Acta Chemica Scandinavica A 38 (1984) 781–787

Carbon-13 NMR Spin-lattice Relaxation Studies on 2-Chloro-1,3,2-dioxarsolane and its Ring-substituted Methyl Derivatives

DAGFINN W. AKSNES and KARI RAMSTAD

Department of Chemistry, University of Bergen, Allegt. 41, N-5000 Bergen, Norway

The carbon-13 spin-lattice relaxation times (T_1) of the dioxarsolanes were measured in the temperature range 274–353 K by use of the inversion recovery method. The variable temperature T_1 measurements show that the spin-lattice relaxation is governed by the dipole-dipole mechanism below ~320 K. At higher temperatures, however, a clear curvature in the Arrhenius plots indicates that the spin-rotation mechanism is also operative. The overall and internal rotational diffusion constants, D and D_{int}, were deduced from the T_1 data on the basis of the stochastic diffusion model. The temperature dependence of D and D_{int} was found to follow an Arrhenius-type behaviour with activation energies of 23–24 and 9–17 kJ mol^{-1}, respectively. The calculations show that the rate of methyl rotation in 2-chloro-4-methyl-1,3,2-dioxarsolane and *trans*-2-chloro-4,5-dimethyl-1,3,2-dioxarsolane is similar and about three times faster than in the *cis* isomer of the latter compound. The internal methyl rotation of the *cis*-4,5-dimethyl groups thus appears to be severely hindered as judged from the relatively slow rotation and high activation energy.

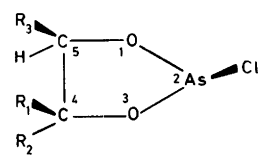
The use of carbon-13 NMR spin-lattice relaxation times (T_1) as a means of investigating molecular dynamics in liquid systems has been well established.[1] T_1 studies can, in particular, yield useful information about rapid molecular motions on a time scale that is far shorter than what is available with more conventional NMR techniques.[1]

Previous ^{1}H and ^{13}C NMR studies on five-membered arsenites and related compounds have largely concentrated on determination and interpretation of chemical shifts and spin-spin coupling constants[2,3] whereas T_1 measurements have received very limited attention in spite of their potential usefulness.[4,5]

In this paper we report the determination of T_1 as a function of temperature of the 1,3,2-dioxarsolanes shown below. The main objective of this investigation was to define the relaxation mechanisms present in these systems, to gain information about overall and internal motions in five-membered arsenites and to study the effect of increasing methyl-substitution on the T_1 times.

RESULTS AND DISCUSSION

The ^{13}C resonance signals for the present compounds have been assigned on the basis of a previous paper.[2g] Compound II has previously been found to exist as a mixture of *syn* and *anti* isomers at 183 K.[2e] However, only exchange-averaged ^{1}H and ^{13}C spectra resulting from rapid



I; $R_1=R_2=R_3=H$
II; $R_2=R_3=H, R_1=CH_3$ (syn)
$R_1=R_3=H, R_2=CH_3$ (anti)
III; $R_2=H, R_1=R_3=CH_3$ (cis)
$R_1=H, R_2=R_3=CH_3$ (trans)

0302-4377/84 $2.50
© 1984 Acta Chemica Scandinavica

intermolecular exchange of chlorine, were observed for compounds I–III in the studied temperature range (274–353 K). The exchange of chlorine proceeds with inversion at arsenic since retention of configuration at arsenic would preserve the chemical shift differences and not lead to the observed averaging.

The chlorine exchange will have a negligible effect on the ^{1}H and ^{13}C line-widths since the substituent at arsenic only introduces small shielding differences[2e,6] in the absence of exchange. Furthermore, the exchange process will not directly affect T_1 but will only give rise to averaged T_1 values for nuclei with exchanging environments like, for example, the *syn* and *anti* methyl groups in II.

