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Abstract

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ON THE QUESTION OF INTRAMOLECULAR REARRANGEMENTS

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In what follows, by a molecule we shall understand any system of atomic nuclei and electrons with limited variation of internuclear distances,* possessing **one** least value of the potential energy, i.e., not only molecules in the usual sense, but also various conformations of molecules, radicals, various low-stability complexes, etc.

By an intramolecular rearrangement we shall understand any act of transformation of a molecule that converts it into one or several other molecules, in particular, into another isomer or into another conformation. In this broad sense, intramolecular rearrangements play a major role in chemistry, since one of the stages of many chemical reactions is the decomposition of some molecule into parts. In considering intramolecular rearrangements we shall regard each molecule as an isolated system. At the same time we shall assume that it is in thermal equilibrium with the surrounding medium and that its properties depend on this medium.

Intramolecular rearrangements are possible only with an appropriate change of certain internal coordinates (distances between nuclei or angles between the planes in which the nuclei are located). However, these changes can occur **only due to intramolecular vibrations** (including rotations about certain bonds). Therefore the possibility of a certain rearrangement **within one molecule** is connected with the possibility of the required change of internal coordinates due to intramolecular vibrations.

For each particular case, determining the possibility of sufficient approach of nuclei during rotation of individual parts of a molecule about certain bonds presents no special difficulty if the geometry of the molecule is known, and we shall not dwell on this. Let us consider the case of true vibrations of a molecule.

Vibrations of molecules leading to intramolecular rearrangements cannot, in essence, be harmonic. But we shall restrict ourselves to consideration of harmonic vibrations, and later take the influence of anharmonicity into account qualitatively.

In the case of harmonic vibrations each internal coordinate is a linear combination of normal coordinates (see ([1–3])). Since at thermal equilibrium the normal coordinates and their rates of change are distributed according to the normal law (4,5), each internal coordinate and the rate of its change are also distributed according to the same law (see (6,7)).

For the coordinate q_j and the rate of its change $\dot{q}_j$, these distributions have the form

$$dW(q_j) = \frac{1}{\sqrt{2\pi}\,\sigma_{q_j}} \exp\left(-\frac{q_j^2}{2\sigma_{q_j}^2}\right) dq_j, \tag{1}$$

$$dW(\dot{q}_j) = \frac{1}{\sqrt{2\pi}\,\sigma_{\dot{q}_j}} \exp\left(-\frac{\dot{q}_j^2}{2\sigma_{\dot{q}_j}^2}\right) d\dot{q}_j; \tag{2}$$

* More precisely, with a sufficiently small probability of large changes in internuclear distances.

where $\sigma_{q_j}^2 = \overline{q_j^2}$ and $\sigma_{\dot{q}_j}^2 = \overline{\dot{q}_j^2}$, taking into account the relation between the form of a normal vibration and the derivative of its frequency with respect to various parameters (3), can be represented in the form

$$\sigma_{q_j}^2 = \hbar \sum_i \frac{\partial \omega_i}{\partial u_{jj}} \operatorname{cth} \frac{\hbar \omega_i}{2kT}, \tag{3}$$

$$\sigma_{\dot{q}_j}^2 = \hbar \sum_i \omega_i^2 \frac{\partial \omega_i}{\partial u_{jj}} \operatorname{cth} \frac{\hbar \omega_i}{2kT} = -\hbar \sum_i \frac{\partial \omega_i}{\partial t_{jj}} \operatorname{cth} \frac{\hbar \omega_i}{2kT} \tag{4}$$

(u_{jj} and t_{jj} are the diagonal elements of the matrices of potential and kinetic energy corresponding to the coordinate q_j; the summation is performed over all normal vibrations in which the coordinate q_j participates).

If the required change in the coordinate q_j, equal to q_0, corresponds to some intramolecular "activated complex," then, repeating the usual arguments of the theory of absolute reaction rates (8) with the appropriate changes, we obtain for the rate constant of the intramolecular rearrangement $\varkappa$ the expression

$$\varkappa = \frac{1}{2\pi} \frac{\sigma_{\dot{q}_j}}{\sigma_{q_j}} \exp\left(-\frac{q_0^2}{2\sigma_{q_j}^2}\right) = \varkappa' \exp\left(-\frac{q_0^2}{2\sigma_{q_j}^2}\right) \tag{5}$$

In formula (5) the pre-exponential factor $\varkappa'$, as follows from (3) and (4), is the appropriately averaged frequency of the vibrations in which the coordinate q_j participates, and therefore it does not exceed 10^{14} sec^{-1}.

We shall assume that the minimum value of $\varkappa$ at which one can still speak of the process as practically occurring is of the order of 10^{-8} sec^{-1}. Then from (5), with the aid of tables (see (9)), we find that

$$q_0/\sigma_{q_j} \simeq 10 \tag{6}$$

approximately determines the condition for occurrence or non-occurrence of the corresponding intramolecular rearrangement.

Anharmonicity has different effects in the case when the rearrangement occurs with an increase in the distance between chemically bonded nuclei (or with a change in the angle of rotation of individual parts of the molecule relative to one another), and in the case when the rearrangement occurs with a decrease in the distance between chemically unbonded nuclei.

