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Prediction and Correlation of the Enthalpies of Gas-Phase Ionic Reactions

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Received October 3, 1975 AIC50723L

In this article, an equation previously derived to predict the enthalpies of reactions of ionic acids and bases is tested. As predicted by theory, this new equation works better than the *E* and *C* equation for the large enthalpies associated with the interaction of ions but not as well for the smaller enthalpies associated with the interaction of neutral acids and bases. The *D* and *O* parameters obtained on the systems for combinations of ions are reasonable in terms of the derived relationship of these quantities in a molecular orbital model and our qualitative notions about the relative importance of ionic and covalent bonding in the resulting compounds. Parameters are also reported which enable one to predict the enthalpies associated with the combination of the corresponding atoms or radicals to produce the same compounds.

Introduction

There have been two reported[2,3] empirical attempts to fit enthalpies of reactions of ionic acids and bases to the *E* and *C* equation

$$-\Delta H = E_A E_B + C_A C_B \tag{1}$$

These attempts were not fully satisfactory in view of the lack of discernible trends in the values of the parameters in one case[2] and the need to exclude proton and hydride systems in the case[3] where reasonable constraints were imposed. Even with the proton excluded, a poor statistical *R* factor ratio resulted. A recent theoretical analysis of this problem,[4] in which a molecular orbital treatment led to an equation of the form of eq 1 for neutral adducts, has suggested that a more appropriate equation for use on the large enthalpies associated with ionic systems is one of the form

$$-\Delta H = [(D_A - D_B)^2 + O_A O_B]^{1/2} \tag{2}$$

The parameters *D* are empirically obtained but are related to the diagonal elements of the MO secular determinant, while the *O* parameters are similarly obtained and related to the off-diagonal elements. The A and B subscripts refer to acid and base which on the systems covered here are cations and anions, respectively.

In this article, we report the success we have had in correlating the enthalpies for a large number of reactions of ionic species with this equation.

Calculations

The empirical data fitting was carried out on an IBM 360/75 using the program previously described for enthalpies of formation of adducts of neutral acids and bases.[4]

We have had no way to evaluate critically much of the data used in this fit. Accordingly, a consistent set of bad experiments bearing on an ion for which there are limited data available could lead to incorrect parameters. Accordingly, Table II should be consulted when applications of the parameters are attempted.

Parameterization of the Data Set. In order to obtain a unique solution to the series of simultaneous equations which result when enthalpies are substituted into eq 2, we must fix at least four of our *D* and *O* numbers.[5] The selection of the ions which are fixed and the values which are assigned to these four parameters is arbitrary, but via this selection, we attempt to impose a meaningful model on the data. The consistency of the empirical parameters with the model one attempts to impose is the means of judging the success or failure of the model. The $O_A O_B$ term of eq 2 which contains the energy involved in the two-center interactions was equated in magnitude to covalency of the ionic–covalent model. We should emphasize that these are not rigorously equivalent and, with our parameterization, we may be mixing the true diagonal and off-diagonal terms. This approximation is necessary because of our inability accurately to calculate dissociation energies for four molecules with molecular orbital theory and to then divide the energy into the corresponding terms[4] of eq 2. Furthermore, most of our qualitative ideas about bonding in these molecules have been formulated in terms of the ionic–covalent model and our resulting parameters can be more meaningfully interpreted and tested in these terms. With the above ionic–covalent model definition of the $O_A O_B$ term, the $(D_A - D_B)$ term has two contributions to it. For the system MX, where M^+ is the acid and X^- the base, it contains the Coulombic energy associated with the attraction between the two ionic charges, as well as the energy gained or lost in the partial transfer of an electron to M^+ to give $M^{\delta+}$ and the partial electron release from X^- to give $X^{\delta-}$. Both of the above contributions to the $(D_A - D_B)^2$ term of MX are expected to be absent in the dissociation energy ΔH_D of a homonuclear diatomic molecule. Therefore, we can assume

$$\Delta H_D(X_2) = [O_{X^+} O_{X^-}]^{1/2}$$

and

$$\Delta H_D(M_2) = [O_{M^+} O_{M^-}]^{1/2}$$

Squaring and rearranging the above equations give

$$O_{X^+} = [\Delta H_D(X_2)]^2 / O_{X^-} \tag{3}$$

and

$$O_{M^-} = [\Delta H_D(M_2)]^2 / O_{M^+} \tag{4}$$

For a heteronuclear diatomic molecule, MX, we would expect the covalent energy to be the same regardless of whether the molecule had been formed from M^+ and X^- or M^- and X^+. Let us define ΔH_- and ΔH_+ as

$$\Delta H_- = \Delta H_D(MX) + I_X - \epsilon_M \tag{5}$$

$$\Delta H_+ = \Delta H_D(MX) + I_M - \epsilon_X \tag{6}$$

where I_X is the ionization energy of X and ϵ_X the electron affinity; I_M and ϵ_M are corresponding values for M.

In other words, ΔH_- represents the total enthalpy of forming the MX molecule from M^- and X^+ whereas ΔH_+ is the usual enthalpy of forming the MX molecule from M^+ and X^-. Equation 2 predicts

$$\Delta H_- = [(D_{X^+} - D_{M^-})^2 + O_{X^+} O_{M^-}]^{1/2} \tag{7}$$

$$\Delta H_+ = [(D_{M^+} - D_{X^-})^2 + O_{M^+} O_{X^-}]^{1/2} \tag{8}$$

However, if $O_{M^+} O_{X^-}$ is simply equated to $O_{X^+} O_{M^-}$, one would find that the covalent energy predicted by eq 7 is not equal to that from eq 8. [For example, in $(50^2 + 10)^{1/2}$ and $(20^2 + 10)^{1/2}$, the quantity 10 does not make the same contribution to the resulting number in each case.] We can circumvent this problem by squaring eq 7 and 8 and rearranging which lead to

$$1 = \frac{(D_{X^+} - D_{M^-})^2}{(\Delta H_-)^2} + \frac{O_{X^+}O_{M^-}}{(\Delta H_-)^2} \tag{9}$$

$$1 = \frac{(D_{M^+} - D_{X^-})^2}{(\Delta H_+)^2} + \frac{O_{M^+}O_{X^-}}{(\Delta H_+)^2} \tag{10}$$

If one examines eq 10, it will be seen that $O_{M^+}O_{X^-}/(\Delta H_+)^2$ is the fraction of the total squared enthalpy that is due to $O_{M^+}O_{X^-}$ and from eq 9 it is seen that $O_{X^+}O_{M^-}/(\Delta H_-)^2$ is the fraction of the total squared enthalpy that is due to $O_{X^+}O_{M^-}$. If we equate the fraction of the total squared enthalpy that is due to the *OO* term regardless of how the MX molecule was formed, we obtain

$$\frac{O_{M^+}O_{X^-}}{(\Delta H_+)^2} = \frac{O_{X^+}O_{M^-}}{(\Delta H_-)^2} \tag{11}$$

Equation 11 does not actually equate the covalent energies in eq 7 and 8. However, since the *OO* term is small compared to $(\Delta H_-)^2$ or $(\Delta H_+)^2$, the error introduced by using eq 11 is much smaller than that from simply equating $O_{M^+}O_{X^-}$ to $O_{M^-}O_{X^+}$. Therefore, this model closely approximates the ionic–covalent model.

