Activation Energies for Fluxional Behavior in Aryl(pentachlorocyclopentadienyl)mercurials, η^1-C_5Cl_5HgR, from ^{35}Cl NQR Relaxation Times *

Norbert Weiden [a], Alarich Weiss [a], Gary Wulfsberg [b], William Ilsley [b], Kevin Benner [b], and William Wourster [c]

[a] Institut für Physikalische Chemie, Technische Hochschule Darmstadt, D-6100 Darmstadt
[b] Department of Chemistry and Physics, Middle Tennessee State University, Murfreesboro, TN, USA
[c] Department of Chemistry, Wayne State University, Detroit, MI, USA

Z. Naturforsch. **45a**, 503–510 (1990); received August 25, 1989

Solid-state activation energies for fluxional behavior in three aryl-subsituted (pentachlorocyclopentadienyl)phenylmercury compounds $RHgC_5Cl_5$: (pentachlorocyclopentadienyl)(pentamethylphenyl)mercury (**I**, R = $C_6(CH_3)_5$, E_{act} = 19.3 kJ mol^{-1}); (pentachlorocyclopentadienyl)(2,4,6-tris(*tert*-butyl)phenyl)mercury (**II**, R = 2,4,6-$C_6H_2(C(CH_3)_3)_3$, E_{act} = 59.5 kJ mol^{-1}); and (pentachlorocyclopentadienyl)(phenyl)mercury (**III**, R = C_6H_5, E_{act} = 62.8 kJ mol^{-1}) have beeb obtained from ^{35}Cl NQR spin-lattice relaxation-time measurements. **II** has also been shown to be fluxional in solution by ^{13}C NMR spectra. **II** was prepared by an exchange reaction between $Hg(C_5Cl_5)_2$ and $Hg(2,4,6\text{-}C_6H_2(C(CH_3)_3)_3)_2$, which reacted readily despite the great steric hindrance present in the latter reagent.

Key words: Fluxional, Nuclear quadrupole resonance (NQR), Pentachlorocyclopentadienylmercury, Spin-lattice relaxation time, Activation energy.

One of the most fascinating properties of many *monohapto*-cyclopentadienyl metal compounds, η^1-$C_5X_5MR_n$, is fluxionality, the rapid relocation of the carbon-metal sigma bond to involve in turn each of the five cyclopentadienyl ring carbons, each relocation generating an equivalent structure [1]. Because of the time scale of this process, it is normally studied by solution NMR, but recently it has been possible to study it in the solid state by wide-angle or magic-angle-spinning NMR techniques [2]. Most studies have been limited to demonstrating that fluxional motion is occurring in certain temperature ranges; only a few studies have been able to assign activation energies to the process. Such data would help answer many interesting questions about fluxional behavior, such as how it is affected by changing the cyclopentadienyl ring substitution, how it is affected by the presence of steric hindrance or of solid-state bonding of ring substituents to mercury atoms in adjacent molecules, and how it is affected on going from solution to the solid state.

Recently we have begun applying ^{35}Cl NQR, which has long been used to study molecular motion in the solid state [3], to the study of fluxional behavior in the solid state [4, 5]. The continuous-wave (CW) NQR technique we used was capable of locating "fade-out" temperatures for fluxional compounds, above which no NQR signals could be located due to reorientation at a rate comparable to or greater than the linewidth, but since the CW-NQR technique does not give true linewidths, nothing could be deduced about the activation energy for the process. In this paper we report additional studies using pulse-Fourier transform (FT) NQR spectroscopy to measure true linewidths and spin-lattice relaxation times T_1, which enabled us to obtain activation energies (E_{act}) for fluxional reorientation in three aryl-substituted (pentachlorocyclopentadienyl)phenylmercury compounds $RHgC_5Cl_5$:

(pentachlorocyclopentadienyl)(pentamethylphenyl)-mercury (**I**, R = $C_6(CH_3)_5$);
(pentachlorocyclopentadienyl)(2,4,6-tris(*tert*-butyl)-phenyl)mercury (**II**, R = 2,4,6-$C_6H_2(C(CH_3)_3)_3$); and
(pentachlorocyclopentadienyl)(phenyl)mercury (**III**, R = C_6H_5).

II has not previously been reported, so its synthesis, and solution and solid-state NMR spectra are also included.

* Presented at the Xth International Symposium on Nuclear Quadrupole Resonance Spectrocopy, Takayama, Japan, August 22–26, 1989.

Reprint requests to Dr. G. Wulfsberg, Department of Chemistry and Physics, Middle Tennessee State University, Murfreesboro, TN 37132, USA.

