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The Photochemical and Radiation-chemical Stability of Molecules. Unimolecular Reactions Involving the Abstraction of a Hydrogen Atom

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The ways in which electronically excited molecular systems are deactivated are examined, a theory of the non-adiabatic and predissociation mechanisms for the decomposition of molecular systems with elimination of a hydrogen atom is described, and the isotope effect in this reaction is discussed and compared with experimental data. The photochemical stability of molecules of different classes, radical-cations, and radicals is explained on the basis of the theoretical results. The evolution of atomic hydrogen (formation of radicals) in low-temperature radiation-chemical experiments is associated with the position of the lowest triplets state of the molecules, their ionisation potentials, the polarity of the medium, and the energies of the C-H bonds in the radical-cations.
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I. INTRODUCTION

One of the fundamental problems in photochemistry and radiation chemistry is that of the relation between the structure of molecules and their resistance to the action of radiation. The theoretical aspects of this problem are examined below for unimolecular reactions involving the abstraction of a hydrogen atom. Reactions of this type are some of the most common in the photochemistry and radiation chemistry of hydrogen-containing compounds[1-3].

Correct ideas about the relation between the structure of molecules and their stability were put forward for the first time by Voevodskii and Molin[4], who related the stability of the molecule to the energy of its lowest excited state. According to their hypothesis[4], molecules in which the energy of the first excited singlet state exceeds the bond dissociation energy are unstable; when the opposite situation obtains the molecular stability increases sharply. It has been shown[5,6] that the decomposition of electronically excited complex molecules with elimination of a hydrogen atom can proceed with an appreciable probability via a predissociative mechanism only in triplet states and molecular stability must therefore be related to the positions of the lowest triplet state. The approaches on which the studies of Voevodskii and Molin[4] and Plotnikov[5,6] were based are similar, the difference consisting only in the nature of the states involved in the molecular decomposition. However, this does not mean by any means that the conclusions reached by the two sets of workers lead to identical results, since there exist molecules (for example the benzene molecule) in which the energy of the lowest triplet state is lower than that of the bond undergoing the dissociation, while that of the lowest singlet state is higher.

The explanation of the radiation-chemical stability of molecules towards the elimination of hydrogen atoms solely with allowance for the decomposition of electronically-excited molecules[2,4,7,8] cannot be complete, because hydrogen atoms can also be formed in the decomposition of electronically-excited radical-cations. The mechanism of the non-adiabatic decomposition of molecular radical-cations, radicals, and molecules with elimination of a hydrogen atom has been discussed[9] and it has been shown that the probability of the reaction is determined mainly by the energy of the bond undergoing dissociation, which is large for molecules and cannot be small for radicals and radical-cations.

In all the studies quoted above, it was assumed that the decomposition with elimination of a hydrogen atom proceeds in electronically excited states. In principle, there is a possibility of another decomposition mechanism, reducing to the transformation of electronic energy into the vibrational energy of the system with its subsequent concentration, by fluctuations, in the bond undergoing dissociation. The rate of such a process ($\sim 10^6$ s^{-1} for molecules with only a few atoms) decreases exponentially with increase of the number of vibrational degrees of freedom of the system[10,11]. Hence it will be necessary to conclude that the stability of the molecules increases with increase of their complexity and that polymeric molecules are stable, which conflicts with experimental data[1-3]. The independence of pressure of the quantum yield of hydrogen atoms[12,13] also shows that the contribution of the fluctuation decomposition mechanism is small, because otherwise an increase of pressure, which leads to an increased rate of vibrational relaxation, should decrease the yield. In a condensed phase the quasi-equilibrium mechanism of the decomposition of polyatomic

systems[10,11] is still less likely, since the lifetime of the vibrationally excited states is extremely short (10^{-11} to 10^{-12} s) in consequence of the vigorous vibrational relaxation processes, which suppress the decomposition process. In the case of systems with only a few atoms (CH_4, H_2O) the vibrational relaxation time is long—up to 10^{-2} s, and the fluctuation mechanism of their decomposition in the ground electronic state (!) cannot be fully ruled out[14-16].

The attempts to describe photochemical reactions with elimination of a hydrogen atom by a mechanism involving a redistribution of vibrational energy cannot be regarded as satisfactory, because they either did not account for the vibrational relaxation[17], or dealt with $\sigma\sigma^*$ and $n\sigma^*$ states of molecules with only a few atoms[18], for which the potential surface is not of the bonding type, and consideration of the redistribution of vibrational energy to a large extent lacked physical significance. It follows from the foregoing that the decomposition of polyatomic electronically excited systems takes place without passing through the stage of the redistribution of vibrational energy by fluctuations. Direct experimental and theoretical evidence for this conclusion will be presented later.

The ways in which electronically excited molecular systems are transformed and the mechanism of the elimination of a hydrogen atom will be considered below, and on this basis the photochemical and radiation-chemical stability of molecular systems will be explained. Since the experimental data for this process have been described systematically in a number of monographs[1-3,19-21] and reviews[22,23], we confined ourselves to giving references to these sources, using the data of original studies only when necessary.

II. ELECTRONIC ENERGY LEVELS OF MOLECULAR SYSTEMS

This section presents information about the nature of the electronically excited states of molecular systems required for further consideration. The Hamiltonian of a molecular system H can be formulated as the sum of the Hamiltonian in the adiabatic approximation H_0, the non-adiabatic operator V, and the spin–orbital interaction operator H_{SO}. The eigenfunctions of the Hamiltonian H_0 consist of product of electronic, vibrational, and rotational functions. For a condensed phase, the rotational motion of polyatomic systems is impossible, and one need consider only the electronic and vibrational functions and the corresponding states.

The states of a system with a Hamiltonian H_0 are characterised by a definite electron spin and may be classified in terms of the multiplicity. The majority of molecules have a singlet ground state (S_0) and can have both singlet (S_1, S_2, ...) and triplet (T_0, T_1, ...) electronically excited states. The triplet state T_0 is the excited state of molecules with the minimum energy. The first excited S_1 state lies somewhat above (by 10^3-10^4 cm^{-1}) the triplet state T_0. Other triplet states are frequently distributed between the T_0 and S_1 states[24]. The ground and first electronically excited states of singly charged radical-ions and radicals derived from organic molecules are doublets. There is very little information about the distribution of quartet states in these systems and they are apparently usually located above the first excited state. (As an example, one may quote the allyl radical, for which calculations with complete allowance for the configuration interaction in terms of the π-electron approximation[25] have shown that the quartet level lies above the first excited doublet.)

Another important characteristic of the electronic states of molecular systems is their orbital nature, determined by the nature of the electronic transition which results in the given state. In molecules of organic compounds it is possible to distinguish three types of electrons: π, σ, and n. The wave function of π and σ electrons are delocalised over the molecule. (In molecules containing heteroatoms, there naturally exist π and σ orbitals, with the maximum values corresponding to the location of the heteroatom. This maximum is usually low and the wave function is delocalised over the entire molecule.) The n-electron wave function is non-zero only in a limited region of the molecular system. The π- and σ-electron orbitals can be both bonding and antibonding, and are designated in the latter case by π^*, and σ^*; n-orbitals are non-bonding.

In conformity with the foregoing, electronic states of the following types are possible in molecular systems: $\pi\pi^*$, $\sigma\sigma^*$, $n\sigma^*$, $\sigma\pi^*$, $\pi\sigma^*$, and $n\pi^*$; these arise as a result of electronic transitions between the above orbitals. All these states are characterised by a definite multiplicity. In molecular spectroscopy and photochemistry the following notation has been adopted for electronic states, indicating their multiplicity and electronic nature: $S_{\pi\pi^*}$, $T_{\pi\pi^*}$, $S_{n\pi^*}$, $T_{n\pi^*}$, etc. (We may note that the eigenvalues of the Hamiltonian H_0 corresponds to these states and are not mixed under the influence of the operators V and H_{SO}. This classification is possible if the distance between the states is significantly greater than the matrix elements of the operators V and H_{SO}, which never exceed ~100 cm^{-1}.) For further consideration, it is important to note that, in all the states except $n\pi^*$ and $n\sigma^*$, the electrons are delocalised over the molecular system. Electrons in the $n\pi^*$, and $n\sigma^*$ states are localised near the heteroatom containing the n electrons.

The radical-cations derived from long paraffinic molecules occupy a special place among molecular systems[26]. Despite the fact that the ground state is of the σ-type, it is localised in a fairly small region of the large molecule. The reason for this is that, on localisation of a hole in the middle part of the molecule, the energy decreases by approximately 0.5 eV owing to the change in the C–C bond length. The localisation region then corresponds to 4–5 bond lengths (6–7 Å).

The electronic excitation of the molecular system entails a change in bond lengths (and in the general case also in bond angles) and in vibration frequencies. The rate of non-adiabatic transitions, including transitions involving the fragmentation of the molecular system, depends on these parameters and also on the extent to which the corresponding vibrations are anharmonic. The changes in bond lengths and vibration frequencies on electronic excitation may be inferred from the vibronic absorption and luminescence spectra of molecular systems. Together with vibrational spectra, they make it possible to determine also the anharmonicity of the vibrations. For many compounds, particularly aromatic compounds and their derivatives, these spectra have been investigated[24,27-29] and it has been found that (1) the change in the vibration frequencies of polyatomic molecules on electronic excitation is small in most cases compared with the vibration frequencies†; (2) the changes in bond lengths are also

† An appreciable change in the vibration frequencies of the C–O group is observed on $n \rightarrow \pi^*$ transitions in carbonyl compounds[27], which is due to the local nature of the transition.

small and, what is particularly important for further discussion, there is no significant change in the C–H bond lengths regardless of the nature of the state; (3) the majority of molecular vibrations can be described in terms of the harmonic approximation but the stretching vibrations of the C–H bonds (and in general R–H bonds) exhibit appreciable anharmonicity. The last conclusion is valid for any system containing a hydrogen atom, because the anharmonicity of the vibrations increases with decrease in the reduced mass of the oscillator.

The absorption spectra of aliphatic compounds are as a rule structureless [1] and it is therefore difficult to determine from them the change in the geometrical parameters of the molecule on electronic excitation. However, one may make the general claim [5,30] that the changes in these parameters are small, in molecules containing a large number of identical bonds, after $\pi \rightarrow \pi^*$, $\sigma \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$, and $\pi \rightarrow \sigma^*$ electronic transitions if one considers states with a comparatively low energy, not exceeding 10 eV (see Section VII). Since the electronic transitions in the above energy range are due to the delocalised electrons of the C–C bonds and the bonds between carbon atoms and the heteroatom [31,32], electronic excitation should alter the lengths of these bonds alone; the C–H (and in general R–H) bonds change insignificantly. This applies also to $n\pi^*$ and $n\sigma^*$ states. Few data are available at present for the electronic spectra of radical-cations (see Pshezhetskii et al. [19] and Bogatyreva and Buchachenko [22] together with the literature which they quote). However, for reasons stated above, one may assume that in these systems too the changes in bond lengths on electronic excitation are small and, what is most important, frequently do not involve the C–H (R–H) bonds.

The above conclusions, which follow from experimental data and theoretical considerations, constitute the basis of the theoretical models for reactions involving the elimination of a hydrogen atom. Certain deviations from such models will be indicated below (see Section VIII).

III. DEACTIVATION PROCESSES INVOLVING EXCITED MOLECULAR STATES

Following optical excitation or excitation by electron impact, the molecular system passes from the ground electronic states to an excited state (in the general case a vibronic state), which corresponds to an eigenvalue of the Hamiltonian H_0. For a long time, this postulate was assumed without proof and conditions under which it is valid were established only comparatively recently [33,34]. These conditions reduce to the following: (1) in the region of the excitation energy there is one state of the system with the Hamiltonian H_0 to which transition from the ground state is allowed; (2) the excitation is due to a source whose spectral line width exceeds the width of the excited state [35]. In classical (non-laser) photochemistry and radiation-chemistry the above conditions are fulfilled.

