products from step (2) would not ordinarily be expected to make a significant contribution to the total reaction products. This, of course, results from the fact that if the chains are long, step (1) and hence (2), would represent only a small per cent. of all the reactions occurring. That the chains in this reaction are short may be deduced from the experiments conducted in a packed reaction flask. The fact that no reduction in rate was observed is good evidence that the thermal decomposition of methyl ethyl ketone proceeds through a short chain mechanism.

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STORRS, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Kinetics of Hot Deuterium Atoms in the Photolysis of Deuterium Iodide[1,2]

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Deuterium atoms with large kinetic energy have been produced by photolysis of gaseous deuterium iodide. The reaction of these hot deuterium atoms with hydrogen, methane, ethane and neopentane has been studied as a function of composition, wave length, temperature and added rare gas. With hydrogenous substrates the ratio of hot atom reaction producing HD to moderation producing thermal D atoms has been measured. The variation of the ratio D_2/HD with experimental conditions is described by a simple mechanism. Efficiencies of moderators are correlated with their molecular properties.

Introduction

The role of hot hydrogen atoms in the photolysis of hydrogen iodide at 2537 Å. has been described by Schwarz, Williams and Hamill[4] who found that the yield of hydrogen was significantly and systematically influenced by dilution with rare gases. In that study the products of hot atom reactions were chemically indistinguishable from the products of thermal atom reactions. That limitation has been removed in the present work by using deuterium iodide as the source of hot deuterium atoms which act upon various substrates containing protium. In this way, the product of hot atom reaction with the substrate (HD) can easily be distinguished from the product of reaction (hot or thermal) with deuterium iodide (D_2).

The results are examined in the framework of a mechanism analogous to that proposed in the previous study, with the addition of steps taking account of the hot atom reaction with and moderation by the substrate, designated in general by RH.

$$\mathrm{DI} + h\nu \longrightarrow \mathbf{D} + \mathrm{I} \tag{1}$$

$$\mathbf{D} + \mathrm{DI} \longrightarrow \mathrm{D_2} + \mathrm{I} \quad \kappa_3 \tag{2}$$

$$\mathbf{D} + \mathrm{RH} \longrightarrow \mathrm{HD} + \mathrm{R}\cdot \quad \kappa_3 \tag{3}$$

$$\mathrm{R}\cdot + \mathrm{DI} \longrightarrow \mathrm{RD} + \mathrm{I} \tag{4}$$

$$\mathbf{D} + \mathrm{DI} \longrightarrow \mathrm{D} + \mathrm{DI} \quad \kappa_5 \tag{5}$$

$$\mathbf{D} + \mathrm{RH} \longrightarrow \mathrm{D} + \mathrm{RH} \quad \kappa_6 \tag{6}$$

$$\mathbf{D} + \mathrm{M} \longrightarrow \mathrm{D} + \mathrm{M} \quad \kappa_7 \tag{7}$$

$$\mathrm{D} + \mathrm{DI} \longrightarrow \mathrm{D_2} + \mathrm{I} \tag{8}$$

$$\mathrm{D} + \mathrm{RH} \longrightarrow \mathrm{HD} + \mathrm{R} \tag{9}$$

$$\mathrm{I} + \mathrm{I} + \mathrm{M} \longrightarrow \mathrm{I_2} + \mathrm{M} \tag{10}$$

The **D** designates a hot deuterium atom. Processes 2 and 3 are the hot atom reactions with DI and substrate, respectively, and similarly κ implies that the quantity measured is the net probability of reaction before thermalization. Processes 5, 6 and 7 are those of moderation (thermalization). RH represents hydrogen, methane, ethane or neopentane while M in process 7 represents a rare gas. Processes 8 and 9 are the reactions of thermal atoms but in most of this work the ratio DI/RH is such that process 9 may be neglected. Further it seems reasonable to neglect process 5, since the heavy DI molecule should be a very poor moderator for D atoms.

