Bromine Nuclear Magnetic Resonance Study of the Reorientation of Bromomercurio-*N*-acetyl-L-phenylalanine, Bromomercuriocinnamic Acid, Bromomercuriobenzoic Acid and Bromomercuriomethane in Water

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Bromine nuclear magnetic relaxation times have been measured for aqueous solutions of KBr at 298 K, containing the bromomercury compounds bromomercuriocinnamic acid (CIN), bromomercurio-*N*-acetyl-L-phenylalanine, bromomercuriobenzoic acid and bromomercuriomethane. Br^- exchanges rapidly with the bromomercury compounds. Average spin-lattice relaxation times of ^{79}Br and ^{81}Br have been measured for solutions containing CIN between 273 and 253 K. Correlation times ($\tau_{rot} \approx 10^{-10}$ s at 298 K) for reorientation of the compounds are probably shorter than the pre-exchange lifetimes of bromine on the compounds. The high activation energy ($E_{rot} = 45$ kJ mol^{-1}) for reorientation measured for CIN suggests that hydrogen bonds are broken during the reorientation.

Nuclear magnetic relaxation times of quadrupolar nuclei, e.g., ^{35}Cl, ^{79}Br, ^{14}N, ^{2}H, have been used to study the reorientation of molecules in neat liquids.[1] Relaxation times of halide ions in water which, because of rapid chemical exchanges, are partly determined by the much shorter relaxation times of the halogen bonded to mercury, have been used to study the reorientation of molecules containing the mercury.[2, 3] This so-called halide probe technique has been further used to study the binding of molecules, labelled with mercury, with macromolecules of biochemical interest,[4-6] and also to determine the stability constants of bromomercury compounds in the presence of other ligands.[7]

We have studied four bromomercury compounds: bromomercuriocinnamic acid (CIN), bromomercurio-*N*-acetyl-L-phenylalanine (PHE), bromomercuriobenzoic acid (BEN) and bromomercuriomethane (ME) in aqueous solutions of potassium bromide, in which fast chemical exchange of bromine occurs. CIN and PHE were chosen because they bind reversibly to the enzyme α-chymotrypsin and a study of this binding, using the halide-probe technique, will be published elsewhere. From a detailed study of the temperature and isotope dependence of the measured spin-lattice relaxation times for CIN the spin-lattice relaxation and correlation times of bromine on the organomercury compounds were determined.

EXPERIMENTAL

PREPARATION AND ANALYSIS

Chloromercuriobenzoic acid and iodomercuriomethane were from Koch-Light but the other mercury compounds were synthesized. Acetoximercuriocinnamic acid was prepared by adding cinnamic acid in methanol solution to an equimolar quantity of mercury(II) acetate in a 10:1 methanol/water solution at 333 K with 0.1 % perchloric acid catalyst. A white precipitate formed after vigorous stirring. The product was dissolved in acetic acid and precipitated by the addition of water. It was homogeneous to t.l.c. Results of microanalysis were C 32.3; H 2.6; Hg 48.3 % (theoretical: C 32.2; H 2.4; Hg 49.6 %). The product had a mass spectrum with principal mass ions in the range 403 to 408 mass units characteristic of the isotopic distribution of a monomercurio derivative.

Acetoxi-*N*-acetyl-L-phenylalanine was prepared by mixing equimolar quantities of L-phenylalanine (Sigma Chemical Co.) in alkaline solution with acetic anhydride. The pH of the solution was adjusted to pH 6, when the *N*-acetylated amino-acid was precipitated. This was recrystallised from a water/methanol mixture. *N*-acetyl-L-phenylalanine and an equimolar quantity of mercury(II) acetate were dissolved separately in methanol and mixed at 333 K. A white precipitate immediately began to grow from solution. This was recrystallised from acetic acid. Results of microanalysis were, C 31.5; H 3.08; N 3.34% (theoretical: C 33.54; H 3.23; N 3.01 %).

