^{1}H and ^{13}C Nuclear Magnetic Resonance Study of Hindered Rotation and Acid–Base Exchange Rates in Benzaldehydes dissolved in Superacid Medium

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Using ^{13}C and ^{1}H n.m.r. line shape analysis, the complex system of inter- and intra-molecular exchange rates in *p*-chlorobenzaldehyde dissolved in superacidic medium has been investigated. The effect of proton exchange on the measured barrier to internal rotation in the protonated species is shown and the population of unprotonated benzaldehyde has been estimated.

DYNAMIC n.m.r. spectroscopy has become a classical method for the estimation of exchange rates.[1] By this method it has been shown that protonation or Lewis acid adduct formation of amides, benzaldehydes, and acetophenones greatly increases the barrier

[1] H. Kessler, *Angew Chem.*, 1970, **82**, 237.

to rotation.[2-6] This has been explained in terms of the enhanced π character of the σ bond through stabilisation of the resonance form B by protonation or

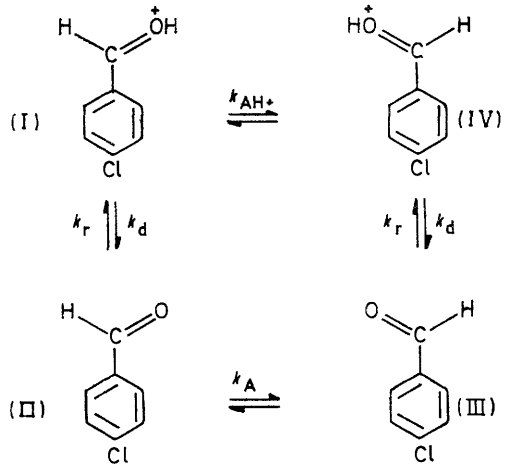
A B

complex formation. In order to show that the rotation rate obtained from n.m.r. line shape analysis is the real rotation rate for the complexed molecule it must be proved either that donor–acceptor exchange is much slower than rotation or that exchange has no effect on the n.m.r. line shape. For some Lewis acid adducts it has been shown that the donor–acceptor exchange is very slow[3] and the rotation rates measured are those for rotation in the complex. On the other hand nobody has tried to estimate the effect of proton exchange on the n.m.r. line shape in such systems.

It is well known that even weak bases undergo protonation in superacidic medium and that the conjugate acid can be observed under long lifetime conditions by n.m.r.[7] To study the effect of proton exchange on the n.m.r. line shape for this type of reaction, we decided to perform a thorough investigation of the system *p*-chlorobenzaldehyde–magic acid–SO_2. In this systm the proton exchange changed by varying the aldehyde: acid ratio. The n.m.r. spectrum of stable protonated *p*-chlorobenzaldehyde[5] at −30° shows three groups of lines: the C=$\overset{+}{O}$H proton as a doublet at δ 13·08 (J 8·0 Hz), the aldehydic proton as a doublet at 9·64 (J 8·0 Hz), and the aromatic protons as an ABCD system centred at 8·20. The lowfield doublets show that there is a slow proton exchange in this superacid solvent. This is not the case when benzaldehydes are dissolved in FSO_3H; no COH^+ proton is observable and there is a narrow singlet for the aldehyde proton.[6]

Line Shape Programs and Evaluation of Exchange Rate Constants.—When the deprotonation rate increases, the low field doublet (COH^+) broadens and vanishes whereas the aldehydic proton doublet reduces to a singlet. The line shape analysis of the COH^+ line broadening cannot be used to calculate the rate of deprotonation because the broadening is not due to a simple two site exchange; it takes into account the exchange between the superacid and traces of protonated water (H_3O^+ peak at δ 10·3). The aldehydic proton signal will be affected solely by the proton exchange, and changed from a doublet (due to spin coupling to the COH^+ proton) at slow proton exchange to a singlet at fast exchange. This process was considered as a simple two site exchange and the line shape was calculated with a computer program based on McConnell's equation.[8] The rate obtained is, however, only half the rate of deprotonation, since if the leaving and the returning protons have the same spin, which will happen at each second exchange, there will be no effect on the aldehydic proton signal.