Applying the ordinary steady-state treatment to D and for the present neglecting the production of HD by process 9, the following expression of the ratio of rates of production of isotopic hydrogen molecules is obtained

$$\frac{\mathrm{D_2}}{\mathrm{HD}} = \frac{\kappa_2}{\kappa_3} \times \frac{(\mathrm{DI})}{(\mathrm{RH})} + \frac{\kappa_6}{\kappa_3} + \frac{\kappa_7}{\kappa_3} \times \frac{(\mathrm{M})}{(\mathrm{RH})} \tag{11}$$

This relation has been applied to the treatment of the results described below.

Experimental

Materials.—Deuterium iodide was prepared from the elements[5] on platinized asbestos at 300°. After several preparations to purge the system, it was possible to obtain DI containing as little as 2.0 mole % HI. Methane, ethane and neopentane were Phillip's Research Grade materials. Hydrogen, neon and helium were obtained from Matheson and were tested for absence of oxygen.

Apparatus.—Most of the photolyses were carried out at room temperature (25°) using the 2537 Å. mercury resonance radiation from a Hanovia SC 2537 lamp. The photolysis cells were cylindrical Vycor tubes having a volume of about 40 ml. The Vycor (Corning 7910) glass served as a filter for 1849 Å. radiation.

In some experiments quartz cells were used in order to admit 1849 Å. radiation. In still another series of runs a quartz cell was irradiated with a General Electric A-H6 capillary mercury arc through a benzene filter. In this case measurement of the spectral intensity combined with the measured absorption coefficients of hydrogen iodide and benzene permitted the estimate of energy absorption *versus* wave length shown in Fig. 1. It is estimated that the average wave length of light absorbed was 2950 Å.

Some experiments were conducted at 100° by enclosing the reaction cell in a quartz steam jacket.

Procedures.—Reaction mixtures were prepared by measuring pressures of reagents in a known volume, followed by condensation into the previously evacuated reaction cell.

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[1] From the doctoral dissertation of R. J. Carter, June, 1955.

[2] Presented at the 127th Meeting of the American Chemical Society, Cincinnati, Ohio, March 29–April 7, 1955.

[3] Eastman Kodak Fellow, 1954–1955.

[4] H. A. Schwarz, R. R. Williams, Jr., and W. H. Hamill, THIS JOURNAL, **74**, 6007 (1952).

[5] Deuterium gas, 99.66 mole % obtained from Stuart Oxygen Co., on authorization by the U.S.A.E.C.

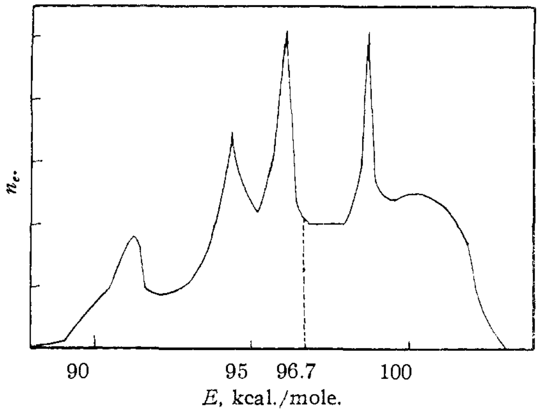

Fig. 1.—Energy absorbed by deuterium iodide in illumination by AH-6 through benzene.

Hydrogen, methane and the rare gases, being non-condensable, were transferred from the known volume to the reaction cell by means of a mercury lift pump. In a typical series of experiments the partial pressures of deuterium iodide and of ethane ranged between 30–150 mm. and 100–700 mm., respectively. The stopcock to the reaction cell was closed, the cell removed from the vacuum manifold and irradiated until the amount of deuterium iodide decreased by approximately 10%. Variations in the rate of photolysis had no effect on the results.

After photolysis, the reaction cell was attached to the vacuum line and products not condensable in liquid nitrogen were transferred by means of a Topler pump to a bulb for mass spectrometric analysis.

