supporting the more recent structure. The Raman spectra in this region are closely paralleled by the IR spectra,[20] which also show a sharp doublet (3570, 3580 cm^{-1}) followed at lower frequencies by two very broad, complex regions of absorption. The broad bands are undoubtedly due to strongly hydrogen-bonded water, but the sharp bands might arise either from hydroxyl (which substitutes for fluoride in the lattice) or from the shorter of the two O–H bonds in the water molecules (0.953 and 0.983 Å, respectively[17]).

Hydroxyl groups in apophyllite occupy Wyckoff sites 4e (0, 0, z; etc.), lying along the fourfold axis but disordered with respect to ±z. This would generate the representation

$$A_{1g}(\text{Raman}) + A_{2g}(\text{inact.}) + A_{1u}(\text{inact.}) + A_{2u}(\text{IR})$$

which plainly does not account for the spectra, most notably for the presence of a doublet in the E$_g$ spectrum. We conclude that the sharp ν(OH) features arise from motion of the shorter of the two bonds of the lattice water. ν(OH) of hydroxyl was not detected, we suggest, because of its low concentration: most apophyllites are fluorine rich.[21]

A set of 16 symmetry-related short O–H bonds on general positions generates half the representation shown as the row "ν(OH)" in Table IB. Thus, appearance of a doublet (3550, 3557 cm^{-1}) in the E$_g$ spectrum is accounted for, as is presence of intensity in both B$_{1g}$ and A$_{1g}$/B$_{2g}$ (3558 cm^{-1}) spectra (Figure 3 and 4). The same selection rules apply for the set of 16 long O–H bonds: the results show ν(OH) intensity below 3400 cm^{-1} for all symmetry species, in accord with these rules. A detailed assignment is not attempted for these bands as δ(OH$_2$) overtones almost certainly complicate the situation.

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Contribution from the Department of Applied Science, Faculty of Engineering, Tohoku University, Sendai, Japan

Vibrational Spectra of Trimethylphosphine Telluride and the P–Te Stretching Force Constant

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The infrared (4000–400 cm^{-1}) and Raman (3200–100 cm^{-1}) spectra of (CH$_3$)$_3$PTe and (CD$_3$)$_3$PTe have been recorded for the solid state. The solution Raman spectra also have been recorded. The spectra have been interpreted on the basis of C_{3v} molecular symmetry. Normal-coordinate analysis has been carried out in terms of symmetry force constants. The PC$_3$ degenerate stretch was found to be mixed with the CD$_3$ rocks in (CD$_3$)$_3$PTe; therefore its assignment was not unequivocal. The P–Te force constant was found to have a value of 2.20 mdyn/Å which is compared with the P–O, P–S, and P–Se force constants in the trimethylphosphine chalcogenides.

Introduction

Although numerous alkyl- and arylphosphine compounds with oxygen, sulfur, and selenium are well-known, phosphine telluride, which is the next homologue to the selenide, is little known. The first example of trialkylphosphine telluride is tributylphosphine telluride prepared by Zingaro.[1] Subsequently several phosphine tellurides have been prepared by the reaction of tellurium with phosphines.[2] Chremos and Zingaro[3] have examined the location of the P–Te stretching vibration for some phosphine tellurides (C$_n$H$_{2n+1}$)$_3$PTe (n = 3–5 and 8) and observed a doublet, one peak around 400 and the other around 450 cm^{-1}. These frequencies are confined in a rather narrow range, even though the P–Se frequency in trialkylphosphine selenides shows dependence on alkyl substituents.[4] The P–Se stretching vibration in tris(dimethylamino)phosphine telluride has been assigned to 519 cm^{-1}, and the force constant has been determined to be 5.89 mdyn/Å, in spite of the P–S force constant being 3.81 mdyn/Å in the corresponding sulfide.[5] Thus, it was felt that precise vibrational analysis would be necessary to place the P–Te vibration and to determine its force constant. However the above compounds containing many atoms are structurally complex and make the analysis intractable.

