



Heats of Combustion and Formation of Some Methoxypolysilane and polysiloxane: Si–O Bond Energy

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Citation: The Journal of Chemical Physics **22**, 1268 (1954); doi: 10.1063/1.1740365 View online: http://dx.doi.org/10.1063/1.1740365 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/22/7?ver=pdfcov Published by the AIP Publishing

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Erratum : Heats of Combustion and Formation of Some Organosilicon Compounds J. Chem. Phys. **22**, 957 (1954); 10.1063/1.1740244

Heats of Combustion and Formation of Some Organosilicon Compounds J. Chem. Phys. **19**, 1330 (1951); 10.1063/1.1748052



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The existence of associated nitric oxide molecules was inferred on the basis of thermodynamic data^{1,2} and it has now been shown that nitric oxide dimerises in the vapor, liquid, and solid states.³⁻⁵

A. L. Smith et al.4 on the basis of the infrared and Raman spectra of liquid and solid nitric oxide have demonstrated the existence of (NO)₂ and suggested that the structure is



This suggested structure is not confirmed by x-ray diffraction work (Dulmage et al.⁵). They favor a rectangular structure

$$\begin{array}{c|cccc} N' & & & \\ \hline N' & & \\ \hline r_1 & & \\ O' & & \\ O' & & \\ \hline N'' & & \\ \end{array} \qquad \begin{array}{c} N'' & & \\ \hline r_1 = 1.10A \\ r_2 = 2.38A. \end{array}$$

The possibility of a rectangular structure for the nitric oxide dimer had been pointed out previously by O. K. Rice.⁶ The decrease in bond length of the shorter NO link indicates that the $\pi^* 2p_z$ electron originally present in the NO monomer has lost its antibonding character. The unusually large N'-O" bond length indicated that this bond is not an ordinary covalent bond. This rectangular structure affords an explanation of why no vibrational frequency has been found which could be assigned to the stretching of the N-N bond in the proposed ONNO structure. There is no frequency in the infrared or Raman spectrum of (NO)₂ which can reasonably be assigned to $\nu(NN)$. This is almost conclusive evidence that no "normal" N-N (or N-O) bond joins the two units of the dimer. Taken in conjunction with the x-ray evidence the ONNO structure (trans or cis) containing a two-electron NN (or NO) bond is ruled out as a possibility.

Turning to the x-ray rectangular configuration it is clear that the bonds (N'-O'') and (O'-N'') must be equivalent. Their length of 2.38A indicates that they do not represent normal covalent bonds. The formation of this rectangular molecule can be pictured as follows (see Fig. 1). Let the plane of the dimer, (NO)₂ be the xz plane. σ and $2p\pi_y$ localized bonds are formed between the



atom pairs, (N'O') and (N''O''). We are left with six $2p_z$ electrons. These are to be fed into molecular orbitals (MO) formed from the O and N:2 p_z atomic orbitals (AO). The suggestion is made that MO's of two different types can be constructed by the overlapping of these similar AO's owing to the rectangular nature of the dimer.

(i) By the overlap of the $(N':2p_z)$ and $(O':2p_z)$ AO's and the N" and (O":2 p_z) AO's localized $2p\pi_z$ MO's can be formed between the pairs of atoms. These MO's can accommodate four electrons. Together with the σ and π_y bonds these π_z bonds give the N'O' and N"O" links their typical "triple" bond properties.

(ii) σ -type MO's can be formed by the overlap of the $N':2p_z$ and $(O'':2p_z)$ AO's and similarly for the atom pair O' and N''.

For the filling of these two σ -type MO's there remain however only two electrons. It is suggested that one electron is fed into each of these σ -type MO's, the electrons having opposite spins thus accounting for the diamagnetism of (NO)2. These one-electron σ bonds offer a partial explanation for the abnormally long bond lengths of these NO links. The mutual repulsion of nonpaired electrons would also operate in favor of a long N'O' bond length.

Each oxygen and nitrogen atom has associated with it one σ bond, two localized π bonds, and a one-electron σ -type bond; i.e., the atoms have four bonding MO's associated with them; they are quadrivalent.

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Heats of Combustion and Formation of Some Methoxy-polysilane and -polysiloxane: Si-O Bond Energy

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PREVIOUSLY, we reported on the heats of combustion and formation of some compared? formation of some organosilicon compounds containing alkyl or phenyl group, etc., and stated the technique used for burning them completely.1 Organosilicon compounds containing only methoxy group are readily burnt completely by themselves without ampoule, by the ignition of the liquid pool in the crucible.

