of calcium cyanamide, we should expect a higher oxalate yield from a given amount of cyanamide than if the cyanamide were all added at once. This method of adding the cyanamide was followed in experiments described below.

Mixtures were digested for six hours at 60 and 80° in a constant temperature bath. The mixtures were stirred continuously during the digestion. Four samples were run at each temperature.

Twenty-five grams of crude calcium cyanide was added in each case to 150 cc. of water heated to the temperature at which the digestion was to be carried out. They were then placed in the water-bath and the stirrers started. To one pair of the mixtures 31.5 g. of calcium cyanamide was added immediately. To the second pair the 31.5 g. of calcium cyanamide was added in twelve equal portions at half-hour intervals.

At the end of six hours' digestion, one of each pair of mixtures was analyzed directly. The two remaining samples were autoclaved for two hours at 75 pounds' pressure.

During the preliminary digestion some cyanide was lost due to volatilization of hydrogen cyanide formed by hydrolysis.

TABLE IV

25.0 g. of crude calcium cyanide; 31.5 g. of calcium cyanamide; 150.0 cc. of water

Time, hours	Temp., °C.	Digestion		Subsequent to six hours' digestion	Cake, g.	% in cake	Calcium oxalate	
		Time	Addition of calcium cyanamide				Grams total	% yield on NaCN
6	60	All at start		Not autoclaved	45.04	13.16	5.92	16.3
6	60	Continuous ^a		Not autoclaved	42.99	14.56	6.25	17.3
6	60	All at start		Autoclaved	46.45	18.42	8.57	23.7
6	60	Continuous		Autoclaved	49.40	20.67	10.22	26.3
6	70	All at start		Not autoclaved	46.50	13.50	6.28	17.4
6	70	Continuous		Not autoclaved	44.86	17.88	8.01	22.2
6	70	All at start		Autoclaved	47.07	19.90	9.36	25.9
6	70	Continuous		Autoclaved	46.80	24.26	11.38	31.4
6	80	All at start		Not autoclaved	44.23	16.20	7.29	20.1
6	80	Continuous		Not autoclaved	46.19	22.30	10.30	29.2
6	80	All at start		Autoclaved	47.53	19.46	9.25	26.3
6	80	Continuous		Autoclaved	48.04	24.12	11.80	32.9

^a The continuous addition of cyanamide refers to the addition of small portions of calcium cyanamide at half-hour intervals.

Application.—Although the percentage yield of oxalate from cyanide by this process is low, it does not follow that the process is without commercial value. Where cyanamide is being autoclaved for ammonia production the addition to the autoclave of small amounts of cyanide, itself produced from cyanamide in a previous operation, is not impractical. All of the nitrogen of both compounds is liberated as ammonia and recovered, and a part of the carbon of both compounds is converted into valuable by-products. The autoclave solids ordinarily thrown away may be treated by a comparatively simple process and the valuable calcium oxalate separated from the excess of calcium carbonate with which it is associated. Return of the autoclave solution to a subsequent operation provides the excess of soluble calcium salts which has been shown to have a favorable influence on the reaction.

The process above described is protected by U. S. Patent No. 1,717,353, assigned to the American Cyanamid Company. The thanks of the authors

are due to this company for permission to publish these results, and to Mr. K. D. Ashley for his cooperation in the work.

Summary

A reaction not previously reported has been found to take place between cyanamide and cyanide, resulting in the formation of an intermediate compound which can be hydrolyzed to oxalate. The velocity of this reaction is dependent on hydrogen-ion concentration.

Autoclaving calcium cyanide and calcium cyanamide with water produces calcium carbonate, calcium oxalate and a solution of calcium formate. Replacing the water with calcium formate solution results in increased yields of oxalate.

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ZIRCONIUM. II. ZIRCONIUM OXALATE AND DIPHENYLDINITROGEN ZIRCONIUM

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Zirconium Oxalate

The fact that an insoluble precipitate was obtained upon the addition of oxalic acid or ammonium oxalate to solutions of zirconyl salts has been known since 1820. Since that time a number of investigations have been made concerning various compounds containing zirconium and the oxalate group, but so far as can be determined there seems to have been no success when efforts were made to obtain the normal zirconium oxalate $Zr(C_2O_4)_2$. The marked success with which the author has prepared other normal zirconium compounds in methyl alcoholic solutions suggested that the oxalate might be prepared in a similar manner.

A methyl alcoholic solution of zirconium tetrachloride was treated with a methyl alcoholic solution of oxalic acid. A reaction took place at once with the formation of a white gelatinous precipitate. This was filtered off, washed, dried and analyzed.

Anal. Calcd. for $Zr(C_2O_4)_2$: Zr, 34.80. Found: Zr, 35.08.

The two figures are close enough together to establish the identity of the compound.

The effects of a number of common solvents were observed. They are given below in table form. It is worthy of note that the normal zirconium oxalate is quite soluble in water, quite contrary to what might be expected from the literature, since the basic salts investigated by other workers are noted for their insolubility.