In a previous paper,[6] the vibrational analyses of (CH$_3$)$_3$PO, (CH$_3$)$_3$PS, and (CH$_3$)$_3$PSe have been reported. This work is also an extension of the vibrational study to the telluride. Trimethylphosphine telluride is the simplest molecule of the phosphine tellurides and convenient for elucidating the P–Te stretching frequency and force constant. Preparation of trimethylphosphine telluride is simple,[7] but it is unstable, which makes the recording of the vibrational spectra difficult by conventional procedures. This difficulty was overcome with the aid of a special sampling technique.

Experimental Section

Infrared Samples. Tellurium was sublimed onto a CsI optical plate in vacuo in an appropriate glass tube. The plate coated with thin film of tellurium was fixed in a low-temperature cell with a small side tube of trimethylphosphine, and after evacuating it and subsequent cooling of the plate with liquid nitrogen, trimethylphosphine was condensed on the tellurium film. The CsI plate was then warmed by expelling

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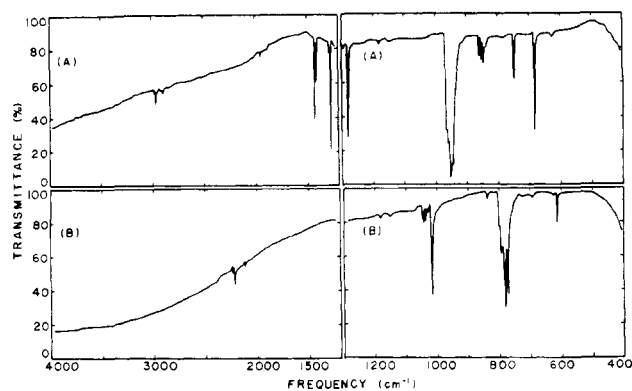(7) Brodie, A. M.; Rodley, G. A.; Wilkins, C. J. *J. Chem. Soc. A* **1969**, 2927.

Figure 1. Infrared spectra of (A) (CH₃)₃PTe and (B) (CD₃)₃PTe recorded in the solid state at -196 °C.

liquid nitrogen, and trimethylphosphine was melted. The reaction took place on the CsI plate, and then immediately the plate was recooled with liquid nitrogen. The excess of trimethylphosphine was collected as a solid on an upper portion of the liquid-nitrogen reservoir. Trimethylphosphine telluride and unreacted tellurium remained on the CsI plate. The unreacted tellurium caused poor transparency in the high-frequency region. Neither improvement in transparency nor enhancement in absorption intensity was attained in spite of repeating such an operation.

Raman Samples. A small amount of tellurium powder was placed in a small glass tube with a side capillary. The tube was connected to a vacuum line, and a quantity of trimethylphosphine corresponding to less than 1 equiv of the tellurium and diethyl ether (or benzene) were successively condensed into it at -196 °C. The tube was then sealed off and warmed in hot water for a few hours, during which color of the solution turned to light yellow. While still hot, the solution was transferred to the capillary tube. After standing overnight at room temperature, transparent crystals and a solution saturated with trimethylphosphine telluride were obtained. The capillary was used to record both the solid and solution Raman spectra. The solution spectra showed no bands attributable to free trimethylphosphine.

The infrared spectra (4000-400 cm⁻¹) were recorded on a Perkin-Elmer Model 337 spectrophotometer. The frequencies were read on a Hitachi QPD-33 recorder by abscissa expansion with a Perkin-Elmer expanded-scale readout kit. The instrument was calibrated with indene.[8] The Raman spectra (3200-100 cm⁻¹) were recorded on a JEOL JRS S-1 laser Raman spectrophotometer equipped with an NEC GLG 108 He-Ne laser at ambient temperature. The spectrometer was calibrated with the emission lines of neon. The infrared and Raman spectra of (CH₃)₃PTe and (CD₃)₃PTe are shown in Figures 1 and 2.

