$Hg(SR)_3$, even though mole ratios of RS^- to $Hg(SR)_2$ in the range 2.0 to 5.0 were used.

The species distribution diagram in Figure 3 shows that, even though the formation constant for addition of the third glutathione ligand to form the $Hg(SG)_3$ complex is much less than those for formation of $Hg(SG)_2$, it is large enough that a significant fraction of the Hg(II) is present as the $Hg(SG)_3$ complex at the concentrations used in the ^{13}C NMR studies. These concentrations are somewhat higher than those used in potentiometric studies;[1,23] however, a significant fraction of the Hg(II) is also present as $Hg(SR)_3$ at the lower concentrations. For example, using the formation constants determined in this work, 16 and 50% of the Hg(II) is calculated to be present as $Hg(SG)_3$ at pH 8 in solutions containing 1×10^{-3} M Hg(II) and 1×10^{-3} M and 7×10^{-3} M GSH, respectively.

The ^{13}C chemical shift data indicates that Hg(II)–ligand binding is exclusively to the deprotonated sulfhydryl groups in the 3:1 complexes of glutathione, cysteine, and penicillamine, with the ammonium groups undergoing titration over essentially the same pH ranges as for the free ligands. However, the ^{13}C NMR results do not provide any information about the geometry of the HgS_3 unit. Vibrational spectroscopy indicates that the mononuclear $Hg(SR)_3$ complexes formed from methanethiolate and *tert*-butylthiolate ligands have a trigonal planar geometry in solution.[24] Assuming this to be the geometry of the $Hg(SR)_3$ complexes of glutathione, cysteine, and penicillamine, the two ligands of $Hg(SR)_2$ and the third ligand to bind become equivalent in the $Hg(SR)_3$ complex and all three ligands have equal probabilities of dissociating to re-form $Hg(SR)_2$ and free ligand. Using the values determined for k_{-1} and k_{-2} for the Hg(II)–glutathione system, the average lifetime of the $Hg(SG)_3$ complex is 7.9×10^{-5} s at pH 6, 1.4×10^{-4} s at pH 7, and 1.57×10^{-4} s at pH 8. Consequently, once formed the complex dissociates very rapidly. Since the three ligands are equivalent in $Hg(SG)_3$ and thus have an equal probability of dissociation, the result is a rapid exchange of free ligand for bound ligand.

In conclusion, it is of interest to use the results of this study to predict the equilibrium and kinetic properties of Hg(II) complexes in vivo. We will take as an example the conditions in human erythrocytes,[25] where the glutathione concentration is $\sim 2.2 \times 10^{-3}$ M and the pH is ~ 7.4. Under these conditions, 9.9, 10.8, and 10.9% of the Hg(II) is predicted to be present as the $Hg(SG)_3$ complex at total Hg(II) concentrations of 1×10^{-4}, 1×10^{-5}, and 1×10^{-6} M, respectively. The average lifetime of the $Hg(SG)_2$ complex before reaction with free glutathione to form $Hg(SG)_3$ is predicted to be 1.1×10^{-3} s while the average lifetime of $Hg(SG)_3$ is predicted to be 1.5×10^{-4} s. Thus, the rate and equilibrium constants determined in this study predict that, even though the stability of $Hg(SG)_2$ is extremely high,[1] exchange of glutathione between its free and Hg(II)-complexed forms will be fast under the conditions present in human erythrocytes, as has been observed experimentally in ^1H NMR studies of Hg(II) binding in intact human erythrocytes.[4] Considering the ubiquity of glutathione in cellular systems,[26] it is likely that the reactions characterized in this work play a major role in the mobility of Hg(II) in biological systems.

Acknowledgment. This research was supported by the Natural Sciences and Engineering Research Council of Canada, by the University of Alberta, and by the National Institutes of Health Grant GM37000. The authors are grateful to Professor R. E. D. McClung and to Joan Pleasants for their help with and the use of their NMR Exchange Programs.

Registry No. Glutathione, 70-18-8; cysteine, 52-90-4; penicillamine, 52-67-5.

