Journal of Molecular Structure, 32 (1976) 393—402

VIBRATIONAL ANALYSIS OF CHLORINATED METHYLPHOSPHONIC ACIDS AND THEIR ANIONS
PART III. $CCl_3PO_3H_2$

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(Received 3 September 1975)

ABSTRACT

The IR and Raman spectra of $CCl_3PO_3H_2$ and its anions are reported. Included are the spectra of aqueous solutions of the anions and solid state IR spectra of the acid and of the Na and K salts. The results of the normal coordinate analysis for the dibasic anion are given.

INTRODUCTION

The IR and Raman spectra of $CCl_3PO_3H_2$ and its anions are analysed. No spectra of the aqueous solutions of undissociated acid molecules could be obtained, as expected from the very acidic character of the first dissociation step, prohibiting the numeric evaluation of the first acidity constant by potentiometric methods[1]. Addition of hydrochloric acid to solutions of the acid caused $CCl_3PO_3H_2$ to precipitate, leaving solutions of too low a concentration for vibrational spectra to be obtained. The spectra reported in this study for the anions of the acid include the aqueous solution IR and Raman, in H_2O and D_2O, and solid state IR in the region 4000—450 cm^{-1}.

EXPERIMENTAL

The dimethyl ester of the acid was prepared by the reaction of CCl_4 with $P(OCH_3)_3$. After distillation, the ester was hydrolysed by reflux in excess concentrated HCl. The acid was purified by recrystallisation from H_2O. The salts were prepared by simple metathesis. The IR spectra were recorded on a Perkin-Elmer 225 grating IR spectrometer, using AgCl as window material. The Raman spectra were taken with a Coderg PHO instrument, equipped with a OIP He—Ne laser.

$CCl_3PO_3^{2-}$ in aqueous solution

The observed frequencies and their proposed assignment are given in Table 1. The maximum symmetry for this anion is C_{3v}. Under this symmetry, the fundamentals are described by

$$\Gamma = 5a_1 + a_2 + 6e$$

The only vibration forbidden in the IR and Raman is the a_2 vibration, corresponding to the torsional motion. The a_1 vibrations can be described as $\nu(PO_3)$, $\nu(PC)$, $\nu(CCl_3)$, $\delta(PO_3)$ and $\delta(CCl_3)$, the e vibrations as $\nu(PO_3)$, $\nu(CCl_3)$, $\delta(PO_3)$, $\delta(CCl_3)$, $\rho(PO_3)$ and $\rho(CCl_3)$.

Compared with other phosphonic acid studies [2—4] and using polarisation data from the Raman spectra, the PO_3 stretches are easily localised. For highly concentrated solutions, in the IR the 1130 cm^{-1} band, attributed to the e-species $\nu(PO_3)$, becomes asymmetric, so under these conditions the C_{3v} symmetry is lowered by asymmetric solvation, causing the e-mode to split. In the PO_3 deformation region, two bands at 558 and 501 cm^{-1}, respectively, are observed in the Raman spectra and due to its clear polarisation, the former is attributed to $\delta(PO_3)$, a_1. Compared with the spectra of $CCl_3SO_3^-$, studied by Miles et al. [5], the strong 402 cm^{-1} band must be due to $\nu(CCl_3)$, a_1. $\nu(PC)$, a_1 and $\nu(CCl_3)$, e are expected in the 900—700 cm^{-1} region and in both the IR and Raman, two bands are observed, near 860 and 760 cm^{-1}, neither of which shows clear polarisation, however in view of its greater intensity in the Raman spectrum, the 760 cm^{-1} band could be attributed to the a_1 vibration. This contradicts the expected value of $\nu(PC)$, which is found to increase in the series $CH_3PO_3^{2-}$—$CHCl_2PO_3^{2-}$ [2—4], and the extrapolated $CCl_3PO_3^{2-}$ is expected above 800 cm^{-1}. The proposition is also contradicted by the solid state IR spectra of the disodium salt; therefore $\nu(PC)$, a_1 is attributed to the 862 cm^{-1} band and $\nu(CCl_3)$, e to the band at 759 cm^{-1}.