The total exchange process can be depicted as in the Scheme. The overall rotation, that is to say (I) ⇌ (IV) + (I) ⇌ (II) ⇌ (III) ⇌ (IV), can be evaluated from the ^1H n.m.r. signals of the aromatic protons



SCHEME Total exchange process for *p*-chlorobenzaldehyde in superacid medium

using the program DNMR3 due to Binsch.[9] It can also be obtained from the line shapes from the ^{13}C signals from the *ortho*- and *meta*-carbon atoms using a two site exchange program to simulate the line shapes.

To distinguish between the effects from the two ways of exchange from (I) to (IV) it is necessary to take all exchanges given in the Scheme into account. This can be done with a four site exchange program, which can be constructed using the method employed by McConnell (for a discussion of multi-site exchange see ref. 10). With this simple formalism only the natural abundance ^{13}C n.m.r. line shapes can be simulated. The proton spectrum is far too complex to be handled as a four site exchange.

In the four site exchange program, four different rate constants are needed: k_d the rate of deprotonation, k_{AH^+} the rotation rate in the protonated aldehyde, k_A the rotation rate in the unprotonated aldehyde, and k_r the rate of reprotonation. k_d Can be obtained from the line shape of the aldehydic proton signal (see above), k_{AH^+} can be evaluated at low aldehyde concentration when the proton exchange is slow and is assumed to be independent of the concentration of aldehyde, k_A can be estimated from the $\Delta G^{\ddagger}$ value (8 kcal mol^{-1} at

[2] E. S. Gore, D. J. Blears, and S. S. Danyluck, *Canad. J. Chem.*, 1965, **43**, 2135.
[3] G. Olofsson, P. Stilbs, T. Drakenberg, and S. Forsén, *Tetrahedron*, 1971, 4583.
[4] A. Greenwald and M. Rabinovitz, *Chem. Comm.*, 1969, 642.
[5] R. Jost, P. Rimmelin, and J. M. Sommer, *Chem. Comm.*, 1971, 879.
[6] A. Ellencweig and M. Rabinovitz, *Tetrahedron Letters*, 1971, 4439.
[7] A. White, D. O'Brien, and G. A. Olah, *Chem. Rev.*, 1970, **70**, 560.
[8] H. M. McConnell, *J. Chem. Phys.*, 1958, **28**, 430.
[9] D. A. Kleier and G. J. Binsch, *J. Magnetic Resonance*, 1970, **3**, 146.
[10] I. O. Sutherland, in 'Annual Reports on NMR Spectroscopy,' ed. E. F. Mooney, Academic Press, London, 1971, vol. 4.

$-100°$) for the rotation in the free aldehyde [11] (k_A *ca.* 10^6 s^{-1} at 10°), and k_r can now be obtained through fitting of experimental and theoretical ^{13}C line shapes.

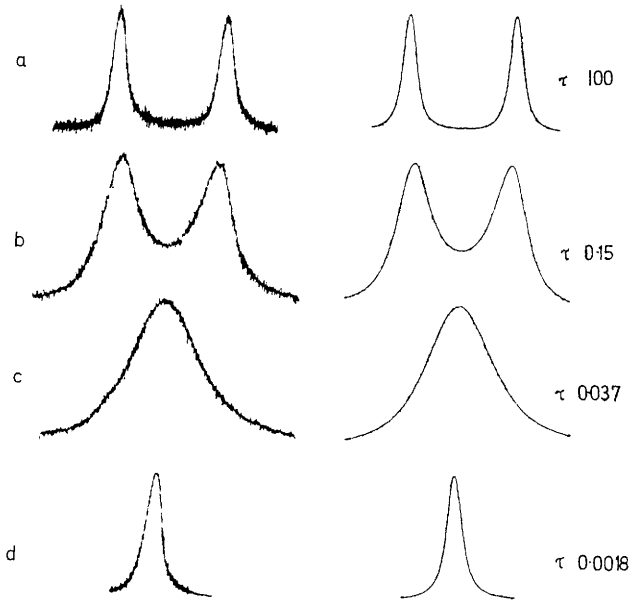


FIGURE 1 Experimental and calculated spectra for the aldehydic proton of protonated *p*-chlorobenzaldehyde at different aldehyde : acid ratios: a, 0·2 : 1; b, 0·6 : 1, C, 0·7 : 1; d, 0·8 : 1

