chemiluminescence correlated with $NDPO_2$ concentrations (Figure 3). It is important to note that the light emission by the $NDPO_2$ through the 634- and 703-nm filters is 53% of the total photoemission. Further $^{1}O_2$ characterization was performed by monitoring the effect of EAS and sodium azide in the monomol emission (Figure 4).

4.2. DABCO Effects. As mentioned above, an increase of $^{1}O_2$ dimol emission by DABCO has been described previously,[21,23,24] but the reason for this enhancement is unknown; it was suggested to be due to a change in the localized concentration of $^{1}O_2$ in solution or in the rate or extent of nucleation of oxygen bubbles.[23] The favoring of the emission due to a simultaneous transition involving a pair of $^{1}O_2$ molecules (dimol) should be accompanied by a decrease in the unimolecular decay (monomol). A decrease in monomol emission by DABCO has been described by Ogilby and Foote.[30] As can be seen in Figure 6, with $NDPO_2$ (Figure 6A) or hypochlorite/H_2O_2 (Figure 6B) as a source of $^{1}O_2$, the relationship between dimol and monomol emission is drastically affected by the presence of DABCO, as would be expected. A concentration of about 50 mM of DABCO is required to quench half of the singlet oxygen present in solution.[31] This value is similar to that which produces half of the loss of the monomol emission, as shown in Figure 6.

Kanofsky[32] reported that DABCO increases the rate of $^{1}O_2$ production in the reaction of H_2O_2 with OCl^- and attributed this catalysis as responsible for the enhancement of $^{1}O_2$ dimol emission described by Deneke and Krinsky.[21,23] As mentioned above, in our experiments DABCO had no effect on the yield in $EASO_2$ with $NDPO_2$ or hypochlorite/H_2O_2 as the $^{1}O_2$ source, and it did not change the decomposition kinetics of $NDPO_2$ (Figure 5A). DABCO increased the dimol signal (Figure 5C). DABCO has been described as being unreactive toward $^{1}O_2$ due to its effect in preventing or retarding the oxidation of known reactive acceptors of $^{1}O_2$.[33] Further studies on the reactivity of DABCO with $^{1}O_2$ using photooxidation with Rose bengal are in progress (Di Mascio, P.; Sies, H., in preparation).

4.3. Calibration of Monomol and Dimol Emission Using $^{1}O_2$ Yield of $NDPO_2$ Thermodissociation. The first derivative of the time course of $NDPO_2$ thermodissociation (Figure 5A) reveals a peak at 6 min at a rate of 75 μM NDP produced/min (not shown). This corresponds to an $^{1}O_2$ production rate of 38 μM/min, calculated with the $^{1}O_2$ yield of 50%. The signals in monomol and dimol emission (Figure 5B,C) give a calibration of 25 μM $^{1}O_2$ min^{-1} mV^{-1} in the monomol reaction and 38 μM $^{1}O_2$ min^{-1} (200 counts)$^{-1}$ s^{-1} at 703 nm in the dimol reaction (uncorrected for filter characteristics). Expressed alternatively, 10 μM $^{1}O_2$/min corresponds to 0.4 mV in the germanium-diode signal (monomol) and to 14 counts s^{-1} in the 703-nm photoemission (dimol), taking into account the second power concentration dependence. This type of calibration can be carried out with different types of geometry and should be used for standardization.

Acknowledgment. We wish to thank Drs. Marisa H. G. Medeiros and Heribert Wefers for stimulating discussions. We also thanks Dr. H. Haddad, Department of Chemistry, Düsseldorf, for ^{1}H NMR and IR spectroscopy analysis. This work was supported by Deutsche Forschungsgemeinschaft, National Foundation for Cancer Research, and Fonds der Chemischen Industrie.

---

(30) Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 3423-3430.

(31) Foote, C. S. In *Biochemical and Clinical Aspects of Oxygen*; Caughey, W. S., Ed.; Academic Press: New York, 1979; pp 613-625.

(32) Kanofsky, J. R. *Biochem. Biophys. Res. Commun.* **1986**, *134*, 777-782.

(33) Ouannes, C.; Wilson, T. *J. Am. Chem. Soc.* **1968**, *90*, 6527-6528.