TABLE 1

Vibrational spectra of $CCl_3PO_3^{2-}$ in aqueous solution

IR (H_2O)		IR (D_2O)		Raman (H_2O)		Raman (D_2O)		Assignment
$\bar{\nu}$ (cm^{-1})	R.I.	$\bar{\nu}$ (cm^{-1})	R.I.	$\bar{\nu}$ (cm^{-1})	R.I.	$\bar{\nu}$ (cm^{-1})	R.I.	
1130	vs, br	1125	vs, br	1130	3	1130	3	$\nu(PO_3)$, e
989	s	984	s	994	45, P	997	45, P	$\nu(PO_3)$, a_1
890~	sh			862	3	864	3	$\nu(PC)$, a_1
750~	sh	752	m	759	13	763	14	$\nu(CCl_3)$, e
500~	sh	550~	w	558	5, P	585	3, P	$\delta(PO_3)$, a_1
				501	3	515	3	$\delta(PO_3)$, e
				402	100, P	405	100, P	$\nu(CCl_3)$, a_1
				328	10	329	9	$\rho(PO_3)$, e
				265	19	267	16	$\delta(CCl_3)$, a_1 + e
				167	13	172	10	$\rho(CCl_3)$, e

The 328 cm^{-1} band in the Raman spectra is attributed to $\rho(PO_3)$. $\delta(CCl_3)$ (a_1 + e) and $\rho(CCl_3)$, e remain to be attributed. The Raman bands at 265 and 167 cm^{-1} have not yet been interpreted. In correlation with the assignments for $CCl_3SO_3^-$ [5], the a_1- and e-type $\delta(CCl_3)$ vibrations are assumed to be accidentally degenerate and give rise to the 265 cm^{-1} band, leaving the 167 cm^{-1} band due to $\rho(CCl_3)$.

$CCl_3PO_3Na_2$ and $CCl_3PO_3K_2$ in the solid state

The observed frequencies, and their proposed assignment, are given in Table 2. Two bands at 1164 and 1118 cm^{-1}, respectively, are observed for the Na_2-salt, in the asymmetric PO_3 stretchings region, compared with one in the symmetric PO_3 stretch region at 997 cm^{-1}. This indicates that the C_{3v} anion has lower symmetry in the crystal. The bands at 590 and 398 cm^{-1}, attributed to $\delta(PO_3)$, a_1 and $\nu(CCl_3)$, a_1, respectively also appear single, as does the e-type $\delta(PO_3)$ and $\rho(PO_3)$. It is not clear whether the doublet 254—231 cm^{-1} is to be attributed to lifting of the accidental degeneracy of the corresponding 265 cm^{-1} band of the aqueous solution, or is caused by the symmetry lowering due to site-effects, in which case, of course, accidental

TABLE 2

IR spectra of $CCl_3PO_3Na_2$ and $CCl_3PO_3K_2$ in the solid state

I		II		Assignment
$\bar{\nu}$(cm^{-1})	R.I.	$\bar{\nu}$(cm^{-1})	R.I.	
		3280	m, vbr	(H_2O)
		1660	w	
		1610	w	
1164	s	1140	vs, br	$\nu(PO_3)$, e
1118	s			
997	s	989	s	$\nu(PO_3)$, a_1
		925	w, br	(H_2O)
859	w	843	w	$\nu(PC)$, a_1
		760~	w, sh	$\nu(CCl_3)$, e
757	s	748	s	
745	s	732	s	
		700~	w, sh	
		660	w	(H_2O)
		584	s	$\delta(PO_3)$, a_1
590	s	565	w, sh	
		556	w	
523	m	498	s	$\delta(PO_3)$, e
398	w	394	w	$\nu(CCl_3)$, a_1
335	w	323	w	$\rho(PO_3)$, e
254	s	250	w	$\delta(CCl_3)$, a_1 + e
231	s			

I, $CCl_3PO_3Na_2$; II, $CCl_3PO_3K_2$.

degeneracy must still be accepted. In view of the observation of single bands for e-type $\delta(PO_3)$ and $\rho(PO_3)$, the former explanation is preferred. It is, however, clear that for none of the a_1-vibrations yet assigned, splitting was observed in this spectrum. Therefore the doublet at 757—745 cm^{-1}, which is to be correlated with the 759 cm^{-1} band of the solution, must be due to an e-type vibration, and consequently is attributed to $\upsilon(CCl_3)$, e, the 859 cm^{-1} band to $\upsilon(PC)$, a_1.