Vibrational Assignments

Assignments were made on the basis of C_{3v} symmetry, which is the presumed geometry of the isolated molecule. The 36 vibrations distribute as $8 A_1 + 4 A_2 + 12 E$, in which the A_1 and E modes are infrared and Raman active and the A_1 modes are polarized in Raman. The A_2 are inactive in both.

The vibrations of the methyl group and the PC₃ stretches appear in almost the same regions as those for trimethylphosphine selenide.[6] A few methyl vibrations are split in the solid as observed in other trimethylphosphine chalcogenides.[6,9]

The Raman spectrum from the solution of (CH₃)₃PTe shows an intense and polarized band at 378 cm⁻¹. The skeletal deformations should appear below 300 cm⁻¹ analogously to the sulfide and selenide;[6] therefore this band is assigned to the P-Te stretch, which is observed to shift to 350 cm⁻¹ on deuteration of the methyl groups. In the region below 300 cm⁻¹, three Raman bands are observed for (CH₃)₃PTe at 264, 226, and 179 cm⁻¹ in the solution spectrum, of which the 226-cm⁻¹ band being the most intense and polarized is assigned to the

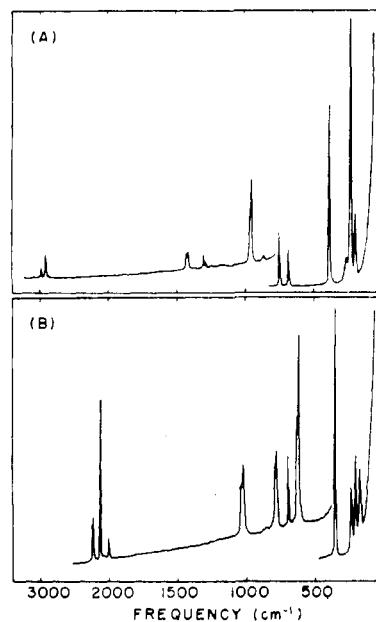(8) Jones, R. N.; Nadeau, A. *Spectrochim. Acta* **1964**, *20*, 1175.
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Figure 2. Raman spectra of (A) (CH₃)₃PTe and (B) (CD₃)₃PTe recorded in the solid state at ambient temperature.

Table I. Fundamental Frequencies (cm⁻¹) and Assignments for (CH₃)₃PTe[a]

IR solid	Raman soln	Raman solid	calcd freq	assignt[b]	PED[c]
2958 w	2980	2967	2964	$A_1 \nu_1$	$\nu_{as}(CH_3)$ 100
2890 w	2908 p	2898	2896	$A_1 \nu_2$	$\nu_s(CH_3)$ 99
1411 1409 } m	1409	1405	1416	$A_1 \nu_3$	$\delta_{as}(CH_3)$ 94
1295 w	1309 p	1294	1308	$A_1 \nu_4$	$\delta_s(CH_3)$ 89, $\nu_s(CH_3)$ 8
942 s	952 p	941	950	$A_1 \nu_5$	$\rho(CH_3)$ 86
681 s	674 p	678	684	$A_1 \nu_6$	$\nu_s(PC_3)$ 84, $\nu(PTe)$ 8
	378 p	376	375	$A_1 \nu_7$	$\nu(PTe)$ 55, $\nu_s(PC_3)$ 11, $\delta_s(PC_3)$ 32
	226 p	222	217	$A_1 \nu_8$	$\delta_s(PC_3)$ 64, $\nu(PTe)$ 33
2976 w	2980	2985	2983	$E \nu_{13}$	$\nu_{as}(CH_3)$ 100
2958 w	2980	2967	2964	$E \nu_{14}$	$\nu_{as}(CH_3)$ 99
2890 w	2908	2898	2892	$E \nu_{15}$	$\nu_s(CH_3)$ 99
1430 s		1421	1432	$E \nu_{16}$	$\delta_{as}(CH_3)$ 96
1420 m		1408	1422	$E \nu_{17}$	$\delta_{as}(CH_3)$ 94
1279 s	1288	1278	1283	$E \nu_{18}$	$\delta_s(CH_3)$ 83, $\nu_s(CH_3)$ 12
950 s		952	957	$E \nu_{19}$	$\rho(CH_3)$ 83
859 851 } m 845		851	854	$E \nu_{20}$	$\rho(CH_3)$ 78, $\nu_d(PC_3)$ 14
746 m	745	743	753	$E \nu_{21}$	$\nu_d(PC_3)$ 69, $\rho(CH_3)$ 23
	264	254	259	$E \nu_{22}$	$\delta_d(PC_3)$ 97
	179	183	184	$E \nu_{23}$	$\rho(PC_3)$ 98

