  Bull. Chem. Soc. Jpn., 57, 1174—1178 (1984) [Vol. 57, No. 5

Regularity in Homolytic Lattice Energies of Anhydrous Formate, Acetate, Oxalate, and Glycolate of Metals**

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(Received July 30, 1983)

The homolytic lattice energy ΔU_R of an ionic crystal M_xA_y was defined as the standard internal energy change at 298.15 K for the following vaporization process to yield neutral species M and A: $(1/x)M_xA_y(c)=M(g)+(y/z)A(g)$. ΔU_R and $[\Delta U_R-(y/x)\Delta H_f^\circ(A,g)]$ were calculated for formates and acetates and for oxalates and glycolates, respectively, of metals, and were analyzed empirically. ΔU_R(formate)$\simeq\Delta U_R$(acetate) holds for every metal. ΔU_R of oxalates and glycolates may be expressed as follows: ΔU_R(oxalate or glycolate)$=a\Delta U_R$(formate or acetate)$+b(y/x)$, where a is the constant close to unity, and b is the constant which is, possibly, close to zero for oxalates and about 40 kJ mol^{-1} for glycolates. The linear relations in ΔU_R were discussed in relation to crystal structure of the salts and carboxyl O-H bond dissociation energy of the corresponding carboxylic acids.

The cohesion energy of an ionic crystal of formula M_xA_y has been usually expressed as the lattice energy U_L which is defined as the standard internal energy change ΔU° for the following heterolytic (ionic) vaporization of the crystal at 298.15 K:

$$M_xA_y(c) = xM^{m+}(g) + yA^{n-}(g), \quad (1)$$

where m and n are the numbers of ionic charges in the units of e. U_L is given as follows:

$$U_L = x\Delta H_f^\circ(M^{m+}, g) + y\Delta H_f^\circ(A^{n-}, g) - \Delta H_f^\circ(M_xA_y, c) - (x+y)RT. \quad (2)$$

For most of polyatomic anions, reliable experimental data of standard enthalpy of formation in gaseous state are not availble at present. Within the extent of the present compounds, reliable data are available only for acetate anion,[1] so it is impossible to carry out a satisfactory empirical analysis in terms of U_L for the present compounds. On the other hand, reliable data are more abundant for the corresponding gaseous neutral species (free radical). A formed by loss of n electrons from a polyatomic anion A^{n-}. Within the extent of the present compounds, ΔH_f°(A,g) has been determined precisely for formate and acetate free radicals.[2,3]

Here, the homolytic lattice energy ΔU_R is defined as the standard internal energy change at 298.15 K of the following homolytic (nonionic) vaporization of an ionic crystal M_xA_y (c):

$$(1/x)M_xA_y(c) = M(g) + (y/x)A(g). \quad (3)$$

ΔU_R is given as follows:

$$\Delta U_R = \Delta H_f^\circ(M, g) + (y/x)\Delta H_f^\circ(A, g) - (1/x)\Delta H_f^\circ(M_xA_y, c) - [(x+y)/x]RT. \quad (4)$$

Correspondingly, the heterolytic lattice energy ΔU_I is defined by the equation: $\Delta U_I=(1/x)U_L$. ΔU_I is related with ΔU_R according to:

$$\Delta U_I = \Delta U_R + \sum_1^m{}_i I(M, i) + C_1 + (y/x)[\sum_1^n{}_j A(A, j) + C_2], \quad (5)$$

where $I(M, i)$ is the i-th ionization energy of species M, $A(A, j)$ is the j-th electron affinity of species A, and C_1 and C_2 are $[\Delta U^\circ(298.15\ K)-\Delta U^\circ(0\ K)]$ for the processes: $M(g)=M^{m+}(g)+me$ and $A(g)+ne=A^{n-}$, respectively where e denotes electron.

** Contribution No. 58 from Chemical Thermodynamics Laboratory, Faculty of Science, Osaka University.

In this paper, ΔU_R of formates and acetates and $[\Delta U_R-(y/x)\Delta H_f^\circ(A, g)]$ of oxalates and glycolates are analyzed empirically and discussed in relation to crystal structure of the salts and O-H bond dissociation energy of the corresponding carboxylic acids.

