Recoil Tritium Reactions with Molecular Hydrogen

Part 2.—Moderation Effects

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Moderation studies of the $T+H_2$ and $T+D_2$ systems moderated by helium, argon and krypton are reported. The derived kinetic parameters indicate that helium is a much poorer moderator in these systems than is either argon or krypton. This observation is rationalised by considering the effect of collisional dissociation of translationally excited product in the different moderators, and the effect of an α_{He} , which declines as the collision energy increases.

1. INTRODUCTION

For more than two decades the reactions of hot atoms have been studied in an effort to understand the factors which govern the nature and efficiency of elementary chemical processes at high energies.^{1, 2} Among the simplest hot-atom reactions are those of tritium atoms with molecular hydrogen and its isotopic analogues. In a previous paper³ we outlined our reasons for embarking on a detailed study of reactions (1.1) and (1.2)

$$\mathbf{T} + \mathbf{H}_2 \to \mathbf{H}\mathbf{T} + \mathbf{H} \tag{1.1}$$

$$T + D_2 \rightarrow DT + D \tag{1.2}$$

and discussed the use of various scavenging species in our experimental system, concluding that iodine monochloride was a satisfactory scavenger for use in the recoil tritium/molecular hydrogen system. In this paper we report the results obtained in carrying out a classic moderation study of reactions (1.1) and (1.2), and, in light of the rather surprising results, consider the implications of our findings for the more widely reported recoil tritium/hydrocarbon systems.

Since the early 1960s the basic methods of hot-atom chemistry have relied largely on the kinetic theory developed by Estrup and Wolfgang.⁴ In our previous paper³ (Part 1) we discussed the extension of the kinetic theory to include effects due to scavenger competition⁵ and the modified kinetic-theory equations will not be developed again here. However, in view of our experimental results, it is necessary to examine briefly the basic kinetic-theory equations and the assumptions required in their derivation. This we do in the following section. The experimental method and the results obtained are then described and the results analysed in terms of the kinetic theory. The kinetic theory parameters derived from this analysis are then considered in relation to parameters obtained by other techniques.

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2. THE KINETIC THEORY OF HOT-ATOM RECTIONS^{2, 4}

The kinetic theory of hot-atom reactions is in fact derived from neutron moderation theory.⁶ The most important assumption of the theory (for our purposes) is that the number density of hot atoms at energy E may be written as eqn (2.1) in the absence of hot-atom absorption (*i.e.* removal by chemical reaction)

$$n(E)\,\mathrm{d}E = \frac{\mathrm{d}E}{\alpha E} \tag{2.1}$$

where α is the mean logarithmic energy decrement, *i.e.* $-\langle \log[(E \text{ after collision})/(E \text{ before collision})]\rangle$ averaged over all collisions between the hot atoms and the molecules of the surrounding medium.

It has long been recognised^{7, 8} that the use of eqn (2.1) with hard-sphere α values does not provide satisfactory agreement between the hot-product-yield equations (see below) and experimentally determined yields, and yet for many years it has been argued that eqn (2.1) may be used as the basis of the kinetic theory by regarding α as an empirically determined constant.

In a medium in which the hot atoms may undergo chemical reactions on collision to yield products in which the hot atom becomes bound, eqn (2.1) becomes

$$n(E) dE = \frac{dE}{\alpha E} \left(1 - \int_{E}^{E_{o}} n(E') f p(E') dE' \right)$$
(2.2)

where f is the probability of collision between the hot atom and reactive component of the medium and p(E) is the probability of reaction to form a bound product on collision at energy E.

It may also be shown⁴ that the fraction of hot atoms which become bound before they are moderated to thermal energies is given by

$$P = 1 - \exp\left(-fI/\alpha\right) \tag{2.3}$$

where

$$I = \int_0^\infty \frac{p(E')}{E'} \mathrm{d}E'. \tag{2.4}$$

To make use of eqn (2.3) for the analysis of experimental data, Estrup and Wolfgang assumed that α for a mixture consisting of a reactant species, r, and a moderator species, m, could be written

$$\alpha = f\alpha_{\rm r} + (1 - f)\alpha_{\rm m} \tag{2.5}$$

where α_i is the average logarithmic energy decrement for collisions between the hot atoms and species *i*.

