

# Estimation of the Dissociation Energies of Donor–Acceptor Complexes of Group 13–15 Element Compounds within the Framework of the Statistical EC Model

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**Abstract**—The parameters of 18 Lewis bases of group 13–15 elements E'H<sub>2</sub>EH<sub>2</sub>·LB (E' = P, As, Sb; E = B, Al, Ga; LB = SMe<sub>2</sub>, NMe<sub>3</sub>) and 18 Lewis acids of group 13 elements ER<sub>3</sub> (R = H, F, Cl, Br, Me, C<sub>6</sub>F<sub>5</sub>) were optimized using a statistical approach within the electrostatic-covalent (EC) model. The EC model allows prediction of dissociation energies of donor-acceptor complexes with an absolute median deviation of ±4 kJ mol<sup>-1</sup>, but this approach is not applicable to estimation of donor-acceptor bond energies.

**Keywords:** group 13–15 elements, ECW model, Lewis acids, Lewis bases, donor-acceptor complexes

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## INTRODUCTION

Hydrogen compounds of group 13–15 elements, which are valence-isoelectronic to hydrocarbons, are promising precursors for the synthesis of valuable semiconductor materials and inorganic polymers [1]. However, they have low stability. One way to stabilize such compounds is donor–acceptor (DA) stabilization due to complexation with Lewis acids or bases [2]. To search for suitable Lewis acids and bases, it is necessary to know the energetics of complexation. This information can in principle be obtained by quantum-chemical calculations, but such calculations for a large number of complexes of group 13–15 element compounds are rather labor-consuming. Therefore, it is important to search for simpler models that make it possible to quickly estimate the dissociation energy of a DA complex and to find promising objects for further experimental studies.

A simple model that allows quantitative description and prediction of the enthalpies of dissociation of donor-acceptor complexes into components was proposed by Drago (ECW model) [3–5]. Within the framework of the ECW model, the enthalpy of complexation during the interaction between a Lewis acid (A) and a Lewis base (B) in solution can be represented as the sum of covalent and electrostatic contributions [4]. The electrostatic contribution is determined by the partial positive charge on the acceptor site of the Lewis acid and the degree of stabilization of the lone electron pair of the Lewis base. The covalent contribution is determined by the overlap integral and the difference between the LUMO energy of the Lewis acid

and the HOMO energy of the Lewis base [5]. ECW is a four-parameter model: the  $E_A$  and  $E_B$  parameters characterize the electrostatic contribution of the Lewis acid and base, respectively, and the  $C_A$  and  $C_B$  parameters characterize their covalent contribution. Since the electrostatic and covalent contributions are considered independent, the expression for the enthalpy of dissociation of the complex into a Lewis acid and base has the form [5]:

$$\Delta_{\text{diss}} H_{298}^{\circ} = E_A E_B + C_A C_B + W. \quad (1)$$

The  $W$  parameter includes all constant (counterpart-independent) contributions to the change in the dissociation enthalpy that are specific for a particular Lewis acid or particular Lewis base. It cannot be selected and determined exclusively within the framework of the model. An example of this contribution is the enthalpy of dissociation of the dimer form of the Lewis acid Al<sub>2</sub>Cl<sub>6</sub> into monomers during the formation of AlCl<sub>3</sub> complexes with Lewis bases [6]. As the main assumption in Drago's approach is that the dissociation enthalpy of a donor–acceptor complex is determined only by the electrostatic and covalent contributions, the model can be called the electrostatic-covalent model, or simply the EC model.

As would be expected, the EC model has limited applicability. Thus, Drago indicated that the EC model neglects the steric factor [7] and  $\pi$ -back donation [8]. These factors lead to significant deviations of the dissociation enthalpies of DA complexes predicted within the EC model from the experimental values in nonaqueous solutions. A more global problem of the

EC model is the choice of reference compounds. If the DA complexes of reference Lewis acids and bases have additional interactions that are not taken into account within the EC model, this may lead to a systematic error in estimating the dissociation enthalpies of the complexes.

The use of the EC model is based on the fact that the electrostatic and covalent Lewis acid–base interactions are fundamental and make the major contribution to the dissociation enthalpy of any donor–acceptor complex. Therefore, it is possible, firstly, to select such reference donor–acceptor complexes for which the contribution of other interactions to the dissociation enthalpy is minimum. Secondly, it is possible to identify donor–acceptor complexes for which there are significant deviations of the dissociation enthalpy from that predicted using the simple EC model. For these complexes, the use of the EC model makes it possible to estimate the contributions of other Lewis acid–base interactions (e.g., dispersion interactions) to the dissociation enthalpy of the donor–acceptor complex.

The main advantage of the EC model is its simplicity: using only four parameters, the model allows us to predict the dissociation enthalpies of donor–acceptor complexes with an accuracy on the order of 1 kcal/mol [5]. Note that Drago’s approach allows us to extend the EC model to similar energy characteristics of the dissociation processes of DA complexes. Thus, the  $E_A$ ,  $C_A$ ,  $E_B$ , and  $C_B$  parameters can be used to estimate not only the experimental dissociation enthalpies of DA complexes in nonaqueous solutions, but also the values obtained by quantum–chemical methods: gas-phase dissociation enthalpies, dissociation energies of DA complexes, and DA bond energies in the complexes.