Multiplying eq 3 by eq 4 yields

$$O_{X^+}O_{M^-} = \frac{[\Delta H_D(M_2)]^2\,[\Delta H_D(X_2)]^2}{O_{M^+}O_{X^-}} \tag{12}$$

Substituting eq 12 into eq 11 gives

$$\frac{O_{M^+}O_{X^-}}{(\Delta H_+)^2} = \frac{[\Delta H_D(M_2)]^2\,[\Delta H_D(X_2)]^2}{O_{M^+}O_{X^-}(\Delta H_-)^2} \tag{13}$$

Solving for $O_{M^+}O_{X^-}$

$$O_{M^+}O_{X^-} = [\Delta H_D(M_2)]\,[\Delta H_D(X_2)](\Delta H_+)/\Delta H_- \tag{14}$$

We will also use the square root of eq 14, namely

$$[O_{M^+}O_{X^-}]^{1/2} = \left[\frac{[\Delta H_D(X_2)]\,[\Delta H_D(M_2)](\Delta H_+)}{\Delta H_-}\right]^{1/2} \tag{14a}$$

Equation 14a is similar to the geometric mean rule given previously,[3] except that the dissociation energies are multiplied by the ratio $(\Delta H_+/\Delta H_-)^{1/2}$. This extra factor appears because we have equated the relative contributions of the covalent energies rather than their absolute values.

Equation 14 was used to set the standards for the fit of enthalpies of reactions of monovalent and divalent (vide infra) acids and bases using eq 2 as follows. We chose to fix the *O* numbers for CH_3^+ and Br^- because we had a large number of fairly covalent molecules with these species in our fit. For CH_3Br, the following data were used (taken from ref 3 and references therein): $\Delta H_+ = 218.0$ kcal/mol, $\Delta H_- = 316.4$ kcal/mol, $\Delta H_D(Br_2) = 46.1$ kcal/mol, $\Delta H_D(CH_3–CH_3) = 85.8$ kcal/mol. From these data, $O_{CH_3^+}O_{Br^-} = 2725$. We will arbitrarily set $O_{CH_3^+} = 50.00$. This leaves O_{Br^-} equal to $2725/50 = 54.50$.

We choose to fix the *D* numbers for K^+ and Cl^- because there were many ionic species in our fit involving these ions. Using eq 14 for KBr and for CH_3Cl, we were able to obtain the $O_{M^+}O_{X^-}$ product as we did for CH_3Br above. With $O_{CH_3^+}$ set at 50.00, O_{Cl^-} can then be calculated. Similarly, O_{K^+} can be calculated from the $O_{K^+}O_{Br^-}$ product because O_{Br^-} is known. The values obtained for O_{K^+} and O_{Cl^-} in this way were not fixed in the final fit but were merely used to determine the D_{K^+} and D_{Cl^-} values which were fixed. The $O_{K^+}O_{Cl^-}$ product determined by the above procedure was 222. A check on this product obtained from eq 14 directly gave a value of 225 leading to a rounded average value of 224.

The total enthalpy of formation of KCl from K^+ and Cl^- is 117 kcal/mol. From the square of eq 2, we obtain

$$117^2 = (D_{K^+} - D_{Cl^-})^2 + 224$$

which can be solved to produce a value of $(D_{K^+} - D_{Cl^-})$ equal to 116.0. Setting $D_{K^+} = 100.00$, leaves $D_{Cl^-} = -16.00$.

In summary, the following values were fixed in order to obtain a unique enthalpy data fit in the final computer analysis of the reported enthalpies: $O_{Me^+} = 50.00$, $O_{Br^-} = 54.50$, $D_{K^+} = 100.00$, $D_{Cl^-} = -16.00$.

Incorporation of Divalent Ions. In all earlier applications of the *E* and *C* equation, we have dealt with only 1:1 adducts, i.e., equations of the general form of eq 2 and 3. We have extended our work with eq 2 to cover 2:1 adducts of the form

$$M^{2+}(g) + 2X^-(g) \rightarrow MX_2(g) \tag{15}$$

and

$$2M^+(g) + X^{2-}(g) \rightarrow M_2X(g) \tag{16}$$

as well as 1:1 adducts of divalent ions

$$M^{2+}(g) + X^{2-}(g) \rightarrow MX(g) \tag{17}$$

Since enthalpy is a state function, we can break up the enthalpy for the reaction represented by eq 15, for example, into two 1:1 type interactions of the form

$$M^{2+} + X^- \xrightarrow{\Delta H_1} MX^+$$

$$MX^+ + X^- \xrightarrow{\Delta H_2} MX_2$$

If the parameters for X^- were known from systems for univalent cations and anions, such an approach would require two parameters for M^{2+} and two more for MX^+ in order to calculate the two 1:1 enthalpies and the total enthalpy. Enthalpy data for MX^+ reacting with several anions would be needed to evaluate the parameters for MX^+. The sparsity of thermodynamic data available on MX^+ species combining with other anions makes this approach impossible. Instead, we averaged the enthalpies for the two steps $((\Delta H_1 + \Delta H_2)/2$ or $\Delta H_{total}/2)$ and attempted to fit this quantity. Accordingly, the parameters reported calculated half the total enthalpy of adduct formation for 2:1 adducts. The resultant *D* and *O* numbers will predict enthalpies for reactions corresponding to univalent cations combining with univalent anions and half the total enthalpy of reactions corresponding to eq 15 and 16.

The systems described by eq 17 are quite uncertain, as the quality of the data is often questionable. Furthermore, data which are fit to equations of the form of (1) or (2) are screened such that systems in which there are potentially large π-bonding or lone pair–lone pair repulsion contributions to the enthalpy are avoided for these should require additional terms in the enthalpy equations. For the specific case of the oxide and sulfide ions, the adducts fall into two classes. In the 2:1 adducts of oxide and sulfide, these bases form two separate single bonds to the acids. The 1:1 adducts of oxide and sulfide (i.e., those involving divalent cations) form only one bond to the acid which may be a multiple bond. Two sets of parameters were used for oxide and sulfide in the data fit. The sets for the 1:1 adducts of oxide and sulfide resulted in a poor fit of these systems and are not reported in Table I. The reported parameters for O^{2-} and S^{2-} reproduce enthalpies of reactions of the form of eq 16.

