New Helium-moderator Anomaly in Recoil Tritium Chemistry

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Summary Moderation studies of the recoil tritium–hydrogen system appear to show that helium is an abnormally poor moderator for hot tritium atoms, a finding which is in sharp contradiction with results from other recoil tritium systems.

THE reactions of recoil tritium atoms with simple gas-phase hydrocarbons have been extensively studied for more than two decades in the hope of elucidating reaction processes at high energies.[1] One of the principal tools of recoil chemistry has been the moderation study,[2] in which an inert-gas moderator is added to the hot atom–reactant system to modify the hot-atom collision density. It has generally been found[2,3] that helium is the best moderator for gas-phase studies, in that, as would be expected from the similarity in mass between ^3H and ^4He, helium exerts the greatest influence on the collision density and hot-product yields of all the noble gases. Thus, helium is attractive as a moderator and when, in the past, abnormalities have been reported[4] in helium-moderated systems, detailed studies[5] of those abnormalities have led to useful advances in our understanding of recoil tritium chemistry.

During a moderation study of the recoil tritium–hydrogen system, in which reaction (1) is the only process which leads to detectable products, we repeatedly observed that helium had a smaller effect on HT yields than the more massive moderators such as argon and krypton. Using a

$$T\cdot + H_2 \rightarrow HT + H\cdot \qquad (1)$$

simplified form[5] of the kinetic theory of hot reactions,[2] the total yield of products, P, under conditions of high moderation and adequate scavenging is related to the mole faction of the reactant molecule, x_r, by equation (2), in which I is

$$\frac{1}{P} = \frac{\alpha_r}{I} + \frac{1 - x_r}{x_r}\,\frac{\alpha'_m}{I} \qquad (2)$$

the reactivity integral of the system, α_r is the mean logarithmic energy decrement for collisions between hot atoms and reactant (r), and α'_m is proportional to the mean logarithmic energy decrement for collisions between hot atoms and the moderating species (m). From equation (2) it follows that a plot of $1/P$ against $(1 - x_r)/x_r$ should yield a straight line with a slope/intercept ratio equal to α'_m/α_r.

The Figure shows yields of HT obtained from reaction (1) plotted in accord with equation (2), for the T + H_2 system moderated by helium and argon. The Figure also shows the results reported by Seewald *et al.* (corrected for recoil range errors) on the T + CH_4 system, again modera-

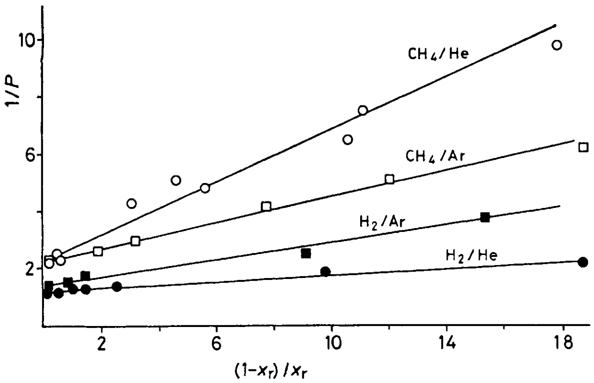

FIGURE. Plot of $1/P$ *vs.* $(1 - x_r)/x_r$ for the total hot-product yields from T + H_2 moderated by helium, ●, and argon, ■; also shown are results from T + CH_4 moderated by helium, ○, and argon, □, taken from ref. 4.

ted by helium and argon.[4] (These latter results are quite consistent with results reported by other workers for a variety of hydrocarbons.) While the yields from the hydrocarbon system indicate $\alpha'_{He} > \alpha'_{Ar}$, which emphasizes that helium is a better moderator than argon, the new results from the T + H_2 system clearly lead to the conclusion that $\alpha'_{He} < \alpha'_{Ar}$.

A complete first-kind kinetic theory analysis[2] of both systems leads to the α_m values given in the Table, which includes the remarkably small value of α_{He} derived from the T + H_2 system. This quite unexpected result, which is reproducible and confirmed by our study of the analogous T + D_2 system, leads to the conclusion that there is a marked anomaly in the behaviour of helium moderator in the T + H_2 system. That this behaviour is anomalous is confirmed by the fact that the relative moderation efficiencies of helium and argon appeared quite normal in our recent study[6] of scavenger effects in the T + H_2 system, where the slopes of scavenger curves were consistent with the conventional moderating efficiencies of these moderators.

While we shall delay speculation on the origins of this anomaly until our studies are completed, it should be noted that previous arguments concerning the presence of T^+ ions in helium-moderated systems[4] are unlikely to account for the present results, as the anomaly appears as a difference in behaviour between two helium-moderated systems (the α_{Ar} values being comparable in both H_2 and CH_4). The reactant species in both systems have similar ionisation energies and in the case of the highly moderated samples, the effect persists in the presence of a low ionisation energy scavenger (Br_2, I_2, or ICl).

TABLE. Relative moderating efficiencies of helium and argon.

	Units α_{H_2}	Units α_{CH_4}
α_{He}	0·040 ± 0·005	0·14 ± 0·01
α_{Ar}	0·15 ± 0·01	0·17 ± 0·01

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