(25) Natelson, S.; Natelson, E. A. *Principles of Applied Clinical Chemistry*; Plenum Press: New York, 1978; p 36.

(26) Meister, A. In *Glutathione: Metabolism and Function*; Arias, I. M., Jakoby, W. B., Eds.; Raven Press: New York, 1976; p 35.

Chlorine NMR Studies of Ionized and Associated Silyl Perchlorates

Joseph B. Lambert*,[1a] and Wojciech Schilf[1b]

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60208. *Received February 5, 1988*

Abstract: ^{35}Cl and ^{37}Cl NMR studies have been carried out on triphenylsilyl (sityl) perchlorate and trimethylsilyl perchlorate in sulfolane. Line widths vary from the kilohertz range at 0.1 M concentrations to a few hertz at millimolar concentrations. Chemical shifts vary in an analogous fashion. These observations are consistent with a two-site, fast exchange between associated (e.g., ion-paired) and fully ionized forms of the silyl perchlorate. Quantitative analysis with explicit consideration of the presence of water yielded the equilibrium constant for dissociation of the associated form to free ions and hence percentages of the two forms at each concentration. These results provide unequivocal evidence for the existence of free silylenium ions in dilute sulfolane solution.

Demonstration of the existence of silylenium ions (R_3Si^+) in solution has been difficult over the years[2] and only recently realized.[3-6] Abstraction of hydride from silyl hydrides by triphenylmethyl perchlorate gives triphenylmethane and silyl perchlorates. The reaction is carried out in solvents of high polarity but low nucleophilicity, such as dichloromethane, sulfolane, and acetonitrile. In dilute solution, cryoscopic measurements demonstrated that the silyl perchlorates exist as two particles and conductance measurements showed that they possess an ionic structure, for the cases of tris(alkylthio)silyl [$(RS)_3Si^+$ (R = Me,

---

(1) (a) Supported by the National Science Foundation (Grant CHE86-09899). (b) On leave from the Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland.

(2) For a review of past efforts, see: Corriu, R. J. P.; Henner, M. *J. Organomet. Chem.* **1974**, *74*, 1-28.

(3) Lambert, J. B.; Schulz, W. J., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 1671-1672.

(4) Lambert, J. B.; McConnell, J. A.; Schulz, W. J., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 2482-2484.

(5) Lambert, J. B.; Schulz, W. J., Jr.; McConnell, J. A.; Schilf, W. *J. Am. Chem. Soc.* **1988**, *110*, 2201-2210.

(6) Lambert, J. B.; McConnell, J. A.; Schilf, W.; Schulz, W. J., Jr. *J. Chem. Soc., Chem. Commun.* **1988**, 455-456.

0002-7863/88/1510-6364$01.50/0

Table I. Chlorine NMR Parameters for Trimethylsilyl Perchlorate in Sulfolane

concn, M	δ	line width,[a] Hz		$^{35}Cl/^{37}Cl$	% free ion[b]
		^{35}Cl	^{37}Cl		
0.584	-28	1960	1100	1.8	20 ± 5
0.292	-24	1720	910	1.9	29 ± 5
0.146	-23	1520	880	1.7	35 ± 7
0.073	-22.5	1320	800	1.65	37 ± 8
0.036	-18	950	530	1.8	52 ± 12
0.0288	-16.6	790	450	1.8	57 ± 13
0.023	-15	650	410	1.6	61 ± 13
0.018	-12	590	360	1.6	67 ± 11
0.0147	-10	470	280	1.7	71 ± 10
0.0118	-7.6	350	200	1.75	77 ± 10
0.0094	0.9	310	160	1.9	89 ± 5
0.0047	4.4	24	21	1.14	98 ± 1

[a] Line width at half-height; the error is probably about 10%. [b] Calculated from the ^{35}Cl line width and chemical shift parameters; the errors represent the range.

