Rate constants for ammonia loss in good agreement with those reported by Al-Shatti et al.[2] were obtained, but overall rates for fluoride loss about one-third of those reported were observed (Table I). For the three acid concentrations accessible in ClO_4^- medium, linear regression leads to $k_{F^-} = (8.1 \times 10^{-6})[H^+] + 4.4 \times 10^{-7}\ s^{-1}$. This rate constant for the acid-catalyzed path is over 3 times greater than, and the acid-independent rate constant about one-fifth of, the values reported earlier by Al-Shatti et al. Since our measurements were directly of fluoride released, while Al-Shatti et al. relied on the absorbance change at an isosbestic point of $[Cr(NH_3)_5H_2O]^{2+}$ and $[Cr(NH_3)_4H_2OF]^{2+}$, we believe our values for k_{F^-} to be more reliable. We noted also that the ammonia loss rate constants were a factor of 2 lower for aquation in hydrochloric acid media. The slight pH dependence of the ammonia rate constant was outside our experimental uncertainty.

The focus of this note, however, is the isomeric nature of the ammonia aquation product, shown in Table I to be 25% trans and 75% cis, independent (as might be expected) of H^+ concentration. Since it has been shown consistently that chromium(III) aquations are stereoretentive (although this is not necessarily true for solutions in ammonia[8] and aprotic[9] solvents), we take this product distribution to reliably reflect the relative rates of loss of the ammonias cis and trans to fluoride.

In interpreting these results, it is necessary to remember the statistical factor of 4 favoring loss of cis ammonia from $[Cr(NH_3)_5Y]^{2+}$, where both cis and trans ammonias have equal individual aquation labilities. With recognition of this, there is no cis-labilizing influence of fluoride in this complex. Indeed the slight imbalance is in favor of trans since the "single ligand" rate constants calculated from our data are $k_{trans} = 1.7 \times 10^{-6}\ s^{-1}$ and $k_{cis} = 1.3 \times 10^{-6}\ s^{-1}$.

It follows that there is no support in this data for the suggestion that fluoride may exert a cis-labilizing influence by the proposed mechanism of π donation from ligand to metal, even though both "single ligand" constants are slightly larger than the "single ligand" rate constant[10] for $[Cr(NH_3)_6]^{3+}$ of $8.1 \times 10^{-7}\ s^{-1}$.

The observation of trans labilization rather than cis is consistent with an earlier study[11] of *cis*-$[Cr(NH_3)_4F_2]^+$, where it was found that the ammonia ligands located trans and cis to fluoride were more labile than those cis to two fluorides by a factor of about 4 (rather uncertain due to resin-catalyzed decomposition). The observed overall rate constant at 50 °C was $8.4 \times 10^{-6}\ s^{-1}$, giving "single ligand" rate constants of 3×10^{-6} and $8 \times 10^{-7}\ s^{-1}$, respectively.

These findings bring into focus the difficulties associated with establishing genuine cis labilization in an ML_5X system. One obtains 80% cis product in the situation of stereoretentive loss of equally labile cis and trans L ligands; very careful cis/trans product analysis is demanded to establish either that cis > 80% or that trans < 20%. In one study[12] it was shown that the relevant product was more than 93% cis, clearly establishing the case for cis labilization, but not all authors have so carefully specified the isomeric purity of their products, and none appear to have explicitly recognized the statistical factor of 4.

Acknowledgment. The authors thank the NSERC and the University of Victoria for financial support.

Registry No. $[Cr(NH_3)_5F]^{2+}$, 19443-25-5.

---

[8] A. D. Kirk and T. L. Kelly, *Inorg. Chem.*, **13**, 1613 (1974).

[9] D. A. Palmer and D. W. Watts, *Aust. J. Chem.*, **21**, 2895 (1968).

[10] J. Bjerrum and C. G. Lamm, *Acta Chem. Scand.*, **9**, 216 (1955).

[11] A. D. Kirk and L. A. Frederick, *Inorg. Chem.*, **20**, 60 (1981).

[12] G. Guastalla and T. W. Swaddle, *Can. J. Chem.*, **52**, 527 (1974).