N.M.R. MEASUREMENTS

The nuclear spin relaxation times T_1 and T_2 of ^{79}Br and ^{81}Br were measured using a Polaron r.f. pulsed spectrometer operating at $2\pi \times 16$ MHz. The probe consisted of a crossed coil arrangement. The coils were wound on a PTFE former; the transmitter coil consisted of 4 turns of 300 s.w.g. Cu wire wound on each side in the Helmholtz manner producing a coil of length 30 mm and 20 mm in diameter. The receiver coil of 8 turns of 32 s.w.g. wire was wound in a solenoid on an 11 mm diameter former. Sample volumes of 0.3 cm^3 were used.

The sample temperature was controlled to $\pm\frac{1}{2}$ K by means of a proportional controller. The sample temperature was measured by a thermocouple in contact with the sample container. T_2, the spin-spin relaxation time, was determined from the free induction decay following a 90° pulse. T_1, the spin-lattice relaxation time, was measured using a $90°$-τ-$90°$ pulse sequence. The length of the 90° pulse was 22 μs and the signal was observed 13 μs after the end of the pulse. As the signal to noise ratio of the free induction decay for 1 mol dm^{-3} KBr solution was 3 :1, the average of 500 measurements was obtained using a boxcar integrator.

RESULTS AND DISCUSSION

BROMIDE ION RELAXATION IN ELECTROLYTE SOLUTION

Average spin-lattice relaxation times ($\overline{T}_1$) of ^{79}Br nuclei in solutions of aqueous KBr containing various concentrations of the mercurials CIN, PHE and BEN at 298 K are shown in fig. 1. All solutions were made up in 0.1 mol dm^{-3} citrate/phosphate buffer at pH 5.5 and contained 1.0 mol dm^{-3} of KBr. The equilibrium binding constants of the mercury compounds with bromide, acetate and water are such that they will be quantitatively converted to bromo-derivatives when dissolved in solutions containing a large excess of bromide.[7] The spin-lattice and spin-spin relaxation times for solutions containing 250 μmol dm^{-3} BEN at 298 K were found to be equal $\overline{T}_1 = 6\ 2 \pm 0.2$ ms and $\overline{T}_2 = 6.2 \pm 0.2$ ms.

In dilute aqueous solutions of KBr the Br nucleus is at the centre of a Br^- ion with noble gas structure, nevertheless the nuclear magnetic relaxation mechanism is quadrupolar and according to Hertz [8] the fluctuating electric field gradients of greatest importance are produced by the reorientation of water molecules in the second hydration sphere and outer regions. The diffusion of cations K^+ in and out of the hydration sphere of Br^- and the rotation of the K^+-Br^- ion pairs, however, generate additional fluctuating field gradients which, at finite ionic concentrations, may contribute to the relaxation rate $1/T_{1\ \text{Br}}$ for Br in the " free " state.[9] The cation RHg^+ has quite a strong affinity for the anion Br^- so that even in low concentrations any RHg^+ will be associated with Br^- in KBr solutions.[7] Whether the bonding in the transient species RHg^+-Br^- is predominantly covalent or ionic, the electric field gradient produced by RHg^+ at Br^- will be much greater than that produced by K^+. Consequently, the relaxation rate $1/T_{1\ \text{RHgBr}}$ for Br in the " bound " state is much faster than the relaxation rate in the " free " state. As each Br^- forms many transient associations with RHg^+, during the time it takes the Br nucleus to relax, an average relaxation time $\bar{T}_1$ is observed, which is shorter than the relaxation time $T_{1\,\mathrm{Br}}$ observed in the absence of RHg^+.