Et, iPr)],[3,5] triphenylsilyl or sityl (Ph_3Si^+),[4,5] and trimethylsilyl (Me_3Si^+).[6] The concentration dependence of the conductance indicated that free ions are in equilibrium with ion-paired or covalent forms.[5] Moreover, the ^{29}Si resonances at high concentrations were clearly characteristic of associated forms.[5,7] The poor receptivity of ^{29}Si prevented measurements from being made at the dilute concentrations at which free ions were indicated by cyroscopy and conductivity. All previous evidence is consistent with the equilibrium of eq 1 between free ions and associated forms that include ion pairs or covalent species.[3-7]

$$R_3Si^+ + ClO_4^- \rightleftharpoons R_3Si^+ClO_4^- \rightleftharpoons R_3SiOClO_3 \qquad (1)$$

We[5,6] and others[7,8] have used the chlorine nucleus as a probe for the nature of the species formed on abstraction of hydride from silyl hydrides. The ^{35}Cl and ^{37}Cl nuclei have spins of $^3/_2$ and large quadrupole moments (respectively, -0.08 and -0.0632 × $10^{-28}Q/m^2$).[9] In the presence of large electric field gradients, chlorine line widths should be quite large. When chlorine is engaged in covalent bonds, line widths indeed are many kilohertz (13 kHz for CCl_4). In the tetrahedral environment of a free perchlorate anion, however, the electric field gradient approaches zero, so that quadrupolar relaxation is ineffective. The ^{35}Cl or ^{37}Cl line width of ionic ClO_4^- therefore should be quite narrow (the situation is analogous to ^{14}N in NH_4^+). When perchlorate is associated in an ion pair or is part of a covalent bond, the ^{35}Cl and ^{37}Cl resonances should be broadened. Even the line width of the spherical Cl^- ion is broadened when it is disturbed by complexation.[10] An equilibrium between free and associated species should give concentration-dependent line widths. We report herein the detailed examination of ^{35}Cl and ^{37}Cl line widths and chemical shifts of sityl perchlorate and trimethylsilyl perchlorate. The results provide a quantitative measure of the percentages of free and associated perchlorate.

Results

All experiments were performed in carefully dried sulfolane. For Me_3SiClO_4, both ^{35}Cl and ^{37}Cl experiments were carried out on the same sample. Table I contains data for Me_3SiClO_4 on chemical shifts, which are essentially the same for both nuclides, and on line widths, which are different for the two nuclides because of differences in nuclear quadupole coupling constants. The line widths vary from the kilohertz range to about 20 Hz in the concentration range examined. The chemical shift varies over a range of about 30 ppm, with movement toward high frequency (low field) at lower concentrations. The variations of line width and chemical shift are illustrated for ^{35}Cl in Figure 1.

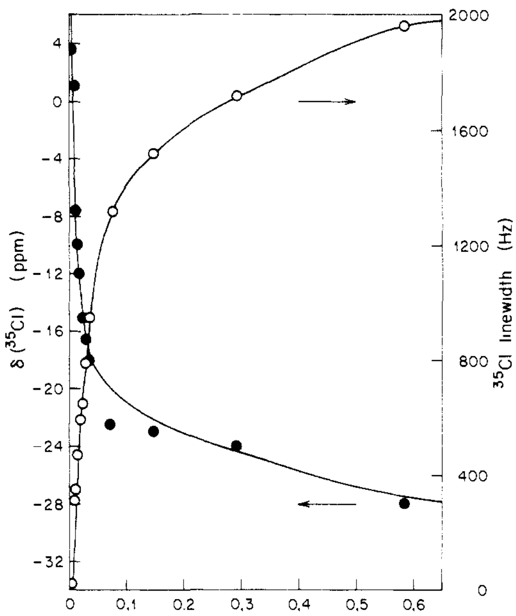

Figure 1. ^{35}Cl line width in Hz (open circles) and the ^{35}Cl chemical shift in δ from dilute $HClO_4$ (filled circles) as a function of concentration for trimethylsilyl perchlorate in sulfolane.

Table II. Chlorine NMR Parameters for Triphenylsilyl Perchlorate in Sulfolane

concn, M	δ	^{35}Cl line width,[a] Hz	% free ion[b]
0.0292	-20.3	530	51 ± 17
0.0234	-20.3	390	56 ± 22
0.0187	-18.6	355	59 ± 20
0.0150	-16.2	330	63 ± 18
0.0120	-13.1	280	68 ± 15
0.0096	-9.1	260	74 ± 11
0.00765	-5.8	200	80 ± 8
0.00612	+2.8	57	96 ± 2
0.00490	+4.1	16	98 ± 1

[a] Line width at half-height. [b] Calculated from the line width and chemical shift parameters; the errors represent the range.