0932-0784 / 90 / 0300-0503 $ 01.30/0. – Please order a reprint rather than making your own copy.

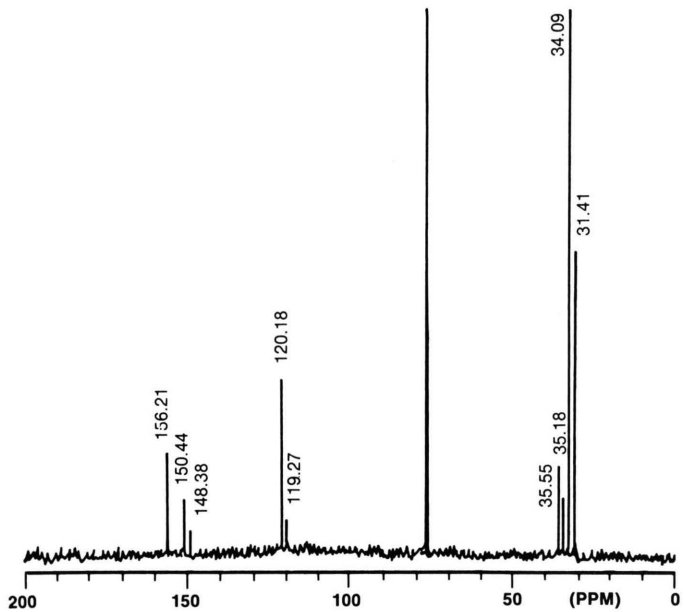

Fig. 1. $CDCl_3$ solution proton-decoupled ^{13}C NMR spectrum of **II**. Chemical shifts are referenced to tetramethylsilane.

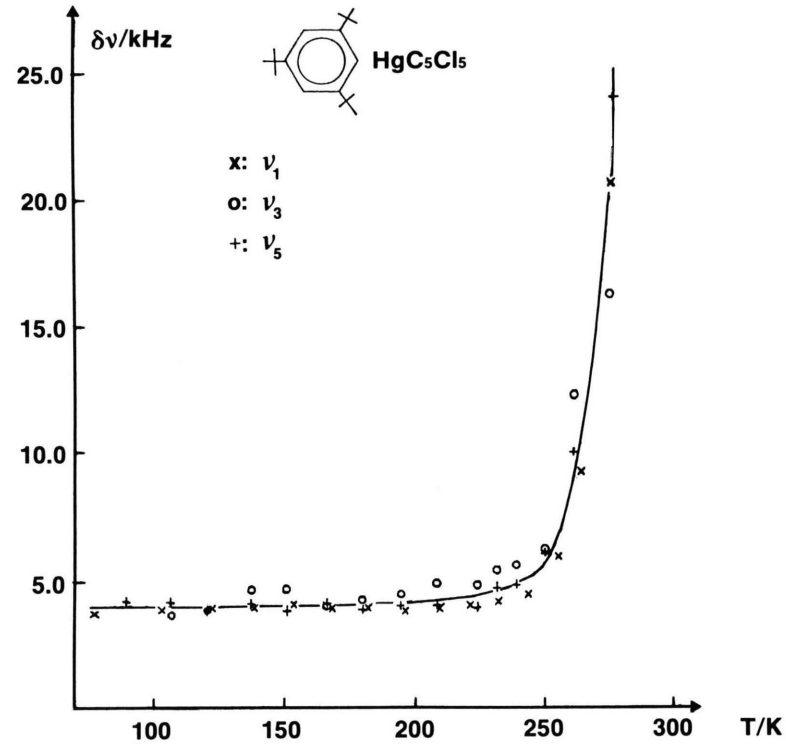

Fig. 6. Linewidths $\delta\nu$ as function of temperature for three frequencies of **II**.

