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PHYSICAL CHEMISTRY

A Graph Theory Method for Determining the Basis of Homodesmic Reactions for Acyclic Chemical Compounds

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Abstract—One of the techniques for theoretically determining enthalpies of formation of organic compounds is the method of homodesmic reactions. In this work, a graph theory interpretation of acyclic chemical compounds was presented, and an algorithm for constructing a basis of homodesmic reactions was developed, which makes it possible to use a homodesmic approach to calculating the enthalpy of formation. Using the developed algorithm was exemplified by building the basis of homodesmic reactions for the butyramide molecule.

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Thermodynamic parameters of chemical compounds, in particular, standard enthalpies of formation $\Delta_f H°$, are fundamental characteristics of energy contents of substances and are necessary for analyzing mechanisms of chemical reactions in engineering calculations. Because of the lack of experimental data, researchers developed various variants of approximate calculations of thermodynamic quantities $\Delta_f H°$ [1–4], including those using modern quantum chemical approaches. In our opinion, the most reliable technique for theoretically predicting the enthalpy of formation of a chemical compound is a comparative calculation method based on homodesmic reactions (HDR), which are defined as isodesmic processes supplemented with a group balance condition [5, 6].

The HDR method is conveniently used as a reaction of separation of groups. A group is taken to mean a polyvalent atom of a molecule together with all of the atom's ligands, i.e., atoms bound to the central atom by single covalent bonds [7]. The compound being studied is decomposed into a set of compounds that contain all its thermochemical groups. A similar approach was applied in our previous work [8], where a basis set of routes (independent subgraphs of the graph of a complex chemical reaction) allowed one to examine submechanisms for compliance with a basis of nonlinear parametric functions of kinetic parameters.

In the general case for an arbitrary chemical compound, the choice of HDR is ambiguous. The determination of all the basis (independent) HDR enables one to make independent estimates of $\Delta_f H°$, control the reproducibility of results, and thereby improve the reliability of the theoretical determination of the standard enthalpy of formation of a chemical compound [6].

This poses the problem of constructing an HDR basis and developing the corresponding algorithm for determining it. Earlier [6], we described the mathematical background and software for a homodesmic method for calculating standard enthalpy of formation. We also characterized the main stages of developing a program that implements an algorithm for determining an HDR basis by analyzing matrices of bonds and groups. In this work, we presented a graph theory interpretation, which also makes it possible to automate the procedure of selecting an HDR basis. Using graphs favors the illustrative geometric interpretation of the bases, which is important for the following physicochemical analysis. The purpose of this work was to develop a graph theory algorithm for constructing an HDR basis implementing a homodesmic approach to calculating enthalpies of formation.

To gain a better insight into the subject, the explanation of theoretical aspects was accompanied by illustrative visualization.

An acyclic chemical compound can obviously be represented as a member of a special class of graphs—a tree. Vertices of the tree of a chemical compound

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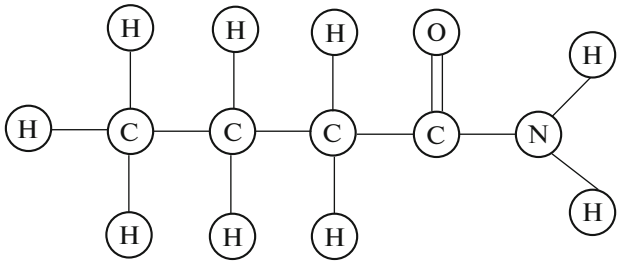

Fig. 1. Graph of butyramide molecule.

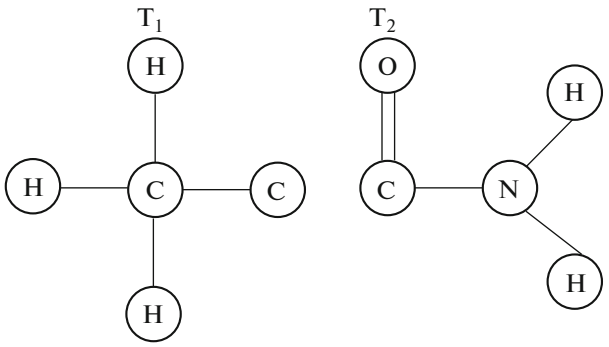

Fig. 2. Terminal groups T_1 and T_2 of butyramide molecule.

represent atoms constituting its molecule. Edges connecting vertices of the tree of a chemical compound are bonds between atoms. As an example, let us consider the tree of a molecule of butyramide $PrCONH_2$ (Fig. 1).