This enables eqn (2.3) to be rewritten as

$$\frac{-1}{\log\left(1-P\right)} = \frac{1-f\alpha_{\rm m}}{f} + \frac{\alpha_{\rm r}}{I}$$
(2.6)

so that if the experimental product yield, P, is determined as a function of f, a plot of $-1/\log(1-P)$ against (1-f)/f should yield a straight line of slope α_m/I and intercept α_r/I , allowing I and α_r to be determined in units of α_m .

The determination of f for any sample requires some assumption to be made about the relative sizes of the reactant and moderator molecules. f may be written as

$$f = \frac{x_{\rm r} S_{\rm r}}{x_{\rm r} S_{\rm r} + x_{\rm m} S_{\rm m}}$$
(2.7)

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where x_i is the mole fraction of component *i*, and S_i is the total cross-section for the hot atoms interacting with component *i*.

Clearly the S_i are likely to be functions of the collision energy,⁹ for much the same reasons as the α_i are, but again it has been common practice⁸ to assume that the energy dependences will be such that little error will be introduced by taking f/α to be energy independent.

3. EXPERIMENTAL

The experimental method and the materials used have already been detailed³ in Part 1. Quartz sample bulbs $(10-20 \text{ cm}^3)$ were filled on a grease-free vacuum line with hydrogen, iodine monochloride, helium-3 and a noble-gas moderator. The bulbs were irradiated with thermal neutrons at the Aldermaston Herald reactor to induce a tritium activity of *ca*. 3×10^4 Bq, through the ³He(n,p)³H process. The bulbs were then broken on a second grease-free vacuum line and the contents analysed by radio-gas chromatography using a 2 m alumina column operated at -196 °C, and twin gas-glow proportional counters. The carrier gas was helium and this was mixed with *ca*. 10 vol % methane before entry to the proportional counters. The HT or DT activity measured during this procedure was converted into a fractional product yield, $P_{\rm HT}$ or $P_{\rm DT}$, based on the total tritium activity induced in each sample bulb. This latter value was estimated from the partial pressure of helium-3 in the bulb, the neutron flux through the bulb (determined from the activity induced in cobalt monitoring wires wrapped around the bulb) and the recoil loss, *L*. No correction to the product yields for the effect known previously as 'wall HT' has been applied in these experiments because of the recent report which suggested that such correction is unnecessary.¹⁰

Experiments in which deuterium has been used as the reactant have had a small correction applied to compensate for the reactivity of the *ca*. 3% isotopic impurity observed in our lecture bottles of D₂ (Matheson, stated purity > 99.5%). This correction was determined by adding to the observed DT yield an amount equal to the observed HT yield multiplied by the ratio of reactivity integrals I_{D_2}/I_{H_2} . In the experiments reported below this correction is small, amounting to < 5% of P_{DT} .

The cross-sections used for the various components in the evaluation of f_i were as follows.¹¹

compound	$S_i/\mathrm{nm^2}$	
 H., D.	0.234	
He	0.200	
Ar	0.275	
Kr	0.292	
O ₂	0.281	
IČI	0.450	

4. ERRORS

Errors arise in recoil tritium experiments from a variety of sources including the sample composition measurements, the neutron flux determination, the recoil loss correction and the determination of the product activity. Our best estimates of the errors associated with sample composition are $\pm 3\%$, and of the errors associated with fractional yields are $\pm 12\%$. In both cases, and for all derived error limits used below, the error ranges refer to reliable errors. In the results recorded below the values are recorded to three places of decimals, with the exception of sample pressures which are recorded to 0.1 Torr.

5. RESULTS AND DISCUSSION

The results obtained from the moderation studies of the $T+H_2$ and $T+D_2$ systems are collected in tables 1 and 2, respectively.¹² In each system three moderators have been used, He, Ar and Kr. Three corresponding kinetic-theory plots of the first type for the $T+H_2$ system [*i.e.* the plots obtained using eqn (2.6)] are shown in fig. 1, and

