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CONCLUSIONS

1. Perfluoro-tert-butanol forms H bonds of the OH...OC—M type with transition metal carbonyl π complexes: $CpM(CO)_3$ ($Cp = \eta^5\text{-}C_5H_5$ and $\eta^5\text{-}Et_5C_5$, M = Mn, Re), $MezM(CO)_3$ ($Mez = \eta^6\text{-}Me_3H_3C_6$, M = Cr, Mo, W), $(\eta^5\text{-}C_5H_5)M(CO)_2PR_3$ (R = Ph, i-Pr, M = Mn, Re) at low temperatures in liquid xenon and at -20°C in CCl_4.

2. For isostructural complexes, the basicity of the O atom of the CO group increases on substitution of one of the CO groups by a phosphine ligand, introduction of alkyl substituents in the π ring, and in going from Mn to Re.

3. Hexacarbonyls $M(CO)_6$ (M = Cr, Mo, W) do not form an H bond with perfluro-tert-butanol.

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VIBRATIONAL SPECTRA AND CONFORMATIONS OF VINYLDICHLOROPHOSPHINE SULFIDE MOLECULES

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Information about the steric structure of vinyldichlorophosphine sulfide (VDCPS) is given in [1], where it was concluded on the basis of the singlet form of the νC═C band in the IR spectrum that the conformation of this compound is of one type. However, our attention is drawn to the fact that the total number of bands in the spectrum of VDCPS is larger than expected for a single conformer (29 instead of 21). This fact prompted us to carry out a conformational study of this compound that was as thorough as possible. We used IR and Raman spectroscopy for this purpose and also calculated the fundamental vibrational modes.

The vibrational spectra of VDCPS were obtained for the three states of aggregation of the substance — gas, liquid, and solid (Table 1). By analyzing Table 1 it can be seen that in the spectra of the liquid and gas there are complex spectral patterns in the region of νPCl_2 (440-520 cm^{-1}), γ: CH (580-610 cm^{-1}), νP═S (660-690 cm^{-1}), and νP═C (760-790 cm^{-1}). In the spectra of the liquid when there is a variation in temperature, a redistribution of intensities of the separate components of the multiplets occurs. As the substance is cooled there is a decrease in intensity of the following bands in the IR spectrum: 520 (shoulder), 584 (shoulder), 668, and 764 cm^{-1}. Under the given experimental conditions it was not possible to obtain an IR spectrum of the crystalline phase. Analogous changes occur in the Raman spectrum of the liquid when the sample is cooled; and when changing to the crystalline state those bands listed above as well as ones at 448 and 390 (shoulder) cm^{-1} are "frozen out." This fact

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TABLE 1. Parameters of Vibrational Spectra and Results of Calculations of Frequencies and Fundamental Vibrational Modes for Vinyldichlorophosphine Sulfide