In this study, we examined the applicability of the EC model for estimating the dissociation energies of DA complexes and the DA bond energies.

## EXPERIMENTAL

The parameters were optimized by the Powell method [9] using the SciPy software package [10] and the objective functions  $f_1$ :

$$f_1(E_{A1} \dots E_{An}, C_{A1} \dots C_{An}, E_{B1} \dots E_{Bn}, C_{B1} \dots C_{Bn}) = \sum_{i=1}^n \sum_{j=1}^n \sqrt{(\Delta_{\text{diss}} E_{0ij} - [E_{Ai} E_{Bj} + C_{Ai} C_{Bj}])^2} \quad (2)$$

and  $f_2$ :

$$f_2(E_{A1} \dots E_{An}, C_{A1} \dots C_{An}, E_{B1} \dots E_{Bn}, C_{B1} \dots C_{Bn}) = \sum_{i=1}^n \sum_{j=1}^n \left( \frac{L}{1 + e^{-k(\text{err}_{ij} - x_0)}} - 1 \right) \text{err}_{ij},$$

where

$$\text{err}_{ij} = \frac{\Delta_{\text{diss}} E_{0ij} - (E_{Ai} E_{Bj} + C_{Ai} C_{Bj})}{E_0}, \quad (3)$$

as well as the binomial function. However, when using the binomial function, less accuracy was achieved than when using the logistic function  $f_2$ . The numerical solution was found with a specified sufficient accuracy of no worse than 0.1 kJ/mol. Unlike Drago’s original works, here the parameters of the EC model were calculated in such a way that the dimensionality of the dissociation energy obtained by substituting them into the equation

$$\Delta_{\text{diss}} E_0 = E_A E_B + C_A C_B \quad (4)$$

was kJ/mol. The optimization procedure is quite simple and the calculation of parameters takes a few hours.

## RESULTS AND DISCUSSION

As objects of study, we chose 18 Lewis bases based on group 13–15 elements  $E'H_2EH_2 \cdot LB$  ( $E' = P, As, Sb$ ;  $E = B, Al, Ga$ ;  $LB = SME_2, NMe_3$ ) and 18 Lewis acids of group 13 elements  $ER_3$  ( $R = H, F, Cl, Br, Me, C_6F_5$ ). As reference data, we used the energies of gas-phase dissociation of DA complexes into free Lewis acid and base calculated by the B3LYP-D3/def2-TZVP quantum–chemical method in [11] (a total of 322 complexes).

As the compounds exist in the form of monomers, the  $W$  parameter for them is zero, and Eq. (1) can be recorded as Eq. (4).

Unlike Drago’s works, in which  $E_A$ ,  $E_B$ ,  $C_A$ ,  $C_B$  were set arbitrarily for reference compounds, the statistical approach was used here to avoid problems associated with the choice of reference acids and bases.

The main equation of the EC model (4) can be written in matrix form:

$$[E_A C_A] \begin{bmatrix} E_B \\ C_B \end{bmatrix} = \Delta_{\text{diss}} E_0(AB). \quad (5)$$

In matrix form the equation can be written for a set of  $n$  acids and  $n$  Lewis bases at once:

$$= \begin{bmatrix} E_{A1} C_{A1} \\ \dots \\ E_{An} C_{An} \end{bmatrix} \begin{bmatrix} E_{B1} \dots E_{Bn} \\ C_{B1} \dots C_{Bn} \end{bmatrix} = \begin{bmatrix} \Delta_{\text{diss}} E_0(A1B1) \dots \Delta_{\text{diss}} E_0(A1Bn) \\ \dots \\ \Delta_{\text{diss}} E_0(AnB1) \dots \Delta_{\text{diss}} E_0(AnBn) \end{bmatrix}. \quad (6)$$

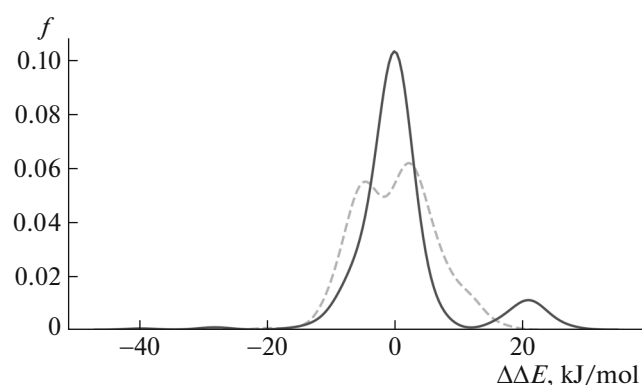
Below we take into account the entire set of parameters  $E_{An}$ ,  $C_{An}$ ,  $E_{Bn}$ ,  $C_{Bn}$  of Lewis acids and bases, unless the particular parameters in question are indicated.