Constraints Placed on Parameters. In trying to fit the enthalpies of both 1:1 and 2:1 reactions involving ionic acids and bases, it was found that the minimum in the series of simultaneous equations of the form of eq 2 was very broad. This is not surprising because, as was the case in the report of the fit of enthalpies of univalent ion reactions with eq 1,[4] there are not enough reversals in the order of donor or acceptor strength toward different acids or bases to define a sharp minimum. Therefore, as in our previous report,[4] it was necessary to impose several constraints on the fit. [In effect, rather than let the computer pick a meaningless minimum, we are going to impose contraints to guide it in selecting one that is consistent with the error in the data set.] The constraints were all of the form of eq 14a involving the O_A and O_B parameters. For symmetrical adducts (e.g., CH_3CH_3 or Cl_2), ΔH_+ must equal ΔH_-. Therefore

$$[O_{X^+}O_{X^-}]^{1/2} = \Delta H_D(X_2) \tag{18}$$

Six equations of the form of eq 18 and 125 equations of the form of eq 14a were added to the 256 equations of the form of eq 2 which were fit with the D and O parameters listed in Table I (vide infra). The adducts for which an equation of the form of eq 14a has been added are noted by an asterisk (*) in Table II. There were 41 acids and 18 bases included in the fit, each with two parameters, but four of the parameters were fixed. Therefore, there were 114 variables that were fit with the above equations. Constraints were placed on all of these variables except the parameters for Zr^{2+}, NO^+, O^{2-}, S^{2-}, Se^{2-}, Te^{2-}, OH^-, and NO_2^-. These parameters were not constrained because a suitable value for the dissociation energy of the corresponding symmetrical molecules could not be found. The parameters for these acids and bases are of use only in predicting enthalpies and cannot be compared to others that have been constrained. For most of the singly charged ions in the fit, the dissociation energies[6] were used in eq 14a. For those singly charged ions with lone pairs of electrons and small ionic radii (e.g., F^-), the dissociation energy of the symmetrical molecule cannot be used to obtain the covalent energy contribution in a molecule where the neighboring atom has no lone pairs. If we had a sharp minimum and a large data block for Cl^+, F^+, etc., it might be possible somehow to incorporate these effects into the parameters in the empirical fit. Without this, we are attempting to pick a reasonable minimum by adding constraints and must use discretion in so doing. For systems in which this is a potential complication and also for doubly charged ions, reported values for the homopolar bond energy, E_H,[7-9] were used in eq 18 instead of $\Delta H_D(X_2)$. (It should be noted that when there were widely differing values of E_H reported in the literature, we first selected Pauling's values, then Huheey's values, and then Sanderson's values.) The E_H value for Ba^{2+} was obtained by extrapolation of reported[7] values of E_H for the other alkaline earth ions. The values of E_H for the first-row transition metals were estimated as follows. It was assumed that all values would fall between the E_H value for Ca^{2+}, 25.0 kcal/mol, and that for Zn^{2+}, 33.5 kcal/mol (see ref 8). It was also assumed that E_H would follow the same trend as the first ionization potential. Therefore, eq 19 was used to estimate these energies for the first-row transition elements, M

$$E_H = 25.0 + \frac{I(M)}{I(Zn)}8.5 \tag{19}$$

where $I(M)$ is the first ionization potential of M. *In view of these approximations for the transition metal ions and other uncertainties in the data, we feel the parameters for these systems should be used only to predict enthalpies and used cautiously in parameter interpretation.*

In order to calculate ΔH for use in eq 14a, it is necessary to have a crude estimate (vide infra) of the electron affinities of the atoms (e.g., $Na + e^- \rightarrow Na^-$) whose ions (e.g., Na^+) are acids in the data set (see eq 5). Unfortunately, these electron affinities are not known very well for the atoms corresponding to singly charged ions and are not known at all for the atoms of most doubly charged ions. Accordingly, one can only guess at a value, but, fortunately, as we will show below, our final $[O_{M^+}O_{X^-}]^{1/2}$ term is not very sensitive to the values employed. The crude scheme used to estimate very crude values for these double electron affinities and the values employed are given as supplementary material to this paper.

The weight factor (see Table II or ref 4) used for the equations of the form of eq 14a was 3.00 if the dissociation energies and electron affinities were known. When any approximations or homopolar bond energies were used, these equations were given a weight factor of 4.00. For equations of the form of eq 18, the weight factor was 0.50 for the CH_3–CH_3, C_2H_5–C_2H_5, Cl–Cl, Br–Br, and I–I molecules. For the C_6H_5–C_6H_5 molecule, the weight factor was increased to 1.732 because of the possibility of carbon–carbon π bonding.

The single electron affinities for the corresponding atoms of singly charged positive ions (e.g., Na) were taken from ref 6 or 10, except that the values for Rb and Cs were taken as equal to that for K.

Results and Discussion

Data Fit. Fitting the available enthalpy data to eq 2 resulted in the best fit D and O parameters of the various cations and anions reported in Table I. The excellent fit of the experimental data to the values calculated using eq 2 and the parameters in Table I is reported in Table A-1 of the supplementary material.

As predicted by theory, eq 2 offers several advantages over eq 1 for ionic reactions. The most important one is that the overall fit of the data is better. The total squared weighted deviation from the experimental values for 101 molecules formed from singly charged ions was 153 as compared to 783 for 95 molecules using[3] eq 1. We mentioned earlier two deficiencies in the fit obtained using eq 1. First of all, a poor statistical R factor ratio between the unrestricted fit and the restricted fit was obtained. Second, systems involving the acid H^+ and the base H^- were so poorly fit by eq 1 that parameters were not reported for these ions. Equation 2 solves both of these problems. The R factor ratio between the completely unrestricted fit and the fit where 98 of the 114 parameters are constrained (by forcing the $O_{M^+}O_{X^-}$ parameters to fit eq 14a, we constrain the D parameters of eq 2 as well, since $-\Delta H$ is fixed) is 1.13. In this restricted fit, the number of degrees of freedom (the number of interactions minus the number of variable parameters) is 142. The R factor ratio obtained when eq 1 is used is 1.91 for a fit where 20 parameters are constrained and there are 36 degrees of freedom.[3] The value of the R factor allows one to reject the use of an ionic–covalent model imposed on eq 1 with 99% confidence (for ions) whereas this model imposed upon eq 2 cannot be rejected at any confidence level. It should be emphasized, however, that the fact that the ionic–covalent model cannot be rejected when applied to eq 2 does not prove that this model is correct. It should be noted, also, that the values of $R(b,n-p,\alpha)$ (see ref 13) are tabulated based on linear equations. *Therefore, the confidence with which one may reject a model cannot be stated with certainty.* However, one can say with certainty that the level of confidence of a rejection of the system based on the use of eq 1 for ions is much higher than that of eq 2.

