"Inert" Moderators in Hot Atom Chemistry

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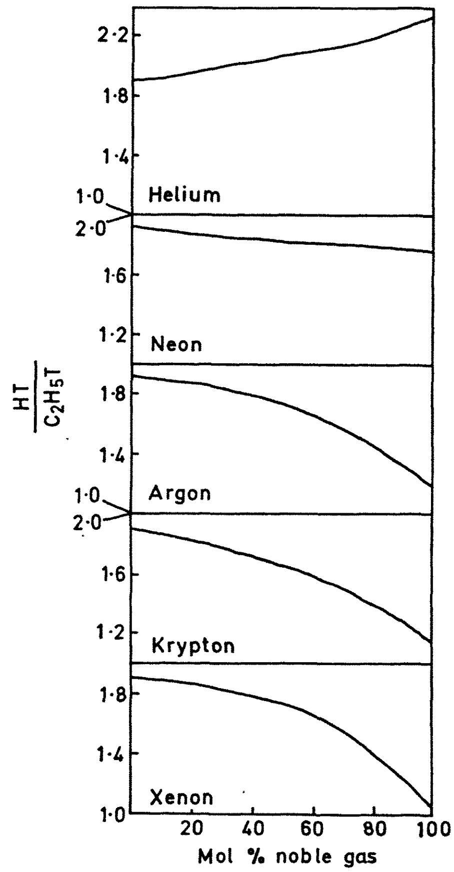
Summary Product ratios change in different ways when different "inert" moderators are used in hot-atom experiments: thus, changes in product ratios can no longer be used to determine relative energies of the hot atoms initiating particular reactions.

HOT tritium atoms, produced by $^3He(n,p)^3H$, can react chemically with hydrocarbon molecules in the gas phase with a high collision efficiency,[1] to produce two main products, labelled parent and HT. If the two reactions were characteristic of hot atoms with different amounts of excess of energy, then the high energy reaction would attenuate the tritium atom flux, (as a function of energy), so reducing the yield of the low energy product. To investigate this effect many experiments have been performed in which increasing amounts of inert moderators, usually rare gases, are added to the system. The yields of high and low energy products are both reduced but it is assumed that the relative attenuation of low energy product is reduced until, in the limit of 100% moderator the competition between various reactions for hot atoms is eliminated. These ideas have been formulated quantitatively in the Estrup–Wolfgang[2] theory of hot reactions and it is possible to determine which products are formed by high and which by low energy hot atoms.[3] Clearly such conclusions should be a function of the hydrocarbon alone and in no way dependent on the moderating gas used in the experiments. However, results of both Urch and Welch[4] and also Seewald and Wolfgang[5] suggest that changing the moderator can affect the conclusions concerning high and low energy products. In these experiments the ratios of scavenger, hydrocarbon, and moderator were all varied. To study the moderator effect of various rare gases independently a series of experiments was performed in which the amounts of hydrocarbon (ethane 20 cm Hg), scavenger (oxygen 5 cm Hg), and helium-3 (2 cm Hg) were all constant and varying amounts of rare gases were added up to a maximum pressure of 240 cm Hg. The variation of the ratio HT/C_2H_5T with mole fraction of moderator is shown in the Figure. Clearly the moderator has a profound effect on HT/C_2H_5T ratio even in the limits of 100% moderator. A naive interpretation of the helium case would suggest that HT was the low energy product whereas for argon, krypton, or xenon the conclusion would be reversed. Seewald and Wolfgang have suggested that the high yield of HT with helium, when compared with neon is due to the presence, at chemically important energies, of un-neutralized tritium ions. The results presented here, however, show a gradation of effect from helium through to xenon; there seems no



FIGURE

justification from assuming[6] that neon is a "good" moderator whilst helium is "bad". It could be that this gradation does in fact reflect a variation in the ability of the noble gases to neutralize tritons but Estrup[7] has shown that rate at which a tritium atom might lose energy in collision with a noble gas atom will be a function of the energy of the tritium atom. The flux of tritium atoms, as a function of energy, could therefore be different for different moderating gases. The limiting ratios would then reflect changes in the number of tritium atoms in particular energy ranges on going from one moderator to another.

Whatever the reason it is clear that many of the conclusions that have been drawn in hot atom chemistry from "moderator studies" must now be regarded as erroneous and more critical experiments must be performed in an attempt to find the relative energies of hot atoms that initiate specific reactions.

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