Reappraisal of an Inconsistency in Recoil Tritium Chemistry

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Summary A major qualitative inconsistency in the yields of hot products from the reaction of recoil tritium atoms with mixtures of hydrogen and methane is re-examined in the light of recent suggestions that collisional dissociation of excited HT plays a significant role in determining the H-abstraction yield.

RECOIL tritium atoms react with saturated hydrocarbons primarily by H abstraction[1] and H substitution:

$$T + RH \rightarrow HT + R\cdot$$

$$T + RH \rightarrow RT + H$$

There has been considerable disagreement as to whether H-abstraction occurs at higher or lower mean energies than H-substitution. Moderation studies with heavy moderators have been interpreted as indication of a higher mean energy for the abstraction reaction. However Root and Rowland recently presented the yields of hot products from the reaction of recoil tritium atoms with mixtures of H_2 with CD_4, and D_2 with CH_4,[2] as evidence of an apparent inconsistency in the kinetic treatment of hot atom data. Wolfgang[3] attempted to resolve this inconsistency by proposing excitation functions for the principal reactions in those systems which could account for the observed trends in the product yields and yield ratios. Recently a new approach to the results of recoil tritium experiments has been presented.[4] It is proposed that HT may be produced from hydrocarbons by a high energy stripping mode of reaction (as suggested by Wolfgang *et al.*[5,6]), but that much of the product so formed remains in a highly excited state—both internally and translationally, and may undergo dissociation on collision with surrounding molecules.

In gathering the available data to provide a test for this theory it was observed that the extent of collisional dissociation was dependent on the mass of species likely to be encountered by excited HT molecules. It has been shown[4] that collision with a low mass species, such as helium, results in much less collisional dissociation, and consequently a greater yield of thermalised HT, than collision with a heavy species such as argon. On this basis one would expect D_2 to behave in a manner similar to helium, although giving results undoubtedly complicated by the diatomic nature and high reactivity of D_2.

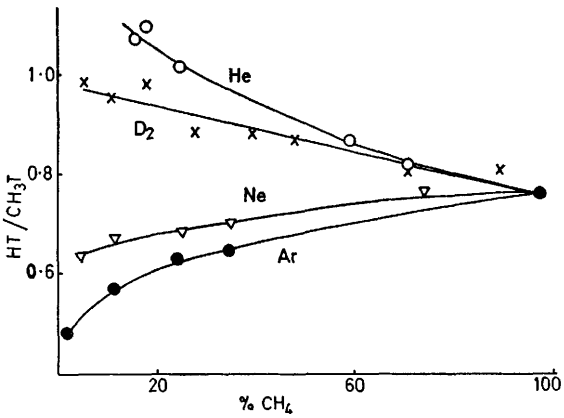

FIGURE. *The variation of the* HT/CH_3T *yield ratio observed in the presence of different moderators, shown as a function of the mol* % CH_4.

The HT/CH_3T yield ratio as a function of the mole percent of CH_4 in the CH_4–D_2 mixtures studied by Root and Rowland[2] are shown in the Figure, along with the results reported by Seewald and Wolfgang[6] for methane moderated by helium, neon, and argon. Clearly the HT/RT ratio increases on the addition of the lightweight species He or D_2, and yet decreases when the heavy moderators Ne or Ar are added. This result is entirely consistent with the suggestion that collisional dissociation of excited HT is of major importance in determining the HT/RT ratio observed in recoil tritium–hydrocarbon systems, and resolves the difficulty quite correctly pointed out by Root and Rowland.

The currently available evidence in support of collisional dissociation of HT as a major influence in results from recoil tritium experiments, also lends weight to the qualitative validity of the semiclassical trajectory studies of Polanyi and his co-workers[7] in which HT was observed as the major product of reaction of T with RH at a tritium atom energy of 12 eV.

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