## DETERMINATION OF STRUCTURES OF MOLECULES OF LOWER HALIDES

OF TRANSITION ELEMENTS BY GAS ELECTRON-DIFFRACTION ANALYSIS.

I. TITANIUM TRICHLORIDE

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A method for the electron-diffraction investigation of unstable halides of transition elements with lower valences is described. The relative pressures of TiCl<sub>4</sub>, TiCl<sub>3</sub>, TiCl<sub>2</sub>, and TiCl vapors in the TiCl<sub>4</sub> + Ti system at 400-2000 °K were calculated. Electron-diffraction patterns of gaseous TiCl<sub>3</sub> at 1100°K were obtained. The effective geometrical and vibrational parameters of the TiCl<sub>3</sub> molecule were determined. The equilibrium structure with  $D_{3h}$  symmetry was found within the harmonic approximation, and the vibrational frequencies and force constants were evaluated.

The literature contains contradictory data on the structure of the titanium trichloride molecule in the gas phase. Thus calculation of the energies of the valence states by the Van Vleck method [1] indicates a pyramidal structure of trihalides of the titanium subgroup (with  $C_{3V}$  symmetry). An estimate of 100° is presented for the Cl-Ti-Cl angle in widely used handbooks of molecular constants [2, 3]. Tables of thermodynamic functions [4, 5] have also been calculated with the use of a pyramidal model of the molecule. There is a rough estimate of the Ti-Cl bond length for gaseous TiCl<sub>3</sub> (2.3 Å) on the basis of an investigation of crystalline titanium trichloride [6].

Although they do not contain a complete set of frequencies, the spectroscopic data for a mixture of gaseous titanium chlorides  $\text{TiCl}_n$  [7] and  $\text{TiCl}_3$  isolated in Ar, Ne, and Kr matrices [8, 9] are clearly not in agreement with the concepts of the pyramidal structure of the titanium trichloride molecule. Thus the absence of frequency  $v_1$  in the IR spectra [7-9] and the prediction of the structure of MCl<sub>3</sub> molecules on the basis of an estimate of the polarizability of the central metal atom [10] provide evidence for a planar structure for the TiCl<sub>3</sub> molecule (with D<sub>3h</sub> symmetry).

Taking into account the incompleteness and contradictory character of the available literature data on the structure and spectrum of the titanium trichloride molecule, we undertook an electron-diffraction investigation of  $TiCl_3$  vapors.

It is known that titanium trichloride is an unstable compound, the direct heating of which leads to disproportionation to  $TiCl_4$  (g) and  $TiCl_2$  (s). To obtain  $TiCl_3$  vapor we therefore used the reduction of titanium tetrachloride with titanium metal by heating in the ampul of a vaporizer of the Knudsen double-effusion cell type. The lower chamber was prepared from nickel and was separated from the upper chamber by means of a dispenser valve. It was located on the outside of the electron-diffraction camera at room temperature since, in accordance with the experimental conditions, it was charged with  $TiCl_4$ , which is a liquid with a vapor pressure of  $\sim 10^{-2}$  atm at 298°K. The upper chamber and the connecting channel were prepared from chemically pure-grade titanium and were equipped with a special heater, which made it possible to maintain the temperature of the upper chamber at 1100°K. The temperature was monitored with a platinum-platinorhodium thermocouple mounted in a specially drilled hollow in the wall of the ampul. The upper chamber was charged with fine titanium turnings, which were changed in each new series of photographs of the electron-diffraction patterns. A similar design can be used to obtain electron-diffraction patterns of other unstable halides of transition elements.