For a set of Lewis acids and bases, the problem is reduced to optimization of the parameters that make it possible to find a numerical solution to the matrix equation (6) without finding an analytical solution. The multidimensional optimization problem was solved by Powell's method [9], which allows determination of the local minima of the objective function (objective function minimization). Objective functions can be selected to control the error distribution of the resulting model. To estimate the dissociation energies of the donor-acceptor complexes, the objective function  $f_1$  is given by Eq. (2).

For the entire set of DA complexes, the parameters of Lewis acids and bases are optimized to achieve the smallest sum of standard deviations  $\Delta\Delta E$  of the dissociation energies calculated by Eq. (4) from the calculated dissociation energies obtained in [11]. Then, using the obtained parameters, it is possible to calculate the dissociation energies of donor-acceptor complexes corresponding to all possible combinations of parameterized Lewis acids and bases using Eq. (4).

The factors that are not taken into account by the EC model (with errors thus introduced in the predicted values) impose restrictions on the sets of initial data that can be used for parameterization of Lewis acids and bases. To eliminate systematic errors in parameterization, as initial data it is necessary to consider the characteristics of a set of donor-acceptor complexes in which the influence of factors not included in the EC model is minimized. When using the statistical EC model, these limitations are mostly mitigated. The proposed method can be used to search for donor-acceptor complexes whose energetics has a significant contribution from the interactions neglected by the EC model. For this, instead of the  $f_1$  function, logistic function  $f_2$  (3) can be used as an objective function in parameter optimization.

This function does not simply correspond to the sum of differences  $\Delta\Delta E$ ; each deviation is assigned a statistical weight that depends on  $\Delta\Delta E$ . The  $x_0$  parameter determines the value of the function at its minimum. As we seek the minimum deviation,  $x_0 = 0$ . The  $E_0$  parameter separates the  $\Delta\Delta E$  values for which the statistical weight asymptotically approaches zero as  $\Delta\Delta E$  increases from the  $\Delta\Delta E$  values for which the statistical weight quickly approaches its maximum as  $\Delta\Delta E$  decreases. We chose  $E_0 = 4.184$  kJ/mol, since Drago noted that the EC model allows an accuracy on the order of one kilocalorie per mole [5]. The  $L$  parameter determines the maximum value of the statistical weight. The  $k$  parameter determines the rate at which the statistical weight of  $\Delta\Delta E$  approaches zero or maximum when  $\Delta\Delta E$  deviates from  $E_0$ . The functions with  $L = 1, 2$  and  $k = 0.25, 0.5, 1, 2, 4$  were tested. The error in the dissociation energy calculation by Eq. (4) is the lowest when the logistic function  $f_2$  is used with  $L = 2$  and  $k = 2$ .

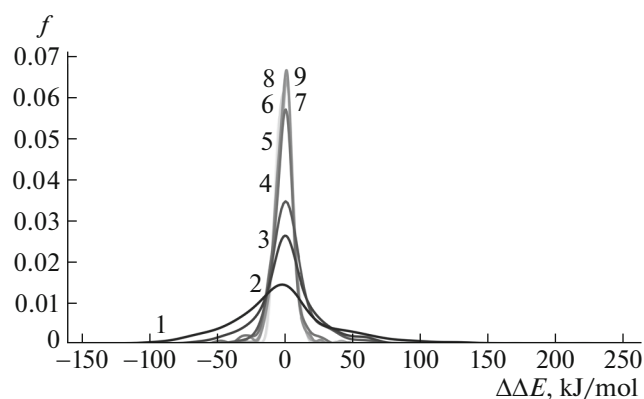


**Fig. 1.** Distribution graph of  $\Delta\Delta E$ . Distribution of differences obtained using the objective functions  $f_1$  (dashed line) and  $f_2$  (solid line).

In the dissociation energy calculation of donor-acceptor complexes with the parameters optimized using the objective function  $f_1$  and substituted into Eq. (4), the average absolute difference  $|\overline{\Delta\Delta E}|$  between the dissociation energies calculated by quantum-chemical methods ( $\Delta_{\text{diss}}E_{\text{QCC}}$ ) and those calculated by Eq. (4) ( $\Delta_{\text{diss}}E_{\text{EC}}$ ) is 5.0 kJ/mol. The absolute median error is  $\mu = 4.3$  kJ/mol, the interquartile range is  $q = 8.7$  kJ/mol, and the standard deviation of the difference is  $\sigma = 6.2$  kJ/mol. Thus, we can determine the error of dissociation energy calculated using the EC model relative to the dissociation energy obtained using quantum-chemical calculations:  $\varepsilon = |\overline{\Delta\Delta E}| + 2\sigma$  [12]. For the given set of donor-acceptor complexes,  $\varepsilon = \pm 17.4$  kJ/mol.