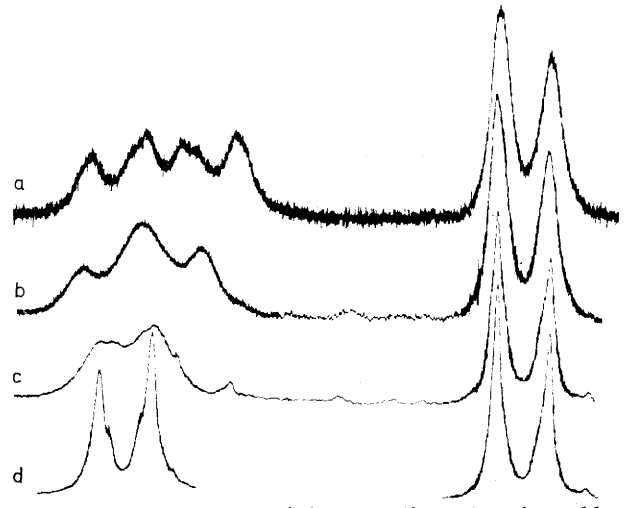


FIGURE 2 N.m.r. spectra of the aromatic protons in *p*-chlorobenzaldehyde at various aldehyde : acid ratios: a, 0·2 : 1; b, 0·5 : 1; c, 0·8 : 1; d, 0·9 : 1

It is not possible to determine the chemical shifts for the unprotonated species, due to its very low concentration. It was, however, possible to show that the line shape of the calculated spectrum was not very sensitive to the chemical shifts choosen for the signals from the unprotonated aldehyde. Thus the chemical shifts obtained for the aldehyde in a non-protonating solvent at low temperature [11] were used.

RESULTS AND DISCUSSION

Figure 1 shows experimental and theoretical spectra from the aldehydic proton for the aldehyde : acid ratio varying between 0·2 : 1 to 0·8 : 1 and the rates of deprotonation are given in the Table. It is easily

Rate constants for deprotonation and overall rotation and the population of the unprotonated aldehyde at various aldehyde to acid ratios.

[Aldehyde] : [acid]	k_d/s^{-1}	$k_{rot}^{overall}/s^{-1}$	p
1·0	10^4	10^{-3}	10^{-3}
0·9	10^4	180	2×10^{-4}
0·8	1100	43	4×10^{-5}
0·7	53	29	4×10^{-5}
0·6	13	23	
0·2	0·01	10 *	

* Equal to k_{AH^+} since there is no proton exchange. k_{AH^+} Is assumed to be concentration independent.

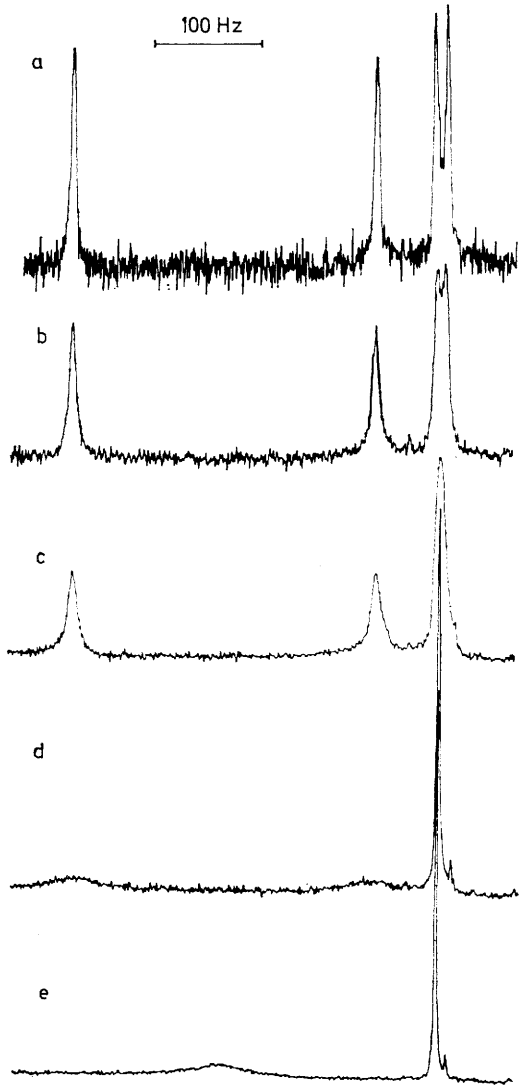


FIGURE 3 Experimental ^{13}C Fourier transform n.m.r. spectra of the *ortho*- and *meta*-carbon atoms of *p*-chlorobenzaldehyde at various aldehyde : acid ratios: a, 0·2 : 1; b, 0·5 : 1; c, 0·7 : 1; d, 0·9 : 1; e, 1 : 1

