their reported values as described should be comparable to the ones determined in this research. It is seen in Table V that the differences are random, indicating a lack of systematic error in either set. The results for $Mo(CO)_6$ and $W(CO)_6$ agree surprisingly well whereas a considerable discrepancy exists for $Cr(CO)_6$. An error of more than ±1 kcal./mole is unlikely in our results, but a considerably larger error could have occurred in measurements made using a Beckman type thermometer. It may be recalled, however, that Sharafov and Rezukhina reported the formation of an appreciable amount of a peculiar dark chromium oxide which they presumably regarded as thermodynamically identical with ordinary Cr_2O_3.

TABLE V

COMPARISON OF PRESENT VALUES WITH THOSE OF SHARAFOV AND REZUKHINA[2]

	ΔH°_{298}		
	Sharafov and Rezukhina		
Compound	As reported	Corrected[a]	This research
$Cr(CO)_6$	−257.08	−249.4	−257.6
$Mo(CO)_6$	−233.12	−235.6	−234.8
$W(CO)_6$	−219.29	−225.3	−227.3

[a] Corrected as described in text by using more recent heats of formation of metal oxides.

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General Relation between Potential Energy and Internuclear Distance. II. Polyatomic Molecules[1]

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The simple form of a general relation between potential energy and internuclear distance derived from a quantum mechanical model is applied to the bonds of a large number of polyatomic molecules. The relation has the form $V = D_e[1 - \exp(-n\Delta R^2/2R)]$, where the parameter n is related to D_e by the equation $D_e = k_eR_e/n$. Using known values of bond stretching force constants as determined from molecular force models with known bond lengths, dissociation energies of bonds in polyatomic molecules have been calculated more accurately than was hitherto possible. One important feature of the method is that no empirically evaluated parameters are used. The relationship between bond dissociation energy and average bond energy as related to the derived potential function is discussed. For non-polar molecules or for polar molecules containing hydrogen or molecules with atoms of atomic number less than nine the calculated dissociation energies agree with the thermochemical bond energies with about 5% accuracy. A number of other applications of this function will be suggested. With due consideration to its limitations this function should be useful as a tool for elucidating other problems of bond formation and structure.

Introduction

Many attempts have been made to derive from quantum theory or to formulate empirically analytic relationships between potential energy and internuclear distance for diatomic molecules.[2] Except for the simplest systems such as the H_2^+ and H_2 molecules quantum theory has not given definite relationships,[3] while empirical internuclear potential functions have not correlated satisfactorily such bond properties as dissociation energy, bond lengths, bond stretching force constants and anharmonicity constants. In no case has it been possible to apply diatomic internuclear potential functions to the bonds of polyatomic molecules and obtain even a qualitative correlation of bond properties.

We have recently derived an internuclear potential function from a quantum mechanical model which has found extensive application in quantitatively predicting and correlating the bond properties of a large number of diatomic molecules.[4] It will be shown that this internuclear potential function can be used to predict and correlate the bond properties of a number of bonds in polyatomic molecules. One important feature of the method is that no empirically evaluated constants are used, since all necessary parameters have been evaluated from a quantum mechanical model.[4]

The form of the function which has been derived previously for diatomic molecules is

$$V = D_e[1 - \exp(-n\Delta R^2/2R)] \qquad (1)$$

where D_e bond dissociation energy referred to the bottom of the potential curve, $\Delta R = R - R_e$, and R_e = equilibrium bond length. The derivation of (1) shows that n may be obtained from the relation

$$n = n_0(I/I_0)_A^{1/2}(I/I_0)_B^{1/2} \text{ cm.}^{-1} \qquad (2)$$

where $(I/I_0)_A$ and $(I/I_0)_B$ are the ionization potentials of atoms A and B in the bond A–B, relative to those of the corresponding atoms in the same

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[1] Presented in part at the 125th Meeting of the American Chemical Society, Kansas City, March, 1954.

[2] P. M. Morse, *Phys. Rev.*, **34**, 57 (1929); Coolidge, James and Vernon, *ibid.*, **54**, 726 (1938); H. M. Hulburt and J. O. Hirschfelder, *J. Chem. Phys.*, **9**, 61 (1941); M. L. Huggins, *ibid.*, **3**, 473 (1935); **4**, 308 (1936); R. Rydberg, *Z. Physik*, **73**, 376 (1932); M. F. Manning and N. Rosen, *Phys. Rev.*, **44**, 953 (1933); G. Poschl and E. Teller, *Z. Physik*, **83**, 143 (1933); E. A. Hylleraas, *ibid.*, **96**, 661 (1935); J. W. Linnett, *Trans. Faraday Soc.*, **36**, 1123 (1940); **38**, 1 (1942); G. B. B. M. Sutherland, *J. Chem. Phys.*, **8**, 161 (1940); *Proc. Indian Acad. Sci.*, **8**, 341 (1938); A. A. Frost and B. Musulin, THIS JOURNAL, **76**, 2045 (1954); *J. Chem. Phys.*, **22**, 1017 (1954).

[3] (a) E. Teller, *Z. Physik*, **61**, 458 (1930); (b) H. M. James and A. S. Coolidge, *J. Chem. Phys.*, **1**, 825 (1933).