Isotope analyses were performed on a Consolidated 21–103 A. mass spectrometer. It was determined that no significant isotope exchange between H_2, HD and D_2 was induced during the analysis. The amount of contaminant protium iodide present in the deuterium iodide was determined by photolyzing a sample of the iodide under conditions identical to those used in the photolyses of reaction mixtures. The presence of protium requires a correction to the ratio (D_2/HD) (obsd.) after photolysis as follows: If f is the mole fraction of deuterium iodide

f^2 = probability of production of D_2 (D + DI)
$2f$ = probability of production of HD (D + HI or H + DI)
$(1 - f^2)$ = probability of production of H_2 (H + HI)

Therefore the observed final pressures of D_2 and HD are to be corrected as

$$P_{D_2}\,(\text{calcd.}) = P_{D_2}\,(\text{obsd.})\left[1 + \frac{2f(1-f)}{f^2} + \frac{(1-f)^2}{f^2}\right] \qquad (12)$$

$$P_{HD}\,(\text{clacd.}) = P_{HD}\,(\text{obsd.}) + P_{H_2}\,(\text{obsd.}) - P_{D_2}\,(\text{obsd.})\left[\frac{2f(1-f)}{f^2} + \frac{(1-f)^2}{f^2}\right] \qquad (13)$$

Only calculated pressures of D_2 and HD are used in the results reported below.

In the experiments with helium, the ionizing voltage in the mass spectrometer was 15.5 volts instead of the usual 70 volts in order to avoid interference by helium at mass 4. The sensitivities of H_2, HD and D_2 were carefully redetermined under these conditions.

In experiments with hydrogen, precision is poor when large proportions of hydrogen are used due to interference with the mass analysis. Also, the presence of hydrogen initially makes it necessary to depend entirely upon masses 3 and 4 for the analysis, in which case equations 12 and 13 are modified by omission of terms involving H_2, *i.e.*, omit P_{H_2} (obsd.) and $(1 - f)^2/f^2$.

Results

For the photolysis of deuterium iodide at 2537 Å. in the presence of ethane the ratio D_2/HD is a linear function of DI/C_2H_6 over a wide range of composition, as shown in Fig. 2. At small values of DI/C_2H_6 (large amounts of ethane) the points fell at abnormally small values of D_2/HD. This is attributed to process 9, the reaction of thermal D atoms with ethane. Experiments at 100° were virtually indistinguishable from those at 25°, except in the region of high ethane concentration.

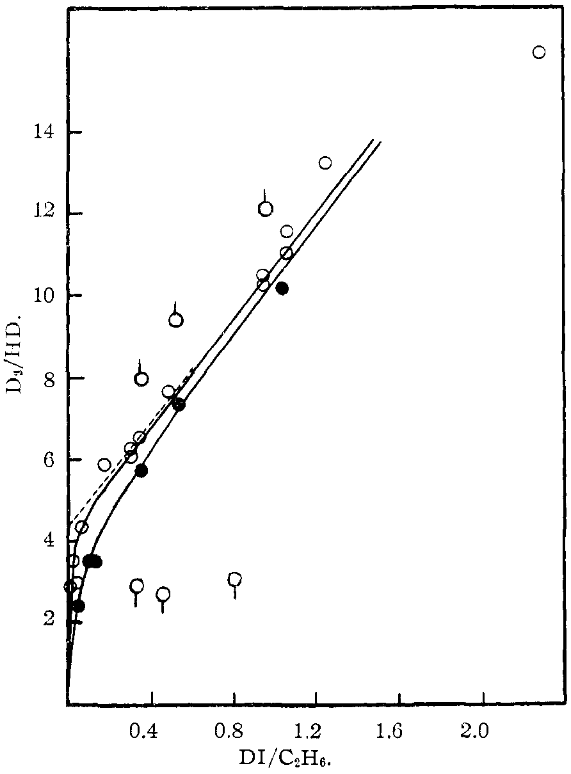

Fig. 2.—Photolysis of deuterium iodide in ethane: ○, 25°; ●, 100°, 2537 Å.; ó, 2950 Å.; ♀, 1849 Å.