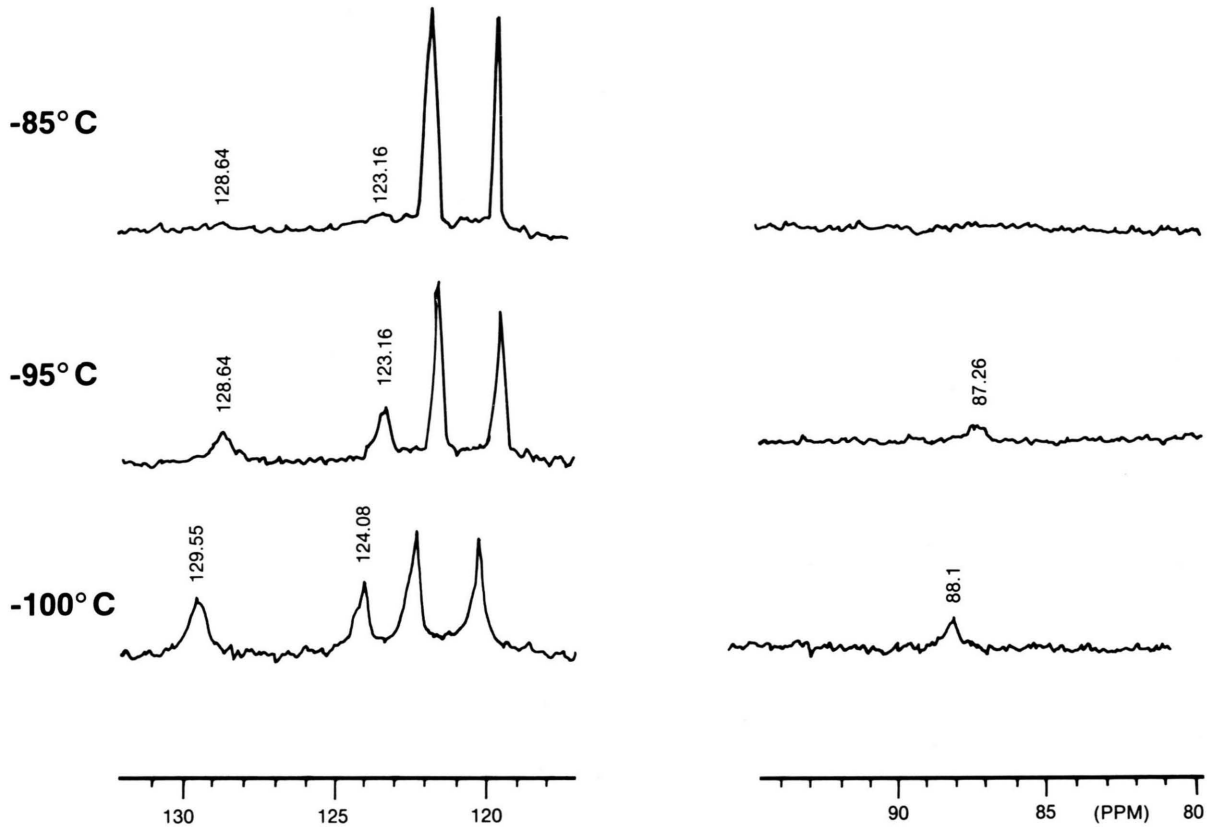

Fig. 2. $CDCl_3$ solution proton-coupled ^{13}C NMR spectrum of **II** at (a) −85 °C, (b) −95 °C, (c) −100 °C.

Experimental

1,3,5-Tris(t-butyl)benzene was synthesized according to Myrhe [6]; this was brominated by the procedure of Pearson [7], and then converted to bis(2,4,6-tris-*tert*-butyl)phenylmercury (**IV**) by the procedure of Huffman [8].

Synthesis of **II**. Into a Schlenk flask were placed 0.43 g (6.23 mmol) **IV** and 0.42 g (6.23 mmol) of bis-(pentachlorocyclopentadienyl)mercury [5] in 5 ml dichloromethane and 5 ml heptane under an atmosphere of argon. The mixture was stirred for about 2 h, after which the solvent was slowly stripped off to give a yellow-white solid, m.p. 96–100°, in a 98% yield.

T_1 of the ^{35}Cl nuclei have been measured by the $\pi-\tau-\pi/2$ pulse technique using polycrystalline samples. The $\pi/2$ pulse width was about 7 μs. From the free induction decay (FID) the linewidth at half intensity was determined after Fourier transformation of the FID. In all experiments the sample was held at constant temperature to within ±0.1 K by a temperature-controlled stream of N_2 gas. The absolute values of the temperature are reliable to ±0.2 K.

Discussion

II was prepared in 98% yield by stirring together equimolar quantities of $[2,4,6\text{-}C_6H_2(C(CH_3)_3)_3]_2Hg$ (**IV**) and $(C_5Cl_5)_2Hg$ in methylene chloride at room temperature for 2 h. Organomercury exchange reactions of this type often proceed through four-centered intermediates in which each mercury is three-coordinated [9]. Examination of the solid-state structure of