In the fit reported here, the proton (twelve enthalpies) and the hydride ion (nine enthalpies) were included in the data set. All of the enthalpies involving these ions, except for H_2 and AgH, are predicted within 9 kcal/mol (about 3%). Equation 2 calculates a smaller enthalpy for H_2 than the experimental value by about 40 kcal/mol. Abnormalities associated with H_2 have been reported previously.[2,3] The direction and magnitude of the miss for H_2 is a function of the value of the dissociation energy of H_2 used in eq 14a for other molecules involving hydrogen, so we shall not speculate on a molecular explanation. A weight factor of 4.0 has been

Table I. *D* and *O* Parameters in Ions

Base	Conditional[a]	*D*	Marginal[a]	Conditional[a]	*O*	Marginal[a]	Ref[b]
			Base Parameters				
F^-	0.96	−42.6	1.28	0.14	94.47	0.16	
Cl^-	*c*	−16.0	*c*	0.07	63.57	0.09	
Br^-	0.84	−10.5	1.21	*c*	54.50	*c*	
I^-	0.83	−3.6	1.19	0.09	47.06	0.11	
O^{2-} (2:1)	5.33	−176.4	5.51	0.14	100.33	0.76	*e*
S^{2-} (2:1)	7.05	−135.0	7.18	0.14	62.06	0.15	*e*
Se^{2-}* [k]	5.68	−122.9[d]	18.4	254.6	9.77[d]	822.8	*e*
Te^{2-}*	6.97	−100.4[d]	33.7	270.1	21.51[d]	1306	*e*
OH^-*	1.75	−48.1	3.48	25.1	211.44	49.7	
CH_3^-	2.06	−58.6	2.40	0.26	152.65	0.45	*f*
$C_2H_5^-$	2.89	−54.6	3.27	6.81	159.35	6.93	*f*
CN^-	4.83	−30.1	4.92	0.11	136.48	0.15	*g*
NH_2^-	2.39	−75.9	2.71	0.22	97.76	0.24	*h*
$C_6H_5^-$	4.42	−39.9	4.75	0.28	150.92	0.28	
NO_2^-*	4.02	−33.8[d]	68.1	35.0	0.07[d]	589.9	*i*
H^-	1.76	−29.8	2.04	0.52	145.22	0.94	
			Acid Parameters				
H^+	1.56	311.6	2.01	0.05	81.95	0.09	
Li^+	2.14	132.6	2.29	0.11	9.14	0.11	
Na^+	2.03	112.6	2.22	0.06	5.86	0.06	
K^+	*c*	100.0	*c*	0.04	3.46	0.05	
Rb^+	2.29	95.6	2.43	0.11	2.65	0.11	
Cs^+	2.30	90.7	2.43	0.11	2.90	0.11	
Cu^+	4.37	160.1[d]	4.42	0.12	27.65[d]	0.13	
Ag^+	2.91	158.0[d]	3.05	0.06	18.87[d]	0.10	
Al^+	2.42	155.1	2.54	0.11	17.54	0.11	
In^+	2.31	132.6	2.44	0.11	8.68	0.11	
Tl^+	2.22	129.3	2.36	0.06	5.74	0.07	
CH_3^+	1.84	204.8	2.11	*c*	50.00	*c*	
$C_2H_5^+$	1.76	173.4	2.06	0.05	40.01	0.10	
n-$C_3H_7^+$	1.91	164.0	2.16	0.11	41.33	0.12	
$C_6H_5^+$	5.86	196.1	6.12	0.14	55.44	0.15	
NO^+*	8.26	140.0[d]	16.6	53.3	35.41[d]	101.0	
Cl^+	1.78	251.8[d]	1.82	3.10	52.73[d]	3.17	
Br^+	1.66	224.5	1.98	0.16	38.48	0.17	
I^+	1.39	196.5	1.66	0.12	25.73	0.13	
Be^{2+}	2.67	329.6	2.79	0.14	25.84	0.15	*j*
Mg^{2+}	2.90	253.7	3.00	0.14	17.75	0.15	*j*
Ca^{2+}	2.40	213.2	2.51	0.14	12.45	0.15	*j*
Sr^{2+}	2.40	199.9	2.51	0.14	9.13	0.15	*j*
Ba^{2+}	2.40	190.6	2.51	0.14	7.50	0.15	*j*
Sc^{2+}	4.36	234.5	4.49	0.14	16.85	0.15	*j*
Ti^{2+}	2.62	253.8	2.71	0.14	17.34	0.15	*j*
Zr^{2+}*	2.61	252.2[d]	12.43	21.5	74.68[d]	101.6	*j*
V^{2+}	2.90	262.5	2.97	0.14	17.53	0.15	*j*
Cr^{2+}	2.67	257.4	2.76	0.14	21.41	0.15	*j*
Mn^{2+}	2.54	255.7	2.64	0.14	17.11	0.15	*j*
Fe^{2+}	2.35	270.8	2.47	0.14	22.49	0.15	*j*
Co^{2+}	4.04	273.1	4.06	0.14	20.47	0.15	*j*
Ni^{2+}	3.30	283.0	3.38	0.14	19.73	0.15	*j*
Cu^{2+}	4.05	293.0	4.18	0.14	21.63	0.15	*j*
Zn^{2+}	2.04	281.4	2.28	0.14	22.44	0.15	*j*
Cd^{2+}	2.14	260.4	2.30	0.14	17.34	0.15	*j*
Hg^{2+}	4.65	294.5	5.08	0.14	6.87	0.15	*j*
Si^{2+}	3.78	295.9	3.94	0.22	24.03	0.22	*j*
Ge^{2+}	3.43	270.3	3.62	0.14	20.65	0.15	*j*
Sn^{2+}	2.73	241.8	2.85	0.14	18.97	0.15	*j*
Pb^{2+}	2.42	232.5	2.52	2.74	10.58	0.35	*j*

[a] The significance of these error limits is discussed in ref 5. [b] References used for electron affinities and ionization potentials of acids and bases, respectively. See ref 11 and 12 unless otherwise noted. [c] These parameters were fixed as standards. [d] These parameters are considered tentative because of sparce or poor data. [e] M. L. Huggins and Y. Sakamoto, *J. Phys. Soc. Jpn.*, **12**, 241 (1957). [f] F. M. Page, *Adv. Chem. Ser.*, No. **36**, 68 (1962). [g] J. Berkowitz, W. A. Chupka, and D. Gutman, *J. Chem. Phys.*, **55**, 2733 (1971). [h] J. Beauchamp, private communication. [i] J. Berkowitz, W. A. Chupka, and T. A. Walker, *J. Chem. Phys.*, 50, 1497 (1969). [j] R. C. Weast, Ed., "Handbook of Chemistry and Physics", 51st ed, Chemical Rubber Publishing Co., Cleveland, Ohio 1970. [k] Asterisks signify parameters which are not constrained.

employed for eq 14a for all hydrogen compounds that employ this constraint. The thermodynamic data for most of the systems involving Ag^+ are not known very well. This accounts for the moderate but reasonable misses in our attempts to fit the experimental enthalpies on molecules involving this ion including AgH. In general, most of the hydride and proton enthalpies are fit to within the experimental uncertainties. Thus, equation 2 is seen to be a greatly improved function for correlating and predicting enthalpies of reactions involving ionic species as was predicted from our theoretical analysis.

Interpretation of the Parameters. The parameters obtained in the data fit are very much dependent upon the constraints placed on the fit. Accordingly, the parameters do not contain as much independent information as in our neutral-molecule

E and *C* fit. However, the parameters do provide us with a quantification of the individual properties of the cations and anions in the context of the model and constraints put on the fit and they do have predictive power.

