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An Electron Diffraction Investigation of Vanadium Tetrachloride

BY WILLIAM N. LIPSCOMB AND A. GREENVILLE WHITTAKER

On the basis of vapor density measurements, Roscoe[1] assigned the formula VCl_4 to vanadium tetrachloride in the gas phase. The physical and chemical properties of this interesting compound have recently been summarized by Simons and Powell.[2]

Prompted mainly by the possibility that the unpaired electron in the monomer might play a steric role leading to a structure different from the common tetrahedral structure, we have undertaken an electron diffraction investigation of vanadium tetrachloride, with the results described below.

Experimental

Vanadium tetrachloride was prepared by the method described by Mertes.[3] Dry chlorine was passed over ferrovanadium (containing about 50% of vanadium and 4% of silicon) in a glass combustion tube at 400° in an electric furnace. The crude product was purified by two successive fractionations through a 30-cm. all-glass column packed with glass spirals.

The final product was analyzed for quadrivalent vanadium by titration with standard permanganate solution. The results indicated 99.3% of vanadium tetrachloride; the impurities were probably chiefly silicon chlorides.

The electron diffraction investigation was carried out with the apparatus described by Brockway.[4] Photographs were taken at camera distances of 10.91 cm. and 20.19 cm. with electrons of wave length 0.0610 Å., as determined by standardization against zinc oxide.[5] The photographs were taken with the sample at about 50°.

Interpretation

The appearance of the photographs, which show measurable features out to s values of about twenty-five $\left(s = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}\right)$, is represented by curve V of Fig. 1. Since the first feature (dotted portion of curve V), which cannot be read from the photographs, is always relatively insensitive to structure, it could be estimated satisfactorily from previous experience with the theoretical curves of other more or less similar molecules.

The radial distribution function[6] was calculated from the visual curve, V, by means of the equation

$$rD(r) = \sum_{s=\frac{\pi}{10}}^{s_{\max}} I(s_i)\, e^{-as_i^2} \sin(rs_i) \qquad (1)$$

where the summation was carried out in steps of $\Delta s = \pi/10$ and a was so chosen that $e^{-as_{\max}^2} = 0.10$. The radial distribution curve thus obtained (curve RD, Fig. 1) indicates two important distances, at $r = 2.04$ Å. and $r = 3.30$ Å., whose ratio 1.618 agrees satisfactorily with the expected ratio for a tetrahedral molecule, $(8/3)^{1/2} = 1.633$. The other smaller peaks of the radial distribution curve are undoubtedly spurious; the only prominent ones, those at 1.57 and at 4.58 Å., do not correspond to sensible interatomic distances for any configuration of this molecule. We assume that the scattering gas contained no significant amounts of molecules other than VCl_4. Hence the radial distribution method indicates that the molecule is tetrahedral.

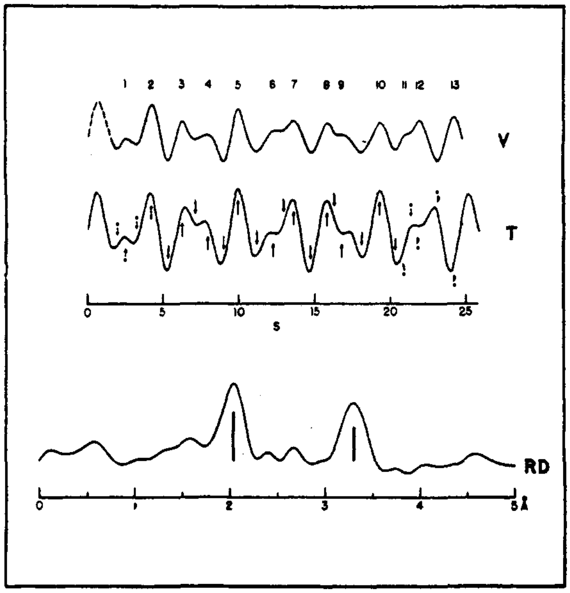

Fig. 1.

The correlation method[7] was used to test the conclusion of the radial distribution treatment. The theoretical intensity curve T was calculated for a tetrahedral model with V–Cl = 2.04 Å. and Cl–Cl = 3.33 Å., according to the formula

$$I(s) = \sum_{i,j} \frac{Z_i Z_j}{r_{ij}} \sin(r_{ij}s) \qquad (2)$$

The major features of this theoretical curve are in agreement with those of curve V. Although some slight discrepancies are apparent, for example with regard to the intensities of the tenth maximum and the eighth and eleventh minima relative to neighboring features, reëxamination of the photographs showed that their appearance is actually entirely consistent with the theoretical curve. In the radial distribution curve the

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[1] H. E. Roscoe, *Ann. Chem.*, Supplement VII, 70 (1870).

[2] J. H. Simons and M. G. Powell, THIS JOURNAL, **67**, 75 (1945).

[3] A. T. Mertes, *ibid.*, **35**, 671 (1913); see also ref. (2).

[4] L. O. Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936).