The experimental T_1 data for compounds I–III are presented in Tables 1–3. All T_1 values were initially plotted as semilogaritmic plots of T_1 *versus* reciprocal temperature and visually checked for linearity as demonstrated in Fig. 1. The linear rise in $\ln T_1$ with decreasing reciprocal temperatures (for temperatures below ~320 K) is indicative of predominating dipolar relaxation.[1] At higher temperatures, however, the clear curvature in the Arrhenius plots shows that the spin-rotation mechanism is also operative (see Fig. 1).

The intramolecular dipolar relaxation time T_1^{DD} is related to the observed relaxation time T_1^{obs} and the nuclear Overhauser effect η through eqn. (1).

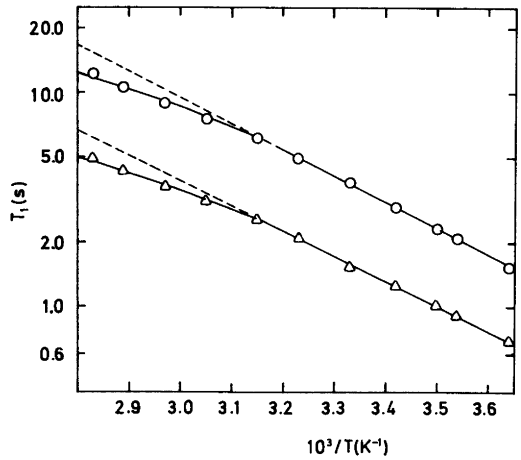


Fig. 1. Carbon-13 spin-lattice relaxation times in 2-chloro-4,5-dimethyl-1,3,2-dioxarsolane plotted *versus* reciprocal temperature. ○ and △, methine and methyl carbons, respectively.

$$T_1^{DD}=2T_1^{obs}/\eta \quad (1)$$

We have measured the nuclear Overhauser effect in compounds II and III. For II the average η values of three runs are identical, within experimental error, for the CH, CH_2, and CH_3 carbons, *viz* 1.9 and 1.8 at 301 and 350 K, respectively. Calculations based on eqn. (1) give the following η values: 1.5, 1.6, and 1.8 for the CH, CH_2, and CH_3 carbons, respectively, and 2.0

Table 1. Carbon-13 spin-lattice relaxation times, effective correlation times and rotational diffusion constants for 2-chloro-1,3,2-dioxarsolane.[a]

Temp. (K)	T_1(s) C-4	$\tau_{eff}(CH_2)$ (ps)	$D(CH_2)^b$ $\times 10^{-10}(s^{-1})$
349.0	7.11(9.62)	2.40	6.88
340.5	6.21(7.83)	3.00	5.60
329.0	5.02(5.83)	4.60	3.59
319.0	4.08(4.47)	5.20	3.20
310.0	3.30	7.10	2.36
303.0	2.68	8.70	1.92
295.5	2.21	10.5	1.58
289.0	1.69	13.8	1.21
279.5	1.15	20.3	0.82
275.5	1.04	22.4	0.74

[a] The values in parentheses are the calculated T_1^{DD} values used for calculating the correlation times and rotational diffusion constants in the high-temperature range. [b] E_a=24.5±1.0 kJ mol.$^{-1}$ The estimated uncertainty in E_a is 90 % confidence limit.

for all carbons at ~300 K. For compound III the average η values of two runs at 351 K are in the range 1.8 to 2.0 for the different carbons. The values calculated by means of eqn. (1) are in the range 1.5 to 1.7. The errors in the measured η values are of the order ±10 %. It is thus seen that the two methods give identical results within experimental error. However, since accurate nuclear Overhausers experiments are difficult, we believe that the dipole-dipole contribution to the relaxation rate is more accurately determined from the temperature dependence of T_1.

