Molecular Structure of Molybdenum Oxide Tetrachloride Studied by Gas Electron Diffraction

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(Received July 27, 1974)

The molecular structure of molybdenum oxide tetrachloride was determined to be a square pyramid by a sector-microphotometer method of gas electron diffraction. The following molecular parameters were obtained by a least-squares method: r_g(Mo–Cl)$=2.279\pm0.003$ Å, r_g(Mo–O)$=1.658\pm0.005$ Å, and r_g(Cl···Cl(s))$=3.142\pm0.008$ Å. The structure of gaseous $MoOCl_4$ is similar to that of gaseous $WOCl_4$. The infrared spectra of $MoOCl_4$ were also measured in solutions.

The molecular structure of MXY_4, where M is a central atom, can be classified into two groups: trigonal bipyramid and square pyramid. The structure of gaseous SOF_4[1,2] was reported to be a trigonal bipyramid, and the structures of $XeOF_4$[3,4] and $WOCl_4$[5,6] in the gas phase were found to be square pyramids, although the OXeF angle (92°) and the OWCl angle (102.4°) differ a great deal from each other. According to infrared spectroscopic study,[7] the $MoOCl_4$ molecule is monomeric and has a square-pyramidal structure in the gas phase as well as in inert solvents. The present study was undertaken in order to determine in more detail the structure of $MoOCl_4$ in the gas phase by the sector-microphotometer method of electron diffraction,[8] in order to see the difference between the configuration of $MoOCl_4$ and those of $WOCl_4$ and $XeOF_4$ and to compare the Mo–O and Mo–Cl bond distances of $MoOCl_4$ with those of other molybdenum compounds such as MoO_2Cl_2,[9] $MoCl_5$,[10] and $MoOCl_3$ (in solid state).[11,12]

The vibrational spectra of $MoOCl_4$ have been measured in the gas phase [7,13] and in solutions.[7,14] We have obtained the infrared spectra of $MoOCl_4$ in inert solvents in a wider range for the purpose of calculating the mean amplitudes of vibration.

Experimental

The sample prepared by refluxing molybdenum trioxide with thionyl chloride[15] was purified by repeated sublimation *in vacuo*. It was then loaded into a high-temperature nozzle in a dry box, vaporized at *ca.* 80 °C. Electron diffraction photographs were taken with an r^3-sector at a camera distance of 144.4 mm. The accelerating voltage was about 40 kV, the exposure times 30∼40 s, and the electron-beam current 0.7 μA. The electron wavelength was determined by means of gold powder patterns. The lattice constant of gold was calibrated by means of X-ray diffraction and checked by an electron diffraction study of CCl_4. Photographs were recorded on Fuji process hard plates. The photographic densities of four plates were measured with a digital microphotometer at intervals of 0.4 mm, and the intensity of each plate was used independently for the structure analysis.

The infrared spectra of $MoOCl_4$ in carbon tetrachloride and cyclohexane solutions were measured in the range 4000∼40 cm^{-1} with a Hitachi EPI-G3 spectrophotometer and a Hitachi FIS-3 far-infrared spectrometer. Carbon tetrachloride and cyclohexane were dried by use of phosphorus pentoxide and sodium metal, respectively, since $MoOCl_4$ readily decomposed with a trace of water in the solvent. Measurement of the Raman spectrum was impracticable because of the intense color of the $MoOCl_4$ solutions.

Structure Analysis

Intensities measured in the range $q=17\sim102$ Å^{-1} were leveled theoretically. The elastic scattering factors of Schäfer *et al.*[16] and the inelastic scattering factors of Cromer and Mann[17,18] were used. The radial distribution is shown in Fig. 1. The N_{ij} functions which fit μ_{ij}[5,19] in a whole range of the scattering angle were as follows:

$$N_{\text{Mo-Cl}} = 1.000$$

$$N_{\text{Mo-O}} = 1.020 + 0.147\exp(-0.00040\,q^2)$$

$$N_{\text{Cl}\cdots\text{Cl}} = 1.202 + 0.076\exp(-0.00028\,q^2)$$

$$N_{\text{Cl}\cdots\text{O}} = 1.245 + 0.395\exp(-0.00060\,q^2)$$

The radial distribution curve, which is very similar to that of $WOCl_4$,[5] suggests that the molecular structure of $MoOCl_4$ is a square pyramid.

