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THE CHEMISTRY OF HOT HYDROGEN ATOMS WITH 1-3 eV ENERGY AND OF EXCITED RADICALS

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I. INTRODUCTION

Many investigations[1-10] of the chemistry of hot tritium atoms produced by the nuclear reactions $^6Li(n,\alpha)T$ and $^3He(n,p)T$ (recoil energy of the T atoms 2.7 and 0.2 MeV respectively) have shown that these atoms can efficiently take part in chemical reactions when slowed down to energies comparable to those of chemical interaction: in particular, they can take part in transfer and substitution reactions proceeding without activation energy

$$T^* + RH \rightarrow HT + R^\cdot \quad (1)$$
$$T^* + RH \rightarrow RT + H \quad (2)$$

For thermal hydrogen atoms the activation energy of reaction (1) is 9-12 kcal mole^{-1}; reaction (2) is not known to occur with thermal H atoms.

Hot T atoms can add on to the double bond of alkenes, giving excited radicals[6,10], and they can also replace individual atoms or even groups of atoms in complicated molecules[1,7]: when this happens the intermediate products can be used in an excited state, and the decomposition mechanisms will be determined by a number of factors (degree of excitation, efficiency of transfer of the excitation energy, etc.[7,8]).

It should be noted that the formation of fast atoms and of excited molecules and radicals is not confined to processes accompanying nuclear transmutations, but it occurs also in radiolysis, photolysis, and even in thermal reactions at high temperatures.

To explain various anomalies in the behaviour of atoms and radicals, many workers in the field of kinetics have put forward the concept of an abnormally high reactivity for the hot hydrogen atoms and radicals obtained in the radiolysis of hydrocarbons and in the photolytic decomposition of excited molecules.

The majority of workers believe that the primary act in the radiolysis of hydrocarbons is fissure of the C-H bond.

The energy excess $E_{excit} - D_{C-H}$ (where D is the dissociation energy of the C-H bond) apportions itself between R and H in inverse proportion to the masses, and is carried away mainly in the form of kinetic energy by the H atom[11].

Hot H* atoms with a kinetic energy of the order of several electron-volts are reactive at low temperatures as well as at ordinary temperatures[12-14]. Armstrong[14] has demonstrated experimentally the existence of hot hydrogen atoms in his study of the low-temperature radiolysis of HCl at -78° and -196°. These atoms are produced by the decomposition of an excited HCl* molecule ($HCl^+ + e \rightarrow HCl^* \rightarrow H^* + Cl$). Radiation yields G of 4.0 and 2.4 respectively were measured for the formation of hot and of thermal H atoms.

The concept of hot H* atoms has been invoked many times in work on the liquid-phase and gas-phase radiolysis of hydrocarbons[15-17]. Reactions between highly excited H* atoms and C_2H_4 molecules have also been detected mass-spectrometrically[18].

However, a quantitative interpretation of reaction schemes involving hot atoms during radiolysis presents serious difficulties, because of the presence of various competing reactions, of the unknown energy spectrum of the hot atoms, etc.

The most convenient route for the preparation of H* atoms is through photochemical reactions, in particular the photodissociation of the hydrogen halides HI and HBr.

II. FORMATION OF HOT HYDROGEN ATOMS DURING PHOTOLYSIS OF HI AND HBr, AND THEIR REACTIONS

Kondrat'ev and coworkers had shown[19], as long ago as in 1934, that the reactivity of H atoms obtained by the photolysis of HI is essentially dependent on their kinetic energy.

Hydrogen iodide has a continuous absorption spectrum in the ultraviolet region, beginning at 3850 Å.[20,21] The maximum extinction coefficient ϵ lies in the region of 2500 Å, and has a value of $\sim 2 \times 10^{-19}$ cm^2 per molecule[20]. Since ϵ_{HI} is high in the region of 2500 Å, and most of the radiation with λ = 2537 Å is absorbed in the first centimeter of optical path at atmospheric pressure, the experiments are usually made at lower HI pressures (~ 10-30 mmHg).

The most commonly used sources of ultraviolet radiation are low-pressure cadmium or mercury resonance lamps of type Hanovia SC 2537 (or lamps type PRK-2 or PKR-4, made in the Soviet Union). For experiments at λ = 1849 Å these lamps are fitted with a Suprasil window[22,23], and with a filter of lithium fluoride irradiated with X-rays or γ-rays,

which transmits ~ 50% of the light with λ = 1849 Å but almost completely suppresses the light of wavelength λ = 2537 Å.

The H* atoms formed in the photolytic decomposition of HI* have a kinetic energy of

$$E_{H^*} = [E_{h\nu} - D_{HI} - E_{I^*}] \times \frac{127}{128} \quad (I)$$

where $E_{h\nu}$ is the energy of the impinging quantum, D_{HI} the dissociation energy of HI, equal to 71 kcal mole^{-1}, and E_{I^*} the electronic excitation energy of an iodine atom to the $I^2P_{1/2}$ state, equal[24] to 21.8 kcal mole^{-1}. Thus, for λ = 3130, 2537, and 1849 Å the energy of hot H* atoms is 20, 41, and 82 kcal mole^{-1} respectively (0.9, 1.8, and 3.6 eV) if the I atom is in the $I^2P_{3/2}$ ground state.

During photolysis of HBr the spectrum of the first formed H* atoms lies in a narrower range of energies, because the first excited state of the bromine atom is 0.4 eV above the ground state[22,24]. In the photolysis of HBr the energy of tne H* atoms is lower than in the photolysis of HI (since the mass of Br is smaller than that of I), and hence the spectrum of H* atoms is narrower and lies in the range 2.5–2.9 eV at λ = 1849 Å. The use of HBr for the production of H* atoms with ~ 3 eV energy also has some other advantages as compared with HI: 1) HBr absorbs weakly in the region of λ = 2537 Å, so that photolysis can be carried out without a filter; 2) the extinction coefficient of Br_2 at λ = 1849 Å is considerably lower than that of I_2; 3) HBr is chemically more stable than HI.

