indicate that the recoil does not free the Br^{80m} from the parent $(Br_2)_n$ unit, or that, if it does, the atom's capability of reacting with the organic medium is removed during the escape process. To test the latter possibility, samples were allowed to stand at 77°K for 2 hr following neutron irradiation. They were then extracted and the organic layer was analyzed for Br^{80} (18 min) which might have been produced by the isomeric transition of Br^{80m} atoms which had recoiled into the organic medium as a result of the n,γ process. The yields were very nearly those predicted on the assumption that the organic yield of the n,γ process is a true indication of the fraction of the Br^{80m} atoms which escape from the $(Br_2)_n$ units.[14]

The fact that the organic yield from the n,γ process in polycrystalline $n\text{-}C_6H_{14}$ is lower (1%) than that of the isomeric transition process (4%) is unexpected. The most obvious interpretation would seem to be that the recoil atom, faced by a solid wall of close-packed surrounding molecules, has a very low probability of escape from the parent cage, and that it has less capability of reacting with the hydrocarbon matrix surrounding the surface of the cluster than does an atom produced by the isomeric transition. This difference in capability may result from the fact that essentially all of the isomeric transition events produce Br^{80} ions which emit conversion and Auger electrons which produce radiolytic fragments from the hydrocarbon matrix, whereas the fraction of $Br^{79}(n,\gamma)Br^{80m}$ events which lead to charged Br^{80m} and electron emission may be no more than 12%.[15]

[14] In making this estimate it was assumed that the fraction of the Br^{80m} atoms escaping the clumps was twice the organic yield since approximately half would enter inorganic combination. It was further assumed that the organic yield for the isomeric transition of those which had escaped would be *ca.* 50%, which is the value for the organic yield of the isomeric transition in very dilute Br_2 in *n*-hexane.

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Kinetics of Thermal Deuterium Atom Reactions with Methane and Ethane[1]

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Abstract: Use of NH_3 as a proton (deuteron) scavenger has permitted a study of the effects of temperature on homogeneous thermal D-atom reactions with CH_4 and C_2H_6 in H^3 β-ray irradiated gaseous $TD\text{-}D_2\text{-}CH_4\text{-}NH_3$ and $TD\text{-}D_2\text{-}C_2H_6\text{-}NH_3$ mixtures between 25 and 220°. Exchange products with CH_4 are CH_3D, CH_2D_2, CHD_3, and CD_4, but ethane is not a detectable product below 125°. C_2H_5D is the only deuterated ethane formed by the atomic sequence in $D_2\text{-}C_2H_6\text{-}NH_3$ mixtures at 25 to 125°. Exchange proceeds *via* H-atom abstraction in both systems. Above ~125° a chain reaction sequence, $D\cdot + RH \rightarrow HD + R\cdot$ (i), $R\cdot + D_2 \rightarrow RD + D\cdot$ (ii), becomes dominant. Activation energies, $E_{\rm i}$ and $E_{\rm ii}$, have been found to be 8.5 ± 0.5 and 12.0 ± 0.7 kcal/mole, respectively, for $RH = CH_4$, and 6.5 ± 0.5 and 13.5 ± 1.0 kcal/mole, respectively, for $RH = C_2H_6$. Estimates of $\Delta S°$ and $\Delta H°$ for *i* provide $k_{(D\cdot + CH_4)} = 6 \times 10^{-11} e^{-8500/RT}$ cc/molecule sec between 25 and 125° and a collision theory (hard sphere, $\sigma = 3$ A, two squared terms) steric factor of 0.1. Results also suggest that D_2 is quite inefficient as a third body for collisional stabilization of excited methane and ethane molecules formed *via* $R\cdot + D\cdot \rightarrow RD^*$, even at D_2 pressures near 1 atm.

Although the reactions of thermal hydrogen atoms with CH_4 and with C_2H_6 have been subjects of many investigations for over 30 years,[3-9] the activation energy for the homogeneous reaction with CH_4 has yet to be established within reasonable limits.[10] Before 1958 values ranging from 4.5[4] to 15 kcal/mole[3] were reported. Recently, the range appears to have been narrowed to approximately 7 to 12 kcal/mole.[5,6,8] Little attention has been given to reactions of hydrogen atoms with C_2H_6 during the last decade. Earlier values of E_A for ethane range from 6 to 9 kcal/mole.[3] This state of affairs attests to difficulties with production of hydrogen atoms at steady rates, avoidance of surface effects, and establishment of necessary relations between measured quantities and parameters of the elementary steps. Shortcomings of flow systems[4,8] for studies of homogeneous reactions and for temperature coefficient measurements are well known. Flame techniques,[6] in particular, as well as photolytic competitive methods,[5] are dependent upon knowledge concerning elementary steps whose kinetic parameters are seldom more firmly established than those to be determined. Investigations employing radiolytically generated hydrogen atoms[7,9] are subject to seriously misleading interpreta-

[1] Based on a dissertation presented in partial fulfillment of requirements for the Ph.D., The Ohio State University, 1965, by R. H. Lawrence, Jr., U.S.A.F., A.F.I.T. Program, 1961–1965.