sample	moderator	$X_{\mathbf{H}_{2}}$	X _{ICI}	$X_{mod}{}^a$	pressure /Torr	P _{HT}
HI	He	0.848	0.031	0.096	1030.1	0.873
H2	He	0.692	0.029	0.254	1053.6	0.869
H3	He	0.578	0.028	0.371	1122.4	0.824
H4	He	0.482	0.027	0.469	1152.7	0.783
H5	He	0.394	0.027	0.555	1132.2	0.786
H6	He	0.285	0.029	0.663	1032.0	0.705
H7	He	0.093	0.028	0.855	1072.0	0.534
H8	He	0.048	0.030	0.889	1038.7	0.496
Al		0.940	0.028	0.000	1102.7	0.827
A2	Ar	0.822	0.029	0.114	1071.1	0.716
A3	Ar	0.674	0.029	0.266	1076.4	0.706
A4	Ar	0.516	0.029	0.421	1057.1	0.731
A5	Ar	0.415	0.030	0.512	1107.4	0.585
A6	Ar	0.307	0.028	0.633	1097.1	0.640
A7	Ar	0.191	0.030	0.746	1039.8	0.646
A8	Ar	0.099	0.029	0.843	1110.4	0.388
A9	Ar	0.031	0.027	0.911	1100.0	0.171
A10	Ar	0.061	0.030	0.885	1248.6	0.262
K 1	Kr	0.853	0.029	0.094	1047.5	0.842
K2	Kr	0.731	0.028	0.218	1069.3	0.772
К3	Kr	0.524	0.030	0.424	1070.1	0.706
K4	Kr	0.426	0.029	0.524	1050.9	0.694
K5	Kr	0.334	0.029	0.617	1037.5	0.608
K 6	Kr	0.180	0.029	0.759	1097.1	0.434
K 7	Kr	0.125	0.028	0.817	1152.5	0.400
K 8	Kr	0.063	0.029	0.881	1230.3	0.324
K9	Kr	0.044	0.031	0.891	1058.6	0.226

TABLE 1.—YIELDS OF HT FROM $T + H_2$ SYSTEM

^a Balance is helium-3.

the analogous plots for the $T+D_2$ system in fig. 2. The derived kinetic-theory parameters are given in table 3. The lines drawn on the kinetic plots were chosen by a least-squares technique to represent the limiting slopes at high moderation, as the kinetic-theory expression [eqn (2.5)] is known to be unreliable^{13, 14} in systems with high product yields, unless in the calculation of α allowance is made for the fraction of collisions with the reactive component which are reactive rather than moderating.

The reactivity integrals obtained in this work differ from the values obtained by Seewald *et al.*¹⁵ ($I_{\rm HT} = 6.9 \pm 0.7 \alpha_{\rm Ar}$ and $I_{\rm DT} = 7.1 \pm 0.7 \alpha_{\rm Ar}$), although the mean ratio of $I_{\rm HT}/I_{\rm DT}$ obtained in the different moderators (1.24±0.14) is in closer agreement with the value reported by Seewald from 1:1 mixtures of H₂ and D₂ (1.15±0.04). However, our experimental ratio is in reasonable agreement with the ratio of 'reaction'

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			<u>.</u>			
					pressure	
sample	moderator	X_{D_2}	$X_{\rm IC1}$	X _{mod}	/Torr	P _{DT}
H101		0.927	0.030	0.000	1119.3	0.821
H102	He	0.784	0.031	0.140	1074.0	0.857
H103	He	0.601	0.030	0.327	1124.1	0.818
H104	He	0.457	0.031	0.467	1075.0	0.744
H105	He	0.388	0.030	0.538	1123.1	0.732
H106	He	0.300	0.030	0.630	1137.6	0.681
H108	He	0.184	0.031	0.741	1099.1	0.592
H109	He	0.087	0.028	0.844	1153.8	0.500
H110	He	0.043	0.028	0.889	1203.8	0.420
A101	Ar	0.930	0.031	0.000	1140.3	0.865
A102	Ar	0.743	0.031	0.189	1069.0	0.797
A103	Ar	0.606	0.031	0.321	1078.8	0.692
A104	Ar	0.465	0.031	0.461	1080.6	0.632
A105	Ar	0.374	0.030	0.552	1065.6	0.569
A106	Ar	0.274	0.029	0.653	1107.7	0.527
A108	Ar	0.191	0.031	0.732	1086.2	0.521
A109	Ar	0.090	0.030	0.838	1153.4	0.285
A110	Ar	0.067	0.030	0.860	1123.7	0.247
K101	Kr	0.791	0.031	0.133	1052.7	0.838
K102	Kr	0.663	0.029	0.268	1132.4	0.796
K103	Kr	0.554	0.031	0.369	1072.2	0.717
K104	Kr	0.332	0.027	0.603	1210.6	0.562
K105	Kr	0.239	0.031	0.690	1136.3	0.491
K106	Kr	0.177	0.031	0.746	1049.1	0.473
K108	Kr	0.119	0.026	0.817	1277.9	0.415
K109	Kr	0.080	0.030	0.846	1076.2	0.311
K110	Kr	0.044	0.032	0.883	1056.6	0.192

Table 2.—Yields^{*a*} of DT from $T + D_2$ system

^a Yields shown are corrected for H_2 impurity in D_2 reagent.



