Acid Dissociation of Chloroform: Use of an Electrostatic Effect to Detect Marginal General Base Catalysis[1]

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Summary The positive charge in $[H_2N(CH_2)_3NMe_3]^+$ makes this amine a particularly effective catalyst for the acid dissociation of chloroform, and general base catalysis of this reaction in dilute aqueous buffer solutions of this amine is therefore easily detectable.

It has been suggested[2] that $CHCl_3$ is an unusual carbon acid in that it is fully normal in the Eigen sense,[3] *i.e.*, that its endothermic reaction with base in aqueous solution is a process in which proton transfer is faster than the subsequent separation of proton transfer products (equation 1). A reaction such as this should show general base catalysis,

$$CHCl_3 + B \underset{}{\overset{\text{fast}}{\rightleftarrows}} CCl_3^-{\cdot}HB^+$$

$$CCl_3^-{\cdot}HB^+ + H_2O \xrightarrow{\text{slow}} CCl_3^-{\cdot}H_2O + HB^+ \qquad (1)$$

but this may be difficult to detect inasmuch as the exponent of the Brønsted relation for the system will be large and catalysis by the hydroxide ion may overwhelm that by other basic species. In an early study of this reaction, general base catalysis in $MeNH_2$ buffers was claimed,[4] but this could not be substantiated by a later, more detailed investigation, and general base catalysis of the process in aqueous solutions of simple amines was therefore declared to be unobservable.[2]

TABLE. Rates of detritiation of $CHCl_3$ in buffers of (I)[a]

10^2 $[RNH_2]$/M	10^6k/s^{-1}
0·77	5·89
1·54	6·20
3·08	6·38
3·85	6·63

[a] $[RNH_2]/[RNH_3^+] = 5$; ionic strength = 0·10 M; T = 25 °C.

We have now demonstrated general base catalysis of the acid dissociation of $CHCl_3$ in amine buffers by using a simple expedient which detects this form of catalysis in marginal cases. The method employs an electrostatic effect to produce positive deviations from the Bronsted relation[5] and thereby increases the general base contribution to the overall reaction rate. Since the ionization of $CHCl_3$ generates a negative charge on the substrate, a rate acceleration of this kind may be achieved by using a positively charged base, *e.g.*, (3-aminopropyl)trimethylammonium ion, $[NH_2(CH_2)_3NMe_3]^+$ (I).[6]

The Table shows that specific rates of dissociation of $CHCl_3$ in buffer solutions of this amine, as measured by the rate of loss of tritium from C^3HCl_3, clearly increase with increasing general base concentration. The change over the concentration range employed amounts to 13%, even though the maximum concentration of undissociated base was limited to 0·04 M in order to keep ionic strengths at a reasonable level (0·1 M). Least-squares analysis of these data provides the relationship $10^6k = 5{\cdot}78 \pm 0{\cdot}05 + (22 \pm 2)[RHN_2]$ and gives a hydroxide ion catalytic coefficient of $(1{\cdot}66 \pm 0{\cdot}02) \times 10^{-1}\,l\,mol^{-1}\,s^{-1}$, in good agreement with the value $(1{\cdot}61 \pm 0{\cdot}01) \times 10^{-1}\,l\,mol^{-1}\,s^{-1}$ measured in NaOH solutions.

By working carefully, we were able also to detect general base catalysis of this reaction in uncharged amine buffers, although the rate changes there were considerably less (3–6% using maximum undissociated base concentrations of 0·1–0·4 M) than with the positively charged catalyst. The data for 7 neutral amines give a good Brønsted relation, $\beta = 1{\cdot}15 \pm 0{\cdot}07$, from which the point for (I) deviates by a factor of 90. Without this deviation the rate increase in the buffer solutions of this amine would have been 0·1% rather than 13%, and general base catalysis would have been undetectable.

It is interesting that the rate constant for hydroxide ion also deviates from this Brønsted relation, and that the (negative) deviation here (500 ×) is even greater than that shown by (I). The difficulty in detecting general catalysis in this system is therefore not the result of normal behaviour by the hydroxide ion, as claimed previously,[2] but is due rather to an unusually large value of β.

We thank the National Science Foundation and the Petroleum Research Fund of the American Chemical Society for support, and Professor H. Koch of Ithaca College for providing facilities.

(*Received*, 1*st August* 1975; *Com.* 879.)

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[1] A portion of this research was done at the Illinois Institute of Technology and is described in a Ph.D. thesis submitted there by A. C. Lin.

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