The dipotassium salt was obtained as a dihydrate. The low frequency for $\upsilon(OH)$, 3280 cm^{-1}, indicates strong hydrogen-bonded H_2O molecules. The bands at 2400 cm^{-1} and the doublet at 1660—1620 cm^{-1} are also attributed to vibrations of the hydrate—water. The splitting of the OH_2 bending probably indicates that two different kinds of water are present in the crystal.

For this salt no splitting is observed for the band attributed to the asymmetric PO_3 stretching. It should be noted that the band attributed to $\upsilon(CCl_3)$, e is decomposed in several components, while only a single maximum is observed for the band attributed to $\upsilon(PC)$, a_1. The decomposition observed in the broad band near 570 cm^{-1} and the appearance of a single sharp maximum near 498 cm^{-1} appears to contradict our assignment of the a_1 deformational PO_3 mode in the aqueous phase Raman spectra, however, the polarisation observed in the latter indicates that the splitting observed for the solid dipotassium salt cannot be due to simple site symmetry effect. The weak band near 660 cm^{-1} is attributed to the libration of the water molecules, while the weak 925 cm^{-1} band is due to an overtone.

$CCl_3PO_3H^-$ in solution

The frequencies observed for the aqueous solution of this anion are gathered in Table 3. The maximum symmetry for this anion is C_s. Under this symmetry, the fundamental vibrations are divided into the symmetry species as:

$$\Gamma = 13\,a' + 8\,a''$$

All of the fundamentals are active in IR and Raman. Except for the OH vibrations, the fundamentals of the monobasic anion can be correlated with those of the dibasic anion following the scheme

$$\begin{tikzcd}
C_{3v} & C_s \\
a_1 \arrow[r] & a' \\
a_2 \arrow[r] & a'' \\
e \arrow[uur] \arrow[ur] &
\end{tikzcd}$$

Bands due to the "A,B,C" - pattern [6] of the OH valence vibrations were observed in neither IR, nor Raman. Furthermore, $\delta(OH)$ and $\gamma(OH)$ vibrations were not found, as they are probably hidden by the strong PO valence bands.

TABLE 3

Vibrational spectra of $CCl_3PO_3H^-$ in aqueous solution

IR (H_2O)		IR (D_2O)		Raman (H_2O)		Raman (D_2O)		Assignment
$\bar{\nu}$(cm^{-1})	R.I.	$\bar{\nu}$(cm^{-1})	R.I.	$\bar{\nu}$(cm^{-1})	R.I.	$\bar{\nu}$(cm^{-1})	R.I.	
1220	s, br	1220	vs, br	1216	1	1220	1	$\nu(PO_2)$, a''
1095	s	1093	s	1101	10, P	1092	10, P	$\nu(PO_2)$, a'
				997	1, P			($CCl_3PO_3^{2-}$)
942	m	930	m	950	7, P	940	6, P	ν(POH), a'
860~	vw, sh			870	3, P	875	4	ν(PC), a'
775~	w	763	m	773	12	776	11	$\nu(CCl_3)$, a' + a''
540~	w	549	w	555	7, P	542	8, P	$\delta(PO_3)$, a'
				479	6	475	5	$\delta(PO_3)$, a' + a''
				404	100, P	406	100, P	$\nu(CCl_3)$, a'
				321	10	319	8	$\rho(PO_3)$, a' + a''
				261	18	260	sh.	$\delta(CCl_3)$, 2a' + a''
				244	11	241	17, P	
				166	11	163	10	$\rho(CCl_3)$, a' + a''

The interpretation of the spectra in the P—O valence vibration region is analogous to that given for other monobasic phosphonates [2—4]. The weak 997 cm^{-1} Raman band is attributed to ν(PO), a_1 of the dibasic anion, which is present due to hydrolysis of the monobasic anion.

