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A Proposed Mechanism for the Conversion of Alcohols to Allophanates

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RECEIVED MARCH 13, 1953

It is suggested that in the conversion of alcohols to allophanates by means of cyanic acid the reaction occurs primarily by means of a concerted attack on the alcohol by two moles of reagent. The route through a carbamate intermediate is held to be of secondary importance.

In a recent review article[1] discussion of allophanate formation from alcohols and cyanic acid its authors have advocated what might be termed the carbamate hypothesis as representing the most advanced thought on the subject. This theory holds that allophanates are formed in two steps: first, one mole of cyanic acid adds to the alcohol to form a carbamate and, second, an additional mole of reagent adds to yield the allophanate. According to Blohm and Becker, the second step is

$$\mathrm{ROH} \xrightarrow{\mathrm{HNCO}} \mathrm{ROCONH_2} \xrightarrow{\mathrm{HNCO}} \mathrm{ROCONHCONH_2}$$

the slow or rate-determining reaction. Werner[2,3] has advanced the view that obligate acid catalysis figures in the conversion of carbamates to allophanates. The reviewers treat this with circumspection, and recognize that cyanic acid itself ($K_a = 2.2 \times 10^{-4}$) may, in certain cases, have sufficient acid strength, and acid catalysis as ordinarily understood is merely facultative. They suggest, however, that zinc chloride, inadvertently introduced into the cyanic acid, may operate as a Lewis acid.

Certain features of the mechanism suggested by Blohm and Becker are not in accord with our experience or the experience of others. We have in mind the conventional preparation of allophanates by the passage of cyanic acid, generated from reasonably pure cyanuric acid, into an alcohol, with or without solvent. It is understood that there is no willful addition of any catalyst.

If the carbamate hypothesis is valid, it is odd that carbamates have seldom been reported as the major product of the reaction of cyanic acid with an alcohol, even though it is a common practice to carry out the reaction with an excess of alcohol.[4] Indeed, if the first step, as stated, is the rapid step, one would scarcely expect to find any significant amount of allophanate produced.

To the best of our knowledge there are no published data which show that acids other than cyanic acid are necessary for the conversion of alcohols to allophanates. Therefore, if we accept the opinion of Werner that acids are indeed necessary for the conversion of carbamates to allophanates, we are forced to conclude that the countless individuals who have prepared allophanates in supposedly neutral media actually had contamination with acidic substances. This involves a burden of proof which should be borne by the advocates of the carbamate hypothesis.

Many of the publications pertaining to allophanate formation contain conflicts of fact as well as interpretation. Furthermore, the experiments cannot be compared critically because of widely varying (or unspecified) conditions under which the investigations have been carried out. It seemed desirable, therefore, to conduct more carefully controlled studies in an effort to throw some light on the mode of action of cyanic acid upon alcohols.

Experimental

Materials.—Cyanic acid was produced in the usual manner by depolymerization of cyanuric acid (Eastman Kodak white label product) in an electrically heated tube. A slow stream of carbon dioxide was used to carry the exit gases through a Dry Ice–acetone trap, where the cyanic acid was condensed and collected as a liquid. The liquid was weighed immediately, then taken up in ice-cold ether and filtered to remove suspended solid (cyanuric acid and cyamelide). The weight of liquid was corrected for the weight of solid thus removed.

Experiment I.—Ordinary ether (12 cc.) containing 2.5 g. (0.058 mole) of cyanic acid was added to a solution of 5.3 g. (0.116 mole) of absolute alcohol in 10 cc. of ether. Crystalline material began to separate in less than 90 minutes. After 8 hours the solution was decanted; the product was washed with 50% ether–Skellysolve B and weighed. The yield of ethyl allophanate was 812 mg., m.p. 192–193°. A close approximation to the amount of product retained in solution was obtained by determining the solubility of the allophanate in 22 cc. of ether containing 5.3 g. of absolute alcohol. When corrected for this amount (135 mg.), the total amount of allophanate produced in 8 hours was 947 mg. (25%).

