LXIV.—*On the Action of Hexabromacetone on Urea.*

By ALFRED SENIER.

SEVERAL years ago, by acting on urea with hexabromacetone, Herzig (*Ber.*, **12**, 170) obtained two acids which he named respectively α - and β -cyanuric acid. In many respects both these compounds behave like ordinary cyanuric acid, but certain differences were observed which it was thought indicated that they were distinct isomeric substances.

The attention of chemists has recently been directed to the question of the constitution of ordinary cyanuric acid, as to whether it is to be regarded as iso or normal, and it seemed at least possible that a

further study of Herzig's acids might furnish the desired standpoint from which to elucidate this problem. With this end in view, I repeated Herzig's experiments, and obtained what seemed to be two cyanuric acids in the manner he has described. When a mixture of urea and hexabromacetone is heated to a temperature above 150°, bromoform and bromide of ammonium are formed, and when the mixture is heated further to 160° or to 170—180° it then yields to water in the one case the β -, and in the other the α -cyanuric acid.

During the preparation of these acids, however, I was led to doubt whether they really differed from ordinary cyanuric acid. There is no very notable dissimilarity between the method employed by Herzig and that by which the ordinary acid is prepared. All three acids are formed by the action of heat on urea. The temperature, too, which Wöhler observed as that corresponding to the conversion of urea itself into ordinary cyanuric acid, 150—170°, includes the temperatures made use of by Herzig.

It is well known that if chlorine is used as suggested by Würtz (*Annalen*, **64**, 307), or hydrochloric acid as employed by De Vrij (*Annalen*, **61**, 248), the ammonia is removed more readily, being eliminated in the one case as nitrogen and hydrogen chloride, and in the other as ammonium chloride. In Herzig's experiment, hexabromacetone seems to act in an analogous manner to these reagents, and to remove the ammonia as tribromacetamide according to a reaction observed by Weidel and Gruber (*Ber.*, **10**, 1145), thus—

No doubt it may be conceived that the hexabromacetone acts in another way, forming bromoform and cyanuric acid, thus—

but of this there is no experimental evidence, and even if it is the fact, the resulting acid would be the ordinary cyanuric acid.

Let us now see whether a careful comparison of the properties said to distinguish Herzig's acid with the corresponding properties of ordinary cyanuric acid, causes the doubt which already arises to disappear, or whether as we proceed it becomes more and more defined and rises to certainty.

The properties of the α -acid on which Herzig chiefly relies as differentiating it from ordinary cyanuric acid are :—I. The solubility in alcohol. II. The amount of water of crystallisation. III. The composition of some of its salts.

I. *Solubility in Alcohol.*

Herzig finds the solubility of ordinary cyanuric acid in 100 parts of alcohol at 22° to be 0·349 part, and that of his α -acid to be 0·556 part. In other words, the α -acid is about one and a-half times as soluble as ordinary cyanuric acid. It is remarkable that, notwithstanding this small difference, only a single determination should have been made. My experiments with ordinary cyanuric acid leave little room for doubt that its solubility in alcohol is influenced considerably by small variations in the experimental conditions.

Six determinations made at temperatures very close to that of Herzig's experiment, give me the following numbers which are seen to exhibit considerable differences:—

I.	II.	III.	IV.	V.	VI.	Mean.
0·088	0·095	0·090	0·090	0·100	0·110	0·095

These results were obtained by allowing hot solutions to cool and then remain with occasional agitation for one or two days. They indicate, on the whole, that the solubility of cyanuric acid in alcohol is less than one-third of that found by Herzig; but the numbers are not as concordant as is usual in such estimations. This is explained by the tendency to form supersaturated solutions in alcohol, which, as will be seen from the next experiments, is clearly characteristic of cyanuric acid. Hot saturated solutions were prepared, and the amount of acid held in solution was determined from time to time. At 22–23° 100 grams of alcohol retained in solution—

	Experiment I. gram.		Experiment I gram.
After two hours....	0·192	After one day....	0·122
After two days....	0·074	After two days ..	0·082
		After three days..	0·090
		After four days..	0·075

It is seen that on standing the solution contains less and less cyanuric acid. If we take the mean of these numbers, the solubility of cyanuric acid in 100 parts of alcohol is 0·106 part. This is, however, a somewhat higher figure than that resulting from the previous determinations (0·095). As the mean of the whole 12 experiments the solubility of cyanuric acid in 100 parts of alcohol at 21–24° is 0·100 part, whilst from one experiment Herzig concludes that its solubility is 0·349 part. Herzig thus finds the solubility to be more than three times as great as my experiments indicate. If the relation of my mean result for ordinary cyanuric acid to Herzig's number, on

the one hand, be compared with that of the numbers found by Herzig for the ordinary, and the α -acids on the other, thus—

$$0.100 : 0.349 \text{ and } 0.349 : 556,$$

then it is evident that the ratio of difference between two observations of the solubility of the ordinary acid is greater than that between the ordinary and the α -acid as given by Herzig. Under these circumstances, a small difference in solubility of two substances can be accepted only very reluctantly as evidence of difference of constitution.