The quantum yield of hydrogen, Φ_{H_2}, during photolysis of HI in the region of λ ≃ 2500 Å is unity, and is independent of temperature between -78° [23] and 190°.[25] The temperature independence of Φ_{H_2} can be explained by a reaction scheme involving hot H* atoms:

$$HI \xrightarrow{h\nu} H^* + I(^2P_{1/2} \text{ or } {}^2P_{3/2}) \quad (3)$$
$$H^* + HI \rightarrow H_2 + I \quad (4)$$
$$H^* + I_2 \rightarrow HI + I \quad (5)$$
$$I + I + M \rightarrow I_2 + M. \quad (6)$$

Chain branching does not take place, because the reaction

$$I + HI \rightarrow I_2 + H \quad (7)$$

is endothermic by 35 kcal mole^{-1}. It has been shown[26] that even $I^2P_{1/2}$ atoms hardly ever undergo transfer reactions of the type (7). The steady-state rate of formation of H_2 and I_2 is

$$\frac{d(H_2)}{dt} = \frac{d(I_2)}{dt} = \frac{I_a}{1 + \frac{k_5}{k_4}\frac{(I_2)}{(HI)}} \quad (II)$$

where I_a is the number of photons absorbed in 1 sec. At low extents of reaction, when the ratio I_2/HI can be treated as constant, the quantum yield of hydrogen Φ_{H_2} is

$$\Phi_{H_2} = \frac{(H_2)_{fin} - (H_2)_{init}}{\int_0^t I_a\,dt} \simeq \frac{1}{1 + \frac{k_5}{k_4}\frac{(I_2)}{(HI)}}. \quad (III)$$

It is evident from Eqn. (III) that $1/\Phi_{H_2}$ is a linear function of the ratio I_2/HI, whose slope gives the ratio k_5/k_4. Schwarz and coworkers[27] examined the photolysis of HI at λ = 2537 Å and found that the ratio k_5/k_4 is 3.8 and does not vary with temperature. Addition of inert moderators (Ne, Ar, He, etc.) results[25] in a decrease of k_4/k_5 from 0.25 to 0.014, and an activation energy $E_4 - E_5 = 4.5 \pm \pm 0.8$ kcal mole^{-1} appears[27].

These results on the effect of temperature and of added inert moderators are difficult to explain in terms of classical kinetics unless the concept of hot atoms is adopted. Thus, the temperature independence of Φ_{H_2} is readily explained if the enhanced reactivity of hot H* atoms is ascribed to the excess kinetic energy of these atoms, which is higher than or equal to the threshold energy required for any particular reaction. The addition of inert moderators to the system causes thermalisation of the hot H* atoms. If we assume that inhibition involves an elastic collision mechanism, the average energy loss per collision, $\Delta\overline{E}/E$, is

$$\frac{\Delta\overline{E}}{E} = \frac{2m_1m_2}{(m_1+m_2)^2} \quad (IV)$$

where m_1 and m_2 are the masses of the colliding atoms. $\Delta\overline{E}/E$ reaches a maximum for $m_1 = m_2$, and therefore He is a more efficient moderator than Ar. The slowing down of H* on HI molecules is a slow process. If He is added, however, the slowing down of H* atoms becomes fast, the probability of reaction (4) decreases, and the ratio k_4/k_5 also decreases. Further experimental confirmation of the reactions of hot H* atoms formed in the photolysis of HI and HBr can be found in the papers of Martin and Willard[22,23] and by Carter and coworkers[28] on the photolysis of HI–RH and HBr–RH mixtures and of their deuterated derivatives at λ = 2537 and 1849 Å, where RH = H_2, CH_4, C_2H_6, C_5H_{12}.

In this case, in addition to reactions (3)–(6), the following reactions occur:

$$D^* + DI \rightarrow D_2 + I \quad (8)$$
$$D^* + RH \rightarrow HD + R^\cdot \quad (9)$$
$$D^* + DI \rightarrow D + DI \quad (10)$$
$$D^* + RH \rightarrow D + RH \quad (11)$$
$$D^* + M \rightarrow D + M \quad (12)$$
$$D + DI \rightarrow D_2 + I \quad (13)$$
$$D + RH \rightarrow HD + R^\cdot \quad (14)$$
$$R + DI \rightarrow RD + I \quad (15)$$

where D* is a hot deuterium atom and D is a slowed deuterium atom. Since the activation energy of (14) is large (~ 7–12 kcal mole^{-1} for thermal hydrogen atoms), it may be assumed that at high concentrations of RH the formation of HD occurs mainly by reaction (9). Then

$$\frac{D_2}{HD} = \frac{k_8}{k_9}\frac{[DI]}{[RH]} + \frac{k_{11}}{k_9} + \frac{k_{12}}{k_9}\frac{[M]}{[RH]} \quad (V)$$

and in the absence of the moderator M we have the linear relationship

$$\frac{D_2}{HD} = \frac{k_8}{k_9}\frac{[DI]}{[RH]} + \frac{k_{11}}{k_9}. \quad (VI)$$

The intercept on the y-axis of the plot of D_2/HD against DI/RH corresponds to k_{11}/k_9, and the slope corresponds to k_8/k_9.

From the slope and the intercept we can, with appropriate assumptions, evaluate the mean probability of reaction per collision in the hot region and the mean energy loss per collision with a hydrocarbon molecule during the thermalisation. Table 1 gives the results of Carter and coworkers[28] and of Martin and Willard[22] for k_8/k_9 and k_{11}/k_9 in the photolysis of DI–RH and HBr(DBr)–RH(RD) mixtures, and also the mean reaction probabilities per collision and the mean energy losses per collision.

The increase of the D_2/HD ratio with increase of wavelength λ, or with addition of an inert moderator, as well as the lack of temperature dependence, is evidence that hot H* atom reactions occur during photolysis of HI.

