Hot Atom Isotope Effect in D-Abstraction from Alkanes

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Summary A major difference between the hard-sphere D-abstraction excitation functions for hot H and T atoms reacting with RD has been observed, suggesting that certain extrapolations between the H and T systems may be invalid.

ONE of the principal reactions of translationally excited hydrogen atoms with simple alkanes is abstraction (1) of hydrogen.[1,2] This reaction has been studied in the gas

$$H^* + RH \longrightarrow H_2 + R\cdot \qquad (1)$$

phase using recoil tritium atoms [formed by the nuclear process $He^3(n,p)T$], which are initially formed with *ca.* 0·2 MeV kinetic energy. The results of such work have led to the suggestion[1,3] that reaction (1) may occur with a high efficiency over a T atom energy range from *ca.* 0·5 to > 10 eV. (At higher energies, it has been argued,[4] collisional dissociation[5] of translationally excited HT product may occur. This would not affect the argument which follows). However, results obtained using H* atoms,[6] generated by photodissociation of HBr or HI (giving an energy range of *ca.* 0·6—3 eV), reacting with deuteriated alkanes, have suggested that the excitation function for reaction (1) (using RD) reaches a maximum at a hot atom energy of *ca.* 1 eV, and thereafter declines.

Unfortunately, experiments in which TBr is photodissociated[7] have not allowed a determination of absolute yield from reaction (1), so that arguments concerning the energy range of hot abstraction have frequently involved a

comparison of results from hot tritium experiments with those from hot hydrogen experiments.[8]

TABLE. Data used in calculations.[a]

Atom	Hard-sphere radius (r/nm)	Mass/a.m.u.
H, D, and T	0·074	1, 2, and 3
R	0·15	12

Abstraction thresholds = 0·5 eV.
Bond dissociation energies, all = 4·5 eV.

[a] All other parameters as given in ref. 9.

One of the many theoretical studies of reaction (1) was carried out using a hard-sphere energy-transfer model.[9] Recently a more exact six-body potential surface trajectory calculation[10] predicted an excitation function for H-abstraction by T atoms that was in surprisingly good agreement with the hard-sphere model result, both excitation functions exhibiting a maximum at *ca.* 7 eV (T atom energy). Thus it was felt that a useful indication of the validity of comparing recoil tritium results with photolytic H* results, could be obtained from the hard-sphere model.

Using the same calculation method as described previously,[9] with the single exception that chatter (*i.e.* successive collisions following a rebound of the struck atom) was permitted,[11] the excitation functions for reactions (2) and (3) were obtained. With the data shown in the Table,[9]

$$T + RD \longrightarrow TD + R\cdot \quad (2)$$

$$H + RD \longrightarrow HD + R\cdot \quad (3)$$

the results given in the Figure were obtained. The function for the reaction (3) has a peak at *ca.* 1 eV, in remarkably good agreement with the results of Gann *et al.*[6] for RD = n-C_4D_{10}. This function shows a much smaller high-energy tail than the corresponding function for the T atom reaction (2). Detailed analysis of the trajectories involved indicates that this results largely from a greatly reduced probability of H attack perpendicular[9] to the R–D bond resulting in stable product formation, compared with the corresponding trajectories for process (2).

Thus on simple dynamic grounds alone, one expects the abstraction excitation function for reaction (3) to have a peak at considerably lower energies than that for reaction (2). Collisional dissociation[5] of excited TD product may, of course, modify the excitation function for reaction (2) deduced from a bulb experiment. However, even taking collisional dissociation into account, the maximum in this abstraction function is predicted to occur above 4 eV with the hard-sphere model. If these results obtained with the model are approximately as reasonable as those for

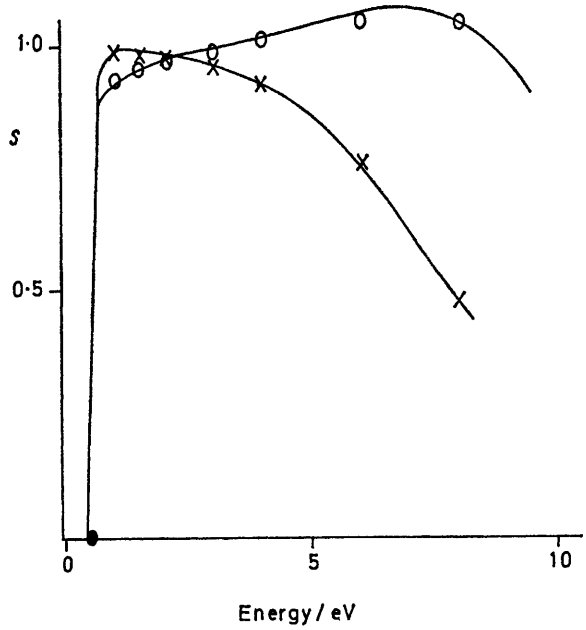

FIGURE. Abstraction cross-section, S (arbitrary units) for the reactions T + RD → TD + R· (○) and H + RD → HD + R· (×), shown as a function of the laboratory energy of the hot atom (eV).

T + RH,[9,10] then it is clear that a simple extrapolation from H* systems to T* systems is of doubtful validity, the large hot atom isotope effect observed here indicating a very significant difference between the two systems.

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