When calculating the dissociation energies of donor-acceptor complexes with the parameters optimized using the objective function  $f_2$  and substituted into Eq. (2),  $|\overline{\Delta\Delta E}| = 4.2$  kJ/mol;  $\mu = 1.2$  kJ/mol;  $q = 2.5$  kJ/mol; and  $\sigma = 7.8$  kJ/mol. When using the logistic function  $f_2$  compared with the case of the objective function  $f_1$ , the error  $\varepsilon$  increases to  $\pm 19.8$  kJ/mol, but the absolute average error, and especially the median error, decreases significantly ( $\mu$  decreases from 4.3 to 1.2 kJ/mol, i.e., more than three times). The graphs of distribution of the differences  $\Delta\Delta E$  obtained using the objective functions  $f_1$  and  $f_2$  are shown in Fig. 1.

The predictive ability of the model was determined by the following procedure. First, the minimum required sample was randomly composed, which included two donor-acceptor complexes of each Lewis base and two complexes of each Lewis acid (a total of 36 complexes). Based on the dissociation energies known for these donor-acceptor complexes, the  $E$  and  $C$  parameters were determined for each Lewis acid and each Lewis base. Then the dissociation energies of all 322 donor-acceptor complexes were calculated by Eq. (4) using the obtained parameters. In subsequent



**Fig. 2.** Distribution graph of  $\Delta\Delta E$  for different sample sizes used to determine the parameters in the EC model. The numbers indicate the sample size  $m$  (Table 1).

iterations, another 36 complexes were added to the sample, which were randomly selected in such a way that they included two complexes of each Lewis base and each Lewis acid. The  $E$  and  $C$  parameters were newly optimized, and the dissociation energies of all 322 donor-acceptor complexes were calculated using Eq. (4). Figure 2 presents the graphs of error distribution for the dissociation energies of the donor-acceptor complexes determined by Eq. (4). The absolute mean values of the difference, absolute median errors, standard deviations of the difference, interquartile range of the difference, and the errors of the dissociation energy of the complex are given in Table 1.

From the data obtained it follows that using only 180 out of 322 dissociation energies of donor-acceptor

**Table 1.** Absolute average values of the error  $|\overline{\Delta\Delta E}|$ , absolute median errors  $\mu$ , standard deviation errors  $\sigma$ , interquartile range of the error  $q$ , and errors  $\epsilon$  in determining the dissociation energy of the complex by Eq. (4) for different sample sizes ( $X$ )

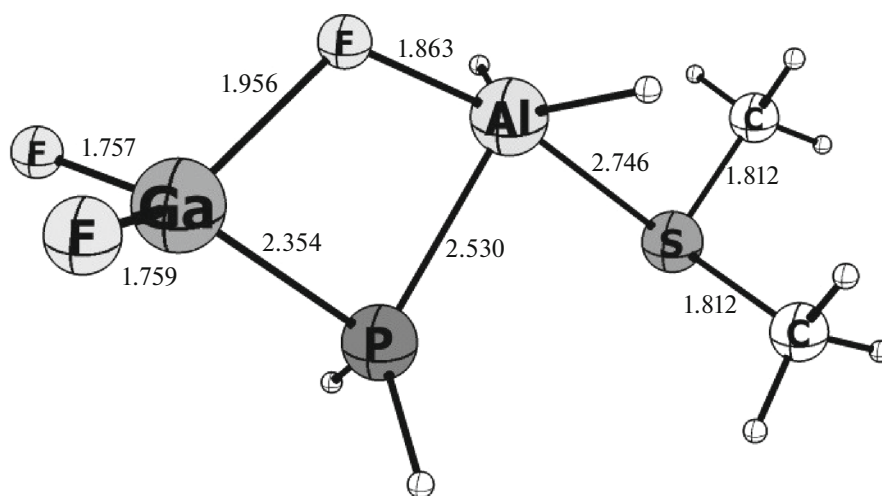
$m$	$X$	$ \overline{\Delta\Delta E} $	$\mu$	$\sigma$	$q$	$\epsilon$
		kJ/mol				
1	36	27.2	17.0	39.7	34.6	106.6
2	72	15.4	8.6	23.3	16.2	62.0
3	108	11.1	3.5	25.2	8.3	61.5
4	144	6.7	4.1	10.4	8.6	27.5
5	180	5.3	3.8	7.4	7.6	20.1
6	216	5.4	4.1	7.8	7.8	21.0
7	252	5.3	3.9	7.3	8.3	19.9
8	288	4.9	3.8	6.5	7.7	17.9
9	322	4.9	4.0	6.2	8.2	17.3

complexes to determine the parameters, we can obtain the values of parameters whose substitution into Eq. (4) makes it possible to determine the dissociation enthalpies for all 322 donor-acceptor complexes with  $\mu \sim 4$  kJ/mol and  $\epsilon \sim 20$  kJ/mol. An increase in the sample size does not lead to a significant reduction in the error. Thus, based on the data on 180 dissociation energies of donor-acceptor complexes calculated using the model, it is possible to estimate the dissociation energies of the remaining donor-acceptor complexes with  $\epsilon = \pm 20$  kJ/mol. The relatively low accuracy of estimation is compensated by the simple calculation procedure and high speed of computing.