TABLE 1. Efficiency of slowing down and probability of hot reactions in the DI–RH and HBr(DBr)–RH(RD) systems.[22,27]

λ, Å	System	Fraction of atoms slowed down	Fraction of atoms reacting with hot atoms	k_0/k_9	k_{11}/k_9	Average reaction probability per collision		Average loss of energy per collision		Reference
						P_s	P_9	f_{tot}	$f_{elastic}$	
2537	DI–H_2	0.58	0.42	5.64	1.40					
	DI–C_2H_6	0 81	0.19	6.40	4.33					27
	DI–CH_4	0.94	0.057	24.3	16 7					
	DI–C_5H_{12}	—	—	4.65	4.80					
1849	HBr–D_2	0.39	0.61	2.04	0.65	0.26	0.17	0.32	0.32	22
	HBr–CD_4	0.94	0.062	81	15		0.0031	0.07	0.091	
	HBr–C_2D_6	0.86	0.14	11.8	6.1		0.018	0.19	0.052	
	DBr–H_2	0.38	0.62	1.54	0.60	0.41	0.35	0.50	0.50	
	DBr–CH_4	0.83	0.17	6.40	5.0		0.002	0.42	0.20	22
	DBr–C_2H_6	0.69	0.31	2.25	2.2		0.14	0.51	0.12	

As the kinetic energy of the H* atom increases, the role of "hot" reactions becomes more important. Thus, in the case of CH_4 and C_2H_6, the fraction of "hot" reactions by hydrogen atoms increases from 6 to 17 and from 19 to 31% respectively as the energy of the H* atoms is raised from 0.9–1.8 eV (λ = 2437 Å) to 2.5–2.9 eV (λ = 1849 Å). The ratio k_1/k_2 for hot T* atoms of energy ~ 3 eV is 3.5–4, as shown[9] by a study of the photolysis of TBr (λ = 1849 Å) mixed with CH_4 and C_2H_6. With tritium recoil atoms having an initial energy of 0.2 MeV, the "hot" reactions (1) and (2) account for 50–70% of the total amount of tritium atoms consumed[1–10].

Hot H* atoms obtained by the photolytic decomposition of HI have an enhanced reactivity, since they can bring about replacement reactions not only at room temperature (in the gas[19,23,28] and in the liquid phase[29,31]) but also, in the solid phase, at temperatures of -78°[22,31] and -196°,[30] as shown for the low-temperature photolysis of HI (0.01–0.1 mole %) in a matrix of 3-methylpentane. The quantum yield Φ_{H^*} is 0.2 in the liquid phase at 298°K and in the solid phase at 123°K; $\Phi_{H_{thermal}}$ = 0.8 at 298°K, falling to 0.2 at 77°K.

With thermal H atoms, low-temperature replacement reactions are effectively excluded by the large activation energy.

III. FORMATION AND REACTIONS OF EXCITED RADICALS OBTAINED BY PHOTOLYSIS OF ALKYL HALIDES AND OTHER COMPOUNDS

Radiolytic and photolytic processes can give rise not only to hot hydrogen atoms having an excess of kinetic energy, but also to "hot" vibrationally excited radicals whose reactivity increases markedly with the energy of the source of excitation.

The reactions of "hot" radicals obtained in the photolysis of alkyl iodides have been most fully investigated. Alkyl iodides have a continuous absorption spectrum in the region 2500–2600 Å. When an excited molecule of alkyl iodide decomposes, the energy excess $E_{h\nu} - D_{R-I}$ apportions itself among the residues in inverse proportion to their masses. For example, in the photolysis of CH_3I at λ = 2537 Å ($E_{h\nu}$ = 112 kcal mole^{-1}), $E_{h\nu} - D_{CH_3-I}$ equals 57 kcal mole^{-1} if I is in the $I^2P_{3/2}$ state and 35 kcal mole^{-1} if I is in the $I^2P_{1/2}$ state. Since the masses of CH_3 and I are very different, ~ 7/8 of this energy will be imparted to the CH_3 radical, and as a result the latter will become vibrationally excited.

Many papers[32–40] give experimental proof of the higher reactivity of vibrationally excited CH_3^* radicals as compared with thermal CH_3 radicals.

One usually considers the following scheme during photolysis of CH_3I:

$$CH_3I \xrightarrow{h\nu} CH_3^* + I \quad (16)$$

$$CH_3^* + CH_3I \longrightarrow CH_4 + CH_2I \quad (17)$$

$$CH_3^* + RH \longrightarrow CH_4 + R^\cdot \quad (18)$$

$$CH_3^* + CH_3I \longrightarrow C_2H_6 + I \quad (19)$$

$$CH_3^* + CH_3I \longrightarrow CH_3 + CH_3I \quad (20)$$

$$CH_3^* + M \longrightarrow CH_3 + M \quad (21)$$

and also the recombination reactions of thermal CH_3 and CH_2I radicals and I_2 addition reactions. It has been shown that the main reactions of the CH_3^* radical are the abstraction reactions (17) and (18), the rate of formation of CH_4 being unaffected by temperature over the range from -78° to 300°, whereas additions of inhibitors (I_2, O_2, NO) and of inert moderators (noble gases, N_2, CO_2) lower the rate of formation of CH_4.[36,38]

Reactions (17) and (18) are observed not only in the gaseous and in the liquid phase, but also in the solid phase at low temperatures. Formation of CH_4 has been reported at a temperature of 4°K in pure CH_3I,[39] at 77°K in hydrocarbon matrices[40,41], and at 20°K in solid inert matrices of Kr, Xe, and N_2 containing C_2H_6 and $(CH_3)_3CH$.[42] On changing from the liquid to the solid phase Φ_{CH_4} decreases by approximately a factor of 5–7, the decrease taking the form of a discontinuity at the phase transition point[40].

The decrease in Φ_{CH_4} on going over to the solid phase may be due to greater efficiency of the deactivation processes experienced by the CH_3^* radicals in the solid phase.

It is important to note that during solid-phase photolysis (77°K) of CH_3I and of solutions of CH_3I and CD_3I in methylcyclohexane, stabilisation of the CH_3^* radicals cannot occur to any significant extent[40,42]: only R• radicals formed by reactions (17) and (18) were detected by the ESR method.

On the other hand, partial stabilisation of the methyl radicals occurs in the photolysis of azomethane, since in this case the proportion of hot CH_3^* radicals (produced by the decomposition of the excited $CH_3–N{=}N–CH_3^*$ molecule) is not large.

The reactivity of CH_3^* increases with the excitation energy. Thus, Φ_{CH_4} values of 0.15×10^{-3}, 3.2×10^{-3}, and 30×10^{-3} have been reported[38] for the photolysis of CH_3I with light of λ = 3130, 2537, and 1849 Å respectively.