Procedure and Results

Most of the standard enthalpies of formation used in the present analysis were taken from Ref. 4. The data from other sources are collected in Table 1. From these data, ΔU_R was calculated according to Eq. (4) and presented in Table 2 for formates and acetates. The plot of ΔU_R (acetate) against ΔU_R (formate) is shown in Fig. 1. A straight line passes close to the plots and the origin in

Table 1. Standard enthalpies of formation at 298.15 K taken from sources other than Ref. 4

Species	$-\Delta H_f^\circ$/kJ mol^{-1}
$HOCH_2CO_2H(g)$	582.4[a)]
$HO_2CCO_2H(g)$	731.6[6)]
$(CH_3CO_2)_2Mg(c)$	1367.7[5)]
$HCO_2(g)$	151±8[2)]
$CH_3CO_2(g)$	208±4[3)]

a) Estimated value. See the text for the method of estimation.

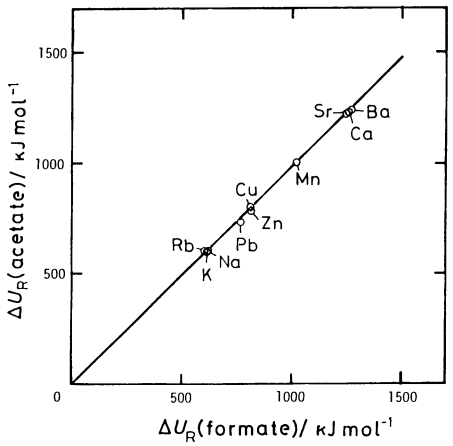

Fig. 1. ΔU_R (acetate) *vs.* ΔU_R (formate) plot. For the definition of ΔU_R, see the text. The straight line is expressed with the equation: ΔU_R (acetate)$=$ 0.9818ΔU_R (formate).

Table 2. Homolytic lattice energies ΔU_R of anhydrous formate and acetate of metals, and $[\Delta U_R-(y/x)\Delta H_f^\circ(A, g)]$ of anhydrous glycolate and oxalate of metals

	ΔU_R		$[\Delta U_R-(y/x)\Delta H_f^\circ(A, g)]$	
	kJ mol^{-1}		kJ mol^{-1}	
	Formate	Acetate	Glycolate	Oxalate
Na(I)	620	603	1003	761
Mg(II)	—	1095	1892	1410
Al(III)	—	1584	—	—
K(I)	613	599	992	758
Ca(II)	1257	1234	2027	1532
Mn(II)	1018	1006	—	1303
Co(II)	990	—	—	1269
Ni(II)	994	—	—	1280
Cu(II)	811	808	1582	—
Zn(II)	810	787	1591	—
Rb(I)	602	605	—	740
Sr(II)	1249	1228	2001	1528
Ag(I)	—	471	—	617
Cd(II)	—	—	—	1018
Cs(I)	—	607	—	—
Ba(II)	1268	1241	2034	1542
Hg(II)	—	455	—	732
Tl(I)	—	497	—	—
Pb(II)	766	736	—	1039

For symbols, see the text.

this figure. Linear regression analysis gave the following result:

$$\Delta U_R(\text{acetate})/\text{kJ mol}^{-1} = 0.9818\Delta U_R(\text{formate})/\text{kJ mol}^{-1}, \quad (6)$$

with standard deviation from the fit s_f of 9 kJ mol^{-1}.