This applies not only to a free molecule, but also to a molecule in a solvent. In this case, during the first instant after excitation, the system is also in a state which is an eigenstate of the Hamiltonian H_0. (For this, it is necessary that the interaction of the vibrations of solvent molecules with the electronic excitation in the given molecule should be weak.) If the initial state is vibrationally excited, it relaxes owing to the interaction of the vibrations of the molecule of the compound with those of the molecules of the solvent. In polyatomic systems the rate of vibrational relaxation is extremely high, amounting to $10^{11}-10^{13}$ s^{-1}. [24] In molecular systems consisting of a small number of atoms (H_2, N_2, CH_4, etc.) the rate of vibrational relaxation may be much smaller (down to 10^{-2} s^{-1}), as stated above, and may depend very markedly on the amount of vibrational energy [14]. This effect is due to the relatively small number of vibrational modes in such systems and the anharmonicity of the vibrations.

The states of the Hamiltonian H_0 are not eigenstates of the system Hamiltonian H and therefore undergo spontaneous radiationless decomposition under the influence of the operators V and H_{SO}. Irreversible radiationless decomposition can occur only when the system in the final state has a continuous (quasi-continuous) energy spectrum [33,34,36,37]. Polyatomic molecules have a quasi-continuous spectrum of vibrational levels when the vibrational excitation energies exceed 1 eV. In the case of molecules with only a few atoms the energy levels are insufficiently closely spaced, and in isolated molecules of this kind radiationless transitions to not occur. In impurity molecules radiationless transitions are always possible, because the overall spectrum of states of the system is quasi-continuous owing to the vibrational states of the solvent molecules. The rate of the radiationless transitions in the condensed phase may depend on the strength of the interaction of the vibrations of the impurity and solvent molecules, i.e. on the rate of vibrational relaxation [38–41]. Another cause of the existence of a continuous spectrum of states of the system is associated with the possible photochemical reactions. We shall consider these possibilities below and here we shall deal with radiationless transitions involving a large number of closely spaced discrete states. By definition, processes of this type do not lead (in the first stage) to chemical transformations in the system and are referred to as conversion processes.

The following instances of conversion are distinguished. If the transition is between electronically excited states with the same multiplicity, the corresponding process is called an internal conversion process. When the distance between the electronically excited states does not exceed ~1 eV, the rate of internal conversion is very high, amounting to $10^{11}-10^{12}$ s^{-1}. [24,27,42] In the vast majority of molecules, the distance between the neighbouring electronically excited states is ≤ 1 eV, and internal conversion processes in such systems are therefore very rapid. The azulene molecule [24], in which the distance between S_1 and S_2 states is ~1.7 eV, constitutes an exception. A process involving a change in the multiplicity of the states as a result of the transition is referred to as intercombination conversion (singlet–triplet or $S-T$ conversion). The rate of such conversion depends very strongly on the spin–orbital coupling of the states of the system and on its other characteristics [24,43,44]. The rate of $S-T$ conversion between $\pi\pi^*$ states of aromatic molecules is 10^6-10^8 s^{-1}. [15] The rate of $S-T$ conversion between $\pi\pi^*$ and $n\pi^*$ states is very high ($\sim 10^{10}-10^{11}$ s^{-1}) owing to the appreciable spin–orbital coupling between them [24,43]. The rate of $S-T$ conversion in aliphatic hydrocarbons should also be high [44]. If the system finds itself in the ground electronic state as a result of a radiationless transition, the process is called degradation of electronic energy. One should then distinguish two types: an internal degradation process (for example an $S_1 \rightarrow S_0$ transition in which the multiplicity of the states does not change) and an intercombination degradation process (involving a change in multiplicity, for example $T_0 \rightarrow S_0$).

In most molecules the S_1 state is located at a considerable distance from S_0 ($\geqslant$2.5 eV). Internal degradation in such systems is unlikely (its rate is $\sim 10^5$ s^{-1}) and cannot compete with the radiative decomposition of the S_1 state and the $S-T$ conversion[42,45]‡. As the energy of the first excited state of the system decreases, the role of the internal degradation process increases, and, in systems in which the energy of the first excited state is less than ~1.5 eV, it may become the main pathway to the deactivation of the excited state[42]. The rate of intercombination (T_0-S_0) degradation also depends very strongly on the energy of the excited state. The characteristic rate of this process in aromatic hydrocarbons at low temperatures is $\sim 10^{-1}$ s^{-1}. For molecules with the lowest $T_{n\pi^*}$ state, the probability of this process is much greater, and its rate is $\sim 10^2-10^4$ s^{-1}.[24,27] Electronically excited states may naturally decompose also via radiative channels. In allowed electronic transitions the rate of radiative decomposition is 10^8-10^9 s^{-1}. In symmetry-forbidden electronic transitions (the $\pi \rightarrow \pi^*$ electronic transition in benzene and the $n \rightarrow \pi^*$ transitions in carbonyl compounds) the rate of the radiative transition is somewhat lower and amounts to 10^5-10^6 s^{-1}. The probability of radiative transitions forbidden by multiplicity is much lower and their rate is $10^{-3}-10^3$ s^{-1}.[24,27]

IV. THE DISTRIBUTION OF VIBRATIONAL ENERGY IN THE INITIAL STATE

The rate and mode of decomposition of an electronically excited system depends significantly on the amount of vibrational energy and particularly on the nature of its distribution among the vibrational degrees of freedom. We are primarily interested in the possibility of the non-equilibrium excitation of the stretching R–H bond vibrations. The degree of excitation of these vibrations depends on the way in which the electronic state is "prepared".

Following optical excitation or excitation by electron impact, the probability of the excitation of vibrational states is determined by the corresponding Franck–Condon factor§. At low temperatures only those vibrations can be excited whose characteristics (frequency and/or equilibrium value of the normal coordinate) change in the electronic transition. In the majority of hydrocarbon molecules and their substituted derivatives the stretching C–H bond vibrations are not of this kind (see Section II), so that one cannot expect their significant excitation. The vibrational energy in such systems during the first instant after the electronic transition is concentrated in the stretching C–C bond vibrations or in the vibrations of a carbon–heteroatom bond.

The vibrational energy is distributed in a different manner if the electronic state $|f\rangle$ is formed as a result of internal conversion from a higher excited state $|i\rangle$. Because of the considerable anharmonicity of the R–H bond vibrations, their significant excitation in this process is to be expected. We shall demonstrate this in relation to a simple model. Suppose that the system has two vibrational degrees of freedoms, one of which is associated with the anharmonic R–H bond oscillator and the other with a vibration which can be described in terms of the harmonic approximation. (In aromatic hydrocarbons the C–C vibrations may be regarded as being of this kind with a high degree of accuracy.) The harmonic vibration is characterised by the difference Δ between the values of the equilibrium coordinate in the $|i\rangle$ and $|f\rangle$ states. For simplicity, we shall assume that the characteristics of the R–H bond vibrations in the $|i\rangle$ and $|f\rangle$ states are identical. The rate of internal conversion from the zero-point vibrational state corresponding to the electron energy level i, accompanied by the excitation of the nth vibration of the R–H bond and the mth harmonic vibration corresponding to the electron energy level f, is proportional to the square of the matrix element:

$$\frac{1}{\mu}\left\langle i\left|\frac{\partial}{\partial x}\right|f\right\rangle\left\langle 0\left|\frac{\partial}{\partial x}\right|n\right\rangle\langle 0|m\rangle. \qquad (1)$$

Here μ and x are the reduced mass and the internal coordinate of the R–H vibration reckoned from the equilibrium value x_0; $|i\rangle$ and $|f\rangle$ are the electronic wave functions and $|0\rangle$, $|n\rangle$, and $|m\rangle$ are the vibrational wave functions. In order to calculate the value of the quantity defined by formula (1), one may employ the Morse functions for the R–H bond and the functions of the harmonic oscillator for the second vibration. The Morse potential is

$$U(x) = D\,(e^{-2\alpha x} - 2e^{-\alpha x}), \qquad (2)$$

where D is the bond dissociation energy, $\alpha = \omega(\mu/2D)^{1/2}$, and ω is the zero-point vibration frequency of the oscillator. The wave functions of the discrete spectrum are of the following form[46]:

$$|n\rangle = \left[\frac{\alpha\Gamma(2s_0-n+1)}{n!\Gamma(2s_0-2n+1)\,\Gamma(2s_0-2n)}\right]^{1/2} y^{s_0-n}e^{-y/2}\cdot F(-n, 2s_0+1-2n, y), \qquad (3)$$

where $s_0 = 2D/\omega - 1/2$, $0 \leqslant n < s_0$, $y = (2s_0+1)e^{\alpha x}$, $\Gamma(z)$ is the gamma-function, and $F(\alpha, \gamma, z)$ is a degenerate hypergeometric function. Using Eqn. (3), it is easy to obtain[47] an expression for the vibrational factor of the R–H bond in formula (1):

$$\left|\left\langle 0\left|\frac{\partial}{\partial x}\right|n\right\rangle\right|^2 = \frac{\alpha^2}{4}n!\,\frac{\Gamma(2s_0+1-n)\,(2s_0-2n)}{\Gamma(2s_0)}. \qquad (4)$$

The calculation of the Franck–Condon factor $\langle 0|m\rangle$ with the functions of the harmonic oscillator presents no difficulty[48]:

$$|\langle 0|m\rangle|^2 = \frac{e^{-\eta}}{m!}\eta^m,\quad \eta = \frac{\Delta^2\mu'\omega'}{2}, \qquad (5)$$

where ω' and μ' are the frequency and mass of the harmonic oscillator. The average values of the quantum number n are presented below as a function of the difference between the electronic energies ΔE_{if} of the i and f electron energy levels and the parameter s_0:

ΔE_{if}, eV	0.5 eV	1 eV	1.5 eV	2 eV
s_0=15	0.1	0.8	3.6	4.6
s_0=30	0.06	0.5	0.96	2.1

The following values of the parameters were selected: ω = 3000 cm^{-1}, ω' = 1500 cm^{-1}, and η = 1. Evidently the probability of the excitation of the R–H bond vibrations in a non-adiabatic transition increases with increasing anharmonicity of the vibrations (with decrease of the bond energy) and with increase of ΔE_{if}. For typical values $\Delta E_{if} \simeq 1-2$ eV, the R–H bond vibrations are significantly excited. This result may be obtained only when account

‡ This also show that decomposition of the majority of molecules cannot proceed via the mechanism involving the concentration of vibrational energy by fluctuations.

§ It is postulated that the corresponding electronic transition is symmetry-allowed.

is taken of the anharmonicity of the R–H vibrations, since in terms of the harmonic approximation the R–H vibrations with $n > 1$ are not excited at all in our model.

It is noteworthy that the above result is comparatively new, because it had been assumed earlier that in the internal conversion the energy is transmitted more or less uniformly to all the vibrational modes of the system. The average energy of the ν-mode is then determined (in terms of the harmonic approximation) by the parameter Δ_ν, the vibration frequencies ω_ν, and the amount of energy converted ΔE if.[49] For higher and lower values of ΔE if, the high-frequency and low-frequency vibrations are excited preferentially. The vibrational energy is always delocalised over the molecule in the harmonic approximation. As shown above, allowance for the anharmonicity of the vibrations leads to the possibility of the localisation of the vibrational energy in an individual bond.

An excited state may arise also as a result of intercombination conversion, which occurs under the influence of the spin–orbital interaction and (in terms of second-order perturbation theory) a non-adiabatic interaction. For intense spin-orbital interaction (~10 cm^{-1}), which depends little on the internuclear distances, the interconversion does not entail a significant excitation of the C–H bond vibrations. An example is provided by the transitions between the $n\pi^*$, and $\pi\pi^*$ states of different multiplicity. If the spin–orbital coupling is weak (~0.1 cm^{-1} for aromatic hydrocarbon molecules), terms describing the contribution of the non-adiabatic interaction may contribute significantly to the probability of the transition. In this case the excitation of the C–H vibrations is more likely in a radiationless transition.