Contribution from the Department of Chemistry,
Arizona State University, Tempe, Arizona 85287

Bond Energies in Solid Oxides

M. O'Keeffe* and J. A. Stuart

Received May 3, 1982

It has been long established that bond energies in a large class of molecules can, to a good first approximation, be considered constant. The energy of atomization of a molecule can thus be considered as the sum of the energies required to break the component bonds. In this procedure one of course uses different bond energies for single, double, etc. bonds. In solids, however, the concept of bond order is more usefully replaced by that of *bond strength*. In a symmetrical environment the bond strength is simply the valence divided by the number of bonds. (Here, and throughout, "valence" is used in the sense of the absolute value of the formal oxidation state of an atom—for the main-group atoms in the compounds considered here, this is just the group number.) Thus, in MgO with octahedral coordination of the atoms the strength of the Mg–O bond is $^1/_3$; in Al_2O_3 with octahedral coordination of Al by O and tetrahedral coordination of O by Al the strength of the Al–O bond is $^1/_2$. For less symmetrical environments, bond strengths can be assigned on the basis of bond-strength–bond-length correlations.[1] A generalization of Pauling's electrostatic valence rule is that, for each atom in a solid, the sum of all the bond strengths is equal to the valence. In a metal oxide, in the absence of metal–metal bonding, the sum of all the bond strengths is just twice the number of oxygen atoms. The range of bond strengths encountered in solid oxides is from $^1/_{12}$ (i.e., for a 12-coordinated K atom) to $^7/_4$ (in perchlorates) with often a wide range, perhaps a factor of 3, for a given atom. It is not therefore practical to assign bond energies in solids in the same way as is done for molecules, many of which contain only bonds of integral order.

In this work we have investigated whether the energy of atomization of solid oxides can be divided into components, not according to the number of bonds but according to the contribution of each metal atom to the total bond strength. Thus, it was investigated whether Mg, for example, contributes the same amount per equivalent to the energy of atomization in $MgAl_2O_4$ (in which it is in tetrahedral coordination) as it does to that of Mg_2SiO_4 (in which it is in octahedral coordination). This was found indeed to be the case of high accuracy. The results should be of considerable interest to those interested in the theory of bonding in oxides and related solids.

Data Analysis

The starting point for the analysis was the heats of formation of solid oxides at 298 K. These were taken first from the compilation of Robie, Hemingway, and Fisher[2] and, for compounds not listed there, from Kubaschewski, Evans, and Alcock.[3] Enthalpies of atomization were then calculated by using enthalpies of atomization of the elements taken from Stull and Prophet.[4] Data for all compounds of 15 main-group elements (those listed in Table I) and Fe(II) were included. For reasons explained below, the data for binary compounds were considered separately. In all, there were data for 16 binary and 95 ternary, etc. oxides. The compounds ranged

---

[1] I. D. Brown and R. D. Shannon, *Acta Crystallogr., Sect. A*, **A29**, 266 (1973).

[2] R. A. Robie, B. S. Hemingway, and J. R. Fisher, *Geol. Surv. Bull.*, (*U.S.*), **No. 1452** (1978).

[3] O. Kubaschewski, E. Ll. Evans, and C. B. Alcock, "Metallurgical Thermochemistry", 4th ed., Pergamon Press, Oxford, 1967.

[4] D. R. Stull and H. Prophet, *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*), **NSRDS-NBS 37** (1971).

0020-1669/83/1322-0177$01.50/0

Table I. Equivalent Bond Enthalpies (kJ mol^{-1}) in Oxides

element	N^a	h^b	h_0	$h - h_0$
H	30	487 (3)	486	1
Li	6	628 (7)	585	43
Be	3	597 (7)	593	4
B	5	535 (4)	523	12
C	14	434 (3)	414	20
Na	13	523 (5)	440	83
Mg	20	506 (5)	499	7
Al	36	511 (2)	513	-2
Si	46	473 (2)	466	7
P	4	382 (4)	341	41
S	10	292 (3)	237	52
K	9	514 (7)	396	118
Ca	29	558 (4)	532	26
Fe(II)	5	464 (7)	466	-2
Sr	4	554 (7)	504	50
Ba	4	553 (7)	491	62

[a] Number of compounds containing that element. [b] Standard deviations are in parentheses.

from those with simple stoichiometry such as KOH and $LiAlO_2$ to more complex oxides such as $Mg_2Al_4Si_5O_{18}$ and $Ca_5(PO_4)_3OH$.

