^{35}Cl NQR SPECTROSCOPY AND PSEUDOROTATION IN SOLID CHLOROPHOSPHORANES

I.A. KJUNTSEL, V.A. MOKEEVA, G.B. SOIFER and I.G. SHAPOSHNIKOV

Radiospectroscopy Laboratory, University of Perm, 614005, Perm (U.S.S.R.)

(Received 20 January 1988)

ABSTRACT

The ^{35}Cl NQR frequency ν and the spin-lattice relaxation time T_1 have been investigated in solid tetrachlorophosphoranes $C_6H_5PCl_4$, $4\text{-}ClC_6H_4PCl_4$ and $2,6\text{-}Br_2\text{-}4\text{-}ClC_6H_2OPCl_4$ at temperatures from 77 K to the melting points. The fading of the NQR signals and the exponential shortening of the T_1 time for the chlorine nuclei in the P–Cl bonds show the existence of the exchange motion (pseudorotation) in these solids which involves three or four chlorine atoms corresponding to their interactions with the environment. The activation energies of the motion are found to lie in the range 40–70 kJ mol^{-1}.

INTRODUCTION

Pseudo-rotation [1] is an intramolecular motion consisting of the spatial rearrangement (exchange of positions) of ligands bonded to a multicoordinated central atom, the rate of such a motion increasing exponentially with temperature. Pseudorotational motion was first observed by means of the NMR method in the liquid and gas phases of pentafluorophosphorane [2], later in the liquid phase and in solutions of a number of compounds of pentacoordinated phosphorus. The results of these investigations show the activation energy of the motion in question to vary somewhat for different substances but not to exceed 80–85 kJ mol^{-1} which makes it probable that pseudorotational motions in the solid phase are also possible. In fact, such motions were observed in the crystalline dimer compounds $(Cl_3PNR)_2$ using the ^{35}Cl NQR method [3,4]; the corresponding values of the activation energy were found to be not greater than 60–100 kJ mol^{-1}, which shows that the pseudorotation rates amount to values registered by the NQR method near room temperatures.

This paper presents the results of an NQR study of pseudorotations in solid tetrachlorophosphoranes $RPCl_4$ ($R=Ar$, OAr); these substances are the chlorinated analogues of the classic subjects for the investigation of this kind of motion in liquids.

EXPERIMENTAL

Temperature dependence of the NQR frequencies ν and the spin–lattice relaxation time T_1 for the ^{35}Cl nuclei is studied in three phosphoranes: $C_6H_5PCl_4$ (**I**), 4-$ClC_6H_4PCl_4$ (**II**), and 2,6-Br_2-4-$Cl \cdot C_6H_2OPCl_4$ (**III**) using the pulse NQR spectrometer and the nitrogen gas cryostat in the temperature range from 77 K to the sample melting points (344, 350 and 390 K respectively). The experimental techniques and the data processing were described earlier [4]. The ^{35}Cl NQR frequencies measured in **I** and **II** at 77 K coincide within the bounds of experimental error with those obtained in refs. 5 and 6. The spectrum of **III** is observed for the first time by us (see ref. 7).

RESULTS AND DISCUSSION

The ^{35}Cl NQR spectra of the P–Cl bonds in the crystals of **I** and **II** are similar to one another (see Table 1). In each case two low-frequency (24–25 MHz) lines belong to the chlorine nuclei in two different axial bonds P–Cl_{ax}, two lines in the range of 33 MHz are due to the chlorine nuclei in the crystallographically nonequivalent equatorial bonds P–Cl_{eq} (the upper line, ~ 36 MHz, in **II** be-

TABLE 1

^{35}Cl NQR spectra and the parameters of eqns. (1)–(3) for the crystalline compounds $C_6H_5PCl_4$ (**I**), 4-$ClC_6H_4PCl_4$ (**II**) and 2,6-Br_2-4-$ClC_6H_2OPCl_4$ (**III**)

Com-pound	Nucleus	77 K		T_f^a (K)	$a \times 10^4$ (s^{-1}K^{-n})	n	b (s^{-1})	E_a (kJ mol^{-1})
		ν (MHz)	T_1 (s)					
I	Cl_{ax}	24.611	0.53	270	0.483	2.45		
	Cl_{ax}	25.515	0.54	270	0.398	2.49	4.12×10^{14}	53.5
	Cl_{eq}	33.584	0.20	270	4.59	2.13		
	Cl_{eq}	33.743	0.29	270	2.19	2.23		
II	Cl_{ax}	25.068	0.74	275	2.36	2.00		
	Cl_{ax}	25.546	0.71	275	3.37	1.93	3.85×10^{13}	50.9
	Cl_{eq}	33.491^b	0.31	275	9.89	1.86		
	Cl_{eq}	33.845	0.37	275	8.80	1.85		
	4-Cl	35.238	0.40	—	3.42	2.03		
III	Cl_{ax}	27.495	0.41	380	6.48	1.89	9.61×10^{12}	68.2
	Cl_{ax}	29.382	0.24	270	9.48	1.89	1.39×10^{12}	41.4
	Cl_{eq}	33.302	0.23	270	10.1	1.88		
	4-Cl	36.302	0.45	—	3.44	2.01		