[5] C. S. Lu and E. W. Malmberg, *Rev. Sci. Instruments*, **14**, 271 (1943).

[6] L. Pauling and L. O. Brockway, THIS JOURNAL, **59**, 2181 (1937); R. A. Spurr and V. Schomaker, *ibid.*, **64**, 2693 (1942).

[7] L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

spurious smaller peaks mentioned above are probably the result of these aspects of the visual curve which we now believe are quantitatively in considerable error, rather than of numerous more subtle errors in the drawing of the visual curve; however, it did not seem worth while to verify this by recalculation of the radial distribution function.

The quantitative comparison of the measurements of the features with the theoretical curve for the tetrahedral model is shown in Table I.

TABLE I

Min.	Max.	$s_{\text{obs.}}$	$s_{\text{calcd.}}$	$s_{\text{calcd.}}/s_{\text{obs.}}$
1		1.94	1.70	(0.877)
	1	2.51	2.40	(0.956)
2		3.24	3.01	(0.927)
	2	4.23	4.15	0.980
3		5.32	5.26	0.989
	3	6.21	6.45	{1.038}
4		7.12	7.14	{1.004}
	4	7.95	7.71	{0.970}
5		8.98	8.74	0.974
	5	9.92	9.94	1.002
6		11.17	11.08	0.992
	6	12.27	12.03	{0.980}
7		12.92	12.42	{0.961}
	7	13.61	13.50	0.992
8		14.76	14.61	0.990
	8	15.82	15.85	1.002
9		16.25	16.85	{1.037}
	9	16.77	17.29	{1.031}
10		18.08	18.18	1.005
	10	19.28	19.31	1.001
11		20.35	20.39	1.002
	11	20.91	21.55	(1.031)
12		21.34	22.00	(1.031)
	12	21.86	22.88	(1.046)
13		23.11	23.97	(1.038)
	13	24.17	25.16	(1.041)
			Av.[a]	0.996
			Av. dev.[a]	0.013

[a] In the calculation of the average and average deviation the values in parentheses were omitted and those in braces were given half weight.

The values in parentheses were omitted from the averages because it is known that the corresponding measurements (of extreme outer and inner rings) are unreliable. Furthermore, the ratios enclosed in braces were given only half weight since the measurements of unsymmetrical rings on which they depend are distorted by what has been called a St. John effect.[4] The quantitative comparison leads, in agreement with the radial distribution function, to the following structural parameters and probable limits of error: V—Cl = 2.03 ± 0.02 Å. and Cl–Cl = 3.32 ± 0.03 A.

An additional theoretical curve, which is not included in Fig. 1, was calculated in which account was taken[8] of the actual ratio of the scattering powers of vanadium and chlorine, $(Z-F)_{\text{Cl}}/(Z-F)_{\text{V}}$. This curve was found to be substantially identical to the one given in Fig. 1.

Discussion

The vanadium–chlorine distance of 2.03 Å. in vanadium tetrachloride is shorter than that found by Palmer[9] in vanadium oxytrichloride (V–Cl = 2.12 Å.). The bond distances in these molecules and those reported for the related compounds chromyl chloride,[9] titanium tetrachloride,[10] and titanium tetrabromide[10] can be brought together in a simple discussion based on values of the covalent radii for titanium, vanadium and chromium, estimated as described below, and on the assumption that six of the nine available central atom orbitals ($3d^5 4s4p^3$) are used, on the average, for bond formation by each of these atoms. This assumption is probably only approximately valid since these three elements will not have the same tendency to employ the available orbitals and since other mechanisms than the formation of multiple bonds may play a role in shortening the bonds.

Plausible values of single-bond covalent radii may be assigned to these three elements. A titanium radius of 1.28 Å. is obtained[10] by multiplication of the octahedral radius of titanium (1.36 Å.) by the value 0.943 found for the ratio of the tetrahedral and octahedral radii in tin and lead compounds. A chromium radius of 1.13 Å. may be obtained by subtracting the chlorine radius[11] 0.99 Å. from the chromium–chlorine distance in chromyl chloride, 2.12 ± 0.02 Å. This radius, which is less than that[9] assumed by Palmer (1.15 Å.), may well be slightly small if more than six orbitals (on the average) are used to form the bonds to chlorine and oxygen or if the bonds are shortened for other reasons. We interpolate, nevertheless, between this chromium radius (1.13 Å.) and the titanium radius (1.28 Å.) to obtain a vanadium radius of 1.20 Å. Although this radius may also be slightly small, we shall employ it in our discussion, its value is the same as that assumed by Palmer.[9]

A double-bond radius for chromium of 1.02 Å. may be obtained by subtracting the double-bond radius of oxygen (0.55 Å.) from the chromium–oxygen distance in chromyl chloride (1.57 Å.). If we assume that this very reasonable difference of 0.11 Å. between the single-bond and double-bond radii for chromium applies also to vanadium and titanium, we obtain 1.09 and 1.17 Å. for the double-bond radii of these two elements, respectively.