The 870 cm^{-1} Raman band, correlated with ν(PC), a_1 of the dibasic anion is, compared with the 773 cm^{-1} band, correlated with $\nu(CCl_3)$, e, clearly polarised. It is however difficult to use this polarisation as a definitive argument for the attributions made for the dibasic anion, as under C_s symmetry, the e-type vibration gives rise to an a' component. In the region near 250 cm^{-1}, where for the dibasic anion an accidental degeneracy of the a_1 and e CCl_3 deformations was accepted, for the monobasic anion two strongly overlapping bands are observed in the Raman spectra. It is more obvious that the observed splitting is due to lifting of the accidental degeneracy than due to the splitting of an e-type fundamental. Although for C_s symmetry the torsional motion is allowed in Raman and IR, no bands due to this vibration have been observed.

CCl_3PO_3HNa and CCl_3PO_3HK in the solid state

The observed IR frequencies for these salts and their proposed assignment, are given in Tables 4 and 5. The Na-salt was obtained as a hydrate. The bands at 3140, 2350 and 1700 cm^{-1} are attributed to ν(OH), the "association-band", and $\delta(OH_2)$ of the hydrate water respectively. The low frequency for ν(OH) indicates strongly hydrogen bonded molecules. The 649 cm^{-1} band, which disappears upon deuteration, is attributed to the librational mode of the water molecules.

The bands observed at 2800 and 1800 cm^{-1} are attributed to bands A and C of the O—H valence vibration of the monobasic anion. The weak 2650 cm^{-1}

TABLE 4

IR spectra of CCl_3PO_3HNa in the solid state

I		II		Assignment
$\bar{\nu}$(cm^{-1})	R.I.	$\bar{\nu}$(cm^{-1})	R.I.	
3140	s, vbr	3160	w, br	(H_2O)
		2950~	w, sh	ν(OH), ν(OD)
2800~	w, sh			
		2650	vw, sh	
		2480	s, br	
2350	m, vbr			
		2100~	w, sh	
		1820	m, vbr	
1800	w, sh			
1700	m, br			(H_2O)
1313	m, br			δ(OH)
1215	s	1232	s	$\nu(PO_2)$, a″
1101	s	1108	s	$\nu(PO_2)$, a′
		1045~	w, sh	
947	s	942	s	ν(POH), a′
		910~	w, sh	δ(OD)
870	w	865	w	ν(PC), a′
800~	vw, sh			$\nu(CCl_3)$, a′ + a″
763	s	764	s	
753	s	753	s	
725~	vw, sh			
		695	w, sh	γ(OD)
649	m			(H_2O)
553	s	540	m, vbr	$\delta(PO_3)$, a′ + a″
487	s	483	w	$\delta(PO_3)$, a′
401	m			$\nu(CCl_3)$, a′
352	m			$\rho(PO_3)$, a′ + a″
326	m			
279	w			$\delta(CCl_3)$, 2a′ + a″
263	m			
236	s			
218	sh			
209	w			

I, CCl_3PO_3HNa; II, CCl_3PO_3DNa.

shoulder is due to an overtone. Upon deuteration, strong shifts occur in this region, although the patterns indicate incomplete deuteration. This implies that besides H_2O and D_2O, HDO molecules are also present, which makes a definite attribution very difficult. Nevertheless, the attributions of the 2950 and 2100 cm^{-1} bands to the A-band of normal, and deuterated salt respectively, and the bands near 3160 and 2480 cm^{-1} to hydrate molecules, appear certain.