Table III. Chlorine NMR Parameters for Perchloric Acid in Sulfolane

concn, M	δ	^{35}Cl line width,[a] Hz
0.146	3.00	25
0.073	3.52	19.5
0.036	3.75	18.4
0.0090	3.99	14.7
0.0045	4.28	13.0
0.00225	4.5	10.0

[a] Line width at half-height.

Table II contains analogous data for Ph_3SiClO_4; ^{37}Cl experiments were not performed in this case. The trends are analogous to those for Me_3SiClO_4, except that the lower solubility of Ph_3SiClO_4 prevented carrying the experiments to higher concentrations.

For comparison, measurements also were carried out on perchloric acid itself (70% aqueous $HClO_4$) in sulfolane (Table III).

Discussion

The expectation for a covalent or ion-paired species is a ^{35}Cl or ^{37}Cl line width in the kilohertz range, which was observed for the trimethylsilyl case above 0.04 M (^{35}Cl) or 0.3 M (^{37}Cl). The expectation for a free ion is a sharp peak (in the 10-Hz range), which was observed below 0.01 M. Thus, these silyl perchlorates appear to exist in rapidly equilibrating free and associated states,

---

(7) Prakash, G. K. S.; Keyaniyan, S.; Aniszfeld, R.; Heiliger, L.; Olah, G. A.; Stevens, R. C.; Choi, H.-K.; Bau, R. *J. Am. Chem. Soc.* **1987**, *109*, 5123-5236.

(8) The application of chlorine NMR spectroscopy to this problem was first suggested by the USC group.

(9) Brevard, C.; Granger, P. *Handbook of High Resolution Multinuclear NMR*; Wiley-Interscience: New York, 1981; p 106.

(10) Sugawara, T.; Yudasaka, M.; Yokoyama, Y.; Fujiyama, T.; Iwamura, H. *J. Phys. Chem.* **1982**, *86*, 2705-2709.

since only one signal is observed at a given concentration. This conclusion is in agreement with the concentration dependence of the conductance.[5,6] Moreover, *the sharp line widths occur in the concentration range at which all previous conductance and cryoscopic experiments were carried out and on which all claims for silylenium ions in solution were based.*[3-6]

The ^{35}Cl NMR spectra of perchloric acid ($HClO_4$) show relatively sharp peaks into the 0.1 M range (Table III). Although this material consequently is primarily in the free-ion state, both line width and chemical shift show the trends expected for association at higher concentrations. The effects, however, are small compared with those of the silyl perchlorates. Extrapolation to infinite dilution suggests a line width of about 7 Hz and a chemical shift of about δ 5.1 for the free ion. These effects have been observed previously for $HClO_4$.[11]

The concentration dependence of the NMR parameters may be analyzed quantitatively in order to obtain relative amounts of the free and associated forms. Equation 2 describes the equilibrium in a dissociative fashion, in which AB is the associated form, A is the silyl cation, and B is the perchlorate ion. It is assumed that the NMR behavior of all associated forms may be treated as if they result from a single species, although it may be only approximately true. The desired equilibrium constant K is given by eq 3. The total concentration in solution of silicon-containing materials c_o is known by measurement and is comprised of the sum of the amounts of associated (AB) and free (A) species, eq 4. Thus, c_{AB} in eq 3 is equal to $c_o - c_A$. If the system were completely dry, c_A would equal c_B in eq 3 and K could be reduced to a single variable (c_A or c_B). Any water would react with A to give R_3SiOH, however, thereby removing some silicon-containing material from the equilibrium. The extent of hydrolysis may be included explicitly in the calculation, since the amount of A is reduced by however much water is present while the amount of B is unaffected ($R_3Si^+ClO_4^- + H_2O \rightarrow R_3SiOH + H^+ + ClO_4^-$), eq 5, in which c_W is the original concentration of water.