FIG. 1.—First-type kinetic theory plots of yields from the recoil tritium + hydrogen system, moderated by helium, argon and krypton, and scavenged by ICl.



FIG. 2.—First-type kinetic theory plots of yields from the recoil tritium + deuterium system, moderated by helium, argon and krypton, and scavenged by ICl.

	mo	oderator (units α_m	(_{bo}
parameter	He	Ar	Kr
α _H ,	24.8+6.0	6.9 + 1.7	6.6+1.6
$\alpha_{D_2}^{n_2}$	18.7 ± 4.5	4.7 ± 1.1	5.2 ± 1.3
$I_{\rm HT}^{D_1}$	30.0 ± 3.6	8.6 ± 1.0	8.2 ± 1.0
$I_{\rm DT}^{\rm III}$	25.0 ± 3.0	6.3 ± 0.8	7.0 ± 0.7

TABLE 3.—KINETIC-THEORY PARAMETERS OF $T + H_2$ and $T + D_2$ systems

integrals' predicted from trajectory studies by Karplus *et al.*¹⁶ (1.37), and our ratio determined from the argon moderation study (*ca.* 1.37) is clearly in remarkable agreement with this theoretical estimate.

Comparison of the α values obtained in this work with the results of Seewald *et al.* is more difficult. In their paper¹⁵ on the T+H₂/D₂ systems these authors do not actually give a value of α_{reac} , although in another publication¹⁷ they quote $\alpha_{D_2} = 2.8 \alpha_{Ar}$ and in fact found¹⁸ $\alpha_{H_2} = 3.1 \alpha_{Ar}$. These values are clearly considerably smaller than the values obtained during the present study (*i.e.* in our work argon has had a smaller effect on the product yields than in theirs) and we are inclined to the view that their low yields from highly moderated systems may have resulted from a depletion of either reactant or product by reaction with the scavenger (I_2) under the conditions of their experiment (91 °C).¹⁸

Probably the most surprising feature of our results may be observed in table 4, where the values of α_{mod} in terms of α_{H_2} and α_{D_2} are collected. While the error limits are rather large, the results obtained from all the H₂ and D₂ systems are consistent within these error ranges and the ratio α_{mod} (in units of α_{D_2})/ α_{mod} (in units of α_{H_2}) is 1.36±0.13. Consequently it is most surprising to find that $\alpha_{He} = (0.26\pm0.03) \alpha_{Ar}$, as all previous reports¹ of recoil tritium experiments have shown $\alpha_{He} > \alpha_{Ar}$. (Seewald *et al.*¹⁷ give $\alpha_{He} = 3.9 \alpha_{Ar}$ from their study the T+CH₄ system.) Furthermore, the

mode	erator	$\alpha_{\rm mod}/\alpha_{\rm H_2}$	$\alpha_{\rm mod}/\alpha_{\rm D_2}$	
Н	e	0.04	0.05	
Α	r	0.15	0.21	
K	r	0.15	0.19	

TABLE 4.— α_{mod} values derived from kinetic analyses

slopes of the scavenger curves obtained in our own experiments on the IC1-scavenged $T + H_2$ system³ were consistent with $\alpha_{H_2} > \alpha_{Ar}$. Using the scavenger-corrected kinetic theory⁵ the slope of a scavenger curve is given by

$$\frac{\partial P_i}{\partial f_s} = -\left(\frac{f_r}{\alpha}\right)\frac{K'_i}{\alpha} \tag{5.1}$$

where K'_i is the scavenger competition integral

$$= \int_0^\infty \frac{p_i(E)}{E} \left(\int_0^\infty \frac{p_s(E')}{E} dE' \right) dE$$

(see Part 1 for details³).