Upon deuteration, the 1313 cm^{-1} band disappears, while a new band appears near 910 cm^{-1}. Although the observed shift is larger than calculated,

TABLE 5

IR spectra of CCl_3PO_3HK in the solid state

I		II		Assignment
$\bar{\nu}$(cm^{-1})	R.I.	$\bar{\nu}$(cm^{-1})	R.I.	
		3500	m, vbr	(H_2O)
2740	m, vbr	2740	m, vbr	ν(OH)
2530	w			
2400~ 2320	m, vbr	2315	m, vbr	
1650	m, vbr	1680 1610	m, vbr	(H_2O)
1290	w, br	1290	w, br	δ(OH)
1214	s	1215	s	$\nu(PO_2)$, a″
		1193	s	
1126	m	1110	w, sh	$\nu(PO_2)$, a′
1069	w, sh	1085~	sh	
1042	s, br	1056	s	
941	w, sh	956	s	ν(POH), a′
936	s	934	s	
872	w	858	w	ν(PC), a′
860	w, sh			
757	s	760~	sh	$\nu(CCl_3)$, a′ + a″
		749	s	
543	s	560	s	$\delta(PO_3)$, 2a′ + a″
517	m	512	m	
468	s	470	s	
399	w			$\nu(CCl_3)$, a′
325	m			$\rho(PO_3)$, a′ + a″
276	w			$\delta(CCl_3)$, 2a′ + a″
252	w			

I, CCl_3PO_3HK, anhydrous; II, CCl_3PO_3HK, hydrated.

it seems appropriate to interpret the bands as δ(OH) and δ(OD). In the spectrum of the deuterated salt a new band is found at 695 cm^{-1}. If this band is attributed to γ(OD), the corresponding γ(OH) is calculated at 955 cm^{-1}. in this region only ν(POH), a′ is found at 947 cm^{-1}. For the normal salt however a weak shoulder is observed near 900 cm^{-1}, probably corresponding to γ(OH). The other bands in the spectra of the Na-salt were attributed with the aid of the spectra obtained from the aqueous solutions.

In the spectrum of the anhydrous K-salt, the bands of the 'A,B,C'-pattern are very clearly observed. Band B shows some fine structure, in accordance with the Fermi-resonance explanation of the pattern [6]. Very remarkable are the shifts in the region of the PO valence vibration upon hydration of the anhydrous salt: the three bands of the latter at 1126, 1069 and 1042 cm^{-1} merge upon hydration and consequently are due to the same vibration of the isolated anion; in view of their position, they are attributed to $\nu(PO_2)$, a′.

The other two PO stretches, both giving rise to single bands in the anhydrous salt, split upon hydration into doublets. It is clear that drastic changes in crystal structure occur during hydration. The other bands in the spectra of the potassium salt are interpreted similar to those of the sodium salt.

$CCl_3PO_3H_2$ in the solid state

The frequencies observed in the IR spectrum of the solid acid, together with their proposed assignment, are given in Table 6. Bands A and B of the O—H valence vibrations are clearly visible. In the lower region, two weak bands are observed at 1560 and 1450 cm^{-1}. The former may be identified with band C of the pattern. It is difficult to interpret the 1450 cm^{-1} band also as a C-band, due to its low frequency: if this low frequency is explained by strong hydrogen bonds, then its low intensity compared with band A cannot be adequately explained. Therefore, the interpretation of this band as a combination- or overtone-band cannot be rejected. In the region of PO valence- and OH deformation- vibrations, a massive absorption with several maxima is observed. Due to the strong overlapping, no strict attribution is possible, and the attributions given in Table 6 must be regarded as approximate.

In the region of the PC stretches, two bands are observed at 873 and 865 cm^{-1}, and only one, at 778 cm^{-1}, is seen in the region of asymmetric CCl_3 stretches. The latter, however, is very broad. These features might indicate that our attributions are wrong. It appears, however, to us that the splitting of $\nu(PC)$ is due to crystal effects, whereby we accept that the

