Variation in the Abstraction Isotope Effect for Energetic Tritium Atoms

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Summary The HT/DT yield ratio from the reaction of energetic tritium atoms with 1:1 mixtures of protonated and deuteriated alkanes, is found to fall on addition of neon.

Energetic tritium atoms, which may be formed by the $He^3(n,p)T$ nuclear process, react with simple hydrocarbons principally by abstracting or replacing a hydrogen atom,[1] *e.g.*

$$T + CH_4 \longrightarrow HT + CH_3 \cdot$$

$$T + CH_4 \longrightarrow CH_3T + H \cdot$$
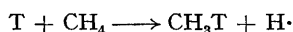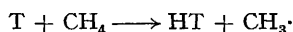
When energetic tritium atoms react with perdeuterio-compounds, the yields of all labelled products are generally smaller than those obtained from the protonated analogues.[1] Measurement of this isotope effect is clearly of importance in providing a test for any fundamental theory of the reaction dynamics. The isotope effect on the abstraction reaction is of particular interest because Rowland and co-workers have demonstrated a correlation between the yield from the abstraction reaction and the bond dissociation energy of the C–H bond involved.[2]

Although there have been earlier measurements of these isotope effects,[1,3] many were performed before the importance of scavenger effects were understood,[4] or before the distinction between reactive and moderating isotope effects were fully appreciated.[1]

We have measured the ratio of yields of HT/DT from recoil tritium reacting with 1:1 mixtures of CH_4/CD_4, C_2H_6/C_2D_6, and C_3H_8/C_3D_8, in the gas phase at atmospheric pressure.[5] In all cases a small quantity (3·5—4·5 mol%) of bromine scavenger was present,[1] although variation of the bromine concentration by a factor of 4 did not effect the measured yield ratio. The

HT/DT ratio was determined as a function of the partial pressure of neon added to the alkane mixture. In order that the results from the different alkanes may be compared under conditions of similar moderation (*i.e.* hot-atom collision density), the HT/DT ratio is shown in the Figure as a function of the ratio of the total substitution yield[6]
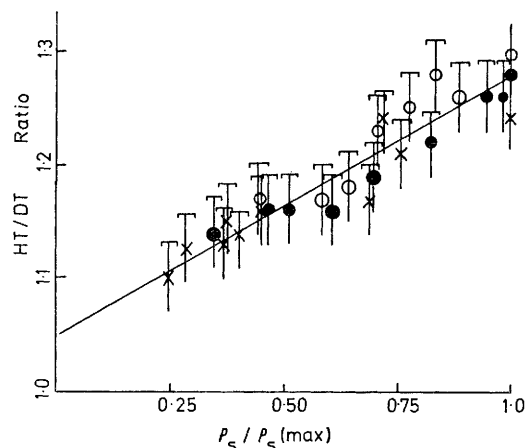

Figure. Variation of the HT/DT yield ratio with the degree of neon moderation of 1:1 alkane mixtures. $X = CH_4/CD_4$, $\bullet = C_2H_6/C_2D_6$, $\bigcirc = C_3H_8/C_3D_8$. The degree of moderation is measured by the ratio of the total substitution yield to that in the absence of neon.

(*i.e.* the yield of all products other than HT and DT) as moderator is added, to the total substitution yield in the absence of moderator, *i.e.* $P_S/P_S(\text{max})$.

Clearly the abstraction isotope effects are similar for each alkane mixture and decreases as the degree of moderation

by neon increases. While there is no justification for assuming a linear dependence with the axes shown in the Figure, straight line extrapolation leads to a common-isotope effect of $1\cdot04 \pm 0\cdot04$ in the limit of infinite neon moderation. Hydrogen atom abstraction by thermal atoms or radicals is expected to show an efficiency closely related to the energy content of the C–H bond under attack. Thus for thermal abstraction from a given alkane one might expect that the isotope effect would be close to the ratio of the C–H/C–D bond stretching frequencies (ca. $1\cdot3$). The present findings for energetic atoms, at high moderation, are clearly much lower than this, suggesting that differences in near-threshold reactivity are not of major importance in connection with these isotope effects.

Rowland[2] has demonstrated a sensitive dependence of the abstraction yield on the R–H bond dissociation energy. While the C–D bond strengths in the alkanes studied here are approximately $3\cdot8$ k Jmol^{-1} larger than their C–H counterparts, the similarity of the isotope effects in the three alkane mixtures studied suggest that, contrary to the earlier hypothesis,[3] the effects do not contain a large bond-energy contribution. $[D_{C-H} = 434\cdot3(CH_4), 413\cdot8(C_2H_6),$ and $404\cdot6(C_3H_8),$ units $=$ kJ mol$^{-1}]$.[7]

Recently it was suggested[8] that a significant contribution to the abstraction-isotope effect may come from the reduced efficiency of the high energy D-abstraction. It has also been proposed that both HT and DT formed by the high-energy abstraction mechanism may be highly vibrationally and translationally excited, and thus liable to dissociate on collision. The extent of this collisional dissociation for HT has been shown to be dependent on the nature of the collision partner;[9] for example a somewhat smaller fraction of the HT initially formed survives in excess neon moderator than in the pure hydrocarbon.[10] In argon, krypton, and xenon moderators this effect is even more pronounced. Since the distribution of excita-

tion energies and the dissociation probabilities will be different for HT and DT, we would anticipate that addition of moderator should alter the HT/DT yield ratio.

For the alkanes studied here, DT is expected to be produced with less internal energy and with a lower translational energy than HT by T atoms of a similar energy. In addition collisional dissociation of DT is expected to be somewhat less efficient than for HT of the same translational energy. As a result one would expect that the HT/DT ratio in these experiments would fall as the opportunity for collisional dissociation increases, i.e. as the degree of moderation by neon increases. Furthermore since the abstraction product which would be susceptible to collisional dissociation will be that formed by high energy T atoms (say > 5 eV), variations in the bond energy of C–H bond from which abstraction occurs should exert relatively little influence on the variation of the isotope effect with moderation, so that the effect produced in the three alkane systems studied should be very similar. Clearly the results shown in the Figure bear out both of these predictions.

Early experiments[3] using helium moderator with CH_4/CD_4 mixtures gave no indication of a lowering of the HT/DT ratio. This is also consistent with the collisional dissociation hypothesis, since helium is expected to stabilise excited HT and (to a lesser extent) DT more effectively than the hydrocarbon. The earlier work in unmoderated CH_4/CD_4 gave an abstraction isotope effect of $1\cdot25 \pm 0\cdot07$, which, within the error limits, is in agreement with the present results in the absence of neon.

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