From eqn (5.1) it follows that the ratio of scavenger curve slopes obtained in two different moderators (m₁ and m₂) under conditions of the same extrapolated (*i.e.* $f_s = 0$) yield, P_i° , and so the same (f_r/α), is given by

$$\left(\frac{\partial P_i}{\partial f_s}\right)_{\mathbf{m}_1} / \left(\frac{\partial P_i}{\partial f_s}\right)_{\mathbf{m}_2} = \frac{\alpha_{\mathbf{m}_1}}{\alpha_{\mathbf{m}_2}}$$
(5.2)

which under conditions of high moderation (*i.e.* $\alpha \approx \alpha_{mod}$) gives

$$\left(\frac{\partial P_i}{\partial f_s}\right)_{\mathbf{m}_1} / \left(\frac{\partial P_i}{\partial f_s}\right)_{\mathbf{m}_2} = \frac{\alpha_{\mathbf{m}_2}}{\alpha_{\mathbf{m}_1}}.$$

Our earlier scavenger curves showed α_{He}/α_{Ar} to be *ca.* 1.2 in Br₂ and ICl-scavenged H₂ (and *ca.* 2.5 in oxygen-scavenged H₂). Clearly a pronounced contradiction has arisen between the relative moderating efficiencies of He and Ar determined by two different methods (*i.e.* first-type kinetic analysis and scavenger curves for the T+H₂ system), and by kinetic analyses of two different systems (T+H₂ and T+CH₄).

We propose a two-fold resolution of these difficulties. Taking first the discrepancy between the α_{He}/α_{Ar} ratios inferred from the moderation and scavenger studies, we note that the hot-product yields are functions of the collision density in the energy region spanned by the hot-product excitation functions, and are consequently influenced largely by the α values in and above this region. Most theoretical studies^{16, 19-22} of the T+H₂ systems have indicated that the excitation functions for reactions (1.1) and (1.2) both peak at collision energies of *ca*. 10 eV (laboratory system).

Theoretical studies^{23, 24} of the reactions between T atoms and scavengers such as Br_2 and ICl suggest that the excitation functions for these reactions are largely confined to the low-energy region and are most important at energies around 1 eV.

Experiments in which inert gas moderators are used to lower the yields of reaction products achieve this effect by lowering the collision density over the energy range in which hot products are formed, so that the α values derived from moderation studies reflect the relative moderating efficiencies of the reactant and moderator at collision

energies around 10 eV (although also covering a wide energy range). On the other hand scavenger curves reflect the competitive reactions between reactant and scavenger, and the hot-atom collision density, in the energy region where the hot-atom–reactant and hot-atom–scavenger excitation functions overlap,⁵ and so are functions of the moderating efficiency of a system at collision energies around 1 eV.

Estrup⁹ has shown that the variation in α_{He} over the energy range 1-10 eV is approximately nine-fold when calculated using a realistic T—He potential, and that α increases as the collision energy decreases. This undoubtedly reflects the relatively low electron density around both nuclei and the 'softness' of the repulsive wall. Estrup's calculations for more massive species (*e.g.* Ar and CH₄) indicated relatively little change in α over this energy range, presumably because of the greater steepness of the repulsive wall associated with the greater electron density around the heavier species.

For the molecule D_2 Estrup's calculations did predict an energy dependent α , although the variation beyond *ca*. 2 eV was much smaller than that predicted for He, being approximately three-fold over the 1-10 eV range.

Thus we suggest that the ratio $\alpha_{\rm He}/\alpha_{\rm Ar}$ derived from the T+H₂ scavenger curves *ca.* 1.2) reflects the greater value of $\alpha_{\rm He}$ in the low-energy region in which scavenger competition occurs, while the ratio derived from moderation studies results both from α values at higher energies (where $\alpha_{\rm He}$ has become smaller while $\alpha_{\rm Ar}$ has remained relatively constant) and from the collisional dissociation factor considered below. Note all previous scavenger curves (in T+H₂, ³T+CH₄^{18, 25} and T+C₂H₆) have been consistent with $\alpha_{\rm He} > \alpha_{\rm Ar} > \alpha_{\rm Xe}$.