The Correlation between Electronegativity Differences and Bond Energies

R. R. Reddy,* T. V. R. Rao, and R. Viswanath

Contribution from the Department of Physics, Sri Krishnadevaraya University, Anantapur 515 003, India.
Received February 2, 1988

Abstract: A new formula relating electronegativity differences and bond energies is proposed. The relation has the form $D_{AB} = \bar{D}_{AB} + 32.058\Delta\chi$, where $\bar{D}_{AB} = (D_{AA}D_{BB})^{1/2}$ and $\Delta\chi$ represents the Pauling electronegativity difference. D_{AA} and D_{BB} are the bond energies of homonuclear molecules of the corresponding atoms of heteronuclear molecules. This relation is shown to yield accurate bond energies for both ionic and covalent bonds. A comparison with Pauling's formula $D_{AB} = \bar{D}_{AB} + 30\Delta\chi^2$ and Matcha's relation are also given. The bond energies estimated with the new formula agree within 3% of Match's bond energies. The corresponding error associated with Pauling's equation is about 45%. The proposed equation is found to be superior to the Pauling equation. This study may also be helpful in constructing the electronegativity scale.

I. Introduction

The bond dissociation energy of diatomic molecules is of fundamental importance in the studies of thermochemistry and astrophysics.[1] Thermal, spectroscopic, and mass spectrometric are the most important experimental methods[2-5] used to evaluate bond energy values. Methods for estimating dissociation energies theoretically continue to be proposed by workers[6-12] anxious to improve on Pauling's well-known relation[13]

$$D_{AB} = \bar{D}_{AB} + 30\Delta\chi^2 \qquad (1)$$

---

(1) Gaydon, A. G. *Dissociation Energies*; Chapman and Hall: London, 1968.

(2) Herzberg, G. *Molecular spectra and Molecular structure*; Van Nostrand: New York, 1955.

(3) LeRoy, Robert L.; Bernstein, Richard B. *J. Mol. Spectrosc.* **1971**, *37*, 109.

(4) Hildenbrand, D. L.; Murad, E. *J. Chem. Phys.* **1969**, *51*, 807.

(5) Litzow, M. R.; Spalading, T. R. *Mass spectrometry of Inorganic and Organometallic Compounds*; American Elsevier: New York, 1973.

(6) Steele, D.; Lipincott, E. R.; Vanderslice, J. T. *Rev. Mod. Phys.* **1962**, *34*, 239.

(7) Somayajulu, G. R. *J. Chem. Phys.* **1963**, *34*, 1449.

(8) Preuss, H. *Theor. Chim. Acta* **1964**, *2*, 362.

(9) Ramani, K.; Ghodgaonkar, A. M. *J. Chem. Educ.* **1981**, *58*, 609.

(10) Reddy, R. R.; Reddy, A. S. R.; Krishna Reddy, V. *Theor. Chim. Acta* **1985**, *67*, 187.

(11) Reddy, R. R.; Reddy, A. S. R.; Krishna Reddy, V. *Can. J. Chem.* **1985**, *63*, 3174.

(12) Reddy, R. R.; Rao, T. V. R.; Reddy, A. S. R. *Proc. Indian Natl. Sci. Acad.* **1987**, *53A*, 506.

0002-7863/89/1511-2914$01.50/0

Table I. Computed Values of Dissociation Energies of Diatomic Molecules (kcal/mol)

molecule	D_{AB}[a]	D_{AB}[b]	D_{AB}[c]	D_{AB}[d]
LiF	136.2	126.9	300.7	126.2
LiCl	111.6	102.6	158.5	109.2
LiBr	99.8	91.8	131.3	96.8
LiI	84.6	78.2	97.6	79.5
NaF	122.9	124.6	313.6	121.9
NaCl	97.5	99.0	163.9	106.0
NaBr	86.2	88.9	136.4	94.8
NaI	77.7	76.1	101.6	78.7
KF	116.9	123.4	328.0	118.6
KCl	100.1	96.6	171.6	103.8
KBr	90.1	87.3	143.1	93.8
KI	77.3	74.9	107.2	78.9
RbF	115.3	122.6	327.2	117.7
RbCl	100.1	95.5	170.2	102.7
RbBr	89.9	86.3	142.1	92.8
RbI	76.1	74.1	106.3	78.0
CsF	118.7	125.4	346.3	118.2
CsCl	105.6	98.3	183.3	105.3
CsBr	96.1	89.1	154.0	96.0
CsI	82.2	76.9	116.4	81.9
CaF	132.0	126.5	300.4	125.8
CaCl	103.0	101.9	157.8	108.5
CaBr	96.0	91.4	130.9	96.4
CaI	78.0	77.8	97.3	79.1
MgF	123.0	123.6	269.0	126.2
MgCl	97.0	99.0	139.3	104.8
MgBr	81.0	88.8	114.3	91.5
MgI	63.0	74.8	83.9	73.1
SrF	132.0	123.3	297.1	122.6
SrCl	112.0	97.9	153.8	104.5
SrBr	97.0	87.8	127.3	92.8
SrI	80.0	74.7	94.1	76.0
BeF	151.0	123.5	230.9	129.5
BeCl	110.0	102.1	121.5	103.3
BeBr	89.0	89.8	98.8	88.0
BeI	69.0	74.6	72.5	68.5
av % deviation		5.5	45.0	