V. NON-ADIABATIC DECOMPOSITION

A molecular system in the adiabatic vibronic state $|i\{n\}\rangle$ has a finite probability of a transition under the influence of the non-adiabatic operator to a continuum of $|f\{s\}\rangle$ states, provided that their multiplicities are identical. $\{n\}$ and $\{s\}$ are understood as sets of indices characterising the wave functions of the nuclei $|\{n\}\rangle$ and $|\{s\}\rangle$. The possibility of a continuous spectrum of $|f\{s\}\rangle$ states in any electronic state is determined by the finite value of the bond energy of the atoms in the system. In the region of energies exceeding the dissociation energy of any of the bonds the energy spectrum is continuous and the corresponding wave functions describe the motion of the decomposition products moving apart to infinity. The transitions of the system to such states will be considered here.

The $|i\{n\}\rangle$ state should be understood as an excited vibronic state of the R–H system. The $|f\{s\}\rangle$ states correspond to a continuous energy spectrum of the R$^\cdot$ + H system. The energy of the $|i\{n\}\rangle$ state should naturally exceed the dissociation energy of the R–H bond in the $|f\rangle$ state. The electronic wave functions $|i\rangle$ and $|f\rangle$ for molecules may be calculated by one of the methods of quantum chemistry; we shall make use of the wave functions found by the LCAO-MO method. The situation is somewhat more complex for wave functions describing the motion of nuclei.

The vibrational wave functions $|\{n\}\rangle$ are products of the functions of normal oscillators of the system. The $|\{s\}\rangle$ wave function can also be represented as the product of the function describing the relative motion of the R and H fragments and the vibrational wave functions of the R fragment. The forms of the normal coordinates in the $|i\rangle$ and $|f\rangle$ states are evidently not the same and the above representation of the $|\{n\}\rangle$ and $|\{s\}\rangle$ functions is unsuitable for the calculation of the rates of transition. It is seen that, when the dispersions of the vibration frequencies of the R–H bonds are neglected, the $|\{n\}\rangle$ and $|\{s\}\rangle$ functions are products of the vibrational functions of individual R–H bonds and the functions of the normal oscillators of the remainder of the molecule. The dispersion of the frequencies of the C–H(R–H) bond vibrations is small (~100 cm^{-1}) compared with the vibration frequency (~3000 cm^{-1}) and particularly the bond dissociation energy; for this reason, its neglect leads to very small changes in the decomposition probability. This is even more valid for anharmonic oscillators, because allowance for anharmonicity leads to an effective decrease of the intensity of their interaction[50].

We shall employ the Morse functions as the vibrational wave functions of R–H bonds. The $|\{n\}\rangle$ wave function is the product of the $|n_\nu\rangle$ wave functions, the discrete states of the Morse potential for individual R–H bonds, and the functions of the normal oscillators in the remainder of the molecule. The wave function of the final state is the product of the wave function $|s\rangle$ of the continuous spectrum of the Morse potential, which describes the motion of the eliminated hydrogen atom, and of the wave functions $|n'_\nu\rangle$ of the rest of the system, including the remaining R–H bonds. The vibrational quantum numbers n'_ν may differ from the initial numbers n_ν. The rate of the transition $|i\{n\}\rangle \to |f\{s\}\rangle$ under the influence of the adiabatic operator is described by the following expression in terms of the first-order perturbation theory[9]¶:

$$k = 2\pi \left| \frac{1}{\mu} \left\langle i \left| \frac{\partial}{\partial x} \right| f \right\rangle_{x=0} \left\langle \{n\} \left| \frac{\partial}{\partial x} \right| \{s\} \right\rangle \right|^2, \quad (\hbar = 1), \tag{6}$$

The vibrational factor defined by Eqn.(6) is

$$\left\langle \{n\} \left| \frac{\partial}{\partial x} \right| \{s\} \right\rangle = \left\langle n \left| \frac{\partial}{\partial x} \right| s \right\rangle \prod_\nu \langle n_\nu | n'_\nu \rangle, \tag{7}$$

where the product of the Franck–Condon factors $\langle n_\nu | n'_\nu \rangle$ is evaluated with respect to all the normal oscillators and bonds except the bond undergoing dissociation. In order to obtain the total probability of the abstraction of any hydrogen atom (per unit time), the expression for k must be summed with respect to finite vibrational states of the fragment R and with respect to all the R–H bonds. Furthermore, Eqn.(6) must be averaged with respect to the initial vibrational distribution.

The wave functions of the continuous spectrum of the Morse potential are of the form

$$|s\rangle = \frac{|\Gamma(-s_0 + is)|}{|\Gamma(2is)|\,(2\pi v)^{1/2}}\, y^{-1/2} W_{s_0+1/2, is}(y), \tag{8}$$

where $v = (2E/\mu)^{1/2} = \alpha s/\mu$, $s = (2\mu E)^{1/2}/\alpha$, and $W_{s_0+1/2, is}(y)$ is the Whittacker function. Function (8) is normalised with respect to the delta-function of energy E, which is reckoned from the dissociation energy L.

¶ It is noteworthy that terms containing derivatives with respect to other coordinates of the molecule may contribute to k. Since the difference between the bond lengths in the $|i\rangle$ and $|f\rangle$ states is small (see Section II) and the integral $\langle n|s\rangle$ for low values of n is therefore close to zero, these terms may be neglected. This applies also to the non-adiabatic interaction term containing second derivatives of the electronic functions with respect to internuclear coordinates. The expression for k is quoted in terms of atomic units.

The Franck–Condon factors reach their maximum value for $n_\nu \simeq n'_\nu$ under the conditions of a small change in the equilibrium value of the coordinate of the oscillator (Δ_ν). When $n = 0$ and for $n'_\nu \ll s_{0\nu}$, when the harmonic approximation is valid, we have [42,48]

$$|\langle 0 | n'_\nu \rangle|^2 = e^{-\eta_\nu} \eta_\nu^{n'_\nu} (n'_\nu!)^{-1}, \quad \eta_\nu = \Delta_\nu^2 \mu_\nu \omega_\nu / 2. \tag{9}$$

Calculation of the integral $\left\langle n \left| \frac{\partial}{\partial x} \right| s \right\rangle$ for an unchanged length ($\Delta = 0$) and vibration frequency of the R–H bond† in the $|i\rangle$ and $|f\rangle$ states gives [47]

$$\left| \left\langle n \left| \frac{\partial}{\partial x} \right| s \right\rangle \right| = S_{ns} = \frac{\mu (2s_0 - 2n)}{8\pi n! s} \frac{|\Gamma(-s_0 + is)|^2 \cdot |\Gamma(s_0 + 1 + is)|^4}{\Gamma(2s_0 + 1 - n) \cdot |\Gamma(2is)|^2}. \tag{10}$$

The integral $\left\langle n \left| \frac{\partial}{\partial x} \right| s \right\rangle$ may be also calculated analytically for $\Delta \neq 0$. When $n = 0$, we have

$$\left| \left\langle 0 \left| \frac{\partial}{\partial x} \right| s \right\rangle \right|^2 = S_{0s} \left[\xi^{s_0+1} F\left(s_0 + 1 + is, s_0 + 1 - is; 1; \frac{1-\xi}{2}\right) + s_0 (\xi - 1) \xi^{s_0} F\left(s_0 + 1 + is, s_0 + 1 - is; 2; \frac{1-\xi}{2}\right) \right]^2, \tag{11}$$

where $\xi = e^{\alpha\Delta}$ and $F(\alpha, \beta; \gamma; z)$ is a hypergeometric function. The expressions for the quantities $\left\langle n \left| \frac{\partial}{\partial x} \right| s \right\rangle$ when $n \neq 0$ can also be represented by the product of S_{ns} and a function $\Phi(s_0, s, n, \Delta)$, which is not quoted here because of its cumbersome form. The fundamental dependence of the factor $\left| \left\langle n \left| \frac{\partial}{\partial x} \right| s \right\rangle \right|^2$ on n is contained in the multiplier S_{ns}.

The expression for S_{ns} when $s_0 \gg 1$, $n \ll s_0$, and $s \geqslant 1$ can be greatly simplified if the asymptotic expression for the gamma-function is used [47]:

$$S_{ns} \simeq \frac{\pi^{1/2}\mu}{n! 2^{2s_0}} s_0^{3/2} (2s_0)^n \left(1 + s^2/s_0^2\right)^{s_0 + 1/2} \exp\left(-2s \arctan \frac{s}{s_0}\right). \tag{12}$$

If the decomposition takes place in the nth vibrational state of the bond undergoing dissociation and all the remaining numbers $n_\nu = 0$, one can write

$$k = \frac{2\pi^{3/2}}{\mu} |\beta|^2 F \prod_\nu \eta_\nu^{n'_\nu} e^{-\eta_\nu} (n'_\nu!)^{-1}, \tag{13}$$

where $\beta = \left\langle i \left| \frac{\partial}{\partial x} \right| f \right\rangle_{x=0}$ and the function

$$F = \pi^{-1/2} \mu^{-1} \left| \left\langle n \left| \frac{\partial}{\partial x} \right| s \right\rangle \right|^2.$$

For the majority of molecules, the parameter η_ν is non-zero only in the case of certain oscillators; under these conditions, its characteristic value is close to unity [48,51]. In this instance the multipliers with $n'_\nu \leqslant 1$ make the maximum contribution to Eqn. (13). Hence it follows that $\prod_\nu \eta_\nu^{n'_\nu} e^{-\eta_\nu} (n'_\nu!)^{-1} \sim 0.1$ and the fragment R can acquire a small amount of vibrational energy during the decomposition process, provided that this is allowed by energy factors. The fundamental dependence of k on the molecular parameters is contained in the multiplier F.

† We may note that the value of $\left\langle n \left| \frac{\partial}{\partial x} \right| s \right\rangle$ for $n \ll s_0$ (this is the case which we are in fact considering) is independent of the bond dissociation energy in the excited state, because the functions $|n\rangle$ are converted into the function of the harmonic oscillator when $n \ll s_0$.

Fig. 1 illustrates the variation of F with s_0 for $n = \Delta = 0$; evidently F decreases sharply with increase of s_0. The dependence of F of the parameter s is illustrated in Fig. 2. When $s = 0$, we have $F = 0$, but, when $s \simeq 0.5$ ($E \simeq 10^2$ cm^{-1}), F already reaches a maximum and then slowly decreases. Fig. 3 illustrates the variation of F with the length of the bond undergoing dissociation in the excited state; evidently the decomposition probability increases as the bond length is diminished. With increase of bond length, F initially decreases somewhat and then assumes a value virtually equal to that corresponding to $\Delta = 0$.

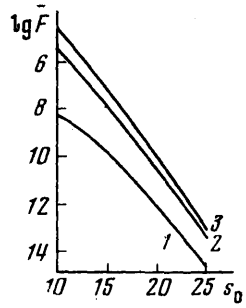


Figure 1. Dependence of the factor F on the parameter s_0 ($\Delta = 0$, $n = 0$); s: 1) 10; 2) 5; 3) 1.

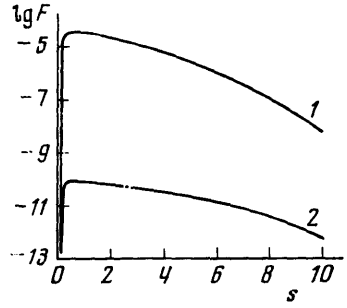


Figure 2. Dependence of the factor F on the parameter s ($\Delta = 0$, $n = 0$); s_0: 1) 10; 2) 20.