The decanted liquid was allowed to stand for an additional 12 hours, during which time 590 mg. of product, m.p. 191–192°, precipitated. The total amount of allophanate produced in 20 hours was, therefore, 1.54 g., or 40%.

The reaction mixture was now taken to near dryness with an air jet. Heating above 30° was avoided to discourage further reaction with remaining cyanic acid and to keep volatilization of any urethan present to a minimum. Dilution with Skellysolve B precipitated 158 mg. of crude ethyl allophanate, m.p. 175–182°, an amount in good agreement with that (135 mg.) calculated to be present in the reaction mixture. The filtrate was carefully concentrated to recover urethan. A total of 308 mg. (6% based on conversion of all cyanic acid to carbamate) of crude ethyl carbamate, m.p. 43–49°, was found.

Experiment II.—A 12-cc. aliquot of the same ethereal cyanic acid solution used in Experiment I was added to a solution of 2.6 g. (0.029 mole) of urethan in 10 cc. of ether. Separation of crystalline material was delayed for 3 hours. After 8 hours the product was isolated as in Experiment I, and found to be 320 mg., m.p. 191–192°. When corrected for the amount of ethyl allophanate (124 mg.) soluble in 22 cc. of ether containing 2.6 g. of urethan, the yield was 444 mg. (12%).

During 12 additional hours of standing the reaction mixture deposited 381 mg., m.p. 180–187°. The 20-hour yield was, therefore, 825 mg. (22%).

As a check on the value (124 mg.) used to represent ethyl allophanate in solution, the reaction mixture was taken to dryness with an air jet. Heating above 30° was avoided. The solid residue was extracted with 50% ether–Skellysolve B to remove the carbamate. The residue of crude ethyl allophanate was 138 mg., m.p. 178–185°.

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[1] H. W. Blohm and E. I. Becker, *Chem. Revs.*, **51**, 471 (1952).

[2] A. E. A. Werner and J. Gray, *Sci. Proc. Roy. Dublin Soc.*, **24**, 77 (1946).

[3] A. E. A. Werner and J. Gray, *ibid.*, **24**, 209 (1947).

[4] M. A. Spielman, J. D. Barnes and W. J. Close, THIS JOURNAL, **72**, 2520 (1950).

Experiment III.—Experiment II was repeated with reagent grade ether, dried over sodium, replacing the commercial ether as a solvent. After 21 hours, only 52 mg. of material which did not melt below 250° was obtained. The solution was allowed to stand an additional 5 days, but still no allophanate was produced.

Experiment IV.—Experiment I was repeated with the addition of 0.5 g. of freshly fused zinc chloride to the ethereal ethanol solution. At the end of 40 hours the crystals were separated and found to amount to 0.1 g., m.p. *ca.* 250° (dec.).

Experiment V.—A reaction mixture containing 2.5 g. of cyanic acid, 5.2 g. of ethyl carbamate and 0.5 g. of freshly fused zinc chloride in 35 cc. of ether was prepared. Separation of crystalline material began in less than one hour. At the end of 16 hours the solid was separated by filtration and washed with a small quantity of cold water. The product (1.3 g.) melted above 250° and was not investigated further.

Experiment VI.—Ether (6 cc.) containing 1.2 g. (0.028 mole) of cyanic acid was added to 2.6 g. (0.056 mole) of absolute alcohol dissolved in 5 cc. of ether containing 0.003 mole of dry hydrogen chloride. There was an immediate vigorous reaction which was moderated by cooling in ice. After the initial reaction was over, the solution was allowed to stand for 2 hours at room temperature. The insoluble material (34 mg., m.p. above 250°) was separated. The filtrate was concentrated to near dryness and diluted with Skellysolve B. The precipitate (1.6 g., 64%) proved to be ethyl carbamate, m.p. 45-50°.

Discussion

In Experiment I it will be noted that considerably more allophanate than carbamate was formed, in spite of the large excess of alcohol. This demonstrates conclusively that, if the carbamate is the intermediate product in the formation of ethyl allophanate, the first step, not the second, is the slow reaction.