The T_1 data for temperatures below ~320 K where the spin-lattice relaxation is governed by the dipole-dipole mechanism, have been fitted to a common two-parameter Arrhenius equation. The listed values for the correlation times and the rotational diffusion constants in Tables 1–3 have been calculated on the basis of the experimental T_1 data, except for the high temperature range where the calculated intramolecular dipolar relaxation times T_1^{DD} (given in parentheses in Tables 1–3) were used. However, only data from the linear part of the semi-logaritmic plots were utilized when calculating the activation energies.

The relative magnitude of the CH_3 relaxation times, in comparison with those of the CH and CH_2 carbons, indicates that the rotation about the C–CH_3 bond is somewhat hindered. However, to directly compare the T_1 data for the different carbons on a quantitative basis, the T_1 values are conveniently converted to effective correlation times.

T_1^{DD} is related to an effective correlation time for overall molecular reorientation, τ_{eff}, under the extreme narrowing condition through eqn. (2).[1a]

$$1/T_1^{DD}=(\hbar^2\gamma_C^2\gamma_H^2 n_H/r_{CH}^6)\tau_{eff} \quad (2)$$

with n_H being the number of directly attached hydrogen atoms. When the molecular reorientation is described as a small-step angular diffusion and the motion of the molecules is isotropic, the effective correlation time is simply related to an isotropic diffusion constant, D, which characterizes the overall molecular reorientation by eqn. (3).[7]

$$\tau_{eff}=1/6D \quad (3)$$

The correlation times and rotational diffusion constants for the CH and CH_2 carbons listed in Tables 1–3 have been calculated by means of eqns. (2) and (3). The first observation to note is that the effective correlation times of the ring C–H vectors increase as the number of methyl groups attached to the ring increase from none to three. This is to be expected, and is a consequence of the Stokes-Debye rule.[8] Secondly, we note that the effective correlation times of the methine carbon in II are somewhat longer than those of the methylene carbon. This observation probably reflects a small anisotropy in the molecular tumbling. In all cases the ring C–H vectors have considerably longer effective correlation times than the methyl C–H vectors. It is noteworthy that comparatively long τ_{eff} values occur in III where a given methyl group is adjacent to another methyl group. On the other hand, the isolated methyl group in II has much shorter effective correlation times. These observations are in accordance with previous findings in methyl-substituted benzenes.[9–10]

The effect of internal motion is to shorten τ_{eff} resulting in a less efficient C–H dipolar relaxation process and a larger value of T_1^{DD}. However, the contribution to τ_{eff} from interconversions between ring-puckered forms is expected to be negligible since the rate of ring inversion is certainly slow on the time scale of the overall molecular reorientation.[4a]

If the internal rotation of a specific group such as CH_3, and the isotropic overall tumbling of the molecule are assumed to be diffusional and described by rotational diffusion constants D_{int} and D, respectively, τ_{eff} is given by the appropriately modified Woessner equation.[11,12]

$$\tau_{eff}=\frac{1}{6D}\left(A+\frac{6B}{6+\rho}+\frac{6C}{6+4\rho}\right) \quad (4)$$

where $\rho=D_{int}/D$, $A=1/4(3\cos^2\theta-1)^2$, $B=3/4\times\sin^2 2\theta$, $C=3/4\sin^4\theta$, and θ is the angle between the axis of rotation and the C–H bond in question. For a methyl group with tetrahedral carbon angles $A=1/9$, $B=8/27$, and $C=16/27$. The simplified model[13] of a rapidly rotating methyl group attached to an isotropically reorienting body, provides a moderately quantitative picture which will reflect the trend in the motional characteristics of the methyl-substituted arsolanes.