[4] E. R. Lippincott and R. Schroeder, *J. Chem. Phys.*, **23**, 1131 (1955); E. R. Lippincott, *ibid.*, **23**, 603 (1955); E. R. Lippincott, to be published.

row and first column of the periodic table.[4] We will assume here that the potential function (1) and relation (2) are valid for bonds in polyatomic molecules, and that the value of n_0 calculated for diatomic molecules can be used with the bonds of polyatomic molecules. The theoretical value of n_0 for the H_2 molecule is 5.34×10^8 cm.$^{-1}$ while for bonds involving multi-electronic atoms n_0 has a value of 6.03×10^8 cm.$^{-1}$. If a geometric mean rule is assumed, the n_0 value for bonds of type H–A is 5.67×10^8 cm.$^{-1}$, thus

$$n_0(H_2) = 5.34 \times 10^8 \text{ cm.}^{-1} \quad n_0(HA) = 5.67 \times 10^8 \text{ cm.}^{-1} \quad n_0(A_2) = 6.03 \times 10^8 \text{ cm.}^{-1} \tag{3}$$

By imposing the conditions for stability that

$$(\partial V/\partial R)_{eq} = 0 \tag{4}$$

and

$$(\partial^2 V/\partial R^2)_{eq} = k_e \tag{5}$$

the following relation can be derived giving the relation of n to bond dissociation energy, equilibrium bond length, and bond stretching force constant, k_e.

$$D_e = k_e R_e / n \tag{6}$$

The use of equations 1, 2 and 6 has been demonstrated previously by correlating and predicting a large amount of spectroscopic data for diatomic molecules.[4] In particular, it was shown that the function (1) was much more accurate and easier to use than the well known Morse potential function,[2] and that with it calculations of bond dissociation energies and bond anharmonicity constants of diatomic molecules are readily made with greater accuracy than was hitherto possible. Relation (2) was originally obtained empirically.[4] The theoretical values of n_0(HA) (5.67×10^8 cm.$^{-1}$) and $n(A_2)$ (6.03×10^8 cm.$^{-1}$) agree remarkably well with the values found previously by empirical methods (5.92×10^8 cm.$^{-1}$ and 6.32×10^8 cm.$^{-1}$ respectively).[4] In order to keep our methods for polyatomic molecules independent of any empirically evaluated parameters we will use the theoretical values of n_0 given in equation 3 in our calculations.

In the following discussion of the application of the potential function for the prediction and correlation of bond properties, we shall group the bonds of polyatomic molecules into the following classifications: (a) single bonds, (b) isolated multiple bonds, (c) adjacent multiple bonds, and (d) bonds for which only the average bond energy is known.

Application to Polyatomic Molecules

The application of the potential function (1) to polyatomic molecules requires consideration of a number of factors. The process of dissociation of a bond in a polyatomic molecule is analogous to the dissociation of a diatomic molecule in the sense that dissociation leads to two fragments, either radicals, molecules or atoms. The dissociation energy of a bond A–B in the molecule M may be defined as the endothermicity of the reaction in which M is decomposed into two fragments R_1 and R_2 formed by breaking bond A–B only.[5] The energy for this process should be computed for the state in which both the reactant M and the products R_1 and R_2 are in the gas phase at zero pressure and 0°K. This dissociation energy is thus unambiguously defined by the description of the initial electronic state of the molecule and the final specified electronic states of the fragments.

However, in using equation 6 to predict the bond dissociation energies of bonds in polyatomic molecules one has the problem of knowing what type of bond stretching force constant to use in the calculations. For diatomic molecules this force constant is unambiguously determined by the vibrational frequency and atomic weights. However, for polyatomic molecules this force constant depends on the vibrational frequency, atomic weights and the type of force field assumed in computing the force constant. In order to test the application of equations 1, 2 and 6 for use with polyatomic molecules we will make separate calculations using bond stretching force constants determined from the following three different types of force fields[6]: (A) a diatomic type force field in which the bond stretching force constant is obtained from the bond vibrational frequency considering the molecule to be diatomic-like. This is obviously a poor approximation and can only be expected to give reasonable results for bonds of molecules which consist of two heavy atoms or of molecules having a light atom attached to a heavier atom. Fortunately these two conditions are usually fulfilled for most molecules where the bond dissociation is known reasonably well; (B) a simple valence force model (SVF). This model assumes that the potential energy of vibration of a molecule can be obtained by considering only the stretching of bonds and the bending of bond angles without any bond–angle, bond–bond, angle–angle, or other interaction terms. Such force constants are known for most of the simple polyatomic molecules. (C) A modified valence force model (MVF). A number of modified valence force models have been used to describe the vibrational motion of a number of molecules depending on the type of interaction terms assumed in the vibrational potential function. However, there is no general agreement among molecular spectroscopists as to the best type of modified valence force field.

The force constants used in equation 6 should be ones determined from zero order vibrational frequencies (corrected for anharmonicity). There is only a limited number of polyatomic molecules where such force constants have been calculated. This anharmonicity correction is about 8% for bonds involving hydrogen and about 3% for bonds which do not contain hydrogen. If force constants determined from zero-order frequencies are not available we will approximate a correction in our calculations by increasing the force constant by 8 or 3%, for A–H or A–B bonds, respectively.

Since the quantum mechanical derivation of the internuclear potential function (1) implies that equation 6 will give dissociation energies it is im-

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(5) M. Szwarc and M. G. Evans, *J. Chem. Phys.*, **18**, 618 (1950).

(6) For a discussion of a number of molecular force field models, see E. B. Wilson, J. D. Decius and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., New York, N. Y., 1955, Chapter 8.