[2] To whom communications concerning this article should be addressed.

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tion unless contributions of ionic reactions can be sorted out unambiguously. The radiolytic method does, however, provide excellent conditions for temperature coefficient measurements in the absence of surface effects.[7] Previous work has indicated that studies of reactions induced by H^3 β rays in gaseous mixtures of D_2, TD, and small quantities of CH_4 at total pressures near 1 atm and as a function of temperature can provide useful information concerning atomic and free-radical steps under precisely controlled experimental conditions, but that ionic reactions play a dominant role below 150°.[7] More recent work has shown that the most significant ionic reactions in such mixtures are effected by a chain sequence of proton and deuteron transfer steps which do not require thermal activation.[11] This work has indicated that small quantities of NH_3, C_2H_6, or other molecules having proton affinities greater than that of CH_4 might be used to inhibit ionic steps sufficiently to permit observation of reactions of radiolytically generated thermal D atoms with CH_4 over a wide range of temperatures. This article reports results of a series of measurements of the rates of D-atom reactions with CH_4 and with C_2H_6 between −78 and 125° in the presence and absence of small amounts of NH_3 which permit assignment of reasonable and consistent activation energies for H-atom abstraction. Data are also presented for the range 150 to 220° which establish occurrence of atomic and free-radical chain exchange mechanisms in the CH_4–D_2 and C_2H_6–D_2 systems and which provide new estimates of activation energies for reaction of CH_3 and C_2H_5 radicals with D_2.

Experimental Section

The experimental apparatus and techniques employed for purification of reagents, preparation of reaction mixtures, maintenance of constant reaction temperatures, sampling, and analysis of reaction mixtures were essentially identical with those employed previously,[7] except for the following modifications. A greaseless high-vacuum threaded glass valve with a Teflon plug (Fischer and Porter 795-609) was used in place of the lightly greased capillary bore stopcock used in the earlier work to provide for admission of reactants to and removal of samples from the reaction vessel. Deuterium was purchased from the Matheson Co., and the D_2–TD mixtures were purified by passage through a heated palladium thimble. D_2–TD mixtures containing small amounts of HD were recovered from reaction mixtures by passage through the palladium thimble and were used in subsequent experiments until the HD/D_2 ratio exceeded approximately 0.05. Aliquots of reaction mixtures containing NH_3 were separated into hydrogen, hydrocarbon, and ammonia fractions by combined use of the palladium thimble and liquid nitrogen cooled traps. Mass spectrometric analyses were performed with a Consolidated 21-620 mass spectrometer with isotope ratio accessory. Analyses for hydrocarbon products were performed by gas chromatography with an F and M 609 flame ionization instrument using an 8-ft, 0.25-in. o.d., 80–100 mesh silica gel column with a 9°/min linear program commencing at 60° at flow rates of 40, 36, and 300 cc/min for H_2, N_2, and air, respectively. Ion current measurements required for dosimetry were performed with a Cary 31 ion chamber and vibrating reed electrometer. Dry nitrogen was used as filling gas for the chamber, and a *W* value of 34.9 ev/ion pair was assumed.[12] Deuterium pressures in each of the reaction mixtures were high enough to ensure that fewer than 1% of the H^3 β rays reached the walls of the 500-cc spherical reaction vessel.[13]

Results and Discussion

TD–D_2/CH_2 System. Previously reported observations[7] of β-ray induced reactions in D_2 containing small quantities of CH_4 demonstrated that CH_3D is the only initial organic product and that it is formed with Arrhenius energies of 1 kcal/mole between 0 and 150° and 14 kcal/mole between 150 and 225°. Absence of more highly deuterated methanes and of ethane suggested that atomic and free-radical steps are relatively insignificant in the lower temperature range, and the very small temperature coefficient below 150° tended to confirm this interpretation. Recent data reported in Table I are generally consistent with those reported earlier with the exception that an improved analytical procedure permits us to observe initial formation of more highly deuterated methanes at 50° and above and of ethane at 125° and above. The temperature coefficient for CH_3D formation below 150° is again found to be inadequate for any reasonable purely atomic and free-radical mechanism.