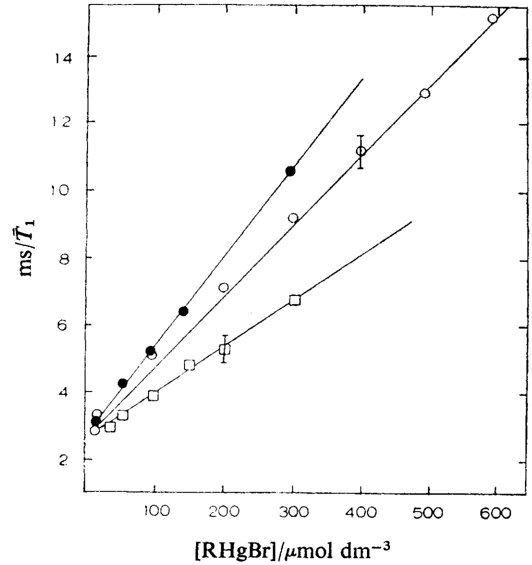

FIG. 1.—Average spin-lattice relaxation rates, $1/\bar{T}_1$, of ^{79}Br in 1 mol dm^{-3}. KBr solutions containing PHE ●, CIN ○ and BEN ☐ against concentration of RHgBr. Measurements were made at 298 K, and at pH 5.5. Straight lines are least-squares fits.

Assuming that $\bar{T}_1 = \bar{T}_2$, and $\tau_{ex} \ll \bar{T}_1$ and that $[Br^-] \gg [RHgBr]$ it has been shown [10] that

$$[\mathrm{Br}^-]/\bar{T}_1 = [\mathrm{Br}^-]/T_{1\,\mathrm{Br}} + [\mathrm{RHgBr}]/(T_{1\,\mathrm{RHgBr}} + \tau_{\mathrm{ex}}) \qquad (1)$$

Where $[Br^-]$ is the concentration of bromide ions, $[RHgBr] \approx [RHg^+]$ is the concentration of the organomercury compound, τ_{ex} is the pre-exchange lifetime of the species RHg^+-Br^-. The data of fig. 1 were fitted to eqn (1) and values of $T_{1\,\mathrm{Br}}$ and $(T_{1\,\mathrm{RHgBr}} + \tau_{ex})$ so obtained are presented in table 1.

TABLE 1.—PARAMETERS FOR ^{79}Br IN EQN (1) OBTAINED FROM THE DATA IN FIG. 1

mercurial	$^{79}T_{1\,\mathrm{Br}}$/ms	$(^{79}T_{1\,\mathrm{RHgBr}} + \tau_{ex})$/ns
BEN	0.43 ± 0.03	71 ± 12
CIN	0.41 ± 0.05	48 ± 8
PHE	0.42 ± 0.04	39 ± 7

$T_{1\,\mathrm{RHgBr}}$ AND τ_{ex}

Fig. 2 shows average relaxation rates of ^{79}Br measured at temperatures between 273 K and 353 K for solutions, buffered at pH 5.5, containing 1.0 mol dm^{-3} of KBr, and similar solutions containing 125 mol dm^{-3} of CIN. The difference between the upper and lower curve is the relaxation enhancement due to CIN. Fig. 3 shows analogous data for ^{81}Br. These data give further insight into the mechanism of

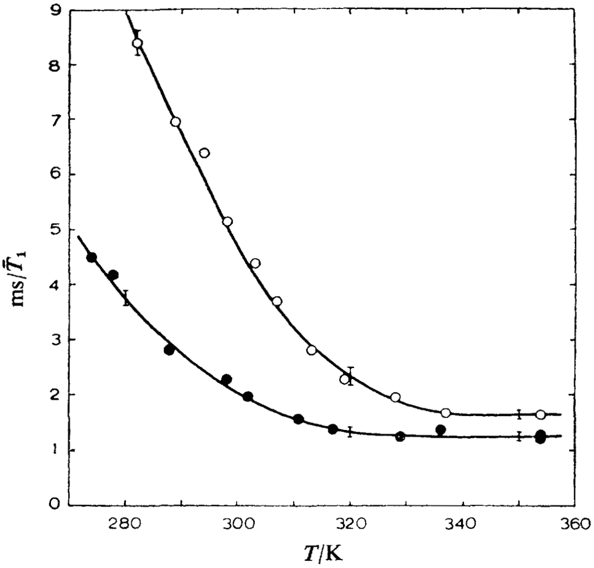

FIG. 2.—Average spin-lattice relaxation rates, $1/\bar{T}_1$, of ^{79}Br in 1.0 mol dm^{-3} KBr solution ●, and 1.0 mol dm^{-3} KBr solution containing 125 μ mol dm^{-3} ClN ○ against $1/T$. Curves are least-squares fits.