It follows from Eqn. (12) that the factor F increases very rapidly with increase of the vibration quantum number of the R–H oscillator in the initial state. Since $2s_0 \geqslant 10$, the excitation of the R–H bond vibrations leads to an increase in the probability of dissociation by more than an order of magnitude for each vibrational quantum.

In the Appendix to the present review it is shown that in many interesting cases $|\beta|^2 \simeq 2$ a.u. The constant for the elimination of a hydrogen atom is then given by

$$k \simeq 10^{14} \cdot F \ (\text{s}^{-1}). \tag{14}$$

The results of the calculation by Eqn. (14) of the rate constants for the decomposition of molecular systems with elimination of a hydrogen atom for different R–H bond energies are presented below:

D, eV	1.5	2.0	2.5	3.0	3.5	4.0	4.5
s_0	7.6	10.3	13.0	15.7	18.4	21.1	23.8
$\lg k$, (s^{-1})	10.7	9.3	7.8	6.3	4.8	3.3	1.7

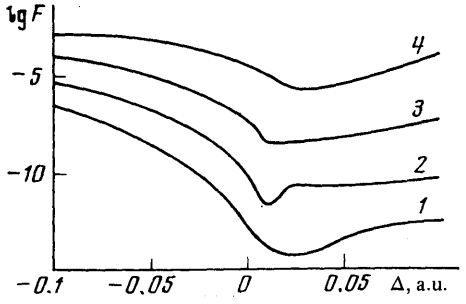


Figure 3. Dependence of the factor F on the parameter Δ ($s = 1$, $n = 0$); s_0: 1) 25; 2) 20; 3) 15; 4) 10.

In all cases it was assumed that $\omega = 3000$ cm^{-1}, $s = 1$, $\Delta = 0$, and $n = 0$. Several important conclusions follow from the above data: (1) the probability of the elimination of a hydrogen atom via a non-adiabatic mechanism from electronically excited molecular systems, for which $D \simeq 4-4.5$ eV (the majority of hydrocarbon molecules), is very low when $n \simeq 0$, and the quantum yield of the dissociation of the R–H bonds cannot exceed $\sim 10^{-3}$. (2) With decrease of the bond energy to 2.5–3.5 eV, the values of k become comparable to the rates of decomposition of the lowest singlet states of the majority of molecules, and the quantum yield of the decomposition in such systems may become appreciable. (3) If the bond energy becomes $\lesssim 2$ eV (paraffin radical-cations), the values of k exceed not only the rate constants for the radiative decomposition, but also the rate constants for internal conversion and vibrational relaxation. In this situation the quantum yield for the elimination of a hydrogen atom approaches unity.

$|\beta|^2 \simeq 2$ a.u. has been estimated for the case where the R–H bond is located in the part of the molecule where the excitation is localised (for example, a C–H bond of benzene). With increase of the distance R between the bond undergoing dissociation and the region where the wave function of the excited state is appreciably different from zero, the matrix element diminishes as R^{-2}. Therefore the constant k should be estimated, for example, in the case of the toluene molecule, from the formula $k \simeq$ $k \simeq 10^{12}F$. This must be taken into account when specific systems are considered.

It follows from the results presented that, other conditions being equal, the weakest R–H bond in the molecule will be preferentially dissociated. In most instances this has been observed experimentally, and henceforth we shall concentrate attention (without additional stipulations) on the description of the dissociation of the weakest R–H bond. One should bear in mind that the energy of the R–H bonds in excited electronic states is frequently smaller than in the ground state. Hence it follows that the probability of decomposition in the highest electronically excited states with formation of the fragment R in an electronically excited state may be much greater than the probability of the process involving the formation of the fragment R in the ground state. This decomposition pathway ($\overset{*}{M} \rightarrow \overset{*}{R} + H$) can be significant in the gas phase, but not in the condensed phase, since the lifetime of the highly excited states of molecular systems is very short in the condensed phase.

VI. PREDISSOCIATIVE DECOMPOSITION

We noted above (Section II) that, owing to the delocalisation of the electronic excitation over the molecular system, there are no significant changes in bond lengths if the number of bonds is large. However, the delocalisation may be infringed if the length of one or several equivalent bonds changes. In this situation a level may arise in the system with the localisation of the excitation energy at an individual bond [30,52], which leads to its dissociation. We shall examine the conditions for the appearance of such a level in a simple model of N equivalent two-electron bonds, weakly interacting with one another. Such are the C–H bonds of the majority of molecules.

The wave function of the ground state of the system can be described in the following form in terms of the zeroth approximation:

$$\Psi_0 = \hat{A} \prod_{n=1}^{N} \varphi_n^0 (R_n, \mathbf{r}_{1n}, \mathbf{r}_{2n}), \qquad (15)$$

where $\hat{A}$ is the antisymmetrisation operator and $\varphi_n^0(R_n, \mathbf{r}_{1n}, \mathbf{r}_{2n})$ is the wave function of the ground state of the nth bond, which depends on its length R_n and the electron coordinates $\mathbf{r}_{1n}$ and $\mathbf{r}_{2n}$. The dependence of the energy of each bond on R_n has the form of the $E^0(R_n)$ Morse curve and the energy of the entire system is

$$\sum_{n=1}^{N} E^0(R_n)$$

reaching a minimum for the equilibrium values of $R_n = R_n^0$.

The wave function of the excited state of the system can be expressed as the product of the wave functions $\varphi^1(R_n, \mathbf{r}_{1n}, \mathbf{r}_{2n})$ of the excited states of individual bonds (the strong bond approximation):

$$\Psi_j = \sum_{n=1}^{N} c_{jn} \hat{A} \varphi_n^1 (R_n, \mathbf{r}_{1n}, \mathbf{r}_{2n}) \prod_{\substack{n'=1 \\ n' \neq n}}^{N} \varphi_{n'}^0 (R_{n'}, \mathbf{r}_{1n'}, \mathbf{r}_{2n'}). \qquad (16)$$

The dependence of the energy $E^1(R_n)$ of an individual bond in the excited state on its length naturally differs from the function $E^0(R_n)$, which actually makes possible the localisation of the excitation energy at an individual bond. Using the variational principle for the energy, we obtain a system of equations defining E_j and c_{nj}:

$$\left[\sum_{\substack{n'=1 \\ n' \neq n}}^{N} E^0(R_{n'}) + E^1(R_n) \right] c_{nj} + \beta (c_{n+1,j} + c_{n-1,j}) = E_j c_{nj}, \qquad (17)$$

where β is the resonance integral for the interaction of adjacent bonds.

We shall consider the dependence of wave functions (16) on the length of one of the bonds. If all the R_n are equal to their equilibrium values R_n^0, then E_j and c_{nj} are defined by the expression

$$E_j = (N-1)E^0(R_n^0) + E^1(R_n^0) + 2\beta\cos\frac{j\pi}{N+1}, \qquad (18)$$

$$c_{nj} = \sqrt{\frac{2}{N+1}}\sin\frac{jn\pi}{N+1}, \quad 1 \leqslant j \leqslant N.$$

In this case excitation delocalised over the entire system corresponds to each value of j. The change in bond order on excitation amounts to $\sim N^{-1}$, which is responsible for the small change in the $E_j(R_n)$ relation in the vicinity of R_n^0 when $N \gg 1$ compared with the $E^0(R_n)$ relation.

The change in the length of one of the bonds alters the matrix element in Eqn. (17) corresponding to this bond. The remaining matrix elements may then be regarded as invariant. The solution of this type of system of equations has been considered[53] and it has been shown that the $(N-1)$th solution again corresponds to the delocalisation of the excitation over the system and is described by an equation of type (18). However, one of the levels has a wave function (for $N \to \infty$) which decreases exponentially with increase of the distance from the selected bond n_0:

$$c_n = \exp[-|n_0 - n|\varkappa(R_{n_0})],$$
$$\sinh\varkappa(R_{n_0}) = [E^0(R_{n_0}) + E^1(R_{n_0}^0) - E^0(R_{n_0}^0) - E^1(R_{n_0})]/2\beta. \qquad (19)$$

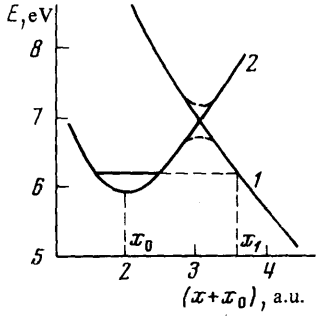


Figure 4. The energy levels of the localised (triplet) (curve *1*) and delocalised (curve *2*) states as a function of the C–H bond length.

It is seen from Eqn. (19) that the excitation may be localised if $\varkappa(R_{n_0}) \neq 0$. This situation is observed when the excitation energy decreases with increase in bond length, which implies that the excitation may be localised when the electron energy level of the excited state of an isolated bond is of the repulsive type. The energy of the system in state (19) is described by a curve with an activation barrier (Fig. 4) and the elimination of a hydrogen atom under the conditions of low excitation energies corresponds to a transition through the barrier.

In the region of excitation energies of hydrocarbons and their substituted derivatives not exceeding ~10 eV, the repulsive electron energy level of the C–H bond is of the triplet type[5]. The functions corresponding to this level describe the relative motion of the hydrogen atom and the radical in the ground electronic state moving apart to infinity.

The problem of the calculation of the rate of decomposition of molecular systems via a mechanism involving the localisation of the electronic excitation energy at the bond undergoing dissociation (which we shall call the predissociative mechanism) has already been examined[5,6]. It has been shown that the bond dissociation corresponds to a transition of a hydrogen atom from the energy level of a binding (delocalised) state to the repulsive energy level of the state where the electronic excitation is localised at an individual bond. Fig. 4 illustrates cross-sections of the potential surfaces for these two states as a function of the coordinate of the stretching vibrations of the R–H bond.

If the initial (delocalised) state is of the triplet type, then the localisation of the energy at an individual bond is due to an electron–electron (exchange) interaction. For a singlet initial state, the transition to a repulsive energy level can occur only under the influence of a relatively weak (see below) spin–orbital interaction. Hence follows immediately the important conclusion that the decomposition with elimination of a hydrogen atom can occur with a high probability only in triplet states.

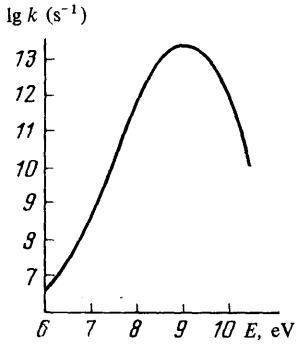


Figure 5. Dependence of the rate constant for the predissociative elimination of a hydrogen atom on the excitation energy.

Evidently the probability of the decomposition will depend on the relative positions of the energy levels of the initial and final states. As shown in Section II, the position of the energy level of the initial state for fairly complex molecules is determined solely by the electronic excitation energy. The position of the repulsive energy level depends on the bond dissociation energy and the energy of the exchange repulsion of the electron of hydrogen from the unpaired electron of the radical. (The remaining interactions are naturally also reflected in the position of the repulsive energy level, but their extent changes little from molecule to molecule.) The C–H bond dissociation energy is reduced in those cases where the unpaired p-electron is delocalised in the radical formed. The greater the degree of delocalisation of the unpaired electron, the smaller the energy of the exchange repulsion between hydrogen and the radical. Thus, as a result of the decreased bond energy, the repulsive energy level is lowered and the dissociation probability is a maximum for the weakest of the R–H bonds. This conclusion is therefore common to non-adiabatic and predissociative mechanisms.