Table I. Initial 100-Ev Yields in TD–D_2CH_4 Mixtures[a]

Temp, °C	100-Ev yields				
	CH_3D	CH_2D_2	CHD_3	CD_4	$CH_3D/CH_2D_2/CHD_3/CD_4$
−100	3.6	0.0	0.0	0.0	
−78	3.6	0.0	0.0	0.0	
−50	3.4	0.0	0.0	0.0	
−25	3.1	0.0	0.0	0.0	
0	4.4	0.0	0.0	0.0	
25	4.3	0.0	0.0	0.0	
50	4.8	0.2	0.0	0.0	1.0/0.04/0.0/0.0
75	5.5	0.5	0.3	0.0	1.0/0.09/0.05/0.0
100	6.4	1.1	0.4	0.0	1.0/0.17/0.04/0.0
125[b]	6.1	2.0	0.45	0.0	1.0/0.33/0.074/0.0
150[b]	10.0	1.3	0.47	0.2	1.0/0.13/0.047/0.02
175[b]	13.6	2.1	0.50	0.3	1.0/0.15/0.037/0.02
186[b]	26.5	3.6	0.61	0.4	1.0/0.14/0.023/0.02
200[b]	30.8	3.7	0.53	0.45	1.0/0.12/0.017/0.02

[a] 98.5 mole % TD–D_2 (1:100)/1.5 mole % CH_4; dose rate = 4.73 × 10^{12} ev/cc sec. [b] Ethane was observed as a product at 125° and higher temperatures, but in each case with a time-dependent *G* value tending toward zero with increasing dose.

In the present investigation it has been observed that the more highly deuterated methanes and ethane formed initially at 125° and above disappear rapidly, if the temperature is lowered and maintained in the 75 to −196° range. Rates of disappearance decrease in the order CD_4, CHD_3, CH_2D_2, and the rate of formation of CH_3D is markedly increased. It is now apparent that failure to observe the more highly deuterated methanes as initial products below 50° may be attributed to two factors. The rate of thermal D-atom reaction with CH_4 is, indeed, quite insignificant at these temperatures, and secondly, a rapid proton–deuteron transfer chain sequence selectively converts the more highly deuterated forms to CH_3D without thermal activation. Estimates of rate constants of the ion–molecule steps responsible for their destruction have been reported,[14] and a more extended discussion of these ionic reactions will be published in the near

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(11) R. H. Lawrence, Jr., and R. F. Firestone, *J. Am. Chem. Soc.*, **87**, 2288 (1965).

(12) J. Weiss and W. Bernstein, *Phys. Rev.*, **98**, 1828 (1955).

(13) L. M. Dorfman, *ibid.*, **95**, 393 (1954).

(14) R. H. Lawrence, Jr., and R. F. Firestone, *J. Am. Chem. Soc.*, **87**, 2288 (1965).

future.[15] For the present discussion it is helpful to set down the sequence of ionic steps which accounts for most of the CH_3D formed below 125° and which otherwise masks the contributions of atomic and free-radical reactions at these temperatures. It is highly probable that the most abundant primary ionic species, D_2^+, reacts quantitatively, or very nearly so, with D_2 in 97.0 to 98.5 mole % D_2 mixtures *via* reaction I.[16]

$$D_2^+ + D_2^+ \longrightarrow D_3 + D\cdot \qquad \text{(I)}$$

All pertinent evidence indicates that the predominant fate of D_3^+ in the presence of 1.5 mole % CH_4 is represented by reaction II,[14,17] and that CH_4D^+ reacts

$$D_3^+ + CH_4 \longrightarrow CH_4D^+ + D_2 \qquad \text{(II)}$$

efficiently with CH_4 *via* reaction III,[14] thus, accounting

$$CH_4D^+ + CH_4 \longrightarrow CH_3D + CH_5^+ \qquad \text{(III)}$$

for a purely ionic contribution to $G(CH_3D)$ equal to or slightly greater than $100/W$, or 3 to 4 molecules/100 ev. In the absence of more highly deuterated methanes and of ethane, the fate of CH_5^+ in D_2-rich mixtures is presumably either neutralization or reaction IV.[7] In

$$CH_5^+ + D_2 \longrightarrow CH_4D^+ + HD \qquad \text{(IV)}$$

the presence of even small traces of more highly deuterated methanes, CH_5^+ lives long enough at room temperature to react with the former *via* the following sequence of reactions[14]

$$CH_5^+ + CD_4 \longrightarrow CHD_4^+ + CH_4 \qquad \text{(V)}$$

$$CHD_4^+ + CH_4 \longrightarrow CHD_3 + CH_4D^+ \qquad \text{(VI)}$$

at which point reaction III regenerates CH_5^+ and the chain is propagated, as well, by reactions VII–X to

$$CH_5^+ + CHD_3 \longrightarrow CH_2D_3^+ + CH_4 \qquad \text{(VII)}$$

$$CH_2D_3^+ + CH_4 \longrightarrow CH_2D_2 + CH_4D^+ \qquad \text{(VIII)}$$

$$CH_5^+ + CH_2D_2 \longrightarrow CH_3D_2^+ + CH_4 \qquad \text{(IX)}$$

$$CH_3D_2^+ + CH_4 \longrightarrow CH_3D + CH_4D^+ \qquad \text{(X)}$$

complete the reduction of all species of formula $CH_{4-i}D_i$, $i > 1$, to CH_3D. Thus, contributions of atomic reactions are relatively small below 125°, and net formation of CH_2D_2, CHD_3, and CD_4 is precluded at these temperatures. Chain termination is most probably effected by neutralization steps, while reaction IV serves to inhibit the chain reaction while adding to the CH_3D yield.

