REACTIVITY OF H· FORMED IN THE RADIOLYSIS OF BENZYL ALCOHOL CONTAINING TETRACYCLINE HYDROCHLORIDE AT 77 K*

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The radiolysis of tetracycline hydrochloride dissolved in benzyl alcohol has been studied at 77 K by ESR. The H· and e⁻ which are formed in the radiolysis of benzyl alcohol at 77 K migrate over a distance corresponding to about 95 and 995 molecules of solvent, respectively, before they are captured by the tetracycline hydrochloride solute. This distance corresponding to H· is smaller than the distance that it migrates in a neopentane matrix. The migration of H· in neopentane matrix is more favoured than in benzyl alcohol matrix. When the mole ratio between solute and solvent is 1 : 10000, the reactivity of H· observed by ESR is the following: a) 20% of H· reacts preferentially with solute because $E_H(\sin \theta)^2 < (E_{mp})$solvent; b) 80% of H· reacts exclusively with the solvent in the first collision because $E_H(\sin \theta)^2 > (E_{mp})$ solvent. The crystal structure of benzyl alcohol presents inherent factors which do not favour the migration of H· at 77 K.

Introduction

Investigations on reactions that occur in the radiolysis and photolysis of mixtures of alkanes at 77 K have revealed an interesting phenomenon.[1,2] When neopentane, containing a small concentration of alkane, is gamma-irradiated or UV-irradiated at 77 K, the radical corresponding to the solute is selectively formed, as a consequence of the selective hydrogen atom abstraction reaction.[3-6] The mechanism of this reaction considers the formation of channels which are constituted by the solvent molecules and so the H· can migrate through them by reacting with the solute.[7,8]

When the concentrations of the sample components are inverted so that the solute is solvent and conversely, the occurrence of selective hydrogen atom abstraction depends on the crystalline solvent. This reaction does not occur for most of the pairs of in-

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verted systems. MIYAZAKI and co-workers[5,6] observed this reaction in the photolysis of the cyclohexane / n-pentane system and vice versa, at 77 K.

When the radiolysis of alkane mixtures at 77 K was compared with results at 4 K, it was observed that the influence of temperature is intimately related to the molecular motion of atoms which take part in the crystalline solvent.[7] The molecular motion of atoms of solvent affects the selective hydrogen atom abstraction.

These facts indicate the importance of the crystalline solvent in the reactions that occur with species formed in the radiolysis at low temperature.

In the radiolysis of organic compounds at 77 K the $H^·$ and e^- can be observed by ESR[9-11] when they are stabilized in some way.[12-14] In methanol, in aqueous and alkaline solutions the tetracycline hydrochloride (TC) solute captures both e^- and $H^·$.[15] Therefore, in the present paper it was possible to estimate the migration distance of e^- and H which are formed in the radiolysis of benzyl alcohol (BA) before they are captured by TC solute, at 77 K. These values indicate that the crystal structure of BA solvent is more adverse than the crystal structure of neopentane with regard to migration of species. The crystal structure of BA presents inherent factors which do not favour the migration of these species. The maximum potential energy (E_{mp}) of the channel walls of solvent molecules affects the reactivity of $H^·$: 20% of $H^·$ reacts with TC solute preferably because they have $E_H(\sin \theta)^2 < (E_{mp})_{BA}$ while 80% of $H^·$ reacts with BA solvent exclusively because they have $E_H(\sin \theta)^2 > (E_{mp})_{BA}$.

Experimental

The TC and BA used were of analytical grade and BA was passed through an activated alumina column. A series of 10 samples containing BA and TC ([TC] $\leqslant$ $\leqslant 0.26$ mol/100 mol of BA) was prepared in a vacuum line on the same day. On the following day these samples were gamma-irradiated simultaneously at 77 K, with a dose of 3 kGy in a ^{60}Co-gammacell 220 source from Atomic Energy of Canada Limited and the ESR spectra were obtained with a JES–ME-3 spectrometer of JEOL at 77 K.

