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Kinetics of Non-Radiative Rotational Isomer Butane Transitions

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A theoretical model for calculation of equilibrium concentrations of isomeric butane molecule forms, and also the forms of hydrocarbons of the alkene series, is proposed. We considered the changes of internal rotational potential energy in respect of reaction coordinate, of rapid conversion of butane isomers from one form to another at room temperature. This is very important for better understanding of the nature of chemical reactions in butane, because the changes of internal rotational potential energy reflect conformational transitions of butane and changes of its chemical and physical properties. The presented model is based on Gribov's system of kinetic equations for isomer–isomer transitions. The canonical ensemble is used to calculate the room temperature probabilities of the rotoisomer conformational states as functions of dihedrial angle, and the obtained results are in good agreement with available ones. Also, in a sense of calculated lifetime of unstable rotoisomers ($< 10^{-10}$ s), our results are comparable with coupled cluster and density functional calculations on alkene derivatives.

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1. Introduction

The existence of the rotational isomers was established by microwave spectroscopy and nuclear magnetic resonance [1], by exploring molecular properties (intensities of spectral lines, dipole moments etc.) averaged during the lifetime of rotoisomers. These molecular conformations are obtained by rotations over C–C bond [2, 3], where rotational angle φ (*dihedrial angle*) can have some characteristic values corresponding to stable conformations (*staggered conformations*), and very unstable ones (*eclipsed conformations*) whose lifetime [4] is very short ($\leq 10^{-10}$ s). This time is smaller or comparable to the period of the frequency of accidental jump over potential barrier between two rotoisomer states.

Generally, potential energy of the rotational hydrocarbon isomers can have complicated form, like in butane, where several stable conformations exist. The value of the potential energy of conformational state which corresponds to dihedrial angle $\varphi = -180°$ (*antistaggered conformations*) is 5 kcal/mol lower in respect of conformational state corresponding to angle $\varphi = 0°$ [1], while the potential energy of conformational states corresponding to angles $\varphi = 60°$ and $\varphi = 300°$ (*staggered conformations*) is 4.1 kcal/mol lower in respect of the same state. At room temperature butane exists in the form of mixture of stable conformational states, which is, on the other hand, in thermodynamical equilibrium with thermal bathroom. Very short lifetime of the butane in nonstable conformations (*eclipsed conformations*) approves their approximate neglect, when stoichiometric ratios between stable states are calculated.

The aim of this work is to establish appropriate theoretical model which could describe internal dynamics of butane molecule, during the short lifetime of its isomers. Very well known ordinary system of kinetic equations, which can be applied to describe interchange between two isomers

$$\frac{\mathrm{d}n_1}{\mathrm{d}t} = -k_1 n_1 + k_2 n_2,$$
$$\frac{\mathrm{d}n_2}{\mathrm{d}t} = k_1 n_1 - k_2 n_2 \qquad (1.1)$$

(n_1, n_2 — concentrations of isomers, k_1, k_2 — rates of reactions) can provide information about equilibrium state, which means that equilibrium constant $K = n_2/n_1$ can be calculated. But there is no information about *nonequilibrium* states within lifetime of isomers — so to explore them we shall employ phenomenon of quantum-mechanical resonance, explained by Gribov [5] in detail. There is another very important experimental fact that justifies introduction of this phenomenon: namely, as it is pointed out in [6], excited rotational spectrum of *pentenyne* molecule shows *coalescence* of two rotational frequencies of two stable isomers — that could be regarded as a quantum state of a mixture of isomers which is a basis of quantum-mechanical resonance.

2. Theoretical model

Theoretical description of the many-particle system exchanging energy with the thermostat, as in the case of butane, is based on the application of the canonic ensemble of particles. Accordingly, we define probability to find

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the system in the equilibrium state shifted in the energy E_i ($\varphi > 0°$) in respect of the state $E_0 = 0$ ($\varphi = 0°$):

$$w_i = \frac{\exp(-\frac{E_0 - E_i}{kT})}{\sum_j \exp(-\frac{E_0 - E_j}{kT})}, \tag{2.1}$$

where T is the temperature, while potential rotational energies in respect of the state $E_0 = 0$ ($\varphi = 0°$) are $E_1 = -4.1$ kcal/mol and $E_2 = -5$ kcal/mol, respectively.