The more marked discrepancy between α_{He}/α_{Ar} ratios derived from moderation studies of T + H₂ and T + hydrocarbon systems we suggest results from the consequences of collisional dissociation of translationally excited HT produced by reaction (1.1) and by the H-abstraction reaction in the respective systems. It has been proposed²⁶ that HT formed by the H-abstraction reaction (III) at relatively high collision energies (*e.g.* > 8 eV) may undergo collisional dissociation (5.4) on collision with components (*e.g.* reactant or moderator) within the system:

$$T^* + CH_4 \to HT^* + CH_3^{\cdot} \tag{5.3}$$

$$HT^* + M \to T + H + M. \tag{5.4}$$

The extent of reaction (5.4) varies with the nature of the collision partner²⁷ and, for the monatomic gases, increases down the series He < Ne < Ar < Kr < Xe. Furthermore, hydrocarbon collision partners tend in this regard to be similar to neon, so that as helium is added to the T+CH₄ system a smaller fraction of the HT initially formed undergoes collisional dissociation, while as argon is added to the system a greater fraction of the HT product dissociates. For this reason the HT/CH₃T product yield ratio observed in the T+CH₄ system increases on helium moderation but decreases on moderation by the more massive moderators, so that in both cases the slope/intercept ratio derived from the first-type kinetic-theory plot is a poor approximation to the α_r/α_m ratio. It has been shown²⁸ that quantities related to α and given by

$$\alpha' = \alpha \frac{S_{\mathrm{T-m}}}{S_{\mathrm{T-r}}}$$

may be obtained from an analysis of the non-HT hot-product yields, and that the α' values are more reliable indications of the relative moderating efficiencies of materials than the α values derived from hot-product yields which include HT. (The use of α' values, which essentially combine the energy dependences of α and S into a single,

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energy-dependent parameter, avoids the necessity of having to consider separately how a variable S may effect the results.) An analysis of this kind performed on the CH₃T yields reported by Seewald¹⁷ leads to $\alpha'_{He}/\alpha'_{Ar} \approx 3.3$, which is equivalent to $\alpha_{He}/\alpha_{Ar} \approx 4.5$ if the conventional (low-energy) cross-sections are assumed, and greater than the ratio of *ca*. 2.5 derived from Seewald's total products yields. (In each case Seewald's data have been corrected for the excessive recoil ranges used in the original paper as described previously.²⁹) Thus the effect of ignoring collisional dissociation of excited HT in the T+CH₄ system, where the product yields are relatively small and the HT yield accounts for about half of the total yield, is to underestimate the ratio α_{He}/α_{Ar} by *ca*. 45%.

This effect is even more pronounced if the moderating efficiencies are estimated on the basis of the HT yields alone. Analysis of Seewald's data for HT yields from the T+CH₄ system leads to $\alpha'_{\rm He}/\alpha'_{\rm Ar} \approx 1.36$, which is equivalent to $\alpha_{\rm He}/\alpha_{\rm Ar} \approx 1.85$ and, as expected, a more serious underestimation (by *ca*. 60%) of the $\alpha_{\rm He}/\alpha_{\rm Ar}$ ratio than that derived from an analysis of the total product yield.

In the $T+H_{2}$ system the effects of collisional dissociation of excited HT product are expected to be even more pronounced than those in the T+CH₄ system because (a) the reactivity of the $T + H_2$ system is greater than that of the $T + CH_4$ system, and (b) the total hot product yield from the $T+H_2$ system is influenced by collisional dissociation, and not just half of it as is the case in T+CH₄. A further difference between the $T+H_2$ and $T+CH_4$ systems which may also contribute to small values of α_{He} found in the present study is that theoretical estimates of the excitation functions for reactions (I) and (III) suggest that HF formed from the $T + H_4$ reaction results from collisions at higher T atom (laboratory) energies than HT formed from the $T + CH_4$ abstraction reaction. While there are considerable uncertainties associated with the excitation functions for the $T + CH_4$ system, no six-atom trajectory study has suggested a mean abstraction energy above 8 eV (Bunker³⁰ gives ca. 7 eV, and Raff³¹ calculations led to a double humped abstraction function with peaks at 2 and 10 eV and a mean of ca. 8 eV). Furthermore these trajectory studies suggest that the abstraction cross-section has become negligible at collision energies > 20 eV, whereas the reaction cross-section for reaction (1) falls to one half of its maximum value at collision energies of ca. 25 eV.²⁰ These factors suggest that not only is collisional dissociation likely to be more important in $T+H_2$ than it is in $T+CH_4$, but that the higher energy of the excitation function in the former system will result in the kinetics of the moderated system being dominated by α_{mod} values at this higher energy, where (as was argued above) α_{He} is small.

