

Dissociation of Excited HT by Collision with Rare-gas Atoms

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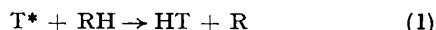
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Summary A simple hard-sphere model is used to study the fate of HT produced by reaction of hot tritium atoms with hydrocarbons in the presence of rare-gas moderators; the results suggest that HT may be produced by a high-energy stripping mode of reaction, but that much of this product may dissociate on collision with the moderator, resulting in some cases in an effective excitation function

which is comparable to that required by the energy cut-off model.

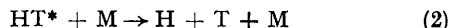
THE reactions of translationally excited tritium atoms with simple hydrocarbons have been extensively studied¹ over the last decade. One of the principal products from such reactions is HT formed by the abstraction (1).

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However, the gross features of the excitation function for reaction (1) remain unknown, except at low energies² (<2 eV). Semi-classical trajectory studies by Polanyi *et al.*³ and the experimental results of Wolfgang *et al.*⁴ suggested that the abstraction function was significant at high energies (>10 eV), and recent results⁵ with a simple hard-sphere model⁶ supported the stripping model of abstraction proposed by Wolfgang.⁴

On the other hand results of studies using 2.8 eV tritium atoms,⁷ a sensitive dependence of the abstraction yield on the R-H bond strength⁷—both in photochemical and nuclear recoil systems—and a sensitive dependence of the abstraction yield on the amount of 'thermal atom' scavenger present in some recoil systems,⁸ all suggest that much of the HT observed from reaction (1) resulted from a comparatively low-energy reaction as predicted by Rowland's 'energy cut-off' model.⁷ Since much of the HT produced in computer simulations using the simple hard-sphere energy transfer model was found to be highly translationally and internally excited,⁵ further calculations have been performed on reaction (2), in order to determine how much



of the abstraction product formed by reaction (1) is likely to survive subsequent collision with the bulk gas.

The calculations were performed using the simple hard-sphere model described previously.⁶ The probability of survival of excited HT was determined as a function of both translational and internal energy (vibration and rotation were not considered separately). The results were then integrated into the excitation function for reaction (1) described previously.⁵ The results for M = He, Ne, and Xe are shown in the Figure as effective excitation functions for HT production in a large excess of those gases. The

functions should be regarded as qualitative at this stage, although details of the calculations will be published later.

These results suggest that collisional decomposition of HT, produced largely in accordance with the stripping model, alters the effective excitation function in such a

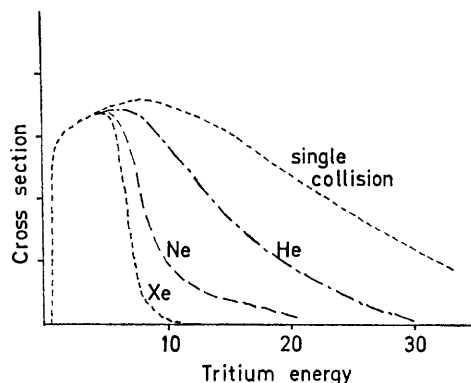


FIGURE. Cross section (in arbitrary units) for reaction (1) as a function of initial T atom energy (eV), for the single collision process (1) and for survival of the product in excess of rare-gas moderators.

manner that the functions become comparable to those required by the energy-cut-off model in systems moderated by heavy rare gases. The three functions shown in the Figure qualitatively account for the variation in the HT yield fraction at infinite moderation in He, Ne, and Xe, observed by Urch *et al.*⁹ in oxygen-scavenged ethane and by Wolfgang *et al.*¹⁰ in bromine-scavenged ethane.

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⁷ See refs. to work of F. S. Rowland *et al.* cited in ref. 1.

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⁹ C. Westhead, D. S. Urch, *Chem. Comm.*, 1971, **8**, 403.

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