In one experiment the materials remaining after complete photolysis and subsequent removal of hydrogen were analyzed and the presence of ethane-*d* was verified. In several other experiments the non-condensable products were examined for methane and methane-*d*. None of the latter was found and the traces of methane were accounted for as an impurity initially present in the ethane.

Experiments with the same system using the band of radiation centering around 2950 Å. showed a distinct increase in the ratio D_2/HD as would be expected from a decreased hot atom contribution. The results are compared with those obtained at 2537 Å. in Fig. 2. Experiments conducted in quartz cells to admit 1849 Å. radiation are regarded as qualitative, since only about 10% of the radiation entering the cell is of the shorter wave length. After subtracting the contribution for 2537 Å. radiation the values shown in Fig. 2 were obtained.

The rare gases neon and helium were added to the deuterium iodide–ethane system as moderators. In the treatment of these results, the measured product ratio, $D_2/HD = R$, is compared with the value expected in the absence of rare gas, obtained from the first two terms on the right-hand side of equation 11. According to that equation, the change in the ratio, ΔR, should be a linear function of M/C_2H_6 with zero intercept. Figure 3 shows the results of these experiments. In the case of neon, no systematic increase of ΔR with increasing proportions of neon is observed, but rather it seems that a small systematic positive error in R appears in these experiments. In the experiment with added helium, points corresponding to low values of DI/C_2H_6 have been weighted more heavily than those corresponding to high values because of the possibility that the deuterium iodide used in these experiments may have been slightly decomposed prior to photolysis.

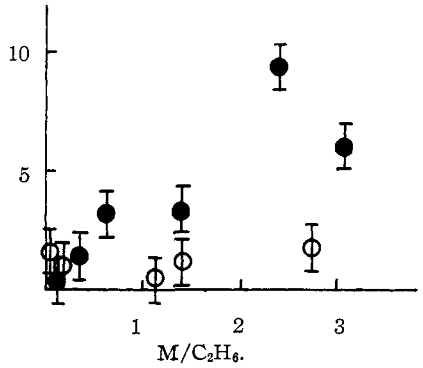

Fig. 3.—Moderation by inert gases: ○, neon; ●, helium.

In the experiments with deuterium iodide–hydrogen mixtures the linear relation required by equation 11 is again observed, as shown in Fig. 4. Experiments at 25 and 100° fall on the same curve. Two experiments were performed with helium added to this system: at $DI/H_2 = 1$ addition of helium to the extent of $1.7P_{H_2}$ increased D_2/HD by 45%; at $DI/H_2 = 0.69$, addition of helium equal to $1.18P_{H_2}$ increased D_2/HD by 59%.

Photolysis of deuterium iodide–methane mixtures was conducted at 2537 Å. and 25° only, with no rare gases added. The results are shown in Fig. 4. In a separate experiment carried to nearly complete consumption of deuterium iodide, the presence of methane-*d* among the products was established by mass spectrometric analysis.

The results of photolysis of deuterium iodide–neopentane mixtures are shown in Fig. 4. Evidence of a thermal reaction (step 9) appears at high proportions of neopentane. In a separate experiment carried to nearly complete consumption of deuterium iodide the presence of neopentane-*d* was established by mass spectrometric analysis of the condensable materials. No other hydrocarbons were detectable in this fraction nor in the non-condensable fraction which would have contained methane, had it been formed.