TABLE 6

IR spectrum of $CCl_3PO_3H_2$ in the solid state

$\bar{\nu}(cm^{-1})$	R.I.	Assignment
2800	m, vbr	$\nu(OH)$
2280	w, br	
2150	w, br	
1560	w, br	
1450	w, br	
1210~	s, vbr	$\delta(OH)$
1138		$\nu(PO)$, a′
1095~		$\delta(OH)$
1025		$\nu(P(OH)_2)$, a″
978		$\nu(P(OH)_2)$, a′
920~	vw, sh	$\gamma(OH)$
900~	vw, sh	
873	w, sh	$\nu(PC)$, a′
865	w	
778	s, br	$\nu(CCl_3)$, a′ + a″
710~	w, br	
549	w, sh	$\delta(PO_3)$, 2a′ + a″
531	m	
483	m	

different components in the region of CCl_3 stretches overlap too strongly to be observed individually. This broadening due to the presence of several components can also explain the massive absorption in the region 1250—900 cm^{-1}.

In the region of the PO_3 deformations also contradictory splittings are observed. The limitation of the spectrum to 450 cm^{-1} however excludes clear conclusions.

NORMAL COORDINATE ANALYSIS

For the dibasic anion, a normal coordinate analysis was made using Wilson's GF-matrix method. The anion was treated in a C_{3v} staggered form. All angles were taken to be tetrahedral. Bond lengths were transferred from other phosphonic acids [2—4]. The same symmetry coordinates as for the dibasic anion of methylphosphonic acid were used [7]. The force constants were calculated using the Matrix Polynomial Expansion Method of Alix [8]. Potential energy distributions were calculated using the formulas given by Alix and Müller [9]. Experimental frequencies were taken from the aqueous phase spectra. In Table 7 we have given those internal force constants that can be obtained unambiguously from the symmetry force constants. In Tables 8 and 9 are presented the potential energy distributions.

TABLE 7

Internal stretching force constants and stretch—stretch interactions of $CCl_3PO_3^{2-}$[a]

	f	Δf
f_{PO}	6.893	0.038
f_{PC}	4.729	0.033
f_{CCl}	2.779	0.030
f_{PO-PO}	0.023	0.038
f_{PO-PC}	0.223	0.009
f_{PO-CCl}	0.055	0.002
f_{PC-CCl}	0.285	0.011
$f_{CCl-CCl}$	0.337	0.023

[a] All data are in mdyne Å^{-1}.

TABLE 8

Potential energy distribution for the A_1 vibrations of $CCl_3PO_3^{2-}$

$\bar{\nu}$	$\nu(PO_3)$	$\nu(CCl_3)$	$\nu(PC)$	$\delta(PO_3)$	$\delta(CCl_3)$
991	0.508	0.024	0.356	0.090	0.020
863	0.446	0.085	0.398	0.003	0.067
558	0.044	0.118	0.002	0.780	0.055
404	0	0.772	0.121	0.079	0.026
265	0	0	0.122	0.046	0.830

TABLE 9

Potential energy distribution for the E vibrations of $CCl_3PO_3^{2-}$

$\tilde{\nu}$	$\nu(PO_3)$	$\nu(CCl_3)$	$\delta(PO_3)$	$\delta(CCl_3)$	$\rho(PO_3)$	$\rho(CCl_3)$
1130	0.943	0	0.042	0	0.010	0.002
760	0.002	0.763	0	0.140	0.051	0.042
501	0.044	0	0.951	0	0	0.003
328	0.005	0.205	0.001	0.274	0.478	0.035
265	0.003	0.016	0.001	0.582	0.370	0.025
169	0	0.014	0.003	0.003	0.089	0.889

CONCLUSION

This part concludes our investigation on chlorinated methylphosphonic acids. For the compounds treated in this article, most of the fundamentals could be assigned. Only the assignment of $\nu(PC)$ and the asymmetric $\nu(CCl_3)$ is not completely certain, although in our opinion, the evidence obtained from the IR spectrum of the disodium salt seems convincing. Nevertheless, structure determination of these compounds by X-ray or neutron diffraction seems to be necessary to enable decisive conclusions to be drawn.

ACKNOWLEDGEMENTS

Prof. Dr. J. Devreese is thanked for computer facilities. Dr. A. Alix from the University of Reims is thanked for many helpful discussions.

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