It is not possible at present to calculate ΔU_R for oxalates and glycolates, since $\Delta H_f^\circ(g)$ is not available for oxalate and glycolate free radicals. Instead, $[\Delta U_R-(y/x)\Delta H_f^\circ(A, g)]$ calculated according to Eq. (4) was given in Table 2 and plotted against ΔU_R (formate) in Figs. 2 and 3. The upper lines express the results of the linear regression analysis of the data of bivalent metal cations. The lower lines were drawn so that they were parallel with the corresponding upper lines with intercepts 141(=282/2) and 399(=798/2), respectively, in Figs. 2 and 3. Thus, the whole data may be expressed by the following equations:

$$[\Delta U_R(\text{oxalate})-(y/x)\Delta H_f^\circ(O_2CCO_2, g)]/\text{kJ mol}^{-1} = 0.9965\Delta U_R(\text{formate})/\text{kJ mol}^{-1} + 282(y/x), \quad (7)$$

with the maximum deviation of 6 kJ mol^{-1} ands s_f of 5 kJ mol^{-1} for uni- and bivalent metal cations, respectively, and

$$[\Delta U_R(\text{glycolate})-(y/x)\Delta H_f^\circ(HOCH_2CO_2, g)]/\text{kJ mol}^{-1} = 0.9728\Delta U_R(\text{formate})/\text{kJ mol}^{-1} + 399(y/x), \quad (8)$$

with the maximum deviation of 5 kJ mol^{-1} and s_f of 6 kJ mol^{-1} for uni- and bivalent metal cations, respectively.

Similar plots, though not shown, were made for the pairs of oxalate-acetate and glycolate-acetate, with

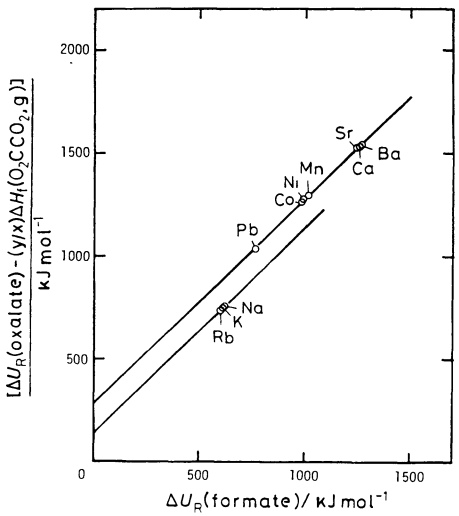

Fig. 2. $[\Delta U_R(\text{oxalate})-(y/x)\Delta H_f^\circ(O_2CCO_2, g)]$ *vs.* ΔU_R (formate) plot.
(y/x) is equal to 1/2 and 1 for mono- and divalent metals, respectively. The straight lines are expressed with the equation: $[\Delta U_R(\text{oxalate})-(y/x)\Delta H_f^\circ(O_2CCO_2,g)]=0.9965\Delta U_R(\text{formate})+282(y/x)$.

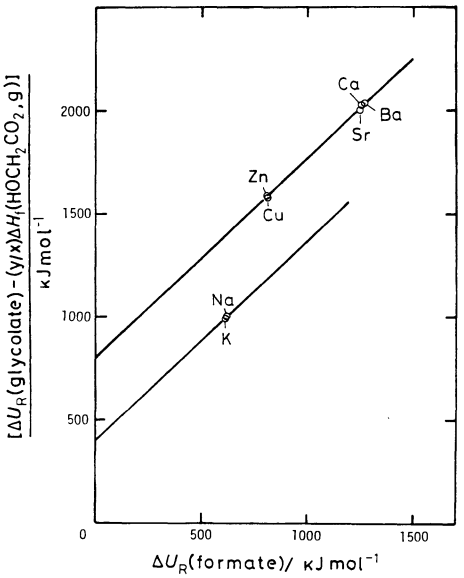

Fig. 3. $[\Delta U_R(\text{glycolate})-(y/x)\Delta H_f^\circ(HOCH_2CO_2, g)]$ *vs.* ΔU_R (formate) plot.
(y/x) is equal to 1 and 2 for mono- and divalent metals, respectively. The straight lines are expressed with the equation: $[\Delta U_R(\text{glycolate})-(y/x)\Delta H_f^\circ(HOCH_2CO_2, g)]=0.9728\Delta U_R(\text{formate})+399(y/x)$.