We measured the heats of combustion of four substances, i.e., methyl ortho-, dí-, tri-silicate and hexamethoxydisilane, using Nenken type adiabatic bomb calorimeter. We have found the products of combustion to be carbon dioxide, water and silica by chemical analysis, without any soot. These samples used for the combustion measurements were prepared by alkolysis of its corresponding polychloro-polysilane and -polysiloxane. After completely dehydrochlorinated,² these products were rigorously distilled through a Stedman column of about 30 theoretical plates. Data on these materials are given in Table I.

TABLE I. Data on the substances used for combustion measurements.

Substance	Formula	b.p. °C/mm H	g d4 ²⁰	$n D^{20}$	Si % Found Calc		
Methyl orthosilicate	$\begin{array}{c} Si (OCH_{2})_{4} \\ Si_{2}O (OCH_{3})_{6} \\ Si_{3}O_{2}(OCH_{3})_{6} \\ Si_{2} (OCH_{3})_{6} \end{array}$	122/760	1.034	1.3688	18.48	18.45	
Methyl disilicate		118.5/30	1.122	1.3818	21.77	21.74	
Methyl trisilicate		95-6/2			23.17	23.12	
Hexamethoxydisilane		98/20	1.095	1.4070	22.99	23.18	

To determine the energy equivalent of the calorimeter at 20°C, we used the value 6319.0 cal/gram³ for the heat of combustion of standard benzoic acid. The resulting molar heats of combustion, at 20°C and 1 atmos constant pressure, are given under $-\Delta H_c$ in Table II. Each value represents the average of four to seven com-

 TABLE II. Heats of combustion and formation and
 Si-O bond energy (kcal/mole).

Formula	Mole wt	$-\Delta H_c$	$-\Delta H_{f^0}$	$-\Delta E$	-ESi-o
$\frac{\text{Si}(\text{OCH}_3)_4}{\text{Si}_2\text{O}(\text{OCH}_3)_6}$ $\frac{\text{Si}_3\text{O}_2(\text{OCH}_3)_8}{\text{Si}_4\text{O}_2(\text{OCH}_3)_8}$	152.23 258.38 364.54	694 1056 1399	300 539 798	1734 2796 3879	102 101 102

bustion measurements and their mean deviations were not over ± 0.1 percent. The corresponding values for the heat of formation from the elements have been computed by using -94.05 kcal,⁴

=

-68.32 kcal,⁴ and -208.14 kcal⁵ for the heats of formation of $\mathrm{CO}_2(g),\,\mathrm{H}_2\mathrm{O}(1)$ and $\mathrm{SiO}_2(\mathrm{amorph.})$ from standard elements, respectively, and are shown under $-\Delta H_f^0$. The heats of formation in the gaseous state from monoatomic gases, ΔE , were calculated using the values presented by Pauling⁶ for the heats of atomization of the constituent elements (except silicon). The value 89.2 kcal/g-atom was used for that of silicon.7 The latent heats of vaporization of these liquids were estimated from Trouton's rule. The value ΔE may be shown by the following expression:

$$\Delta E = aE_{\rm Si-O} + bE_{\rm Si-Si} + cE_{\rm C-O} + dE_{\rm C-H}$$

In this expression E represents the energy value of bond corresponding to each suffix and the factors a, b, c, and d the number of bonds in the molecules in question. As the energy terms of C-Oand C-H bonds are well known from many studies, we can evaluate the Si-O bond energy. In the case of hexamethoxydisilane Si-Si bond energy was considered as equal to the negative value of half of atomization heat of silicon. Si-O bond energy computed in this manner is shown in Table II, using the values proposed by Pauling⁶ for C-O and C-H bond energies.

In the past several values have been reported for Si-O bond energy, and of these the value obtained by Thompson⁵ is indicative of the considerable deviations in his results. We are not also satisfied with others.^{6,8} The Si-O bond energy derived here from four substances is in good agreement.

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The Rule of Mutual Exclusion*

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T is well known that in molecules possessing a center of inversion spectral lines corresponding to fundamental, overtone, and combination frequencies are mutually exclusive in Raman and infrared spectra, i.e., lines appearing in Raman effect are forbidden in infrared absorption and vice versa. The object of this note is to show that this rule is not universally true in crystals.

In molecules, the center of inversion is unique and it commutes with all other symmetry elements. The point group G of the molecule can be written as the direct product of two groups in the form $G = G_1 \times G_2$ where G_2 is the group of order 2 consisting only of the elements E and i. Each irreducible representation of G can be designated g (gerade) or u (un-gerade) according as the trace of iin the representation is positive or negative. Further every eigenfunction can be described as symmetric or antisymmetric with respect to i. Modes of vibration which are symmetric with respect to *i* are permitted only in Raman effect and modes which are antisymmetric with respect to i are permitted only in infrared spectrum.