Least-squares calculations were carried out in order to refine the molecular parameters. Least-squares analyses of background[20] and molecular intensity[21] values were repeated alternately. An experimental background was approximated using a polynomial of 7th degree, and the weight function given by Konaka and Kimura[22] was assumed.

The molecule was assumed to be a trigonal bipyramid C_{2v}. The OMoCl(equatorial) angles 90°, 100°, 110°, 120°, and 130° with the OMoCl(polar) angle 90° were used as initial values for the least-squares calculations. No convergence was obtained for 90° or 130°. For the other cases, the OMoCl(polar) and OMoCl(equatorial) angles as well as the Mo–Cl(polar) and Mo–Cl(equatorial) distances converge to

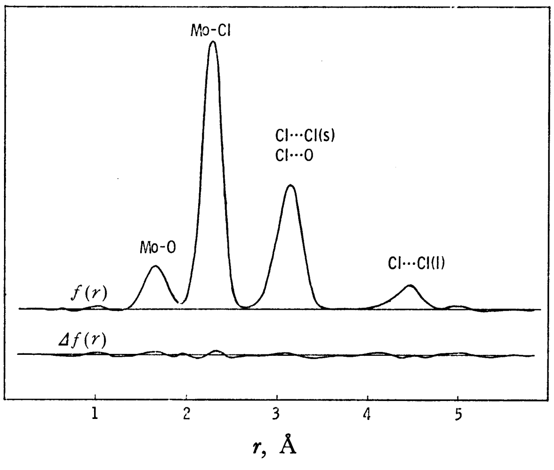

Fig. 1. Experimental radial distribution, $f(r)$, and the difference between the experimental and calculated ones, $\Delta f(r)$. A damping factor, $\exp(-0.0002\,q^2)$, was used.

the same values within the limits of error, indicating that the molecular structure of $MoOCl_4$ is a square pyramid, C_{4v}.

The index of resolution, r(Mo–Cl), r(Mo–O), r(Cl···Cl(s)), and four root-mean-square amplitudes l(Mo–Cl), l(Mo–O), l(Cl···Cl(s)), and l(Cl···Cl(l)) were determined by the least-squares analysis with C_{4v} (Table 1), where l(Cl···O) was fixed because of a large correlation between l(Cl···Cl(s)) and l(Cl···O). The value was obtained by the normal coordinate analysis. Asymmetry parameters for the Mo–Cl and Mo–O were estimated by the diatomic molecule approximation[23] to be 4.0×10^{-6} and 0.6×10^{-6} Å^3, respectively. The parameter in the Morse function, a, was assumed to be 2.0 Å^{-1}, the frequencies of Mo–Cl and Mo–O stretching vibrations 450 and 1015 cm^{-1}, respectively,[7] and the asymmetry parameters for nonbonded distances zero.

The results of the analysis are given in Table 2. r_g parameters were calculated from r_a parameters by means of $r_g=r_a+l^2/r_a$. Random errors were estimated to be 2.5 σ_1 or 2.5 σ_2.[21,24] Systematic errors were estimated from the error in the lattice constant of the reference material (0.06%) and errors in the optical measurement of the diffraction patterns of gold (0.08%) and of the camera distance (0.04%). Correlation matrices[25] are given in Table 3, and the observed and best-fit theoretical intensity curves are shown in Fig. 2.[26] The least-squares computations were carried out by the use of a FACOM 230—60 computer at Nagoya University Computing Center.