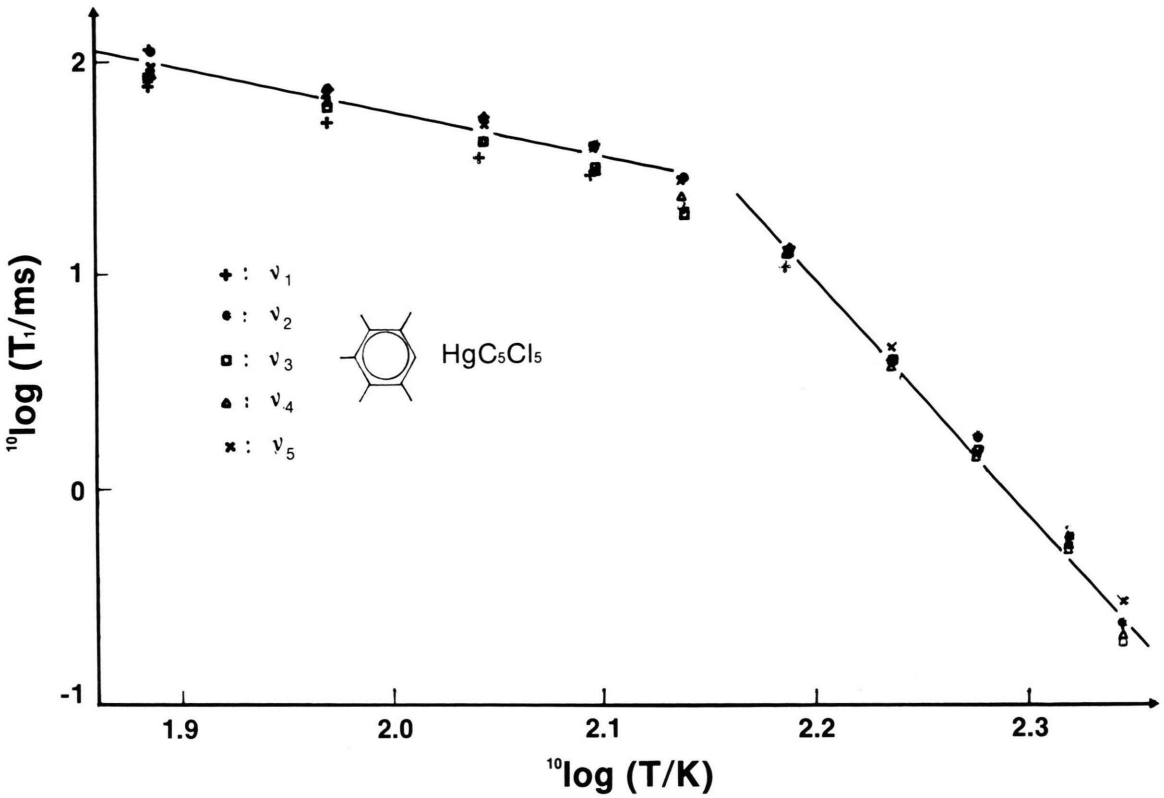

Fig. 3. Logarithm of the spin-lattice relaxation time (T_1 in ms) versus logarithm of temperature for **I**.

IV [8], which shows strong effects of steric crowding, led us to expect that the normal four-centered exchange process would be impossible; hence the smooth, quick reaction was surprising.

Once **II** was prepared, it was of interest to see whether fluxional behavior would be possible in it, or whether steric hindrance would be excessive. The solution ^{1}H NMR spectrum of **II** is simple and typical of 2,4,6,-tris(*tert*-butyl)phenyl derivatives: there are two methyl resonances at 1.57 and 1.34 ppm due to the ortho and para *tert*-butyl methyls, respectively, and one aromatic resonance at 7.50 ppm.

The ^{13}C NMR spectrum exhibits four resonances in the methyl region (Figure 1). The peaks at 31.41 and 34.09 ppm arise, respectively, from the para and ortho *tert*-butyl methyl carbons, and the peaks at 35.18 and 35.55 ppm are due to the quaternary carbons of the para and ortho *tert*-butyl methyl groups, respectively. The aromatic peaks appear at 148.38, 156.21, 120.18, and 150.44 ppm and have tentatively been assigned to the ipso-, ortho-, meta-, and para-carbons, respectively. The C_5Cl_5 resonance appears as a signal at 119.27 ppm, in agreement with its location in **I**, **III**, and related compounds [5]. The fact that only one peak is observed confirms the fluxional behavior of the C_5Cl_5 group at room temperature.

The 119 ppm peak only is very much weakened as the temperature of the NMR measurement is lowered to 10° and even more so at −5 °C; it is absent at −35 °C. At −85 °C (Fig. 2) two new peaks appear at 123.16 ppm and 128.64 ppm, and at −95 °C a third peak appears at 87.26 ppm; in comparison with other spectra of C_5Cl_5 derivatives, the former two can be assigned to the vinylic carbons and the latter to the allylic carbon of the C_5Cl_5 ring [5]. The low-temperature spectra clearly show that **II** is fluxional in solution. However, the quality and number of spectra are insufficient to do a line-shape analysis and obtain a solution E_{act} for the fluxional process in **II**.