The formula per equivalent of an oxide of elements A(1), A(2), ... may be written $A(1)_{\nu_1}, A(2)_{\nu_2}, ..., O_{1/2}$. The stoichiometric coefficients and corresponding valences, z_i, are related by

$$\sum z_i \nu_i = 1 \qquad (1)$$

The process of atomization may be written

$$A(1)_{\nu_1}, A(2)_{\nu_2}, ..., O_{1/2}(s) \rightarrow \sum(\nu_i z_i)[(1/z_i)(A(i)(g)) + \tfrac{1}{2}O(g)] \qquad (2)$$

Thus, for $MgAl_2O_4(s)$

$$Mg_{1/8}Al_{1/4}O_{1/2}(s) \rightarrow \tfrac{1}{4}[\tfrac{1}{2}Mg(g) + \tfrac{1}{2}O(g)] + \tfrac{3}{4}[\tfrac{1}{3}Al(g) + \tfrac{1}{2}O(g)]$$

The enthalpy change for this reaction is the equivalent heat of atomization, ΔH_a. If each element contributes a constant amount per equivalent, h_i, to ΔH_a, then

$$\Delta H_a = \sum \nu_i z_i h_i \qquad (3)$$

For solid compounds, h_i is equivalent to the single-bond enthalpy in molecules. It is conveniently termed the *equivalent bond enthalpy* and is equal to the bond enthalpy per unit bond strength.

A least-squares fit of the data to eq 3 gave the equivalent bond enthalpies recorded in Table I. The squared multiple correlation was >0.99, indicating that the experimental data are extremely well described by eq 3 with constant values of h_i. The predictive value of eq 3 was further investigated by estimating each of the 95 heats of atomization in turn by using the data for the other 94 cases to determine the h_i. The average magnitude of the deviation from the experimental value was 3.9 kJ mol^{-1}, which is to be compared to a mean experimental value of 484 kJ mol^{-1}. No account in the analysis has been taken of experimental uncertainties (all cases were assigned equal weight), but it might be noted that the experimental errors are typically of the order of several kJ mol^{-1}.

As mentioned above, data for the binary oxides (gases in the cases of H_2O, CO_2, and SO_3) were not included in the analysis. However, from them we can calculate an equivalent heat of atomization for the binary compounds, h_0. These are also listed in Table I.

Discussion

A striking feature of the results is that, excepting data for C, P, and S, the equivalent bond enthalpy for different atoms varies over only a small range. This implies that, for a given bond strength, bonds to oxygen have approximately equal energy. It is interesting in this connection that it is observed[1] that, for a given row of the periodic table, bonds of equal strength (such as Mg in tetrahedral coordination and Al in octahedral coordination) have very nearly equal lengths.

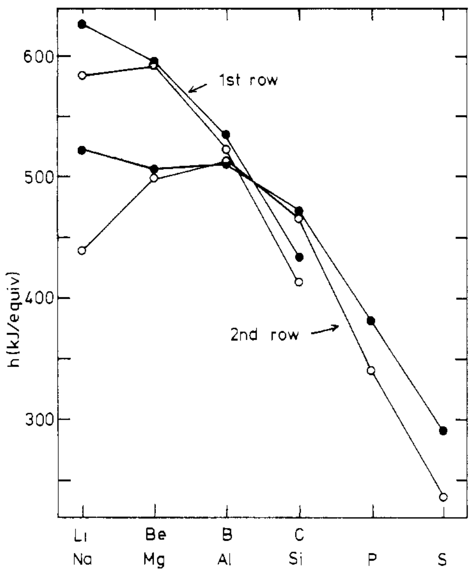

Figure 1. Equivalent bond enthalpies, h_0, for binary oxides (open circles) and for ternary etc. oxides (filled circles) as a function of periodic group number.

For elements such as the alkali and alkaline earths and, to a lesser extent, B and Al, which have variable coordination numbers in the compounds considered, the fact that a constant equivalent bond enthalpy can be assigned suggests that, for a given atom, bond strength is directly proportional to bond energy. Thus, the bond enthalpy of six Mg–O bonds of strength $^1/_3$ is the same as that for four Mg–O bonds of strength $^1/_2$.

For C, Si, P, and S the bond enthalpies refer to one kind of bond (in CO_3, SiO_4, PO_4, and SO_4, respectively), and it is not safe to generalize to bonds of different strengths. It is well-known that for bonds of high order (e.g., C—C, C=C, C≡C) the bond energy is only approximately proportional to bond strength. An extreme example is provided by $SiO_2(g)$ with Si–O bonds of strength 2. From the heat of formation a bond enthalpy of 633 kJ mol^{-1} is calculated: this is much less than twice the enthalpy of a single Si–O bond (Table I).