Discussion

In the absence of rare gas, the last term on the right-hand side of equation 11 is zero and the relation is a simple linear function which describes the results adequately, except at large proportions of substrate. The appearance of a positive intercept may be taken as evidence of the applicability of the hot atom mechanism proposed, for if only a simple thermal atom competition between processes 8 and 9 were involved, a simple proportion between D_2/HD and DI/C_2H_6 would be expected; this was not found. The increase of D_2/HD with increasing wave length and with addition of rare gases serves to substantiate the hot atom mechanism. The observed absence of a temperature coefficient is also to be expected for a hot atom reaction.[6,7]

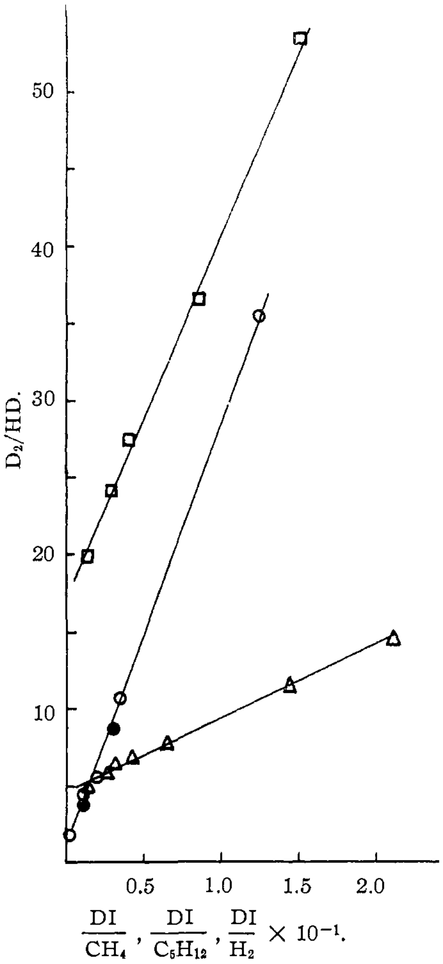

Fig. 4.—Photolysis of deuterium iodide at 2537 Å.: ○, in H_2 at 25°; ●, in H_2 at 100°; □, in CH_4; △, in C_5H_{12}.

The slopes and intercepts of the curves of Figs. 2 and 4 have been evaluated by the method of least-squares and are given in Table I. In the case of the deuterium iodide–hydrogen system, both slope and intercept are multiplied by a factor of 2

TABLE I

REACTION AND MODERATION EFFICIENCIES FOR HOT D ATOMS

System	Slope κ_2/κ_3	Intercept κ_6/κ_3	1/Slope κ_3/κ_2	Intercept/slope κ_6/κ_2
$DI-C_2H_6$	6.40	4.33	0.156	0.677
$DI-H_2$	5.64	1.40	.177	0.248
$DI-CH_4$	24.3	16.7	.041	0.687
$DI-C_5H_{12}$	4.65	4.80	.215	1.03

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(6) W. H. Hamill, R. R. Williams, Jr., H. A. Schwarz and E. E. Voiland, AECU-1321, March, 1951.

(7) J. L. Magee, *Proc. Nat. Acad. Sci.*, **38**, 764 (1952).

in obtaining κ_2/κ_3 and κ_6/κ_3, since process 3 will be followed by H + DI → HD + I yielding a second molecule of HD which does not appear with hydrocarbons.

Values of slopes and intercepts are not given for the experiments at wave lengths other than 2537 Å. since only qualitative support of the hot atom mechanism was obtained in these cases as appears from Fig. 2.

In experiments with added helium, the data in Fig. 3 yields a rather uncertain value of $\kappa_7/\kappa_3 = 2.2$ or $\kappa_7/\kappa_2 = 0.34$. No clear evidence of moderation by neon is present, but this substance because of its large atomic mass would be expected to be a much poorer moderator for hot D atoms than would helium. If moderation occurs simply by elastic collision with rare gas atoms, neon would be expected to be about $^1/_5$ as effective as helium, in which case $\kappa_7/\kappa_3 = 0.44$, a value which would be hardly measurable in the range of conditions covered.