similar results. The linear relations are expressed as follows:

$$[\Delta U_R(\text{oxalate})-(y/x)\Delta H_f^\circ(O_2CCO_2, g)]/\text{kJ mol}^{-1} = 1.0239\Delta U_R(\text{acetate})/\text{kJ mol}^{-1} + 275(y/x), \quad (9)$$

with the maximum deviation of 8 kJ mol^{-1} and s_f of 8 kJ mol^{-1} for uni- and bivalent metal cations, respectively, and

$$[\Delta U_R(\text{glycolate})-(y/x)\Delta H_f^\circ(HOCH_2CO_2, g)]/\text{kJ mol}^{-1} = 0.9965\Delta U_R(\text{acetate})/\text{kJ mol}^{-1} + 397(y/x), \quad (10)$$

with the maximum deviation of 5 kJ mol^{-1} and s_f of 11 kJ mol^{-1} for uni- and bivalent metal cations, respectively.

While univalent metals are limited to alkali metals for the pairs of oxalate-formate, glycolate-formate, and glycolate-acetate, Ag(I) is also included in the plots of the pair oxalate-acetate. This shows that the linear relation for univalent metals is not specific to alkali metals.

Discussion

Prior to the discussion of each of relations in ΔU_R given in Eqs. (6)—(10), two remarks are presented here. Firstly, it is to be noted that the linear relations hold even for compounds of Mn(II), Co(II), Ni(II), and Cu(II), which are the cations with unfilled 3d orbitals. In order to study the effect of the d-orbital splitting on ΔU_R, the difference in ΔU_I between these compounds and the corresponding Ca compounds Ca_xA_y was calculated using equation (2) and the definition: $\Delta U_I = U_L/x$,

$$\Delta U_I(M_xA_y) - \Delta U_I(Ca_xA_y) = \Delta H_f^\circ(M^{2+}, g) - \Delta H_f^\circ(Ca^{2+}, g) - \Delta H_f^\circ(M_xA_y, c) + \Delta H_f^\circ(Ca_xA_y, c). \quad (11)$$

As shown in Table 3, the difference in ΔU_I changes significantly with cation species, but it barely depends on anion species. Thus, the stabilization energy due to the d-orbital splitting of each cation is nearly independent of anion species. The stabilization energy was evaluated by the crystal field theory,[7] resultant values up to 300 kJ mol^{-1}. More recently, a molecular orbital approach[8] was reported, giving the values of several hundred kJ mol^{-1} or less. Whatever the exact values may be, the conclusion derived above, together with the fact that the coefficients of the first terms on the right-hand sides of Eqs. (6)—(10) are close to unity, shows that even if the effect of the 3d-orbital splitting was corrected, the resultant values would satisfy these equations.

Secondly, the linear relations in ΔU_R given in Eqs. (6)—(10), in connection with Eq. (5), leads to the corresponding linear equations in ΔU_I, although it is unknown whether the proportionality holds for the pair of formate-acetate.

Now, the discussion on each linear relation is started. For the pair of formate-acetate, ΔU_R (formate)$\simeq\Delta U_R$ (acetate) holds. Crystal structure has been determined for formates of Na,[9] Ca,[10,11] Sr,[10] Ba,[11] and Cu(II).[12] These crystals are characterized by the coordination of the metal cations with four or more carboxyl oxygen atoms. Hence, ΔU_R may be divided into two parts: The contribution from metal-oxygen interactions and that from the other interactions, both in the crystalline states. The former is considered to be more dominant than the latter. The observed approximate equality in ΔU_R suggests that the crystal structures of formates and acetates of a metal are similar and, in view of the similarity of chemical structure of the anions, the magnitude of metal-oxygen interaction energy is also similar between formate and acetate of a metal.