The absolute yields of CH_3D reported in Table I for the range −25 to 125° are markedly greater than those reported previously,[7] whereas the yields of Table I are smaller at 175 through 200°. The discrepancies in the lower range suggest inhibition of the ionic chain sequence in the earlier work, almost certainly by traces of water vapor formed radiolytically from traces of O_2 in TD–D_2 mixtures prior to preparation of reaction mixtures. Passage of TD–D_2 mixtures through a palladium thimble rigorously excluded such impurities in the present work.

Figure 1 illustrates effects of temperature on $G(CH_3D)$ in TD–D_2/CH_4 mixtures. Since it has been demonstrated[14] that the ionic sequence, reactions I–X, proceeds without thermal activation, and, because the more highly deuterated methanes and ethane emerge as detectable products between 50 and 125°, it is apparent that thermally activated D-atom reactions with CH_4 and/or ionic steps requiring thermal activation occur at lower temperatures and tend toward predominance at 150° and upward. It has been shown[14,15] that addition of small quantities of NH_3 (1.5 mole %) to TD–D_2/CH_4–CD_4 mixtures halts completely the destruction of CD_4, and we observe that C_2H_6, as well, but not Xe, is a very effective inhibitor of the ionic sequence. These observations are based upon data summarized in Table II. Since the proton affinities rank in the order $NH_3 > C_2H_6 > CH_4 > Xe > D_2$,[14] these observations indicate that use of minimal quantities of NH_3 or C_2H_6 sufficient to inhibit the proton–deuteron transfer sequence should make it possible to observe products of D-atom reactions without ionic interference. NH_3 is clearly the better choice, because of its relative inertness to hydrogen atoms ($E_A \simeq 14$ kcal/mole[18]). In addition it possesses a desirably lower ionization potential than CH_4, and the ammonium ion is sufficiently stable and chemically inert that we may expect its predominant fate to be neutralization.

Table II. Effects of Temperature and Additives in TD–D_2/CH_4–CD_4 Mixtures

Temp, °C	Additive[a]	$G(CH_3D)$	$G(CD_4)$
25	None	1×10^2	132
25	Xe	5×10	5×10
25	C_2H_6	1.24	0.0
25	NH_3	0.74	0.0
−78	None	1×10^2	140
−78	Xe	1×10^2	1×10^2

[a] 97% TD–D_2 (1:100)/1.5% CH_4–CD_4 (23:1)/1.5% additive.

TD–D_2/CH_4–NH_3 System. Table III shows that in 97% TD–D_2 (1:100)/3% NH_3–CH_4 mixtures at 25°, $G(CH_3D)$ decreases from 4.2 molecules/100 ev in the absence of NH_3 to 0.23 at NH_3/CH_4 = 5:1 to 10:1. Data of Table III also show that the presence of NH_3 at the 5:1 ratio permits formation of CH_2D_2 and CHD_3 at detectable initial rates over the −78 to 125° range. $G(CD_4)$ and G(ethane) are two and three orders of magnitude, respectively, less than $G(CH_3D)$ at 100 to 125° and are immeasurably small at lower temperature. NH_2D is the only deuterated ammonia detectable and is formed at the same rate within 15% at 25 and 75°, indicating that NH_3 does not react with D atoms or radicals in these mixtures at these temperatures. We estimate $G(NH_2D)$ at approximately 2 molecules/100 ev but its absolute value is somewhat uncertain because of ammonia's strong tendency to adsorb on metal surfaces in the mass spectrometer inlet system.

It is apparent that NH_3 protects the higher deuterated methanes and ethane from species bearing transferrable protons and that temperature dependent yields of CH_3D, CH_2D_2, and CHD_3 persist in the NH_3/CH_4 = 5:1 to 10:1 range. The unscavengable temperature

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[15] R. F. Firestone and R. H. Lawrence, Jr., Advances in Chemistry Series, No. 58, American Chemical Society, Washington, D. C., in press.

[16] D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.*, **23**, 1353 (1955).

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[18] K. T. Oganesyan and A. B. Nalbandyan, *Dokl. Akad. Nauk SSSR*, **160**, 162 (1965).