relaxation. If it were true that $\tau_{ex} \gg T_{1\ \mathrm{RHgBr}}$ then, as the temperature increased, τ_{ex} would become shorter and the enhancement would increase. This would be most likely to be true at low temperatures but fig. 2 and 3 clearly show that the enhancement decreases with increasing temperature throughout the whole range. This trend is expected in the extreme narrowing situation ($\omega_0\tau_c \ll 1$) if $T_{1\ \mathrm{RHgBr}} \gg \tau_{ex}$. Therefore the values entered in table 1 under ($T_{1\ \mathrm{RHgBr}} + \tau_{ex}$) were taken to be values of $T_{1\ \mathrm{RHgBr}}$ at 298 K.

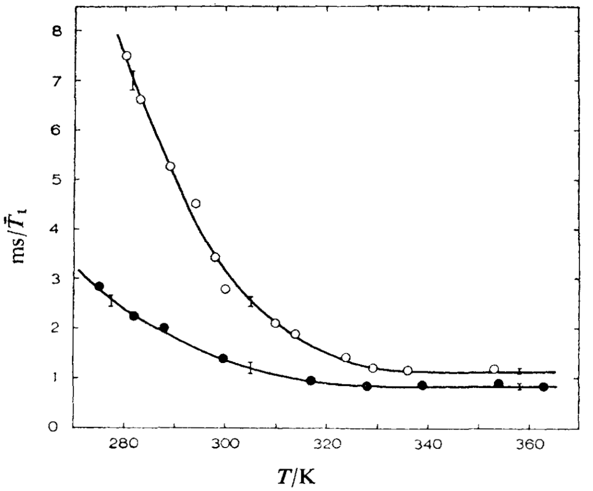

FIG. 3.—Average spin-lattice relaxation rates, $1/\bar{T}_1$, of ^{81}Br in 1.0 mol dm^{-3} KBr solution (●), and 1.0 mol dm^{-3} KBr solution containing 125 μ mol dm^{-3} ClN (○) against $1/T$. Curves are least-squares fits.

MECHANISMS FOR $T_{1\,\mathrm{Br}}$

Following Hertz,[9] the relaxation rate of Br in the solutions containing finite concentrations of KBr only is given by

$$1/T_{1\mathrm{Br}} = \frac{6\pi(2I+3)}{5I^2(2I-1)}\left[\frac{eQ(1+\gamma_\infty)\bar{P}}{\varepsilon_0 h}\right]^2 \times\left[\frac{p^2_{\mathrm{H_2O}}[\mathrm{H_2O}]\tau_{\mathrm{H_2O}}}{r_0^5}+\frac{2e^2[K^+]}{3a^3}f\left(\frac{a}{\alpha}\right)\tau_{\mathrm{KBr}}\right] \tag{2}$$

where $I = 3/2$, e is the electronic charge, Q is the quadrupole moment, γ_∞ is the antishielding factor, $\bar{P}$ is a polarization factor for large separations, $p_{\mathrm{H_2O}}$ is the electric dipole moment of a H_2O molecule, $[H_2O]$ and $[K^+]$ are concentrations of H_2O and K^+ ions respectively, ε_0 is the permittivity of free space, r_0 is the distance between the Br nucleus and the point dipole on the H_2O molecule, a is the distance of closest approach of Br^- and K^+, α is the radius of the ion cloud, $f(a/\alpha)$ is given by Hertz[9] (as $a/\alpha \rightarrow 0$, $f(a/\alpha) \rightarrow 1$ and as $a/\alpha \rightarrow \infty$, $f(a/\alpha) \rightarrow 0$), $\tau_{\mathrm{H_2O}}$ is the correlation time for reorientation of the H_2O molecule, τ_{KBr} is the angular correlation time for the ion pair K^+-Br^-.