A value for the vanadium–chlorine bond distance in vanadium tetrachloride can now be obtained. If, on the average, six orbitals are in-

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(8) R. Spitzer, W. J. Howell, Jr., and V. Schomaker, THIS JOURNAL, **64**, 62 (1942).

(9) K. J. Palmer, *ibid.*, **60**, 2360 (1938).

(10) M. W. Lister and L. E. Sutton, *Trans. Faraday Soc.*, **37**, 393 (1941).

(11) L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, p. 164ff.

volved in bond formation to the four chlorine atoms each bond has $^{1}/_{2}$ double bond character. From the vanadium–chlorine single bond distance of $1.20 + 0.99 = 2.19$ Å. and the double bond distance of $1.09 + 0.89 = 1.98$ Å. together with the resonance curve relating interatomic distance with the amount of double bond character[11] we predict the value 2.04 Å. for the vanadium–chlorine distance; this value is in good agreement with the observed distance 2.03 Å. The unpaired electron in vanadium tetrachloride probably occupies one of the 3d orbitals not involved in bond formation. It is interesting that this electron does not play a significant steric role (similar to that ordinarily played by an unshared electron pair) in the structure of this compound; the observed tetrahedral configuration is that which would be expected if this electron were absent.

In vanadium oxytrichloride, however, five of the six orbitals are required for the three bonds to chlorine atoms and for the double bond to the oxygen atom, thus leaving one orbital to form multiple bonds. If we assume that this extra bond resonates equally among the four atoms surrounding the vanadium atom, we expect a vanadium–chlorine distance of 2.09 Å., corresponding to $^{1}/_{4}$ double bond character, and a vanadium–oxygen distance slightly shorter than the double bond distance of $1.09 + 0.55 = 1.64$ Å. This shortening can be calculated from the double-bond and triple-bond distances of 1.64 and 1.49 Å., respectively, with the use of the resonance curve and with the assumption of $^{1}/_{4}$ triple bond character; thus the vanadium–oxygen distance of $1.64 - 0.08 = 1.56$ Å. is expected. These values are in good agreement with the distances observed in vanadium oxytrichloride: V–Cl = 2.12 ± 0.03 Å. and V=O = 1.56. ± 0.04 Å.

Some shortening of the vanadium–sulfur distance in the unusual crystal sulvanite[12] might also be expected from these considerations, inasmuch as the vanadium atom has only four closest sulfur neighbors (along with six copper neighbors, somewhat further away, with which it undoubtedly interacts rather strongly). The observed distance is 2.19 or 0.05 Å. less than the sum of the single bond radii.

In titanium tetrachloride we may expect a value of 2.12 Å. from the sums of the single-bond radii ($1.28 + 0.99 = 2.27$ Å.) and double-bond radii ($1.17 + 0.89 = 2.06$ Å.) if we make use of the resonance curve. Similarly, we might expect a value of 2.27 Å. in titanium tetrabromide from the single-bond and double-bond radius sums of 2.42 and 2.21 Å., respectively. The observed values[10] (Ti–Cl = 2.18 ± 0.04 Å. and Ti–Br = 2.31 ± 0.02 Å.) are somewhat larger, suggesting somewhat less double bond character, as if titanium actually had a tendency to employ less than six orbitals in bond formation in these tetrahalides.

Acknowledgment.—We wish to thank Professor Linus Pauling and Dr. Verner Schomaker for helpful discussions.

Summary

An electron diffraction study of vanadium tetrachloride shows it to have the regular tetrahedral structure with the bond distance V–Cl = 2.03 ± 0.02 Å. (Cl–Cl = 3.32 ± 0.03 Å.).

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[12] L. Pauling and R. Hultgren, *Z. Krist.*, **84**, 204 (1933).

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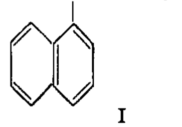
Some Factors Influencing the Ultraviolet Absorption Spectra of Polynuclear Aromatic Compounds. II. The Spectra of Aryl Carbinols and Polybenzfluorenes

BY R. NORMAN JONES

The ultraviolet absorption spectrum of the compound A—(CR$_2$)$_n$—B in which A and B are chromophorically active groups, and R is an alkyl group or a hydrogen atom, should approximate closely to the spectrum calculated for an equimolar mixture of the compounds A—CH$_3$ and B—CH$_3$, since the saturated aliphatic chain can only modify the energy states of the chromophorically active groups through hyperconjugation, or in some other secondary manner, and such effects should not be greatly influenced by the nature of the alkyl group or alkylene chain.

Numerous examples of the "insulation" between two chromophorically active groups provided by a polymethylene chain are recorded in the literature, and a further example is shown in Fig. 1 where the spectra of 2-(1-naphthyl)-ethylamine (I), 1-naphthylamine, and 1-methylnaphthalene are compared. Here the interposed dimethylene chain inhibits interaction between the naphthalene ring system and the potential auxochromic labile electrons of the amino group.

If the chromophorically active groups are separated by one saturated carbon atom only ($n = 1$),



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the same conditions should hold, although some modification of the spectrum might be caused by