It is also found that the probability of the "hot" reaction (19) increases with the excitation energy, as shown by experiments on the influence of added inhibitors and inert moderators on the yield of C_2H_6.

The formation of "hot" $C_2H_5^*$ radicals during photolysis of C_2H_5I (λ = 2537 Å) in the liquid and in the solid phase was demonstrated by Luebbe and Willard[43] in spite of the much lower excitation energy of $C_2H_5^*$ as compared with CH_3^* (a consequence of the greater mass of the C_2H_5 radical).

"Hot" radicals appear also in various other photochemical processes. Thus, the flash photolysis of azo-

methane (λ = 3000–4000 Å) can give CH_3^* radicals in the primary act:

$$CH_3{-}N{=}N{-}CH_3^* \rightarrow N_2 + 2\,CH_3^* \quad (22)$$

followed by extraction of hydrogen from the neopentane present in the system as a second component:

$$CH_3^* + RH \rightarrow CH_4 + R^* \quad (23)$$

$$CH_3 + CH_3 \rightarrow C_2H_6. \quad (24)$$

The proportion of CH_3^* in this case is not large (~ 1% of the total number of CH_3 radicals formed), as shown by the low (~ 0.03) ratio of CH_4/C_2H_6.[40,43] When λ is increased from 3000 to 4000 Å this ratio decreases[43] by a further factor of 3–4. The lower yield of CH_3^* radicals in azomethane as compared with CH_3I is due to the fact that two bonds are broken when $CH_3{-}N{=}N{-}CH_3^*$ decomposes, and the energy excess is divided among at least three particles.

Several hot particles can form when the quantum energy of the incident light is increased. Thus, the photolysis of acetone in the vacuum ultraviolet region (λ = 1236 and 1470 Å) can result in the simultaneous production of CH_3^* radicals and hot hydrogen atoms[44]. The formation of hot acetyl radicals during the photolysis of ketones at λ = 2537 Å has been reported[45].

Several workers have shown[46,47] that the photolysis of diethyl ketone (λ = 2200–3100 Å) produces "hot" propionyl radicals $CH_3CH_2CO^*$ which subsequently decompose into C_2H_4, CO, and H. Hot halomethyl radicals produced in the photolysis of halomethanes also show enhanced reactivity towards displacement reactions[48].

The possibility of forming vibrationally excited radicals has been demonstrated, in the case of the photolysis of azoethane $(C_2H_5)_2N_2$, by changing from 3600 to 2300 Å.[49]

IV. FORMATION OF VIBRATIONALLY EXCITED ALKYL RADICALS BY THE ADDITION OF ATOMIC HYDROGEN TO ALKENES

"Hot" radicals can be obtained not only in photochemical processes and in radiolysis, but also in ordinary chemical reactions. The heat attending the addition of H atoms to C=C bonds is known to be ~ 40 kcal mole^{-1}. This reaction gives rise to vib.ationally excited alkyl radicals, which can decompose in the absence of stabilising collisions or extract hydrogen from RH, as was reported[50–52] for "hot" $C_3H_7^*$ radicals:

$$C_3H_7^* \rightarrow C_2H_4 + CH_3 \quad (25)$$

$$C_3H_7^* + H_2 \rightarrow C_3H_8 + H \quad (26)$$

$$C_3H_7^* + C_3H_6 \rightarrow C_3H_8 + C_3H_5^*. \quad (27)$$

The rate of decomposition of $C_3H_7^*$ depends on the structure of the radical: for n-$C_3H_7^*$ the rate of decomposition is 100–1000 times higher than for iso-$C_3H_7^*$. When H atoms add on to alkenes of higher molecular weight, the number of possible decomposition routes for the "hot" radicals increases. Thus, for $C_4H_9^*$ radicals two decomposition paths are possible[53]:

$$C_4H_9^* \rightarrow CH_3^* + C_3H_6 \quad (28)$$

$$C_4H_9^* \rightarrow C_2H_5^* + C_2H_4. \quad (29)$$

The decomposition constant of the $C_4H_9^*$ radical at 305°K is independent of pressure[54] over the range 0.036–115 atm.

A great deal of work has been done on the reactivity of vibrationally excited $C_2H_5^*$ radicals obtained by the reaction

$$H + C_2H_4 \rightarrow C_2H_{5\,vibr}. \quad (30)$$

We know from chemical kinetics that the basic reactions of thermal ethyl radicals obtained by the photolysis of diethylketone[55–57], acetaldehyde[58,59], azoethane[49,60], etc. are recombination and disproportionation reactions:

$$C_2H_5^* + C_2H_5^* \rightarrow C_4H_{10} \quad (31)$$

$$C_2H_5^* + C_2H_5^* \rightarrow C_2H_6 + C_2H_4 \quad (32)$$

with k_{32}/k_{31} = 0.1–0.2, and $E_{32} - E_{31}$ = 0.8 ± 0.2 kcal × × mole^{-1}.[61] If, however, the ethyl radicals are obtained in a vibrationally excited state by the addition of H atoms to C_2H_4 — mercury photosensitised Hg6($^3P_1$) decomposition of C_2H_4, etc. — the ratio k_{32}/k_{31} increases, but the scatter of experimental results is quite large (from 0.1 to 0.8) and the ratio depends on various factors such as the pressure in the system, the intensity of irradiation, the amount of mercury, the presence of inert additives, etc.[62–66]

The increased yield of C_2H_6 has been explained in various ways. It is suggested that vibrationally excited $C_2H_5^*$ radicals undergo disproportionation reactions more readily than thermal C_2H_5 radicals[65], and that they are able to extract hydrogen[64], but a unified point of view on this problem is still lacking. $C_2H_5^*$ radicals are relatively long-lived, and can experience up to 10^4–10^6 collisions before becoming thermalised, the efficiency of slowing down of $C_2H_5^*$ on C_2H_4, H_2, He, Ne, etc. showing large differences.