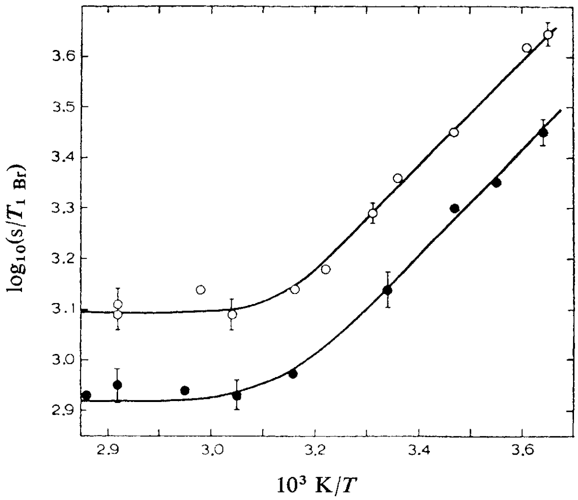

FIG. 4.—Relaxation rates for KBr solution $1/T_{1\,\mathrm{Br}}$, obtained from fig. 2 and 3, versus $1/T$. ^{79}Br – ○, ^{81}Br – ●. Curves calculated from the lower curves shown in fig. 2 and 3.

In fig. 4, $1/T_{1\,\mathrm{Br}}$ is plotted against $1/T$ and it is seen that $^{81}T_{1\,\mathrm{Br}}/^{79}T_{1\,\mathrm{Br}} = 1.49 \pm 0.12$ over the whole range of temperature. It is known from n.q.r. that $(^{79}Q/^{81}Q)^2 = 1.43$,[11] which shows that the relaxation is determined by quadrupolar interactions as given by eqn (2). On the other hand, fig. 4 is divided into two regions: the apparent activation energy below 310 K is $19 \pm$ kJ mol^{-1}, and above 310 K is <3.5 kJ mol^{-1}. Hertz has reported[12] values of 13.8 kJ mol^{-1} (273-298 K) and 12.1 kJ mol^{-1} (308-353 K) for $T_{1\,\mathrm{Br}}$ in KBr solution and 19.2 kJ mol^{-1} (273-298 K) and 13.8 kJ mol^{-1} (308-353 K) for $\tau_{\mathrm{H_2O}}$ in pure water. The simplest interpretation would be that the relaxation is determined by $\tau_{\mathrm{H_2O}}$ in both regions, but that above 310 K the activation energy of reorientation is lower. An alternative interpretation is that relaxation in the high and low temperature regions is determined by two different correlation times, say τ_{H_2O} and τ_{KBr} respectively, in which case the apparent activation energy at low temperatures, obtained by subtracting the estimated contribution of the high temperature process from the observed relaxation rate, would be approximately 40 kJ mol^{-1}.

MECHANISM FOR $T_{1\ \mathrm{RHgBR}}$

The relaxation rate for Br when bound to the organomercury compound is given by the equation [13]

$$1/T_{1\ \mathrm{RHgBr}} = \frac{3(2I+3)}{40I^2(2I-1)}\omega_Q^2\tau_{\mathrm{RHgBr}} \tag{3}$$

where $I = 3/2$, ω_Q is the electric quadrupole coupling constant, τ_{RHgBr} is the correlation time of the electric field gradient at the Br nucleus in the species RHg^+Br^-.

TABLE 2.—PARAMETERS FOR ^{79}Br

mercurial	$^{79}\omega_Q^2\tau_{\mathrm{RHgBr}}$/MHz	τ_{RHgBr}/ps	V/nm^3	τ_θ/ps
PHE	260 ± 49 [a]	54 ± 10 [b]	0.85 [f]	199
CIN	210 ± 35 [a]	43 ± 7 [b]	0.53 [f]	124
BEN	140 ± 25 [a]	29 ± 5 [b]	0.25 [f]	59
BEN (^{35}Cl)	0.35 [c]	6 [c]		
ME	65 ± 5 [d]	13 ± 2 [b]	0.10 [f]	23
$HgBr_4^{2-}$	15 [e]	3 [b]	0.20 [f]	47
	97 [g]	20 [g]		

