POLAROGRAPHIC STUDY OF THE KINETICS AND EQUILIBRIA OF THE REACTION OF BENZALDEHYDES WITH HYDRAZINE

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Whereas formation of imines, oximes, and semicarbazones has been investigated in some detail, there is surprisingly little information available concerning the equilibria, kinetics and mechanisms of the addition of hydrazines to carbonyl compounds. In the former the attacking nucleophile possesses only a single reactive center. The bifunctionality of hydrazine results in two types of complications: First, the nucleophile can exist as a base, but also in a mono- and diprotonated form. Whereas the diprotonated form does not posses a free electron pair on nitrogen, which is necessary for the nucleophilic attack by amines, both the monoprotonated form of hydrazine and the unprotonated one can act as nucleophiles. The positive charge on the adjacent nitrogen atom increases the reactivity of the free amino group in the monoprotonated form of hydrazine. Second, the formation of the hydrazone in the reaction of on molecule of the carbonyl compound with one molecule of hydrazine may be followed by a reaction with the second molecule of the carbonyl compound. This reaction results in a formation of an azine of the type ArCH=N-N=CHAr.

Preliminary experiments indicated that in aqueous buffered solutions, containing a substituted benzaldehyde and an excess of hydrazine, the hydrazone is formed as the predominant product. On the other hand in a buffered solution of hydrazine, containing an excess of the studied benzaldehyde, the azine is formed.

Polarography offers the opportunity to follow continuously the reactions of benzaldehydes and hydrazine under both conditions. In the presence of an excess of hydrazine, it is possible (using reduction waves of the formyl group and the azomethine formed) to follow concentration changes of both the benzaldehyde and of the hydrazone formed. It is possible to follow this reaction also spectrophotometrically, but the wave of the hydrazone formed is better separated from the wave of the parent benzaldehyde than corresponding absorption bands. Improvement of the latter is possible when the changes of absorbance are followed at several wavelengths and a suitable computer program is used for verifying of the rate equation used and for finding the best values of rate constants.

Still greater advantage offers polarography - in comparison with spectrophotometruy - in the investigation of the reaction of the hydrazine in the presence of an excess of benzaldehyde. Here the small changes in absorbance of benzaldehyde in the course of the reaction does not allow following the kinetics spectrophotometrically. On the other hand, changes in the anodic wave of hydrazine with time allows to follow the kinetics continuously at pH>8 by using polarography. For the study of reactions at pH<8, it is necessary to take samples from the reaction mixture and determine the concentration of the unreacted hydrazine using its anodic wave at a higher pH.

After separation of the unreacted benzaldehyde, for example by extraction at a lower pH, it is possible to prove the structure of the azine formed using classical methods. Confirmation, based on comparison of the pH dependences of currents and half-wave potentials with authentic samples of azines, is possible.

Attempts have been made to follow the opposite reaction, namely hydrolysis of azines, but its kinetics were proven to be rather complex one. To be able to correlate the rate of hydrolysis with structure of the carbonyl compound, the rate determining steps, the intermediates and their cleavage and the dependence of the rate on pH have first to be elucidated and interpreted.

The present study represents the case where the use of polarography as an analytical tool in investigations of kinetics and mechanism of organic compounds is particularly advantageous.