In the study of the mechanism of chemical conversions, the question of the degree of their adiabaticity is of interest. Let us consider this problem for reactions of substitution in methyl halides.

If the rate constant of the reaction obeys an Arrhenius law, then according to the quantum mechanical theory of chemical reactions in polar media [1], a system consisting of reagents (products) and a polar medium can be separated into classical and quantum subsystems. In the most general case, the quantum subsystem can contain several subsystems, differing appreciably in characteristic relaxation times (in their rates of motion).

We shall call the reaction "completely adiabatic" if in the transitional region the more rapid portion of the quantum subsystem keeps pace with the movement of its slower portion. In this case the slow portion of the quantum subsystem adiabatically follows the movement of the classical subsystem. If the more rapid portion of the quantum subsystem does not keep pace with the movement of its slower portion, and the latter with the movement of the classical subsystem, we will call the reaction "completely nonadiabatic." The intermediate variation corresponds to a "partially adiabatic" process.

In general the criterion of the occurrence of a reaction with one degree of adiabaticity or another takes a rather complex form [2]. However, a sufficient condition for a reaction to be entirely nonadiabatic is the fulfillment of the following inequality:

\[ \gamma = 2 |V| V_c |^2 \ll 1 \]  

in which \( V \) is a nondiagonal matrical element of the potential of interaction \( \tilde{V} \) leading to the reaction, while \( V_c \) is the critical value of \( V \) [1]. The exchange integral \( V \) is calculated with the functions of the initial (\( \Psi_f \)) and final (\( \Psi_f \)) states of a quantum subsystem, i.e.,

\[ V = \langle \Psi_f | \tilde{V} | \Psi_i \rangle \]  

For completely adiabatic reactions, condition (1) is of the reverse nature (\( \gamma \gg 1 \)).

In the case of the processes of nucleophilic substitution in methyl halides under consideration

\[ \text{CH}_3\text{Y} + \text{X}^- \rightarrow \text{CH}_3\text{X} + \text{Y}^- \]  

where \( X(Y) = \text{Cl}, \text{Br}, \text{or I} \), the quantum subsystem consists of electrons and protons, and therefore, generally speaking, cases of completely adiabatic, completely nonadiabatic, and partially adiabatic occurrence of reaction (1) are possible.

According to [1], to estimate \( \gamma \) it is necessary to know the exchange integral \( V \). In the Born–Oppenheimer approximation, the wave functions of the electron–proton subsystem can be written in the form of a product of electronic (\( \phi_{1,e} \)) and protonic (\( \phi_{1,p} \)) wave functions

\[ V = \langle \phi_{1,e} | \tilde{V} | \phi_{1,p} \rangle, \]  

The electronic wave functions and the potential $V$, entering into expression (3), depend weakly (in comparison with $\psi_{HF}$) on the coordinates of the protons ($Q$), and in the case of integration with respect to $Q$ in the Condon approximation, can be removed from under the integral sign. Denoting as $L_{e}$ the exchange integral between the electronic wave functions of the potential $\tilde{V}$, let us rewrite (3) in the form

$$V = L_{e} \langle \psi_{i} | \psi_{f} \rangle$$

In order to calculate the overlapping integral $\langle \psi_{i} | \psi_{f} \rangle$ in analytical form, let us use the oscillator wave function* and let us introduce a system of normal coordinates. In the system of normal coordinates, the vibrational wave functions are represented in the form of the product of unidimensional oscillator wave functions, corresponding to dynamic variables, i.e., $\psi_{i, f}$

$$= \prod_{n} \psi_{n}^{i, f}(Q_{n})$$

The system under consideration, CH$_{2}$Y + X$^-$, consists of six particles, and its description necessitates the knowledge of 12 normal coordinates, not associated with translational and rotational movement of the system as a whole. Part of them describe the motion of the quantum particles (protons) and part the movement of classical particles. To find the normal coordinates of the reagents and products, let us use the Wilson method.

Let us denote as $q_{i}$ the internal coordinates (i.e., the changes in the equilibrium interatomic distances and equilibrium angles between lines of bonds), and as $p_{i}$ their coupled momenta. Then according to [3], in the approximation of small vibrations, the total energy of the system can be written in the form

$$E = \frac{1}{2} \sum_{i, j} g_{ij} q_{i} p_{j} + \frac{1}{2} \sum_{i, j} f_{ij} q_{i} q_{j}$$

where $g_{ij}$ are the elements of the inverse matrix of the kinetic energy, while $f_{ij}$ are the elements of the matrix of the force constants. It is convenient to select natural coordinates as the 12 internal coordinates - the changes in the bond lengths $\Delta r_{1}$, $\Delta r_{2}$, $\Delta r_{3}$, $\Delta r_{4}$, and $\Delta r_{5}$ from the change in the valence angles $\Delta \alpha_{12}$, $\Delta \alpha_{23}$, $\Delta \alpha_{34}$, $\Delta \beta_{1}$, $\Delta \beta_{2}$, and $\Delta \beta_{3}$ (Fig. 1). In natural coordinates the problem of determining the normal vibrations is reduced to diagonalization of the matrix $\tilde{H} = \tilde{g}^{T}$. The solution of this problem is simplified after the introduction of the coordinates of symmetry. In the model of a linear complex (according to the calculations of [4], such a configuration is most probable), the system under consideration has the symmetry $C_{nv}$. The corresponding normalized coordinates of symmetry (5) take the form

Symmetry $A_{1}$

$$S_{1} = (\Delta r_{1} + \Delta r_{2} + \Delta r_{3})/\sqrt{3}$$

$$S_{2} = (\Delta \alpha_{12} + \Delta \alpha_{23} + \Delta \alpha_{34} - \Delta \beta_{3} - \Delta \beta_{2} - \Delta \beta_{1})/\sqrt{6}$$

$$S_{3} = \Delta \alpha_{x}$$

Symmetry $E$

$$S_{5}^{a} = (2\Delta r_{1} - \Delta r_{2} - \Delta r_{3})/\sqrt{6}$$

$$S_{5}^{b} = (\Delta r_{2} - \Delta r_{3})/\sqrt{2}$$

$$S_{6}^{a} = (2\Delta \alpha_{23} - \Delta \alpha_{12} - \Delta \alpha_{34})/\sqrt{6}$$

$$S_{6}^{b} = (\Delta \alpha_{12} - \Delta \alpha_{34})/\sqrt{2}$$

$$S_{7}^{a} = (2\Delta \beta_{1} - \Delta \beta_{2} - \Delta \beta_{3})/\sqrt{6}$$

$$S_{7}^{b} = (\Delta \beta_{1} - \Delta \beta_{2} - \Delta \beta_{3})/\sqrt{2}$$

$$S_{8}^{a} = \Delta \gamma_{1}$$

$$S_{8}^{b} = \Delta \gamma_{2}$$

In the coordinates of symmetry the matrices $\tilde{f}$ and $\tilde{g}$ are blocked diagonals. Thus, the matrix $\tilde{f}$ takes the form

$$\tilde{f} = \begin{pmatrix} \tilde{f}_{A_{1}} & \tilde{f}_{E} \\ \tilde{f}_{E}^{T} & \tilde{f}_{E}^{T} \end{pmatrix}$$

where $\tilde{f}_{A_{1}}$, $\tilde{f}_{E}^{a}$, and $\tilde{f}_{E}^{b}$ are fourth-order symmetrical matrices. The matrix $\tilde{g}$ is analogous in structure.

*If the harmonic approximation is insufficient, the overlapping integral can be calculated by numerical integration.