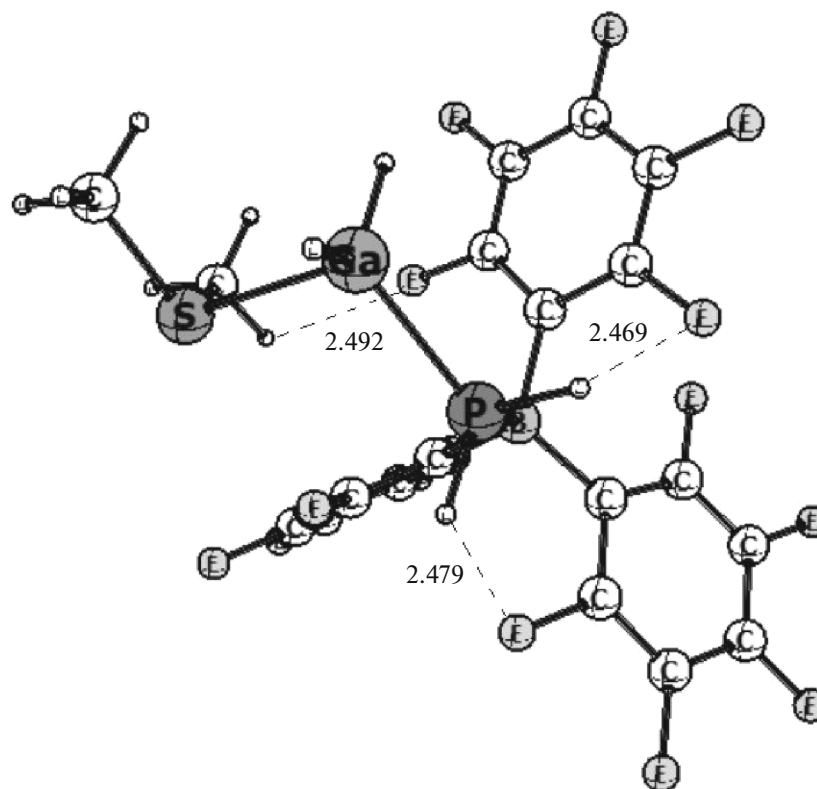
The reason for the high error may be the high energy of rearrangement of the acceptor fragment of the complex during complexation, which is not included in the EC model. Another reason may be additional Lewis acid–base interactions during complexation.

The use of the  $f_2$  function makes it possible to detect, among the donor-acceptor complexes for which the values of the dissociation enthalpy (or other selected thermodynamic or energy characteristic) are known, those complexes whose dissociation enthalpies calculated by Eq. (4) differ significantly from the experimental ones or from the ones obtained by quantum-chemical methods. Such differences will indicate that the donor-acceptor complex has interactions that are not included in the EC model. It is possible to detect individual pairs of Lewis acids and bases, interacting with occurrence of some specific processes, as well as Lewis acids or bases whose donor-acceptor complexes (all or majority) show deviation of the experimental dissociation enthalpies from the values predicted by the EC model. In the latter case, we can draw conclusions about the peculiarities of complexation of a particular Lewis acid or base. Thus, the largest absolute value of  $\Delta\Delta E = -39.7$  kJ/mol is characteristic of the compound  $\text{GaF}_3 \cdot \text{PH}_2\text{AlH}_2 \cdot \text{SMe}_2$ , whose optimized structure is shown in Fig. 3. This cyclic structure has a fluoride bridge between the gallium and aluminum atoms, which increases the energy of dissociation of the complex into components. Thus,  $\Delta_{\text{diss}} E_{\text{EC}}$  is underestimated compared with  $\Delta_{\text{diss}} E_{\text{QCC}}$ , just as the EC model underestimates the dissociation enthalpy of donor-acceptor complexes in which  $\pi$ -back donation is observed [8]. Additional stabilization due to intramolecular interactions also leads to negative  $\Delta\Delta E$  values [13]. An example is the  $\text{B}(\text{C}_6\text{F}_5)_3 \cdot \text{PH}_2\text{GaH}_2 \cdot \text{SMe}_2$  complex ( $\Delta\Delta E = -6.4$  kJ/mol, Fig. 4), which has two H–F short contacts, which are smaller than the sum of the van der Waals radii of hydrogen and fluorine (2.57 Å [14]).

The reason for the significant positive values of  $\Delta\Delta E$  may be the high energy of fragment rearrangement during complexation. Since significant structural changes in the Lewis acid and base during complexation overestimate  $\Delta_{\text{diss}} E_{\text{EC}}$  compared with



**Fig. 3.** Cyclic structure obtained by geometry optimization of the  $\text{GaF}_3 \cdot \text{PH}_2\text{AlH}_2 \cdot \text{SMe}_2$  donor-acceptor complex. The bond lengths are given in Å.



**Fig. 4.** Optimized geometry of the donor-acceptor complex  $\text{B}(\text{C}_6\text{F}_5)_3 \cdot \text{PH}_2\text{GaH}_2 \cdot \text{SMe}_2$ . The H–F internuclear distances are given in Å.