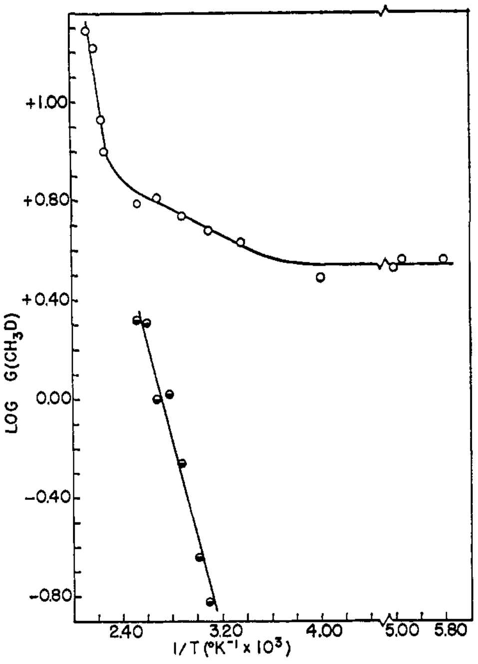

Figure 1. Initial 100-ev yield of CH_3D as a function of temperature: ○, TD–D_2/CH_4, gross yields; ◒, TD–D_2/CH_4–NH_3, nonionic yields.

independent CH_3D yield amounts to 6% of the total CH_3D yield from ionic processes, which is close to the electron fraction of CH_4 and may be attributed to processes induced by direct energy absorption in CH_4 and/or energy transfer from excited neutral D_2.

Table III. Initial 100-Ev Yields of Major Products in TD–D_2/CH_4–NH_3 Mixtures

Temp, °C	(NH_3)/ (CH_4)	CH_3D	CH_2D_2	CHD_3	CH_3D/ CH_2D_2/CHD_3[a]
−78	5	0.17	0.06	0.04	
0	5	0.19	0.09	0.05	
25	1	0.74		0.18	
25	5	0.23	0.07	0.11	
25	10	0.23	0.08	0.05	
50	5	0.35	0.13	0.10	1.0/0.4/0.4
62	5	0.43	0.15	0.11	1.0/0.4/0.3
75	5	0.75	0.26	0.21	1.0/0.4/0.4
87	5	1.25	0.61	0.27	1.0/0.5/0.2
100	5	1.20	0.57	0.26	1.0/0.5/0.2
112	5	2.26	0.79	0.34	1.0/0.4/0.15
125	5	2.30	0.79	0.23	1.0/0.3/0.09

[a] Temperature-dependent portions.

Roughly one-fifth of the scavengable CH_3D ionic yield is observable with equimolar quantities of NH_3 and CH_4 and a simple calculation[19] based on seemingly reasonable assumptions indicates that NH_3 is four to five times as efficient as CH_4 in the competition for transferrable protons and deuterons.

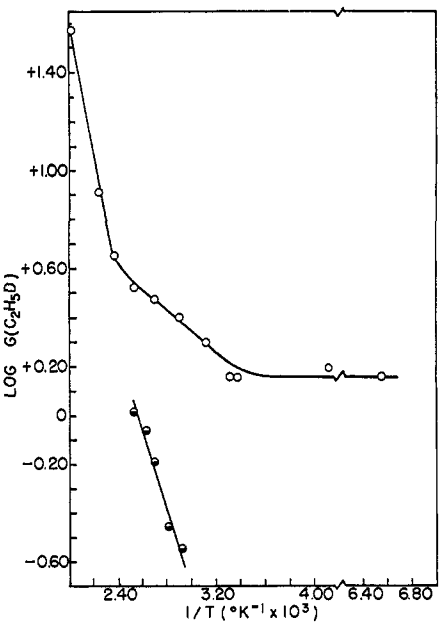

Figure 2. Initial 100-ev yield of C_2H_5D as a function of temperature: ○, TD–D_2/C_2H_6, gross yields; ◒, TD–D_2/C_2H_6–NH_3, nonionic yields.

Deduction of the unscavengeable temperature-independent yields of CH_3D (0.20 ± 0.02 molecule/100 ev), CH_2D_2 (0.07 ± 0.01), and CHD_3 (0.04 ± 0.01) from the respective total yields of Table III provides data which indicate that thermal D-atom reactions begin to contribute significantly between 25 and 50°. The temperature-sensitive nonionic yield of CH_3D increases with an Arrhenius energy of 8.5 ± 0.5 kcal/mole between 50 and 125° as illustrated in Figure 1, and those of CH_2D_2 and CHD_3 parallel the thermal CH_3D yield within experimental error as indicated by data in the last column of Table III. It is apparent that thermal reactions become predominant in the unscavenged TD–D_2/CH_4 system at approximately 150°. CH_3D is formed by a thermal chain sequence at these temperatures, and deduction of the temperature-independent ionic yield (3.4 ± 0.2 molecules/100 ev) provides an Arrhenius energy of 12.0 ± 0.7 kcal/mole between 125 and 200° in the unscavenged system.

