High-pressure Effects on the Proton Nuclear Magnetic Resonance Spectra of Palladium(II) Complexes of Cyclic Sulphides. Estimation of Activation Volumes for Inversion about Sulphur

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The dynamic ^{1}H n.m.r. spectra of the complexes *trans*-$[\mathrm{PdBr_2(SCH_2CMe_2CH_2)_2}]$, *trans*-$[\mathrm{PdCl_2(SCH_2CH_2CH_2)_2}]$, and *trans*-$[\mathrm{PdCl_2\{S(CH_2)_5\}_2}]$ in $\mathrm{CHCl_3}$ and *trans*-$[\mathrm{PdCl_2(SCH_2CMe_2CH_2)_2}]$ in $\mathrm{CH_2Cl_2}$ solvent have been measured for pressures up to 220 MPa. In each case a very small (0 ± 2 cm^3 mol^{-1}) volume of activation is found. These $\Delta V^‡$ values indicate no dissociative, associative, or solvent participation in the inversion process at sulphur, and substantiate the proposal that the major contribution to the entropy is the reorganizational effect on achieving ring planarity.

Dynamic nuclear magnetic resonance spectroscopy has been widely used to study intramolecular exchange processes. Among the systems attracting current interest is the pyramidal inversion about a co-ordinated thioether ligand.[1] Recently a number of detailed studies have been published on the inversion about sulphur in a series of cyclic sulphide complexes of palladium(II) and platinum(II).[2-6] These studies have concluded that the exchange processes are intramolecular and involve inversion about the ring sulphurs. Line shape analysis on n.m.r. spectra collected over a range of temperatures shows that there are significant differences in $\Delta S^‡$. A more direct probe of any associative, dissociative, or solvent contributions to the transition state can be made by measurement of any activation volume changes.[7]

In view of these variations in $\Delta S^‡$ between the complexes, and because there are no reported n.m.r. volume measurements in the literature on such intramolecular processes in inorganic or organometallic systems, we have measured the ^{1}H n.m.r. spectra of the series of complexes *trans*-$[\mathrm{PdCl_2(SCH_2CMe_2CH_2)_2}]$, *trans*-$[\mathrm{PdBr_2(SCH_2CMe_2CH_2)_2}]$, *trans*-$[\mathrm{PdCl_2(SCH_2CH_2CH_2)_2}]$, and *trans*-$[\mathrm{PdCl_2\{S(CH_2)_5\}_2}]$ over a pressure range up to 220 MPa. These complexes were selected because of their solubility characteristics and because their reported $\Delta S^‡$ values at ambient pressure range between +2.3 and −44.6 J K^{-1} mol^{-1}. The latter variation may suggest differences in transition-state solvation in the series of complexes.

Results

Spectra were obtained as a function of temperature and pressure. Experimental data obtained for *trans*-$[\mathrm{PdBr_2(SCH_2CMe_2CH_2)_2}]$ at 18 and 28 °C are shown in the Figure. The increase in inversion rate with temperature and the absence of a significant pressure effect is evident from these spectra. The data at 18 °C are near the coalescence temperature where the line shape should be most sensitive to pressure effects. Using literature chemical shift data,[2] line shapes for two-site exchange including inhomogeneity were calculated and compared with the observed spectra. An inversion rate of 170 s^{-1} was obtained as compared to 196 s^{-1} calculated from activation parameters.[2] Furthermore, the computed line shapes showed that a 20% change in rate over the pressure range studied should have been detectable. Since none was observed we conclude that $\Delta V^‡ = 0 \pm 2$ cm^3 mol^{-1},