[a] Abbreviations used: w, weak; m, medium; s, strong; p, polarized. Raman intensities are not given since photomultiplier sensitivity varies in a wide range within the spectral region. [b] The numbering used for trimethylarsine oxide[10] is applied to the analogous vibrations of trimethylphosphine telluride. [c] The potential energy distribution is defined as $x_{ij} = 100 F_{ii} L_{ij}^2 / \Sigma F_{ii} L_{ij}^2$. Abbreviations used: s, symmetric; as, asymmetric; d, degenerate; ν, stretching; δ, deformation; ρ, rocking.

PC₃ symmetric deformation. The other two bands are assigned to the degenerate and the rocking PC₃ modes, respectively. The Raman spectrum from the solution of (CD₃)₃PTe shows three bands at 227, 202, and 164 cm⁻¹, of which the 202-cm⁻¹ band is polarized. Similarly the three bands are assigned to the degenerate, the symmetric, and the rocking PC₃ modes for (CD₃)₃PTe, respectively.

Vibrational frequencies and assignments are listed in Tables I and II, in which the numbering used for trimethylarsine

Table II. Fundamental Frequencies (cm^{-1}) and Assignments for $(CD_3)_3PTe^a$

IR solid	Raman soln	Raman solid	calcd freq	assignt	PED
2218 w	2230	2224	2210	$A_1 \nu_1$	$\nu_{as}(CD_3)$ 99
2115 w	2126 p	2119	2107	$A_1 \nu_2$	$\nu_s(CD_3)$ 97
1029 w		1026	1020	$A_1 \nu_3$	$\delta_{as}(CD_3)$ 96
1014 s	1024	1015	996	$A_1 \nu_4$	$\delta_s(CD_3)$ 78, $\nu_s(CD_3)$ 11, $\nu_s(PC_3)$ 11
770 s	783 p	774	767	$A_1 \nu_5$	$\rho(CD_3)$ 65, $\nu_s(PC_3)$ 14, $\delta_s(PC_3)$ 10
614 m	610 p	611	610	$A_1 \nu_6$	$\nu_s(PC_3)$ 65, $\rho(CD_3)$ 26, $\nu(PTe)$ 6
	350 p	348	350	$A_1 \nu_7$	$\nu(PTe)$ 60, $\delta_s(PC_3)$ 23, $\nu_s(PC_3)$ 12
	202 p	198	194	$A_1 \nu_8$	$\delta_s(PC_3)$ 71, $\nu(PTe)$ 26
2233 w	2233	2239	2223	$E \nu_{13}$	$\nu_{as}(CD_3)$ 98
2218 w	2230	2224	2210	$E \nu_{14}$	$\nu_{as}(CD_3)$ 97
2115 w	2126	2119	2113	$E \nu_{15}$	$\nu_s(CD_3)$ 95
1041 w		1035	1032	$E \nu_{16}$	$\delta_{as}(CD_3)$ 92
1034 w	1024	1026	1027	$E \nu_{17}$	$\delta_{as}(CD_3)$ 95
1014 w		1015	1009	$E \nu_{18}$	$\delta_s(CD_3)$ 59, $\nu_s(CD_3)$ 13, $\nu_d(PC_3)$ 21
780 s	783	777	779	$E \nu_{19}$	$\rho(CD_3)$ 43, $\delta_s(CD_3)$ 16, $\nu_d(PC_3)$ 30
691 w	690	690	674	$E \nu_{20}$	$\rho(CD_3)$ 18, $\rho(CD_3)$ (ν_{19}) 50, $\nu_d(PC_3)$ 22
626 w	627	625	609	$E \nu_{21}$	$\nu_d(PC_3)$ 17, $\rho(CD_3)$ (ν_{20}), 75
	227	232	226	$E \nu_{22}$	$\delta_d(PC_3)$ 92
	164	167	166	$E \nu_{23}$	$\rho(PC_3)$ 96