To determine whether **II** is fluxional in the solid state, the CP-MAS ^{132}C NMR spectrum was obtained at ambient temperature; spinning sidebands were identified by varying the spinning rate and were excluded. The *tert*-butyl region showed three peaks at

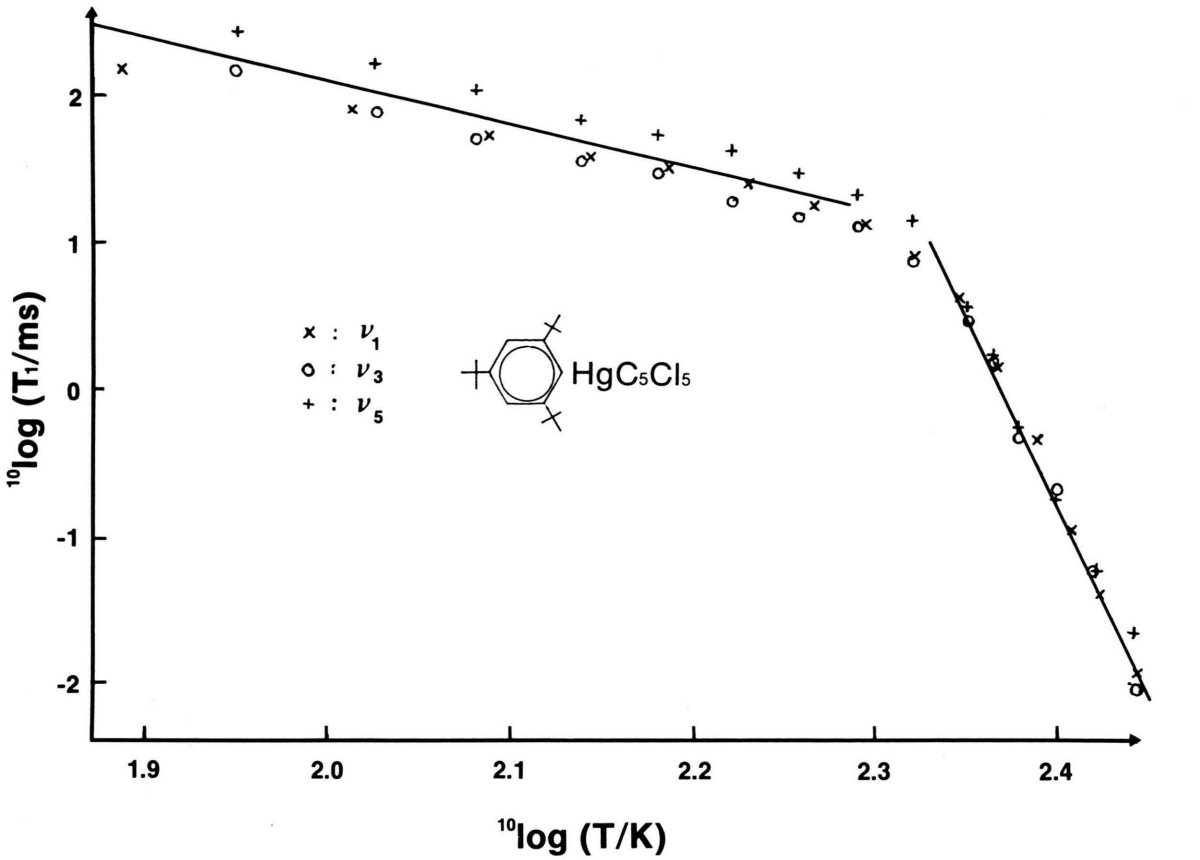

Fig. 4. Logarithm of the spin-lattice relaxation time (T_1 in ms) versus logarithm of temperature for **II**.

32.47, 35.29, and 35.86 ppm, in contrast to the nine peaks observed in this region for the parent compound **IV** in the solid state [10]. This suggests that the rotations of the *tert*-butyl groups are more hindered in **IV** than in **II** (molecular models suggest that this hindrance should not as be severe in **II** as in **IV**). **II** gave solid-state NMR aromatic-region peaks at 149.46, 153.77, and 157.31 ppm, and a broad peak at 119.92 ppm, which arises from both the C_5Cl_5 group and the meta carbons of the aromatic ring. Since the C_5Cl_5 resonance is not resolvable, it was not possible to use solid-state NMR to examine ring fluxional behavior in the solid state.