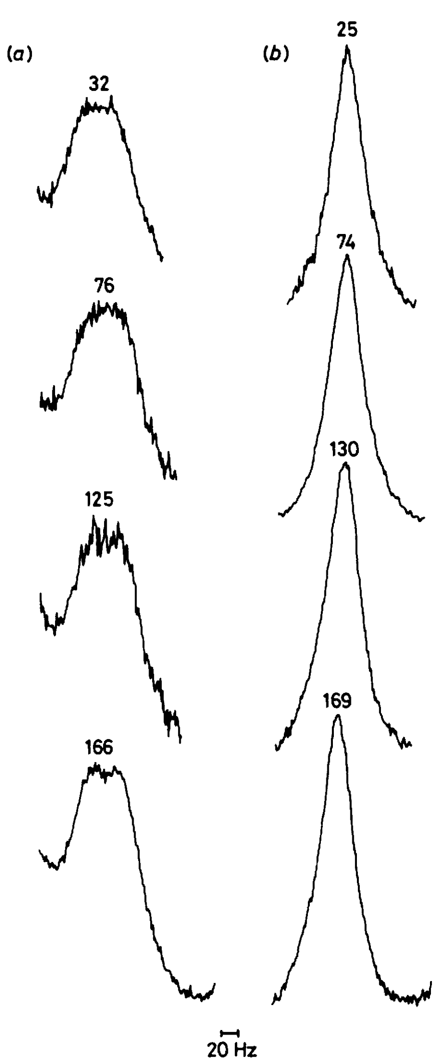

Figure. Proton n.m.r. spectra in the methylene region for *trans*-$[\mathrm{PdBr_2(SCH_2CMe_2CH_2)_2}]$ in $\mathrm{CHCl_3}$ at (*a*) 18 and (*b*) 28 °C over a range of pressures (MPa). Field inhomogeneity (due to the bomb), W_0 = 6.5 Hz using the equation $d\ln k/dP = -\Delta V^{\ddagger}/RT$. The compound *trans*-$[PdCl_2(\overline{SCH_2CH_2CH_2})_2]$ was studied at 26 °C and the data were treated in a similar manner. An inversion rate of 140 s^{-1} was found, as compared to the literature value[2] of 113 s^{-1}; from the fit $\Delta V^{\ddagger} = 0 \pm 2$ cm^3 mol^{-1}. In this compound the β-methylene group was in the fast-exchange region but gave lines partially overlapping the α-methylene groups, so their contribution was included in the computed line shapes. The compound *trans*-$[PdCl_2\{\overline{S(CH_2)_5}\}_2]$ was studied at −3 °C, near the coalescence temperature of the α-methylene groups. The spectrum is complicated due to the existence of axial and equatorial conformations of the ligands which have significantly different chemical shifts of the methylene groups.[4] Since the conformer equilibrium (ring reversal) is rapid at −3 °C the chemical shifts for ⟨ax′ eq′⟩ at −37 °C were used initially in calculating line shapes (see Table 3 in ref. 4). We found, however, that a better fit could be obtained using 50 Hz at −3 °C rather than the 40 Hz observed at −37 °C for the α-methylene chemical shifts. This is reasonable since the relative amounts of ax′ and eq′ should change with temperature. An inversion rate of 90 s^{-1} was obtained compared to 103 s^{-1} calculated from activation parameters.[4] By comparing the line shapes at different pressures a $\Delta V^{\ddagger}$ of 0 ± 2 cm^3 mol^{-1} was obtained. A spectrum of this compound taken at 200 MHz and −3 °C helped confirm the temperature dependence of the chemical shifts. Comparison of computed line shapes at 200 MHz gave a rate of 105 s^{-1}. In general, the component linewidths used for calculating line shapes were uncertain and greater than the inhomogeneity due to unresolved spin–spin splitting. The excess linewidths were comparable to the coupling constants producing the splitting.[2,4] These values were varied in computing spectra and found not to be critical in reaching the conclusions given above.

Discussion

The $\Delta V^{\ddagger}$ values reflect changes in volume between the initial and transition states of the system. Changes in solute, solvent, and their interactions are involved, and some compensation among these factors can be expected. Our measured $\Delta V^{\ddagger}$ values, which are within ± 2 cm^3 mol^{-1} of zero, suggest that intramolecular processes are involved in which solvation changes are small. For *trans*-$[PdCl_2(\overline{SCH_2CMe_2CH_2})_2]$ the inversion rate may be slightly slower at 220 MPa, indicating a slight positive value for $\Delta V^{\ddagger}$. It has been previously suggested that the measured $\Delta S^{\ddagger}$ values reflect changes in internal entropy on going to a 'planar' transition state.[6] Our results reinforce such a postulate that the variations in $\Delta S^{\ddagger}$ values are not a consequence of volume changes in the transition state which would result from solvent involvement. This result also leads to the conclusion that any changes in local dipole moment about sulphur upon attainment of the planar transition state are not sufficiently large to be reflected in transition-state volume changes.