Table 1. Results of the least-squares analysis (r_a and l in Å)

Parameter		σ_1	σ_2
r_a(Mo–Cl)	2.2774	0.0003	0.0005
r_a(Mo–O)	1.6570	0.0018	0.0004
r_a(Cl···Cl(s))	3.1374	0.0028	0.0019
l(Mo–Cl)	0.0613	0.0004	0.0012
l(Mo–O)	0.0431	0.0037	0.0047
l(Cl···Cl(s))	0.1253	0.0017	0.0034
l(Cl···Cl(l))	0.1231	0.0033	0.0014
R	0.9597	0.0044	0.0143

Table 2. Distances and mean amplitudes (in Å)

	r_g	l_{obsd}	l_{calcd}
Mo–Cl	2.279±0.003	0.061±0.003	0.050
Mo–O	1.658±0.005	0.043±0.012	0.035
Cl···Cl(s)	3.142±0.008	0.125±0.009	0.104
Cl···Cl(l)	4.440±0.011	0.123±0.008	0.071
Cl···O	3.108±0.013	0.099 (assumed)	0.099
∠OMoCl	102.8±0.7°		
∠ClMoCl	87.2±0.3°		

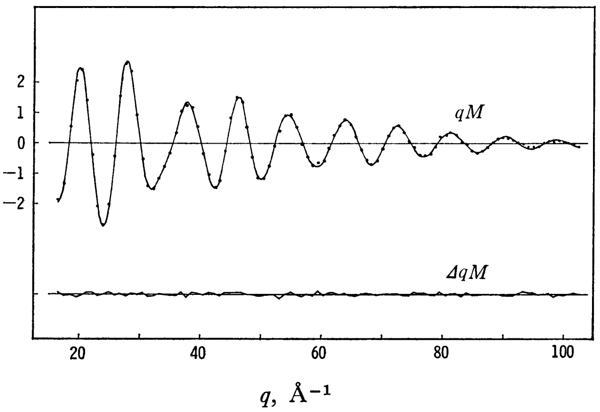

Fig. 2. Observed (dots) and calculated (curve) molecular intensities, qM, and the difference between the observed and calculated ones, ΔqM.

The infrared spectra for $MoOCl_4$ were assigned by analogy with the spectra of related molecules such as $WOCl_4$,[27,28] IF_5, BrF_5, ClF_5, and $XeOF_4$.[29] Since the vibrational frequencies of $MoOCl_4$ are similar to those of $WOCl_4$, the frequencies for the B_1 and B_2 modes, which are infrared-inactive, were assumed to be equal to the corresponding values for $WOCl_4$.[28] The fundamental frequencies are given in Table 4. The valence force constants were calculated by the GF matrix method. The mean amplitudes for the bonded and nonbonded distances were calculated by a normal coordinate analysis. The results are given in Table 2.

Discussion

The structure of $MoOCl_4$ in the gas phase is found to be a square pyramid similar to those of $WOCl_4$,[5] $XeOF_4$,[4] and IF_5.[30] The OMoCl angle (102.8±0.7°) is essentially equal to the OWCl angle (102.4±1.3°) in $WOCl_4$ but is much larger than the corresponding angles in $XeOF_4$ (92°) and in IF_5 (81°), where the small angles in the latter molecules can be explained in terms of a nonbonding valence electron pair of central atoms.[31]

The Mo–Cl bond distance in gaseous $MoOCl_4$ (2.279±0.003 Å) is equal to that in $MoCl_5$ (2.27±0.02 Å)[10] and also to that in MoO_2Cl_2 (2.28±0.03 Å).[9] The Mo–O bond distance in MoO_2Cl_2 (1.75±0.10 Å) can not be compared exactly with that in $MoOCl_4$ (1.658±0.005 Å) because of the large experimental errors. The molybdenum atom in $MoOCl_3$