It is worth pointing out, however, that the Si–O bond enthalpy in molecules is close to that determined for crystals. From the data of O'Neal and Ring[5] for the contribution of the Si–O bond to heats of formation of molecules, an equivalent bond enthalpy of 455 kJ mol^{-1} is calculated. However, in the calculation of bond enthalpies in molecules a number of complex schemes for correcting for next-nearest etc. neighbors have been developed.[6,7] A more direct method of evaluating the enthalpy of the Si–O bond in molecules and crystals is to compare heats of atomization of assemblies each containing the same numbers of bonds. Thus compare (at 298 K)

$$Si(OCH_3)_4 \rightarrow Si + 4O + 4C + 12H$$

$$\Delta H = 8179 \text{ kJ mol}^{-1}$$

$$SiO_2(\text{quartz}) + 2(CH_3)_2O \rightarrow Si + 4O + 4C + 12H$$

$$\Delta H = 8202 \text{ kJ mol}^{-1}$$

---

(5) H. E. O'Neal and M. A. Ring, *Inorg. Chem.*, **5**, 435 (1966).
(6) S. W. Benson and J. H. Buss, *J. Chem. Phys.*, **29**, 546 (1958).
(7) G. J. Janz., *Q. Rev., Chem. Soc.*, **9**, 229 (1955).

In each case 4 Si–O, 4 C–O, and 12 C–H bonds are broken.

In Figure 1 the periodic trends of h_0 and h_i are displayed. The values of h increase in general with increasing difference in electronegativity from oxygen, as might be expected. For the alkali and, to a lesser extent, the alkaline earth elements, there is considerable difference between h and h_0 and the values of h_0 do not show such simple trends across the periodic table. What is striking is that the difference $h - h_0$ for a given group increases monotonically with atomic number. For Li, Na, and K this difference is 43, 83, and 118 kJ mol^{-1}, and for Be, Mg, Ca, Ba, and Sr it is 4, 7, 26, 50, and 62 kJ mol^{-1}, respectively. It is thought that the differences reflect the increasing importance of nonbonded repulsions between the metal atoms in cation-rich compounds such as especially the binary alkali-metal oxides in which each oxygen is coordinated by eight metal atoms. (Compare an oxide such as Na_2SiO_3 in which each oxygen is surrounded by four metal atoms.) Further discussion of this point is better deferred for another occasion.

In conclusion, the main result of this work might be emphasized. It is that the heat of atomization (bond energy) of complex oxides can be accurately represented as a sum of equivalent-bond enthalpies that apparently do not depend on crystal structure.

Acknowledgment. This work is part of a program of research into crystal chemistry supported by the National Science Foundation (Grant DMR-8119061).

Communications

Synthesis and Structural Characterization of Bis(tetraphenylphosphonium) Bis(diethyldithiocarbamato)bis(thiophenolato)tetrakis(μ_3-sulfido)tetraferrate(2II,2III), $(Ph_4P)_2[Fe_4S_4(SPh)_2(Et_2dtc)_2]$. A "Cubane" Type Cluster with Mixed Terminal Ligands and Two Different Modes of Ligation on the Fe_4S_4 Core

Sir:

Synthetic analogues for the 4Fe-4S centers in non-heme-iron proteins are well-known. The molecular and electronic structures and reactivities of various of these complexes have been studied extensively mainly by Holm, Ibers, and coworkers.[1] In the structurally characterized clusters of this type the iron atoms in the Fe_4S_4 cores are tetrahedrally coordinated by three of the triply bridging sulfide ions and a terminal RS^- (R = alkyl or aryl) or Cl^- ligand. Mixed terminal ligand clusters of the type $[Fe_4S_4(SR)_{4-n}X_n]^{2-}$ ($n = 1$–4; X = Cl^-, OAc^-) have been identified in solution and characterized by electronic spectroscopy, electrochemical studies, and ^1H NMR spectroscopy.[2] Interest in the latter type of complexes derives from the possible presence of such species in certain metalloproteins which contain 4Fe-4S centers with unusual Mössbauer spectra and electronic spin ground states. In the oxidized 4Fe-4S "P clusters" of nitrogenase, which show Mössbauer spectra consistent with two distinct iron sites and an uncommon electronic-spin ground state ($S \geq {}^3/_2$),[3] significant differences in the ligation of the Fe_4S_4 cores may account for the unique spectral properties. It has been suggested[3] that such differences in ligation could include expansion to five-coordination for the iron atoms or replacement of thiolate terminal ligands by other nucleophiles.

