Proton Magnetic Resonance Study of Proton Exchange Kinetics in Molten Ammonium Hydrogen Sulphate

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Summary ^{1}H n.m.r. spectra of molten ammonium hydrogen sulphate indicate that proton scrambling occurs both between cations and between cations and anions; rate constants for both processes are determined by Abragam–Bloch analysis.

Although many physicochemical properties of molten salts have been investigated in recent years, precise studies of rapid chemical processes in the homogeneous liquid phase have not hitherto been reported. We have carried out a ^{1}H n.m.r. study of proton exchange in pure molten ammonium hydrogen sulphate (m.p. 146·9 °C). The proton spectrum just above the melting point consists of a singlet due to HSO_4^- and a triplet due to NH_4^+ (relative shift 3·9 p.p.m.; J_{NH} 53 Hz). Upon heating the salt, the lines of the spectrum broaden and coalesce finally to a single line at about 202 °C. Addition of a small quantity of water to the sample at the melting point gives rise to a broadened HSO_4^- peak shifted upfield (*i.e.* there is rapid proton exchange between HSO_4^- and H_2O) but the triplet is substantially unaffected.

The major constituents of the molten pure salt are thus NH_4^+ and HSO_4^- and possible minor species are NH_3 and H_2SO_4. Protons may be exchanged between the major species contributing to the observed spectrum by three formal processes (1)—(3). These equations are not intended to be mechanistic, but to indicate overall proton-exchange or proton-scrambling reactions.

$$HSO_4^- + H^*SO_4^- \rightarrow H^*SO_4^- + HSO_4^- \qquad (1)$$

$$H_3\overset{+}{N}H^* + NH_4^+ \rightarrow NH_4^+ + H^*\overset{+}{N}H_3 \qquad (2)$$

$$HSO_4^- + H^*\overset{+}{N}H_3 \rightarrow H^*SO_4^- + NH_4^+ \qquad (3)$$

The spectra have been analysed by a four-site model, treated by the Abragam–Bloch theory.[1] It is assumed that quadrupolar relaxation of ^{14}N is very slow, since the triplet is sharp at the melting point and increasing temperature should further reduce the effectiveness of relaxation by this mechanism. Thus the ^{14}N nucleus establishes three spin levels for the protons of the ammonium ion (*spectral* sites). It should be noted that there is no spin–spin coupling between the protons of the ammonium ion and the bisulphate ion involved in exchange and that the system is formally equivalent to a four-site problem without coupling. Simultaneously, we allow for proton exchange between ammonium ions in a formal three-site exchange submatrix.

The total magnetic resonance absorption spectrum is generated by the equation:

$$u(\omega) = \mathrm{Im}\left\{i\omega_1[R + iI]^{-1}M_0\right\}$$

$$R = \mathrm{diag}(1/T_{2i}) + K$$

$$I = \mathrm{diag}(\omega - \omega_i)$$

$$K = \begin{bmatrix} -k_c & \frac{fk_a}{4} & \frac{fk_a}{4} & \frac{fk_a}{4} \\ \frac{k_a}{3} & \left(-\frac{fk_a}{4} - \frac{2k_b}{3}\right) & \frac{k_b}{3} & \frac{k_b}{3} \\ \frac{k_a}{3} & \frac{k_b}{3} & \left(-\frac{fk_a}{4} - \frac{2k_b}{3}\right) & \frac{k_b}{3} \\ \frac{k_a}{3} & \frac{k_b}{3} & \frac{k_b}{3} & \left(-\frac{fk_a}{4} - \frac{2k_b}{3}\right) \end{bmatrix}$$

Where

$$f = [HSO_4^-]/[NH_4^+]$$

$$k_a = \frac{-d[HSO_4^-]}{dt} / [HSO_4] \text{ in process (3)}$$

$$k_b = \frac{-d[NH_4^+]}{dt} / [NH_4^+] \text{ in process (2)}$$

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First-order proton exchange rate constants k_a *and* k_b *from analysis of* ^{1}H *n.m.r. spectrum of ammonium hydrogen sulphate*

T/°C	k_a/s	k_b/s
165	65 ± 3	38 ± 2
175	120 ± 6	60 ± 3
185	159 ± 8	75 ± 4
195	255 ± 13	125 ± 6
205	347 ± 18	163 ± 8

The present results are restricted to the case $f = 1$.