The structure of a chemical compound is represented as a set of groups: internal and terminal. In a terminal group, the central atom is bound to one and only one polyvalent ligand. In an internal group, there are no less than two polyvalent ligands.

Thus, using Benson's notation of thermochemical groups [7], one can see that the $PrCONH_2$ molecule is constituted by two types of terminal groups (T_1, T_2) and three types of internal groups (I_1, I_2, I_3) (Figs. 2, 3). Multiple edges connecting the vertices corresponding to C and O atoms indicate double bonds. In Benson's terms, atoms bound to each other by multiple bonds enter into the composition of thermochemical groups (both internal and terminal) as a single complex atom.

The $PrCONH_2$ molecule contains chemical bonds of five types: C–H, C–C, N–H, N–C, and C=O.

Let us refer to a group comprising several adjacent internal groups of a compound as a complex internal group (Fig. 4).

To decompose a compound, it is necessary to determine all possible combinations of internal and complex internal groups. Note that, in each of such combinations, the number of various internal groups is equal to the number of such groups in the compound being studied. If the molecule is symmetric, combinations in the basis are fewer.

An algorithm for constructing an HDR basis of cyclic chemical compounds consists of the following stages:

(1) Determine all possible combinations of internal groups constituting the chemical compound.

A combination of internal groups is taken to mean the sum of combinations of m internal groups forming the chemical compound, taken n at a time ($n < m$). Such combinations are independent (different from each other) subgraphs of the molecular graph.

(2) For each term consisting of one or several internal groups, select terminal groups from those occurring in the chemical compound. If there are no suitable terminal groups among them, construct a new one produced from an adjacent simple internal group by replacing the ligand by a hydrogen atom H. Form the right-hand sides of HDR.

(3) To determine a reactant (reactants) for the chemical compound, take into account the group composition of the products of the right-hand sides of HDR. The reactants are assembled from terminal groups occurring in the products. Determine the stoichiometric coefficients in HDR according to the group balance, i.e., the conservation of the number of (internal and terminal) groups of each type.

The $PrCONH_2$ molecule (Fig. 1) is characterized by five independent subgraphs: I_1, I_2, I_3, I_1I_2, and I_2I_3 (Figs. 3, 4). From them, three independent combinations can be made: $I_1 + I_2 + I_3$, $I_1I_2 + I_3$, and $I_1 + I_2I_3$.

For each term in a combination, suitable terminal groups should be selected. Let us illustrate the formation of a product of HDR by the example of internal group I_2. The tree corresponding to internal group I_2 contains six vertices and six edges. The vertices describe three carbon (C) atoms, two hydrogen (H) atoms, and one oxygen (O) atom. The edges characterize chemical bonds C–H, C–C, and C=O. Bearing in mind that the doubled number of chemical bonds is equal to the sum of the valences of atoms of the chemical compound, we can solve the equation $4 \times 3 + 2 \times 1 + 1 \times 2 + 1 \times x = 2(6 + x)$, where x denotes the number of H atoms that should be taken to complement internal group I_2. Hence, we have $x = 4$ and obtain term $T_1I_2T_3$, where T_3 is a new terminal group produced from I_3 by replacing the N atom by H.

Thus, for terms in the determined combinations, we have $T_1I_1T_1$, $T_1I_2T_3$, $T_1I_3T_2$, $T_1I_1I_2T_3$, and $T_1I_2I_3T_2$. These compounds are a set of possible products of the basis HDR.

Further, to determine reactants, account should be taken of the group balance: the conservation of the number of groups of each type in HDR. For example, the first combination contains three terminal groups T_1, one group T_2, and one group T_3. The compound being studied has one terminal group T_1 and one ter-

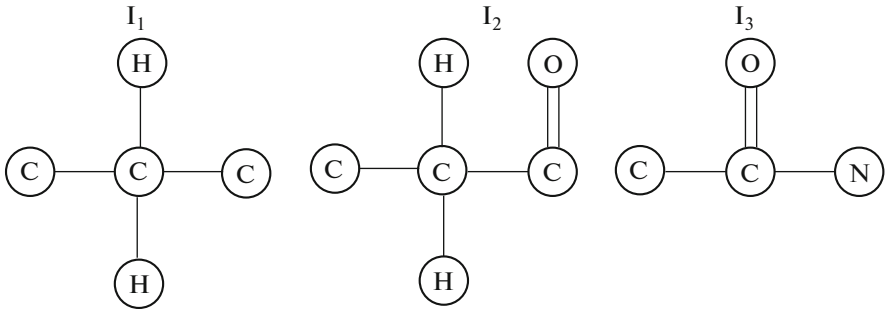

Fig. 3. Internal groups I_1, I_2, and I_3 of butyramide molecule.