In the framework of further mathematical procedure, we shall write the system of kinetical equations [7], which describes temporal population of the two conformational states (rotational isomers) of butane

$$\frac{\mathrm{d}n_1}{\mathrm{d}t} = -k_1 n_1 + k_2 n_2 - k_w \cos^2(\omega t) + k_w \sin^2(\omega t),$$

$$\frac{\mathrm{d}n_2}{\mathrm{d}t} = k_1 n_1 - k_2 n_2 + k_w \cos^2(\omega t) - k_w \sin^2(\omega t), \tag{2.2}$$

where k_1, k_2 and k_w are reaction rates, while oscillatory terms $\cos^2(\omega t)$ and $\sin^2(\omega t)$ represent phenomenon of quantum-mechanical resonance.

An explanation of this experimentally established phenomenon [8, 9] was given by Gribov in his monograph [5]. Simply stated, by exciting butane (thermally, irradiating...) there appears significant overlap of the electronic-vibrational wave functions of the two degenerate electronic-vibrational states (1) and (2) belonging to the close isomer forms of the butane, which gives rise to periodical oscillation back-and-forth between these two close structural states. In this approach, the (quasi)classical problem of many-electron energy-configuration hypersurface $E_\mathrm{e}(x)$, not adiabatically well-defined when traversing between two adjacent local minima (1) and (2), is replaced by better defined problem of the two (virtually intersecting) isomeric many-electron hypersurfaces (hyperparaboloids) serving as potential hypersurfaces for the two vibrational (isomeric) problems. Then, by *external perturbation* of the isomers, at this very intersection the conditions for electronic-vibrational non-radiative resonant transitions between the two isomers (1) and (2) are achieved: these resonance electronic-vibrational states of two isomers are transformed from the corresponding (nonperturbed) products of electronic and vibrational stationary wave functions $(\phi_\mathrm{e}^{(1)}(r,x)\phi_\mathrm{v}^{(1)}(x), \phi_\mathrm{e}^{(2)}(r,x)\phi_\mathrm{v}^{(2)}(x))$ into (perturbed) symmetrized stationary superposition $[\phi_\mathrm{e}^{(1)}(r,x)\phi_\mathrm{v}^{(1)}(x) \pm \phi_\mathrm{e}^{(2)}(r,x)\phi_\mathrm{v}^{(2)}(x)]/\sqrt{2}$, and their (nonperturbed) energies from resonating (equal) superposition of the ground electronic energies of corresponding minima of many-electron energy-configuration hypersurface and vibrational energies of higher excited states $(E_\mathrm{e}^{(1)} + E_\mathrm{v}^{(1)} = E_\mathrm{e}^{(2)} + E_\mathrm{v}^{(2)})$ into (perturbed) slightly split energy doublet $(E_\mathrm{e}^{(1)} + E_\mathrm{v}^{(1)} + (1/2)\Delta E,\ E_\mathrm{e}^{(2)} + E_\mathrm{v}^{(2)} - (1/2)\Delta E)$, with $\Delta E = 2(E_\mathrm{e}^{(1)} + E_\mathrm{v}^{(1)})S_\mathrm{ev}^{(1,2)}$ (where electronic-vibrational overlap integral between the two resonating isomeric states (1,2) is $S_\mathrm{ev}^{(1,2)} = \iint \phi_\mathrm{e}^{(2)}(r,x)\phi_\mathrm{v}^{(2)}(x)\phi_\mathrm{e}^{(1)^*}(r,x)\phi_\mathrm{v}^{(1)^*}(x)\,\mathrm{d}r\mathrm{d}x \approx S_\mathrm{v}^{(1,2)}S_\mathrm{e}^{(1,2)}$, while $S_\mathrm{v}^{(1,2)}$ and $S_\mathrm{e}^{(1,2)}$ are corresponding overlap integrals of vibrational and electronic components).