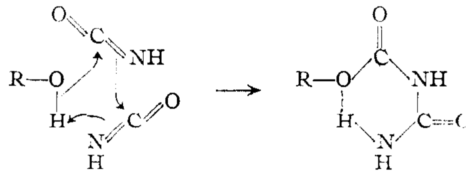
In the second experiment ethyl carbamate was converted to ethyl allophanate by means of cyanic acid; however, the reaction proceeded only slowly under the usual operating conditions (commercial reagents). With pure reagents (experiment III) the reaction did not go at all.[5] This establishes that, while the carbamate *can* be an intermediate, it cannot be an important one in the usual manner of making allophanates. If the reaction in Experiment I proceeds through the carbamate, the yield of final product can approach the yield of Experiment II only as the rate of carbamate formation approaches infinity. But the first experiment shows that the alcohol to carbamate reaction is, as a matter of fact, slow. The carbamate hypothesis, then, would predict that there would be much less allophanate in Experiment I than in Experiment II; but the opposite is true, for at 8 and at 20 hours, the yield of allophanate in the first experiment is twice that of the second. There can be no question of extrinsic acid catalysis, for all chemicals came from corresponding lots and were therefore impure to identical degrees. Stated simply, the alcohol is a better starting material for the synthesis of allophanates than is the carbamate. This can only be interpreted to mean that most of the alcohol was converted to the allophanate by some route other than through the carbamate.

The fourth and fifth experiments were carried out in order to evaluate the role of zinc chloride, suggested by Blohm and Becker, as a possible Lewis acid in promoting allophanate formation. The data show clearly the deleterious effect of this reagent in the conversion of *either* ethanol or ethyl carbamate to the allophanate.

Experiment VI shows the tremendous effect of hydrogen chloride which so enhances the rate of alcohol-to-carbamate conversion that, in the absence of excess cyanic acid, no allophanate whatever is produced. This is consistent with the Blohm and Becker theory of the relative rapidity of this reaction but only within the scope of the experiment; *i.e.*, as catalyzed by strong acid. There is no direct bearing on the mechanism of the reaction as ordinarily carried out (in the absence of acid), especially since it is highly probable that in the presence of hydrogen chloride, the reagent is not cyanic acid but carbamyl chloride.[2]

A second mechanism of historical significance is embodied in the proposal of Davis and Blanchard[6] that cyanic acid exists in solution as "dicyanic acid" which is capable of converting alcohols directly to allophanates. The theory has met with vigorous opposition[2,3,7] and may be regarded as substantially overthrown if it is held to require the existence of a stable, distinct molecular species answering to the description of dicyanic acid.[8]

A development which follows logically from the dicyanic acid theory is the modern concept of concerted attack,[9] wherein a molecule of cyanic acid may associate with one of the alcohol, but is *normally* incapable of consummating the reaction until a second molecule of reagent enters the reaction environment and provides the necessary impetus. By adopting the chelate structure of Blohm and Becker for the product, one may then represent the concerted attack as shown. There is no direct evidence for the hypothesis, but it is consistent with all known facts. We propose that this is the major route under the usual conditions by which allophanates are produced from alcohols.



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(5) This confirms the experience of Werner and Gray (ref. 2) who found cyanic acid to be inert to urethan in neutral ether solution. It is also in harmony with the report of J. Grandière, *Bull. soc. chim.*, [4] **35**, 187 (1924), that cyanic acid does not react with butyl, hexyl, benzyl and methylcyclohexyl carbamates. Finally, L. Birckenbach and H. Kolb, *Ber.*, **68**, 895 (1935), found that carbamates do not yield allophanates with cyanic acid in the absence of mineral acid.

(6) T. L. Davis and K. C. Blanchard, THIS JOURNAL, **51**, 1806 (1929).

(7) E. A. Werner and A. E. A. Werner, *Sci. Proc. Roy. Dublin Soc.*, **23**, 137 (1943).

(8) In this connection Birckenbach and Kolb (ref. 5) have shown that if dicyanic acid is present, the amount is less than 2%.

(9) C. G. Swain and J. F. Brown, Jr., THIS JOURNAL, **74**, 2538 (1952), and earlier papers of the same series.