The use of the formula of the first-order perturbation theory to calculate the rate constant for predissociation with rupture of the R–H bond yields the expression

$$k = 2\pi|\beta|^2|\langle n\}|\{s\rangle|^2, \qquad (20)$$

where β is the matrix element of the electron–electron (spin–orbital) interaction between the initial and final states and $|\{n\}\rangle$ and $|\{s\}\rangle$ designate, as before, the wave functions of the nuclei in the initial and final states. Owing to the weak dependence (for slight displacements of the nuclei) of the operators of the electron–electron and spin–orbital interactions, Eqn.(20) includes the factor governing the overlapping of the nuclear functions of the initial and final states. It is noteworthy that Eqn.(20) is applicable in the region where the potential curves of the localised and delocalised states differ little from the true curve plotted taking into account their interaction. In the region of the intersection of the potential curves Eqn.(20) yields only an approximate estimate, somewhat smaller than the exact value. This region diminishes with increase in the number of bonds in the molecule.

The wave functions $|\{n\}\rangle$ are chosen in the same form as in the description of the non-adiabatic decomposition. Since the decomposition takes place, as a rule, in vibrational states with small quantum numbers ($n \leqslant 3$), the harmonic oscillator function may be adopted as the vibrational wave functions. This makes it possible to obtain, without loss of accuracy, an expression for k in a form suitable for calculation.

The wave functions $|\{s\}\rangle$ have a more complex form than those described in Section V. The point is that the potential surface of the final state is of the repulsive type not only in the direction of the stretching vibrations of the bond undergoing dissociation, but also in the direction of its deformation vibrations. Depending on the stretching vibration coordinate x, a function Ax, where A is the slope of the plot of the repulsive energy level, may be fitted to the potential surface. The parabolae By^2, where $B < 0$, may be fitted to the dependence of the repulsive electron energy level on the deformation displacements of the hydrogen atom [6]. Accordingly, the products of the Airy function [46] and two Whittacker functions [47] are used as the functions of the final state of the bond being dissociated. For the remaining bonds, the harmonic oscillator functions are used.

The calculations [6] yield an expression for k:

$$k = \frac{\sqrt{3}\pi|\beta|^2}{2}\prod_\nu \frac{\eta_\nu^{n_\nu'}e^{-\eta_\nu}}{n_\nu'!}\int_{-\infty}^{+\infty}\cosh^{-1}\left(\frac{\pi z}{2}\right)e^{\frac{\pi z}{6}}S^2\left(\delta-\frac{\omega_2}{A}+\frac{z\omega_2}{\sqrt{3}A}\right)dz, \qquad (21)$$

where $\delta = x_1 - x_0 = (E_0 - E)/A$, where E_0 is the energy of the repulsive triplet level at the point of equilibrium (in the ground state) of the R–H bond, E is the energy of the initial state after the subtraction of the energy transformed into the energy of the vibrational excitation of the fragment R, and ω_2 is the deformation vibration frequency of the R–H bond. E_0 in most cases exceeds significantly (by 2–4 eV) the energy of the R–H bond. The remaining notation is the same as in Eqn.(9). The function $S(y)$ is defined by

$$S(y) = \left(\frac{2^{10}\mu}{A^2\pi^2\omega_1^3}\right)^{1/12}(2^n n!)^{-1/2}\left[\frac{\partial^n}{\partial t^n}S(t)\right]_{t=0},$$

$$S(t) = \exp\left(t^3-\frac{a^3}{\alpha^3}t+\frac{a}{2}y+\frac{b}{2}\right)\Phi\left(yc+d-\frac{2c}{\alpha}t\right), \qquad (22)$$

where μ is the reduced mass, ω_1 the frequency of the stretching vibrations of the R–H bond, n the vibrational quantum number characterising the excitation of the stretching vibrations of the R–H bonds in the initial electronic state, $\alpha = \sqrt{\mu\omega_1}$, $c = (2\mu A)^{1/3}$, $a = c^3/\alpha^2$, $b = c^6/6\alpha^6$, $a = c^4/4\alpha^4$, and $\Phi(z)$ is the Airy function. In order to obtain the complete rate of elimination of hydrogen atoms, Eqn.(21) must be averaged with respect to the initial vibrational (electronic) states and summed with respect to the possible final states.

For rough estimates, the following formula may be used to calculate k: [5,54]

$$k = \frac{2\pi}{A}|\beta|^2\prod_\nu\frac{\eta_\nu^{n_\nu'}e^{-\eta_\nu}}{n_\nu'!}\Omega_n^2(\delta), \qquad (23)$$

where $\Omega_n(\delta)$ is the function of the harmonic (anharmonic) oscillator of the stretching R–H bond vibration. The wave function $\Omega_0(\delta)$ is of the form

$$\Omega_0(\delta) = \left(\frac{\mu\omega_1}{\pi}\right)^{1/4}\exp(-\mu\omega_1\delta^2/2). \qquad (24)$$

Hence it is seen that, when the parameter δ (i.e. the excitation energy) is altered, k passes through a maximum, where $E = E_0$ and $\delta = 0$. A similar variation of k is obtained when Eqn.(22) is used.

The parameter β has been estimated [5,55,56]. In the case of decomposition in triplet $\pi\pi^*$ states of aromatic (unsubstituted) hydrocarbons β is defined by the expression $\beta \simeq 10^{-2}N^{-1}$ a.u., where N is the number of carbon atoms in the molecule. Hence it is seen that the probability of the elimination of a hydrogen atom decreases as N^{-1}. For the lowest triplet states of aromatic hydrocarbons, β is defined by the expression $\beta \simeq 10^{-2}N^{-1/2}$ a.u., so that the probability of the decomposition of the molecule with elimination of a hydrogen atom is independent of molecular size for aliphatic hydrocarbons. A similar situation obtains also for the $n\sigma^*$ states of substituted aliphatic hydrocarbons.

Bearing in mind that, as in Section V, the quantity $\prod_\nu \exp(-\eta_\nu)\eta_\nu^{n_\nu'}(n_\nu'!)^{-1} \simeq 0.1$ and using $\beta = 10^{-2}$ a.u., we obtain the following expression for k:

$$k(s^{-1}) \simeq 10^{12}\int_{-\infty}^{\infty}\cosh^{-1}\left(\frac{\pi z}{2}\right)\exp\left(\frac{\pi z}{6}\right)S_n^2\left(\delta-\frac{\omega^2}{A}+\frac{\omega_2 z}{\sqrt{3}A}\right)dz. \qquad (25)$$

The evaluation of the integral in Eqn.(25) does not present difficulties in most cases [6]. Since $n_\nu' \lesssim 1$, the vibrational energy of the fragment R cannot be large. Fig.5 illustrates the variation of k with the parameter E calculated by Eqn.(25) for the following values of other parameters: $\omega_1 = 3000$ cm^{-1}, $\omega_2 = 1100$ cm^{-1}, $A = 0.1$ a.u., $E_0 = 9$ eV, and $n = 0$.

The $k(E)$ relation for decomposition in excited singlet states is of the same type. Since β for the dissociation of R–H bonds does not exceed several cm^{-1} in this instance [44], the values of k are reduced compared with decomposition in triplet states by 6–7 orders of magnitude. This means that the rate of decomposition in singlet states cannot be significant even for high excitation energies.

A few words may be said about the temperature dependence of the rate of decomposition. As already mentioned at the beginning of this Section, when the excitation energies do not exceed E_0, the elimination of a hydrogen atom is a process involving penetration through an activation barrier. k is independent of temperature at low values of the latter, in the present instance when $T < \omega k_B^{-1}$, where k_B is the Boltzmann constant, and ω is the C–H bond vibration frequency. Since $\omega \gtrsim 1000$ cm^{-1}, k acquires its low-temperature (quantum) value already at

300–400°C. At higher temperatures k increases with increase of T.

If the lowest triplet state of the molecule is located in the region of the maximum on the $k(E)$ curve, the molecule decomposes with a high probability in this state and the process involves elimination of a hydrogen atom. (We do not take into account other possible photochemical reactions.) With decrease of the energy of the lowest triplet state, the probability of decomposition diminishes. In this case, when the energy of the lowest triplet state is smaller than the bond dissociation energy, the elimination of a hydrogen atom is possible only in the highest excited triplet states. Internal conversion, which in most cases is very rapid and suppresses the predissociation process, competes with the above process. In certain molecules the rate of internal conversion may be reduced owing to the characteristics of their structure (see Section IX).

One should bear in mind that, for molecules with a small (smaller than E_0) ionisation potential, the maximum in the function $k(E)$ is in the region of the ionised states of the molecule. The excited (superexcited or autoionisation) states ionise rapidly in this situation (10^{13}–10^{15} s^{-1}). This pathway to the decomposition of molecules, which does not itself lead to chemical changes in the molecule, constitutes an additional factor increasing the stability of molecules with respect to the elimination of a hydrogen atom. We may note that in the condensed phase the ionisation potential is lower than its value in the gas phase [57,58].

The stability of the molecules (in relation to the elimination of a hydrogen atom) is thus related to the positions of the triplet states, the ionisation potential, and the probability of deactivation processes‡. When specific systems are considered, one must of course bear in mind also the efficiency of the formation of triplet states. All the foregoing considerations are applicable (except for the names of the states) also to radicals and radical-cations. For this reason and also because the energy of the excited states of these systems is usually low [3,22,59,60] and the predissociative mechanism cannot therefore make a large contribution, the latter will not be discussed in detail.

VII. THE ISOTOPE EFFECT

The isotope effect in elimination reactions, which is defined as the ratio of the rate constants for the elimination of H and D atoms, can be used to test theoretical ideas about the process mechanism. Since the quantum yield is the main experimental characteristic of photochemical reactions, we shall consider briefly the conditions whose fulfilment is necessary for the observation of the influence of the isotope effect on the yield of the reaction [56].

We shall designate the rate constant for the dissociation of the C–H bond by k_H and that for the dissociation of the C–D bond by k_D. Suppose that the rate of deactivation of the excited states by all the pathways except decomposition is characterised by the constants k and k' respectively in the case of light and deuterated molecules. Then the quantum yield of the dissociation of the C–H and C–D bonds can be formulated thus:

$$Q_H = \frac{k_H}{k_H + k}, \quad Q_D = \frac{k_D}{k_D + k'}.$$

For low irradiation times, the rate of accumulation of products (the yield) is proportional to the quantum yield of the decomposition and we have for the ratio of the rates of accumulation of the light and deuterated molecules during photolysis

$$\frac{u_H}{u_D} = \frac{k_H}{k_D} \cdot \frac{k_D + k'}{k_H + k}. \qquad (26)$$

If $k = k'$, $k' \gg k_D$, and $k \gg k_H$, then $u_H/u_D = k_H/k_D$, so that only in this case is the experimental ratio of the rates of accumulation of products equal to the ratio of the bond dissociation rate constants. Since the inequality $k_D + k' < k_H + k$ always holds, the ratio u_H/u_D gives the lower limit of the true value of the isotope effect.

It follows from the results presented in Sections V and VI that the isotope effect and its dependence on the excitation energy differ for the non-adiabatic and predissociative mechanisms. We shall consider initially the predissociative decomposition mechanism. The replacement of a hydrogen atom by a deuterium atom leads to an increase of μ by a factor of ~ 2 and to a decrease of ω_1 by a factor of $\sim\sqrt{2}$. It is readily seen that, for all the values of the parameter E, the change in the transition energies of the molecule on deuteriation may be neglected in the calculation of k_H/k_D without appreciable error. We then obtain from Eqn. (24)

$$\frac{k_H}{k_D} = 2^{-1/4} \exp[\mu\omega_1\delta^2(\sqrt{2}-1)] = 2^{-1/4} \exp\left[\frac{\mu\omega_1}{A^2}(E - E_0)^2(\sqrt{2}-1)\right]. \qquad (27)$$

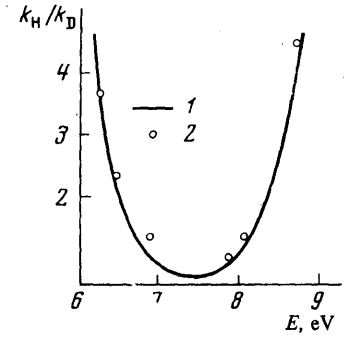


Figure 6. The isotope effect in the predissociative elimination of a hydrogen atom: 1) theory; 2) experiment [61].