TABLE I

PREDICTED BOND DISSOCIATION ENERGIES OF SINGLE BONDS IN POLYATOMIC MOLECULES

Molecule	$n(10^{-8})$, cm.$^{-1}$	$k(10^{-5})$, dynes/cm.[a] Rptd.	Type	Cor.	D, kcal./mole Calcd.	Exptl.	Error, kcal./mole	Error, %	E, kcal./mole	Ref. for D	k
H_3C-H	8.22	4.72	Di-a	5.10	93	101 ± 1	8	8.0	98.2	b	
		5.04	SVF	5.44	100		1	1.0			c
			MVF	5.394*	99		2	2.0			d
H_5C_2-H	8.22	4.82	Di-a	5.21	96	98	2	2.0	98.2	e	
		4.79	SVF	5.17	96		2	2.0			f
			MVF	5.35*	99		1	1.0			d
H_5C_6-H	8.22	5.49	Di-a	5.93	108	102	6	5.9	98.2	g	
		5.05	SVF	5.45	99		3	2.9			h
		5.065	MVF	5.47	99		3	2.9			i
Cl_3C-H	8.22	5.37	Di-a	5.80	105	89 ± 2	16	18.0		j	
		4.80	MVF	5.18	92		3	3.4			k
H_2N-H	9.30	6.22	Di-a	6.72	101	104 ± 2	3	2.9	92.2	l	
		6.42	SVF	6.93	104		0	0.0			c
			MVF	7.171*	108		4	3.9			m
$HO-H$	9.07	7.47	Di-a	8.07	117	118 ± 0.7	1	0.8	109.4	n	
		7.76	SVF	8.38	122		4	3.4			c
			MVF	8.428*	123		5	4.2			o
$HS-H$	8.05	3.93	Di-a	4.24	97	90 ± 5	7	7.8	88	p	
		3.96	SVF	4.28	98		8	8.9			q
			MVF	4.01*	92		2	2.2			r
H_3C-CH_3	12.60	4.36	Di-a	4.49	78	80 ± 6	2	2.5	80	s	
		5.62	SVF	5.79	100		20	25.0			f
			MVF	4.57*	79		1	1.3			d
H_3C-NH_2	14.34	4.88	Di-a	5.03	73	~80	7	8.8	66	p	u
H_3C-OH	13.99	4.86	Di-a	5.01	75	~90	15	16.7	79	t	u
H_3C-Br	14.43	2.78	Di-a	2.86	54	67	13	19.4	66.5	v	
		2.82	SVF	2.90	55		12	17.9			w
		2.863	MVF	2.949	56		11	16.4			x
H_3C-I	13.82	2.25	Di-a	2.32	51	53	2	3.8		y	
		2.23	SVF	2.30	50		3	5.7			w
		2.25	MVF	2.32	51		2	3.8			z
H_2N-NH_2	16.28	3.62	Di-a	3.73	47	60–64	13	21.7	37	l	
O_2N-NO_2	16.28	1.13	Di-a	1.16	16	13	3	23.1		na	c
		1.47	SVF	1.51	21		8	61.5			
		1.36	MVF	1.40	20		7	53.8			bb
$ON-Cl$	15.72	2.0	SVF	2.06	36	37	1	2.7		t	bb
$ON-Br$	16.32	1.5	SVF	1.55	29	28	1	3.6		j	bb
$HO-OH$	15.32	3.85	Di-a	3.97	54	53	1	1.9	34	cc	
		3.84	MVF	3.96	54		1	1.9			dd
$HS-SH$	12.18	2.52	Di-a	2.60	62	72–78	10	13.9		p	

Av. error (kcal./mole); MVF = 3.5; SVF = 5.3; Di-a = 8.0

[a] The force constants have been corrected (column 3) for anharmonicity—3% for all molecules except where one of the atoms in the bond is hydrogen. These have been corrected 8%. (Column 2) Di-a, diatomic approximation; SVF, simple valence force field; MVF, modified valence force field; the asterisk (*) is used to denote the force constants calculated from zero-order frequencies—thus no anharmonicity correction was necessary. [b] H. C. Anderson, G. B. Kistiakowsky and E. R. Van Artsdalen, *J. Chem. Phys.*, **10**, 305 (1942); H. C. Anderson and G. B. Kistiakowsky, *ibid.*, 11, 6 (1943); P. M. Doty, *ibid.*, **12**, 399 (1944). [c] G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand and Co., Inc., New York, N. Y., 1945. [d] G. E. Hansen and D. M. Dennison, *J. Chem. Phys.*, **20**, 313 (1952). [e] H. C. Anderson and E. R. Artsdalen, *ibid.*, **12**, 479 (1944). [f] J. B. Howard, *ibid.*, **5**, 442 (1937). [g] M. Szwarc and D. Williams, *ibid.*, **20**, 1171 (1952). [h] R. C. Lord, J. E. Ahlberg and D. H. Andrews, *ibid.*, **5**, 649 (1937). [i] B. L. Crawford, Jr., and F. A. Miller, *ibid.*, **17**, 249 (1949). [j] M. Szwarc, *Chem. Revs.*, **47**, 75 (1950); V. Braunwarth and H. J. Schumaker, *Kolloidzschr.*, **89**, 184 (1939). [k] J. P. Zietlow, F. F. Cleveland and A. G. Meister, *J. Chem. Phys.*, **18**, 1076 (1950). [l] M. Szwarc, *Proc. Roy. Soc.* (*London*), **A198**, 267 (1949). [m] J. Duchesne and I. Ottelet, *J. Chem. Phys.*, **17**, 1354 (1949). [n] R. J. Dwyer and O. Oldenberg, *ibid.*, **12**, 351 (1944). [o] D. M. Dennison, *Rev. Mod. Phys.*, **12**, 175 (1940). [p] T. L. Cottrell, "The Strengths of Chemical Bonds," Academic Press, Inc., New York, N. Y., 1954. [q] J. B. Lohman, F. P. Reding and D. F. Hornig, *J. Chem. Phys.*, **19**, 252 (1951). [r] J. Duchesne and L. Burnelle, *ibid.*, **19**, 1191 (1951). [s] F. O. Rice and M. D. Dooley, THIS JOURNAL, **55**, 4245 (1933). [t] A. Terenin and H. Neujmin, *J. Chem. Phys.*, **3**, 436 (1935). [u] F. Kohlrausch, "Der Smekal Raman Effekt," Verlag von Julius Springer, 1931. [v] M. Ladacki and M. Szwarc, *Proc. Roy. Soc.* (*London*), **A219**, 341 (1953). [w] T. Wu, "Vibrational Spectra and Structure of Polyatomic Molecules," 2nd Edition, J. W. Edwards, Ann Arbor, Mich., 1946, p. 242. [x] H. B. Weissman, R. B. Bernstein, S. E. Rosser, A. G. Meister and F. F. Cleveland, *J. Chem. Phys.*, **23**, 544 (1955). [y] G. A. McDowell and B. G. Cox, *ibid.*, **20**, 1496 (1952). [z] P. F. Fenlon, F. F. Cleveland and A. G. Meister, *ibid.*, **19**, 1561 (1951). [aa] F. H. Verhoek and F. Daniels, THIS JOURNAL, **53**, 1250 (1931). [bb] H. Siebert, *Z. anorg. Chem.*, **275**, 224 (1954). [cc] P. A. Giguere and I. D. Liu, THIS JOURNAL, **77**, 6477 (1955). [dd] P. A. Giguere and O. Bain, *J. Phys. Chem.*, **56**, 340 (1952).

