Isotope Effect on the Lifetime of Excited Ethane

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Summary The mean lifetimes of excited C_2H_5T and C_2D_5T are estimated from pressure dependence studies of the unimolecular decomposition reactions of these molecules following the substitution reaction with recoil tritium.

Excited ethane molecules are formed by the reaction of ethane with energetic hydrogen atoms.[1] If the hot hydrogen is in the form of the tritium isotope, excited molecules containing a radioactive label are formed [equation (1)].

$$T^* + RH \rightarrow (RT)^* + H \qquad (1)$$

These excited molecules may either become stabilised by collision with the surrounding media or may undergo unimolecular decomposition to give methyl radicals according to the scheme proposed by Johnston *et al.*[2]

$$C_2H_5T \xleftarrow{k_2} (C_2H_5T)^* \xrightarrow{k_1} CH_2T + CH_3$$

Using the experimental procedure described previously,[3] hot tritium atoms from the nuclear reaction, $^3He(n,p)T$, reacted with C_2H_6 or C_2D_6 in the presence of bromine (*ca.* 2 cm Hg) which acts both as a thermal atom scavenger[4] and as a reagent for trapping methyl radicals in the form of methyl bromide. The ratio R = yield of T-labelled ethane/yield of labelled methyl bromide, was obtained as a function of the hydrocarbon pressure, and the results are shown in the Figure. The pressure dependence of R from C_2H_6 is essentially the same as obtained previously,[2,5] but R obtained from C_2D_6 shows a considerably greater pressure dependence.

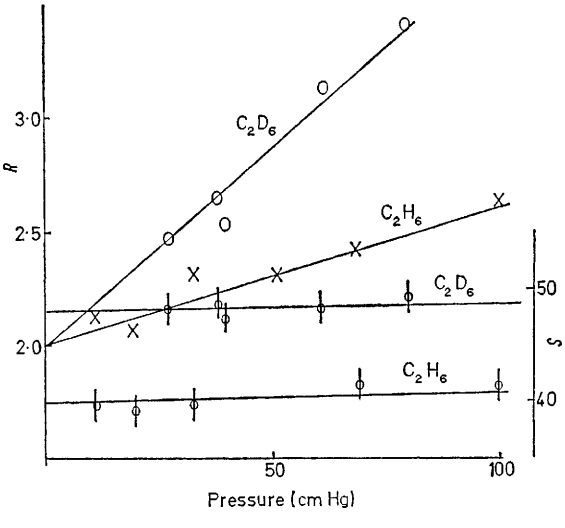

Figure. *Variation of R and S with ethane pressure. The points representing S are those showing error bars, which were estimated from the number of radioactive counts observed. The lines drawn also pass close to points obtained at ca.* 300 cm *pressure.*

Within the limits of experimental error (estimated[3] to be $\pm 5\%$) the zero pressure intercept is the same for both reactants, indicating that, as before,[2] about 66% of the T-labelled molecules initially formed contain insufficient energy to rupture the C–C bond (*i.e.* $< 3{\cdot}7$ eV). The pressure dependence of the remaining 34% may be written as equation (2) where p = hydrocarbon pressure. From

$$0{\cdot}34R = (1 - 0{\cdot}34) + (k_2/k_1)p \qquad (2)$$

the data in the Figure $(k_2/k_1)_{C_2D_5T^*} = 30{\cdot}56$ l mol^{-1} and $(k_2/k_1)_{C_2H_5T^*} = 87{\cdot}18$ l mol^{-1}. Assuming $k_2 = Z\lambda$, where Z is the rate of collision of an excited molecule and is taken to be 8.5×10^{10} l mol^{-1} s and λ, the efficiency of the deactivating collision, is taken to be the same in both reactants, we obtain $((k_1)_{C_2D_5T^*} = 0{\cdot}98\ (\pm 0{\cdot}06) \times 10^{10}$ s^{-1} and $(k_1)_{C_2H_5T^*} = 2{\cdot}79\ (\pm 0{\cdot}17) \times 10^{10}$ s^{-1}, corresponding to mean lifetimes of those excited ethane molecules which have energies $> 3{\cdot}7$ eV of $\tau_{C_2D_5T^*} \simeq (36/\lambda) \times 10^{-12}$ s and $\tau_{C_2H_5T^*} \simeq (104/\lambda) \times 10^{-12}$ s

These findings are qualitatively consistent with the greater energy-level density in deuteriated ethane which results from the lower vibration frequency of C–D bonds compared with C–H bonds. The extent to which the magnitudes are influenced by differences in the hot-atom collision density in C_2D_6 and C_2H_6 is unknown.[6]

Also detected in these experiments were small yields of labelled ethyl bromides. The ratio S = yield of labelled ethane + labelled methyl bromide/yield of labelled ethyl bromide, is shown in the Figure as a function of hydrocarbon pressure and is clearly independent of pressure within the limits of these experiments.[5] The absence of a pressure effect in both hydrocarbons could arise for two reasons: (i) the labelled ethyl radicals could result from a "double-knock" process [equation (3)],[7] or (ii) the radicals could be

$$T^* + C_2H_6 \longrightarrow C_2H_4T\cdot + 2H \qquad (3)$$

produced by unimolecular decay of excited and labelled ethane [equation (4)]. Since no variations in S (from

$$(C_2H_5T)^* \longrightarrow C_2H_4T\cdot + H \qquad (4)$$

ca. 40 in C_2H_6 and *ca.* 50 in C_2D_6, and within $\pm 5\%$) were observed, even up to hydrocarbon pressures of 300 cm Hg, (ii) would require mean lifetimes for *ca.* 3% of the labelled ethanes formed of $< (30/\lambda) \times 10^{-12}$ s for both $C_2H_5T^*$ and $C_2D_5T^*$. This would, of course, be quite consistent with the results given above for the decomposition to methyl radicals. However, this experiment does not allow a definitive statement on the mechanism of ethyl radical production, although it is clear that slightly more C_2H_4T radicals are formed (*ca.* 3%) than C_2D_4T radicals (*ca.* 2%).

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