TD–D_2/C_2H_6 System. The thermal activation energy for H-atom abstraction by D atoms from C_2H_6 appears to be reasonably well established at about 6.8 kcal/mole[3,20] in the 25–150° range. Thus, analysis of the effects of temperature and NH_3 on rates of product formation in TD–D_2/C_2H_6 mixtures provides a relatively firm basis for evaluating the reliability of our analysis of data from the TD–D_2/CH_4–NH_3 system. Tables IV and V present 100-ev yields of products of 98.7% TD–D_2 (1:100)/1.3% C_2H_6 and 97% TD–D_2 (1:100)/3% NH_3–C_2H_6 (10:1) mixtures from −120 to 222° and −78 to 125°, respectively. Arrhenius energies of the C_2H_5D yields in the unscavenged system corresponding to the three temperature ranges of Figure 2 are 13 ± 1, 2.0 ± 0.2, and 0.0 kcal/mole. Deduction of the unscavengable ionic yield (0.13 molecule/100 ev) from

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(19) Let f_1 = fraction of D_3^+ ions which form CH_4D^+, and let f_2 = fraction of CH_4D^+ ions which transfer protons to NH_3 and CH_4, thereby forming CH_3D. Then f_1f_2 = fraction of the scavengeable yield observable at a given ratio, (NH_3)/(CH_4) = R, and is equal to

$$f_1f_2 = \frac{1}{(\epsilon R + 1)} \frac{{}^5/_4\epsilon R + 1}{{}^{25}/_{16}\epsilon R + 1}$$

if the probability of a proton transfer to an acceptor is four times that of a deuteron transfer, and, if the efficiency of NH_3 relative to CH_4, ϵ, is the same for D_3^+ as for CH_4D^+. This leads to f_1f_2 = 0.17 at R = 1 and 0.03 at R = 5, if ϵ is assigned the value 4.5. Observed values are 0.17 and 0.00 at R = 1 and 5, respectively.

(20) M. R. Berlie and D. J. LeRoy, *Discussions Faraday Soc.*, **14**, 50 (1953).

Table IV. Initial Product Yields in TD–D_2/C_2H_6 Mixtures[a]

Temp, °C	$G(C_2H_5D)$	$G(C_2H_4D_2)$	G(methane)	G(propane)	G(butane)
−120	1.4	0.4	0.2	*b*	*b*
−35	1.5	0.5	*c*	*b*	*b*
25	1.4	0.2	*c*	*c*	*c*
30	1.4	*c*	0.5	0.2	0.2
50	2.00	*c*	0.3	0.1	*b*
75	2.45	*c*	0.4	0.2	0.7
100	2.93	*c*	0.4	0.2	1.0
125	3.32	*c*	*c*	*c*	*c*
150	4.34	*c*	0.5	0.4	1.7
175	8.21	*c*	*c*	0.3	1.6
222	38.0	*c*	2.5	1.5	2.5

[a] 1.3 mole % C_2H_6. [b] Dose-dependent 100-ev yield observed; initial value not determined. [c] Not determined.

Table V. Initial Product Yields in TD–D_2/C_6H_3–NH_3 Mixtures[a]

Temp, °C	$G(C_2H_5D)$	$G(C_2H_4D_2)$	$G(C_2H_3D_3)$
−78	0.13	0.10	0.03
25	0.34	0.07	0.04
72	0.41	0.11	0.08
85	0.48	0.14	0.02
100	0.77	0.08	0.02
110	0.99	0.12	. . .
125	1.15	0.08	0.05

[a] 0.27 mole % C_2H_6.

$G(C_2H_5D)$ values obtained in the presence of NH_3 provides an Arrhenius energy of 6.5 ± 0.3 kcal/mole for the thermal mechanism at 25 to 125°.

It is noteworthy that the $C_2H_4D_2$ and $C_2H_3D_3$ yields in the scavenged system are unaffected by temperature in contrast to the behavior of $G(CH_2D_2)$ and $G(CHD_3)$ in the TD–D_2/NH_3–CH_4 system. $C_2H_4D_2$ and $C_2H_3D_3$ appear to be produced for the most part by ionic reactions.

As in the case of CH_4 a thermal atomic and free-radical chain sequence becomes dominant above 125° in TD–D_2/C_2H_6 mixtures. The Arrhenius energy for this region is 14 ± 1 kcal/mole after deduction of the temperature-independent ionic yield observed in the absence of NH_3.

Atomic and Free-Radical Mechanisms. In both TD–D_2/NH_3–CH_4 and TD–D_2/NH_3–C_2H_6 systems, formal step (1) represents radiation-induced and secondary ionic D-atom forming reactions. The

$$D_2 \rightsquigarrow 2D\cdot \qquad (1)$$

most important of these will be $D_2^+ + D_2 \rightarrow D_3^+ + D\cdot$ and $D_2 \rightsquigarrow D_2^* \rightarrow 2D\cdot$, and the anticipated "primary yield" of D atoms should be in the range 3 to 12 atoms/100 ev.[21] For the CH_4 case the following steps represent anticipated reactions of D atoms and methyl radicals

$$D\cdot + RH \longrightarrow HD + R_1 \qquad (2)$$

$$R_1 + D\cdot \underset{k_{3c}}{\overset{k_3}{\rightleftharpoons}} R_1D^* \begin{cases} \xrightarrow{D_2} R_1D & (3a) \\ \longrightarrow R_2 + H\cdot & (3b) \end{cases}$$

with similar steps for formation and destruction of R_2D^* $(CH_2D_2^*)$, etc.