portant that we compare our calculated results with the former quantities. Unfortunately, there is only a limited number of bonds in polyatomic molecules where the bond dissociation energy is

TABLE II

PREDICTED BOND DISSOCIATION ENERGIES OF ISOLATED MULTIPLE BONDS IN POLYATOMIC MOLECULES

Molecule	$n(10^{-8})$, cm.$^{-1}$	$k(10^{-5})$, dynes/cm.[a] Rptd.	Type	Cor.	D (kcal./mole) Calcd.	Exptl.	E (kcal./mole)	Ref. for k	D
HC≡CH	12.60	15.80	SVF	16.27	220	234	198	b	c
			MVF	17.2*	233	170		f	d
						<187			e
$H_2C=CH_2$	12.60	9.57	SVF	9.86	150	<162	145	b	g
			MVF	10.886*	166			h	
HC≡N	14.34	17.9	SVF	18.4	210	223	209	h	i
		18.6	MVF	19.2	219	164		j	k
$H_2C=O$	13.99	12.70	MVF	13.08	160		173	l	
$F_3P=O$	14.09	11.39	MVF	11.73	172	130		l	m
$Cl_3P=O$	14.09	9.98	MVF	10.28	150	122		l	m
$Br_3P=O$	14.09	9.59	MVF	9.88	145	119		l	m

[a] See footnote *a* Table I. [b] See *c*, Table I. [c] See *p*, Table I (L_c = 172 kcal./mole). [d] See *p*, Table I (L_c = 140 kcal./mole). [e] W. C. Price, *Phys. Rev.*, **47**, 444 (1935). [f] See *w*, Table I. [g] W. C. Price, *Phys. Rev.*, **45**, 843 (1934). [h] B. L. Crawford, J. E. Lancaster and R. G. Inskeep, *J. Chem. Phys.*, 21, 678 (1953). [i] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," circular of the Natl. Bureau of Standards 500, 1952. [j] E. Bright Wilson, J. C. Decius and P. C. Cross, "Molecular Vibrations," McGraw–Hill Book Co., Inc., New York, N. Y., 1955, pp. 178. [k] See *q*, Table I. [l] See *bb*, Table I. [m] T. Charnley and H. A. Skinner, *J. Chem. Soc.*, 450 (1953).

known with sufficient accuracy to check equation 6. The molecules containing single bonds which appear to have reliably known dissociation energies are given in Table I. In making this selection we have made extensive use of the review by Szwarc and the recent book by Cottrell as well as the recent literature.[7,8]

Single Bonds.—In Table I we have tabulated the calculated dissociation energies for single bonds using the three types of bond stretching force constants (diatomic type, SVF and MVF, respectively). The calculated D_e values have been corrected for the zero point vibrational energy, but no corrections to 0°K. have been made since this correction is considerably smaller than the error inherent in the method of prediction as well as experimental error in the observed dissociation energy. The calculated values for the bond dissociation energies are surprisingly close to the experimental values, the MVF constants giving a 3.5 kcal./mole average deviation, the SVF constants giving a 5.3 kcal./mole average deviation and the diatomic-like force constants giving an 8.0 kcal./mole average deviation. The agreement is surprising in that it has generally been accepted that any such relation between dissociation energy, force constant and bond length would involve parameters which would require a detailed knowledge of the molecular vibrational force field and thus vary in a rather obscure way from molecule to molecule.[5,6] It appears that the effect of any such parameters on the bond energies is at least no greater than the uncertainty in the present bond stretching force constants for polyatomic molecules. As expected the MVF bond stretching constants give the best results, but the results with the SVF bond stretching constants are nearly as good with the exception of the C–C bond in C_2H_6. In both cases the predicted values seem to be within the 5% level, a result consistent with similar calculations for diatomic molecules. The use of the diatomic approximation gives results which are definitely too low but it is surprising that one can obtain reasonable values. In any case, it is clear that the internuclear potential function (1) and equations 2 and 6 are applicable to most of the single bonds of the collection of polyatomic molecules given in Table I if one uses MVF constants or SVF constants. It would be desirable to check this potential function with a wider selection of molecules, but unfortunately the desired experimentally determined bond dissociation energies are not available.