In summary we conclude that the hot-product yields from the moderated $T + H_2$ and $T + D_2$ systems are influenced both by collisional dissociation of translationally excited product on collision with the moderating species and by the moderating efficiency of the moderator in the high- collision-energy (> 10 eV) region. Our results suggest that helium is an inefficient moderator in this high-energy region compared with the more massive moderators argon and krypton, although the moderator dependence of the extent of collisional dissociation indicates that relative moderating efficiencies derived from conventional kinetic analyses may contain substantial errors.

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- ¹ D. S. Urch, Radiochem., 1975, 2, 1.
- ² R. Wolfgang, Prog. React. Kinet., 1965, 3, 97.
- ³ D. J. Malcolme-Lawes, G. Oldham and Y. Ziadeh, J. Chem. Soc., Faraday Trans. 1, 1981, 77, 187.
- ⁴ P. Estrup and R. Wolfgang, J. Am. Chem. Soc., 1960, 82, 2661 and 2665.
- ⁵ D. J. Malcolme-Lawes, J. Chem. Phys., 1972, 57, 2476.
- ⁶ K. T. Tang and M. Karplus, J. Chem. Phys., 1968, 49, 1676.
- ⁷ R. Wolfang, J. Chem. Phys., 1963, 39, 2983.
- ⁸ D. S. Urch, Int. Rev. Sci., series 2, Radiochemistry, ed. A. G. Maddock (Butterworths, London, 1975), vol. 8, p. 49.
- ⁹ P. J. Estrup, J. Chem. Phys., 1964, 41, 164.
- ¹⁰ D. J. Malcolme-Lawes, G. Oldham and Y. Ziadeh, J. Inorg. Nucl. Chem., in press.
- ¹¹ J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, The Molecular Theory of Gases and Liquids (J. Wiley, Chichester, 1954), pp. 1110–1111.
- ¹² D. J. Malcolme-Lawes, G. Oldham and Y. Ziadeh, J. Chem. Soc., Chem. Commun., in press; Y. Z. Ziadeh, Ph.D. Thesis (Loughborough University of Technology, 1981).
- ¹³ F. S. Rowland and P. Coulter, Radiochim. Acta, 1964, 2, 163.
- ¹⁴ R. N. Porter and S. Kunt, J. Chem. Phys., 1970, 52, 3240.
- ¹⁵ D. Seewald, M. Gersh and R. Wolfgang, J. Chem. Phys., 1966, 45, 3870.
- ¹⁶ M. Karplus, R. N. Porter and R. D. Sharma, J. Chem. Phys., 1966, 45, 3871.
- ¹⁷ D. Seewald and R. Wolfgang, J. Chem. Phys., 1967, 47, 143.
- ¹⁸ D. Seewald, Ph.D. Thesis (Yale University, 1967).
- ¹⁹ D. J. Malcolme-Lawes, J. Chem. Soc., Faraday Trans. 2, 1972, 68, 1613.
- ²⁰ D. J. Malcolme-Lawes, J. Chem. Soc., Faraday Trans. 2, 1975, 71, 1183.
- ²¹ J. T. Adams and R. N. Porter, J. Chem. Phys., 1973, 59, 4105.
- ²² J. S. Wright, S. K. Gray and R. N. Porter, J. Chem. Phys., 1979, 83, 1033.
- ²³ D. J. Malcolme-Lawes, Radiochim. Acta, 1972, 18, 111.
- 24 D. J. Malcolme-Lawes, J. Chem. Soc., Faraday Trans. 2, 1978, 74, 182.
- ²⁵ R. B. Hall and D. J. Malcolme-Lawes, J. Chem. Soc., Faraday Trans. 1, 1974, 70, 648.
- ²⁶ D. J. Malcolme-Lawes, J. Chem. Soc., Chem. Commun., 1972, 1285.
- ²⁷ D. J. Malcolme-Lawes, Radiochim. Acta, 1973, 19, 113.
- 28 R. T. K. Baker and D. J. Malcolme-Lawes, J. Chem. Soc., Faraday Trans. 1, 1973, 69, 1858.
- ²⁹ D. J. Malcolme-Lawes, J. Chem. Soc., Faraday Trans. 1, 1980, 76, 860.
- ³⁰ T. Valencich and D. L. Bunker, J. Chem. Phys., 1974, 61, 21.
- ³¹ L. M. Raff, J. Chem. Phys., 1974, 60, 2220.

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