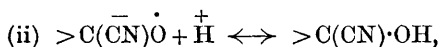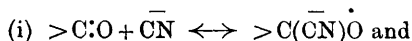CXXII.—*Reactions Involving the Addition of Hydrogen Cyanide to Carbon Compounds.   Part II.   Cyanohydrins Regarded as Complex Acids.*

By ARTHUR LAPWORTH.

IN a recent communication (Trans., 1903, **83**, 995) the effect of catalytic agents on the velocity of addition of hydrogen cyanide to carbon compounds was described, and it was shown that the observations could best be accounted for on the assumption that the process occurs in two stages; the initial stage was supposed to consist in the formation of a complex cyanide ion, the subsequent union of these with hydrogen ions affording the synthetical products.

In the simplest case, namely, where the addition occurs at a carbonyl group, the hypothetical process was represented by:

(i) $>C\!:\!O + \overset{-}{C}N \longleftrightarrow >C(\overset{-}{C}N)\overset{\cdot}{O}$ and

$$(ii) \quad >C(\overset{-}{C}N)\overset{\cdot}{O} + \overset{\cdot}{\overset{+}{H}} \longleftrightarrow >C(CN)\cdot OH,$$

a process involving the conclusion that the cyanohydrins are acidic in character.   Although from other considerations this appeared in the highest degree probable, since these compounds are cyano-derivatives of alcohols, and should therefore be more markedly acidic than the latter, which form metallic derivatives, no direct proof of the acidic character of the cyanohydrins was brought forward.

In attempting partially to reconcile the idea with prevailing views on organic compounds, it was remarked that the accelerating influence of bases in promoting the additions of hydrogen cyanide might temporarily be regarded as the result of the initial addition of a salt of the acid, thereby affording a salt of the cyanohydrin; thus, with potassium hydroxide as the base,

$$>C\!:\!O + KCN \longleftrightarrow >C(CN)\cdot OK,$$
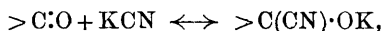
with the reservation that this explanation applies to one side of the question only.

Regarded from either standpoint, the conception involves (1) that the cyanohydrins are acidic in character, and (2) that their salts are formed, although possibly only to a minute extent, when hydrogen cyanide, for example, in presence of bases or potassium cyanide, reacts with the carbonyl compounds.

It must be made clear that there is no trustworthy process of reasoning whereby their degree of acidity might be foretold, but it is natural to surmise that they should be more acidic than the saturated fatty alcohols. The application of the theory of Abegg and Bodländer (*Zeit. anorg. Chem.*, 1899, 20, 475) to the case may appear at first sight to be straightforward, as, according to this view, the complex ion should have a greater capacity for the negative charge than the simple one, hence the cyanohydrins should be more powerful acids than H·C⁝N. There are, however, several reasons which render it impossible to attach any confidence to this mode of reasoning—firstly, because it is not yet possible to guess, even approximately, the affinity of H·C⁝N, in the absence of precise knowledge as to the nature of a solution of hydrogen cyanide in water owing to the exhibition of tautomerism, and, secondly, it is doubtful whether it will be found possible to maintain the universal correctness of the above-mentioned principle. In regard to the latter point, it seems reasonable to suppose, if indeed it is not highly probable, that the phenomena attending the electrolysis of complex electrolytes may frequently be the result of the breaking down of the complex ions after discharge, rather than the selective discharge of simple ions which may or may not be present in appreciable amounts. The potential of the complex ion may conceivably be greatly influenced by its configuration so as to rise even above that of the simple ion, and this appears more likely to occur when the "free affinity" of the complex ion is transferred to a point on the neutral component, as is perhaps usually the case, and is undoubtedly so in the foregoing instance.

The work described in the present communication was carried out with the object of ascertaining whether, in presence of excess of potassium cyanide, the additive products of that salt with carbonyl compounds could be isolated; secondly, to determine whether these products are electrolytes, in which case the complex ions of the type previously assumed must certainly exist; and, lastly, to gain a rough idea as to the relative affinities, as acids, of hydrocyanic acid and the cyanohydrins.

It was found that crystalline products could be prepared by the direct action of potassium cyanide on benzaldehyde and camphorquinone, and that these products have approximately the composition of hydrated potassium salts of the corresponding cyanohydrins, the

divergence probably originating in the fact that it was not found possible to recrystallise them except from solutions which contain considerable quantities of the products of hydrolytic and molecular dissociation.

So far as could be ascertained, these compounds behaved consistently, as should be anticipated on the assumption that they are electrolytes which, on dissolution in water, afford the complex cyanide ion, $CN \cdot CR_1R_2 \cdot O \cdot$, of the cyanohydrins, which must therefore be distinctly acidic in character. Attempts to estimate the approximate affinities of the cyanohydrins were only partially successful, but it seems quite clear that they are much weaker than the ordinary phenols, and their salts must be hydrolytically dissociated to a very considerable extent ; further, the presence of water determines the decomposition of the salts into potassium cyanide and the carbonyl compound from which they are derived.