IR spectrum		Raman spectrum			Calculation		
gas, ν, cm^{-1}	liquid	liquid		crystal	ν, cm^{-1}		assignment*
	ν, cm^{-1}	ν, cm^{-1}	ρ	ν, cm^{-1}	φ 12°	φ 150°	
		98 w			99	98	Torosional PC
		170 m	0,86	174 w	168	166	δ_sPC, δ_{as}ClPS
	181 w	182 s	0,86	181 m	181	183	δPCl$_2$
	214 m	215 m	0,80	215 m	221	229	rPS
	254 s	254 m	0,85	252 m	252 255	249 254	tPCl$_2$, wPCl$_2$
	378 m	381 v.s	0,05	380 v.s	373		δPCC, δHCC
	394 v.w	390 sh	–	–		376	
449 w	447 s	448 m	0,10	–		448	ν_sPCl$_2$
483 m, 490 m	480 v.s	482 v.s	0,10	483 v.s	482		
503 s, 510 sh	502 v.s	500 sh	0,80	505 m	500		ν_{as}PCl$_2$
	520 sh	520 sh				532	
597 sh	584 sh	580 v.w	0,45	–		578	γCHP, $\chi^{CHP}_{CH_2}$, γCH$_2$
603 s, 610 m	603 v.s	600 v.w	0,75	600 v.w	597		
660	658 v.s	660 m	0,25	658 m	660		νPS, νPC
683 sh, 690 m, 693 sh	688 s	690 w	0,20			673	νPS
777 s	764 s	763 m	0,20	–		763	νPC, νPS
781 s, 789 v.s, 793 s	778 v.s	775 m	0,20	775 m	767		
963 w	958 m	958 v.w	–		957	957	γCH$_2$, $\chi^{CHP}_{CH_2}$, γCHP
970 sh, 977 m, 983 w	982 v.s	982 v.w			985	985	γCH$_2$, γCHP, $\chi^{CHP}_{CH_2}$
1010 sh, 1013 m, 1022 sh	1010 s	1012 v.w	0,65		1012	1013	rCH$_2$, δPCH, νPC
1260 v.w	1260 w	1260 m	0,15	1261 w	1260	1260	δPCH, νC=C
1371 sh,	1380 v.s	1383 m	0,25	1383 w	1404	1402	δCH$_2$$\delta$PCH
1377 s,							Overtone νP–C
1387 m							
1547 sh							
1574 w	1590 sh	1580 v.w	–			1594	νC=C, δPCH, δCH$_2$
1609 w	1600 m	1602 s	0,10	1602 s	1602		
2980	2962 v.w	2962 w	0,25				Combination tone νC=C+δ :CH
	3010 w	3010 m	0,10		3014	3014	ν_s :CH$_2$
3020	3034 m	3037 m	0,40		3041	3041	ν :CH
3101	3094 w	3094 m	0,55		3118	3118	ν_{as}CH$_2$

*γ — nonplanar fan vibrations; χ — "twisting" vibrations about the C=C bond.

indicates that the frequencies at 390, 448, 520, 584, 688, and 764 cm^{-1} belong to a less stable comformer (II). The bands at 480, 502, 603, 658, and 778 cm^{-1}, the intensities of which increase on cooling, can be assigned to a correspondingly more stable conformer (I).

Using a modified form of the Van't Hoff equation based on the temperature dependence of the intensities of the bands belonging to different molecular forms [2], the differences in enthalpy ΔH^{I-II} of the given conformers were determined for the following pairs of bands: 603/584 (γ:CH), 658/688 (νP=S), and 778/764 cm^{-1} (νP—C). The values obtained were 555, 801, and 684 cal/mole, respectively. The most reliable value is evidently 801 cal/mole, since it was obtained for the pair of νP=S bands, which have very little overlap. Thus ΔH^{I-II} was taken as equal to 800 ± 100 cal/mole. The error is indicated by s_b, the standard deviation of the slope of the respective graph [3].

In the Raman spectrum in the region 400-800 cm^{-1} the only low-polarized band is the shoulder at 500 cm^{-1} (Table 1). The value given in Table 1 was obtained by resolving the observed profile into separate components. The value of ρ, and also the reduction in intensity when changing from the IR spectrum (very strong) to the Raman spectrum (weak) indicates that it belongs to ν_{as}PCl$_2$ of the stable conformer (I). The second component of this doublet, the shoulder at 520 cm^{-1}, should be assigned to conformer (II), judging by its dependence on temperature. The sharply polarized line at 448 cm^{-1}, which "freezes out" when the substance is crystallized, can be assigned to ν_sPCl$_2$ of conformer (II). Consequently, the polarized line at 480 cm^{-1}, the intensity of which increases when the temperature is lowered, should be assigned to ν_sPCl$_2$ of the stable form (I) of VDCPS.