Results and discussion

The $H^·$ and unidentified radicals ($BA^·$) were formed when BA is gamma-irradiated at 77 K. When BA containing TC is gamma-irradiated at 77 K a singlet is observed in the ESR spectrum besides these species (Fig. 1). The species corresponding to this singlet is denoted in the present work by TC^-.

Figure 2 shows the effect of TC addition to BA in the relative yields of species: $RY_{(H^·)}$, $RY_{(TC^-)}$, $RY_{(BA^·)}$. The $RY_{(TC^-)}$ and $RY_{(BA^·)}$ were obtained by subtrac-
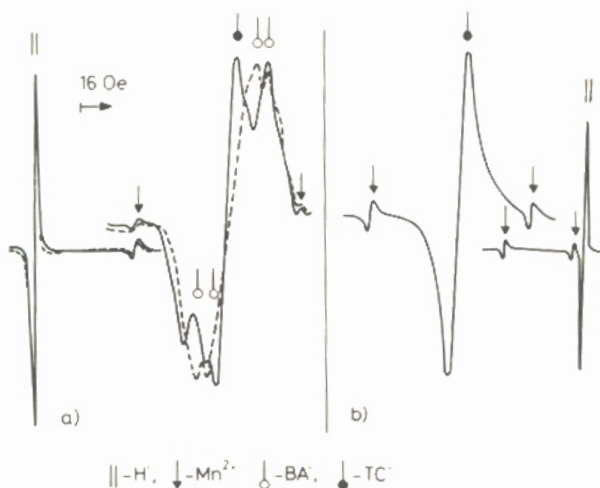
Fig. 1. Radiolysis of BA containing TC at 77 K. (a) - - - - spectrum of BA solvent; ——— spectrum of BA solvent containing [TC] = 0.02 mol/100 mol of BA; (b) spectrum of TC in powder form
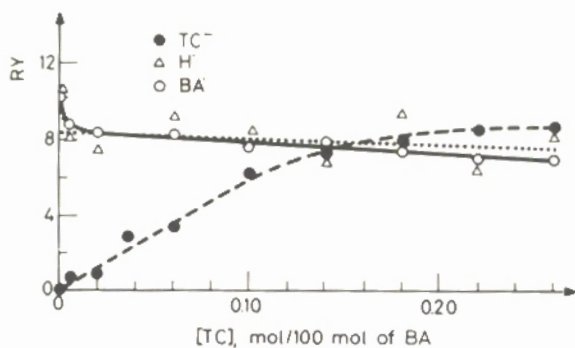

Fig. 2. Effect of TC addition on the RY of paramagnetic species formed in the radiolysis of BA at 77 K
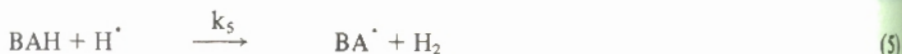
tion of simulated spectra using computer programs. The $RY_{(H·)}$ was obtained by the ratio between heights of the hydrogen peak and the Mn^{2+} standard peak. When TC is added to BA the $RY_{(H·)}$ and $RY_{(BA·)}$ decrease in the same way as a consequence of competitive reactions between solute and solvent with H· formed in the radiolysis of BA at 77 K. The TC⁻ was not formed by rupture of C–H, O–H or C–OH bonds of TC, as a consequence of selective abstraction reaction,[1]⁻[6] because the OH· was not observed in the radiolysis of BA containing TC, at 77 K, and the $RY_{(TC⁻)}$ *increases*

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more pronouncedly than $RY_{(H·)}$ decreases. The $RY_{(TC^-)}$ does not increase linearly when TC is added to BA. The energy of gamma-radiation is transferred to the solute indirectly by e^- formed in the radiolysis of BA, at 77 K. The TC^- species is a consequence of a reaction of capture of e^- by the TC solute.[15-21]

It is interesting to observe the behaviour of TC solute and species formed in the radiolysis of BA, at 77 K (Fig. 2): a) when [TC] = 0.01 mol/100 mol of BA, 20% of $H·$ reacts with solute preferentially while 80% of $H·$ reacts with the solvent exclusively and it is sufficient to capture almost all $H·$ that react with solute; b) when [TC] = = 0.18 mol/100 mol of BA it is sufficient to capture almost all e^-.