$$R_3SiClO_4 \rightleftharpoons R_3Si^+ + ClO_4^- \tag{2a}$$

$$AB \rightleftharpoons A + B \tag{2b}$$

$$K = c_A c_B / c_{AB} \tag{3}$$

$$c_o = c_A + c_{AB} \tag{4}$$

$$c_A = c_B - c_W \tag{5}$$

Thus, after hydrolysis there would be a slight excess of B over A (the presence of R_3SiOH in solution would have little or no effect on the chlorine NMR parameters). The equilibrium constant may be rewritten as eq 6 by consolidating eq 4 and 5. This expression now has two unknowns, the amount of free perchlorate (c_B) and the original amount of water (c_W). The mole fraction of free perchlorate is given by eq 7 in terms of concentrations and by eq 8 in terms of NMR observables (the observable m may be either chemical shift or line width; m is the observed value, m_B is the value for the free perchlorate, and m_{AB} is the value for the associated perchlorate). This expression assumes that the equilibrium between A and AB is fast on the NMR time scale. The expressions of eq 7 and 8 may be equated and used to substitute for c_B in eq 6. Solving for the experimentally known c_o then gives the final closed expression, eq 9.

$$K = (c_B - c_W)c_B / (c_o - c_B) \tag{6}$$

$$X_B = c_B / (c_B + c_{AB}) = c_B / c_o \tag{7}$$

$$X_B = (m - m_{AB}) / (m_B - m_{AB}) \tag{8}$$

$$c_o = (m_{AB} - m_B)[m(K - c_W) - Km_B + c_W m_{AB}] / (m_{AB} - m)^2 \tag{9}$$

Table IV. Parameters for Free and Associated Silyl Cations

	Me_3SiClO_4	Ph_3SiClO_4
K from line width (^{35}Cl)	0.04 ± 0.01	0.04 ± 0.01
K from line width (^{37}Cl)	0.04 ± 0.01	
K from δ	0.03 ± 0.02	
line width (^{35}Cl) free ion (m_A), Hz	10 ± 4	10 ± 4
line width (^{37}Cl) free ion (m_A), Hz	10 ± 4	
δ free ion (m_A)	5 ± 1	5 ± 1
line width (^{35}Cl) assod ion (m_{AB}), Hz	2600 ± 100	1700 ± 100
line width (^{37}Cl) assod ion (m_{AB}), Hz	1500 ± 100	
δ assod ion (m_{AB})	−33 ± 2	−33 ± 2
concn H_2O (c_W), M	<0.004	0.004 ± 0.002

We have fitted eq 9 to the experimental data by means of a locally written least-squares program, which allows four parameters to vary: K (the dissociation constant), c_W (the amount of water originally present), m_A (the chemical shift or line width for free perchlorate), and m_{AB} (the chemical shift or line width for associated perchlorate). When sufficient data are recorded (Tables I and II, respectively, have 12 and 9 points), these parameters may be calculated. Table IV lists the results.

Calculations were carried out for trimethylsilyl perchlorate on three independent data sets: ^{35}Cl line widths, ^{37}Cl line widths, and chemical shift (identical for the two nuclides). Remarkably consistent results were obtained for the equilibrium constant by these three independent calculations (Table IV). The ^{35}Cl line width for the associated form is about 2600 Hz (1500 Hz for ^{37}Cl). These figures may be underestimates, as we found that the calculation is sensitive to the upper limit of concentrations used. Visual examination of the data (Figure 1), however, suggests that a value in the mid 2000s (Hz) for ^{35}Cl is reasonable. Similarly, the chemical shift of the associated form appears to be well defined in the low −30s (ppm). The figures for the free ions (line width about 10 Hz, chemical shift about δ 4) are consistent with our own observations in sulfolane for normally ionic materials such as $HClO_4$ (Table III) and Ph_3CClO_4. From the values of m_B and m_{AB}, the mole fractions of free ions could be calculated for each concentration. These results are presented in Table I as percentages. For trimethylsilyl perchlorate at 0.0047 M, there is 98% free ion, whereas at 0.584 M there is only about 20%.