^{a} See footnotes to Table I.

Table III. Symmetry Force Constants for $(CH_3)_3PTe^a$

A_1 species		E species	
F_1	4.671 (35)	F_{13}	4.735 (30)
F_2	4.679 (166)	F_{14}	4.670 (29)
F_3	0.517 (8)	F_{15}	4.602 (150)
F_4	0.562 (46)	F_{16}	0.527 (7)
F_5	0.585 (19)	F_{17}	0.528 (7)
F_6	3.159 (69)	F_{18}	0.541 (43)
F_7	2.207 (563)	F_{19}	0.603 (17)
F_8	0.691 (225)	F_{20}	0.483 (19)
$F_{2,4}$	−0.332 (214)	F_{21}	3.375 (182)
$F_{4,6}$	−0.278 (79)	F_{22}	0.770 (55)
$F_{7,8}$	−0.133^b	F_{23}	0.620 (60)
		$F_{15,18}$	−0.420 (166)
		$F_{18,21}$	−0.166 (57)
		$F_{20,21}$	−0.090 (42)

^{a} The subscripts refer to the vibrational numbers in Table I. Stretching force constants are in mdyn/Å, bending constants in mdyn·Å·rad^{-2}, and stretch–bend interactions in mdyn·rad^{-1}. The dispersions of the force constants are given in parentheses. ^{b} Force constant constrained.

oxide[10] is applied to the analogous vibration of the tri-methylphosphine telluride.

Normal-Coordinate Analysis

The normal-coordinate analysis was undertaken to determine the P–Te force constant and to compare it with those of the corresponding P–O, P–S, and P–Se bonds. The analysis was made by using the Wilson GF matrix method[11] and programs designed by the author.[12]

Since the molecular parameters of trimethylphosphine telluride are not known, those of the trimethylphosphine moiety were taken from those of trimethylphosphine selenide;[13] $r(P-C)$ = 1.816 Å, $r(C-H)$ = 1.100 Å, $\angle CPTe$ = 113.8°, and $\angle PCH$ = 109.9°, and the P–Te bond length was assumed as sum of double-bond radii for P and Te;[14] $r(P-Te)$ = 2.247 Å.[15,16] The symmetry coordinates for trimethylphosphine group were similar to those employed for trimethylarsine–borane.[17]

The infrared frequencies were used for the calculation except the vibrations below 400 cm^{-1}, for which the Raman frequencies were used. The individual frequencies were weighted

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(15) There are no large differences in molecular parameters of $(CH_3)_3PX$ (X = O, S, and Se)[13,16] aside from the P–X bond lengths. Bond lengths of P–S (1.940 Å)[16] and P–Se (2.091 Å)[13] are close to the double-bond values (1.947 and 2.091 Å, respectively).[14] In this treatment the P–Te double-bond value (2.247 Å) was assumed rather than the single-bond value (2.47 Å). Error in this bond length will lead to errors in the G matrix elements, but owing to the large mass of tellurium there are found no substantial disparities in the G matrix values from those for $(CH_3)_3PSe$ aside from that of the P–Te stretch, for which the P–Te bond length has no effect. Consequently the error in the P–Te bond length actually leads to no substantial error in the F matrix values. Among many isotopes of tellurium, the mass of the isotope ^{130}Te was used in calculation of the G matrix.
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as $w_i = 1/\lambda_i$. The split infrared frequencies were averaged. Since the torsional modes were not observed, these were neglected in the E symmetry species.