Hence it is seen that the isotope effect exhibits a characteristic dependence on the excitation energy. For low excitation energies ($E < E_0$), the isotope effect is large. It decreases with increase of excitation energy, passes through a minimum when $E = E_0$, and then rises to high values again. Eqn. (27) refers to the decomposition in the zero-point vibrational state. A similar although more complex dependence has been observed also for the decomposition in vibrational excited states.

‡ Studies have been published recently [94,95] in which it has been shown that the decomposition of hydrocarbon molecules in T states takes place with elimination of a hydrogen atom via a predissociative mechanism.

The dependence of the isotope effect on the excitation energy has been studied experimentally[61] in relation to the two-quantum decomposition of triphenylmethane with dissociation of the central C–H bond. The triphenylmethane molecule satisfies the requirements specified at the beginning of this Section, and the measured ratio $u_H/u_D = k_H/k_D$.[56]

Fig. 6 presents the dependence of k_H/k_D on E, calculated by Eqn. (21), together with the experimental values[61]. The only parameter which was varied in order to obtain the best agreement with experiment was the energy of the vertical transition to the repulsive E_0 energy level. Thus $E_0 = 7.4$ eV was found. Evidently not only qualitative but also quantitative agreement between the theoretical and experimental variations of k_H/k_D with E is observed. This result constitutes a convincing demonstration of the predissociative mechanism for the decomposition of electronically excited polyatomic molecules with elimination of a hydrogen atom. We shall present below (Section VIII) yet another experimental result of this kind.

The isotope effect in a non-adiabatic elimination reaction depends very strongly on the bond energy. The replacement of a hydrogen atom by a deuterium atom leads to an increase of the parameter s_0 in Eqn. (10) by a factor of $\sim\sqrt{2}$. The data in Section V show that the rate of decomposition decreases almost by an order of magnitude for bond energies $\lesssim 2$ eV and by more than an order of magnitude for higher bond energies. Unfortunately no experimental data are at present available for the isotope effect in a non-adiabatic elimination reaction.

VIII. PHOTOCHEMICAL STABILITY OF MOLECULAR SYSTEMS

In this Section we shall show in relation to specific examples how the photochemical stability of molecules can be related to their structures using the above theoretical results. In conformity with the initial task, we shall consider only the photochemical R–H bond dissociation reactions. Before proceeding to the consideration of specific systems, we shall define yet again the region of applicability of the concepts described. The most important hypothesis among these is that the change in the potential surface of the molecule in the excited state is little different from that in the ground state. Molecules with a small number of atoms (of the type of H_2O), in which there is a significant change in the geometrical characteristics of the system on electronic excitation due to the small number of bonds, constitute an evident exception. Molecules containing either a weak R–H bond, the excited orbitals of which have the minimum energy, constitute a less evident exception. The lowest excited state of such a system corresponds to local excitation of this bond, with a significant change in the nature of the dependence of the potential curve on the bond length. A characteristic example of this is provided by molecules containing an S–H bond (mercaptans). This can be readily demonstrated by comparing the absorption spectra of mercaptans and aliphatic sulphides. The absorption spectra of mercaptans are located further towards long wavelengths than the spectra of the sulphides[62]. The opposite relation is observed in oxygen- and nitrogen-substituted aliphatic compounds when O–H (N–H) bonds are replaced by O–C (N–C) bonds[1]. Aliphatic compounds containing C–C, C–H, C–N, C–O, C–S, N–H, and O–H (but not S–H) bonds are therefore the objects of our consideration.

In modern photochemistry, there are two situations differing in the methods whereby excited states are generated. For low intensities of the exciting light, the system in an excited state has not had sufficient time to absorb a second quantum. The evolution of the electronic states of the system in this situation is described by a simple kinetic scheme, where there is a possibility of transitions to the lowest electronic states only (at low temperatures). For high light intensities, the system, which is in the triplet state, can absorb a second light quantum with a high probability, this being accompanied by a transition to highly excited triplet states§. The photochemistry of molecules is in this case referred to as two-quantum photochemistry[23] and differs from the classical one-quantum photochemistry. As can be seen from the foregoing factors, in a theoretical treatment these two cases must also be distinguished. We shall examine the one-quantum case first.

1. Aromatic Hydrocarbons

The energy of the C–H bond in the molecules of aromatic hydrocarbons is 4.5 eV.[63] The rate of elimination of atoms from such systems cannot therefore exceed 10^2 s^{-1} if the decomposition takes place from the ground vibrational state. The lifetime of the lowest singlet state of the benzene molecule, the energy of which is sufficient for the dissociation of the C–H bond, amounts to 10^{-7} s.[24] It follows from this that the quantum yield of the elimination of hydrogen atoms on excitation by the light corresponding to the first absorption band cannot exceed 10^{-5}. This value agrees with numerous experimental data[1].

When the benzene molecule is excited to high singlet states ($\lambda < 1849$ Å), the quantum yield of the cleavage of the C–H bond in the gas phase increases[65], which can be explained by several causes: (1) singlet–triplet conversion may lead to highly excited triplet states, where decomposition via a predissociative mechanism takes place. (2) Internal conversion can result in the formation of a highly vibrationally excited benzene molecule in the first singlet state, where the probability of the dissociation of a C–H bond may become very appreciable, in conformity with Eqn. (12). (3) Non-adiabatic decomposition with formation of a C_6H_5 radical in an electronically excited state may also make a definite contribution. All these mechanisms are unlikely in the condensed phase, where the rates of internal conversion and vibrational relaxation are high.

The introduction of alkyl substituents into the benzene molecule diminishes somewhat the photochemical stability of the molecule under the same excitation conditions. This was to be expected in view of the results described in Section V, because these molecules contain a C–H bond in the alkyl substituent with a dissociation energy of approximately 3.6 eV. Despite the fact that the bond is remote from π-electron system of the molecule, where the excitation is localised, calculations (see Section VI) have shown that the rate of its dissociation exceeds by

§ For still higher excitation intensities, transitions from the lowest excited S_1 state to the upper singlet states also become significant[64], but transitions of this kind do not introduce any significantly new features into the photochemical behaviour of molecules, because this situation corresponds to low intensities of the high-frequency excitation field.

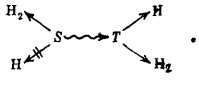
more than an order of magnitude the rate of dissociation of the bonds in the benzene ring. The quantum yield of the dissociation of the C–H bonds in the alkyl substituents of benzene (toluene, ethylbenzene, t-butylbenzene, mesitylene, and others[1]) exceeds 10^{-4}, which is greater by an order of magnitude than the corresponding value for benzene and agrees well with the estimated value of k quoted here.

Aromatic compounds (naphthalene, anthracene, etc.) having a more extensive chain of conjugated bonds than benzene and their substituted derivatives are still more stable. This is associated with the fact that the energy of the lowest singlet (and even more so triplet) states is insufficient for the dissociation of the C–H bonds.

2. Aliphatic Hydrocarbons

The dissociation energy of the C–H bonds in aliphatic hydrocarbons is approximately 4 eV.[63] Decomposition via a non-adiabatic mechanism cannot therefore contribute much to the formation of atomic hydrogen in the photolysis of paraffins, the quantum yield of which is approximately 0.1.[1,12,13] Decomposition via a predissociation mechanism in the singlet state arising on photoexcitation is forbidden, as shown in Section VI. The only real mechanism of the decomposition of paraffin molecules with elimination of a hydrogen atom therefore involves predissociative decomposition in the triplet states, whose energy (~6–7 eV) [44,46] is more than sufficient for this reaction. According to Plotnikov's estimates[44], the rate of the singlet–triplet conversion in paraffins should be high ($\sim 10^9-10^{10}$ s^{-1}). Quantities of the same order of magnitude may be obtained also for the rate of elimination of a hydrogen atom in triplet states. The molecular elimination of H_2 [67] and certain other processes compete with the singlet–triplet conversion. Only the fraction of the molecules which pass to the triplet states undergo decomposition with elimination of a hydrogen atom. This in fact explains the finding that, despite the high rate of elimination of a hydrogen atom, the quantum yield of this process is appreciably less than unity on photoexcitation of paraffin molecules. The atom produced should possess a considerable kinetic energy ($\geqslant 1$ eV).

The set of experimental and theoretical results makes it possible to postulate a mechanism for the photochemical decomposition of paraffin in the lowest excited states with formation of hydrogen:



3. Aldehydes and Ketones

The lowest singlet state of aliphatic aldehydes and ketones is the $n\pi^*$ state, the energy of which is ~3.4–3.7 eV.[1,24] The experimental dissociation energies of the H–COR bond in aldehydes show an appreciable scatter, but the overall trend is for the bond energy to increase somewhat with increasing size of the alkyl group R. Thus the lowest energy of the C–H bond is estimated as 3.02 eV in formaldehyde and 3.69 eV in the CH_3CHO molecule[68]. If this is so, the dissociation of the C–H bond in formaldehyde via a non-adiabatic mechanism should be much faster than in the molecules of more complex aldehydes. Experimental data[1] confirm this conclusion: the elimination of atomic hydrogen is significant only in the photochemistry of formaldehyde and is not observed for more complex aldehydes.

The C–H bond dissociation energy in ketones is approximately 4 eV,[63] so that it exceeds the energy of the lowest excited singlet state. This explains the experimental finding that the elimination of a hydrogen atom on excitation of ketones with light corresponding to the first absorption band is not observed. Only for very high excitation energies (~6–7 eV), where predissociative decomposition via triplet states becomes possible, is there an appreciable contribution by reactions involving the elimination of a hydrogen atom (acetone in the gas phase)[1].

4. Substituted Aliphatic Compounds

The energy of the lowest singlet excited state of aliphatic alcohols, ethers, and amines is of the $n\sigma^*$ type and amounts to ~6 eV,[1,69] while the C–H bond dissociation energy in these compounds is ~4 eV.[63] It is seen from these data that, although the dissociation of C–H bonds via a non-adiabatic mechanism in $S_{n\sigma^*}$ states is possible, its contribution is small. The predissociative decomposition in triplet states, which are located in the vicinity of the lowest singlet, is much more effective. Since the elimination of an H_2 molecule competes with the intercombination conversion process which precedes the decomposition, as in aliphatic hydrocarbons, the elimination of a hydrogen atom is not the only (and perhaps not the decisive) reaction. The introduction into the molecule of O, N, S, etc. atoms with a nuclear charge greater than that of a carbon atoms leads to an increase of the rate of the singlet–triplet conversion[44], which should result in an increased role of the hydrogen atom elimination reaction of such molecules, compared with hydrocarbon molecules. Here one must of course take into account the change in the position of the lowest triplet state on substitution. It may turn out that substitution leads to a sharp decrease of the energy of the T state, which increases the stability of the molecule. (This in fact occurs when an S atom is introduced into the molecule of an aliphatic sulphide.) The experimental data available hitherto[1] confirm this tendency, since the yield of atomic hydrogen in the photolysis of alcohols, ethers, and amines is always higher than in the photolysis of paraffins. Unfortunately the mechanism of the photolysis of aliphatic compounds with substituents has been studied less thoroughly than that of aliphatic hydrocarbons. This factor precludes a quantitative comparison of the theoretical and experimental results.

Aromatic alcohols, ethers, and amines are much more stable than their aliphatic analogues, which can be accounted for by the low energy of the triplet states of aromatic compounds

5. Certain Radicals

The bond energy D of the hydrogen atom in many radicals is greatly reduced compared with its value in the initial molecules[63]:

R	H–CO	C_2H_5	C_3H_5	H–CHOH
D, eV	~0.8	~1.7	~1.7	~1.2

Comparison of the above data with the results in Section V shows that radicals are as a rule less stable than the parent molecules. Indeed, for a bond energy $\leqslant 2$ eV, the rate of elimination of the hydrogen atom exceeds 10^9 s^{-1}, i.e. is higher than the rate of radiative transitions. For bond energies less than ~1 eV, the decomposition takes place with a quantum yield of ~1, if the excitation energy exceeds the energy threshold of the reaction, regardless of the position of the lowest excited state. The available experimental data for photochemical reactions of radicals [22] confirm this conclusion.