$$R_4 + D\cdot \underset{k_{6c}}{\overset{k_6}{\rightleftharpoons}} R_4D^* \xrightarrow{D_2} R_4D \qquad (6a)$$

$$H\cdot + D_2 \longrightarrow HD + D\cdot \qquad (7)$$

$$R_i + D_2 \longrightarrow R_iD + D\cdot \qquad (8)$$

$$R_i + R_j \longrightarrow R_iR_j \qquad (9)$$

including $i = j$

$$2D\cdot \xrightarrow{M} D_2 \qquad (10)$$

where M represents a third body or wall. Reaction 7 will be quantitative for H atoms over the full 25–200° range at 1 atm of D_2.[22]

Appropriate steady-state expressions lead to the following expressions for the 25–125° range in the presence of NH_3

$$d(H)/dt = k_{3b}(R_1D^*) + k_{5b}(R_3D^*) - k_7(H)(D_2) = 0$$

$$(R_1D^*) = (k_3/k_3')(R_1)(D), \quad (R_2D^*) = (k_4/k_4')(R_2)(D\cdot), \quad \text{etc.}$$

where $k_i' = k_{ia} + k_{ib} + k_{ic}$; $k_3 = k_4 = k_5 = k_6$; and

$$G_1I - 2k_3(D\cdot)\sum_{i=1}^{4} f_i(R_i) - 2k_{10}(D\cdot)^2(M) = 0$$

where I is the dose rate (100 ev/cc sec) and f_i is the fraction of R_iD^* which is stabilized by collision. The relative temperature-dependent yields of the deuterated methanes suggest that collisional stabilization of R_iD^* is quite inefficient, and we assume that $2k_3(D\cdot)\sum_{i=1}^{4} f_i(R_i)$ is negligible relative to G_1I and $2k_{10}(D)^2(M)$. This, of course, implies that a substantial portion of each of the deuterated methanes is formed *via* reaction 8. This seems quite reasonable at prevailing D_2 pressures, assuming $E_8 \simeq 12$ kcal/mole.

Since

$$d(R_1)/dt = k_2(D\cdot)(RH) - k_8(R_1)(D_2) - (k_3/k_3')(k_{3a} + k_{3b})(R_1)(D\cdot) = 0$$

it follows that

$$d(CH_3D)/dt = k_2(D\cdot)(CH_4)\left[\frac{k_8(D_2) + (k_3/k_3')k_{3a}(D\cdot)}{k_8(D_2) + (k_3/k_3')(k_{3a} + k_{3b})(D\cdot)}\right]$$

The term in brackets can be assumed to be essentially independent of temperature and assigned the symbol B, such that $G(CH_3D) = Bk_2(CH_4)[G_1/(2k_{10}(M)I)]^{1/2}$

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(21) The minimum value for G_1 is $100/W = 2.8$ atoms/100 ev. In the presence of 3% NH_3–CH_4 or 3% NH_3–C_2H_6 it is virtually certain that only an insignificant fraction of D_3^+ is neutralized,[15] ruling out D_3^+ as an immediate precursor of D atoms. The maximum possible yield of D atoms from dissociation of excited neutral deuterium molecules is approximately 9 atoms/100 ev, but a more reasonable guess is that roughly one neutral molecule dissociates per ion pair formed, for a yield of roughly 6 D atoms/100 ev from excitation events. The yield of D atoms from neutralization of NH_3D^+ obviously depends upon the neutral fragments, but all H atoms so formed will react quantitatively with D_2 at 25° upward at prevailing D_2 pressures to produce an equal number of D atoms. A reasonable estimate of D atoms from neutralization of ammonium ions is probably approximately 3 atoms/100 ev.

(22) D_2 reacts quantitatively with H atoms in TOH–HOH/D_2 gaseous mixtures ($G_1 = 12$ atoms/100 ev) at 100° and $P_{D_2} = 10$ mm in similar reaction vessels (*cf.* R. F. Firestone, *J. Am. Chem. Soc.*, **79**, 5593 (1957)). Assuming E_7 is approximately 7 kcal/mole, the 11-fold smaller value of k_7 at 25° will be more than compensated for by a 75-fold increase in P_{D_2}.

$E_{\text{obsd}} = RT^2\,\mathrm{d}(\log G)/\mathrm{d}t = 8.5 \pm 0.5$ kcal/mole $= E_2 - E_{10}/2$. Assuming the latter to be zero, we assign 8.5 ± 0.5 kcal/mole as the activation energy for the reaction $\mathrm{D\cdot + CH_4 \rightarrow HD + CH_3\cdot}$ between 25 and 125°.