^{a}The fade-out temperature.
^{b}The authors of [5] give the value of 33.420 MHz.

longs to the ^{35}Cl nuclei in the C–Cl bonds). These spectra show that the molecules of **I** and **II** have no symmetry elements and the aromatic radicals are in the equatorial position. However, in compound **III** two equatorial chlorine nuclei give a single line (33.302 MHz at 77 K, double intensity compared with other lines); this fact is evidence for the existence of the molecular plane of symmetry passing through the oxygen and chlorine atoms of the trihalogenphenoxy radical (the O–P bond being in the equatorial plane) and through two axial chlorine atoms. A considerable nonequivalence of the axial chlorine atoms, which is expressed by a large difference in frequency of the two lower-frequency lines (27 and 29 MHz), is due to the fact that the angle POAr < 180°. The resonance line about 36 MHz (like the crystal **II**) belongs to the chlorine nucleus in the aryl radical.

The character of temperature variation of the NQR frequency and the relaxation time T_1 for the chlorine nuclei in the analogous chemical bonds is the same in all three crystals. As an example we shall consider the results obtained for the crystal **III**. As a result of the heating of this crystal, the resonance lines belonging to the chlorine nuclei in the axial and equatorial P–Cl bonds fade out, the ^{35}Cl signal from one axial P–Cl bond fading out appreciably later than the ^{35}Cl signals from the other P–Cl bonds (Fig. 1). In all the cases, the fading of the signals follows the exponential shortening of the relaxation time T_1 which begins somewhat previously (Fig. 2). This fact indicates that the axial and equatorial chlorine atoms participate in a thermoactivated jump motion of the
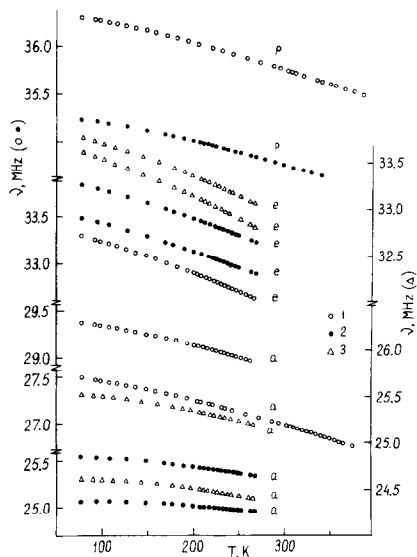

Fig. 1. Temperature dependence of the ^{35}Cl NQR frequencies: (I) 2,6-Br$_2$-4-ClC$_6$H$_2$OPCl$_4$; (2) 4-ClC$_6$H$_4$PCl$_4$; (3) C$_6$H$_5$PCl$_4$. The letters a and e mark the axial and equatorial positions of chlorine atoms in the molecules, p marks the *para* position of chlorine atom in aryl radicals.
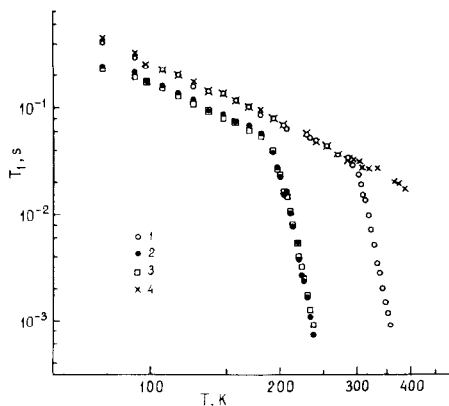
Fig. 2. Temperature dependence of the ^{35}Cl T_1 time in crystal 2,6-Br_2-4-$ClC_6H_2OPCl_4$: (1) Cl_{ax} (27 MHz); (2) Cl_{ax} (29 MHz); (3) Cl_{eq}; (4) 4-Cl.

Arrhenius type. The jump motion is not the reorientations of the molecule as a whole. Indeed, the NQR signal from chlorine nuclei in aryl radicals is observed up to the sample melting and its $T_1(T)$ dependence reveals only the usual power law (Fig. 2, Table 1) for molecular crystals which is caused by the molecular librations. Thus the observed thermoactivated process involves only the P–Cl bonds and is a position exchange of the pseudorotation type. The experimental results show that in the crystal **III** there are two exchange motions: less hindered, in which two equatorial and one axial chlorine atoms participate, and more hindered, in which the second axial chlorine atom takes part. Obviously, the former motion is similar to the exchange process in the $(Cl_3PNR)_2$ crystals [4] which takes place by "the trigonal twist" mechanism [1]. The latter motion is most probably a simultaneous exchange of all four chlorine atoms.