Table 3. The difference between heterolytic lattice energy ΔU_I of formate, acetate, oxalate, and glycolate of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II), and ΔU_I of the corresponding Ca compounds

Cation M(II)	$[\Delta U_I(M_xA_y) - \Delta U_I(Ca_xA_y)]$/kJ mol^{-1}			
	Formate	Acetate	Oxalate	Glycolate
Mn(II)	251	262	—	261
Co(II)	402	—	—	406
Ni(II)	489	—	—	500
Cu(II)	522	542	523	524
Zn(II)	457	457	468	—

For the pairs of oxalate-formate and oxalate-acetate, it is clear from Eqs. (7) and (9), that ΔU_R (oxalate) is expressed by a linear function of ΔU_R (formate) or ΔU_R (acetate), with a coefficient close to unity and a second term proportional to (y/x). Furthermore, from the similarity in chemical structure of the anions as a whole, the relation: ΔU_R(formate)$\simeq\Delta U_R$(oxalate)$\simeq\Delta U_R$ (acetate), is expected to hold for every metal. Substitution of an assumed value of ΔH_f° (O_2CCO_2, g)$=-279$ kJ mol^{-1}, into Eqs. (7) and (9), leads to the following approximate equality relations:

$$\Delta U_R(\text{oxalate})/\text{kJ mol}^{-1} = 0.9965\Delta U_R(\text{formate})/\text{kJ mol}^{-1} + 3(y/x), \quad (12)$$

and

$$\Delta U_R(\text{oxalate})/\text{kJ mol}^{-1} = 1.0239\Delta U_R(\text{acetate})/\text{kJ mol}^{-1} - 4(y/x). \quad (13)$$

The assumed value of $\Delta H_f^\circ(HOCH_2CO_2, g)$ was then used to calculate the mean O-H bond dissociation energy $\bar{D}$(O-H) of oxalic acid, which was defined as ΔU° (298.15 K) for the reaction: $(1/2)HO_2CCO_2H(g) = (1/2)O_2COO_2(g) + H(g)$. $\bar{D}$(O-H) was calculated to be 443 kJ mol^{-1}. Similarly, corresponding O-H bond dissociation energies D(O-H) of formic and acetic acids, defined as ΔU°(298.15 K) of the reactions: $RCO_2H(g) = RCO_2(g) + H(g)$, where R is H or CH_3, were calculated to be 443 and 440 kJ mol^{-1}, respectively. Agreement of the calculated value of $\bar{D}$(O-H) of oxalic acid with D(O-H) of formic and acetic acids strongly suggests that $\Delta H_f^\circ(O_2CCO_2, g)\simeq-279$ kJ mol^{-1} and the relation: ΔU_R(formate)$\simeq\Delta U_R$(oxalate)$\simeq\Delta U_R$(acetate) holds. Thus, ΔH_f°(g) of oxalate biradical, which would be determined experimentally only with difficulty, could be estimated with some grounds. In addition, the coefficients of the first terms of Eqs. (11) and (12) which are close to unity, suggest the similarity in the character of crystal structure and the magnitude of metal-oxygen interaction energy of a metal oxalate with formate and acetate of the same metal.

For the pairs of glycolate-formate and glycolate-acetate, Eqs. (8) and (10) show that ΔU_R(glycolate) is expressed by a linear functions of ΔU_R(formate) or ΔU_R(acetate), with a coefficient close to unity and a second term proportional to (y/x). The assumption that ΔU_R(formate)$\simeq\Delta U_R$(glycolate)$\simeq\Delta U_R$(acetate), or equivalently that $\Delta H_f^\circ(HOCH_2CO_2, g)=-398$ kJ mol^{-1}, leads to the result: D(O-H)$=400$ kJ mol^{-1} for carboxyl O-H of glycolic acid. ΔH_f°(g) of glycolic acid used in this calculation was obtained by estimation

using the group contribution method,[13,14] with an estimated value of $[C-(CO)(O)(H)_2]=-34.3$ kJ mol^{-1}. Hence, this value is more uncertain than the rest. Even so, the value of D(O-H) given above is significantly smaller than the corresponding values of formic and acetic acids.