Initial force constants for the trimethylphosphine group were taken from the values reported for the selenide,[6] and that for the P–Te stretch was assumed to be 2.4 mdyn/Å as the average of 1.6 and 3.2 mdyn/Å estimated for a single and a double bond by Zingaro et al.[2] The calculations were carried out in terms of symmetry force constants to fit the calculated frequencies to the observed ones for $(CH_3)_3PTe$ and $(CD_3)_3PTe$ simultaneously in a manner similar to that employed for other trimethylphosphine chalcogenides.[6]

The interaction constant between the methyl rock and the symmetric PC_3 deformation introduced in the calculation for trimethylphosphine chalcogenides[6] was smaller than 0.02 in magnitude and found not to improve the fit; therefore this interaction was constrained to zero. Instead of this, it was necessary to include the interaction constant between the P–Te stretch and the symmetric PC_3 deformation to improve the fit.

The final set of force constant is listed in Table III. In Tables I and II, the calculated frequencies are compared with the observed frequencies and the potential energy distributions are also given.

Discussion

The decreases in frequency of the PC_3 deformations have been observed from the oxide to the selenide.[6] In the present compound, the corresponding frequencies decrease further. Aside from the PC_3 deformations and slight lowering of the methyl rock frequencies, the other frequencies of the trimethylphosphine group are almost the same as those of trimethylphosphine selenide.[6] Since values of the G matrix elements are not substantially different from those for the selenide, except that of the P–Te stretch,[15] the frequency lowering of the skeletal deformations and the methyl rocks essentially comes from the decrease in their force constants.[18]

As in the other trimethylphosphine chalcogenides,[6] the PC_3 degenerate stretch couples strongly with the CD_3 rocks. Although the 625–627-cm^{-1} band was assigned to the PC_3 degenerate stretch, ν_{21}, in Table II, the assignment is not

(18) Although the geometry of the trimethylphosphine part in the telluride was assumed to be the same as that in the selenide, it is not likely there is no structural difference between the telluride and the selenide. But from inspecting the geometries of the other trimethylphosphine chalcogenides,[13,16] we conclude that the difference will be small. Thus, the frequency lowering of the skeletal deformations and the methyl rocks should for the most part arise from the decrease in the force constants.

unequivocal from the potential energy distribution.

Deformation vibrations of CCC in alkanes and of CCP in trialkylphosphines were found to fall in the 500–400-cm^{-1} region.[19,20] The compound in this study has no such puzzling modes and the 600–300-cm^{-1} region is completely clear aside from the 376-cm^{-1} band (solid $(CH_3)_3PTe$). Consequently the 376-cm^{-1} band has been confidently assigned to the P–Te stretching vibration. As expected from the heavier mass of tellurium, the P–Te frequency is lower than the P–Se frequency (441 cm^{-1} for $(CH_3)_3PSe$[6]). No bands were found in the region corresponding to ones around 400 and 450 cm^{-1} assigned to the P–Te stretching mode in trialkylphosphine tellurides[3] and at 519 cm^{-1} assigned to the P–Te stretch in tris(dimethylamino)phosphine telluride.[4]

The P–Te stretching force constant was found to have a value of 2.20 mdyn/Å. The P–X force constants (7.04 (P–O), 3.73 (P–S), and 2.84 mdyn/Å (P–Se)[6]) in the trimethylphosphine chalcogenides decrease in the order from O to Se.

As anticipated from this trend, the calculated P–Te force constant is smaller than the P–Se constant. Zingaro et al.[2] have estimated the force constant and frequency of a P–Te bond by Gordy's rule,[21] using estimated bond distances upon an approximation of an isolated harmonic oscillator, as 1.6 mdyn/Å and 331 cm^{-1} for a single bond or 3.2 mdyn/Å and 472 cm^{-1} for a double bond. The observed frequency of 376 cm^{-1} for the P–Te stretch is close to the estimated single-bond frequency, but the force constant is approximately an average of the single- and double-bond values.