6. Radical-cations Derived from Organic Molecules

The R–H bond energy in radical-cations derived from organic molecules depends very markedly on their structure. Its value (D^+) may be expressed in terms of the energy of the R–H bond in the initial molecule (D) and the difference between the ionisation potentials (ΔI) of the molecule and the radical: $D^+ = D - \Delta I$. In most cases $\Delta I > 0$ and $D^+ < D$. Hence it follows that radical-cations are as a rule less stable than the initial molecules. (There are also exceptions. Thus $\Delta I < 0$ for the aniline molecule.)

ΔI for aliphatic compounds is 2–3 eV, [63] but in the case of aromatic compounds it is appreciably less. Thus it amounts to ~1.4 eV for the toluene molecule [63]. These data show that the energy of the C–H(R–H) bond in radical-cations derived from aliphatic molecules is 1–2 eV, while the value for radical-cations obtained from aromatic molecules is much higher, being close to ~3 eV. We may note that the C–H bond energy in the CH_2 groups of the radical-cations derived from aliphatic hydrocarbons is smaller by 0.5 eV than the corresponding value for the CH_3 groups.

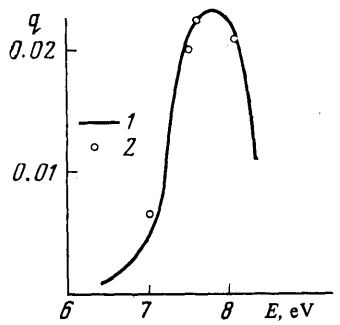


Figure 7. Dependence of the quantum yield of the elimination of a hydrogen atom from the triphenylmethane molecule on the triplet excitation energy: 1) theory; 2) experiment [61].

Comparison of the above data with the results of Section V shows that the radical-cations of aliphatic compounds are much less stable than those of aromatic compounds. This conclusion has been confirmed experimentally [70,71]. The fact that the energy of the first excited doublet state of the radical-cations is frequently small (~1–2 eV) [26,59,60] provides further justification for the above conclusion. Whereas the rate constant for the elimination of a hydrogen atom from aliphatic compounds is high and the elimination process may compete with internal conversion, in aromatic compounds it is almost completely suppressed. The hydrogen atom should be eliminated with a high probability from the central part of the radical-cations derived from paraffins.

We shall now consider briefly the two-quantum excitation of organic molecules. Such excitation gives rise to highly excited triplet states, where C–H bonds may be dissociated via a predissociative mechanism [72]. (This process is not of course the only one possible. Highly excited triplet states very frequently undergo ionisation or preionisation, and not predissociation, particularly when polar solvents are used [23,73].) The case of the two-quantum excitation of molecules is of particular interest, since it makes it possible to compare the theoretical result for the dependence of the probability of predissociation on the energy of the excited state (see Section VI) with experiment.

The $k(E)$ relation has been studied experimentally [61]. Fig. 7 illustrates the theoretical relation, calculated by Eqn. (25) using the parameters characteristic of the C–H bond, together with the experimental results. Evidently there is not only qualitative, but also quantitative agreement between the theoretical and experimental data.

The above examples show how the causes of the different photochemical stabilities of molecular systems having different structures may be understood using theoretical conclusions.

IX. RADIATION-CHEMICAL STABILITY OF MOLECULAR SYSTEMS

The yield of stabilised radicals is used as a quantitative criterion of the stability of molecules in the radiation chemistry of condensed media at low temperatures, because hydrogen atoms are not detected in most cases. The possibility of employing these data to compare the theoretical conclusions of Sections V and VI with experiment is not evident. Strictly speaking, the theory described is applicable to the yield of atomic hydrogen and its use to describe the yield of radicals may be to some extent qualitative. The point is that unimolecular reactions are not the only possible pathway to the formation of radicals. Radicals whose structure is identical with that of the radicals obtained from the parent molecules following the elimination of a hydrogen atom may arise as a result of the ion–molecule reaction

$$RH^+ + RH = R^\cdot + RH_2^+$$

and others. The relative contributions of unimolecular and other radical-generating processes are not at present known with sufficient accuracy [21], but the yield of radicals is usually appreciably (by a factor greater than 2) higher than that of stabilised electrons and therefore radical-cations [19]. Hence follows the conclusion that the unimolecular pathway to the formation of radicals is one of the most important. Apart from the causes already indicated, yet another factor prevents a quantitative comparison of theoretical conclusions with experiment: the amount of radicals detected may not agree with its initial value, because the initial radicals may disappear in numerous reactions (disproportionation, recombination, isomerisation, etc.). For this and other reasons (see

below), in comparing the conclusions of Sections V and VI with experiment one must employ data obtained at temperatures as low as possible.

In describing unimolecular hydrogen elimination process in radiation chemistry, one must bear in mind the following two factors. The effect of ionising radiation on molecular media leads to the formation of not only neutral excited molecules, but also of electronically excited radical-cations. According to estimates [74], the yields of ionised and electronically excited species are approximately the same. The decomposition of radical-cations with elimination of a hydrogen atom and subsequent recombination of the radical-cation R^+ with an electron constitutes an additional pathway (unimolecular in the sense of the formation of hydrogen atoms) to the formation of radicals in radiolysis, compared with photolysis. The natures of the primary excited states of molecules formed on radiolysis and on excitation by light are different. Under the conditions of radiolysis, excitation takes place when electrons collide with the molecules. The optically forbidden singlet–triplet transitions become allowed under these conditions (particularly for the resonance energies of the electrons) and the possibility of the excitation of triplet states, bypassing singlet states, arises.

There is yet another possibility of the direct excitation of triplet states, associated with the recombination reactions of radical-cations and electrons. The ratio of the amount of triplet states formed under these conditions to the amount of singlet states is three, provided that the orientations of the spins of the unpaired electron of the radical-cation and the electron with which it recombines are independent [75]. Under real conditions, this ratio depends also on a number of factors [the spin relaxation time and the distribution of radical-cations and electrons (see, for example, the paper of Magee and Huang [76] and the literature quoted therein¶)].

The direct formation of excited triplet molecules on radiolysis should lead to an increase of the yield of atomic hydrogen compared with its yield on photolysis. Experimental data confirm this conclusion. Thus the ratio of the yield of atomic hydrogen to that of molecular hydrogen is close to unity in the radiolysis of aliphatic hydrocarbons [3]. In photolysis the ratio is approximately 0.1 (see Section VIII).

We shall now consider specific systems. In order to demonstrate the generality of the approach, we shall divide molecules into groups in terms of their radiation-chemical stabilities and not chemical classes. All organic compounds can be divided arbitrarily into three groups: compounds in which the yield of radicals per 100 eV of absorbed energy $G > 1$, compounds for which $G \simeq 1$, and compounds for which $G \ll 1$. The reasons for this subdivision will be made clear below.

1. The first group of compounds includes aliphatic hydrocarbons, alcohols, ethers, amines, and many polymers. Table 1 lists the experimental values of G for these compounds and includes the energies of the lowest triplet state (E_T) and the C–H bond dissociation energies in a neutral molecule (L). [63] The value of E_T for the majority of molecules was determined as the difference between the energy of the lowest singlet state [1,68] and the singlet–triplet splitting. The latter was assumed to be 1 eV for aliphatic hydrocarbons ($\sigma\sigma^*$ states) and 0.5 eV for the remaining compounds ($n\sigma^*$ states) [44]. The values of E_T thus obtained are apparently somewhat higher than the true values [66], but for our purposes an improvement in the accuracy of E_T is unimportant. We may also note that all these compounds, with the exception of amines, have a high ionisation potential ($\geqslant$9 eV). Depending on the molecular structure, its value for amines varies from 7.6 eV to 9 eV. [63] The data in Table 1 permit the conclusion that there is a high probability of the elimination of hydrogen atoms via a predissociative mechanism from molecules of compounds in the first group in the excited triplet state.

Table 1. The values of G, E_T, and D for compounds of the first group.

Compound	G	References	E_T, eV	D, eV
Cyclohexane	4	77	7	4.08
n-Hexane	4.7	20	7	4.1
n-Heptane	4.4	20	7	4.1
n-Decane	3.6	20	7	4.1
Methyl alcohol	5.2	78	6.4	3.96
Ethyl alcohol	6.4	78	6.4	3.9
Aliphatic amines	3–5	79	5.1	4.05
Ethers	2–4	79	6	3.9
Polyethylene	5.8	8	7	4
Polypropylene	4.8	8	7	3.9
Poly(vinyl alcohol)	2.8	8	6	3.9
Polyvinylformal	5	8	6.4	3.9
Polyamides	2.4–3.1	8	5.3	3.9
Poly(ethylene glucol)	4–4.8	8	6	3.9

Since the ionisation potentials of the compounds listed in Table 1 are high, one may expect the formation of a large number of highly excited triplet states on charge recombination. The hydrogen atom formed in this reaction has a high kinetic energy and in its first collision may abstract a hydrogen atom from a neighbouring molecule. This may explain the stereospecificity of the formation of radical pairs in solid paraffins [80]. The energy of the C–H (O–H, N–H) bonds in the radical-cations derived from the molecules of the first group is ~1 eV. [21,71] In conformity with the results in Section V, this leads to high rate constants for the elimination of a hydrogen atom from electronically excited radical-cations.

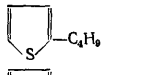
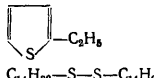
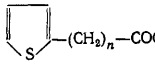
Thus both pathways to the formation of radicals discussed here occur with a high probability for compounds of the first group. It is so far difficult to estimate their relative contributions.

2. The second group includes compounds with $G \simeq 1$. Table 2 presents examples of some of them. The data listed in this table show that the energy E_T is in most cases (where it is known exactly) lower than the energy of the C–H bond. In conformity with the results in section VI, the probability of the elimination of a hydrogen atom from the excited molecules is determined by the ratio of the rate constants for the elimination and internal conversion processes. It is readily seen that the latter depends in this instance on the molecular structure. In

¶ Apart from the factors quoted by Magee and Huang [76], the ratio of the yields of triplets and singlets is also influenced by processes involving the polarisation of the medium, the electronic matrix element of the transition, and the Franck–Condon factor of the vibrations of the molecules and the medium. These problems have not as yet been investigated theoretically.

highly excited reactive $\sigma\sigma^*$ and $\pi\sigma^*$ ($\sigma\pi^*$) states the excitation is delocalised over the entire molecule. The lowest triplet state is localised in a comparatively small part of the molecule (at a benzene ring, a double bond, or an S–S bond). The spatial separation of the excited states causes a decrease of the rate of internal conversion between highly excited states and the $\pi\pi^*$ ($n\sigma^*$) state with increase of the number of CH_2 group (N) as N^{-1}. When $N \gg 1$, conversion processes cannot suppress the decomposition processes. All the foregoing considerations apply also to the excited states of the radical-cations derived from the molecules of the second group.

Table 2. The values of G, E_T, and D for compounds of the second group.