In the first case condition (6) is **sufficient** for the occurrence of the corresponding rearrangement (of course, if all conservation laws can be satisfied), and formula (5) determines the **lower limit** of the rate constant of the process. In the second case condition (6) is **necessary** for the occurrence of the corresponding rearrangement; formula (5) determines the **upper limit** of the rate constant of the process.

It is necessary to emphasize that the concept of activation energy, generally speaking, is inapplicable to intramolecular rearrangements. From (5) and (3) it follows that one can speak of an activation energy only in the case of temperatures much higher than the Debye temperatures of all normal vibrations in which the coordinate q_j participates. From these same formulas follows the fundamental possibility of intramolecular rearrangements even at absolute zero. All this becomes understandable if one takes into account that intramolecular rearrangements are effected by intramolecular vibrations, and the latter occur also at absolute zero, the quantum properties of the vibrations being essential up to temperatures much higher than the corresponding Debye temperatures.

Calculation by formula (5) can be carried out if the value of q_0 is known (it is assumed that the parameters σ_{q_j} and $\varkappa'$ can be found by means of calculation of the vibrations of the corresponding molecule). However, some qualitative conclusions can be obtained from this formula even without knowing the value of q_0.

For one and the same value of q_0, the rate constant determined by formula (5) depends strongly on the value of σ_{q_j}. A small increase (decrease) of the latter may substantially increase (decrease) this constant. Meanwhile, the value of σ_{q_j} depends on the conditions in which the molecule is found (or the bond, if q_j corresponds to some bond). Thus, for example, the values of σ_{q_j} for polar bonds should, as a rule, increase if the molecules are in polar solvents; the value of σ_{q_j} for the O—H bond increases when a hydrogen bond is formed, etc. This circumstance may substantially affect the direction and rate of many chemical processes.

Thus, the quantity σ_{q_j} is of great interest* and we shall consider it in somewhat greater detail.

From (3), after simple transformations, we obtain

$$\sigma_{q_j}^2 = \frac{2}{N}\frac{\partial F}{\partial u_{jj}}; \qquad \frac{\partial \sigma_{q_j}^2}{\partial T} = -\frac{2}{N}\frac{\partial S}{\partial u_{jj}}; \qquad \frac{\partial^2 \sigma_{q_j}^2}{\partial T^2} = -\frac{2}{NT}\frac{\partial C}{\partial u_{jj}}, \tag{7}$$

where F is the molar free energy, including the zero energy of intramolecular vibrations; N is Avogadro’ s number; S is the molar entropy; C is the molar heat capacity**.

Expressions (7) are in agreement with the general principles of statistical thermodynamics (^{5}) and reveal the thermodynamic meaning of $\sigma_{q_j}^2$ and its derivatives with respect to temperature. At the same time, they relate changes in the corresponding thermodynamic quantities to changes in force constants (for example, upon dissolution of a substance in polar solvents) and make it possible to estimate the accuracy of calculating these quantities under possible variations in the calculation of force constants.

The practical calculation of σ_{q_j} is carried out by the formula

$$\sigma_{q_j}[\text{Å}] = 0.184\,\frac{1}{\sqrt{m_0}}\left[\sum_i \frac{\partial \omega_i'}{\partial u_{jj}}\ \text{cth}\ 0.719\,\frac{\omega_i'}{T'}\right]^{1/2}, \tag{8}$$

where m_0 is the “spectroscopic mass” in units of atomic weight; u_{jj} are the force constants in 10^6 cm^{-2}; ω_i' are the frequencies in 10^3 cm^{-1}; T' is the absolute temperature in 10^3 °K.

The calculation of χ' is carried out by the formula

$$\chi' = 2.998 \cdot 10^{13}\,\frac{\left[\sum_i \omega_{i'}^2 \frac{\partial \omega_i'}{\partial u_{jj}}\ \text{cth}\ 0.719\,\frac{\omega_i'}{T'}\right]^{1/2}}{\left[\sum_i \frac{\partial \omega_i'}{\partial u_{jj}}\ \text{cth}\ 0.719\,\frac{\omega_i'}{T'}\right]^{1/2}} \tag{9}$$

(the summation in (8) and (9) is carried out only over those vibrations in which the coordinate q_j takes a noticeable part).

If the coordinate q_j is not used in the calculation of the vibrations and is a linear combination

$$q_j = \sum_{k=1}^{l} \alpha_k q_k$$

of l coordinates used in this calcula-

* This quantity is also of great importance for electron diffraction. In a number of cases it can be determined directly from electron-diffraction data (see review ([10])).

** Analogous formulas with the replacement of $\partial/\partial u_{jj}$ by $-\partial/\partial t_{jj}$ are valid, as follows from (4), for $\sigma^2_{q_j}$.

then, for each frequency ω'_i, it is necessary first to compute

$$\frac{\partial \omega'_i}{\partial u'_{ij}} = \sum_{m,k} \alpha_m \alpha_k \frac{\partial \omega'_i}{\partial u'_{mk}}$$

and then use formulas (8) and (9).

Note added in proof. Recently it became known to me that an expression equivalent to (5) had previously been obtained by Slater [11]. Familiarization with the cited work showed, however, that there this expression is introduced purely formally. The essential conclusions following from it and having fundamental significance—in particular, the conclusion concerning the possibility of the corresponding reactions at absolute zero—are regarded without justification as an indication of the inadequacy of such a quantum approach.

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