There are undoubtedly a large number of effects incorporated into the parameters in addition to those discussed in the derivation[4] of eq 2. For example, any changes in the bond angles of the methyl group in the various CH_3X compounds would be incorporated. The parameters must also contain information about the internuclear distance between the acid and base.

In fitting the experimental data empirically, only the difference in the *D* parameters is used so that an identical fit would be obtained if a constant were added to every D_{M^+} and every D_{X^-}. We define a unique set of parameters by our choice of standards as mentioned above. Since we chose our D_{M^+} standard as $D_{K^+} = 100.0$ and the ionization energy of potassium is 100.1, it is of interest to see if the D_{M^+} parameters for other ions are related to the ionization energy of the appropriate atom. This relationship is not expected to hold for all cases because the charge-transfer terms neglected in the derivation[4] of eq 2 should be incorporated in the parameters of ions that form covalent molecules. Thus, the deviation of the parameters from the ionization potential should increase roughly with increasing tendency to form covalent bonds. For the alkali metals, the D_{M^+} parameters should and do parallel the ionization energy of the atoms quite closely. The ionization energies of Li, Na, K, Rb, and Cs are about 124, 119, 100, 96, and 90 kcal/mol, respectively. From Table I, D_{M^+} values for the corresponding ions are 133, 113, 100, 96, and 90, respectively. For ions that tend to form highly covalent compounds, a significant amount of electron transfer is expected. A large amount of electron transfer will tend to destabilize the energy level. Therefore, one would expect D_{M^+} to be less than the value of the ionization energy of the corresponding atom. Looking at some examples, such as CH_3^+, I^+, and Ag^+, we find that this is true. Ionization energies for CH_3, I, and Ag are 225, 241, and 175 kcal/mol, respectively. In this context, the value of D_{M^+} for Li^+ is higher than one would expect it to be and could be in error.

The D_{X^-} parameters are standardized by the choice of D_{Cl^-} being equal to −16.0. This value is obtained from the enthalpy of adduct formation for K^+ and Cl^-. This number is about 100 kcal/mol less than the electron affinity for Cl. The correlation between the electron affinity of the corresponding atom and D_B is not as close as is the relationship between D_A and the ionization energy of the corresponding atom.

In view of the more complicated functional form of eq 2 than that of eq 1, we cannot look directly at the parameters in Table I and gain the same insight about reactivity as we could with the *E* and *C* parameters. However, as mentioned earlier, we expect that $O_{M^+}O_{X^-}$ would represent the contribution that covalency makes to the total squared enthalpy. We can use the quantity, $[O_{M^+}O_{X^-}]^{1/2}$, to estimate a percent covalent character in the MX bond, P_c, by dividing it by the dissociation energy and multiplying it by 100, leading to the equation

$$P_c = \frac{[O_{M^+}O_{X^-}]^{1/2}}{\Delta H_D} \times 100 \qquad (20)$$

All of the adducts, MX, which are included in our fit have the more electronegative atom as the base, X. Reversal of the charges of the acid and the base, as in eq 5, should not change the magnitude of the covalent energy or the magnitude of P_c. However, we cannot use eq 20 to calculate P_c for an adduct from the parameters for M^- and X^+ when the actual polarity in the molecule is $M^{\delta+}X^{\delta-}$, because, from eq 11, we see that

$$O_{M^+}O_{X^-} = O_{X^+}O_{M^-}(\Delta H_+/\Delta H_-)^2 \qquad (21)$$

If one wants to calculate the percent covalent character in the MX bond from the parameters for M^- and X^+, then one must use

$$P_c^- = \frac{[O_{X^+}O_{M^-}]^{1/2}}{\Delta H_D}(\Delta H_+/\Delta H_-) \times 100 \qquad (22)$$

P_c^- in eq 22 should equal P_c in eq 20.

The values of P_c for representative adducts are compared with previously published values of percent covalent character in Table A-2 of the supplementary material. The agreement is quite good. For 2:1 adducts, the value of ΔH_D that is used to calculate P_c is half the dissociation energy of MX_2 because the $O_{M^{2+}}$ parameters are those which predict half the total enthalpy.

Error Analysis. The marginal and conditional standard deviations[3] for our *D* and *O* parameters are included in Table I. These have been calculated from the deviations of all 389 equations (equations of the form of eq 2, 14a, and 18) from the experimental values. The effect of including the restrictions can be easily seen by comparing the standard deviations of the parameters that were not restricted to those of the parameters that were. The acids and bases whose parameters were not restricted are marked with an asterisk in Table I. It is seen that the effect of adding the restrictions to our fit is to define a sharper minimum in the series of simultaneous equations to be solved. Without the added restrictions, the minimum would be so broad that the parameters could not be defined. (Marginal standard deviations in the parameters obtained in an unrestricted fit would frequently be as high as 100% or greater.) Accordingly, it is probable that several alternative models could be equally well imposed on the system.

The acids F^+, CN^+, OH^+, and NH_2^+ which appeared in the report[3] of the fit of enthalpies of ionic reactions with eq 1 were not included in this fit. These acids were omitted because the sparsity of data on these systems would have allowed their heats to fit exactly, but the resultant parameters would have values that would be meaningless. Constraining these parameters would result in more meaningful values; however, the values of the dissociation energy of the appropriate symmetrical molecules for these four acids (i.e., F_2, C_2N_2, H_2O_2, and N_2H_4) are all expected to contain contributions from lone-pair repulsions or π-bonding interactions. Therefore, we felt that these acids should be omitted from the fit until better data become available.

Prediction of Enthalpies of Dissociation. The prediction of the enthalpies of dissociation is a more straightforward procedure than the prediction of the enthalpies of the ionic reactions. All of the difficulties associated with calculating $-\Delta H_+$ and $-\Delta H_-$ are circumvented. If it were not for our interest in the acid–base aspect of this problem, the recommended procedure for estimating enthalpies of ionic reactions would involve predicting the dissociation energy and using measured ionization potentials and electron affinities to calculate the enthalpy of the ionic reaction. To distinguish the atomic parameters from the ionic ones, we shall use D_A', D_B', O_A', and O_B' and correlate enthalpies of dissociation, i.e.

$$\Delta H_D = [(D_A' - D_B')^2 + O_A'O_B']^{1/2} \qquad (23)$$

Equation 23 was used to fit dissociation energies of 102 compounds. The reactants in this fit are neutral atoms or radicals (i.e., Na^0, CH_3^0, etc.). However, the parameters for an atom or radical acting so as to lose electron density (i.e., the H atom in $H\cdot + Cl\cdot \rightarrow HCl$) will be different from the parameters of the same atom or radical acting so as to gain electron density (i.e., the H atom in $Na\cdot + H\cdot \rightarrow NaH$). In the discussion that follows, in order to avoid confusion, the parameters used in the fit of the dissociation energies for an atom or radical acting so as to lose electron density will be designated by a plus sign in parentheses following the species (i.e., the D' parameter for H· acting so as to lose electron density will be denoted as $D'_{\mathrm{H}(+)}$). Likewise, the parameters for an atom or radical that gains electron density will have a minus sign in parentheses following the species (i.e., the D' parameter for H· acting to form a hydridic compound will be $D'_{\mathrm{H}(-)}$). However, it should be understood that the parameters are used to calculate dissociation energies for neutral species.