The interpretation of the ^{1}H n.m.r. spectrum in terms of proton lifetimes in various sites (reciprocal first order rate constants) is independent of any assumed mechanisms; the only chemicokinetic assumptions in the analysis are the overall transfer probabilities between those sites of the major species linked by exchange processes. The contribution to the spectrum from minor species (including intermediates) is considered negligibly small. Process (1) has no effect on the spectrum since the HSO_4^- resonance consists of a singlet. Process (2) (cation proton exchange) leads to a collapse of the ammonium ion triplet in which the band retains its symmetry about the central line throughout. Process (3) (cation–anion proton exchange) leads to a total collapse of the spectrum during which the triplet collapses asymmetrically. It is clear from the appearance of the observed spectra (in particular the relative line intensities during collapse) that both processes (2) and (3) actually occur. The Figure shows computed spectra matched to observed spectra at three temperatures. Best values of the independent rate constants k_a and k_b at five temperatures are listed in the Table. The activation energy for both processes is approximately 40 kJ mol^{-1}.

Proton exchange between ammonium and substituted ammonium ions in aqueous solution has been extensively studied by Grunwald and his collaborators,[2] who have identified two contributing reactions, one involving a bridging water molecule, the other a direct process between the ammonium ion and its conjugate base. For the various ions studied these alternative protolyses make comparable contributions to the overall proton exchange. It is clear that the study of molten ammonium salts in the presence of small quantities of species containing labile protons will be of great interest.

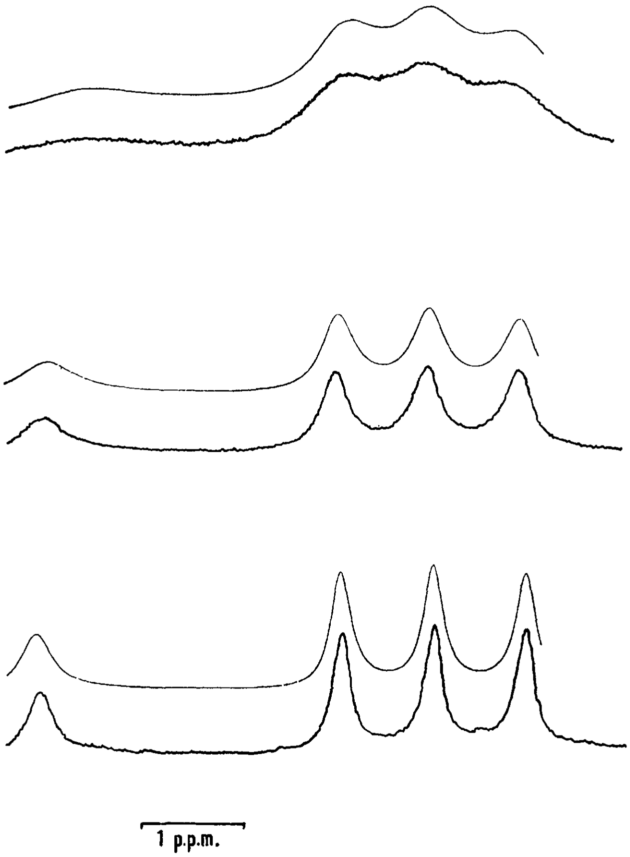

FIGURE. *Computed and observed* ^{1}H *n.m.r. spectra of molten ammonium hydrogen sulphate at* 195 (*upper*), 175 (*middle*), *and* 165 °C (*lower*).

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[1] C. S. Johnson jun., *Adv. Magn. Resonance*, 1966, **1**, 33; C. Hall, D. W. Kydon, R. E. Richards, and R. R. Sharp, *Proc. Roy. Soc.*, 1970, A**318**, 119.

[2] E. Grunwald, *J. Phys. Chem.*, 1963, **67**, 2208.