In the case of crystals, the center of inversion is not unique. Instead, we have an infinity of centers of inversion and they do not necessarily commute with the other symmetry elements. The modes of vibration can no longer be designated symmetric or antisymmetric with respect to the centers of inversion, nor even with respect to one center of inversion. However, all permitted fundamentals in crystals correspond to modes in which equivalent atoms in neighboring unit cells move in phase.1 Such modes can be described symmetric or antisymmetric with respect to any one i (and therefore with all i) and the rule of mutual exclusion is still valid. However, the following example shows that the rule breaks down in general.

The finite space group O_h^{7} obtained by taking twice the Bravais primitive translations as equivalent to the identity element is of order 48×8 . This group has twenty irreducible representations, 4 one-dimensional, 2 two-dimensional, 4 three-dimensional, 4 sixdimensional, 4 four-dimensional, and 2 eight-dimensional. The one-, two-, and three-dimensional representations correspond to the irreducible representations of the isomorphic point group O_h . We give below the characters of the four three-dimensional and the four six-dimensional representations of our extended group. The first row refers to the order of the conjugate class. Typical symmetry elements in the first six conjugate classes are E, C_3, C_2 , σ , S₄, and *i*. Modes coming under F₂ are Raman active (infrared

	1	32	12	12	4 8	4	32	24	24	48	12	6	24	32	12	12	4	32	12	1
71	3 3	0 0	$-1 \\ -1$	-1_{1}	-1^{1}	3	0 0	$-1 \\ -1$	-1	-1^{1}	-1_{1}	3 3	$-1 \\ 1$	0	-1	$-1 \\ -1$	33	0	-1	3 3
3	ŝ	Ő	-1	-1	1	-3	Õ	Ĩ	1	-1	1	ŝ	-1	Ő	-1_{1}	-1	-3	Ŏ	Ĩ	3
$\overline{H_1}$	6	0	2	2	-1	-0	0	Ő	-0	0	0	-2^{3}	$-\frac{1}{2}$	Ő	2	$-\frac{1}{2}$	-3	ŏ	-0	6
$\frac{1}{1}$	6 6	0	$^{-2}_{2}$	-2^{0}	0	0	0	0	2 0	0	$-2 \\ 0$	$-2 \\ -2$	02	0	-2^{0}	$^{2}_{-2}$	0	0	$-2 \\ 0$	6 6
14	6	ŏ	$-\overline{2}$	ō	ŏ	ŏ	ŏ	ŏ	$-\tilde{2}$	ŏ	ž	$-\overline{2}$	ō	ŏ	ō	2	ŏ	ŏ	ž	Ğ.

in-active) while those coming under F_4 are infrared active (Raman in-active). Modes coming under all other representations are forbidden in both Raman and infrared absorption. The symmetry species of the combination modes of oscillations coming under H_1 and H_2 are given by the relation

$$H_1 \times H_2 = F_1 + F_2 + F_3 + F_4 + H_1 + H_2 + H_3 + H_4$$

This shows that the corresponding combination line is permitted in both spectra. Diamond is a specific case coming under the space group O_{h^7} . (See p. 157, Theory of Groups and its Application to Physical Problems by S. Bhagavantam and T. Venkatarayudu, 1951). Fuller details on the combination and overtone lines in this context will be published separately.

The author's thanks are due Professor D. M. Dennison and Professor G. B. B. M. Sutherland for their interest in this work.

* This work was sponsored by the U. S. Army Signal Corps under Con-tract DA-36-039 SC-5581. ¹ S. Bhagavantam and T. Venkatarayudu, Proc. Indian Acad. Sci. 9A, 224 (1939).

Force Constants of the Hydrides of the Second and Third Periods

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YMBOLS: k_e —force constant; *n*—number of valence elec-**S**YMBOLS: R_e —norce constant, n manner; A, B, a, α , β —trons of the element; Z—atomic number; A, B, a, α , β constants.

Recently Mitra¹ has shown that $k_e^{\frac{1}{2}}$ is linear with *n* for the hydrides of the 2nd and 3rd periods.

It was shown by King² and Sheline³ on semitheoretical grounds that $\log k_e$ should be linear with $\log Z$.

 $k_{\bullet} = BZ^{A}$.

Z = a + n

$$\log k_e = A \, \log Z + \log B \tag{1}$$

Now for each period

or

hence

or

$$k_e = B(a+n)^A$$

$$k_e^{1/A} = \alpha + \beta n \tag{2}$$

i.e., some power of k_e should be additive.

When Eq. (1) is tested for the 2nd group hydrides "A" comes out nearly 1.9, so the linearity of $k_e^{\frac{1}{2}}$ is justified in this case. But for the 3rd group hydrides, "A" is nearly 4. Hence $k_e^{\frac{1}{2}}$ should give