[a] Experimental data from ref 13, 15, and 16. [b] Computed with $D_{AB} = \bar{D}_{AB} + 32.058\Delta\chi$ with $\bar{D}_{AB} = (D_{AA}D_{BB})^{1/2}$. [c] Computed with Pauling's formula $D_{AB} = \bar{D}_{AB} + 30\Delta\chi^2$ with $\bar{D}_{AB} = (D_{AA}D_{BB})^{1/2}$. [d] Computed with Matcha's relation $D_{AB} = \bar{D}_{AB} + K(1 - \exp(-\alpha\Delta\chi^2)$, with $\alpha = 0.29$, $K = 103$, and $\Delta\chi$ = Pauling's electronegativity difference.

Here, $\bar{D}_{AB}$ is the geometric mean of the bond energies of the homonuclear molecules: $\bar{D}_{AB} = (D_{AA}D_{BB})^{1/2}$ and $\Delta\chi = \chi_A - \chi_B$ (Pauling electronegativity difference).

Noting the success of Matcha's relation[14]

$$D_{AB} = \bar{D}_{AB} + Ki \tag{2}$$

where K is an adjustable parameter and i is Pauling's "ionic character", defined as $i = 1 - \exp(-\Delta\chi^2/4)$, as well as our own adaptions of it, we now propose the simpler formula

$$D_{AB} = \bar{D}_{AB} + 32.058|\Delta\chi| \tag{3}$$

Table II. Computed Value of Dissociation Energies (kcal/mol)

molecule	D_{AB}[a]	D_{AB}[b]	D_{AB}[c]	D_{AB}[d]
NH	93.1	92.1	93.4	87.8
HF	134.6	122.6	145.0	170.0
HCl	103.1	106.5	103.7	102.0
HBr	87.5	91.7	87.1	84.0
HI	71.4	74.1	68.5	66.1
SiH	70.4	76.0	67.6	69.1
SiO	88.1	91.8	91.5	124.1
SiC	69.3	81.7	75.2	74.0
OH	110.6	113.6	114.7	117.6
CH	98.3	105.8	98.9	97.8
CO	84.0	84.5	88.5	82.5
SH	81.1	85.6	83.2	77.6
CF	105.3	103.2	102.2	122.9
AsCl	68.9	74.8	69.1	72.8
AsBr	56.5	63.8	54.8	57.3

[a] Experimental data from ref 13, 15, and 16. [b] Computed with $D_{AB} = \bar{D}_{AB} + 32.058\Delta\chi$ with $\bar{D}_{AB} = (D_{AA}D_{BB})^{1/2}$. [c] Data from ref 14. [d] Computed with Pauling's formula $D_{AB} = \bar{D}_{AB} + 30\Delta\chi^2$ with $\bar{D}_{AB} = (D_{AA}D_{BB})^{1/2}$.

II. Results and Discussion

Estimated bond energies from the eq 1–3 are presented in Tables I and II. Bond energies obtained with our formula (eq 3) are in excellent agreement with the experimental values.[15,16] The average percentage deviation in Table I indicates that estimates obtained with Pauling's equation are considerably differ from the experimental values. By utilizing Pauling's electronegativities in Matcha's relation, the bond energies are estimated and are presented in both Tables I and II for comparison. As seen from the results it is concluded that Matcha's relation still holds its accuracy. But, our relation is simple and compares with Pauling's and Matcha's relations. Our results coincide better with Match's predicted bond energies within the error of 3%. In the case of BeF and SiC, the estimated bond energies differ considerably. Earlier literature[11] values coincide with the present estimated bond energy value of BeF. It is concluded from the above that the experimental value may be in error. The equation proposed in the present paper is found to be comparatively superior to Pauling relation for the ionic bonds and this study may also be helpful in constructing the electronegativity table.

---

(13) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, 1960.

(14) Matcha, R. L. *J. Am. Chem. Soc.* **1983**, *105*, 4859.

(15) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979; Vol. IV.

(16) Huheey, J. E. *Inorganic Chemistry*, 2nd ed.; Harper International: New York, 1978.