Current, Cvetanovich, Rabinovitch, and others[67–70] have made detailed studies of the stabilisation and decomposition of vibrationally excited ethyl radicals obtained by adding H and D atoms to C_2D_4 and C_2H_4. They postulated the reactions

$$C_2H_4 + D \rightleftarrows C_2H_4D^* \quad (33)$$

$$C_2H_4D^* \rightarrow C_2H_3D + H \quad (34)$$

$$C_2H_4D^* + M \rightarrow C_2H_4D + M. \quad (35)$$

The influence of pressure (0.05–3 mmHg) and temperature in the range from -78° to 160° on the ratio k_{35}/k_{34} was investigated, and the experimental results were analysed by Kassel's theory. It was shown that k_{34} is relatively insensitive to temperature, varying from 2.5 × 10^7 to 6.5 × × 10^7 s^{-1} between 195° and 300°K in the case of the $C_2H_2D_3$ radical. The ratio k_{35}/k_{34} is likewise insensitive to temperature, having the values 3.0 and 2.0 at 195° and 300°K respectively for $C_2H_2D_3$. However, a large isotope effect was noted in reactions (34) and (35): thus, for the $C_2H_3D_2^*$ radical under the same conditions k_{35}/k_{34} was 18 and 6.3 at 195° and 300°K respectively, i.e. significantly higher than for the $C_2H_2D_3^*$ radical[67].

It should be noted that vibrationally excited radicals can also be produced in reactions other than the addition of H atoms to alkenes (for example, in polymerisation[71] or in the addition of oxygen or halogen atoms to the C=C bond[72]). Studies of the reactivity of such radicals are very valuable in understanding a number of important processes (hydrocarbon oxidation, halogenation, etc.).

V. REACTIONS BETWEEN HOT H* ATOMS OBTAINED BY PHOTOLYSIS OF HI AND ETHYLENE

A great deal of work has been devoted to the study of the reactivity towards alkanes of hot H* atoms obtained in the photolytic decomposition of HI, but very little information

exists on the interaction between hot hydrogen atoms and alkenes. Yet, this problem is clearly very relevant from the point of view of explaining the influence of the kinetic energy of the H* atoms on the degree of excitation and on the reactivity of the resulting alkyl radical. Studies of the reactions of tritium recoil atoms have shown that alkenes can undergo not only extraction and substitution reactions, as in the case of alkanes, but also addition of a hot hydrogen atom to the double bond with formation of excited radicals[73] which subsequently decompose:

$$T + CH_3(CH_2)_2CH=CHCH_3 \rightarrow CH_3(CH_2)_3\dot{C}HTCHCH_3 \rightarrow CHT=CHCH_3 + CH_3(CH_2)_2. \quad (36)$$

The decomposition of excited radicals is a unimolecular process, analogous to the decomposition of the vibrationally excited radicals obtained by the addition of thermal hydrogen atoms to alkenes[53]. Lee and Rowland[6] have shown that the probability of stabilisation of excited radicals in a condensed phase at low temperatures is higher than in the gas phase

$$T^* + CH_3-CH=CH-CH_3 \rightarrow (CH_3-\dot{C}H-CHT-CH_3)^* \quad (37)$$

$$(CH_3-\dot{C}H-CHT-CH_3)^* \xrightarrow{RH} CH_3CH_2CHT-CH_3 \quad (38)$$

$$(CH_3-\dot{C}H-CHT-CH_3)^* \rightarrow CH_3CH=CHT+CH_3 \quad (39)$$

There is an almost complete lack of data on the reactions of hot H* atoms obtained by the photolysis of HI with alkenes. A systematic study of the reactions between hot H* atoms with 0.9–1.8 eV energy and ethylene was carried out in the Nuclear and Radiation Chemistry laboratory of the Institute of Chemical Physics of the Academy of Sciences of the USSR. The results have been partially reported in a number of papers[74-76]. Photolysis (λ = 2537 Å) of HI–C_2H_4 mixtures was found to give C_2H_6 and H_2 as the main products: butane and other hydrocarbons were not detected. The rate of formation of ethane ($W_{C_2H_6}$) is independent of temperature over a wide range (0–250°). Additions of inert moderators (helium and argon) affect $W_{C_2H_6}$ in different ways: argon has no effect, but helium causes a decrease in $W_{C_2H_6}$. The results are difficult to explain in terms of conventional kinetics. Let us consider the probable reaction scheme in the C_2H_4–HI system. Since C_2H_4 does not absorb in the 2500 Å region, the decomposition of HI with formation of a hot H* atom and an I atom is the only possible primary process resulting from photon absorption:

$$HI \xrightarrow{h\nu} HI^* \rightarrow H^* + I(^2P_{1/2} \text{ or } ^2P_{3/2}). \quad (40)$$

Hot H* atoms with 0.9–1.8 eV energy can undergo an abstraction reaction

$$H^* + HI \rightarrow H_2 + I \quad (41)$$

$$H^* + C_2H_4 \rightarrow H_2 + C_2H_3^* \quad (42)$$

or they can become thermalised

$$H^* + HI \rightarrow H + I \quad (43)$$

$$H^* + C_2H_4 \rightarrow H + C_2H_4. \quad (44)$$

Thermal H atoms will, on the whole, add to the C=C bond, because abstraction from RH involves a large activation energy (~ 7–12 kcal mole^{-1}):

$$H + C_2H_4 \rightarrow H + C_2H_5\,{}_{vibr}. \quad (45)$$

Vibrationally excited C_2H_5 radicals dissociate into H and C_2H_4, or become thermalised. Thermal C_2H_5 radicals can recombine, disproportionate, be captured by I_2, or combine at the C=C bond (thus creating a polymerisation chain):

$$C_2H^{\cdot} + C_2H_5^{\cdot} \rightarrow C_4H_{10} \quad (46)$$

$$\rightarrow C_2H_6 + C_2H_4 \quad (47)$$

$$C_2H_5^{\cdot} + I_2 \rightarrow C_2H_5I + I \quad (48)$$

$$C_2H_5^{\cdot} + C_2H_4 \rightarrow C_4H_9^{\cdot} \xrightarrow{C_2H_4} C_6H_{13}, \text{ etc.} \quad (49)$$

The absence of butane and higher molecular weight hydrocarbons among the photolysis products, whilst H_2 and C_2H_6 are present, means that the experimental results are incompatible with the above scheme. We cannot ascribe the formation of C_2H_6 to disproportionation of C_2H_5 radicals, because for thermal C_2H_5 radicals k_{47}/k_{46} = 0.1–0.2.