Isolated Multiple Bonds.—We will now consider the application of relations (2) and (6) to isolated double and triple bonds. With diatomic molecules it was found that multiple bonds could be treated by the same methods which were used for single bonds. The results for the nitrogen and oxygen molecules were good. There appears to be no need to modify the method when applied to multiple bonds of polyatomic molecules. In Table II we have compared the calculated bond dissociation energies of multiple bonds with experimentally determined bond dissociation energies and bond energies.

In cases where the experimental bond dissociation energies depend on an assumption concerning the heat of sublimation of carbon we have listed alternative experimental values. With the exception of the phosphoryl halides, the predicted dissociation energies are in reasonable agreement with the experimentally determined values, if the heat of sublimation of carbon is 172 kcal./mole. The discrepancy for the phosphoryl halides may be due to dissociation into radicals one of which is in an excited state compared to the state assumed in the thermochemical calculations.

Adjacent Multiple Bonds.—In Table III we have tabulated the calculated bond dissociation energies of some molecules containing adjacent multiple bonds along with experimentally determined bond dissociation energies and bond energies. The agreement for dissociation energies in most cases is poor and it is concluded that the potential function is not applicable to such bonds without modification. The failure may be due to the possibility that these molecules dissociate into

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(7) M. Szwarc, *Chem. Revs.*, **47**, 75 (1950).

(8) T. L. Cottrell, "Strengths of Chemical Bonds," Academic Press, Inc., New York, N. Y., 1954.

TABLE III

PREDICTED BOND DISSOCIATION ENERGIES OF ADJACENT MULTIPLE BONDS IN POLYATOMIC MOLECULES

Molecule	$n(10^{-8})$, cm.$^{-1}$	$k(10^{-5})$, dynes/cm.[a] Rptd.	Type	Cor.	D (kcal./mole) Calcd.	Exptl.	E (kcal./mole)	Ref. for k	D
OC=O	13.99	16.8	SVF	17.3	205	127	192	b	c
		15.5	MVF	16.0	189			d	
SC=S	12.42	8.1	SVF	8.34	149	86	131	b	c,e
		7.5	MVF	7.73	138	52		d	c,e
NN→O	15.82		MVF	11.50*	122	40		f	c
ON=O	15.82	9.13	SVF	9.40	101	73	111	b	c
OO→O	15.44	4.92	MVF	5.07	59	25	72	g	c
OS=O	13.70	9.97	SVF	10.27	153	150	122	b	h
						127			i
O_2S=O	13.70	10.77	SVF	11.09	165	82	109	b	h

[a] See footnote *a* Table I. [b] See *c*, Table I. [c] See ref. *i*, Table II. [d] See *j*, Table II. [e] See *p*, Table I. [f] W. S. Richardson and E. Bright Wilson, Jr., *J. Chem. Phys.*, **18**, 694 (1950). [g] F. F. Cleveland and M. J. Klein, *ibid.*, **20**, 337 (1952). [h] W. H. Evans and D. D. Wagman, N. B. S. Report No. 1037, June 14, 1951. [i] G. St. Pierre and J. Chipman, THIS JOURNAL, **76**, 4790 (1954).

TABLE IV

COMPARISON OF OBSERVED BOND ENERGIES WITH PREDICTED BOND DISSOCIATION ENERGIES OF INORGANIC MOLECULES

Molecule	$n(10^{-8})$, cm.$^{-1}$	$k(10^{-5})$, dynes/cm.[a] Rptd.	Type	Cor.	D (calcd.), kcal./mole	E, kcal./mole	Error, kcal./mole	Error, %	Ref. for k	E
$SnBr_4$	13.23	2.28	SVF	2.35	62	65	3	4.6	b	c
		2.281	MVF						d	
$SnCl_4$	12.75	2.80	SVF	2.88	75	77	2	2.6	b	c
$GeBr_4$	13.63	2.58	SVF	2.66	65	66	1	1.5	b	e
		2.581	MVF						d	
$GeCl_4$	13.13	3.27	SVF	3.37	76	80	4	5.0	b	c
		3.297	MVF						d	
GeF_4	14.87	5.20	SVF	5.36	86				f	
		5.09	MVF						f	
GeH_4	7.77	2.355	MVF	2.543	68				d	
$SiBr_4$	12.73	2.92	SVF	3.01	73	73	0	0.0	b	c
$SiCl_4$	12.27	3.75	SVF	3.86	91	90	1	1.1	b	c
SiF_4	13.89	7.16	SVF	7.37	116	136	20	14.8	b	c
		7.16–2.86	MVF						g	
SiH_4	7.255	2.84	SVF	3.07	86	81	5	6.1	b	c
		2.826	MVF						d	
BBr_3	12.34	3.66	SVF	3.77	82	74	8	10.1	b	e
BCl_3	11.89	4.63	SVF	4.77	99	94	5	5.4	b	e
		4.02	MVF						h	
BF_3	13.46	8.83	SVF	9.09	124	139	15	10.8	b	e
		7.27	MVF						h	
PH_3	8.28	3.09	SVF	3.34	79	76.4	2.6	3.4	b	c
		3.24	MVF						b	
S_8	12.18	2.042	MVF	2.103	51	49.5	1.5	3.0	i	c
P_4	12.90	2.06	MVF	2.12	52	51.3	0.7	1.0	h	c
Av. dev. in kcal./mole		5.0								
Av. % error		5.0								