Table 3. Correlation matrices for molecular parameters of $MoOCl_4$[a]

	r_{Mo-Cl}	r_{Mo-O}	$r_{Cl\cdots Cl(s)}$	l_{Mo-Cl}	l_{Mo-O}	$l_{Cl\cdots Cl(s)}$	$l_{Cl\cdots Cl(l)}$	R
r_{Mo-Cl}	1.0	−0.253	0.038	−0.030	0.007	0.034	−0.001	−0.013
r_{Mo-O}		1.0	0.114	0.139	0.004	0.117	0.020	0.195
$r_{Cl\cdots Cl(s)}$			1.0	0.014	0.001	−0.551	−0.015	0.018
l_{Mo-Cl}				1.0	0.127	0.275	0.065	0.720
l_{Mo-O}					1.0	0.076	0.020	0.199
$l_{Cl\cdots Cl(s)}$						1.0	0.052	0.388
$l_{Cl\cdots Cl(l)}$							1.0	0.091
R								1.0

a) The elements are defined as $\rho_{ij}=B_{ii}^{-1}/(B_{jj}^{-1}\times B_{ij}^{-1})^{1/2}$.

Table 4. Fundamental vibrational frequencies of $MoOCl_4$ (in cm^{-1})

		Obsd	Calcd			Obsd	Calcd
A_1	ν_1	1015a)	1015	B_2	ν_6	220b)	220
	ν_2	450a)	450	E	ν_7	396	396
	ν_3	143	143		ν_8	256	257
B_1	ν_4	400b)	400		ν_9	172	172
	ν_5	148b)	148				

a) Ref. 7. b) Ref. 27.

has a distorted octahedral arrangement due to bridging of chlorine atoms in the crystal state.12) The terminal Mo–Cl and Mo–O distances in $MoOCl_3$ are 2.26±0.02 Å and 1.63±0.04 Å, respectively. They agree with the corresponding distances in $MoOCl_4$ in the gas phase, although the bridging Mo–Cl is much greater than the terminal one. The OMoCl(terminal) angle in $MoOCl_3$ (103.8±1.4°) is also in good agreement with that in $MoOCl_4$ (102.8±0.7°).

By a normal coordinate analysis the force constants for the Mo–O and Mo–Cl bonds in $MoOCl_4$ were estimated to be 8.29 and 2.68 md/Å, respectively. The Mo–O force constant and the observed Mo–O distance give a good fit to the correlation curve between the distances and the force constants for the Mo–O bond.32) Although the Mo–O bond in $MoOCl_4$ is formally a double bond, its bond order is estimated to be 3 from the correlation curve between the distance and the bond order.32) Gray and Hare33) gave the same bond order in their molecular orbital treatment for the Mo–O bond in the MoO^{3+} group, whose electronic structure consists of Mo^{5+} of [Krypton]$4d^1$ and oxide ion. Since the electronic structure of Mo^{6+} in $MoOCl_4$ is [Krypton]$4d^0$, the properties of the Mo–O bond would differ considerably from that of MoO^{3+}. However, the smallness of the Mo–O distance in $MoOCl_4$ might be mainly due to the double π-bonds formed between the $2p_x$ and $2p_y$ of oxygen and the $4d_{xz}$ and $4d_{yz}$ of molybdenum as in the Mo–O bond in MoO^{3+}.

The elastic scattering factor and the phase angle calculated by means of the Thomas-Fermi-Dirac (TFD) potential34) were also used for molybdenum atom, a remarkable increment of 0.013 Å being found in the Mo–O mean amplitude but no changes in the bond distances. The case is very similar to the results of tetramethyltin given by Nagashima *et al.*35) It seems that the phase angle for the molybdenum atom from the TFD potential is too small.

All the mean amplitudes we obtained are significantly larger than those calculated from the normal vibrations, especially with regard to Cl···Cl(1). This is probably due to the lack of accuracy in the frequencies of the B_1 and B_2 modes. A similar discrepancy between the observed mean amplitude of Cl···Cl(1) and the calculated value was reported by McAdam *et al.*6) in their electron diffraction study of $WOCl_4$ in which they suggested the effect of an anharmonic vibration of the WCl_4 group.

A grant from the Ministry of Education is acknowledged.

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