In order to define a unique set of parameters, four parameters again must be fixed as standards.[3] The standards were chosen by the following procedure. For a symmetrical molecule, we can square eq 23 and write

$$(O'_{\mathrm{X}(+)})(O'_{\mathrm{X}(-)}) = [\Delta H_{\mathrm{D}}(\mathrm{X}_2)]^2 \qquad (24)$$

To set the scale, we make the arbitrary assumption that $O'_{\mathrm{X}(+)} = O'_{\mathrm{X}(-)}$. The O' parameters for K· acting so as to lose electron density and NH_2· acting so as to gain electron density are then calculated to be

$$O'_{\mathrm{K}(+)} = \Delta H_{\mathrm{D}}(\mathrm{K}_2) = 11.8 \text{ kcal/mol}$$

$$O'_{\mathrm{NH}_2(-)} = 78.0 \text{ kcal/mol}^{12}$$

The D standards were chosen from[4] the ΔH_{D} for KBr of 91 kcal/mol. Using a value $O'_{\mathrm{Br}(-)}$, equal to $\Delta H_{\mathrm{D}}(\mathrm{Br}_2)$, it can be shown that $(D'_{\mathrm{K}(+)} - D'_{\mathrm{Br}(-)})$ is equal to 88.0. This was assigned[15] as $D'_{\mathrm{K}(+)}$ equal to 143.31 and $D'_{\mathrm{Br}(-)}$ equal to 55.31.

The restrictions placed on the fit included eight equations of the form of eq 24 for the adducts CH_3–CH_3, C_2H_5–C_2H_5, C_6H_5–C_6H_5, C_2N_2, N_2H_4, Cl_2, Br_2, and I_2. A very low weight (a high weight factor) was given to C_2N_2 because of the possibility of carbon–carbon π bonding.[3] N_2H_4 was also given a low weight because of the possibility of lone-pair repulsions.[3] The other 35 restrictions placed on the fit consisted of adding dissociation energies calculated with the polarity of the acid and base pair reversed. For example, CH_3F was included as "$CH_3^{\delta+}$, $F^{\delta-}$," as well as "$CH_3^{\delta-}$, $F^{\delta+}$". This procedure enabled a better definition of the parameters for some of the species for which very few data are available (i.e., $D_{\mathrm{F}(+)}$, $D_{\mathrm{OH}(+)}$, etc.). The parameters necessary for calculating the dissociation energies from eq 23 for about 250 compounds are listed in Table II.

The R factor ratio[13] between this restricted fit and the completely unrestricted fit was 1.14. Therefore, this restricted fit is consistent with the experimental values at all reported confidence levels.

For comparison purposes, eq 2 was used to fit the enthalpies for the ionic reaction of the 101 compounds reported here. The only restrictions placed on this fit were the eight equations of the form of eq 24 (see above). The value of the σ statistic for this fit of the enthalpies of reaction of ionic acids and bases is 1.8. Thus, the fit of dissociation energies with eq 23 is comparable to the fit of enthalpies of reactions of ionic acids and bases with eq 2.

Equation 2 reproduces the enthalpies of the ionic systems much better than the original E and C fit we have reported.[3] We have also shown here that, as required in our theoretical analysis, quantities which are constant for a given acid or base can be incorporated into the D and O parameters without significant loss of accuracy. In this connection, the functional form of eq 2 or 23 is very much different from that of eq 1. It has been shown[14] that the adducts of neutral acids and bases are so parameterized that a constant contribution can often be independently determined.

It was of interest to determine the ability of the parameters to incorporate the $(1 - S^2)$ quantity (S is the overlap integral) that was neglected in the theoretical development. Accordingly, the data on 42 systems whose overlap integrals could be calculated were found to give a range of $(1 - S^2)$ values from 0.85 to 0.95 and to fit eq 25 as well as eq 23.

$$\Delta H(1 - S^2) = [(D_{\mathrm{A}}'' - D_{\mathrm{B}}'')^2 + O_{\mathrm{A}}''O_{\mathrm{B}}'']^{1/2} \qquad (25)$$

Table II. Parameters for Predicting Dissociation Energies[a]

Atom of radical of positive polarity	$D(+)'$	$O(+)'$	Atom of radical of negative polarity	$D(-)'$	$O(-)'$
CH_3	66.3	82.3	F	27.9	126.2
C_2H_5	69.3	77.6	Cl	47.3	75.5
C_6H_5	70.8	93.9	Br	55.3[a]	56.0
Li	146.7	31.8	I	69.2	39.1
K	143.3[b]	11.8[b]	OH	62.4	108.4
Cs	145.0	13.4	NH_2	52.7	78.0[b]
H	85.9	118.5	NO_2	70.6	50.0
Ag	108.9	30.1	CN	45.0	147.0
Al	151.0	48.3	C_6H_5	95.8	91.3
Tl	125.0	20.5	CH_3	91.3	89.5
F	−3.4	28.1	C_2H_5	92.2	81.1
Cl	37.4	42.3	H	120.8	87.7
Br	51.8	37.3	Na	93.0	141.9
I	68.9	30.0	Rb	90.9	187.3
NO	76.5	1.3			
NH_2	44.1	49.1			
OH	4.1	5.7			
CN	54.1	119.0			

[a] In order to compare this fit to the fit of enthalpies of ionic interactions, a statistic that is independent of the magnitude of the observables must be used because the enthalpies of ionic interactions merely contain constants added onto the dissociation energies. One such criterion for testing the goodness of a fit is the σ statistic defined as[13] $\sigma = [\Sigma_i(F_i^{\mathrm{calcd}} - F_i^{\mathrm{exptl}})^2 W_i^2/(N - P)]^{1/2}$ where F_i^{calcd} is the ith calculated value, F_i^{exptl} is the ith experimental value, W_i is the weight given to the ith equation, N is the number of equations, and P is the number of variable parameters. The σ value for the fit described above is 2.2. This indicates that the agreement between the experimental enthalpies and the values calculated from eq 23 is excellent. [b] These parameters were fixed as standards.

Our theory thus predicts that, depending on circumstances, one must select eq 1 or eq 2 to predict enthalpies. The discussion in the next section will review the criteria to be employed in making the selection.

Conclusion

The results of the various correlations described in this article have provided strong support of the predictions which have arisen from our theoretical analysis of the energetics of complex formation in terms of a molecular orbital model. Not only has this treatment indicated why the E and C equation is inappropriate for ionic reactions, but an appropriate alternative was offered and shown to provide an excellent fit of the data available. In both instances (i.e., eq 1 and 2), we have attempted to provide qualitative insights into the parameters by equating the one-center terms of the molecular orbital description with ionic contributions to the bonding of the qualitative ionic–covalent model. It should be emphasized, by considering the enthalpy of a reaction, that our concern is with differences in the one-center terms of the free acids and bases or free cations and anions compared to those of the adducts or compounds formed. In a similar fashion, the two-center terms are equated with covalency. The resultant parameters are physically meaningful in terms of this imposed model.