The D_{int} values for the methyl groups in II and III given in Tables 2 and 3, have been evaluated

Table 2. Carbon-13 spin-lattice relaxation times, correlation times and rotational diffusion constants for 2-chloro-4-methyl-1,3,2-dioxarsolane.[a]

Temp (K)	T_1(s)[b] C-4	C-5	4-CH_3	τ_{eff}(CH) (ps)	τ_{eff}(CH_2) (ps)	τ_{eff}(CH_3) (ps)	D(CH)[c] $\times 10^{-10}$(s^{-1})	D_{int}(CH_3)[d] $\times 10^{-10}$(s^{-1})
353.0	13.5(17.7)	7.97(10.1)	6.39(7.2)	2.63	2.31	2.15	6.34	3.5
350.0	12.5(16.3)	7.38(9.3)	5.97(6.8)	2.86	2.51	2.28	5.83	3.5
345.0	12.0(14.6)	6.94(8.3)	5.53(6.2)	3.19	2.80	2.50	5.22	3.5
339.0	11.0(12.7)	6.34(7.3)	5.16(5.5)	3.67	3.21	2.82	4.54	3.3
336.0	10.5(11.7)	6.01(6.7)	4.76(5.1)	3.98	3.49	3.04	4.19	3.3
327.5	8.41(9.7)	4.86(5.5)	4.01(4.4)	4.83	4.23	3.52	3.45	3.1
318.0	6.91(7.5)	4.06(4.3)	3.39(3.5)	6.19	5.40	4.44	2.69	2.8
313.0	6.24	3.56	3.04	7.47	6.54	5.11	2.23	2.7
304.0	5.06	2.94	2.54	9.21	7.92	6.11	1.81	2.4
299.0	4.39	2.49	2.20	10.6	9.35	7.06	1.57	2.1
297.0	4.10	2.36	2.10	11.4	9.87	7.39	1.46	2.1
290.0	3.30	1.87	1.77	14.1	12.5	8.77	1.18	2.0
286.5	2.94	1.67	1.59	15.9	13.9	9.77	1.05	1.8
284.5	2.67	1.52	1.47	17.5	15.3	10.6	0.95	1.7
279.5	2.23	1.28	1.23	20.9	18.2	12.6	0.80	1.5
274.0	1.78	1.03	1.07	26.2	22.6	14.5	0.64	1.5

[a] The values in parentheses are the calculated T_1^{DD} values. [b] Due to rapid exchange of chlorine only averaged NMR parameters of the *syn* and *anti* isomers are observed. [c] E_a=22.9±1.0 kJ mol^{-1}. The estimated uncertainty in E_a is 90 % confidence limit. [d] E_a=9.3±1.4 kJ mol^{-1}.

Table 3. Carbon-13 spin-lattice relaxation times, correlation times and rotational diffusion constants for 2-chloro-4,5-dimethyl-1,3,2-dioxarsolane.[a]

Temp. (K)	T_1(s) C-4[b] *cis*	*trans*	4-CH_3[b] *cis*	*trans*	τ_{eff}(CH)(ps) *cis*	*trans*	τ_{eff}(CH_3)(ps) *cis*	*trans*	D(CH)[c] $\times 10^{-10}$(s^{-1}) *cis*	*trans*	D_{int}(CH_3) $\times 10^{-10}$(s^{-1}) *cis*	*trans*
353.0	12.1(15.5)	10.2(13.6)	4.85(6.1)	5.25(6.2)	3.01	3.43	2.55	2.50	5.55	4.87	2.4	4.6
346.0	10.5(13.0)	8.84(11.4)	4.31(5.2)	4.58(5.4)	3.58	4.09	2.99	2.88	4.65	4.08	2.2	4.3
337.0	8.96(10.4)	7.47(9.0)	3.62(4.2)	3.97(4.4)	4.48	5.17	3.70	3.53	3.72	3.22	1.8	4.0
328.0	7.60(8.3)	6.45(7.1)	3.11(3.4)	3.45(3.6)	5.62	6.55	4.57	4.31	2.97	2.54	1.6	3.6
317.0	6.11	5.16	2.53	2.83	7.62	9.03	6.14	5.49	2.19	1.85	1.3	3.3
310.0	4.97	4.17	2.08	2.34	9.37	11.2	7.47	6.64	1.78	1.49	1.1	2.9
300.0	3.85	3.20	1.63	1.85	12.1	14.6	9.53	8.39	1.38	1.14	0.9	2.4
292.0	2.95	2.41	1.25	1.48	15.8	19.3	12.4	10.5	1.06	0.86	0.7	2.1
285.5	2.32	1.88	1.00	1.21	20.1	24.8	15.5	12.8	0.83	0.67	0.6	1.9
282.5	2.10	1.69	0.91	1.10	22.2	27.6	17.1	14.1	0.75	0.60	0.6	1.8
275.0	1.52	1.21	0.68	0.86	30.6	38.5	22.8	18.1	0.54	0.43	0.5	1.6