The absence of C_4H_{10} may be due to inhibition of the C_2H_5 radical by iodine. Also, according to Benson and others[77], the activation energy for the removal of hydrogen from HI by thermal alkyl radicals is 1–2 kcal mole^{-1}. Therefore, the formation of ethane (but not of butane) in the system may be explained by postulating the reaction

$$C_2H_5^{\cdot} + HI \rightarrow C_2H_6 + I. \quad (50)$$

However, if the C_2H_5 radicals are thermal, the difference between the effects of He and Ar inert moderators on the rate of formation of ethane is difficult to understand.

A kinetic analysis in which only thermal particles were considered also failed to agree with the experimental results.

The present writer has stated a hypothesis according to which hot $C_2H_5^*$ radicals are formed, during photolysis, by the combination of H* and C_2H_4, the reactivity of $C_2H_5^*$ being determined by the kinetic energy of the hot hydrogen atom:

$$H^* + C_2H_4 \rightarrow C_2H_5^*. \quad (51)$$

Hot $C_2H_5^*$ radicals with $E_{C_2H_5^*} = Q + E_{H^*}$ (where Q is the heat of addition of H to a C=C bond, 40 kcal mole^{-1}) can extract hydrogen from RH:

$$C_2H_5^* + RH \rightarrow C_2H_6 + R^{\cdot} \quad (52)$$

where RH = HI or C_2H_4, and reaction (52) proceeds either without activation energy (in the case of HI) or possibly with a small activation energy for extraction from hydrocarbons.

This hypothesis allows us to explain the experimental results. Thus, if the $C_2H_5^*$ radical is hot it will not be captured by iodine and will mainly give rise to C_2H_6 by reaction (52). If the radical is unable to react by (52) and becomes thermalised the resulting $C_2H_5^*$ is captured by iodine with formation of C_2H_5I. Additions of He lower $W_{C_2H_6}$ because H* rapidly loses energy by collisions with He (as a result of the comparable masses of H and He), and consequently the probability of reaction (51), and therefore also (52), decreases. Additions of Ar (Fig. 1) have no effect on $W_{C_2H_6}$ because the thermalisation of H* atoms is much slower on argon than on helium. This is confirmed by the negligible effect of Ar additions on W_{H_2}, showing once again that reactions (41) and (42) are "hot" reactions.

In order to explain the effect of composition on W_{H_2} and $W_{C_2H_6}$, the photolysis of HI–C_2H_4 mixtures was investigated over a wide range of concentrations of the two components. The experiments were made under steady state conditions at a constant pressure of HI (30 mmHg), so that the initial rate of formation of H atoms was constant. When photolysis is carried out in mixtures containing an excess of HI the main reaction of the H* atoms is (41), and only a small

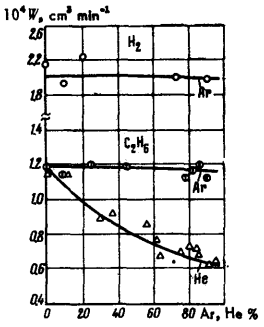


Fig. 1. Effect of He and Ar additions on W_{H_2} and $W_{C_2H_6}$ in the (C_2H_4 : HI = = 6 : 4)–Ar(He) system.

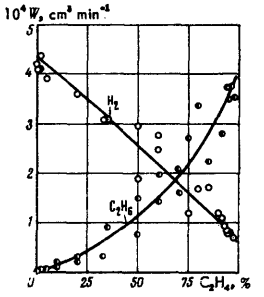


Fig. 2. Effect of composition on W_{H_2} and $W_{C_2H_6}$ in the HI–C_2H_4 system at 25° (P_{HI} = 30 mmHg).

fraction of the H* atoms will escape reaction (41) and take part in reactions (42) and (51). As the concentration of C_2H_4 in the mixture is increased, the contribution of reactions (42) [and particularly of reaction (51)] increases. The resulting $C_2H_5^*$ radicals can decompose, become thermalised, or take part in abstraction and addition reactions:

$$C_2H_5^* + HI \rightarrow C_2H_6 + I \quad (52a)$$

$$C_2H_5^* + C_2H_4 \rightarrow C_2H_6 + C_2H_3^{\cdot} \quad (53)$$

$$C_2H_5^* + C_2H_4 \rightarrow C_4H_9^* \quad (54)$$

$$C_2H_5^* + M \rightarrow C_2H_5^{\cdot} + M \quad (55)$$

$$C_2H_5^* \rightarrow H + C_2H_4 \quad (56)$$

Curves for the variation of W_{H_2} and $W_{C_2H_6}$ with composition are shown in Fig. 2. It can be seen that the decrease of W_{H_2} with increase of $[C_2H_4]$ is almost linear, whereas the increase of $W_{C_2H_6}$ shows a large departure from linearity.

It is important to note that the sum $W_{H_2} + W_{C_2H_6}$ is equal to the initial rate of formation of hydrogen in pure HI, to an accuracy of ±20%, over the whole concentration range. It follows that most of the H* atoms are consumed in reactions (41), (42), and (51), and that $C_2H_5^*$ radicals, unlike thermal $C_2H_5^{\cdot}$ radicals, contribute mainly to the abstraction reactions (52) and (53) rather than to the addition reaction (54).

Introducing the condition

$$(W_{H_2})_0 \simeq (W_{H_2})_t + (W_{C_2H_6})_t \quad (VII)$$

and considering reactions (41)–(55), we can derive a kinetic equation of the form

$$\frac{W_{H_2}}{W_{C_2H_6}} = \frac{k_{42}}{k_{51}} + \frac{k_{41}}{k_{51}} \frac{[HI]}{[C_2H_4]}. \quad (VIII)$$

The plot of $W_{H_2}/W_{C_2H_6}$ against $[HI]/[C_2H_4]$ shown in Fig. 3 is evidently linear: from the intercept and slope of this straight line we can find k_{42}/k_{51} and k_{41}/k_{51}, and therefore also k_{42}/k_{41}. It turns out that $k_{42}/k_{41} \simeq 0.1$, in fair agreement with earlier results[22,28] for reactions of hydrogen abstraction from alkanes. Thus, the main reactions in the photolysis of HI–C_2H_4 mixtures are (41) or (51), according to whether HI or C_2H_4 is present in excess in the system. The ratio k_{53}/k_{52}, estimated by successive approximations, is also close to 0.1.