The whole of the evidence, then, tells in favour of the view which has been advanced as to the mechanism of the action of hydrogen cyanide on carbonyl compounds. The most important point in that theory, namely, that the complex ion formation precedes that of the cyanohydrin or its salt, is advantageous because of its greater simplicity (compare Trans., 1903, **83**, 1001) as compared with the opposite view, as it involves the union of two instead of three individuals, and, moreover, explains the observation that acids greatly retard the union of camphorquinone with hydrogen cyanide in aqueous solution, even when care is exercised to employ materials free from traces of impurities of a basic nature, the presence of which would tend to vitiate the conclusion drawn. It is to be hoped that before long it may be found possible by measurements of the reaction velocities in this or in similar cases to throw further light on this most important question.

EXPERIMENTAL.

The Potassium Cyanide Derivative of Benzaldehyde,

$$C_6H_5 \cdot CH {<}^{OK}_{CN} \; + \; Aq.$$
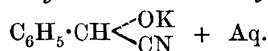
It was shown in the previous communication (*loc. cit.*, p. 1003) that when benzaldehyde is shaken at the ordinary temperature with an aqueous solution of hydrogen cyanide, an unexpectedly large quantity of the cyanohydrin is formed ; if special precautions are taken, still more interesting results are obtained.

When hydrogen cyanide was passed into an ice-cold solution of potassium hydroxide containing benzaldehyde in suspension, it was noticed that the opalescent liquid became almost transparent at a

certain stage, and subsequently returned to its original opaque condition. This suggested that the hypothetical potassium salt of the cyanohydrin was more stable than at first supposed, and attempts to isolate it were therefore instituted.

If an ice-cold saturated solution of potassium cyanide is added gradually to benzaldehyde, also at 0°, with constant stirring, a milky emulsion is at first produced, but this quickly becomes clear and homogeneous. If the vessel is removed from the cooling mixture, it gradually becomes opaque once more, and so sensitive is the solution to rise of temperature that if the hand is applied to the sides of the vessel, local decomposition is caused. The oil which separates under these conditions was found to be a mixture of benzaldehyde and its cyanohydrin.

If an excess of saturated potassium cyanide solution is added to the clear liquid obtained as above, and the solution left at 0°, a white, crystalline salt separates, the formation of which is promoted by scratching the sides of the vessel, and the whole may become semi-solid.

The material may be separated by filtration, and as it was found impossible to recrystallise it in the ordinary way, it was prepared for analysis by spreading it in a very thin layer over highly absorbent earthenware, which was subsequently placed beneath a bell-jar together with a vessel containing an alkali hydroxide to remove carbon dioxide. The dry salt was afterwards washed with a little ice-cold water, dried over sulphuric acid and potassium hydroxide in a vacuum, and finally washed with dry chloroform, which was removed by exposure over solid paraffin.

A specimen prepared in the above way was analysed, the total carbon being estimated by combustion in a tube containing lead chromate, and then continuing the process after the addition of some finely divided silica to the residue in the boat. The water of crystallisation could not be estimated directly, as the substance decomposed rapidly at temperatures considerably below 100°. The cyanogen was estimated by adding excess of a decinormal solution of silver nitrate to a weighed quantity of the salt dissolved in water, and determining the excess of silver after acidifying with nitric acid.

0·3458 gave 0·1371 K_2SO_4.   K = 17·8.
0·7672   ,,   0·3050 K_2SO_4.   K = 17·9.
0·4748 required 23·05 c.c. $N/10$ $AgNO_3$.   CN = 12·6.
0·4171 gave 25·45 c.c. nitrogen at 16° and 747 mm.   N = 6·8.
0·2392   ,,   0·3856 CO_2 and 0·1072 H_2O.   C = 43·9 ; H = 5·0.
$C_7H_6O,KCN,2\frac{1}{2}H_2O$ requires K = 18·1 ; CN = 12·0 ; C = 44·4 ; H = 5·1 ;
N = 6·5 per cent.

The amounts of potassium and cyanogen in a number of other specimens were estimated and found to vary considerably, but were in most cases nearly in equivalent proportions. Thus it seems unquestionable that the substance is an additive product of the aldehyde with potassium cyanide with an uncertain quantity of water, probably less than $2\frac{1}{2}$ molecular proportions.

