The Effect of Temperature on Hydrogen Atom Scavenging by Ethylene in the γ-Radiolysis of Liquid Cyclopentane

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Summary The relative rate of addition to ethylene compared with H-atom abstraction from cyclopentane for H-atoms produced by the γ-radiolysis of liquid cyclopentane is markedly dependent upon temperature.

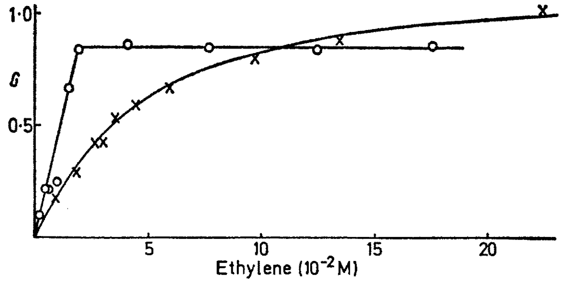

FIGURE. *Ethylene iodide yields;* ○ *radiolysis at* 195K; × *radiolysis at* 298K.

HYDROGEN yields from γ-irradiated liquid alkanes *e.g.* n-hexane[1] and cyclopentane,[2] decrease with decreasing temperature below 298K. One possible explanation for this phenomenon is that as the temperature decreases H-atom addition to product olefin becomes of importance even at very low olefin concentration since the rate of the competing process, H-atom abstraction from the alkane, decreases due to the activation energy requirements. Little is known of the reactions of H-atoms in organic liquids and even less of the effect of temperature on their rates. During a study of the scavenging of H-atoms by ethylene in γ-irradiated olefin-free, liquid cyclopentane we have obtained confirmation that, with decreasing temperature, reaction 1

$$\mathrm{H}\cdot + \mathrm{C_2H_4} \rightarrow \mathrm{C_2H_5}\cdot \qquad (1)$$

becomes much more efficient relative to reaction 2

$$\mathrm{H}\cdot + \text{cyclo-}\mathrm{C_5H_{10}} \rightarrow \mathrm{H_2} + \text{cyclo-}\mathrm{C_5H_9}\cdot \qquad (2)$$

The yield of ethyl radicals was obtained by scavenging with a very low concentration of iodine (*ca.* 10^{-4}M) containing ^{131}I as tracer.[3] The total dose was 2×10^{17} ev/ml cyclopentane, so that the concentration of cyclopentene produced by radiolysis was negligibly small. C_2H_5I was separated by g.l.c., trapped in iso-octance at 195K, and counted with a scintillation counter.

The Figure shows $G(C_2H_5I)$ at 195K and 298K as a function of ethylene concentration. At the higher temperature the curve has the same shape as that for cyclohexane[4] but the absolute yields are lower by about 15%.

At 195K, H-atom scavenging is complete in the presence of 2×10^{-2}M-ethylene with $G(\mathrm{H}\cdot) = 0{\cdot}85$. The ratio of rate constants for reactions 1 and 2, k_1/k_2 therefore increases significantly with decreasing temperature. The curve before the plateau cannot be used to obtain a value of k_1/k_2 to compare with that of 250 obtained for cyclohexane at ambient temperature[4] since the competition will be mainly between reaction 1 and reaction 3

$$H\cdot + I_2 \rightarrow HI + I\cdot \qquad (3)$$

In the absence of iodine, complete scavenging will almost certainly occur at olefin concentrations less than 10^{-3}M. Decreasing the iodine concentration at ethylene concentrations below 2×10^{-2}M causes an increase in $G(C_2H_5I)$.

These results, confirmed by similar experiments with n-hexane, show that it is impossible to obtain meaningful "initial" $G(H_2)$ values for saturated liquid hydrocarbons at 195K by extrapolation of hydrogen yields obtained at experimentally practicable doses. Reported "initial" G values which decrease with decreasing temperature may for the most part simply reflect this experimental difficulty. Such has been shown to be the case in the radiolysis of liquid ethane at 195K.[5,6]

At the highest ethylene concentrations $G(C_2H_5I)$ becomes greater at 298K than at 195K. The explanation for this is not immediately apparent. There might be some effect of temperature on the H-atom yield, but complications due to ion–molecule reactions which occur at these ethylene concentrations do not allow an immediate calculation of $G(H\cdot)$ from the results obtained at 298K.[4]

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