Physical Chemistry

1958

SovietRxiv

Abstract

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Physical Chemistry

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A Scheme for Calculating the Physicochemical Properties of Derivatives of Paraffin Hydrocarbons

(Presented by Academician B. A. Kazanskii, 2 VIII 1957)

The regularities of a number of physicochemical properties of various classes of hydrocarbons can be successfully represented with the aid of the concepts introduced by V. M. Tatevskii concerning the types and subtypes of carbon–carbon and carbon–hydrogen bonds (^{1}). A scheme for calculating the physicochemical characteristics of hydrocarbons based on these concepts (^{2}) gives good agreement between experimental and calculated values of physicochemical quantities and, consequently, makes it possible to find the physicochemical characteristics of compounds that have not yet been investigated and even have not yet been obtained, the possibility of whose preparation is predicted by the theory of chemical structure.

Of great theoretical and practical interest is the question of the applicability of the indicated concepts to the development of a scheme for calculating the physicochemical properties of other classes of organic compounds (besides hydrocarbons). In the present work we shall consider, for example, derivatives of paraffin hydrocarbons of the general formula

$$\mathrm{C}_n\mathrm{H}_{2n+2-m}\mathrm{X}_m, \tag{1}$$

where X is a monovalent substituent group.

Extending the concepts of subtypes of chemical bonds* to compounds of this structure, we assume that the properties of a bond, as in the case of hydrocarbons, are determined mainly by the influence of the atoms participating in its formation and of the atoms directly bonded to the latter. We shall denote bonds $\mathrm{C-C}$, $\mathrm{C-H}$, and $\mathrm{C-X}$ of different subtypes for compounds of structure (1), in general form, as follows:

$$\mathrm{C}_i^k - \mathrm{C}_j^l, \qquad \mathrm{C}_i^k - \mathrm{H}, \qquad \mathrm{C}_i^k - \mathrm{X}, \tag{2}$$

where i and j indicate the primary, secondary, tertiary, or quaternary character of the carbon atoms forming the bond ($i, j = 1, 2, 3, 4$), and the indices k and l

show how many groups X are directly bonded to the given carbon atom ($k, l = 0, 1, 2, 3$). The bond subtypes characteristic of derivatives of ethane and methane may be disregarded, since they are not encountered in the higher homologues.

Let us now attempt to represent some physicochemical property P (molecular volume, refraction, energy of formation from atoms, etc.) for a substance (1) through the corresponding partial properties p_{ij}^{kl}, $p_i^k(\mathrm{H})$, $p_i^k(\mathrm{X})$, attributable to individual chemical bonds of the indicated subtypes, the number of which in the given compound is determined by the coefficients n_{ij}^{kl}, $n_i^k(\mathrm{H})$, $n_i^k(\mathrm{X})$; then

$$P_{C_n\mathrm{H}_{2n+2-m}\mathrm{X}_m} = \sum_{ij}^{kl} n_{ij}^{kl} p_{ij}^{kl} + \sum_{i}^{k} n_i^k(\mathrm{H})\, p_i^k(\mathrm{H}) + \sum_{i}^{k} n_i^k(\mathrm{X})\, p_i^k(\mathrm{X}). \tag{3}$$

It turns out, however, that the coefficients $n_i^k(\mathrm{H})$ and $n_i^k(\mathrm{X})$ depend on the coefficients n_{ij}^{kl} and can be represented as linear combinations of the latter:

$$\begin{aligned}
n_1^0(\mathrm{H}) &= 3\left(n_{12}^{00} + n_{12}^{01} + n_{12}^{02} + n_{13}^{00} + n_{13}^{01} + n_{14}^{00}\right),\\
n_1^1(\mathrm{H}) &= 2\left(n_{12}^{10} + n_{12}^{11} + n_{12}^{12} + n_{13}^{10} + n_{13}^{11} + n_{14}^{10}\right),\\
n_1^2(\mathrm{H}) &= n_{12}^{20} + n_{12}^{21} + n_{12}^{22} + n_{13}^{20} + n_{13}^{21} + n_{14}^{20},\\
n_2^0(\mathrm{H}) &= n_{12}^{00} + n_{12}^{10} + n_{12}^{20} + n_{12}^{30} + 2n_{22}^{00} + n_{22}^{01} + n_{22}^{02} + n_{23}^{00} + n_{23}^{01} + n_{24}^{00},\\
n_2^1(\mathrm{H}) &= \tfrac{1}{2}\left(n_{12}^{01} + n_{12}^{11} + n_{12}^{21} + n_{12}^{31} + n_{22}^{01} + 2n_{22}^{11} + n_{22}^{12} + n_{23}^{10} + n_{23}^{11} + n_{24}^{10}\right),\\
n_3^0(\mathrm{H}) &= \tfrac{1}{3}\left(n_{13}^{00} + n_{13}^{10} + n_{13}^{20} + n_{13}^{30} + n_{23}^{00} + n_{23}^{10} + n_{23}^{20} + 2n_{33}^{00} + n_{33}^{10} + n_{34}^{00}\right),\\
n_1^1(\mathrm{X}) &= n_{12}^{10} + n_{12}^{11} + n_{12}^{12} + n_{13}^{10} + n_{13}^{11} + n_{14}^{10},\\
n_1^2(\mathrm{X}) &= 2\left(n_{12}^{20} + n_{12}^{21} + n_{12}^{22} + n_{13}^{20} + n_{13}^{21} + n_{14}^{20}\right),\\
n_1^3(\mathrm{X}) &= 3\left(n_{12}^{30} + n_{12}^{31} + n_{12}^{32} + n_{13}^{30} + n_{13}^{31} + n_{14}^{30}\right),\\
n_2^1(\mathrm{X}) &= \tfrac{1}{2}\left(n_{12}^{01} + n_{12}^{11} + n_{12}^{21} + n_{12}^{31} + n_{22}^{01} + 2n_{22}^{11} + n_{22}^{12} + n_{23}^{10} + n_{23}^{11} + n_{24}^{10}\right),\\
n_2^2(\mathrm{X}) &= n_{12}^{02} + n_{12}^{12} + n_{12}^{22} + n_{12}^{32} + n_{22}^{02} + n_{22}^{12} + 2n_{22}^{22} + n_{23}^{20} + n_{23}^{21} + n_{24}^{20},\\
n_3^1(\mathrm{X}) &= \tfrac{1}{3}\left(n_{13}^{01} + n_{13}^{11} + n_{13}^{21} + n_{13}^{31} + n_{23}^{01} + n_{23}^{11} + n_{23}^{21} + n_{33}^{01} + 2n_{33}^{11} + n_{34}^{10}\right).
\end{aligned} \tag{4}$$

Substituting in equation (3), in place of the coefficients $n_i^k(\mathrm{H})$ and $n_i^k(\mathrm{X})$, their expressions (4) in terms of the coefficients n_{ij}^{kl}, and grouping the terms in the corresponding way, we obtain for the physicochemical property P the equation

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* The types of bonds in these compounds are

$$\mathrm{C-C}, \quad \mathrm{C-H}, \quad \mathrm{C-X}.$$

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

$$P_{C_n\mathrm{H}_{2n+2-m}\mathrm{X}_m} = \sum_{ij}^{kl} n_{ij}^{kl} P_{ij}^{kl}, \tag{5}$$

which contains no terms with coefficients n_i^k. The new constants P_{ij}^{kl} are combinations of the partial properties p_{ij}^{kl}, $p_i^k(\mathrm{H})$, $p_i^k(\mathrm{X})$ associated with the subtypes of the C—C, C—H, and C—X bonds introduced above; we do not give these expressions for P_{ij}^{kl}, so as not to encumber the exposition.

Thus, the physicochemical property P of a substance is ultimately represented through the numbers of chemical C—C bonds of different subtypes and certain quantities P_{ij}^{kl}, which, according to the calculation scheme, should retain approximately constant values for all compounds of a given class. At present these constants cannot be calculated theoretically. The suitability of formula (5), and therefore of the concepts introduced above, can be tested by determining the quantities P_{ij}^{kl} from experimental values of the physicochemical property P for various compounds of type (1) with a given substituent X, or by determining P_{ij}^{kl} from data for some one group of compounds of a definite class and comparing the values of the property P calculated from these constants with the experimental values of the latter for another group of compounds.