Trimethylphosphine telluride is so unstable that, in the air and at room temperature, trimethylphosphine is released from the solid complex, leaving tellurium behind. Trimethylarsine selenide has a similar tendency, but dissociation rate is small enough to be able to make a KBr pellet for infrared measurement. The As–Se force constant has been calculated to be 2.55 mdyn/Å.[22] The P–Te force constant is smaller than the As–Se constant, suggesting that the P–Te bond is weaker than the As–Se bond in accord with chemical evidence.

Registry No. $(CH_3)_3PTe$, 76773-16-5; $(CD_3)_3PTe$, 76773-17-6.

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X-ray Photoelectron Spectroscopic Study of Organometallic Nitrosyl Compounds of Chromium, Molybdenum, and Tungsten

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Gas-phase core electron binding energies of organometallic nitrosyl complexes of chromium, molybdenum, and tungsten are reported. On going from Cr to W in the series $CpM(NO)_2Cl$ (M = Cr, Mo, W), back-bonding to the NO groups increases and electron density is withdrawn from the Cl atoms. The data for $CpM(NO)_2Cl$ and $CpM(CO)_2NO$ (M = Cr, Mo, W) indicate that the back-bonding in the Mo and W compounds is significantly different from that in first-row transition-metal nitrosyls. Electron density is mainly transferred to the nitrosyl oxygen atom, whereas, in first-row nitrosyls, approximately equal amounts of electron density are transferred to the oxygen and nitrogen atoms.

Previous X-ray photoelectron spectroscopic (XPS) studies of transition-metal nitrosyls and carbonyls in the gas phase have established that NO groups are stronger π acceptors than CO groups[2] and that the 1s binding energies of the atoms of these ligands are linearly related to the corresponding N–O or C–O stretching force constants.[3–5] We now report the results of a gas-phase XPS study of a series of organometallic nitrosyl complexes of chromium, molybdenum, and tungsten. The measured core binding energies, listed in Table I, allow us to compare the π-donor and σ-acceptor properties of the group 6 transition-metal atoms. The data also allow us to compare the donor and acceptor properties of the nitrosyl group with those of other groups such as the carbonyl group, the cyclopentadienyl group, and the chloro group.

Spectra

The carbon 1s spectrum of $CpCr(CO)_2NO$ (Cp = η^5-C_5H_5) is shown in Figure 1. The spectrum is readily deconvoluted

into two peaks, separated by 1.7 eV. An unrestricted least-squares fit of the spectrum yields an intensity ratio of 3.8:1, although the ratio of Cp to CO carbon atoms in the compound is 2.5:1. This result is not unexpected; the C 1s and O 1s peaks of carbonyl groups usually lose considerable intensity to shake up peaks at higher binding energy.

The nitrogen 1s spectrum of $CpCr(NO)_2NO_2$ (Figure 2) shows, on the high binding energy side, a strong band due to free nitric oxide from decomposition of the sample. A peak at approximately 407.7 eV due to $CpCr(NO)_2NO_2$ can be clearly resolved. Because there are twice as many NO groups as NO_2 groups and because the nitrogen binding energy of the analogous compound $CpCr(NO)_2Cl$ is fairly close to 407.7 eV, we believe that the binding energy of the NO groups in $CpCr(NO)_2NO_2$ is approximately 407.7 eV. The nitrogen of the NO_2 group either has about the same binding energy as the nitrogen of the NO group or, more likely, has a higher binding energy. Indeed it is possible to fit the spectrum quite well with peaks at 407.5 and 408.5 eV, having an intensity ratio of 2:1, respectively. However, because of the interference of the nitric oxide band, we have little faith in this deconvolution and prefer simply to conclude that the binding energy of the NO_2 group is probably greater than 407.7 eV.

The oxygen 1s spectrum of $CpCr(NO)_2NO_2$ (Figure 3) also shows a peak due to free nitric oxide; however in this case the nitric oxide peak is well separated from the peaks due to the

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