The concentration of water proved to be negligible, insofar as it would affect the line-width and chemical shift parameters recorded in these experiments. The actual value from the calculation was slightly less than zero, so we artificially imposed values of 5, 10, and 15 ppm (Karl Fischer titrations[5] of the solvent indicated water in the 5–15 ppm (ca. 0.001 M) range). These impositions did not alter the results. Thus, water at the level of the experiment has an imperceptible effect on the enormous changes in line width and chemical shift seen in Figure 1.

The lower solubility of triphenylsilyl (sityl) perchlorate permitted a smaller range of concentrations for the experiments (Table II). Measurements were begun at concentration levels for which an entirely clear solution could be obtained. The equilibrium constant for sityl perchlorate is essentially the same as that for trimethylsilyl perchlorate (Table III). Measurements were not carried out in this case for ^{37}Cl. The ^{35}Cl line width for the associated form appears to be somewhat less than that for trimethylsilyl, although this result may be an artifact of the lower value of the upper limit to concentration. The concentration of water (ca. 0.004 M) according to the calculation may be comparable to that of the lowest point but is probably lower.

The relative line widths of the ^{35}Cl and ^{37}Cl resonances provide information about the possibility of slow exchange between the free and associated forms. Previous extensive work in biochemical systems[12] offers background for this area. For the present small

---

[11] Akitt, J. W.; Covington, A. K.; Freeman, J. G.; Lilley, T. H. *Trans. Faraday Soc.* **1969**, *65*, 2701–2711. Masuda, Y.; Kanda, T. *J. Phys. Soc. Jpn.* **1954**, *9*, 82–87.

[12] Forsén, S.; Lindman, B. *Methods Biochem. Anal.* **1981**, *27*, 289–486. Falke, J. J.; Pace, R. J.; Chan, S. I. *J. Biol. Chem.* **1984**, *259*, 6472–6480.

molecules it is expected that the extreme narrowing limit holds. Our experiments with the two isotopes of chlorine provide a test for whether exchange is slow. If the line width were controlled by slow exchange, transverse relaxation should be essentially independent of the isotopic identity. The ratio of ^{35}Cl and ^{37}Cl line widths should then be unity.[12] On the other hand, if exchange is fast, the ratio of line widths should go as the square of the ratio of quadrupole moments ($1.26^2 = 1.6$).[9,12,13] Indeed, except for the lowest concentration, the ratio of line widths is in the range 1.6–1.9. Thus, throughout the range of concentrations, exchange between free and associated perchlorate is fast. A possible alternative explanation, that the line broadening derives from exchange between environments with a very large chemical shift difference, is excluded by the observation of only a 38 ppm chemical shift difference (Table IV) between the species. We may conclude that each perchlorate ion must visit a silyl cation many times on the time scale of transverse relaxation, even at 0.584 M.[14]

Conclusions

Triphenylsilyl and trimethylsilyl perchlorates exist in an equilibrium between free silylenium ions and an associated form that may be covalent or ion-paired. The chlorine resonances change from a broad peak of line width in excess of 1000 Hz above 0.1 M to a sharp peak of line width less than 30 Hz below 0.005 M. The chemical shift responds in like manner, moving from a value of about δ −30 for the associated form to about δ 5 for the free ion. The ^{35}Cl/^{37}Cl line width ratio of about 1.6 requires that exchange between free and associated forms be fast. The equilibrium constant between free and associated forms and the percentages of individual species may be calculated from a least-squares analysis of the data. For both trimethylsilyl and triphenylsilyl, the free ion is present at the 50% level at about 0.03 M and at the 98% level at 0.005 M. By 0.5 M, free Me_3Si^+ has dropped to 20%. The amount of water in solution both by direct measurement and from the least-squares calculation is below 0.004 M and can have no palpable effect on the observations.