So far, the scheme presented has been tested only in calculating certain physicochemical properties of monohydric alcohols (X = OH).

To illustrate the accuracy of these calculations, Figs. 1 and 2 give graphs showing the agreement between experimental and calculated values.

molecular volumes and refractions of certain alcohols. The points on the abscissa axes correspond to individual isomeric alcohols of the series $C_9H_{19}OH$: 1—nonanol-1, 2—nonanol-3, 3—nonanol-5, 4—3-methyloctanol-4, 5—2,5-dimethylheptanol-5, 6—2,5-dimethylheptanol-4, 7—2,2,4-trimethylhexanol-4, 8—3,5,5-trimethylhexanol-3, 9—2,4-dimethyl-3-ethylpentanol-3, 10—2,2-dimethyl-3-ethylpentanol-3, 11—2,2,3,4-tetramethylpentanol-3.

Fig. 1. Experimentally obtained (1) and calculated (2) values of molecular volumes V^{20}, in ml/mole, for certain alcohols of the series $C_9H_{18}OH$

Fig. 2. Experimentally obtained (1) and calculated (2) values of molecular refractions MR_D^{20}, in ml/mole, for certain alcohols of the series $C_9H_{18}OH$

The thick line in the figures is constructed from the experimental data, the thin line from the calculated values. The agreement of these lines is satisfactory; the course of the curves is reproduced well. Without introducing the concept of subtypes of bonds, in these cases (for structural isomers with the same molecular weight) constant values of the physicochemical characteristics would have been obtained, which would have contradicted the experimental data.

Table 1

Values of the constants P_{ij}^{kl}, in ml/mole, for calculating the molecular volumes and refractions of monohydric alcohols

P_{ij}^{kl}	V^{20}	MR_D^{20}	P_{ij}^{kl}	V^{20}	MR_D^{20}
P_{12}^{10}	35.32	9.404	P_{23}^{10}	2.37	3.806
P_{12}^{01}	38.57	8.806	P_{23}^{01}	4.77	3.921
P_{13}^{10}	26.67	8.191	P_{24}^{10}*	(−3.81)	(3.454)
P_{13}^{01}	31.50	7.347	P_{33}^{01}	−5.91	2.528
P_{14}^{10}	–	–	P_{34}^{10}	−15.61	1.590
P_{22}^{01}	13.74	5.262			

* The values of this constant were obtained from only one equation.

The values of the constants P_{ij}^{kl} for calculations of the molecular volumes and refractions of monohydric alcohols, given in Table 1, were determined by the least-squares method from the experimental values of these characteristics for 54 alcohols (for which data on d_4^{20} and n_D^{20} are available in the literature). The values of the constants P_{ij}^{kl} (k and $l = 0$) for C—C bonds remote from the hydroxyl group coincide with the values of the corresponding constants for alkanes, calculated in the works of Tatevskii et al., and may be taken from (2). Recently the scheme was also used for calculating the magnetic susceptibilities of certain alcohols (3), and the convergence of the exper–

the agreement between the experimental and calculated values of the magnetic susceptibility is also quite satisfactory.

It would be very interesting to test the suitability of the proposed scheme for calculating the physicochemical properties of compounds of other classes ($X = F$, Cl, Br, I, NH_2, etc.). Nevertheless, it is already clear that the possibilities for explaining and predicting the values of the physicochemical properties of organic compounds afforded, in particular, by such concepts of the theory of chemical structure as the valence state of the atom and the type and subtype of chemical bond prove to be broader than was shown earlier (2), both with respect to the range of compounds covered and with respect to the range of physicochemical properties covered.

Received
17 XI 1956

CITED LITERATURE

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Properties, Moscow, 1953. [3] V. A. Ziborov, Yu. A. Pentin, V. M. Tatevskii, ZhFKh, **32**, issue 3 (1958).

Note: Figure translations are in progress. See original paper for figures.