The Effect of Helium Moderator in Studies of Hot Hydrogen Reactions with Hydrocarbons

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Summary The relative H-abstraction yield obtained by the recoil tritium reaction with ethane is found to rise in the presence of helium, suggesting that the collisional dissociation of excited HT plays a major role in determining the final product ratio.

Energetic tritium atoms react with simple hydrocarbons primarily by reactions (1) and (2).[1] In studying the

$$T^* + RH \longrightarrow HT + R \qquad (1)$$

$$T^* + RH \longrightarrow RT + H \qquad (2)$$

kinetics of such reactions in the gas phase it has been common practice to investigate the variation of product yields as a function of the amount of an inert "moderator" species present in the reaction mixture. A good moderator for hot atoms is one which exerts a large influence on the hot atom–reactant collision density.[1] The low atomic mass of helium suggests that this substance should be an efficient moderator for tritium atoms, and indeed for many years helium was widely used for this purpose.[2] However, Seewald and Wolfgang[3] argued that the high ionisation potential of helium, coupled with its high moderating power, could allow tritium ions to reach chemical energies, (*i.e.* 0—100 eV), before complete neutralisation by charge exchange processes. Those workers suggest that such ions could give rise to spurious HT, and that the high HT/RT ratio from recoil tritium–methane systems moderated by a large excess of helium may be directly attributed to this source. For this reason other moderators, such as neon,[3,4] have largely superceded helium in kinetic studies of hot hydrogen chemistry.

Using the experimental technique described elsewhere,[1–4] we have investigated the effect of adding helium to a system in which recoil tritium [produced by the $^3He(n,p)T$ reaction] reacts with ethane in the presence of a large amount of bromine, the latter acting both as a scavenger for thermal atoms and radicals,[1,5] and as a low ionisation potential collision partner for hot tritium species. Samples containing C_2H_6 (*ca.* 10 cm Hg), Br_2 (*ca.* 30 cm), ^3He (*ca.* 2 cm), and varying amounts of ^{4}He, were irradiated with thermal neutrons. The ratio of yields from reactions (1) and (2) were determined and the results are shown in the Figure, corrected for recoil loss, wall HT, and unimolecular decomposition of labelled ethane.[1] The estimated uncertainties in these ratios are $< 3\%$.

Addition of only *ca.* 26 cm of helium caused the HT/RT ratio to increase from 1·2 to 1·3. Since the absolute yield of HT under these conditions is of the order of 10% (of available tritium), the observed increase is greater than could reasonably be attributed to spurious HT produced by ions.[3] The most plausible explanation of the rise in the HT/RT ratio on addition of helium seems to us to be the more efficient thermalisation of translationally and vibrationally excited HT on collision with helium, compared with the extensive collisional dissociation of this product predicted[6] to occur on collision with more massive species such as neon, hydrocarbon, or bromine.

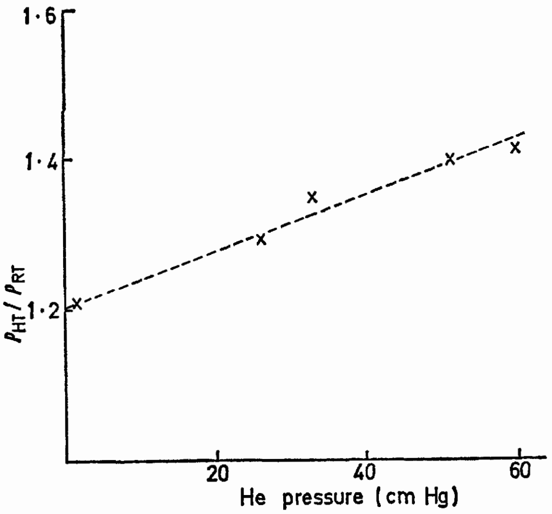

FIGURE. *Variation of* P_{HT}/P_{RT} *with added helium moderator.*

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