The salt forms thin, rectangular plates which have straight extinction, and probably belong to the orthorhombic system; it dissolves readily in ice-cold water, but is partially decomposed and a milky liquid results; if some potassium cyanide is present, however, a clear solution may be obtained: this, when warmed, becomes opalescent. It dissolves in strong alcohol, and on adding benzene a deposit of glistening plates is obtained; these, however, consist of pure potassium cyanide. As was to be anticipated from the latter observation, potassium cyanide dissolves somewhat freely in 95 per cent. alcohol containing benzaldehyde, although it is very sparingly soluble in pure alcohol of that strength.

The salt is very stable towards chloroform or benzene, but if washed with moist ether it is slowly decomposed, and potassium cyanide, nearly free from benzaldehyde, remains.

On exposure to a moist atmosphere containing carbon dioxide, the compound becomes sticky, and is finally converted into a mixture of potassium carbonate, mandelonitrile, benzaldehyde, and benzoin, the whole appearing reddish-brown. If, however, the substance is kept in a desiccator over an alkali hydroxide and sulphuric acid, it may be preserved with little alteration for some weeks or months.

An aqueous solution of the substance is decomposed by very weak acids, such as hydrocyanic acid and even phenols, the free cyanohydrin being deposited as an oil.

The Potassium Cyanide Derivative of Camphorquinone,

$$C_{10}H_{14}\left\langle \begin{array}{l} C{<}^{OK}_{CN} \\ | \\ CO \end{array} \right. + Aq.$$
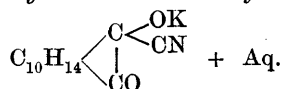
Camphorquinone forms a very well defined additive product with potassium cyanide, which may be prepared as follows.

An ice-cold, nearly saturated, solution of potassium cyanide is gradually added to the quinone, which is contained in a mortar and constantly triturated. The yellow powder gradually becomes replaced by a white, potassium salt, which may be transferred to a porous plate, dried over sulphuric acid and an alkali hydroxide, and washed with a considerable amount of chloroform to remove unaltered quinone. It is perhaps more satisfactory, however, to add the requisite amount of

potassium cyanide dissolved in water to the quinone, finely powdered and suspended in its own weight of alcohol ; in this case, the powder first dissolves to a nearly colourless solution, and finally separates in the form of the additive product.

The method which gave the best products was the following : the quinone was dissolved in chloroform, and to the solution was added a moderately strong solution of potassium cyanide in excess, the whole being finally cooled to $0°$, when it became colourless, and eventually the solid compound separated in well-formed crystals, and was purified and dried in the manner previously indicated.

The compound is more stable than that of benzaldehyde, and may be recrystallised by dissolution in ice-cold water containing a small quantity of potassium cyanide, and allowing the filtered solution to evaporate in a vacuum over sulphuric acid ; it is very doubtful, however, if any real advantage is thereby gained.

A specimen prepared by the second of the above methods was analysed.

0·1675 gave 0·0522 K_2SO_4. $K = 13·9$.
0·4077   ,,   0·1254 K_2SO_4. $K = 13·8$.
0·4402 required 16·3 c.c. $N/10\,AgNO_3$. $CN = 9·6$.
0·1676 gave 0·2818 CO_2 and 0·1211 H_2O. $C = 45·8$; $H = 8·0$.
$C_{10}H_{14}O_2,KCN,3H_2O$ requires $K = 13·7$; $CN = 9·3$; $C = 46·3$; $H = 7·7$
per cent.

The approximate agreement of the analytical results with the formula suggested is probably accidental. A considerable number of specimens, prepared in various ways, were analysed, and gave varying results. Three specimens gave respectively (a) $K = 16·4$, $CN = 10·2$; (b) $K = 12·9$, $CN = 9·1$; (c) $K = 13·7$, $CN = 10·1$ per cent. As a general rule, the ratio $K : CN$ was somewhat too low, suggesting that some free cyanohydrin was present. In all cases, the specimens analysed were free from colour, and therefore from unaltered camphorquinone.

The salt crystallised in thin, usually four-sided, rectangular plates having straight extinction. It may be dissolved, with care, in ice-cold water, affording a clear, colourless solution, which, when warmed, becomes yellow and finally turbid at a temperature which depends on the concentration. A very small quantity of potassium cyanide raises the temperature at which this takes place. If the yellow solution is shaken with ether, the latter is found to extract a mixture of camphorquinone and its cyanohydrin (compare Trans., 1903, 83, 1003). If carbon dioxide or hydrogen cyanide is passed into the clear, aqueous solution, a turbidity at once appears, and a colourless oil is finally obtained ; this is found to be nearly pure camphorquinone cyano·

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hydrin, as it affords an excellent yield of the corresponding amide on treatment with fuming sulphuric acid (*loc. cit.*).

