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MECHANISMS OF ACID-BASE CATALYSIS AND
STUDIES IN DEUTERIUM OXIDE AS SOLVENT

Final Report

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ABSTRACT

A set of recent studies has revealed that simple cyanocarbon acids are nearly normal in the Eigen sense and that chloroform, as well as some substituted chloromethanes are entirely normal. The investigative tools which have led to these conclusions involved: following the kinetics of proton transfer by means of tritium labeling; determining primary isotope effects utilizing a newly developed procedure; measuring entropies of activation in water and mixed solvents; determining the presence of general base catalysis for a fully normal acid by studying it in mixed solvents where the revealing characteristic is parallelism between rates and the H_- function. Utilizing these techniques, it has been found that chloroform behaving as an acid is fully normal, i.e. in all of its characteristics it is indistinguishable from such acid groups as oxygen acids and nitrogen acids. The simple cyanocarbon acids are very nearly normal but show two anomalies. First, for the rapid "reverse reaction" between carbon anion and general acid the rate is about a factor of 10 less rapid than expected for a simple diffusion controlled process. Second, the reaction of cyanocarbon acids with hydroxide ion is anomalously slow. This latter feature is of experimental significance since its presence permits determination of Brønsted β of unity in aqueous solution. Explanations have been advanced for the hydroxide anomaly and for the mostly normal behavior of these classes of carbon acids.

For this recent period, this program has been concerned with the mechanism of ionization of carbon acids as studied by kinetics, isotope effects and associated tools. A principal focus of the work was understanding the acidity of a group of simple cyanocarbon acids of the general formula $(CN)_xRH$. In sharp contrast to most of the carbon acids which have previously been studied, these cyanocarbon acids are virtually normal in the Eigen sense. By this is meant that the slow proton removal stage occurs with a general base catalysis which is characterized by a Brønsted coefficient β of unity. The reverse reaction between carbon anion and general acid, which is not the rate determining step, is simultaneously characterized by a reaction rate in aqueous solution of within about a factor of 10 the expected value for a diffusion controlled process.

There is a second standpoint from which these acids are not fully normal. This is that, for the slow step, the rate of proton removal by hydroxide ion tends to be anomalously slow by factors of from 100 to 1000. Actually this "slow" reaction rate of hydroxide is essential in permitting a measurement of the general base catalysis with unit β which is characteristic of these reactions.

Supporting evidence for the normality of these acids and for the fact that it, in the slow step, is the proton removal which is rate determining and diffusion which is rate determining in the reverse, has been obtained by use of the following auxiliary tools: primary hydrogen isotope effects; solvent isotope effects; ionization constants of the acids;

entropies of activation for the reactions. The overall conclusion is internally consistent and persuasive, and the data are important in revealing that carbon acids can be virtually normal. Explanations have been advanced for the particular characteristics of these cyanocarbon acids. The phenomenon of relatively poor hydrogen bonding has been invoked to explain the "slow" reactions with hydroxide ion.

Included in these studies were a set of experiments on the rate of reaction of some of these cyanocarbon acids in mixed solvents of H_2O - DMSO. These studies have served two rather different functions. In the first place, it has been shown that the proton removal reaction of these cyanocarbon acids can serve as an interesting and useful Basicity Probe for examination of mixed solvents. As a second and rather different item, it has been found that studies of entropies of activation in the mixed solvents offers useful evidence on the reaction mechanism itself.

In a search for a carbon acid which would be fully normal, a series of studies were made with the acid chloroform, Cl_3CH . The conclusions from these studies, which utilized the same investigatory tools as for the reactions just discussed, was that chloroform was an example of a carbon acid which was, in the Eigen sense, fully normal in all respects.

Given this important characteristic of chloroform, a set of studies was made on substituted methanes containing both chlorine and cyano substituents, and it has been found that the normality can persist for $\text{Cl}_2(\text{CN})\text{CH}$ when one cyano group is present and is virtually there when two are present.

As a consequence of these studies, our understanding of the characteristics of carbon acids has been greatly clarified, and it now becomes possible to turn ones attention to comparable studies of other classes of cyanocarbon acids and to more detailed experiments which will reveal the special role of the aqueous solvent in all of these reactions. As part of such an extended program, some preliminary studies have been made with substituted acetylenes.

The results of these various studies have been embodied in a series of publications, a partial list of which is given below. In addition, the results have been presented to several meetings of the American Chemical Society, to Gordon Conferences, and in seminars at several universities throughout the nation.

Recent Publications

1969

E. A. Walters and F. A. Long, Proton Transfer from Cyanocarbon Acids. I. General Base Catalyzed Detritiation of 1,4 Dicyano-2-butene-1-t in Aqueous Solution. Journal of the American Chemical Society, 91, 3733 (1969).

H. H. Huang and F. A. Long, The Decarboxylation of Azulene-1-carboxylic Acid. II. Carbon-13 Isotope Effects, Journal of the American Chemical Society, 91, 11 (May 21, 1969).

F. Hibbert, F. A. Long, and E. A. Walters, A Kinetic Probe for Basicity and Its Application to Mixed Aqueous Solvents, Journal of the American Chemical Society, 91, 2381 (1969).

1971

F. Hibbert, F. A. Long and E. A. Walters, Proton Transfer from Cyanocarbon Acids. II. General-Base-Catalyzed Detritiation and Bromination of Malononitriles. Rates of the Reverse Reactions. Journal of the American Chemical Society, 93, 2829 (1971).

F. Hibbert and F. A. Long, Proton Transfer from Cyanocarbon Acids. III. Primary and Solvent Kinetic Isotope Effects in the Ionization of Malononitriles. Journal of the American Chemical Society, 93, 12 (1971).

F. Hibbert and F. A. Long, Proton Transfer from Cyanocarbon Acids. IV. Kinetic Ionization Behavior of p-Nitrobenzyl Cyanide and Bromomalononitrile. Journal of the American Chemical Society, 94, 2647 (1972).

1972

F. Hibbert and F. A. Long, Detritiation of Malononitriles in Mixed Aqueous Solvents and in Salt Solutions. A Kinetic Probe for Solvent Basicity. Journal of the American Chemical Society, 94, 7637 (1972).

D. B. Dahlberg, Aqueous Solution Structure as Determined from Thermodynamic Parameters of Transfer from H_2O to D_2O . Journal of Physical Chemistry, 76, 2045 (1972).

Zafra Margolin and F. A. Long, Dimethyl Sulfoxide-Water for Study of "Unobservable" General Base Catalysis and Anomalous Behavior of Hydroxide Ion. Journal of the American Chemical Society, 94, 5108 (1972).

E. A. Walters and F. A. Long, Isotope Effects on Hydroxide Ion in Aqueous Solution. Journal of Physical Chemistry, 76, 362 (1972).

D. B. Dahlberg and F. A. Long, Solvent Effects on the Kinetics and Equilibria Associated with the Interconversion of 3-Methylacetyltonone in H_2O - D_2O Mixtures. Accepted for publication in the Journal of the American Chemical Society.

Zafra Margolin and F. A. Long, The Acidic Behavior of Chloroform. Accepted for publication in the Journal of the American Chemical Society.

Recent Publications cont'd

Zafra Margolin and F. A. Long, The Acidic Behavior of Mono and Dichloro Acetonitrile. To be published in the Journal of the American Chemical Society.