The solubility of cyanuric acid which, in accordance with Herzig's experiment, has found its way into chemical literature (for example, see Beilstein, *Handbuch Org. Chem.*, 2nd Ed., 1006), is therefore too high. If from the twelve experiments I have made, two which are clearly cases of supersaturation are removed, the mean of the remaining ten, 0.09, may be taken as very accurately representing the solubility of the ordinary cyanuric acid in 100 parts of alcohol at 21—24°.

In the next place the relative solubility of the ordinary acid and of Herzig's α -acid must be examined.

The difference of solubility in the case of these two acids as observed by Herzig, and as the result of two experiments of my own, is as follows:—

	Herzig.	Senier.	
		I.	II.
Ordinary cyanuric acid	1.00	1.00	1.00
Herzig's α -acid	1.59	2.15	1.22

The solubility of the ordinary acid is taken as unity for purposes of comparison. In agreement with Herzig, I find the α -acid more soluble than the ordinary acid. But although in my first experiment it is more than twice as soluble, in my second experiment its solubility is not much greater than that of the ordinary acid.

It was observed by Herzig that his α -acid could not be converted into a salt and separated therefrom without being changed into the ordinary acid. Regeneration from a barium salt gave him an acid having the same solubility in alcohol as the ordinary acid. I have repeated the observation and can confirm this statement, thus:—

	Herzig.	Senier.
Ordinary cyanuric acid	1.00	1.00
α -Acid regenerated from a barium salt	0.97	1.10

The most probable explanation of these observations is that minute quantities of foreign substances are present which are sufficient to

increase the solubility of the acid. The purer the acid the more it approaches to the solubility of ordinary cyanuric acid. Conversion of the acid into a salt and regeneration therefrom does not appear to be a process of intermolecular change, but simply a method of purification. If this is true, then the solubility of the α -acid should be reduced when it is purified by recrystallation, for instance, from alcohol. Here are the results of some experiments to determine this compared with the numbers already obtained:—

Ordinary cyanuric acid.	α -Acid.			
	Crystallised from water.	Regenerated from barium salt.	Recrystallised from alcohol.	
1·00	2·15	1·10	I. 1·15	II. 1·09

Recrystallisation from alcohol itself, then, it is evident, is enough to so purify the α -acid that its solubility in alcohol is reduced very closely to that of ordinary cyanuric acid.

Numerous attempts have been made to discover the impurity the presence of which is the cause of the difference in solubility observed in the case of the acid prepared by the use of hexabromacetone. These inquiries have not, however, led to a perfectly satisfactory conclusion. It is deserving of mention, nevertheless, that when cyanuric acid itself is recrystallised from a solution containing small quantities of biuret, its solubility in alcohol is much increased.

Herzig's observation that fuming nitric acid also converts the α - into the ordinary acid is quite in accordance with the explanation to which I have been led of the behaviour of the α -acid when regenerated from a salt or recrystallised from alcohol, namely, that both these processes are cases of simple purification. This very method was employed long ago by Liebig and Wöhler (*Berz. Jahresbericht*, **11**, 83) as a means of purifying ordinary cyanuric acid. These observers dissolved the crude cyanuric acid in hot oil of vitriol, and to the solution added nitric acid, afterwards precipitating the pure cyanuric acid by water.

II. Water of Crystallisation.

The proportion of water held by crystals of ordinary cyanuric acid was determined by Liebig and Wöhler (*Pogg. Ann.*, **20**, 369). When the acid is freshly recrystallised and pressed between paper, it contains 21·8 per cent. of water, corresponding to two molecules. Herzig found in the case of his α -acid only one molecule. His results

are 11.73 and 12.13, corresponding very well with one molecule, which requires 12.24 per cent.

Repeating this experiment with a specimen of the α -acid which I prepared, I found, after freshly recrystallising from water and drying between paper, that it contained 17.6 per cent. water, which was given off at 120°. This specimen was then recrystallised from alcohol, and again from water, when its power of combining with water had risen very nearly to that of the ordinary acid. It contained 19.9 per cent. of water, whereas a determination in the case of the ordinary acid gave me 20.6 per cent. Thus by purification it is seen that the percentage of water of crystallisation which the acid is capable of fixing increases until a number is reached not far removed from that given by the ordinary acid.