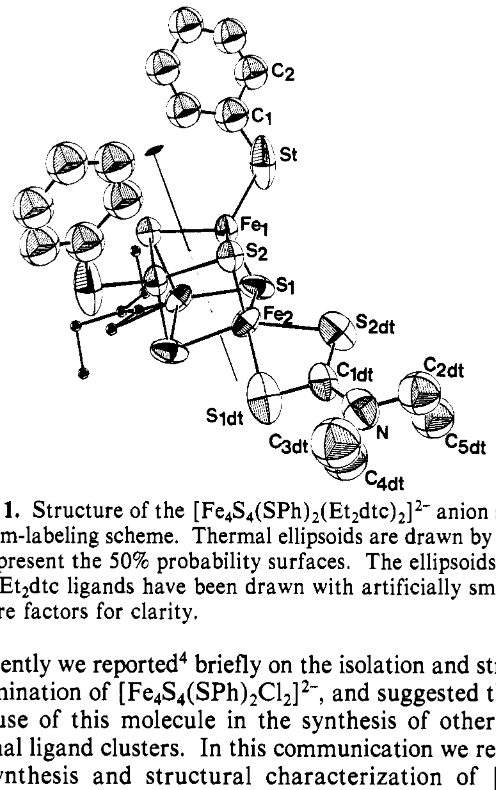

Figure 1. Structure of the $[Fe_4S_4(SPh)_2(Et_2dtc)_2]^{2-}$ anion showing the atom-labeling scheme. Thermal ellipsoids are drawn by ORTEP[18] and represent the 50% probability surfaces. The ellipsoids for one of the Et_2dtc ligands have been drawn with artificially small temperature factors for clarity.

Recently we reported[4] briefly on the isolation and structure determination of $[Fe_4S_4(SPh)_2Cl_2]^{2-}$, and suggested the possible use of this molecule in the synthesis of other mixed terminal ligand clusters. In this communication we report on the synthesis and structural characterization of $[Fe_4S_4(SPh)_2(Et_2dtc)_2]^{2-}$ (I), a new mixed terminal ligand cluster that shows differences in ligation for the iron atoms in the Fe_4S_4 core.[5]

The reaction of $(Ph_4P)_2[Fe_4S_4(SPh)_2Cl_2]$ with sodium diethyldithiocarbamate, $NaEt_2dtc$, in acetonitrile at ambient temperature, in a 1:2 molar ratio, proceeds readily. Following filtration of the reaction mixture and addition of ether to incipient crystallization, black crystals of I form and are isolated in ~90% yield. Anal. Calcd for $Fe_4S_{10}P_2C_{70}N_2H_{70}$ (M_r = 1.544): Fe, 14.51; S, 20.73; C, 54.42; N, 1.81; H, 4.53. Found: Fe, 14.68; S, 20.03; C, 55.37; N, 1.88; H, 4.72. The synthesis of I (in ~80% yield) can be accomplished also by

---

(1) (a) Holm, R. H. *Acc. Chem. Res.* **1977**, *10*, 427 and references therein. (b) Laskowski, E. J.; Frankel, R. B.; Gillum, W. O.; Papaefthymiou, G. C.; Renaud, J.; Ibers, J. A. Holm, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 5322. (c) Ibers, J. A.; Holm, R. H. *Science (Washington, D.C.)* **1980**, *209*, 223.

(2) (a) Johnson, R. W.; Holm, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 5338. (b) Que, L., Jr.; Bobrik, M. A.; Ibers, J. A.; Holm, R. H. *Ibid.* **1974**, *96*, 4168.

(3) (a) Münck, E.; Rhodes, H.; Orme-Johnson, W. H.; Davis, L. C.; Brill, W. J.; Shah, V. K. *Biochim. Biophys. Acta* **1975**, *400*, 32. (b) Zimmermann, R.; Münck, E.; Brill, W. J.; Shah, V. K.; Henzl, M. T.; Rawlings, J.; Orme-Johnson, W. H. *Ibid.* **1978**, *537*, 185. (c) Huynh, B. H.; Henzl, M. T.; Christner, J. A.; Zimmermann, R.; Orme-Johnson, W. H.; Münck, E. *Ibid.* **1980**, *623*, 124. (d) Münck, E. In "Mössbauer Spectroscopy and Its Chemical Applications"; Stevens, J. G., Shenoy, G. K., Eds.; American Chemical Society: Washington, DC, 1981; Adv. Chem. Ser. No. 194, p 305.

(4) Coucouvanis, D.; Kanatzidis, M.; Simhon, E.; Baenziger, N. C. *J. Am. Chem. Soc.* **1982**, *104*, 1874.

(5) The synthesis of the $[Bu_4N][Fe_4S_4(Et_2dtc)_4]$ and $Fe_4S_4(Et_2dtc)_4$ complexes has been accomplished recently. The magnetic and Mössbauer properties of these complexes have been investigated: Silverthorn, W. E.; Wells, F. V.; Wickman, H. H., submitted for publication in *Inorg. Chem.* Wickman, H. H., private communication.

0020-1669/83/1322-0179$01.50/0 © 1983 American Chemical Society