Experimental

The complexes *trans*-$[PdCl_2(\overline{SCH_2CMe_2CH_2})_2]$, *trans*-$[PdBr_2(\overline{SCH_2CMe_2CH_2})_2]$, *trans*-$[PdCl_2(\overline{SCH_2CH_2CH_2})_2]$, and *trans*-$[PdCl_2\{\overline{S(CH_2)_5}\}_2]$ were prepared by published procedures.[3] Saturated solutions were made in $CHCl_3$ or CH_2Cl_2 as solvent.

The n.m.r. spectra were obtained using a Bruker WH-90 Fourier-transform spectrometer. For the probe arrangement the tank circuit used a 4-mm radio frequency (r.f.) coil double tuned to the ^1H and ^2H frequencies. The lock sample was D_2O, except for the spectra of *trans*-$[PdCl_2(\overline{SCH_2CMe_2CH_2})_2]$ and those at −3 °C, where the lock solution was 30% $LiClO_4$ in D_2O. The lock sample was contained in a n.m.r. tube (outside diameter 4 mm) and the sample solution in a Wilmad precision glass capillary (outside diameter 2 mm). The two solutions were coaxially arranged in the cell. The pressurizing fluid was CCl_4, except for solutions of the complex *trans*-$[PdCl_2(\overline{SCH_2CMe_2CH_2})_2]$ where $CDCl_3$ was used. Sample solutions were separated from the pressurizing fluid by a nylon cap inside the sample tube, and a Teflon cap over it. The titanium–aluminium alloy bomb containing the doubly tuned r.f. coil and thermocouple was constructed along the general lines of those used by Merbach and co-workers.[8,*] Electrical connections were made through a self-sealing arrangement of brass cones and titanium or berylco plugs, insulated with Torr-seal epoxy resin. The bomb was placed in a modified Bruker probe head containing the necessary tuning capacitors. A deuterium lock was used for field stabilization and the experimentally found inhomogeneity was 5—10 Hz. The ^1H n.m.r. signals of the methylene groups nearest the sulphur in the complexes were used for rate measurements. Spectral quality was solubility limited, and multiple pulses (100—500) were collected to obtain acceptable line shape. Temperature checks were made both before and after data collection, and as a general check on the apparatus and procedure the tautomerization of *NN*-dimethylacetamide was studied. A value of 11 ± 1 cm^3 mol^{-1} was obtained for $\Delta V^{\ddagger}$; lit.,[9] 10.3 cm^3 mol^{-1}.

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References

1 E. W. Abel, R. P. Bush, F. J. Hopton, and C. R. Jenkins, *Chem. Commun.*, 1966, 58.
2 E. W. Abel, M. Booth, and K. G. Orrell, *J. Chem. Soc., Dalton Trans.*, 1979, 1994.
3 E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell, and V. Sik, *J. Chem. Soc., Dalton Trans.*, 1980, 1169, 1175.
4 E. W. Abel, M. Booth, and K. G. Orrell, *J. Chem. Soc., Dalton Trans.*, 1980, 1582.
5 E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell, and V. Sik, *J. Chem. Soc., Dalton Trans.*, 1980, 2208, 2220.
6 E. W. Abel, G. W. Farrow, K. G. Orrell, and V. Sik, *J. Chem. Soc., Dalton Trans.*, 1977, 42.
7 T. Asano and W. J. Le Noble, *Chem. Rev.*, 1978, **78**, 407.
8 W. Earl, H. Vanni, and A. E. Merbach, *J. Magn. Reson.*, 1978, **30**, 571.
9 H. D. Lüdemann, R. Rauchschalbe, and E. Lang, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 331.

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* Details may be obtained from the authors.