III. *Composition of some of its Salts.*

1. *Silver Salts.*—Herzig describes two silver salts of his α -acid. A complete analysis of the one led him to give it the formula

which requires 57.14 per cent. of silver. This is probably, as Herzig himself remarks, the same salt that Wöhler (*Annalen*, **62**, 244) prepared, but to which the somewhat different formula

is ascribed, which is based, however, merely on a silver determination. This formula requires 57.29 per cent. of silver.

A trisilver salt of the ordinary acid of the composition

which requires 69.23 per cent. of silver, was prepared by Liebig (*Annalen*, **62**, 123), and afterwards by Wöhler (*Annalen*, **62**, 245). Now following the method of Liebig, Herzig obtained in the case of the α -acid salts containing from 57 to 59 per cent. of silver, and this is noted as characteristic of the α -acid.

I have repeated this experiment and have obtained salts with various proportions of silver both from the α - and the ordinary acid. By the careful employment of an excess of ammonia, according to Liebig's method, I obtained, however, from both acids the trisilver salt, as the following analytical numbers indicate:—

	Theory.	Silver salt of cyanuric acid.	Silver salt of α -acid.
Silver	69.23	69.5	68.7

When the ammonia is not in excess throughout the operation, salts

are produced containing a less proportion of silver. Such salts were observed by Wöhler in the case of cyanuric acid and Herzig's salts the α -acid probably belong to this class. One which I obtained gave me 58.1 per cent. of silver.

2. *Barium Salts*.—Wöhler (*Annalen*, 62, 251) discovered monobarium cyanurate, which he prepared by dropping a solution of barium hydroxide into a boiling solution of cyanuric acid until, the still liquid remaining acid, the first permanent cloudiness appears. The solution is then kept at 60° for several hours, when the salt is precipitated in beautiful crystals. With ordinary cyanuric acid, Herzig working in this manner obtained Wöhler's salt, $C_3N_3(Oba)(OH)_2 + H_2O$.

Herzig's analysis gave—

	Theory.	Experiment.
Barium	31.93	29.72

Now the same experiment in the case of the α -acid led to a different compound, and this is regarded by Herzig as a characteristic property of this acid. The salt obtained contained 41.29 per cent. of barium, corresponding to the formula $C_3N_3(Oba)_2(OH) + 4H_2O$.

But repeating this experiment I arrived at results which are in accord with the general outcome of my previous experiments. I have found when operating with the α - as well as with the ordinary acid, that the same monobarium salt is formed which Wöhler first observed. Thus I obtain the following numbers :—

	Theory.	Cyanuric acid.	α -Acid recrystallised from alcohol.
Barium	31.93	31.73	29.77

The percentage of silver which my α -barium salt contained is the same as that found by Herzig in the salt of the ordinary acid.

By the use of larger proportions of barium hydroxide salts richer in barium are easily produced. From the α -acid I have prepared salts or mixtures of salts containing 41.4 per cent. and 50.23 per cent. of barium, and from the ordinary acid one containing 45.4 per cent.; both these salts and Herzig's salt, which gave 41.29 per cent. of barium, are very probably mixtures.

The doubt which was felt during the preparation of this α -acid as to whether it is to be looked on as a distinct isomeride of ordinary cyanuric acid or not, has gradually become stronger, and the conclusion to which I am led by the whole investigation is that the acid produced by the action of hexabromacetone and heat on urea and known as Herzig's α -cyanuric acid, is identical with ordinary cyanuric acid.

Note on β -Cyanuric Acid.—This acid is produced in the same reaction as the α -acid, but at a somewhat lower temperature. Whilst

the α -acid requires a temperature rising to 180° , the β -compound is formed between 150 — 160° . It is more soluble in alcohol than the α -acid, but Herzig gives no determination of its solubility. It crystallises from water in anhydrous crystals. Further, it is distinguished from both the α - and the ordinary acid by not giving cyanic acid when heated, and by not forming cyanuric chloride when treated with phosphorus pentachloride. Finally, when dissolved in soda solution and the solution warmed, it does not give the sparingly soluble trisodium salt, which, as pointed out by Hofmann (*Ber.*, **3**, 769), is so characteristic of ordinary cyanuric acid.

My experiments give me somewhat different results. I have undoubtedly obtained cyanuric chloride by the action of phosphorus pentachloride. This I have isolated from the crude product of the reaction, and found it to melt at 144° . Moreover, it is easy with my specimen of the β -acid to obtain the difficultly soluble trisodium salt. That it is really the β -acid described by Herzig is proved by the fact that it did not give cyanic acid when heated in a small tube, a test which never fails, even with small quantities, in the case of pure cyanuric acid. Whether, therefore, this β -acid is a distinct isomeric compound cannot as yet be decided with certainty, although the previous work on the α -acid renders this improbable, and a final judgment must await further experiments.

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