Hence, the principal reactions of hot H* atoms with E = 0.9–1.8 eV are those of extraction and addition at a π-bond, with formation of an excited radical. The excited $C_2H_5^*$ radical appears to be fairly long-lived, and is able to take part in chemical reaction (hydrogen abstraction) with RH until it decomposes.

The above estimates of k_{53}/k_{52} and k_{42}/k_{41} show that the cross-sections of these reactions depend to some extent on the strength of the bond, though the dependence is very much weaker (by several orders of magnitude) than in the case of thermal H atoms or $C_2H_5^{\cdot}$ radicals.

It is important to note that the reactions of excited radicals are relatively insensitive to small additions of oxygen (Fig. 4), an efficient acceptor for thermal ethyl radicals.

Since the activation energy of reaction (50) is small (~ 1.5–2 kcal mole^{-1}), this reaction will compete with the "hot" reaction (52) only at elevated temperatures. Thus, it is interesting to examine the effect of temperature on $W_{C_2H_6}$ over a wide range of concentrations of HI–C_2H_4 mixtures. Fig. 5 shows temperature plots of $W_{C_2H_6}$ for 69, 90, 95, and 98% C_2H_4 respectively in the mixture. It is evident from the figure that even at 98% C_2H_4, when the hot reaction (41) can be effectively ignored, $W_{C_2H_6}$ is independent of temperature: this is evidence for the high efficiency of reaction (53). Helium additions cause the appearance of an activation energy (Figs. 5 and 6), the maximum value of E_{act} under full thermalisation of the hot H* atoms being ~ 1.5–2 kcal mole^{-1} (in agreement with the activation energy for the extraction of hydrogen from HI by thermal alkyl radicals). It must be noted that $W_{C_2H_6}$ decreases only by a factor of 2–3 at room temperature when H* atoms are fully slowed down. At lower temperatures (< 0°) the contribution of reaction (50) becomes less important, and $W_{C_2H_6}$ decreases more sharply.

It is interesting to consider the behaviour of excited radicals at low temperatures, when the thermal radicals are usually in a stabilised state. It has been reported[40,42] that CH_3^* could not be detected by ESR in the photolysis of CH_3I, although CH_4 was observed even at very low temperatures. When HI was photolysed in a matrix of 3-methylpentane[30] containing added alkenes (C_2H_4, etc.), ethyl, butyl, and other radicals were detected by ESR, though the authors consider that these were produced by the addition of thermalised hydrogen atoms to the alkenes. There are also data[32] on the photolysis of HI at 77°K in alkene matrices (C_2H_4, C_3H_6, see Table 2).

It is interesting to note that, as in our experiments on the gas-phase photolysis of HI–C_2H_4 mixtures, the main hydrocarbon product is C_2H_6 and the concentration of C_4H_{10} is low. Significant amounts of C_2H_5I are present: this

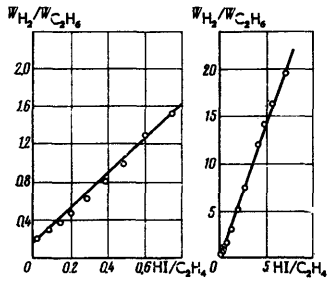


Fig. 3. Kinetic curve for Eqn. (VIII).

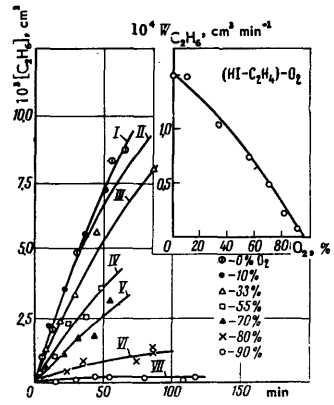


Fig. 4. Effect of added O_2 on the yield of C_2H_6 in the (C_2H_4 : HI = 6 : 4)–O_2 system: kinetics of the formation of C_2H_6 and $W_{C_2H_6}$ as a function of added O_2:
I) 0% O_2; *II*) 10% O_2; *III*) 33% O_2; *IV*) 55% O_2; *V*) 70% O_2; *VI*) 80% O_2; *VII*) 90% O_2.

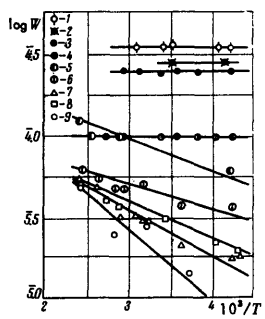


Fig. 5. Effect of temperature on $W_{C_2H_6}$ in the photolysis of HI–C_2H_4 and (HI–C_2H_4)–He mixtures:
1) HI : C_2H_4 = 2 : 98; 2) HI : C_2H_4 = 5 : 95; 3) HI : C_2H_4 = 1 : 9; 4) HI : C_2H_4 = 4 : 6; 5) (HI : C_2H_4 = 1 : 9) + 85% He; 6) (HI : C_2H_4 = 4 : 6) + 50% He; 7) (HI : C_2H_4 = 4 : 6) + 85% He; 8) (HI : C_2H_4 = 4 : 6) + 92% He; 9) (HI : C_2H_4 = 4 : 6) + 98% He.

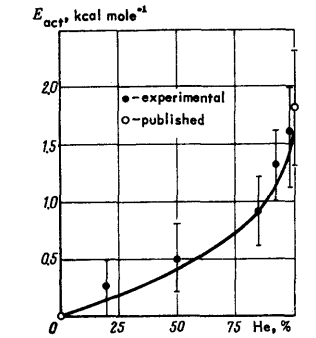


Fig. 6. Variation of the activation energy for hydrogen abstraction by ethyl radicals with concentration of added helium in the photolysis of the ternary mixture (HI : C_2H_4 = = 4 : 6)–He. The open circles are E_{act} data for hydrogen extraction from HI by thermal alkyl radicals.[77]

TABLE 2. Photolysis of HI–C_2H_4 and HI–C_3H_6 mixtures at 77°K (after Hughes and Purnell[32]).