In contrast to vinyldichlorophosphine oxide (VDCPO) [4], the νC=C region in the vibrational spectra of VDCPS is conformationally less sensitive, judging by the data obtained. In fact, the symmetrical band at 1600 cm^{-1} in the IR spectrum has a very weak shoulder at 1590 cm^{-1}, which is more clearly identified only in the Raman spectra. It was not possible to analyze this region in the spectrum of the solid crystal because of the unsatisfactory signal to noise ratio. Because of the high instability of the substance, it also proved impossible to obtain spectra of solutions.

Spectra of VDCPS in the gas phase were obtained after passing the substance beforehand through a chromatographic column. From a comparison of the intensities of the conformationally sensitive bands, it transpires that the fraction of stable conformer increases in the gas phase. Thus, the ratio of optical densities D_{660}/D_{690} of $\nu P{=}S$ increases from 2.2 in liquid to 2.8 in gas. As the less polar form must be stabilized in the gas phase, it can be assumed from the results obtained that the more stable conformer (I) has a lower dipole moment.

In the gas phase there are three bands in the $\nu C{=}C$ region at 1609, 1574, and 1547 cm^{-1}. The first two we have assigned to conformers (I) and (II), respectively. The band at 1547 cm^{-1} is likely to be an overtone $\nu P{-}C$ vibration.

For a more detailed interpretation of the spectra, the frequencies and fundamental vibrational modes of the different rotational isomers of VDCPS were calculated. The geometric and potential parameters of the molecule were assumed to be identical to the parameters of VDCPO in [4], with the exception of the P=S bond, the length of which was taken to be equal to 1.92 Å and the force constant equal to $7.8 \cdot 10^6$ cm^{-2}. The dihedral angle φ between the plane of the vinyl group and the plane containing the P=S and P–C bonds is not known. It can only be assumed that in the less polar conformer (I) $0° < \varphi \leq 60°$, while in (II) $120° \lesssim \varphi < 180°$. Symmetrical cis ($\varphi = 0°$) and trans ($\varphi = 180°$) conformations were not considered, since measurement of the degrees of depolarization of the Raman spectral lines indicate the absence of symmetry elements in both conformers. In the Raman spectrum of VDCPS, with the exception of those at 182 and 170 cm^{-1} there are no strongly depolarized lines caused purely by deformational vibrations (Table 1). Because of the uncertainty about the angle φ we had to assume arbitrarily that $\varphi = 12°$ for (I) and $\varphi = 150°$ for (II) by analogy with VDCPO [4]. In this case the calculations quite correctly convey the conformational sensitivity of the vibrational frequencies of VDCPS. It should be noted that when φ is varied from 12 to 60° and from 150 to 120° there is no substantial change in the frequencies calculated theoretically. Refinement of the potential field of VDCPS was carried out according to the method in [5]. The final values of the force constants (in 10^6 cm^{-2}) are: $K_{C=C} = 13.100$; $K_{PC} = 5.260$; $K_{P=S} = 7.860$; $K_{PCl} = 3.650$; $K_{PCC} = 1.210$; $K_{PCH} = 0.830$; $K_{SPC} = 0.860$; $K_{ClPC} = 1.120$; $K_{ClPS} = 1.700$; $K_{ClPCl} = 1.100$; $K_{HCC} = 0.790$; $K_{\gamma CH_2} = 0.330$; $K_{\gamma CHP} = 0.299$; $K_{\chi} = 0.730$; $K_{tors} = 0.142$; $H_{PC}^{PS} = 0.770$; $H_{PS}^{PCl} = 0.790$; $H_{PCl}^{PCl} = 0.230$; $A_{PC}^{PCH} = 0.050$; $A_{PC}^{SPC} = -0.300$; $A_{PCl}^{ClPC} = -0.050$; $A_{PCl}^{ClP} = 0.300$; $A_{PCl}^{ClPCl} = 0.340$; $l_{PCC}^{SPC} = 0.160$; $l_{PCH}^{HCC} = 0.080$; $l_{SCC}^{ClPC} = -0.110$; $l_{SPC}^{ClP} = -0.200$; $l_{ClPC}^{ClPS} = l_{ClPC}^{ClPC} = -0.170$; $l_{ClPS}^{ClPS} = -0.050$; $l_{ClPC}^{ClPCl} = -0.130$; $l_{\gamma CH_2}^{\gamma CHP} = 0.046$; $l_{\gamma CH_2}^{\chi} = 0.004$; $l_{\gamma CHP}^{\chi} = -0.017$. Other force constants are the same as for VDCPO [4].