Consistent with predictions from the theoretical analysis, we found that when eq 2 was used to fit 143 enthalpies of reactions of adducts of neutral acids and bases, the resultant fit was good, but not quite as good as the fit obtained with eq 1. The weighted root-mean-square deviation between the experimental enthalpies and the enthalpies calculated using eq 2 was 0.029 kcal/mol. Using eq 1 for over 280 enthalpies of reactions of neutral acids and bases, the root-mean-square deviation was 0.016 kcal/mol. This result is expected, for some of the correction terms neglected in deriving eq 2 are significant compared to the small enthalpies of reactions of neutral acids and bases but negligible compared to the large enthalpies of ionic reactions. Thus, eq 1 is the preferred equation for fitting enthalpies of adduct formation of neutral acids and bases, whereas eq 2 is the preferred equation for fitting enthalpies of adduct formation of ionic acids and bases.

An analysis of the approximations used to arrive at equations of the form of (1) and (2) indicates the conditions under which the E and C equation (eq 1) or the D and O equation (eq 2) exceed the limits of applicability. The use of the charge correction equations (eq 11 of ref 4) in the derivation of eq 1 restricts its applicability to prediction of enthalpies of interactions where the amount of electron density transferred from the base to the acid is small enough so that the energy of the acid and base orbitals can be approximated by a linear function of charge. Since in most neutral adducts the amount of charge transfer is expected to be less than 0.5 of an electron, this is a good approximation. For all of the acid–base interactions to which eq 1 and 2 have been applied, the change in the occupation numbers has been less than unity. One would not expect these equations to predict the enthalpy of a reaction where more than one electron is transferred as, for example, in F^+ reacting with CH_3^- to produce CH_3F.

The relative error introduced by eliminating the square root term in the derivation[4] of eq 1 can be approximated by $[2S^2H_AH_B/(H_A - H_B)^2]^2$ where H_A and H_B represent the diagonal Hamiltonian matrix elements of the acid and base, respectively, and S represents the overlap integral. If an arbitrary upper limit of 5% (0.05) is imposed on the error which will be accepted, the condition that results is

$$\frac{2S^2H_AH_B}{(H_A - H_B)^2} \leqslant 0.05^{1/2} = 0.22$$

Using a value of 0.1 for S (which is a reasonable value for adducts of neutral acids and bases), it is found that $H_AH_B \leq 11(H_A - H_B)^2$. If electron affinities, ϵ_A, are used to approximate H_A and ionization energies, I_B, are used to approximate H_B, it can be seen that the above condition holds when ϵ_A and I_B are sufficiently different for a given acid and base. As these two energies become similar, that enthalpy becomes larger and the error introduced in expansion of the square root becomes larger. Equation 1 should not be employed to correlate experimental enthalpies of systems of this type. The term $S^2(H_A - H_B)$ which has been incorporated in product type parameters can be fit by a product function over only limited ranges and will cause complications as H_A approaches H_B.

In conclusion, limitations on the applicability of eq 1 to predict enthalpies of acid–base interactions can be formulated in terms of the ionization energies and electron affinities of the bases and acids, respectively. In order to confine the error generated by elimination of the square root to less than 5%, the electron affinity of the acid and the ionization energy of the base must fall within a range such that the product of ϵ_A and I_B is less than 11 times the square of the difference between ϵ_A and I_B. Furthermore, if ϵ_A and I_B lie outside the range of acids and bases currently in the system (roughly, 30–75 kcal/mol for ϵ_A and 175–300 kcal/mol for I_B), caution should be used in extending eq 1 to cover them until it is established that $S^2/(H_A - H_B)$ can be fit to a product function for all of the systems in the correlation. The ionic systems do not meet these requirements and accordingly eq 2 should be utilized.

The limitation placed on the use of eq 2 occurs as a result of the assumption that H_A and H_B for a given acid or base can be approximated by a constant; i.e., no charge correction term is utilized. As mentioned earlier, the error generated by this approximation is estimated to be a few kilocalories per mole. When this error amounts to a significant fraction of the enthalpy (i.e., enthalpies of adduct formation below about 30 kcal/mol), the E and C equation should be utilized. For enthalpies larger than about 30 kcal/mol, eq 2 may be used quite generally.

It is of interest to point out that our fit of the dissociation energies is significantly better than that of the Pauling equation used to derive electronegativities

$$K(\chi_A - \chi_B)^2 = D_{AB} - [D_{AA}D_{BB}]^{1/2}$$

where χ is the electronegativity, K is a proportionality constant, and D refers to a dissociation energy. Statistical analysis indicates that the imposition of the electronegativity model on the data can be rejected with high confidence. A better criterion for electronegativity could probably be developed from our treatment, but in view of the qualitative way in which electronegativity usually is employed, we feel the present values are adequate.

Acknowledgment. The authors acknowledge support of this work from the National Science Foundation through Grant US NSF GP 31431X and from the Atomic Energy Commission through the award of a Special Fellowship in Nuclear Science and Engineering to A.P.M.

Registry No. F^-, 16984-48-8; Cl^-, 16887-00-6; Br^-, 24959-67-9; I^-, 20461-54-5; Se^{2-}, 22541-48-6; Te^{2-}, 22541-49-7; OH^-, 14280-30-9; CH_3^-, 15194-58-8; $C_2H_5^-$, 25013-41-6; CN^-, 57-12-5; NH_2^-, 17655-31-1; $C_6H_5^-$, 30922-78-2; NO_2^-, 14797-65-0; H^-, 12184-88-2; hydrogen, 1333-74-0; lithium, 7439-93-2; sodium, 7440-23-5; potassium, 7440-09-7; rubidium, 7440-17-7; cesium, 7440-46-2; copper, 7440-50-8; silver, 7440-22-4; aluminum, 7429-90-5; indium, 7440-74-6; thallium, 7440-28-0; CH_3^+, 14531-53-4; $C_2H_5^+$, 14936-94-8; *n*-$C_3H_7^+$, 19252-52-9; $C_6H_5^+$, 17333-73-2; NO^+, 14452-93-8; chlorine, 7782-50-5; bromine, 7726-95-6; iodine, 7553-56-2; beryllium, 7440-41-7; magnesium, 7439-95-4; calcium, 7440-70-2; strontium, 7440-24-6; barium, 7440-39-3; scandium, 7440-20-2; titanium, 7440-32-6; zirconium, 7440-67-7; vanadium, 7440-62-2; chromium, 7440-47-3; manganese, 7439-96-5; iron, 7439-89-6; cobalt, 7440-48-4; nickel, 7440-02-0; zinc, 7440-66-6; cadmium, 7440-43-9; mercury, 7439-97-6; silicon, 7440-21-3; germanium, 7440-56-4; tin, 7440-31-5; lead, 7439-92-1; fluorine, 7782-41-4; NH_2^+, 15194-15-7; OH^+, 12259-29-9; CN^+, 17247-95-9.