A portion of the specimen the analysis of which is given above was sent to Prof. James Walker, who kindly undertook some measurements of the conductivity of its solution in water, alone and in presence of potassium cyanide. He reports : " It is difficult to interpret the results owing to the possibility of the occurrence of several kinds of hydrolysis. The conductivity of potassium cyanide falls on combination with camphorquinone to an extent which cannot be accounted for solely on the assumption that the negative complex ion has a very small velocity of migration and the fall is greater for the first $\frac{1}{2}$ molecule of the quinone than for the second. It is therefore clear that a diminution in the amount of ionisation must have taken place ; nevertheless, in my opinion, the new compound is a moderately good electrolyte."

Affinity of the Cyanohydrins as Acids.—A considerable number of attempts were made to obtain a satisfactory comparison of the affinities of the cyanohydrins with that of hydrocyanic acid. Qualitative experiments showed that on adding a reactive ketone or an aldehyde to an aqueous solution of potassium cyanide containing free hydrocyanic acid and coloured with phenolphthalein, an increase in the red colour was always produced. This observation indicated that the solution became more strongly alkaline, but might be accounted for by the existence of an unstable compound of the phenolphthalein with hydrocyanic acid, the concentration of which would be diminished on the partial removal of hydrocyanic acid from the solution by the ketone or aldehyde.

Efforts were now made to compare the speeds with which relatively small quantities of ethyl formate are hydrolysed by aqueous solutions of potassium cyanide, alone and with the addition of ketones and aldehydes. In the former case, by removing portions of the reaction mixture, diluting largely with ice-cold water, precipitating the cyanide by addition of silver nitrate, and finally removing the latter by sodium chloride, sharp results could be obtained on titration with standard alkali ; in presence of aldehydes and ketones, however, the numbers were not so concordant, but in every case it was found that the apparent end point in the hydrolysis was reached much more rapidly when benzaldehyde or camphorquinone was present, indicating a greater initial alkalinity in the presence of the carbonyl compound.

Another mode of investigation was also adopted, namely, a direct comparison of the cyanohydrin, $CN \cdot CMe_2 \cdot CH_2 \cdot CMe(OH) \cdot CN$, with β-naphthol, as regards the effect of alkali on their solubilities in water. This cyanohydrin was chosen on account of its relatively

great stability, and because its equivalent is nearly the same as that of β-naphthol.

0·0460 gram of the cyanohydrin dissolved without difficulty and within 3 minutes in 15 c.c. of water at 16°, whilst the same weight of β-naphthol did not dissolve in 50 c.c. of water at that temperature after 4 days. This weight of each of these compounds was then covered with 1 c.c. of water, and the smallest amount of N/10 sodium hydroxide required to bring them completely into solution was determined. It was found that 5·8 c.c. were required for the cyanohydrin, and 6·3 c.c. for the naphthol (the equivalent volume of the alkali is 3·0 c.c. in each case). Hence, whilst the cyanohydrin is very much more readily soluble in water, the excess of soda required to keep the substance in solution at a concentration approximately about N/20 is not very different in the two cases. It may safely be concluded, therefore, that this cyanohydrin is a much weaker acid than β-naphthol, and therefore *a fortiori* than hydrocyanic acid.

Numerous aldehydes and ketones besides the two above dealt with were investigated, in the hope of being able to obtain from them similar potassium cyanide additive compounds, but with indifferent success.

In the case of fatty aldehydes, no solid salts were isolated, but it was frequently found that the aldehydes were more readily soluble in ice-cold potassium cyanide solution than in water; heat was generated, and in many cases condensation of the aldehyde took place to some extent. The nitrobenzaldehydes reacted very rapidly, but secondary reactions occurred.

Both o- and p-bromobenzaldehydes dissolved very rapidly in concentrated potassium cyanide solutions and gave clear solutions at the ordinary temperature, so that the additive compounds are apparently more stable than that of benzaldehyde itself : this is perhaps what might be anticipated, as the tendency to the formation of negative complex ions should, other things being equal, increase with the "negativeness" of the neutral component. Colourless, crystalline compounds were isolated from these solutions, but these can scarcely be of a simple character, as they contained only about one-half the required proportion of potassium, the proportion of cyanide being comparatively high; this suggests that they were mixed with free cyanohydrins.

Saturated fatty and aromatic monoketones did not appear to dissolve in ice-cold potassium cyanide to any marked extent ; moreover, their cyanohydrins, which are very easily obtained if acid is added, were rapidly decomposed by ice-cold alkalis. Their behaviour suggests that the aldehydes differ from the ketones mainly in that they yield more stable additive compounds, rather than that they afford them

more readily ; that is to say, the velocity of the breaking down of the complex ion as compared with that of its formation is, in these cases, relatively high.

The author's thanks are due to the Research Fund Committee of the Chemical Society for a grant which defrayed part of the cost of this investigation.

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