Therefore, the TC solute captures e^- and $H·$ which are formed in the radiolysis of BA at 77 K and it competes with the solvent in the reaction with $H·$:

$$BAH \longrightarrow \begin{cases} BA· + H· & \text{(1)} \\ \\ BAH^+ + e^- & \text{(2)} \end{cases}$$

$$TC + e^- \xrightarrow{k_3} TC^- \tag{3}$$

$$TC + H· \xrightarrow{k_4} \text{products} \tag{4}$$

$$BAH + H· \xrightarrow{k_5} BA· + H_2 \tag{5}$$

where k_3, k_4, k_5 are rate constants of the Reactions (3), (4), (5), respectively; BAH is another symbol of benzyl alcohol solvent; $BA·$ and BAH^+ are radicals and cations corresponding to the solvent, respectively. TC^- is a paramagnetic species that produces a singlet in the ESR spectrum at 77 K.

Reaction (1) corresponds to the rupture of C–H or O–H bonds with the formation of radicals. Reaction (2) corresponds to the ionization of solvent molecules. Both reactions take place as a consequence of energy absorption from gamma-radiation by the solvent molecule. The TC solute participates in the capture Reactions (3) and (4).[15-1] In the competitive Reactions (4) and (5), the TC solute and the BA solvent react with $H·$ that was formed in the radiolysis of BA solvent at 77 K.

The value of constant k_5 can be estimated as being: 1.8×10^{13} dm$^3 \cdot$ mol$^{-1} \cdot$ $\cdot$ s$^{-1} \leqslant k_5 \leqslant 7.6 \cdot 10^{13}$ dm$^3 \cdot$ mol$^{-1} \cdot$ s^{-1}. These values are rate constants of the abstraction reaction of hydrogen atom from benzene and toluene, respectively.[22] As $k_4 = 2.9 \cdot 10^5$ dm$^3 \cdot$ mol$^{-1} \cdot$ s^{-1},[15] it is not expected that 20% of $H·$ formed in the radiolysis of solvent should be captured by TC when [TC] = 0.01 mol/100 mol of BA. The TC solute captures e^- and competes with the solvent in the reaction with $H·$, although [TC] = 0.26 mol/100 mol of BA.

MIYAZAKI and co-workers[7,8] explain that the H· which is formed in the radio-lysis of the solvent at 77 K, can migrate a long distance by a succession of glancing collisions with the channel walls of solvent molecules and then react with an alkane solute selectively. Therefore, it is expected that the e^- and H· can migrate through the channels of BA matrix and react with TC.

A rough estimate of the average distance that e^- and H· are able to travel can be calculated from the $RY_{(TC^-)}$ and from the RY of H· that reacts only with the solute, $RY_{(H·)TC}$, as a function of [TC]. The species migrate through some volume of matrix. When the species meet one solute molecule in this volume, they are captured by solute. Equation (6) relates the RY with the distance n that the species travel through the matrix[5]:

$$-\log (1 - RY/RY_0) = n[TC] \log e/100 \qquad (6)$$

where n is the number of solvent molecules in that volume and RY_0 is the relative yield of species at infinite solute concentration.
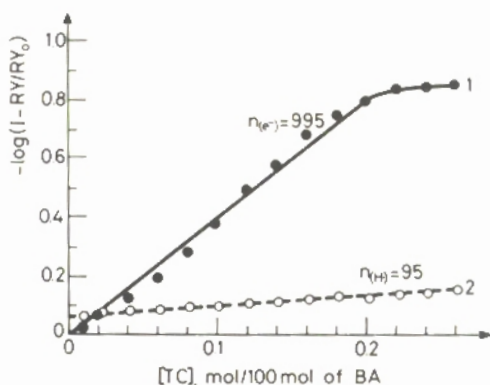