[a] calculated from $T_{1\ \mathrm{RHgBr}} + \tau_{ex}$ in table 1, using eqn (4), assuming $T_{1\ \mathrm{RHgBr}} \gg \tau_{ex}$. [b] calculated from $^{79}\omega_Q^2\tau_{\mathrm{RHgBr}}$ assuming $^{79}\omega_Q = 2\pi \times 350$ MHz. [c] calculated from data in ref. (4) for chloromercuriobenzoic acid. [d] calculated from one measurement of $\bar{T}_1 = 0.25$ ms in a solution of 1.0 mol dm^{-3} KBr and 250 μ mol dm^{-3} ME at 298 K. [e] calculated from data in ref. (3). [f] calculated from molecular models, assuming $\eta = 10^{-3}$ N s m^{-2}. [g] calculated from data in ref. (2).

Values of $^{79}\omega_Q^2\tau_{\mathrm{RHgBr}}$ were calculated from the data in table 1 using eqn (3) and are entered in table 2. Also given in table 2 are the following data: for ME obtained from one measurement; for BEN calculated from Baldeschweiler's data[4]; for $HgBr_4^{2-}$ calculated from O'Reilly's data.[3] τ_{RHgBr} is given by the relation [24]

$$1/\tau_{\mathrm{RHgBr}} = 1/\tau_{rot} + 1/\tau_{ex} \tag{4}$$

where τ_{rot} is the correlation time for reorientation and τ_{ex} is the pre-exchange lifetime for the RHg^+Br^-.

Fig. 5 shows a plot of $[\mathrm{RHgBr}]/T_{1\ \mathrm{RHgBr}})$ versus $1/T$ for ^{79}Br and ^{81}Br. The data were obtained from fig. 2 and 3 using eqn (1) and assuming $T_{1\ \mathrm{RHgBr}} \gg \tau_{ex}$. As was found for $T_{1\ \mathrm{Br}}$ (fig. 4), the graph in fig. 5 is divided into two regions. The apparent activation energy below 330 K is 45±kJ mol^{-1} and above 330 K is <14 kJ mol^{-1}. The ratio $^{81}T_{1\ \mathrm{RHgBr}}/^{79}T_{1\ \mathrm{RHgBr}} = 1.53 \pm 0.25$, determined from fig. 5, supports the assumption that the relaxation rate is determined by quadrupolar interactions as given by eqn (3), except at low temperatures.

Eqn (4) shows that τ_{RHgBr} is equal to the shorter of τ_{rot} and τ_{ex}. It was shown previously that $\tau_{ex} < T_{1\ \mathrm{RHgBr}}$, consequently for CIN at 298 K (table 1) $\tau_{ex} < 50$ ns. Furthermore, the upper limit for the rate of chemical exchange (diffusion controlled) at 298 K in aqueous solutions is of order 0.1 ns,[15] therefore 50 ns $> \tau_{ex} >$ 0.1 ns.

Rotational correlation times τ_θ given in table 2, were derived from the Stokes–Einstein equation:

$$\tau_\theta = \eta V/kT \tag{5}$$

where V is the effective volume of the molecule (estimated from space-filling models and entered in table 2) in a solvent of viscosity η. It is well known, however, that τ_{rot} derived from n.m.r. measurement for a quadrupolar nucleus tends to be shorter than τ_θ because small molecules do not reorientate diffusionally by many small steps.[1] For ClN at 298 K $\tau_\theta = 0.124$ ns consequently it may be assumed that $\tau_{rot} \approx 0.1$ ns. These estimates indicate that $\tau_{ex} > \tau_{rot}$, therefore $\tau_{RHgBr} = \tau_{rot} \approx 0.1$ ns. These conclusions are also supported by the increase in τ_{RHgBr} with increasing size of the species RHg^+Br^- ($\propto V^{3/2}$) which can be seen from the entries in table 2. This trend would be expected for τ_{rot} but not for τ_{ex}.