The 77 K ^{35}Cl NQR spectra of the new mercurial **II** was recorded on a Decca NQR spectrometer and is given in Table 1; fade-out of the CW-NQR signal, suggesting fluxional behavior, was observed near 281 K.

In order to obtain more information on the fluxional behavior of the three compounds we have measured the linewidths $\delta\nu$ and T_1 for a number of ^{35}Cl NQR frequencies in these substances. For **I** this was done for all five ^{35}Cl NQR lines. The results of the T_1 measurements are shown as a log T_1 versus log T plot in Figure 3. The figure reveals clearly that all five signals exhibit the same behavior, which proves that the five chlorine atoms are all engaged in the same process. For **II** the investigations have been carried out for three of the five signals (Fig. 4) and for **III** for two ^{35}Cl NQR lines (Figure 5). Again it can be seen that the ^{35}Cl NQR signals belonging to one compound show the same features. Thus in principle the investigation of a single line for each substance of this type should suffice.

For nuclei with spin $I=3/2$ librations of the molecules lead to a relationship for the temperature dependence of T_1 of the form:

$$T_1^{-1} = a\,T^n \tag{1}$$

with $n=2$ [11, 12]. From Figs. 3–5 it can be seen that this relation is fulfilled rather well only on the low

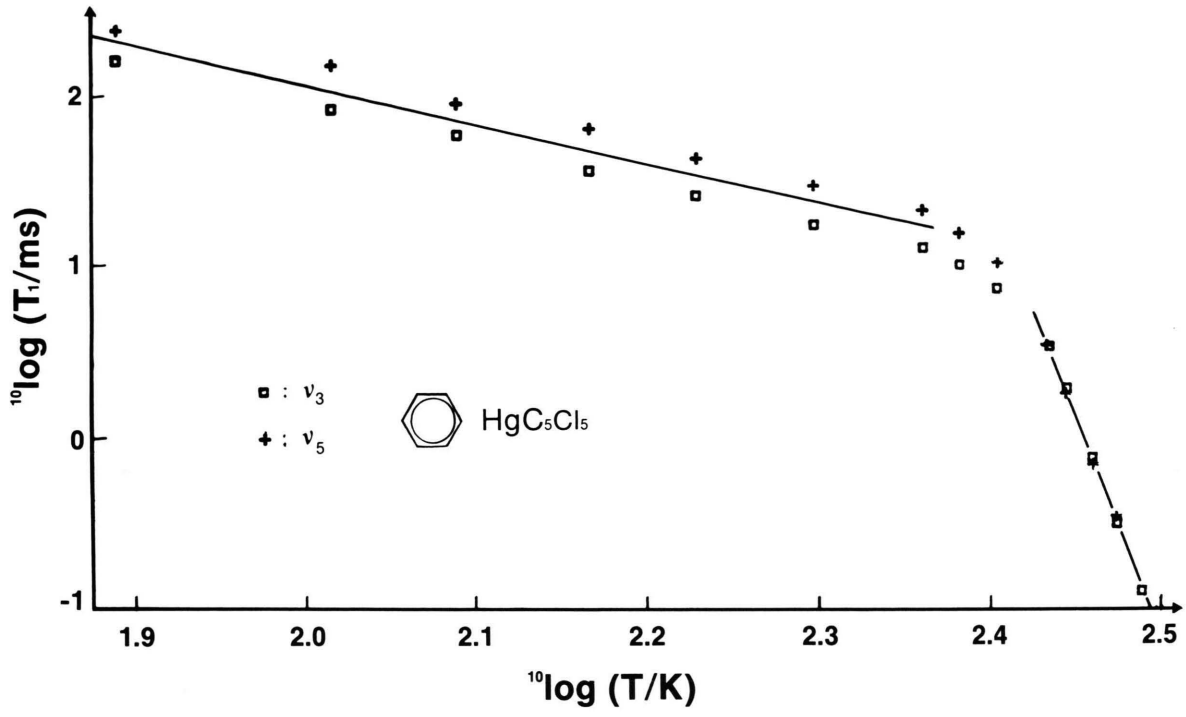

Fig. 5. Logarithm of the spin-lattice relaxation time (T_1 in ms) versus logarithm of temperature for **III**.

temperature regime for all three substances. On the other hand, the onset of molecular motion in the form of hindered rotation leads to a relationship

$$T_1^{-1} = b \exp(-E_{act}/RT) \quad (2)$$

for T_1 [11]. Combination of (1) and (2) leads to

$$T_1^{-1} = a T^n + b \exp(-E_{act}/RT). \quad (3)$$

Equation (3) has been used to fit the experimental $T_1 = f(T)$ data. The results for E_{act} (with estimated errors of $\pm 5\%$) and n, and the corresponding temperature ranges are given in Table 1.