seen that the deprotonation rate changes from a very slow exchange at the lowest aldehyde concentration ($k_d < 10^{-2}$ s^{-1}) to a very fast exchange at the highest concentration ($k_d > 10^4$ s^{-1}). This system is hence

[11] J. M. Sommer, R. Jost, and T. Drakenberg, unpublished results.

very suitable to study the effect from proton exchange on the n.m.r. line shape.

Figure 2 shows experimental ^1H n.m.r. spectra from the aromatic protons, an ABCD system at slow exchange, changing to an AA'BB' system at fast exchange. The overall exchange rate constants obtained from these spectra are given in the Table and it is obvious, both from line shapes and the rate constants, that the rate of proton exchange has a large effect on the overall exchange. This can be explained in the following way. Even though the population of the unprotonated species is very small (can never be observed by n.m.r.) due to the rapid internal rotation in the unprotonated species, there is a measurable competition between two pathways, either rotation in the protonated aldehyde or deprotonation–rotation in the unprotonated aldehyde followed by reprotonation.

Figure 3 shows the experimental ^{13}C spectra of the *ortho*- and *meta*-carbon atoms at various aldehyde concentrations. The results from the best fitting line shapes, using the four site exchange program, shows that the population of the unprotonated aldehyde even for the highest concentration is low ($p = 10^{-3}$). The reprotonation rate, k_r, did not show any pronounced concentration dependence, but appeared to be constant ($k_r = 1{\cdot}0 \pm 0{\cdot}5 \times 10^7$ s^{-1}). We have also performed a series of calculations with the four site exchange program, assuming fast proton exchange ($k_d = 10^4$ s^{-1}) and varying the population of the unprotonated aldehyde. These calculations show that the population of the unprotonated species has to be $<10^{-6}$ under these conditions to assure that there is no effect on the overall rotation rate constant from rotation in the unprotonated aldehyde.

The conclusion which can be drawn from these results is that one must be very careful when evaluating rate parameters from n.m.r. line shapes for systems where there is more than one possible route of exchange even though the population of the species in one of these routes is very small. Especially, for the type of exchange we have dealt with here, one should be suspicious of results which have been obtained from systems where the n.m.r. signal from the COH^+ proton has not been observed.

EXPERIMENTAL

Samples.—'Magic acid' [SbF_5–FSO_3H (1 : 1)] was obtained from Cationics Inc. and used without further purification. Sulphur dioxide was dried over P_2O_5. *p*-Chlorobenzaldehyde was purified by recrystallisation of the commercial product. The sample with the lowest concentration in benzaldehyde was prepared by mixing at dry ice temperature a sulphur dioxide solution of the superacid with the benzaldehyde directly in a 10 mm n.m.r. tube under vigorous stirring. The following samples were obtained through addition of successively more aldehyde. The aldehyde : acid ratio varied from 0·2 : 1 to 1 : 1 (the accuracy in these concentrations are, however, only *ca.* 10%).

Measurements.—All n.m.r. spectra were recorded with a Varian XL-100-15 spectrometer equipped with the Varian FT-100 Fourier transform system. The proton spectra were recorded in the continuous wave (CW) mode with all settings adjusted to obtain as good line shapes as possible and the ^{13}C spectra were obtained in Fourier transform (FT) mode with proton noise decoupling. For both ^1H and ^{13}C measurements the spectrometer was locked on [$^2H_6$]acetone kept in the space between the 10 and 12 mm n.m.r. tubes. Typical settings for the ^{13}C spectra were spectral width 1000 Hz, acquisition time 2·0 s, pulse width 60 μs, and 1000 transients.

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