To describe the time evolution of this quantum-mechanical resonance we depart from the nonstationary Schrödinger equation

$$\mathrm{i}\hbar\frac{\partial \Psi_\mathrm{ev}(r,x,t)}{\partial t} = (\hat{H}_0 + \Delta H)\,\Psi_\mathrm{ev}(r,x,t), \tag{2.3}$$

where ΔH is a nondifferential step-like perturbation operator. We represent the solution of Eq. (2.3) in the form [5]:

$$\Psi_\mathrm{ev}(r,x,t) = a(t)\,\Psi_\mathrm{ev}^{(1)}(r,x,t) + b(t)\,\Psi_\mathrm{ev}^{(2)}(r,x,t), \tag{2.4}$$

where

$$\Psi_\mathrm{ev}^{(1)}(r,x,t) = \frac{1}{\sqrt{2}}\left[\phi_\mathrm{e}^{(1)}(r,x)\phi_\mathrm{v}^{(1)}(x) + \phi_\mathrm{e}^{(2)}(r,x)\phi_\mathrm{v}^{(2)}(x)\right]\exp(-\mathrm{i}\omega t),$$

$$\Psi_\mathrm{ev}^{(2)}(r,x,t) = \frac{1}{\sqrt{2}}\left[\phi_\mathrm{e}^{(1)}(r,x)\phi_\mathrm{v}^{(1)}(x) - \phi_\mathrm{e}^{(2)}(r,x)\phi_\mathrm{v}^{(2)}(x)\right] \times \exp(-\mathrm{i}\omega t)[\cos(\Delta\omega t) - \mathrm{i}(\sin\Delta\omega t)] \tag{2.5}$$

are the solutions of the nonstationary Schrödinger equation without perturbation,

$$\mathrm{i}\hbar\frac{\partial \Psi_\mathrm{ev}(r,x,t)}{\partial t} = \hat{H}_0\,\Psi_\mathrm{ev}(r,x,t), \tag{2.6}$$

with $\omega = (E_\mathrm{e}^{(1)} + E_\mathrm{v}^{(1)})/\hbar \approx 10^{15}$ Hz and $\Delta\omega = \Delta E/\hbar = 2(E_\mathrm{e}^{(1)} + E_\mathrm{v}^{(1)})S_\mathrm{ev}^{(1,2)}/\hbar \approx 10^{10}$ Hz [8], and time-dependent unknown functions $a(t)$ and $b(t)$. These functions can be determined by inserting of Eq. (2.4) into Eq. (2.3) (having in mind that electronic-vibrational wave functions of Eqs. (2.5) are solutions of Eq. (2.6), so that one can get two differential equations, $\mathrm{i}\hbar\partial a/\partial t = a\Delta H$ and $\mathrm{i}\hbar\partial b/\partial t = b\Delta H$. In this way, for the initial condition $|\Psi_\mathrm{ev}(r,x,0)|^2 = \left|\phi_\mathrm{e}^{(1)}(r,x)\phi_\mathrm{v}^{(1)}(x)\right|^2$, when $a(0) = b(0) = 1/\sqrt{2}$, we obtain the solutions $a(t) = b(t) = \exp(-\mathrm{i}\Delta Ht/\hbar)$. By inserting Eqs. (2.5) and solutions for $a(t)$, $b(t)$ into Eq. (2.4), after some algebra, the time-dependent probability density of the electronic-vibrational wave function of the system may be represented in the form

$$|\Psi_\mathrm{ev}(r,x,t)|^2 = \frac{1}{2}\left|\phi_\mathrm{e}^{(1)}(r,x)\right|^2\left|\phi_\mathrm{v}^{(1)}(x)\right|^2\cos^2\left(\frac{\Delta\omega}{2}t\right) + \frac{1}{2}\left|\phi_\mathrm{e}^{(2)}(r,x)\right|^2\left|\phi_\mathrm{v}^{(2)}(x)\right|^2\sin^2\left(\frac{\Delta\omega}{2}t\right). \tag{2.7}$$

¿From this equation, it can be concluded that system alternatively excites two isomer-conformational states with periodicity $\tau = 1/\Delta\omega \approx 10^{-10}$ s, which is macroscopically manifested as a temporal oscillatory change in concentration of the two isomers, providing the origin for oscillatory terms in Eq. (2.2).