$\Delta_{\text{diss}}E_{\text{QCC}}$ , and additional Lewis acid–base interactions underestimate  $\Delta_{\text{diss}}E_{\text{EC}}$  compared with  $\Delta_{\text{diss}}E_{\text{QCC}}$ , their mutual influence can lead to low absolute values of  $\Delta\Delta E$ , which increases the accuracy of the model.

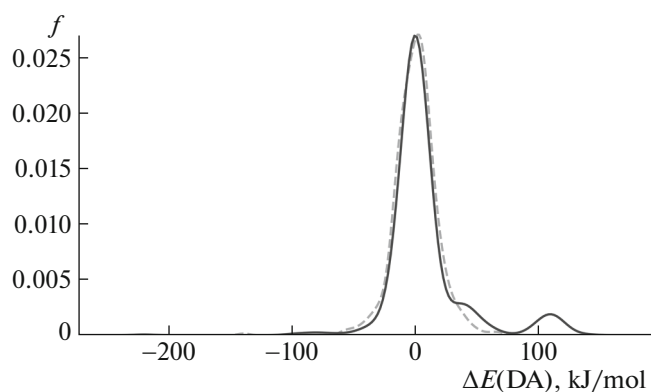
The dissociation energies obtained by quantum-chemical calculations and Eq. (4), as well as their differences for a number of complexes, are given in Table 2. In general, the analysis shows that the EC model gives much worse predictions for the dissocia-



**Table 2.** Dissociation energies obtained by quantum-chemical calculations  $\Delta_{\text{diss}}E_{\text{QCC}}$  and those calculated by Eq. (4)  $\Delta_{\text{diss}}E_{\text{EC}}$  using the parameters optimized with the objective function  $f_2$  and their differences  $\Delta\Delta E$  for some complexes

Compound	$\Delta_{\text{diss}}E_{\text{QCC}}$ , kJ/mol	$\Delta_{\text{diss}}E_{\text{EC}}$ , kJ/mol	$\Delta\Delta E$ , kJ/mol
$\text{BH}_3 \cdot \text{PH}_2\text{AlH}_2 \cdot \text{SMe}_2$	106.6	108.0	1.4
$\text{BH}_3 \cdot \text{AsH}_2\text{AlH}_2 \cdot \text{SMe}_2$	82.6	88.6	6.0
$\text{BH}_3 \cdot \text{SbH}_2\text{AlH}_2 \cdot \text{NMe}_3$	62.2	63.9	1.7
$\text{GaF}_3 \cdot \text{PH}_2\text{AlH}_2 \cdot \text{SMe}_2$	178.0	138.3	-39.7
$\text{GaF}_3 \cdot \text{AsH}_2\text{AlH}_2 \cdot \text{SMe}_2$	120.2	124.6	4.4
$\text{GaF}_3 \cdot \text{SbH}_2\text{AlH}_2 \cdot \text{NMe}_2$	103.2	103.2	0.0
$\text{BCl}_3 \cdot \text{AsH}_2\text{BH}_2 \cdot \text{NMe}_3$	40.5	66.1	25.6
$\text{GaCl}_3 \cdot \text{PH}_2\text{AlH}_2 \cdot \text{SMe}_2$	142.0	141.1	-0.9
$\text{GaCl}_3 \cdot \text{SbH}_2\text{AlH}_2 \cdot \text{SMe}_2$	110.8	111.4	0.6
$\text{AlBr}_3 \cdot \text{PH}_2\text{AlH}_2 \cdot \text{SMe}_2$	145.9	145.1	-0.8
$\text{AlBr}_3 \cdot \text{AsH}_2\text{AlH}_2 \cdot \text{SMe}_2$	132.0	130.5	-1.5
$\text{Al}(\text{C}_6\text{F}_5)_3 \cdot \text{SbH}_2\text{AlH}_2 \cdot \text{NMe}_3$	104.9	111.0	6.1
$\text{AlMe}_3 \cdot \text{PH}_2\text{AlH}_2 \cdot \text{SMe}_2$	60.3	63.6	3.3
$\text{AlMe}_3 \cdot \text{AsH}_2\text{AlH}_2 \cdot \text{SMe}_2$	52.2	52.1	-0.1
$\text{AlMe}_3 \cdot \text{SbH}_2\text{AlH}_2 \cdot \text{SMe}_2$	38.2	38.2	0.0
$\text{B}(\text{C}_6\text{F}_5)_3 \cdot \text{PH}_2\text{AlH}_2 \cdot \text{SMe}_2$	98.5	93.7	-4.8
$\text{GaBr}_3 \cdot \text{SbH}_2\text{BH}_2 \cdot \text{NMe}_3$	91.0	107.7	16.7
$\text{B}(\text{C}_6\text{F}_5)_3 \cdot \text{AsH}_2\text{AlH}_2 \cdot \text{SMe}_2$	75.4	72.9	-2.5

tion energies of the Lewis base complexes  $\text{EH}_2\text{BH}_2 \cdot \text{LB}$  ( $\text{E} = \text{P}, \text{As}, \text{Sb}$ ;  $\text{LB} = \text{NMe}_3, \text{SMe}_2$ ) than for the dissociation energies of the complexes  $\text{EH}_2\text{AlH}_2 \cdot \text{LB}$  and