Fig. 3. The distance that H· and e^- migrate through BA matrix containing TC solute at 77 K:
curve 1 corresponding to e^- when $RY = RY_{(TC^-)}$; curve 2 correspondent to H· when $RY = 10 - RY_{(BA·)} = RY_{(H·)TC}$ (RY_0 is the RY of species at infinite solute concentration and $RY_0 = 10$)

As may be seen in Fig. 3, straight lines are obtained for e^- and H· in the radio-lysis of BA/TC at 77 K. The slopes give $n_{(e^-)} = 995$ and $n_{(H·)} = 95$. In the BA matrix, the e^- and H· collide with 995 and 95 solvent molecules before they react with the solute, respectively. This distance corresponding to H· is smaller than the distance that it migrates through a neopentane matrix (Table 1).

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Table 1

Distance of Migration of H· and e⁻ Through Various Systems at 77 K

System	Source of species	Type of reaction	Migration distance[c]
neo-C_5H_{12} / 2,3 DMB [a]	Radiolysis of solvent	Selective H· abstraction by H·	2630[d]
neo-C_5H_{12} / c-C_6H_{12}	Radiolysis of solvent	Selective H· abstraction by H·	970[e]
neo-C_5H_{12} / i-C_4H_{10}	Photolysis of HBr or of HI	Selective H· abstraction by H·	560[e]
c-C_3H_6 / C_2H_6	Radiolysis of solvent	Selective H· abstraction by H·	360[e]
i-C_4H_{10} / C_3H_8	Photolysis of HI	Selective H· abstraction by H·	100[e]
i-C_4H_{10} / C_3H_8	Radiolysis of solvent	Selective H⁻ abstraction by H·	40[e]
TMB[b] / C_3H_8	Radiolysis of solvent	Selective H· abstraction by H·	100[e]
TMB[b] / C_3H_8	Photolysis of HI	Selective H· abstraction by H·	90[e]
BA/TC	Radiolysis of solvent	Capture of e⁻ by solute	995[f]
BA/TC	Radiolysis of solvent	Capture of H· by solute	95[f]

[a] 2,3–dimethylbutane;
[b] 2,2,3,3–tetramethylbutane;
[c] This distance is the number of solvent molecules;
[d] Value obtained by GUEDES;[5]
[e] Value obtained by MIYAZAKI and co-workers;[5]
[f] Value obtained in the present work.

MIYAZAKI calculated the maximum potential energy for $H^\bullet$ in the channels of neopentane matrix: $(E_{mp})_{neopentane} = 9.3$ kcal/mol^8, and he correlated E_{mp} with the energy of $H^\bullet$, (E_H), and with the angle of incidence of $H^\bullet$ into the channeling (θ). When the E_{mp} is highest the percentage of species that react with solvent is smallest. The selectivity of reaction between the species that migrate through matrix and solutes present in small concentration depends on E_{mp}. When E_{mp} is highest, this selectivity is also highest. Therefore, 20% of $H^\bullet$ that react preferentially with TC solute enter into the channeling, so that $E_H(\sin \theta)^2 < (E_{mp})_{BA}$ and they migrate by a succession of glancing collisions with about 95 solvent molecules; while 80% of $H^\bullet$ enters into the channeling, so that $E_H(\sin \theta)^2 > (E_{mp})_{BA}$, reacting exclusively with BA solvent in the first collision.

The crystal structure of benzyl alcohol presents inherent factors which did not favour the migration of $H^\bullet$ at 77 K.

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