3. Numerical results

For further analysis, it is necessary to establish a relationship of reaction rates with ensemble probabilities of butane molecules, i.e. rotational isomers corresponding to stable conformations. Starting from the fact that the characteristic time of the system corresponds to the period of the frequency of accidental jump over potential barrier between two rotoisomer states, $\nu \approx 10^{10}$ Hz, $T \approx 10^{-10}$ s [1], and taking into account the relationship $k_i = \nu w_i$, it is clear that system of Eq. (2.2) can be rewritten in the form better suited for the analysis, where the adopted time unit is 10^{-10} s

$$\frac{\mathrm{d}n_1}{\mathrm{d}t} = -w_1 n_1 + w_2 n_2 - w\cos^2(\omega t) + w\sin^2(\omega t),$$

$$\frac{\mathrm{d}n_2}{\mathrm{d}t} = w_1 n_1 - w_2 n_2 + w\cos^2(\omega t) - w\sin^2(\omega t). \quad (3.1)$$

By inserting $E_0 = 0$, $E_1 = -4.1$ kcal/mol and $E_2 = -5$ kcal/mol into Eq. (2.2), and probabilities $w_1 = 0.75$, $w_2 = 0.25$, and $w = 0.5$ which corespond to the room temperature $T = 300$ K, for initial values $n_1 = 1.0$ and $n_2 = 0$, the numerical solution of the system (3.1) is presented graphically in Fig. 1.

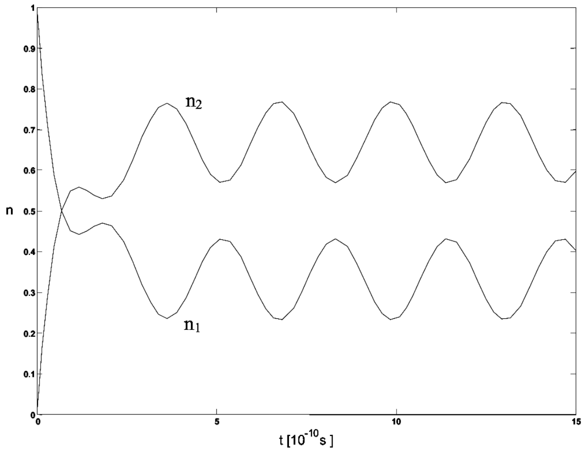

Fig. 1. The kinetics of the time dependent butane concentrations n_j (in relative units) in the model photochemical reaction of isomer transitions, for two-isomeric butane system with each isomer in possible ground and excited electronic-vibrational states (see Eq. (3.1) and the text for details).

Analyzing this graph we find the maximal value of the coefficient of stoichiometric ratio of these two butane isomeric concentrations

$$K = \frac{n_{2\,\max}}{n_{1\,\min}} = \frac{0.75}{0.25} = 3.$$

This ratio is in full agreement with values obtained independently by the well known method for finding difference in the free energy of the two conformational states, $\Delta G = -2.303RT\log K$ [10, 11], wherefrom $\Delta G = -0.67$ kcal/mol for $T = 300$ K, quoted in most textbooks of organic chemistry.

4. Conclusions

The obtained results show that our model gives satisfactory theoretical description of the numerous interesting properties of rotational isomers. The equilibrium ratios of concentrations of stable conformations obtained within the model, are in good agreement with well known empirically obtained results. The obtained time dependence of populations of rotational isomers of butane, is in agreement with experimental data on lifetimes of rotational isomers. Our results are comparable with calculations regarding to rotational isomerization about the carbon–carbon single bond done via density functional theory and checked with two-dimensional infrared vibrational echo spectroscopy. The model presented in this work is much less computer expensive. All this reveals a possibility to generalize the model to more complex situations with more rotoisomers, and even structural isomers and related biophysical phenomena. Accordingly, the future plans are directed to theoretical studies of rotational spectra of excited molecules, treated experimentally via methods able to examine picosecond isomerizations.

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