Matrix	Irradiation time, min	Photolysis products	Amount, mol. %
HI 150 μmole C_2H_4 15 μ mole	65	C_2H_6	29
		n-C_4H_{10}	1
		C_2H_5I	70
		C_2H_2, C_4H_9I, C_4H_6, C_6H_{14}, C_3H_3I, C_1- and C_3-iodides	<1
HI 125 μmole C_3H_6 25 μ mole	40	C_3H_8	28
		2,3-dimethylbutane	2
		n-C_3H_7I	3
		i-C_3H_7I	67
		allene, diallyl, cyclopropane, C_3H_5I, methylacetylene	traces

may be ascribed to capture of ethyl radicals by I_2. The authors have put forward a hypothesis involving the formation of a reactive complex in the matrix when a photon is absorbed, followed by reactions within a cell. However, their results can be interpreted in terms of the formation of "hot" C_2H_5 radicals, produced by reaction (51), which are highly reactive even at liquid nitrogen temperature and can therefore abstract hydrogen from RH.

The results discussed above demonstrate that hot H* atoms with 1–3 eV energies have some special features as compared with thermal hydrogen atoms and very fast atoms (such as tritium recoil atoms): in particular, a weak temperature dependence of the rate of the abstraction reaction is possible near the chemical reaction threshold. When the energy is increased in the range 1–3 eV and above, the reactivity of the H* atoms increases. Studies of the reactivity of hot H* atoms in the energy range of a few electron-volts are particularly important, because these atoms can be formed in many photolytic reactions and during radiolysis. In particular, by reacting with alkenes these atoms can produce excited radicals as reactive intermediates which influence the final product distribution.

The formation of hot $C_2H_5^*$ radicals in the radiolysis of C_2H_4 and NH_3 was demonstrated by the present writer[17].

Hot H* atoms are formed by the radiolytic decomposition of excited RH molecules:

$$RH^* \rightarrow R^{\cdot} + H^* \qquad (57)$$

where RH = C_2H_4, NH_3, etc.

The ratio $C_2H_6 : C_4H_{10}$ serves as a measure of the energy of the $C_2H_5^*$ radicals. This ratio is appreciably higher than 0.1–0.2 (the value of k_{disp}/k_{rec} for thermal C_2H_5 radicals), and can approach unity [17,75,78-81] in the radiolysis of C_2H_4 and exceed unity in the radiolysis of C_2H_4–NH_3 mixtures [17,75]. The ratio is not a function of the pressure in the system or of temperature (in the range from +50° to -78°), and decreases when He is added to C_2H_4 or to a C_2H_4–NH_3 mixture [17,75]. Thus, as in the photolysis of HI–C_2H_4 mixtures, the enhanced yield of C_2H_6 in the radiolysis of pure ethylene and of ethylene mixed with RH can be explained starting from the hypothesis that a reactive intermediate (the excited ethyl radical) is formed. It is significant that in the radiolysis of NH_3–C_2H_4 mixtures small additions of O_2 affect the yield of C_4H_{10} (Fig. 7) more strongly than that of C_2H_6: this is difficult to understand on the assumption that these products are formed exclusively by reactions (46) and (47). An interesting observation made on the radiolysis of C_2H_4 at -196° is that not only did the $C_2H_6 : C_4H_{10}$ ratio not fall off, but it was even greater than unity, showing that the reactive $C_2H_5^*$ radical can be formed even at low temperatures [80].

The formation of reactive $C_2H_5^*$ radicals is obviously not specific to ethylene. The features obtained should be observable, to a greater or lesser extent, in the addition to alkenes of hot hydrogen atoms obtained both by the decomposition of excited molecules in radiolytic and photolytic processes and in chemical reactions accompanying nuclear transformations.

In contrast to the excited radicals obtained by the decomposition of a molecule, we have the new concept of an excited $C_2H_5^*$ radical formed by the collision of an ethylene molecule with a fast hydrogen atom. Whether under these conditions a vibrationally excited radical is formed, or whether electronic excitation can occur, is still not fully clear, because the electronic levels of $C_2H_5^*$ are not known.

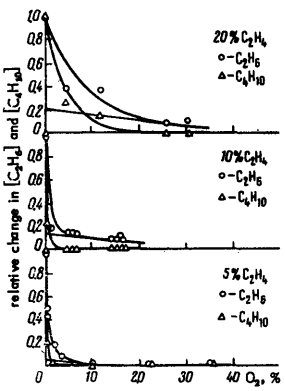


Fig. 7. Effect of added O_2 on the relative change in the yield of C_2H_6 and C_4H_{10} during radiolysis of (NH_3–C_2H_4)–O_2 mixtures. (Dose rate 1.2×10^{14} eV cm^{-3} s^{-1}, irradiation time 40 h.)

We know that the C_2H_4 molecule has low-lying electronic levels: 1.7, 4.4, 7.7, and 9.2 eV. [82] Since the levels of the $C_2H_5^*$ radical must lie below those of the $C_2H_4^*$ molecule, we cannot exclude the possibility of excitation of the electronic levels of $C_2H_5^*$ ($E_{C_2H_5^*} \simeq Q + E_{(H^*)} \simeq 3.8$ eV). When discussing kinetic mechanisms it is essential to make allowance for the possible formation of excited particles having enhanced reactivity. This is specially important in the case of photochemical processes occurring in the vacuum ultraviolet region (λ = 1236, 1440 Å) and during radiolysis, when hot atoms and radicals having several electron-volts of excess energy can be formed. "Hot" intermediate products (molecules, atoms, radicals) can be expected to form also in the reactions of recoil atoms, particularly tritium, with alkanes [2,9] as well as with alkenes [10].

Studies of the reactions of hot atoms and radicals having energies of the order of a few electron-volts should help to fill a gap in one of the most interesting regions of chemical kinetics: the region of intermediate energies, comparable with the energy of the chemical bond, which (unlike the high energy and the thermal energy regions) is as yet inadequately investigated.

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