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Abstract

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Formation of Excited Ethyl Radicals in the Interaction of Hot Hydrogen Atoms with Ethylene

(Presented by Academician V. N. Kondrat̕ ev on March 6, 1964)

In various areas of high-energy chemistry (photochemistry, radiation chemistry), concepts concerning the special chemical behavior of excited (“hot”) radicals are often invoked to explain specific phenomena (see, for example, ([1], [2])). However, in most cases such reasoning is purely qualitative and sometimes unsubstantiated. In the present communication we give some data on the formation, stability, and reactivity of hot ethyl radicals.

In studying ([3]) reactions of hot tritium atoms with ethylene, and also in the radiolysis of ethylene-containing mixtures in an atomic reactor, we observed anomalously high ethane/butane ratios, inconsistent with the reaction schemes of ethyl radicals generally accepted in thermal chemistry ([4]). These results can be explained on the basis of the idea that the reactivity of ethyl radicals formed upon addition of atomic hydrogen to ethylene depends on the energy of the H atoms.

Since, however, in nuclear reactions in the system and during radiolysis, very high energies, exceeding the ionization potential, are transferred to molecules, in principle a number of competing processes (in particular, ion-molecular ones) may occur, which makes it difficult to determine the mechanism of the phenomenon unambiguously.

In this connection, an attempt was made to obtain and study hot ethyl radicals under “softer” conditions, ensuring a clearer interpretation of the experimental data. For this purpose, photolysis was carried out of mixtures of hydrogen iodide with ethylene, enclosed in a thermostated quartz cell, followed by analysis of the products by gas chromatography, IR spectrometry, and manometrically. Irradiation was performed with the light of a PRK mercury lamp, in whose ultraviolet spectrum there are lines with λ 2483, 2537, 2652, 2804 Å, with intensity ratios respectively 0.4 : 1.0 : 0.9 : 0.4. In this region of the spectrum C_2H_4 is not directly subjected to photolysis, while HJ decomposes according to the scheme ([5])

$$\mathrm{HJ} \xrightarrow{h\nu} \mathrm{HJ} + \mathrm{J}^*, \tag{1}$$

Fig. 1. Dependence of the rate of C_2H_6 formation (cm^3/min) on temperature. a –system HJ : C_2H_4 = 9 : 1 (I), b –system (I) : He = 2 : 8

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$$\mathrm{H} + \mathrm{HJ} \rightarrow \mathrm{H}_2 + \mathrm{J}, \tag{2}$$

$$\mathrm{J} + \mathrm{J} \rightarrow \mathrm{J}_2. \tag{3}$$

The quantum yield $\Phi = 2$ and does not depend on temperature or on ethylene additions. H atoms are formed in photolysis (1) with increased nonequilibrium energy

$$E(\mathrm{H}^*) = [E_\gamma - D_{\mathrm{HJ}} - E(\mathrm{J}^*)] \cdot \frac{127}{128}.$$

At λ 2537 Å ($E_\gamma = 4.9$ eV = 112 kcal/mol) and $D_{\mathrm{HJ}} = 71$ kcal/mol, the kinetic energy of the H atoms is $E(\mathrm{H}^*) = 19$ kcal/mol (0.8 eV), if J is formed in the state $^2P_{1/2}$ ($E^*_{\mathrm{J}} = 22$ kcal/mol), and reaches 41 kcal/mol

(1.8 eV) in the case of $\mathrm{J}(^2P_{3/2})$. This corresponds to average thermal-motion energies at temperatures of 10^4—$2.1 \cdot 10^4$ °K.

V. N. Kondrat' ev and co-workers, using the oxidative photolysis of HJ as an example, first showed (^{6}) that the chemical activity of such hot H-atoms depends on their kinetic energy.

In an HJ–C_2H_4 mixture, hot H-atoms are consumed mainly in process (2), but some fraction of them adds to ethylene

$$\mathrm{H}^* + \mathrm{C_2H_4} \rightarrow \mathrm{C_2H_5^*}, \tag{4}$$

as a result of which excited ethyl radicals $C_2H_5^*$ are generated with $E^* = q + E(\mathrm{H})$ ($q = 38$ kcal/mole–the heat effect of the reaction of addition of an H-atom to ethylene (^{7})).