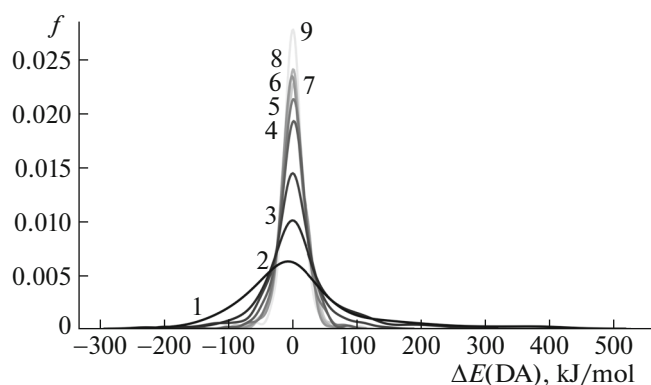
**Fig. 5.** Distribution graph of  $\Delta E(\text{DA})$ . Distribution of differences obtained using the objective functions  $f_1$  (dashed line) and  $f_2$  (solid line).

$\text{EH}_2\text{GaH}_2 \cdot \text{LB}$  ( $\text{E} = \text{P}, \text{As}, \text{Sb}$ ;  $\text{LB} = \text{NMe}_3, \text{SMe}_2$ ). As for Lewis acids, the EC model gives worse predictions for the dissociation energies of the complexes of group 13 halides than for the complexes of hydrides and trimethyl and perfluoro derivatives. The reason for this may be short contacts of Lewis acid halogen atoms with the protons of methyl groups at the nitrogen and sulfur atoms of the Lewis bases, most appreciable for boron-containing compounds, since the smallest radius of the boron atom allows the Lewis acid to be located closer to the  $\text{NMe}_3$  or  $\text{SMe}_2$  group.

For compounds with large absolute values of  $\Delta\Delta E$ , the  $\Delta\Delta E$  values are assigned nearly zero statistical weights during parameterization, which has minimum effect on the optimized  $E$  and  $C$  parameters. Excluding these compounds from the sample does not significantly improve the predictive ability of the model because their near-zero statistical weights. However, excluding the compounds for which the model predicts the dissociation energy with the largest error allows prediction of dissociation energies for a reduced set with smaller average and median errors. Thus, exclusion of 34 donor-acceptor complexes with the largest absolute values of  $\Delta\Delta E$  followed by re-optimization of parameters using the objective functions  $f_1$  and  $f_2$  gave the distributions of  $\Delta\Delta E$  for the remaining 288 complexes with the following parameters: when using the objective function  $f_1$ ,  $|\overline{\Delta\Delta E}| = 3.0$  kJ/mol;  $\mu = 2.0$  kJ/mol;  $q = 4.0$  kJ/mol;  $\sigma = 4.5$  kJ/mol;  $\varepsilon = \pm 12.0$  kJ/mol; when using the objective function  $f_2$ ,  $|\overline{\Delta\Delta E}| = 2.8$  kJ/mol;  $\mu = 2.7$  kJ/mol;  $q = 5.4$  kJ/mol;  $\sigma = 3.3$  kJ/mol;  $\varepsilon = \pm 9.4$  kJ/mol.

The EC model can also be used to calculate other energy characteristics of donor-acceptor complexes. Thus, we used the donor-acceptor bond energies in complexes obtained by quantum-chemical methods [11] to determine the donor-acceptor bond energy using the EC model. When calculating the donor-acceptor bond energies with the parameters optimized using  $f_1$  and substituted into Eq. (4), the average absolute difference  $|\overline{\Delta E(\text{DA})}|$  between the dissociation energies  $E(\text{DA})_{\text{QCC}}$  and  $E(\text{DA})_{\text{EC}}$  calculated by quantum-chemical methods by Eq. (4) is 21.9 kJ/mol;  $\mu = 12.0$  kJ/mol;  $q = 26.8$  kJ/mol;  $\sigma = 28.8$  kJ/mol;  $\varepsilon = \pm 79.5$  kJ/mol.

When calculating the donor-acceptor bond energies with the parameters optimized using  $f_2$  and substituted into Eq. (4),  $|\overline{\Delta E(\text{DA})}|$  is 10.0 kJ/mol;  $\mu = 3.8$  kJ/mol;  $q = 7.4$  kJ/mol;  $\sigma = 21.6$  kJ/mol. The error  $\varepsilon$  in the case of using  $f_2$  compared to the case of using  $f_1$  is reduced to  $\pm 53.2$  kJ/mol. The distribution graphs of the differences  $\Delta E(\text{DA})$  obtained using the objective functions  $f_1$  and  $f_2$  are shown in Fig. 5. Thus, the error in estimating the donor-acceptor bond energy within the EC model exceeds the error of the dissociation energy of the donor-acceptor complex 2.85-fold and is



**Fig. 6.** Distribution graph of  $\Delta E(\text{DA})$  for different sample sizes used to determine the parameters in the EC model. The numbers indicate the sample size  $m$  (Table 1).

unsatisfactory. The distribution graphs of errors in determining the dissociation energy of donor-acceptor complexes by Eq. (4) are shown in Fig. 6. Table 3 presents the absolute mean value of the difference, absolute median error, standard deviation of the difference, interquartile range of the difference, and error of the dissociation energy of the complex.