[a] The values in parentheses are the calculated T_1^{DD} values. [b] C-4 and C-5 have identical environments due to rapid exchange of chlorine. [c] E_a=23.5±0.3 and 24.6±0.6 kJ mol^{-1} for the *cis* and *trans* isomers, respectively. The estimated uncertainty in E_a is 90 % confidence limit. [d] E_a=17.1±0.5 and 11.4±0.8 kJ mol^{-1} for the *cis* and *trans* isomers, respectively.

from the T_1 data by means of eqns. (2)–(4). Our calculations show that the rate of methyl rotation in II and *trans*-III is similar ($\rho \approx 1-4$) and about three times faster than in *cis*-III. This observation indicates that the methyl rotation is considerably hindered in the *cis* isomer, presumably due to steric interactions. Further support of this conclusion is found in the very high activation energy calculated for the *cis*-4,5-dimethyl groups in III (*vide infra*) and its 2-phenyl analogue (18–19 kJ mol^{-1}).[4b]

If the rotational diffusion is a thermally activated process the temperature dependence is usually expressed by an Arrhenius-type equation[1]

$$D = A \exp(-E_a/RT) \quad (5)$$

where A and the activation energy E_a, are adjustable parameters. We have thus obtained the apparent activation energies for the overall reorientation and the internal methyl rotation by fitting the calculated D values to eqn. (5) (Tables 1–3). The activation energies for the overall molecular tumbling are similar in the investigated compounds (23–24 kJ mol^{-1}) and close to the values found for the 2-phenyl analogues of II and III (~25 kJ mol^{-1}).[4b] The calculated activation energies for the methyl groups are relatively high (*ca.* 9, 11, and 17 kJ mol^{-1} for II, *trans*-III, and *cis*-III, respectively) and also quite close to the observed values in the related 2-phenyl-1,3,2-dioxarsolanes.[4b]

It has been claimed[14] that the Arrhenius activation energy (E_a) for a methyl group hindered by a three-fold potential barrier, is only 2–4 % lower than the barrier height. On this basis it is reasonable to assume that the high E_a values found for the methyl-substituted arsolanes, the *cis* isomer in particular, indicate that the internal methyl rotation is severely hindered in these systems. This conclusion is consistent with the relatively slow internal reorientation rates already calculated for the methyl groups.

EXPERIMENTAL

The syntheses of the 2-chloro-1,3,2-dioxarsolanes have been described in previous papers.[2] Solutions of the freshly distilled compounds added 30 % v/v benzene-d_6, were transferred to 10 mm o.d. NMR tubes, degassed by four freeze-pump-thaw cycles, and sealed under vacuum. The spin-lattice relaxation measurements were performed at 22.63 MHz on a Bruker CXP 100 spectrometer. The sample temperature was regulated and stabilized to within ±0.5 K in the high-temperature range (above 293 K) and to within ±1 K in the low-temperature range (below 293 K) by means of a Bruker B-ST 100/700 c temperature control unit. The temperature was measured before and after each experiment by a thermometer immersed in liquid in a spinning NMR tube.