The character of the $T_1(T)$ dependence for the chlorine nuclei in the axial and equatorial P–Cl bonds is due to the effects of two independent additive mechanisms: the librations of the molecule as a whole and the above-mentioned exchange motion (Fig. 2)

$$(T_1^{-1})_{exp} = (T_1^{-1})_{libr} + (T_1^{-1})_{exch} \qquad (1)$$

where

$$(T_1^{-1})_{libr} = aT^n \qquad (2)$$

$$(T_1^{-1})_{exch} = b \times \exp(-E_a/RT) \qquad (3)$$

The Arrhenius contribution (3), which is most interesting, can be found by subtracting the $a \times T^n$ contribution from the experimental $T_1^{-1}(T)$ dependence (the $a \times T^n$ law is easily determined from the low-temperature part of

experimental curves where it dominates). The result of the subtraction is shown for the crystal **III** in Fig. 3 by two groups of points: A and D.

The least-squares fitting of the data obtained according to the rule mentioned above with relation (3) (see straight lines on Fig. 3) gives the values of the activation energy E_a for the chlorine position exchange (Table 1). The high value of E_a for the rearrangement involving the low-frequency axial chlorine atom in the crystal **III** (see Table 1) is accounted for by the interaction of this atom with trihalogenphenoxy radical which creates additional hindrances to the exchange motion.

The exchange motion is also observed in solid tetrachlorophosphoranes **I** and **II** where it leads to the simultaneous fading of the ^{35}Cl NQR signals from all the P–Cl bonds (as in the crystal **III**, the observation of the NQR signal from the C–Cl chlorine nuclei up to the sample melting and the power law of the temperature dependence of spin–lattice relaxation rate for these chlorine nuclei in the crystal **II** give evidence for the absence of the reorientations of the molecule as a whole). The temperature dependence of the exchange contributions in $T_1^{-1}(T)$ in the crystals of **I** and **II** is shown in Fig. 3 (the straight lines B and C). As is seen from Fig. 3, in this case the exchange contributions are equal for all the axial and equatorial P–Cl chlorine nuclei, i.e. these atoms participate simultaneously in the same motion which makes them indistinguishable. The last circumstance makes it impossible to accept the existence of the reorientations of the PCl$_4$ fragment by a 180° turn around the P–Ar bond.

The activation energies E_a which are obtained for the exchange motion in the crystals **I** and **II** using the experimental data processing with eqs. (1)–(3) are shown in Table 1.
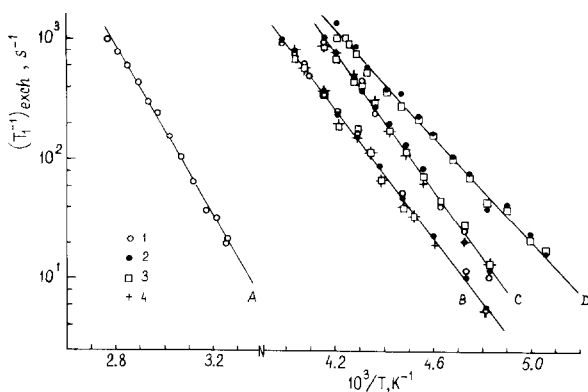

Fig. 3. Temperature dependence of the exchange contribution to the ^{35}Cl spin–lattice relaxation rate in crystals: (A,D) 2,6-Br$_2$-4-ClC$_6$H$_2$OPCl$_4$; (B) 4-ClC$_6$H$_4$PCl$_4$; (C) C$_6$H$_5$PCl$_4$. (1) Cl$_{ax}$ (low-frequency line); (2) Cl$_{ax}$ (high-frequency line); (3) Cl$_{eq}$ (low-frequency line); (4) Cl$_{eq}$ (high-frequency line).

All the data reported above lead to the conclusion that the ^{35}Cl NQR method makes it possible to reveal the intramolecular rearrangements (the exchange motion of the pseudorotation type) of the chlorine atoms in crystalline tetrachlorophosphoranes. It is found that the exchange motion in the solid phase of these compounds can involve three or four ligands corresponding to their intra- and intermolecular interactions with the environment.

REFERENCES

1 V.I. Sokolov, Vvedenie v Teoreticheskuyu Stereokhimiyu, Nauka, Moscow, I982.
2 H.S. Gutowsky, D.W. McCall and C.P. Slichter, J. Chem. Phys., 21 (1953) 279.
3 G.E. Kibrik, I.A. Kjuntsel, E.S. Kozlov, V.A. Mokeeva and G.B. Soifer, J. Mol. Struct., 83 (1982) 113.
4 G.E. Kibrik, I.A. Kjuntsel, E.S. Kozlov, V.A. Mokeeva and G.B. Soifer, Magn. Reson. Chem., 23 (1985) 903.
5 V.I. Svergun, V.G. Rozanov, E.F. Grechkin, B.R. Timokhin, Yu.K. Maksutin and G.K. Semin, Izv. Akad. Nauk SSSR, Ser. Khim., 8 (1970) 1918.
6 M. Kaplansky, R. Clipsham and M.A. Whitehead, J. Chem. Soc. A, (1969) 584.
7 E.S. Kozlov, I.A. Kjuntsel, V.A. Mokeeva and G.B. Soifer, Zh. Obshch. Khim., 57 (1987) 953.