[a] See footnote *a*, Table I. [b] See *c*, Table I. [c] M. L. Huggins, THIS JOURNAL, **75**, 4123 (1953). [d] K. Venkateswarlu and Sundayan, *J. Chem. Phys.*, **23**, 2365 (1955). [e] See *p*, Table I. [f] A. D. Caunt, L. N. Short and L. A. Woodward, *Trans. Faraday Soc.*, **48**, 873 (1952). [g] F. L. Voetz, A. G. Meister and F. F. Cleveland, *J. Chem. Phys.*, **19**, 1084 (1951). [h] See *j*, Table II. [i] H. J. Bernstein and J. Powling, *J. Chem. Phys.*, **18**, 1018 (1950).

radicals one of which is not in the ground state assumed for the thermochemically calculated dissociation energy or to effects caused by the delocalization of the π electrons. A comparison with the experimental bond energies gives better agreement. This agreement is partly due to the fact that the force constants used are in general ones based on the totally symmetric bond stretching frequencies. The corresponding mode of vibration, therefore, leads to atomization of the molecule. This suggests that for such molecules one might obtain better agreement if a comparison is made with average bond energies.

Comparison with Bond Energies

Since experimentally determined bond energies are available for a wide selection of polyatomic molecules it is logical to investigate the conditions for which equation 6 may be expected to predict dissociation energies which have values near the corresponding bond energies. Thus there may be a collection of molecules for which the dissociation energy is nearly the same as the bond energy, E. Certainly the dissociation energy of a bond A–B in a polyatomic molecule is not necessarily the same as the bond energy of bond A–B. In general the bond energy will depend on the environment of

TABLE V

COMPARISON OF PREDICTED BOND DISSOCIATION ENERGIES WITH THERMOCHEMICAL BOND ENERGIES FOR CARBON COMPOUNDS

Molecule	$n(10^{-8})$, cm.$^{-1}$	$k(10^{-5})$, dynes/cm.[a] Rptd.	Type	Cor.	D (calcd.), kcal./mole	$E(L_c$ 172), kcal./mole	Error, %	$E(L_c$ 140), kcal./mole	Error, %	Ref. for k	Ref. for E
H_3C-H	8.22	5.04	SVF	5.44	100	98	2.0	91	9.9	b	c
			MVF	5.394*						d	
$HCC-H$	8.22	5.92	SVF	6.39	114	102	11.8	94	21.3	b	e
			MVF	6.24*						f	
H_3C_2-H	8.22	5.08	SVF	5.49	100	101	1.0	93	8.6	h	e
			MVF	6.13*						g	
$HC\equiv CH$	12.60	15.80	SVF	16.27	220	198	11.1	145	51.7	b	c
			MVF	17.2*						f	
$H_2C=CH_2$	12.60	9.57	SVF	9.86	150	145	3.3	110	26.7	b	e
			MVF	10.886*						g	
H_3C-CH_3	12.60	5.62	SVF	5.79	100	80	25.0	66	51.5	k	c
			MVF	4.57*	-					d	
H_3C-NH_2	14.34	4.88	Di-a	5.03	73	66	10.6	51	43.1	i	c
$HC\equiv N$	14.34	17.9	SVF	18.4	210	209	0.5	155	35.5	b	c
		18.6	MVF							j	
H_3C-OH	13.99	4.86	Di-a	5.01	75	79	5.1	72	4.2	i	c
$H_2C=O$	13.99	12.70	MVF	13.08	160	173	7.5	149	7.4	k	c
$OC=O$	13.99	16.8	SVF	17.3	205	191	7.3	174	17.8	b	e
		15.5	MVF							j	
F_3C-F	15.74	9.14	SVF	9.41	116	116	0.0	108	7.4	b	e
		9.15-6.24	MVF							l	
H_3CS-CH_3	12.42	3.05	SVF	3.14	66	62	6.5	53	24.5	m	e
$SC=S$	12.42	8.1	SVF	8.34	149	131	13.7	114	30.7	b	e
		7.5	MVF							j	
Cl_3C-Cl	13.90	4.38	SVF	4.51	81	79	2.5	71	14.3	b	e
		3.65-2.98	MVF							l	
H_3C-Cl	13.90	3.46	SVF	3.56	65	79	17.2	71	8.5	f	e
Br_3C-Br	14.43	3.66	SVF	3.77	65	67	3.0	58	12.1	b	e
		2.95-2.34	MVF							n	
H_3C-Br	14.43	2.82	SVF	2.90	55	66	16.7	57	3.6	j	c
		2.863	MVF							o	
H_3C-I	13.82	2.23	SVF	2.30	50	54	7.4	44	13.6	j	c
		2.25	MVF							p	
					Av. % error		6.7		21.3		