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Percentage in the gaseous mixture of molecules, %	r <sub>a</sub> (Ti→Cl), Å	l (Ti-Cl), Å	r <sub>a</sub> (ClCl), Å	l (CiCl), Å	Cl—Ti—Cl, deg	R <sub>f</sub> , %
93,6	2,205(3)	0,080(3)	3,774(48)	0,245(21)	117,8	5,8

TABLE 1. Effective Structural and Vibrational Parameters of the Molecule

TABLE 2. Experimental Structural and Vibrational Parameters of  $\text{TiCl}_3$  within the Harmonic Approximation

$r_e^h$ (Ti-Cl), 2		$\angle_{e}^{h}$ CI-TI-CI, deg		R <sub>f</sub> , %			
Model with C <sub>3v</sub> symmetry							
2,183	1	119,5	l	6,31			
Model with $D_{3v}$ symmetry							
2,183(6)	I	(120)	l	6,25			
F, mdyn/Å							
F <sub>11</sub> 2,10(18)	$F_{22} \\ 0,036(7)$	$F_{33}$ 2,50(8)	F 0,05	$\begin{bmatrix} 44 \\ 3(3) \end{bmatrix} \begin{bmatrix} F_{34} \\ -0,047 \end{bmatrix}$			

The following reduction reactions, which lead to the production of gaseous products, are possible in the reaction of  $TiCl_4$  vapors with heated titanium metal:

$$\begin{split} & \operatorname{3TiCl}_4(g) + \operatorname{Ti}(s) = 4\operatorname{TiCl}_3(g), \\ & \operatorname{TiCl}_4(g) + \operatorname{Ti}(s) = 2\operatorname{TiCl}_2(g), \\ & \operatorname{TiCl}_4(g) + 3\operatorname{Ti}(s) = 4\operatorname{TiCl}(g), \\ & \operatorname{TiCl}_4(g) = \operatorname{TiCl}_2(g) + \operatorname{Cl}_2(g). \end{split}$$

The ratio of the gaseous components  $TiCl_4$ ,  $TiCl_3$ ,  $TiCl_2$ , and TiCl varies as a function of the temperature and the pressure of the vapor stream emerging from the vaporizer nozzle. To select the optimum conditions, prior to the start of the experimental studies we made preliminary calculations of the relative pressures of the  $TiCl_4$ ,  $TiCl_3$ ,  $TiCl_2$ , and TiCl vapors at 400-2000°K with the aid of handbook data [3]. We found that near 1000°K there is a region of significant preponderance of  $TiCl_3$  as compared with all of the other components of the system (the  $TiCl_4$  pressure is lower by a factor of ~10; the  $TiCl_2$  pressure is lower by three orders of magnitude as compared with the  $TiCl_3$  pressure; the TiCl pressure is negligibly low). Taking into account the approximate character of the calculation, as well as the fact that in our experiments the conditions may be nonequilibrium, the composition of the gas mixture was varied during the structural analysis.

The electron-diffraction patterns were obtained with a modernized electron-diffraction camera from Moscow State University for high-temperature investigations [11] at a vaporizernozzle temperature of 1100°K; the accelerating voltage was 60 kV, the distance between the nozzle of the vaporizer ampul and the photoplate was 515.35 nm, and the photographs were obtained on diapositive plates coated with a thin layer of India ink to avoid spoiling of the photographs by exposure to light as a result of incandescence of parts of the ampul. The  $r^3$  sector, with a maximum radius of 100 mm, was used to obtain the photographs. The electrondiffraction patterns were processed with a Joyce Löbl microdensitometer. The molecular component of the intensity sM(s) was obtained in the interval s = 2-20 Å<sup>-1</sup>.

The structural analysis of the electron-diffraction data was carried out by the standard method with the use of the program in [12] and a BÉSM-6 computer under the assumption that the vapor consists of TiCl<sub>3</sub> and TiCl<sub>4</sub> molecules. The parameters of the TiCl<sub>4</sub> molecule were taken from [13] and were not varied. Variation of the composition of the gaseous TiCl<sub>3</sub> + TiCl<sub>4</sub> mixture leads to a minimum value of the error factor when 93(6)% TiCl<sub>3</sub> is present in