Compound	G	References	E_T, eV	D, eV
$Ph-C_{17}H_{35}$	0.8	81	3.5	3.7
$Ph-C_9H_{19}$	0.59	81	3.5	3.7
$Ph-C_7H_{15}$	0.46	81	3.5	3.7
$Ph-C_6H_{11}$	0.55	82	3.5	3.7
$Ph-C_4H_9$	0.24	81	3.5	3.7
$Ph-C_2H_5$	0.19	81	3.5	3.7
	0.8	79	<4	~4
	0.2	79	<4	~4
$C_{14}H_{29}-S-S-C_{14}H_{29}$	1.1	79	<4	~4
$C_{12}H_{25}-S-S-C_{12}H_{25}$	1	79	<4	~4
$C_8H_{17}-S-S-C_8H_{17}$	0.35	79	<4	~4
$C_4H_9-S-S-C_4H_9$	0.2	79	<4	~4
	1	79	<4	~4

The second group thus includes compounds where one or both of the given pathways to the formation of radicals are incompletely suppressed. Some of the compounds of the second group should be included in the third group. We placed them in Table 2 in order to demonstrate the continuity of the transition from the second to the third group.

The term intramolecular energy transfer is used in radiation chemistry instead of the term internal conversion. In other respects the above ideas are the same as those developed in studies by Voevodskii and coworkers[2].

3. The third group includes compounds with the highest radiation-chemical stability (Table 3). The data in Table 3 show that the energy of the lowest triplet state[24,27] of these compounds is lower than the C–H bond dissociation energy. One should not expect for these compounds anomalously long internal conversion times in the highest triplet states, since the excited states of these compounds are not spatially separated. The elimination of a hydrogen atom from the molecules in the highest triplet states is suppressed by internal conversion. An increase of the number of π electrons leads to a decrease of the rate constant for the elimination of a hydrogen atom (see Section VI) and to an increase of the internal conversion rate constant owing to the increase of the density of electronic states. This explains the decrease of G with the increase of the number of conjugated bonds in the molecule.

The energy of the bonds involving the hydrogen atoms in the radical-cations derived from the majority of the compounds listed in Table 3 is high (~3 eV [63,71]), so that the non-adiabatic reaction involving the elimination of a hydrogen atom from a radical-cation cannot compete with the decomposition reactions in the excited states. The ionisation potentials of all the compounds in the third group do not exceed 9 eV [63] and decrease sharply on passing to the condensed phase[57,58]. This means that the probability of the formation of highly excited triplet states on charge recombination is low and that their lifetime is short owing to ionisation processes. With increase of the polarity of the medium, the probability of the formation and the lifetime of the highest triplet states diminish, which may explain the decrease of G with increasing polarity of the medium (cf. for example, benzene and benzoic acid).

Table 3. The values of G, E_T, and D for compounds of the third group.

Compound	G	Refs.	E_T, eV	D, eV
Toluene	0.3	2	3.55	3.7
Benzene	0.2	2	3.66	4.7
Phenylacetylene	0.08	83	3.1	4.7
Diphenylacetylene	0.04	83	3.1	4.7
Biphenyl	0.05	82	2.8	4.7
Diphenyl disulphide	0.06	79	3.5	4.7
Thiophen	0.18	79	<4	4.7
Benzoic acid	0.05	2	3.35	4.7
Polystyrene	0.2	8	3.5	3.7
Poly(ethylene terephthalate)	0.4	8	3.5	3.7

The above results demonstrate the usefulness of the attempt to explain the low-temperature radiation-chemical stability of molecules (in the narrow sense under consideration) taking into account only the unimolecular radical formation reactions. The absence of contradictions between the theoretical and experimental data permits certain hypotheses concerning the possible role of the remaining radical formation processes, in the first place the role of ion–molecule reactions: the role of these processes at low temperatures is either small or the probability of their occurrence is correlated with the probability of unimolecular reactions. The discussion of this problem is outside the scope of the initial aim of this review and we shall therefore confine ourselves to certain general remarks.

The widely held view in radiation chemistry that ion–molecule reactions in the condensed phase make an appreciable (decisive according to some workers[19]) contribution to the formation of radicals in low-temperature radiolysis is based on the high cross-sections of these reactions in the gase phase[71,84,85]. However, it is incorrect to assume that these results are also valid for the condensed phase.

It follows from the general theory of reactions involving a change in charge distribution in the condensed phase[86-88] that their rates depend on the energy of the reorganisation (repolarisation) of the medium, decreasing exponentially with its increase. This leads to a non-zero activation energy for ion–molecule reactions in the condensed phase. The presence of an activation energy has been noted for ion–molecule reactions even of weakly polarised compounds such as molecular hydrogen[89]. At low temperatures ($k_BT \ll E_a$, where E_a is the activation energy) ion–molecule reactions therefore make a small contribution to the formation of radicals (naturally provided that $E_a \neq 0$).

The values of E_a are at present unknown, so that it is difficult to specify the temperature below which ion–molecule reactions are unimportant for the given system. Experimental studies of the temperature dependence of the yield of radicals at $T < 77$ K may be of primary importance in this connection. Since the rates of unimolecular reactions involving the elimination of atomic hydrogen are independent of temperature, such data make it possible to estimate the contributions of different pathways to the formation of radicals at low temperatures. (We may note that the yield of CH_3 radicals in the radiolysis of methane at 4.2 K is the same as the yield of atomic hydrogen[90].)

Another important difference between the condensed and gas phases, which must be taken into account in considering ion–molecule reactions, is that the lifetime of the separated charges in non-polar media is extremely short ($\lesssim 10^{-10}$ s).[3,91] The recombination process will thus compete with ion–molecule reactions, increasing the contribution of the unimolecular radical formation process.

Unfortunately there is as yet no common point of view on the problem of the relation between ion–molecule reactions and the electronic structures of the species involved in them. One can only claim that aliphatic molecules and cations show a greater tendency to undergo such reactions than aromatic species, because the ionisation of aromatic molecules does not involve R–H (C–H) bonds. The probability of ion–molecule reactions is particularly high for aliphatic alcohols and amines, because the ionisation of their molecules involves the elimination of an n electron, together with an oxygen or nitrogen atom, and a significant decrease of the proton elimination energy.

Thus it is to be expected that the probability of ion–molecule radical-formation reactions is correlated with the probability of unimolecular reactions, and that the contribution of the latter at low temperatures is decisive, although exceptions are possible.

The contents of this section are part of the general theory of the radiation-chemical behaviour of molecules The creation of this theory is a task for the future.

X. CONCLUSION

The results quoted demonstrate the usefulness of the application of theoretical considerations in the interpretation of the photochemical and radiation-chemical properties of molecular systems. There is no doubt that interesting results are to be expected along these lines in the future. We believe that the theory will develop along two paths: the refinement of the models already examined and the development of models of processes which have not as yet been investigated. In refining the models, one should bear in mind primarily the possibility of reactions involving the elimination of a hydrogen atom and the formation of radicals in electronically excited states. This path is of considerable importance in the vacuum photolysis of gas-phase molecules. Among problems which have not been investigated as yet, the development of the theory of the non-adiabatic and predissociative elimination of molecular hydrogen, of the dissociative addition of electrons, and of the formation of excited states by recombination is important. The problem of the theoretical description of ion–molecule reactions in the condensed phase is of particular interest. The successful solution of such problems requires further experimental investigation of the spectra of radicals and radical-cations and of the temperature dependence of the yield of radicals in radiolysis.

XI. APPENDIX

Here we shall describe the estimation of the electronic component of the matrix element of the non-adiabatic operator. The expression for β can be transformed into

$$\beta = \left\langle i \left| \frac{\partial U}{\partial x} \right| f \right\rangle_{x=0} [\Delta E_{fi}(0)]^{-1}, \qquad (A.1)$$

where U is the operator of the Coulombic interaction of the electrons and nuclei of the system and $\Delta E_{fi}(0)$ is the difference between the electronic energy levels f and i at the point corresponding to the equilibrium configuration. By choosing the system in such a way that the x axis coincides with the direction of the R–H bond, one can obtain for the derivative $\partial U/\partial x$

$$\frac{\partial U}{\partial x} = \sum_i \left[\frac{z_1 e^2 m_2 (X_1 - x_i)}{(m_1 + m_2) |\mathbf{R}_1 - \mathbf{r}_i|^3} - \frac{z_2 e^2 m_1 (X_2 - x_i)}{(m_1 + m_2) |\mathbf{R}_1 - \mathbf{r}_i|^3} \right], \qquad (A.2)$$

where m_1 and m_2 are the masses, z_1 and z_2 the effective charges, $\mathbf{R}_1$ and $\mathbf{R}_2$ the radius-vectors, X_1 and X_2 their x components for the nuclei of the hydrogen atom and the atom to which it is linked, and $\mathbf{r}_i$ and x_i are the radius vector and its x component for the ith electron. The operator (A.2) is of the one-electron type and the general expression for its matrix elements between arbitrary configurations can be found in Kaplan's book[92]. If $|i\rangle$ is the excited state and $|f\rangle$ is the ground state, then

$$\left\langle i \left| \frac{\partial U}{\partial x} \right| f \right\rangle = \sqrt{2} \left\langle \varphi_i \left| \frac{\partial U}{\partial x} \right| \varphi_f \right\rangle, \qquad (A.3)$$

where φ_i and φ_f are the molecular orbitals between which the electronic transition takes place. In other cases the expression for the numerator in Eqn. (A.1) differs from that in Eqn. (A.3) by an unimportant numerical multiplier. When φ_i and φ_f are described by a linear combination of atomic orbitals. The main contribution to β comes in most cases from two-centre integrals for the interaction of the electrons of the atom to which the hydrogen atom is linked with the nucleus of the hydrogen atom. Their calculation presents no difficulty, since they are expressed in terms of the derivatives of two-centre quantum-chemical integrals with respect to the internuclear distance R.[93] For example, in the case of $\pi - \pi^*$ transitions of aromatic molecules, this integral is

$$\gamma = \left[2p_z 2p_z \left| \frac{X_1 - x}{|\mathbf{R}' - \mathbf{r}|^3} \right| \right] = \frac{1}{R^3} - \frac{18}{\alpha^3 R^4} + \\ + \left(\frac{18}{\alpha^2 R^4} + \frac{18}{\alpha R^3} + \frac{8}{R^3} + \frac{2\alpha}{R} + \frac{\alpha^2}{4} \right) e^{-\alpha R}, \qquad (A.4)$$

where α is the Slater charge of the carbon atom for the $2p_z$ functions. Assuming that $R = 2$ a.u., and $\alpha = 3$, we obtain $\gamma \simeq 0.15$ a.u. The integrals with other functions of the valence shell of the carbon atom and other atoms in the Second Period have similar values. The expression $\gamma = R^{-2}$ can be used for estimates, provided that $R > 3$ a.u.

Taking into account only two-centre integrals for the interaction of atoms with the nearest carbon atom, we obtain the following expression for β in the decomposition of aromatic hydrocarbons in the $\pi\pi^*$ states:

$$\beta = C_{ni} C_{nf} \gamma (\Delta E_{if}(0))^{-1},$$

where C_{ni} and C_{nf} are the coefficients of the expansion of φ_i and φ_f with respect to the atomic orbitals of the carbon atom from which the hydrogen atom is eliminated. If the

molecule contains N carbon atoms, then $C_{ni} \simeq C_{nf} \simeq N^{1/2}$ and $\beta \simeq N^{-1}\gamma[\Delta E_{if}(0)]^{-1}$. After summation with respect to all the hydrogen atoms, we find that $k \simeq N^{-1}$. Thus the stability of molecules increases with increase in the number of conjugated bonds. The values $N \lesssim 6$ are of real interest. Bearing in mind that $\Delta E_{if} \simeq 0.1$ a.u., we obtain $|\beta|^2 \simeq 2$ a.u. For molecules containing a large number of bonds, $|\beta|^2$ is much smaller than this value.

In the decomposition of molecules in $\sigma\sigma^*$ states, which can be described in terms of the strong bond approximation, k is independent of N, and the same value (i.e. 2 a.u.) may be used for $|\beta|^2$. If the decomposition takes place in the $n\pi^*$ and $n\sigma^*$ states of molecules or $\sigma\sigma^*$ states of radical-cations, then k is independent of molecular size owing to the localisation of states, and it may be assumed that $|\beta|^2 \simeq 2$ a.u.

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