Supplementary Material Available: Fit of enthalpies of ionic acids and bases, representative percent covalent characters, and estimation of double electron affinities (three tables plus text) (17 pages).

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which differ only in sign. The positive set was chosen: $D_{K(+)} = 143.41$; $D_{Br(-)} = 55.31$. These values, however, could have been merely arbitrarily chosen because only the difference in the D parameters is used in calculating the dissociation energies.

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Crystal Structure of 2-Sulfanilamidopyrimidinesilver(I)

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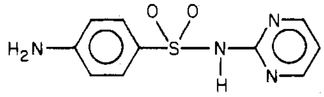
Received September 9, 1975 AIC506708

The crystal structure of 2-sulfanilamidopyrimidinesilver(I), $Ag(C_{10}H_9N_4O_2S)$, a burn treatment compound, was determined from single-crystal automated x-ray diffractometer measurements. The crystal data are: $a = 6.173$ (2), $b = 9.600$ (5), $c = 20.30$ (2) Å, $\beta = 96.22$ (8)°, d(measured) = 1.982 (3), d(calcd) = 1.983, $Z = 4$, $P2_1/c$, 1719 total reflections, 1151 present, $R_1 = 0.053$, $R_2 = 0.031$, from full matrix least squares. The nitrogen atoms of the pyrimidine ring coordinate to two different silver atoms to form polymeric chains extending through the crystal. Each silver atom in this chain is also coordinated to one oxygen atom from the sulfonyl group of the 2-sulfanilamidopyrimidine molecule in the chain. A second identical chain (related by center of symmetry) is joined to the first chain by the coordination of the silver atom from each chain to the imido nitrogen atom of the 2-sulfanilamidopyrimidine molecule in the other chain. In addition, the silver atoms in one chain are only 2.916 (1) Å from the symmetry-related silver atom in the other chain. The double stranded chains are further hydrogen bonded by the amine hydrogen atoms and sulfonyl oxygen atoms to form planar sheets of the double-stranded chains. The coordination about silver is a distorted trigonal bipyramid.

Introduction

The crystal structure of 2-sulfanilamidopyrimidinesilver(I), a burn treatment compound, was undertaken to determine the coordination about silver and to verify the presence or absence of the imido hydrogen atom. [The common name for 2-sulfanilamidopyrimidine is sulfadiazine; for brevity, the complex will be called silver sulfadiazine in the text.] Silver sulfadiazine is too insoluble in alcohol to permit a good NMR spectrum; in dimethyl sulfoxide the spectrum is ambiguous due to decomposition to form a silver mirror and peak broadening from nitrogen quadrupole coupling. Powder diagrams of silver sulfadiazine made by treating sodium sulfadiazine with silver nitrate and by treating sulfadiazine directly with silver nitrate are identical. This observation coupled with the crystal structure described below indicates that it is Ag(I) which is complexed and that the imido hydrogen atom is absent.



2-sulfanilamidopyrimidine ≡ sulfadiazine

Experimental Section

Crystals of silver sulfadiazine were made by mixing two 500-ml solutions of approximately 2×10^{-3} M sulfadiazine and silver nitrate in boiling 95% ethyl alcohol and cooling the solution from 63 °C to room temperature over a 12-day period in a 50-l. water bath. Chemical analysis of the crystals gave the following. Found [theoretical]: Ag, 30.22 (3) [30.20%]; C, 33.3 (3) [33.6%]; N, 15.7 (1) [15.7%]; H, 1.9 (3) [2.5%].

The colorless crystals are monoclinic, space group $P2_1/c$ with $a = 6.173$ (2) Å, $b = 9.600$ (5) Å, $c = 20.30$ (2) Å, $\beta = 96.22$ (8)°, $V = 1195.86$ Å^3; d(pycnometrically) = 1.982 (3) g/cm^3, d(from cell dim) = 1.983 with $Z = 4$, formula weight for $C_{10}H_9N_4O_2SAg$ = 357.15, $F_{000} = 352$. Linear absorption coefficient = 17.8 cm^{-1}. The cell dimensions were determined from 12 reflections with 2θ between 32 and 45° with Mo Kα_1 = 0.70926 Å.

Intensity data were obtained by the 2θ scan method on a Picker diffractometer. Background counts were made for 10 s on each end of the scan of 1.5°, scan rate = 1°/min; oriented graphite monochromated Mo Kα radiation was used. The integrated intensity and standard deviation in the net intensity were calculated as in previous work.[1] Lorentz and polarization corrections were made, but an absorption correction was not made since the absorption correction would range only between the limits of 0.88 to 0.98. The crystal, 0.01 mm along b^*, 0.06 mm along c^*, and 0.59 mm along a^*, was mounted with its rotation axis approximately along a^*.

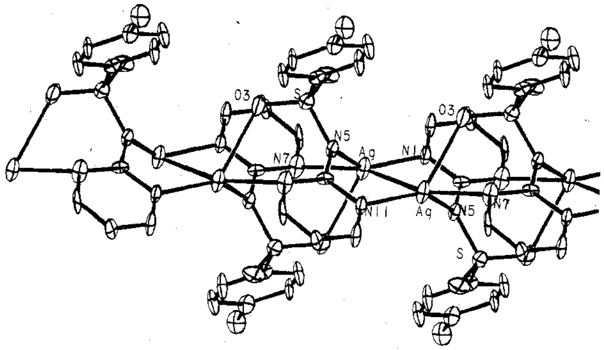


Figure 1. Structure of 2-sulfanilamidopyrimidinesilver(I) showing the interlinked double-stranded chain.

Nonhydrogen-scattering factors and dispersion corrections were taken from ref 2, and the hydrogen scattering factors used were those of Stewart, Davidson, and Simpson.[3] The real portion of the dispersion correction to the scattering factors of silver and sulfur was included in all calculations, and the imaginary part was included in the last two cycles of refinement.

The structure was solved using heavy-atom techniques. Least-squares refinements were initially by block-diagonal methods, but the last cycles were by full-matrix methods. The initial difference map to locate hydrogen atoms (after isotropic refinement $R_1 = 0.09$) showed all hydrogen atoms except one from the pyrimidine ring, one from the phenyl ring, one from the amino group, and one from the imido hydrogen. Including hydrogen atoms in the structure factor calculation did not significantly lower the discrepancy factor at this stage in refinement.[4] Weights used during refinement were the reciprocals of the variances of the observed structure factors; they ranged from 0.01 to 5.4. Absent reflections were given a rather arbitrary weight of 1.0 to force the parameters to correspond to these data, as a rather conservative criterion was used in establishing present reflections.[1] The discrepancy factors, $R_1 = 0.0533$ and $R_2 = 0.0306$, were obtained on the final least-squares cycle which refined on anisotropic temperature factors for all atoms except hydrogen, all coordinates except hydrogen, included all anomalous dispersion corrections, and assumed the imido hydrogen atom was absent. The values of the variables