Effect of Xenon Moderator in Hot Hydrogen Reactions with Deuterium Hydride

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Summary Kinetic-theory parameters are used to determine the extent to which the hot products from the reaction T* + HD undergo collisional decomposition; it is shown, using expressions developed recently by Baer and Amiel, that when xenon moderator is present, collisional decomposition could exceed (70 ± 12)%.

The question of the fate of translationally excited products of hot-atom reactions subsequent to their formation has been examined by a number of workers recently.[1-4] It has been suggested that collisional decomposition could have a significant effect on the yields of hot products. If collisional decomposition of the primary products of hot-atom reaction occurs, it should be greatest when the mass of the recoil atom is large or comparable to that of the product molecule and when the inert-gas moderator is a heavy atom.[1]

To determine the extent to which HT, a common product from the reactions of recoil tritium with hydrocarbons, undergoes collisional decomposition, quartz ampoules containing xenon and deuterium hydride at a total pressure of 200 cm together with small amounts of iodine chloride as scavenger[5] and He-3 were irradiated with neutrons to produce recoil tritium by the process $^3He(n,p)^3T$. Techniques adopted for radiochemical analysis of the products have been described previously.[6,7]

Kinetic-theory plots for the reaction of recoil tritium with HD in the presence of xenon are shown in the Figure. A least-squares analysis of the kinetic theory type-1 plot (Figure a) yields values of 0·14 ± 0·01 for the slope and an experimental value of α_{HD}, the average logarithmic energy decrement for tritium in a collision with a molecule of HD (6·3 ± 1·3) α_{Xe}.

The above value for the slope together with a value for the slope when the moderator present is argon[7] giving more weight to the high moderator points *viz* 0·12 ± 0·01, is substituted in the following expressions derived from the equation for the KT I asymptote given by Baer *et al.*[2,8]

$$\frac{\text{KT } I \text{ slope (Xenon)}}{\text{KT } I \text{ slope (Argon)}} = \frac{\alpha_{Xe}}{\alpha_{Ar}} \frac{I_0(1-J_{Ar})}{I_0(1-J_{Xe})}$$

$$\text{now } \frac{\alpha_{Xe}}{\alpha_{Ar}} = \frac{1-\beta_{Xe}}{1-\beta_{Ar}}$$

$$\text{and } \beta = [(M-m)/(M+m)]^2$$

A value of 0·30 ± 0·12 is obtained for $(1-J_{Xe}):(1-J_{Ar})$ where J_i is the average probability of the hot molecules, in this case HT and DT, undergoing dissociation on collision with the moderator i. Since $J_{Ar} > 0$ it follows that $J_{Xe} >$ 0·70 ± 0·12. The absence of curvature in the KT I plot[8] corresponds to the case $J_m = J_r$.

The comparatively high reactivity of the recoil tritium system studied limits the range of moderator concentrations over which kinetic-theory analyses can be applied with any great validity[9], and prevents the determination of individual decomposition probabilities by the methods adopted by either Spicer[1] or Alfassi *et al.*[2] However, the greater internal energy gained by HT as it becomes

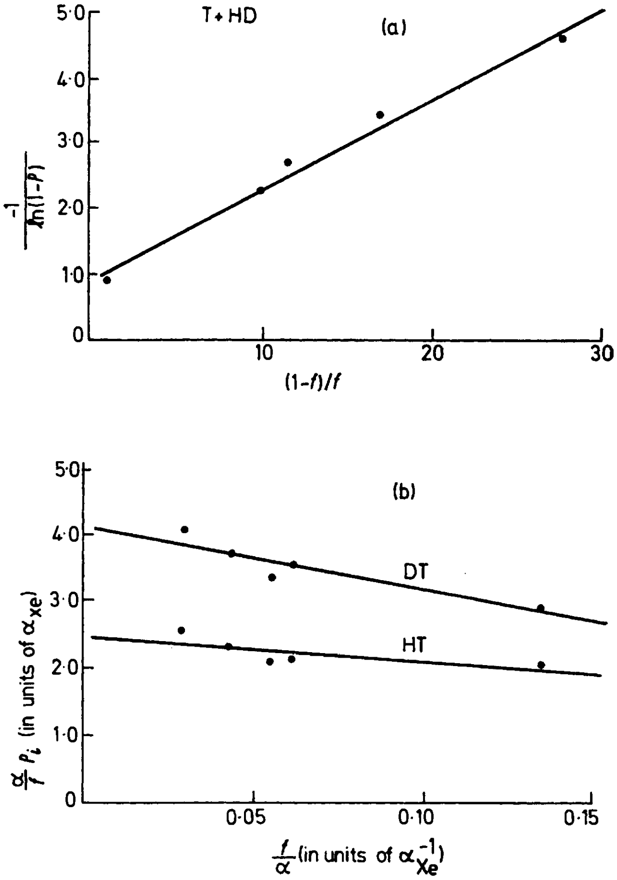

Figure. Kinetic theory plots of (a) total and (b) individual product yields: system T + HD.

thermalized together with its lower bond energy suggests that the major portion of the collisional dissociation figure of (70 ± 12)% for HT + DT can be attributed to the HT.

While not allowing individual decomposition probabilities to be obtained, the use of HD does allow a kinetic theory type-2 plot to be drawn and internal consistency checks applied to test the sensitivity of the present kinetic theory[6] to collisional decomposition. From the intercepts of such a plot (Figure b) I_{HT}, the reactivity integral for HT = $(2·5 \pm 0·3)\alpha_{Xe}$ and $I_{DT} = (4·2 \pm 0·4)\alpha_{Xe}$. The energy shadowing terms K_{HT} and K_{DT} equal $(3·6 \pm 0·7)\alpha_{Xe}^2$ and $(9·5 \pm 1·9)\alpha_{Xe}^2$ respectively. Poor correlation is obtained when these figures are substituted in the equations $I = \Sigma I_1$ and $\frac{1}{2}I^2 = \Sigma K_1$ used to test for internal consistency. Further, the failure of the two sets of data available on the reaction of recoil tritium with HD (Seewald's argon[7] and our xenon) to give colinear k.t.-2 plots, as predicted by the kinetic theory, also reflects the sensitivity of the kinetic theory to collisional dissociation.

An isotope effect of 0·6 ± 0·2, revealed by the ratio of $I_{HT}:I_{DT}$, is in accord with the computer study done by Malcolme-Lawes of this system.[3] This study suggests departures from the theoretical value of 1·1—1·2 would arise in a xenon moderated system, from significant dissociation of excited HT.

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