From the data obtained it follows that when using only 180 out of 322 donor-acceptor bond energies for parameterization, it is possible to obtain the values of parameters whose substitution into Eq. (4) makes it possible to determine the DA bond energies for all 322 donor-acceptor complexes with  $\mu \sim 9$  kJ/mol and  $\varepsilon \sim 50$  kJ/mol.

**Table 3.** Absolute average values of error, absolute median errors, standard deviations of error, interquartile range of error, and errors of the donor-acceptor bond energy determined by Eq. (4) for different sample sizes ( $X$ )

$m$	$X$	$ \overline{\Delta E(\text{DA})} $	$\mu$	$\sigma$	$q$	$\varepsilon$
		kJ/mol				
1	36	68.5	48.2	94.3	101.4	271.3
2	72	48.0	16.9	85.9	34.3	116.6
3	108	21.4	11.8	35.2	23.1	67.6
4	144	17.7	11.0	28.1	21.6	60.9
5	180	13.9	8.7	23.1	17.4	48.7
6	216	12.9	8.8	20.8	18.0	48.9
7	252	14.0	9.2	21.1	19.0	52.0
8	288	13.0	9.1	18.5	17.8	48.6
9	322	12.5	9.7	18.0	19.7	51.9

To summarize, an algorithm for calculating the parameters of the EC model has been proposed, which does not require the introduction of parameters for reference compounds and can be implemented with modern computer facilities. The results show the possibility of using the statistical EC model with data from quantum-chemical calculations on the energies of dissociation of donor-acceptor complexes into free Lewis acids and bases for fast estimation of the dissociation energies of the donor-acceptor complexes that are other combinations of these Lewis acids and bases with an absolute median error of 4.3 kJ/mol. It was shown that the EC model is inapplicable for estimating the donor-acceptor bond energy.

#### SUPPLEMENTARY INFORMATION

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#### CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

#### REFERENCES

1. A. Staubitz, A. P. M. Robertson, M. E. Sloan, and I. Manners, *Chem. Rev.* **110**, 4023 (2010). <https://doi.org/10.1021/cr100105a>
2. U. Vogel, A. Y. Timoshkin, and M. Scheer, *Angew. Chem. Int. Ed.* **40**, 4409 (2001). [https://doi.org/10.1002/1521-3773\(20011203\)40:23<4409::AID-ANIE4409>3.0.CO;2-F](https://doi.org/10.1002/1521-3773(20011203)40:23<4409::AID-ANIE4409>3.0.CO;2-F)
3. R. S. Drago and B. B. Wayland, *J. Am. Chem. Soc.* **87**, 3571 (1965). <https://doi.org/10.1021/JA01094A008>
4. A. P. Marks and R. S. Drago, *J. Am. Chem. Soc.* **97**, 3324 (1975). <https://doi.org/10.1021/ja00845a008>
5. G. C. Vogel and R. S. Drago, *J. Chem. Educ.* **73**, 701 (1996). <https://doi.org/10.1021/ed073p701>
6. R. S. Drago, G. C. Vogel, and T. E. Needham, *J. Am. Chem. Soc.* **93**, 6014 (1971). <https://doi.org/10.1021/ja00752a010>
7. R. S. Drago, *Coord. Chem. Rev.* **33**, 251 (1980). [https://doi.org/10.1016/S0010-8545\(00\)80456-7](https://doi.org/10.1016/S0010-8545(00)80456-7)
8. R. S. Drago and C. Bilgrien, *Polyhedron* **7**, 1453 (1988). [https://doi.org/10.1016/S0277-5387\(00\)81774-X](https://doi.org/10.1016/S0277-5387(00)81774-X)

9. M. J. D. Powell, *Comput. J.* **7**, 155 (1964).  
<https://doi.org/10.1093/comjnl/7.2.155>
10. P. Virtanen, R. Gommers, T. E. Oliphant, et al., *Nat. Methods* **17**, 261 (2020).  
<https://doi.org/10.1038/s41592-019-0686-2>
11. A. V. Pomogaeva, A. S. Lisovenko, and A. Y. Timoshkin, *Russ. J. Gen. Chem.* **93**, 900 (2023).  
<https://doi.org/10.1134/S1070363223040175>
12. I. I. Eliseeva and M. M. Yuzbashev, *General Theory of Statistics* (Finansy Statistika, Moscow, 2004), p. 138 [in Russian].
13. S. Ketkov, E. Rychagova, R. Kather, and J. Beckmann, *J. Organomet. Chem.* **949**, 121944 (2021).  
<https://doi.org/10.1016/j.jorgchem.2021.121944>
14. M. Mantina, A. C. Chamberlin, R. Valero, et al., *J. Phys. Chem. A* **113**, 5806 (2009).  
<https://doi.org/10.1021/jp8111556>

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