Carbon-13 Spin–Lattice Relaxation and Solvation of Organic Ions: n-Butylamine and n-Butylammonium Ion

By GEORGE C. LEVY

(*General Electric Corporate Research and Development, Schenectady, New York* 12301)

Summary Carbon-13 spin–lattice relaxation times in n-butylammonium ion show marked internal or segmental motion in the ion relative to the parent amine.

CARBON-13 spin–lattice relaxation measurements on small, straight chain organic ions can be used to study generalized and specific solvation effects and ion pairing or clustering in all kinds of solvent systems. Observed ^{13}C spin-lattice relaxation times (T_1) yield data on overall molecular tumbling rates and also on internal or segmental motion along the aliphatic chain (which in turn probes the anchoring of the ionic site in the solvent lattice).†

Thus far, segmental motion in aliphatic chains has been observed only in long (>9 carbon) chains[1,2] or in shorter chains that are connected to branching points such as in *NN*-di-n-butylformamide[3] or the side chain of cholesteryl chloride.[4] Segmental motion was found to occur near the aliphatic end of the ten carbon chain in liquid decan-1-ol because intermolecular hydrogen bonding constrained molecular motion near the functional group.[1] In neat

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† These arguments assume ^{13}C–^{1}H dipole–dipole interactions completely dominate the protonated carbon relaxation behaviour but this assumption is justified for the molecules discussed here.

butan-1-ol, however, only a small degree of segmental motion was observed.[3] It was thought that a sizeable molecular constraint on motion was required, in addition to the presence of intermolecular interactions at one end of the molecule. The ^{13}C spin-lattice relaxation behaviour of n-butylamine is analogous to that in butan-1-ol, although all the T_1s are longer, indicating faster overall molecular reorientation. The T_1s for neat n-butylamine are given in the Table. Only a small degree of segmental motion is indicated, the *effective* molecular correlation time (τ_c^{eff}) for the δ-CH_3 carbon being *ca.* 1·3 times τ_c^{eff} for the α-CH_2 carbon.‡ By contrast, when n-butylamine is protonated to the ammonium ion in CF_3CO_2H, the T_1s (Table) indicate that τ_c^{eff} is *ca.* 5 times longer for the CH_3 carbon than for the α-CH_2 carbon. The T_1 data also indicate a distinct increase in τ_c^{eff} for the CH_2 carbons sequentially removed from the ionic site.

TABLE. *Carbon-13 spin-lattice relaxation times for n-butylamine and n-butylammonium ion*[a]

	T_1, (s)[b]			
	α-CH_2	β-CH_2	γ-CH_2	δ-CH_3
Bu^nNH_2 (neat)	13·4	13·4	15·0	12·1
$Bu^nNH_3^+$ $CF_3CO_2^-$				
19·3 mol % in CF_3CO_2H	0·97	1·50	2·13	3·46
10 mol % in CF_3CO_2H	1·54	2·30	3·12	3·98
In CH_2Cl_2–CD_3COCD_3[c]	0·90	1·65	2·49	3·85
	0·92	1·68	2·33	3·95

[a] Determined at 25·16 MHz and 38° on a Varian XL-100-15 Ft n.m.r. spectrometer system using an inversion-recovery pulse sequence. [b] Estimated maximum error ± 5—10%. [c] 1·9 g of the salt in a solvent mixture of 4 ml CH_2Cl_2 and 0·8 ml CD_3COCD_3. Two sets of measurements are given (for the same sample).

The overall shortening of T_1s in the ion by an order of magnitude relative to the free amine arises from electrostatic solute ordering effects as well as intermolecular interactions between the ammonium ion, its counter ion and the solvent shell.

The Table lists T_1s determined for n-butylammonium ion in three solvent systems/concentrations. At two concentrations in CF_3CO_2H the relaxation behaviour was very similar. Some shortening of τ_c and lowering of segmental motion is observed at the lower concentration. In the relatively nonpolar medium CH_2Cl_2–CD_3COCD_3 some increase in segmental motion is evident, although the effect borders on the limit of experimental accuracy.

Studies of cations and anions in various solvent systems are under way to learn what kinds of solute–solvent interactions and what other solvation influences can be studied by this technique.

(*Received*, 18*th April* 1972, *Com.* 659.)

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‡ In calculating reorientation times the number of directly attached protons must be taken into account. Thus CH_2 and CH_3 systems with the same τ_c^{eff} will have T_1s in a ratio of 3 : 2. Sequental motion in the n-butylamine is partly masked by the faster overall reorientation of the amine relative to the alcohol or ammonium ion.

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[2] J. C. Metcalfe, N. J. M. Birdsall, J. Feeney, A. G. Lee, Y. K. Levine, and P. Partington, *Nature*, 1971, **233**, 199.

[3] G. C. Levy and G. L. Nelson, *J. Amer. Chem. Soc.*, 1972, **94**, in the press.

[4] A. Allerhand, D. Doddrell, and R. Komoroski, *J. Chem. Phys.*, 1971, **55**, 189.