The T_1 values were measured by using the inversion recovery method $(180° - \tau - 90° - T)_n$ with $T \geqslant 5T_1$.[1] The number of cycles (n) for each τ value varied from 32 to 64 depending on the signal-to-noise ratio. Short and long τ values in the range ~0 to 1.5 T_1 were alternated in order to minimize systematic errors due to spectrometer imperfections.

Exponential weighting was applied to the 8K free induction decays. The T_1 values were calculated from 10–14 pairs of experimental points (including the equilibrium point $\tau > 5T_1$) by using exponential three-parameter fitting of peak heights.[15,16] The calculated standard deviations of T_1 were of the order 2–4 %.

REFERENCES

1. a. Lyerla, J. R. and Levy, G. C. *Topics in ^{13}C NMR Spectroscopy,* Wiley, New York 1974, Vol. 1, Chapter 3; b. Levy, G. C., Lichter, R. L. and Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy,* Wiley, New York 1980; c. Wehrli, F. W. and Wirthlin, T. *Interpretation of Carbon-13 NMR Spectra,* Heyden, London 1978; d. Berger, S. *Advances in Physical Organic Chemistry,* Academic, New York 1978, Vol. 16, p. 239.
2. a. Aksnes, D. W. and Vikane, O. *Acta Chem. Scand. 26* (1972) 835; b. Aksnes, D. W. and Vikane, O. *Acta Chem. Scand. 26* (1972) 2532; c. Aksnes, D. W. and Vikane, O. *Acta Chem. Scand. 27* (1973) 1337; d. Aksnes, D. W. and Vikane, O. *Acta Chem. Scand. 27* (1973) 2135; e. Aksnes, D. W. and Bjorøy, M. *Acta Chem. Scand. A 29* (1975) 672; f. Aksnes, D. W., Amer, F. A. and Bergesen, K. *Acta Chem. Scand. A 30* (1976) 109; g. Aksnes, D. W. and Lie, A. *Org. Magn. Reson. 21* (1983) 417.
3. a. Bentrude, W. G. and Tan, H.-W. *J. Am. Chem. Soc. 98* (1976) 1850; b. Revel, M., Roussel, J., Navech, J. and Mathis, F. *Org. Magn. Reson. 8* (1976) 399; c. Besserre, D.

and Coffi-Nketsia, S. *Org. Magn. Reson 13* (1980) 313; d. Besserre, D. and Coffi-Nketsia, S. *Org. Magn. Reson. 13* (1980) 235.
4. a. Aksnes, D. W. and Holak, T. A. *Org. Magn. Reson 17* (1981) 285; b. Aksnes, D. W. and Ramstad, K. *Org. Magn. Reson. In press.*
5. Deslauriers, R. and Smith, I. C. P. *Topics in ^{13}C NMR,* Wiley, New York 1974, Vol. 2, Chapter 1.
6. Adler, O. and Kober, F. *Monatsh. Chem. 108* (1977) 65.
7. Hubbard, P. S. *Phys. Rev. 131* (1963) 1155.
8. Abragam, A. *The Principles of Nuclear Magnetism,* Oxford Univ. Press, Oxford 1962, Chapter VIII.
9. Alger, T. D., Grant, D. M. and Harris, R. K. *J. Phys. Chem. 76* (1972) 281.
10. Wehrli, F. W. *Topics in ^{13}C NMR Spectroscopy,* Wiley, New York 1976, Chapter 6.
11. Wallach, D. *J. Chem. Phys. 47* (1967) 5258.
12. Woessner, D. E., Snowden, B. S. and Meyer G. H., Jr. *J. Chem. Phys. 50* (1969) 719.
13. Hertz, H. G. *Prog. Nucl. Magn. Reson. Spectrosc. 16* (1983) 115.
14. Kowalewski, J. and Liljefors, T. *Chem. Phys. Lett. 64* (1979) 170.
15. Brunetti, A. H. *J. Magn. Reson. 28* (1977) 289.
16. Aksnes, D. W. *Unpublished results. Computer program available on request.*

Received March 28, 1984.