[a] See footnote *a*, Table I. [b] See *c*, Table I. [c] K. S. Pitzer, THIS JOURNAL, **70**, 2140 (1948); and reference *p*, Table I. [d] See *d*, Table I. [e] H. A. Skinner, *Trans. Faraday Soc.*, **41**, 642 (1945). [f] See *w*, Table I. [g] B. L. Crawford, J. E. Lancaster and R. G. Inskeep, *J. Chem. Phys.*, **21**, 678 (1953). [h] See *f*, Table I. [i] See *u*, Table I. [j] See *j*, Table II. [k] See *bb*, Table I. [l] E. L. Pace, *J. Chem. Phys.*, **16**, 47 (1948); C. E. Deckler, A. G. Meister and F. F. Cleveland, *ibid.*, **19**, 784 (1951); and B. I. Stepanov, *Acta Physicochim.*, **20**, 174 (1945). [m] See *g*, Table IV. [n] J. P. Zietlow, F. F. Cleveland and A. G. Meister, *J. Chem. Phys.*, **18**, 1076 (1950); T. S. Simanouti, *ibid.*, **17**, 245 (1945); J. C. Decius, *ibid.*, **16**, 214 (1948); B. I. Stepanov, *Acta Physicochim.*, **20**, 174 (1945). [o] See *x*, Table I. [p] See *z*, Table I.

bond A–B in the molecule. Since this environment varies in a rather obscure way from molecule to molecule the relationship between average bond energy and bond dissociation energy has not always been clearly defined. For our purposes it is sufficient to accept the definition of average bond energy given by Szwarc and Evans.[5] In particular they have shown that the relationship between the two requires consideration of the type of molecular force field used to approximate the vibrational motion of the molecule. If one assumes a simple valence force model the average bond energy becomes identical with the bond dissociation energy.[5] On this basis a collection of molecules for which the SVF model gives an adequate description of the vibrational motion of the molecule should have bond dissociation energies which are not greatly different from the corresponding average bond energies. However, in general one needs to demonstrate that the SVF model is a good approximation to the vibrational motion of the molecule under study. Two ways to check this are (A) to work with isotopically substituted molecules for which the same set of force constants are obtained from both isotopically substituted molecule; (B) to work with molecules for which the SVF bond stretching constants are nearly the same as the bond stretching constants determined from more elaborate MVF models.

The first method can be applied to hydrogen containing molecules by studying their deuterium derivatives. In nearly all cases the SVF constants for type A–H bonds agree within a few per cent. of the constants for type A–D bonds.

In Table IV we have listed a number of molecules for which SVF constants are known along with MVF constants if also known. In most but not all cases the MVF constants agree reasonably well with the SVF constants. The SVF constants listed here are ones which have been calculated using totally symmetric frequencies. The use of these latter constants for our purposes appears justified in that the totally symmetric mode of vibration is the one which leads to dissociation or atomization of the molecules, and thus should lead to better correlation with dissociation and bond energies.

We have applied equation 6 to the molecules listed in Table IV. The calculated dissociation energies are compared with the thermochemically determined bond energies and to experimentally determined bond dissociation energies if available. Carbon compounds are not included in this table due to the uncertainty of the heat of sublimation of carbon, L_c.

The average deviation of the calculated dissociation energies from the known bond energies is 5.0 kcal./mole.

A comparison of calculated dissociation energies with bond energies from (6) for carbon compounds is confused by the uncertainty associated with the heat of sublimation of carbon.[8-11] Consequently, in Table V we have compared our calculated values of dissociation energies of bonds in carbon compounds with two sets of bond energies, the first corresponding to $L_c = 140$ kcal./mole and the second to $L_c = 172$ kcal./mole. With few exceptions the predicted dissociation energies agree better with bond energies based on $L_c = 172$ kcal./mole, the average per cent. error from the thermochemical bond energies being 6.7. This furnishes indirect evidence that the heat of sublimation of carbon must be chosen as 172 kcal./mole, if the bond energies of tetravalent carbon compounds are to be consistent with the bond energies of inorganic compounds.

However, a serious difficulty with equation 6 is that the predicted bond energies for a number of polar molecules are considerably in error. The molecules for which we have found serious discrepancies are CH_3F, CH_3Cl, AsF_3, $AsCl_3$, PCl_3, PBr_3 and $SbCl_3$. In general it appears that the predicted bond dissociation energy agrees with the thermochemical bond energy for non-polar molecules and for polar molecules containing hydrogen or atoms with atomic numbers less than nine.

We have no good explanation for the failure of the proposed relation on the polar molecules of the heavier elements. The SVF model may be a poor approximation to the molecular force field. The thermochemical bond energies may differ greatly from the true bond dissociation energies. For the latter situation agreement would certainly not be expected.

Other Applications

Because of the simple form of the proposed function it is possible to apply it to a number of other problems. Using (1) as a starting potential we have formulated a one-dimensional model for hydrogen bonding which predicts or correlates the main features associated with hydrogen bond systems, such as bonded OH distances, OH frequency shifts, hydrogen bond energies, etc. Good agreement is obtained when these predictions are compared with experimental studies of hydrogen bond systems.[12]

One interesting application which may prove very useful is to use the simple potential function as a starting point for the derivation of supplementary relations between force constant and bond length or dissociation energy and bond length which are valid under certain specified conditions such as constant n. We have worked out two such relations and they appear applicable to any collection of molecules in their ground states which have constant n values.

The success of the potential function relation described here in predicting bond dissociation energies justifies its use in constructing potential curves showing the variation of potential energy with internuclear distance.

Another possible application is the construction of potential energy surfaces and calculation of activation energies for chemical reactions. Other applications include calculation of other heats of sublimation and atomization, calculation of molecular ionization potential, prediction of fluorescent properties, etc.