The small intercept observed in the case of deuterium–iodide–hydrogen mixtures raised a question as to whether or not the reactions might be entirely thermal, since this would yield a zero intercept. However, experiments with added helium show a distinct increase in the D_2/HD ratio and are taken as evidence that the production of HD from H_2 under the conditions used is indeed almost entirely a hot atom process.

In the preceding section, the deviation from linearity of the points at large proportions of ethane (see Fig. 2) was attributed to reaction of thermal D atoms with ethane. This process (equation 9) has an activation energy of *ca.* 8 kcal./mole[8] in contrast to the reaction with deuterium iodide (equation 8) which has an activation energy of *ca.* 4 kcal./mole.[4] The more complete expression for D_2/HD *versus* DI/C_2H_6 has been derived taking account of step 9. This modified expression includes the ratio of rate constants κ_9/κ_8 as well as the other parameters which appear in equation 11. Taking the values of κ_2/κ_3 and κ_6/κ_3 from the linear portion of the curve in Fig. 2 a curve which includes the points at low DI/C_2H_6 has been constructed using k_9/k_8 0.0012 at 25° and k_9/k_8 0.0087 at 100° for best fit. The curves corresponding to this treatment are shown in Fig. 5 where mole fraction of HD and mole fraction of C_2H_6 are chosen as variables to display more detail in the region of large proportions of ethane. The dashed line shows the behavior predicted by equation 11 without modification.

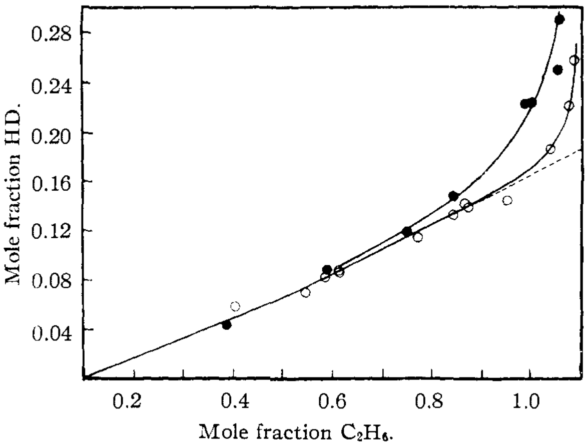

Fig. 5.—Photolysis of deuterium iodide in ethane: ○, 25°; ●, 100°.

The value of k_9/k_8 estimated at 25° corresponds to an activation energy difference of *ca.* 4 kcal./mole, assuming equal frequency factors. The temperature coefficient of k_9/k_8 corresponds to an activation energy difference of *ca.* 6 kcal./mole. The approximate agreement with previous information on these processes substantiates the interpretation of the data at large proportions of ethane.

In the last two columns of Table I the relative efficiences of hot atom reaction with and moderation by the various substrates have been computed using the hot atom reaction with deuterium iodide as the common denominator in all cases.

The reaction of hot D atoms with methane is much less efficient than the corresponding reaction with hydrogen, ethane and neopentane. This is attributed to the fact that the activation energy for the process is 12–13 kcal./mole[8] while the activation

$$D + CH_4 \longrightarrow HD + CH_3$$

energies of the corresponding reactions with C_5H_{12}, C_2H_6 and H_2 are much lower, in the region of 6–8 kcal./mole. Therefore a hot D atom, produced orginally with some 47 kcal./mole of kinetic energy falls below the energy threshold for reaction with methane much earlier in its life than with ethane, hydrogen and neopentane.

The relative moderating efficiencies of the various substrates also show an interesting regularity. Although from the standpoint of elastic collisions alone hydrogen should be the best moderator, it is in fact the poorest, while neopentane is the best. This is taken to mean then internal degrees of freedom absorb energy in the moderating collisions and that moderating efficiency increases with increasing number of available internal degrees of freedom.

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[8] E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd ed., Reinhold Publ. Corp., New York, N. Y., 1954.