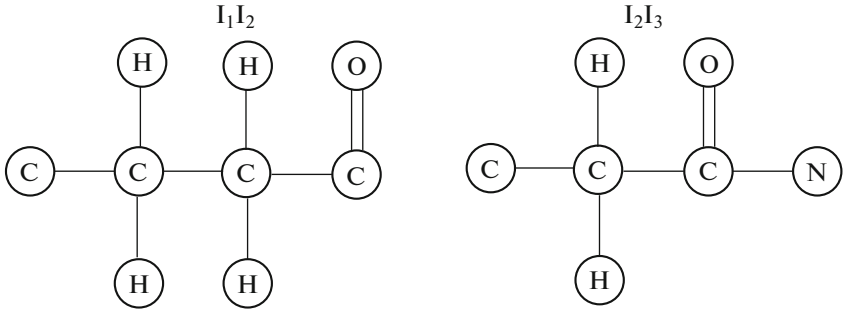

Fig. 4. Complex internal groups I_1I_2 and I_2I_3 of butyramide molecule.

minal group T_2. Thereby, two reactants, T_1T_1 and T_1T_3, are found. Checking the material and bond balances—the conservation of the numbers of atoms and bonds of each type—showed that the stoichiometric coefficients of HDR are 1. That is, the first HDR can be written as

$$T_1I_1I_2I_3T_2 + T_1T_1 + T_1T_3 \rightarrow T_1I_1T_1 + T_1I_2T_3 + T_1I_3T_2 \quad (1)$$

or, in terms of chemical formulas,

$$PrCONH_2 + C_2H_6 + MeCHO \rightarrow C_3H_8 + EtCHO + MeCONH_2.$$

Similarly,

$$T_1I_1I_2I_3T_2 + T_1T_3 \rightarrow T_1I_1I_2T_3 + T_1I_3T_2 \text{ or} \quad (2)$$

$$PrCONH_2 + MeCHO \rightarrow PrCHO + MeCONH_2,$$

$$T_1I_1I_2I_3T_2 + T_1T_1 \rightarrow T_1I_1T_1 + T_1I_2I_3T_2 \text{ or} \quad (3)$$

$$PrCONH_2 + C_2H_6 \rightarrow C_3H_8 + EtCONH_2.$$

For practical calculations of $\Delta_f H°$ of butyramide, the standard enthalpies of formation of reactants and products of homodesmic reactions (1)–(3) are necessary, which were taken from the database [10]. The absolute enthalpies of these compounds and the studied amide were calculated by the G3 composite method [11]. All the quantum chemical calculations were made using the Gaussian 09 software, Revision C.1 [12]. From these data, the heats of HDR (1)–(3) are easy to calculate, which are 0.2, 0.5, and 0.3 kJ/mol, respectively. Note the superior fulfillment of the thermoneutrality condition by all the reactions, which suggests the absence of uncompensated noncovalent interactions in the constructed HDR. Knowing the heat of HDR and $\Delta_f H°$ of the other participants in the reaction, one can readily calculate the standard enthalpy of butyramide. We found the following $\Delta_f H°(PrCONH_2)$ values (kJ/mol): HDR (1), –277.2; HDR (2), –279.9; and HDR (3), –277.9. The $\Delta_f H°$ values calculated using independent HDR are well reproducible and agree well with the experimental value $\Delta_f H = -279.17 \pm 0.88$ kJ/mol [10]. Similar calculations we performed [6] for a test set of 53 CHNO-containing compounds were characterized by a mean absolute deviation of the calculated values from the experimental data of as low as 1.7 kJ/mol, which allows one to consider the HDR method a reliable technique for theoretically determining enthalpies of formation of organic compounds.

Thus, in this work, we presented a graph theory interpretation of chemical compounds, which underlay the development of an algorithm for calculating ratios between parameters in constructing participants in HDR. We developed software in Delphi [13, 14] for determining HDR basis and calculating enthalpies of formation.

Using the developed algorithm, we examined the enthalpies of formation of a test set of CHNO-con-

taining compounds of various classes for compliance with homodesmic reactions [6].

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