The onset of fluxional behavior is connected with an increase of the linewidth $\delta\nu$. This is mainly due to the fact that the T_1 values become very short. For **I** this broadening is not very pronounced, since the linewidths at 77 K are already of the order of 20 kHz. Similar reasons hold for **III**, but for **II** the linewidths are about 4 kHz for all five ^{35}Cl NQR signals at 77 K. (**II** is thermally the most stable of these three compounds, and may best have survived sample shipment.) So the line broadening leading to a "fade-out" of the signals in **II** is very pronounced, as can be seen from Figure 6.

Table 1. Values for the exponent n and the activation energy E_{act} for $RHgC_5Cl_5$.

Comp.	ν(77 K) MHz	Temp. range/K	n	Temp. range/K	E_{act} kJ mol^{-1}
I	36.230	77–125	2.0	150–220	18.7
	36.444	77–125	2.0	150–220	18.7
	36.534	77–125	2.0	150–220	20.9
	36.831	77–125	2.1	150–220	20.0
	37.412	77–125	1.8	150–220	18.4
II	36.362	77–185	2.3	255–278	58.4
	36.555	–	–	–	–
	36.723	77–185	3.0	225–278	61.4
	37.184	–	–	–	–
	38.451	77–185	3.1	225–278	58.6
III	36.212	–	–	–	–
	36.265	–	–	–	–
	36.737	77–230	2.3	265–320	63.8
	36.865	–	–	–	–
	37.350	77–230	2.3	265–320	61.7

In Table 2 are presented E_{act} values in solution and solid state for some cyclopentadienyl mercurials and also for some fluxional cyclooctatetraenyl metal carbonyls. (For purposes of evaluating trends we also list "fade-out" temperatures, the highest temperature at

Table 2. Fade-out temperatures and activation energies for fluxional cyclopentadienyl mercurials and cyclooctatetraenyls.

Compound [a]	Solid state		Solution	
	$T_{fade\text{-}out}$ [b]	E_{act} [c] kJ mol^{-1}	$T_{fade\text{-}out}$ [b]	E_{act} [c] kJ mol^{-1}
I	256 K	19.3 [d]	<243 K	– [e]
II	281 K	59.5 [d]	188 K	– [e]
III	327 K	62.8 [d]	198 K	– [e]
Cp_2Hg	–	23.6; [f] 26.2	<153 K	– [g]
CpHgCl	–	39.7; [f] 42.7	174 K	32.2 [g]
Cp*HgCl	–	–	>193 K	46 [h]
$(COT)Fe(CO)_3$		37.9; [i] 38.9		
$(COT)Fe_2(CO)_5$	<77 K	7.9; [i] 8.9		
$(COT)_2Ru_3(CO)_4$		21.6; [i] 25.2		

[a] Cp = cyclopentadienyl; Cp* = pentamethylcyclopentadienyl; COT = cyclooctatetraenyl.
[b] $T_{fade\text{-}out}$ = highest temperature at which the resolved NQR or ^{13}C NMR peaks are still detectable. Due to the enormous differences in inherent linewidths of NMR and NQR signals, our NQR fade-out temperatures for **I**, **II**, and **III** cannot be directly compared with the NMR temperatures for the same compound.
[c] Activation energy, in kJ mol^{-1}. In case in which two such energies are given, the first is based on T_1 and the second on $T_{1\rho}$ measurements.
[d] This work. [e] Ref. [4]. [f] Ref. [14]. [g] Ref. [15].
[h] A. Razavi, M. D. Rausch, and H. G. Alt, J. Organometal. Chem. **329**, 281 (1987).
[i] Ref. [13].

which the resolved ^{35}Cl NQR or ^{13}C NMR peaks of the distinct ring positions are still detectable.) We note that the solid-state E_{act} follows the sequence **I** < **II** < **III**; this is the same trend found earlier [4] for the solid-state NQR fade-out temperatures of these compounds, and is consistent with the order for NMR fade-out temperatures for these compounds in solution (**II** < **III**; low solubility did not allow the detection of the low-temperature resolved spectrum of **I**).