Conclusions

The successful application of the derived relation between potential energy and internuclear distance in the prediction and correlation of bond dissociation energies in polyatomic molecules indicates that potential curves for bonds in polyatomic molecules have a universal form to which the function (1) is a reasonable approximation. The derivation of (1) from a quantum mechanical model gives further justification for its use since polyelectronic systems can be handled in such a way that the essential features associated with bond formation can be described in terms of a one dimensional equation.

Although the potential function appears applicable to a number of molecules having polar properties, there are indications that it should be modified for strongly polar molecules such as HF, CH_3F and NaCl.

For adjacent multiple bonds the calculated dissociation energies agree better with thermochemical bond energies rather than experimental dissociation energies.

Its application to bonds which involve atoms of the transition series or rare earth series of metals has not been fully investigated.

If one wishes to use relation (6) to predict bond energies, simple valence force bond stretching constants should be used if available.

The use of the simple potential in predicting or correlating bond anharmonicity constants of polyatomic molecules has not been fully investigated. There is some indication that this may be a rather limited application.

Although the proposed function has a number of limitations, it is surprising that such a simple function can correlate and predict successfully such

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a large number of bond properties for polyatomic molecules. With due consideration to its limitations, its use as a tool for elucidating other problems seems justified.

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COLLEGE PARK, MD.

[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORY, THE OHIO STATE UNIVERSITY]

The Properties and Infrared Absorption Spectra of Complexes of Cobalt(III) with Pentadentate Ethylenediaminetetraacetic Acid and Hydroxyethylethylenediaminetriacetic acid

BY MELVIN L. MORRIS AND DARYLE H. BUSCH

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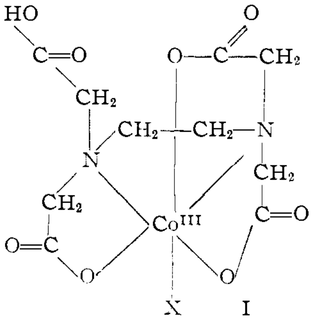
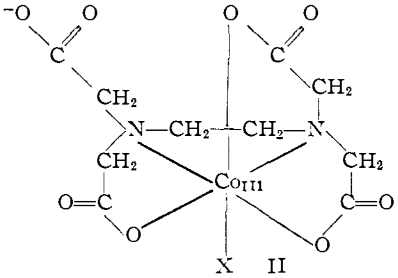
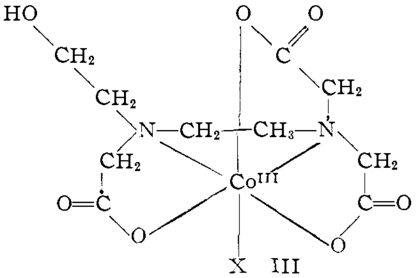
A series of complex compounds containing pentadentate ethylenediaminetetraacetic acid and pentadentate hydroxyethylethylenediaminetriacetic acid have been prepared and characterized. These compounds have the general formulas Na[Co(HY)X] and Na[Co(YOH)X], respectively, where Y represents the tetranegative anion of the first-named ligand, YOH represents the trinegative anion of the second ligand, and X is Cl^-, Br^- or NO_2^-. In addition to the acid salts of the complexes of ethylenediaminetetraacetic acid, the neutral salts, $Na_2[Co(Y)X]$, have been prepared. The infrared spectra of the complexes have been measured and interpreted in considerable detail. The structures of the complexes as inferred from their chemistries have been found to be compatible with the spectral data. It has also been shown that the study of infrared spectra should generally make possible the identification of complexed carboxyl groups and carboxylic acid groups in the presence of each other, while the distinction between complexed carboxyl groups and free carboxylate ions may be definitive only when the metal ion has a great tendency to form covalent bonds.

Cobalt(III) complexes of pentadentate ethylenediaminetetraacetic acid were first prepared by Schwarzenbach.[1] He reported a number of compounds of the general formula $M^I[Co(HY)X]$, where M^I is an alkali metal ion, Y is the tetranegative anion of ethylenediaminetetraacetic acid, and X is Br^- or NO_2^-. The conclusion that the polyfunctional ligand is pentadentate in these compounds was based on chemical studies. His conclusion was substantiated by the study of the C=O stretching vibrations in the infrared spectra of the compounds by Busch and Bailar.[2] The structure of this type of anion is shown below (I).


I

The corresponding compound in which the monodentate group is chloride ion has now been prepared, and, in addition, the "neutral" salts (structure II), $Na_2[Co(Y)X]$, have been prepared for the same series of monodentate groups X. A third related series of compounds involving hydroxyethylethylenediaminetriacetic acid also has been prepared. These may be represented by the general formula Na[Co(YOH)X], where YOH is the trinegative anion of hydroxyethylethylenediaminetriacetic acid and the remaining symbols have the same meaning as given above (structure III).


II


III

In structures I, II and III, the two nitrogen atoms and three carboxyl groups are coördinated to the cobalt(III) ion and the sixth functional group of the hexafunctional organic molecule is free. The only variation indicated by these three structures is in the nature of the unattached group.

In recent years, infrared spectroscopy has received considerable attention as a tool in the determination of the structures of complex inorganic compounds. Because of experimental difficulties, the application has been restricted, for the most part, to the study of organic functional groups and the effect which complex formation has on these groups. The carboxyl group has been the subject of several studies of this kind. The first work along this line was carried out by Douville, Duval and Lecompte[3] on the oxalato complexes of several

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