Fig. 1. Dependence of the rate of formation of C_2H_6 (cm^3/min) on temperature. **a** –system HJ : C_2H_4 = 9 : 1 (I), **b** –system (I) : He = 2 : 8

Fig. 2. Dependence of the yield of C_2H_6 on additions of argon and helium: **a** –system (I)–Ar, **b** –system (I)–He

The number of collisions necessary for thermalization of hot H* atoms in a medium of heavy molecules (HJ, C_2H_4) is sufficiently large, which ensures the

Fig. 2. Dependence of the yield of C_2H_6 on additions of argon and helium: a —system (I)—Ar, b —system (I)—He

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preferential formation of excited $C_2H_5^*$ even at low concentrations of C_2H_4 in a mixture with HJ. The ethyl radicals excited according to (4) also dissipate their energy slowly. Thermal C_2H_5 radicals readily react with iodine.

Indeed, if, in the photolysis of HJ—C_2H_4 mixtures ($t^\circ \simeq 20^\circ$C), sufficient concentrations of thermal ethyl radicals were formed, then, as a result of recombination and disproportionation processes,

$$C_2H_5\cdot + C_2H_5\cdot \begin{cases} \rightarrow C_4H_{10} \\ \rightarrow C_2H_4 + C_2H_6 \end{cases} \tag{5}$$

butane and ethane should have been formed in a ratio of 4 : 1 (^{4}). However, chromatographic analysis of the products of photolysis of mixture (I) HJ : C_2H_4 = 9 : 1 ($p \simeq 100$ mm Hg) shows the absence of butane in the presence of significant amounts of ethane.

The yield of ethane in the temperature interval studied, from 0 to 250°C, does not depend on temperature (see Fig. 1). The absence of a temperature dependence is also observed for mixture (II), rich in ethylene: HJ : C_2H_4 = 3 : 7.

The rate of ethane formation changes only very slightly when even large amounts of Ar are introduced into the system (up to 80% of the composition of the ternary mixture—Ar : (I) = 8 : 2), but drops sharply upon addition of He (see Fig. 2).

If a mixture "deactivated" by helium additions, (He : (I) = 8 : 2), is heated during photolysis, then, in contrast to the pure system (I : HJ : C_2H_4 = 9 : 1), an Arrhenius dependence is observed for the yield of ethane (see Fig. 1). The effective activation energy of the ethane-formation process is $E = 3.5$ kcal/mole, which is close to the value calculated by the Semenov—Polanyi rule (^{7}) for the reaction

$$C_2H_5 + HJ \rightarrow C_2H_6 + J. \tag{6}$$

The results considered indicate the occurrence of excited ethyl radicals when hot H^* atoms add to ethylene (4), and the formation of ethane by the reaction

$$C_2H_5^* + HJ \rightarrow C_2H_6 + J \tag{7}$$

(and by an analogous reaction with C_2H_4 in mixtures (II), rich in ethylene).

Although the activation energies of the reactions $C_2H_5^* + HJ \to C_2H_6$ ($E_I =$ 3.5—5 kcal/mole) and $C_2H_5 + C_2H_4 \to C_2H_6$ ($E_{II} =$ 15—17 kcal/mole) differ very substantially, the ratio of the C_2H_6 yields in systems (I) and (II) is independent of temperature and is equal to 1.3—1.4.

The chemical activity of $C_2H_5^*$ is determined by the degree of excitation E^*, which depends on the mean energy of the hot H^* atoms. The latter can be regulated by introducing helium, which (owing to the closeness of the masses) is an effective moderator of hot hydrogen atoms. In the limit, with complete thermalization of H atoms, reaction (7) is replaced by (6). The excited ethyl radicals prove to be sufficiently stable and manage to react chemically before thermalization. Relaxation of their energy proceeds slowly both in collisions with diatomic HJ molecules (transfer to vibrational levels) and in collisions with argon (transfer to translational degrees of freedom). Since in the present case $E(H) \lesssim q$, the degrees of excitation of the so-called "thermal" ($E_{vib} = q = 38$ kcal/mole) and "hot" ($E = q + E(H)$) $C_2H_5^*$ radicals do not differ very greatly. The qualitative difference in the chemical behavior of $C_2H_5^*$ and C_2H_5 is possibly associated with a difference in the nature of the excitation: fast H atoms may cause excitation of the electronic levels of the radical and impart angular momentum to the radical in a noncentral collision with C_2H_4. It may be assumed that ethyl radicals excited electronically and rotationally (in addition to E^*_{vib}), for which energy relaxation is hindered, possess enhanced chemical activity.

The ideas set forth may prove useful in considering experimental data on the radiolysis and photolysis of organic substances and in studying the chemical consequences of nuclear transformations in organic media.

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