Instead, it was assumed that D(O-H)=443 kJ mol^{-1} for carboxyl O-H of glycolic acid, in accordance with those of formic and acetic acids. This implies that $\Delta H_f^\circ(HOCH_2CO_2, g)=-355$ kJ mol^{-1}. Substitution of this value to Eqs. (8) and (10) leads to the following equations:

$$\Delta U_R(\text{glycolate})/\text{kJ mol}^{-1} = 0.9728\Delta U_R(\text{formate})/\text{kJ mol}^{-1} + 44(y/x), \quad (14)$$

and

$$\Delta U_R(\text{glycolate})/\text{kJ mol}^{-1} = 1.0239\Delta U_R(\text{acetate})/\text{kJ mol}^{-1} + 42(y/x), \quad (15)$$

Among the glycolates, crystal structure has been determined only for Cu(II) glycolate.[15] In this crystal, Cu(II) is coordinated with four carboxyl and two hydroxyl oxygen atoms of glycolate anions, *i.e.* glycolate anion is tridentate, whereas formate and acetate anions are bidentate. In addition, each hydroxyl oxygen atom forms a remarkably short intermolecular hydrogen bond 0.257 nm long to the carboxyl oxygen atom of a second neighbouring complex. The short O-H···O hydrogen bond corresponds to the hydrogen bond energy of about 40 kJ mol^{-1}.

For Cu(II) glycolate, the second terms of Eqs. (14) and (15) may be interpreted in terms of (1) the intermolecular hydrogen bond in the crystal, which is cleaved in the gaseous state, and (2) the change in the electronic structure and probably the molecular structure as well, of the hydroxyl moiety of glycolate anions, accompanying homolytic vaporization. Contributions from these sources to ΔU_R(glycolate) are clearly proportional to (y/x) and independent of metal species. It is to be noted that the contribution from the former source is sufficiently large to account for mostly the second terms by itself. The latter contribution is considered to be smaller than the former. The other possible extra effects arising from the fact that glycolate is a tridentate anion, may not be included in the causes of the second terms, since it seems unlikely that these extra effects are independent of metal species.

Equations (14) and (15) suggest that crystal structure of every glycolate is similar to that of Cu(II) glycolate. Intermolecular hydrogen bond would be present and metal cations would be coordinated with carboxyl and hydroxyl oxygen atoms, in the crystal of every glycolate. The total magnitude of metal-oxygen interaction energy does depend on metal species, but is independent of the kind or the combination of coordinating oxygen atoms (carboxyl and hydroxyl), as is reflected in the coefficients of the first terms which are close to unity.

Thus, it has been shown that the empirical analysis of crystal cohesion energy in terms of ΔU_R can be used to obtain various informations on crystal structure and inter-ion interactions in the crystal, at least within the extent of the present compounds.

Table 4. Estimated standard enthalpies of formation in crystalline state of metal formates, acetates, glycolates, and oxalates

Cathion	$-\Delta H_f^\circ(M_xA_y, c)$/kJ mol^{-1}			
	Formate	Acetate	Glycolate	Oxalate
Mg(II)	1276(A)	—	—	—
Al(III)	1749(A)	—	2452(A)	3428(A)
Mn(II)	—	—	1514(F)	—
Co(II)	—	970(F)	1343(F)	—
Ni(II)	—	969(F)	1342(F)	—
Cu(II)	—	—	—	963(FA)
Zn(II)	—	—	—	959(FA)
Rb(I)	—	—	916(FA)	—
Ag(I)	350(A)	—	586(A)	—
Cd(II)	634(O)	621(O)	1412(O)	—
Cs(I)	698(A)	—	930(A)	1371(A)
Hg(II)	711(A)	—	1192(A)	—
Tl(I)	481(A)	—	715(A)	933(A)
Pb(II)	—	—	1347(FA)	—

F, A, and O in the parentheses show that ΔU_R of the corresponding formate, acetate, and oxalate, was used to derive the estimated value, respectively. The values with parenthesized FA are the mean values of those obtained by correlation with ΔU_R of formate and that of acetate.

Apart from the analysis of ΔU_R described so far, the regularity in ΔU_R or $[\Delta U_R-(y/x)\Delta H_f^\circ(A,g)]$ enables us to estimate $\Delta H_f^\circ(c)$ of a compound M_xA_y, from that of another compound of the same metal, by using equations (6)—(10) and then Eq. (4). The estimated values are presented in Table 4.

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