The frequencies of the conformers calculated using these force constants and their theoretical interpretation are given in Table 1. It can plainly be seen that not all experimentally observed changes in vibrational frequency of VDCPS when there is internal rotation are exactly reproduced in the calculation, in other words, the difference in vibrational frequencies of the conformers cannot be accounted for solely by kinematic factors.

EXPERIMENTAL

IR spectra were obtained on a Specord 75 IR spectrophotometer in the region 400-4000 cm^{-1} and on a JFS-113V Fourier spectrometer in the region 100-600 cm^{-1}. Raman spectra were recorded on an RNO-82 spectrometer with a He–Ne laser as radiation source and on a Bruker RTI-30 spectrometer with an Ar laser (spectral width of aperture 5 cm^{-1}, power of laser 100 mW). The recording conditions on the other instruments are given in [4].

Vinyldichlorophosphine Sulfide. A mixture of 32.9 g of phosphorus pentasulfide and 74 g of vinyldichlorophosphine oxide was heated for 8 h in a current of dry Ar in the presence of 0.1 g of hydroquinone and with agitation and bath temperature of 135°C. From the reaction mixture were distilled off clear products, which were washed with ice-cold water until pH 7 was reached. After two successive distillations from a flask fitted with a fractionating column (ℓ 14 cm), 45 g (54%) of vinyldichlorophosphine sulfide was obtained, with bp 53°C (10 mm), d_4^{20} 1.3859, n_D^{20} 1.5615, S_P 72 ppm (cf. [6]).

Immediately before recording the spectrum the substance was distilled. All operations were carried out in a dry box in an atmosphere of Ar. Because of the instability of the substance each experiment was repeated no less than three times in order to obtain reliable results.

CONCLUSIONS

1. The changes observed in the vibrational spectra of vinyldichlorophosphine sulfide when the phase and temperature were varied indicate that the compound has more than one conformer.

2. A study of these changes, measurement of the degrees of depolarization of the lines in the Raman spectra, and also correlation of the experimental and calculated vibrational frequencies make it possible to conclude that the predominant and energetically favorable form is the less polar conformation with the P=S and C=C bonds close to shielding each other. The conformer in which the vinyl group and P=S group are unfolded is the energetically less favorable form.

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MASS-SPECTRAL CHARACTERISTICS OF SATURATED TRICYCLIC HYDROCARBONS WITH THE COMPOSITION $C_{13}H_{22}$

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In a continuation of our research on the mass spectrometry of saturated hydrocarbons we studied the mass spectra of isomeric tricyclic hydrocarbons with the composition $C_{13}H_{22}$, which consist of six- and/or five-membered rings (I)-(V).

The mass spectra of tricyclanes with the compositions $C_{11}H_{18}$ and $C_{12}H_{20}$ were previously studied and it was shown that the principal pathways of fragmentation of their molecular ions (MI) involve cleavage of the C–C bonds at the most substituted C atom. Another factor that initiates the fragmentation of the MI is the presence of strain caused by nonbonded interactions or distortions of the bond angles and bonds [1].

Each of the hydrocarbons (I)-(V) exists in the form of several stereoisomers that differ with respect to the type of fusion of the condensed rings and the relative orientation of the rings that do not have C atoms in common. The peculiarities of their three-dimensional structures and their nomenclature were described in [2, 3].

In a series of stereoisomers with the same structure the intensity of the MI peak decreases on passing from the more stable to the less stable isomer (Table 1). In contrast

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