Solid-state E_{act} values for fluxional behavior in these compounds are likely to be controlled by contributions from (a) the solid-state lattice potential, (b) the partial breaking of the C–Hg chemical bond in the transition state, and (c) any intramolecular steric hindrance which must be overcome. At first glance E_{act} for **I** seems strikingly low for a solid-state process, but there is known a lower value for a cyclooctatetraenyl iron carbonyl compound, [13] and Campbell [14] found that the solid-state E_{act} of C_5H_5HgCl is only 8–10 kJ mol^{-1} higher than its solution value [15]. Hence the solid-staste lattice potential does not necessarily greatly increase E_{act} for fluxional behavior.

Although it may be the case that E_{act} in **II** is higher than in **I** because of intramolecular steric hindrance between phenyl *tert*-butyl groups and ring chlorines in **II**, this does not explain the observation of an even higher E_{act} in **III**. Hence explanations involving differing lattice potentials or differing properties of the Hg–C_5Cl_5 bond must also be considered to explain the observed trends. In the current absence of crystal structures of **I** and **II** these could only be speculation.

Schoeller [16, 17] has done theoretical calculations on cyclopentadienylboranes and phosphanes, which generally (but not always) indicate that E_{act} values for fluxional behavior in pentachlorocyclopentadienyls should exceed those in the corresponding pentamethylcyclopentadienyls or unsubstituted cyclopentadienyls. The E_{act} values we have obtained are for compounds for which the corresponding pentamethylcyclopentadienyls or cyclopentadienyls are unknown. The largest body of E_{act} data is that for C_5X_5HgCl (Table 2); for C_5Cl_5HgCl we know only that fade-out does not occur near 333 K. (In this compound there is evidence for intermolecular organochlorine-mercury coordination [18], a factor which would be expected to influence significantly the activation energy for fluxional behavior.) It is well known that FT-NQR measurements of T_1 are much more sensitive to molecular motion than are observations of fade-out: in **II** T_1 begins to shorten about 40 K below the temperature at which appreciable line broadening begins. Hence re-examination of the NQR spectra of selected additional compounds by the FT-NQR method, and additional solid-state NMR work, would be worthwhile.

Acknowledgements

We thank the Alexander von Humboldt Foundation, the Deutsche Forschungsgemeinschaft, and the M.T.S.U. Faculty Research Fund for financial support of this work.

[1] J. W. Faller, Adv. Organometal. Chem. **16,** 211 (1977).
[2] C. A. Fyfe, Solid State NMR for Chemists, Guelph, CFC Press 1983, p. 412.
[3] H. Chihara and N. Nakamura, Adv. Nucl. Quadrupole Reson. **4,** 1 (1980).
[4] G. Wulfsberg, A. C. Buchanan, I. Rubin, A. Weiss, D. A. Davis, K. Bass, R. W. Todd, and C. C.-C. Jui, Z. Naturforsch. **41a,** 175 (1986).
[5] G. Wulfsberg, J. S. Frye, A. C. Buchanan, III, A. Weiss, C. C.-C. Jui, D. A. Davis, K. Bass, and R. W. Todd, Organometallics **6,** 2363 (1987).
[6] P. C. Myrhe, T. Rieger, and J. T. Stone, J. Org. Chem. **31,** 3425 (1966).
[7] D. E. Pearson, M. G. Frazer, V. S. Frazer, and L. C. Washburn, Synthesis **1976,** 621.
[8] J. C. Huffman, W. A. Nugent, and J. K. Kochi, Inorg. Chem. **19,** 2749 (1980).
[9] F. R. Jensen and B. Rickborn, Electrophilic Substitution of Organomercurials, McGraw-Hill, New York 1968.
[10] K. S. Benner, M. S. Thesis, Middle Tennessee State University, Aug. 1988.
[11] D. E. Woessner and H. S. Gutowsky, J. Chem. Phys. **39,** 440 (1963).
[12] J. van Kranendonk and M. B. Walker, Can. J. Phys. **46,** 2441 (1968).
[13] A. J. Campbell, C. E. Cottrell, C. A. Fyfe, and K. R. Jeffrey, Inorg. Chem. **15,** 1321 (1976).
[14] A. J. Campbell, C. E. Cottrell, C. A. Fyfe, and K. R. Jeffrey, Inorg. Chem. **15,** 1326 (1976).
[15] F. A. Cotton, D. L. Hunter, and J. D. Jamerson, Inorg. Chim. Acta **15,** 245 (1975).
[16] W. Schoeller, Z. Naturforsch. **38b,** 1635 (1983).
[17] W. Schoeller, J. Chem. Soc. Dalton Trans. **1984,** 2233.
[18] G. Wulfsberg, R. West, and V. N. M. Rao, J. Organometal. Chem. **86,** 303 (1975).