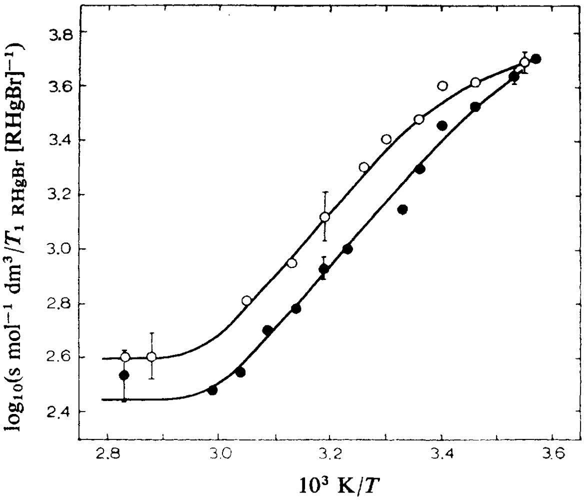

FIG. 5.—Relaxation rates for RHgBr. [RHgBr]/T_1 RHgBr obtained from the data for ClN in fig. 2 and 3, versus $1/T$. ^{79}Br ○, ^{81}Br ●. Points calculated from the lower curve and upper points in fig. 2 and 3, Curves calculated from the curves shown in fig. 2 and 3.

The magnitude of the electric quadrupole coupling constant for Br depends on the kind of bonds in which it is involved. It is greatest when the bonding is strong and assymmetrical, as in CH_3Br (ME) in the gas phase for which the coupling constant for ^{79}Br is reported to be $2\pi \times 350$ MHz[16]; and least when the bonding is weak and symmetrical as in aquated Br^-. Taking $2\pi \times 350$ MHz as the upper limit for the coupling constant in the species RHg^+Br^- then, using eqn (3), the shortest possible value of $\tau_{rot} = 0.043$ ns for ClN at 298 K. Minimum values of τ_{rot} for the other organomercury compounds were calculated in the same way and are given in table 2. On the other hand, the value of $\tau_{rot} \approx 0.1$ ns, estimated previously for ClN at 298 K, leads to an estimate of the coupling constant of $2\pi \times 230$ MHz. The nature of R should not significantly affect the Hg—Br bond, therefore one explanation is that when molecules RHgBr are dissolved in water the Hg—Br bond is weakened, which is to be expected as the chemical exchange of Br^- is rapid. Alternatively, an explanation that could account for some of the discrepancy between the correlation time obtained from n.m.r. and that obtained from molecular size is that relaxation is less efficient for non-spherical molecules.[17] As a result correlation times obtained using eqn (3), which is valid only for spherical molecules, are underestimated.

The apparent activation energy for reorientation of ClN below 330 K is 45 ± 3 kJ mol^{-1}. This is remarkably large and suggests that the hydration sphere surrounding the molecule breaks out of one hydrogen-bonded configuration and reorients into another.[18] Hydrogen bonding may be less important above 330 K and the small temperature dependence suggest that reorientation occurs by the Stokes–Einstein mechanism.

Assuming that τ_{rot} has an Arrhenius-type temperature dependence below 330 K the pre-exponential factor for CIN $\tau^{\circ}_{rot} \approx 10^{-18}$ s is extraordinarily short compared even to the time scale for molecular vibration. The re-orientation of other molecules is aqueous solution also appear to have short pre-exponential factors for the correlation time for reorientation obtained from n.m.r. experiments, e.g., $\tau^{\circ}_{rot} \approx 10^{-16}$ s for $HgBr_4^{2-}$, estimated from the data of O'Reilly,[3] and $\tau^{\circ}_{H_2O} \approx 10^{-15}$ s for H_2O, estimated from the data of Hertz.[12] On the other hand, values of τ°_{rot} obtained for some molecules in neat liquids are more normal, e.g., 6×10^{-14} s for Cl_2CH_2[19] and 10^{-13} s for CPO_3F.[20]

CONCLUSION

This work has shown that the halide-probe technique should be able to detect the binding of CIN and PHE to α-chymotrypsin at room temperature and further work, which it is hoped to report elsewhere, has confirmed this prediction. Interpretation of the data was hampered by uncertainty in the magnitude of the quadrupole coupling constants, nevertheless it was shown that the correlation time for reorientation of CIN is of order 10^{-10} s at 298 K.

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