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Molecular	Frequency									
symmetry	v <sub>1</sub>	v <sub>2</sub>	٧ <sub>3</sub>	v4	ture					
TiCl <sub>3</sub>										
C 37	(530)*	(275)*	(590)*	(260)*	[3]					
C	_	(110±12)*	505±10 **	(135±12)*	[2]					
0.0		110±10(N <sub>2</sub> )**	505±10 ** 505,0(Ne)** 497,1(Ar)**		[7] [8] [8]					
D <sub>3h</sub> D <sub>3h</sub>	(350±30) <b>*</b> 320(30)	(110±15)* 129(20)	491,0(R1)** 496,1(Ar)** $(500\pm10)*$ 498(16)	(135±15)* 107(7)	[9] [9] [12] This study					
TiCla										
$T_d$	389**	144**	498**	136**	[ [2]					
${\rm TiCl}_2$										
$D_{\infty h}$	(279)*	122±12 **	486±30 **		[2] [7] [8]					

TABLE 3. Vibrational Frequencies of the  $TiCl_2$ ,  $TiCl_3$ , and  $TiCl_4$  Molecules

\*Estimated values.

\*\*Data from the IR spectra of the gas and in mixtures.

the mixture. The thermally average structural and vibrational parameters of titanium trichloride are presented in Table 1. The  $3\sigma_{MLS}$  value (MLS = method of least squares) is presented as the error. It must be noted that the 117.8° value of angle Cl-Ti-Cl that we found for the effective structure of TiCl<sub>3</sub> in the gas phase significantly exceeds the estimated values previously presented in [2, 3].

Additional information regarding the composition of the vapor of the investigated mixture was obtained from an analysis of the radial-distribution curve calculated from the experimental intensity curve by means of the program in [14]; the radial-distribution curve contained only two peaks at  $r \approx 2.20$  and 3.70 Å, and the ratio of their areas (1:1) indicated a stoichiometry that was very close to that for the TiCl<sub>3</sub> molecule. From this it was concluded that other molecular forms, including dimers, are not present in appreciable amounts under the conditions of the electron-diffraction experiments.

Further decoding of the electron-diffraction data was carried out by the method in [15], which makes it possible to solve the vibrational problem, in each stage, for molecules with  $C_{av}$  or  $D_{ah}$  symmetry within the harmonic approximation of the potential function; the parameters of the problem are the harmonic force constants and the equilibrium internuclear distances. However, since the number of vibrational characteristics that enter into the intensity equation is insufficient for the determination of the total generalized valence-force field of molecules of the XY<sub>3</sub> type, we used the method of progressive rigidity in the solution of the vibrational problem. In this connection the independently determinable values were only the diagonal elements of the force matrix in symmetry coordinates  $F_{11}$ ,  $F_{22}$ ,  $F_{33}$ , and  $F_{44}$ . At this stage we analyzed the intensity curve obtained from  $sM(s)_{exp}$  after subtracting 7% of the contribution from the TiCl<sub>4</sub> molecule. In the interpretation of the experimental data with respect to both possible models we obtained the same value  $r_e^h(Ti-C1) = 2.183$  Å with virtually the same error factor (R<sub>f</sub> pprox 6.3%). However, for the model with C<sub>sv</sub> symmetry we found an equilibrium value of 119.5° for angle C1-Ti-C1 (Table 2); within the limits of the experimental error, this makes it possible to assume that the molecule is planar. We therefore subsequently limited ourselves to an examination of this model, for which the parameters of the force field were obtained from the experimental data (see Table 2). The set of frequencies obtained on the basis of these parameters is in good agreement with the spectroscopic data; this is particularly the case for frequency  $v_3$  (Table 3). At the same time, one must note that we have obtained for the first time the experimental value of frequency  $v_1$ , which is absent in the IR spectrum because of the planar character of the model of the  $TiCl_3$  molecule. In addition, the  $v_1$  value that we obtained is significantly lower than the estimates of this frequency previously presented in handbooks of molecular constants [2, 3].

The frequencies of the vibrations found and estimated for TiCl<sub>4</sub> and TiCl<sub>2</sub> are presented in Table 3 for comparison. Vibrational frequencies  $v_2$  and  $v_3$  in the TiCl<sub>4</sub>, TiCl<sub>3</sub>, and TiCl<sub>2</sub><sup>-</sup> molecules are close, while frequency  $v_1$  displays a regular decrease on passing from TiCl<sub>4</sub> to TiCl<sub>2</sub>.

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