Experimental Section

All NMR spectra were recorded on a Varian XLA-400 spectrometer (^{35}Cl at 39.17 MHz, ^{37}Cl at 32.61 MHz). Chlorine chemical shifts are reported with respect to external dilute $HClO_4$ in D_2O. The solvent sulfolane was dried over BaO initially and distilled. It was then dried over CaH_2, again distilled, and stored over CaH_2. The silyl perchlorates were prepared by the reaction of the appropriate silane with trityl perchlorate, as described previously.[5] Dilutions were carried out by removing a portion of the sample and replacing it with the same amount of solvent. Measurements for ^{35}Cl and ^{37}Cl were carried out on the same solutions in consecutive experiments in order to achieve identity of concentration and temperature. All experiments were repeated and found to be reproducible.

---

(13) Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy*; Pitman: London, 1983; p 232.

(14) We appreciate useful comments of a reviewer regarding the isotopic ratios of chlorine line widths.

Solid-State ^{2}H NMR Investigation of Internal Motion in 2′-Deoxythymidine

Agustin Kintanar, Todd M. Alam, Wen-Chang Huang, Deborah C. Schindele,[†]
David E. Wemmer,[‡] **and Gary Drobny***

Contribution from the Department of Chemistry, University of Washington,
Seattle, Washington 98195. *Received January 28, 1988*

Abstract: ^{2}H NMR spectroscopy is used to characterize the dynamics of 2′-deoxythymidine in the solid state. Three different specifically deuteriated nucleosides were prepared, with labels at the methyl group, at the C6 position, and at the 5′-methylene group, respectively. The ^{2}H NMR quadrupole echo line shapes and spin–lattice (T_1) relaxation times were analyzed to determine the mechanism and rate of motion of the labeled moieties. Only the methyl group undergoes large-amplitude motion, which consists of 3-fold jumps about the C_3 symmetry axis with a room-temperature correlation time $\tau_c \sim 3.0$ ps. The apparent activation energy (E_a) for this process is 5.9 kJ/mol. The data also indicate that the entire pyrimidine base undergoes a rapid, small-amplitude motion, which we have modeled as a ±9° libration about the equilibrium position. At 298 K, the libration occurs with correlation time $\tau_c \sim 1.0$ ps. The motion of the pyrimidine base also affects the methyl group, but the added motion causes only a small variation in the room-temperature methyl jump correlation time, $\tau_c \sim 4.2$ ps. The librational motion makes only a small contribution to the spin–lattice relaxation of the methyl deuterons, and this likely does not contribute significantly to the unusually low value of the apparent activation energy that is observed. The 5′-methylene group also appears to be undergoing a similar libration (±10°) as the pyrimidine base but with a much longer correlation time, $\tau_c \sim 200$ ns at room temperature. From the models of motion and the experimental line shapes, we are able to determine the static values of the asymmetry parameter (η) and the quadrupole coupling constant for deuterons at the various sites. The static asymmetry parameter was assumed to be zero for the methyl and methylene deuterons, while $\eta_{static} \sim 0.03$ for the deuteron at the 6-position on the pyrimidine base. The static quadrupole coupling constants are 159, 174, and 179 kHz for the methyl, methylene, and base deuterons, respectively.

The realization that proteins, DNA, and RNA are highly dynamic structures has focused interest on the role of internal motion in the function of these biomolecules.[1] Solid-state ^{2}H NMR spectroscopy is a powerful method for investigating these dynamic processes. The rate and type of motion of various deuteriated moieties may be deduced from analysis of the powder pattern line shapes and the spin–lattice (T_1) relaxation times of ^{2}H NMR spectra.[2-6]

[†] Present address: Ultra Diagnostics Corp., Seattle, WA 98105.

[‡] Present address: Department of Chemistry, University of California, Berkeley, CA 94720.

(1) (a) Gurd, F. R. N.; Rothgeb, T. M. *Adv. Protein Chem.* **1979**, *33*, 73–165. (b) Karplus, M.; McCammon, J. A. *CRC Crit. Rev. Biochem.* **1981**, *9*, 293–349. (c) Holbrook, S. R.; Kim, S.-H. *J. Mol. Biol.* **1984**, *173*, 361–388. (d) Kearns, D. R. *CRC Crit. Rev. Biochem.* **1984**, *15*, 237–290.

0002-7863/88/1510-6367$01.50/0