Assuming that activation energies for H-atom and D-atom reactions with CH_4 are equal within 0.5 kcal/mole and employing the Whittle and Steacie[23] value for the reverse reaction, $E_f - E_r = -1.5 \pm 0.8$ kcal/mole. Known or estimated $\Delta H_f°$ and $S°$ values[24] provide $\Delta H°$ (−2 kcal/mole) and $\Delta G°$ (−4 kcal/mole) at 298°K, and we find by means of the relation $\Delta G° = -RT \ln (k_f/k_r)$ and the Arrhenius equation that $A_f/A_r = 1.1 \times 10^2$ at 298°K. This value provides a collision theory steric factor equal to 0.08 (σ = 3 A, two squared terms) for $\mathrm{H\cdot + CH_4 \rightarrow H_2 + CH_3\cdot}$, and leads to the expression $k_{\mathrm{H}} = 5.7 \times 10^{-11} e^{-8500/RT}$ cc/molecule sec. Similarly, assuming $E_A = 10.9$ kcal/mole for $\mathrm{CH_3\cdot + HD \rightarrow CH_4(CH_3D) + D\cdot(H\cdot)}$, the mean of values for $\mathrm{CH_3\cdot + D_2}$ and $\mathrm{CH_3\cdot + H_2}$,[23] and that $\log (A/T^{1/2})$ is the mean of corresponding values, we have a collision theory steric factor equal to 0.1 (σ = 3 A) for $\mathrm{D\cdot + CH_4 \rightarrow HD + CH_3\cdot}$ and the expression $k_{\mathrm{D}} = 6.3 \times 10^{-11} e^{-8500/RT}$, or more realistically, $k_{\mathrm{H}} \simeq k_{\mathrm{D}} = 6 \times 10^{-11} e^{-8500/RT}$ cc/molecule sec, and $P = 0.1$.

For the C_2H_6 system it is necessary in principle to add the following additional steps to the previous set of reactions

$$\begin{tikzcd}[column sep=large] & & \mathrm{Et_1D} & \text{(11a)} \\ \mathrm{Et_1 + D\cdot} \arrow[r, shift left, "k_{11}"] & \mathrm{Et_1D^*} \arrow[l, shift left, "k_{11c}"] \arrow[ur, "\mathrm{D_2}"] \arrow[r] \arrow[dr] & \mathrm{Et_2 + H\cdot} & \text{(11b)} \\ & & \mathrm{R_1 + R_2} & \text{(11d)} \end{tikzcd}$$

with similar steps for formation and destruction of $\mathrm{Et_2D^*}$ ($\mathrm{C_2H_4D_2^*}$), etc., and

$$\mathrm{Et}_j + \mathrm{D_2} \longrightarrow \mathrm{Et}_j\mathrm{D} + \mathrm{D\cdot} \qquad (17)$$

where Et_j represents an ethyl radical and R_i again represents a methyl radical. This leads *via* appropriate steady-state equations to

$$G_1I - 2k_{11}(\mathrm{D\cdot}) \sum_{j=1}^{6} f_j(\mathrm{Et}_j) - 2k_3(\mathrm{D\cdot}) \sum_{i=1}^{4} f_i(\mathrm{R}_i) - 2k_{10}(\mathrm{D\cdot})^2(\mathrm{M}) = 0$$

The most probable path for dissociation of $\mathrm{Et}_j\mathrm{D^*}$ is, of course, that leading to formation of methyl radicals (eq 11d, 12d, etc.), and consistently, we observe no multiply deuterated ethanes from the abstraction sequence. Darwent and Steacie have reported evidence from the Hg-sensitized photolysis of C_2H_6 which suggests that the sequence $\mathrm{H\cdot + C_2H_5\cdot \rightarrow C_2H_6^* \rightarrow 2CH_3\cdot}$ occurs readily at 50 mm of ethane, but is strongly inhibited above 200 mm.[25] It is not unreasonable to predict that deuterium is one or more orders of magnitude less efficient than ethane as a third body for collisional stabilization of vibrationally excited ethane.

The only seemingly relevant new evidence we can offer is merely suggestive and is concerned with the surprisingly low yields of C_2H_5D from the $\mathrm{D\cdot + C_2H_6}$ abstraction sequence relative to the total yields of deuterated methanes from the $\mathrm{D\cdot + CH_4}$ sequence at equal temperatures. This is partly attributable to the use of smaller C_2H_6 concentrations, $(CH_4)/(C_2H_6)$ in their respective systems being 1.8:1.0. The abstraction reaction is first detectable about 25° lower in the C_2H_6 system, as anticipated, but the rate of the abstraction sequence in the CH_4 system becomes equal to that in C_2H_6 (corrected for the concentration difference) at about 50° and exceeds it at higher temperatures. This can be attributed to an improbable difference in steric factors of approximately 10^3 or more ($E_{2,\mathrm{CH_4}} - E_{2,\mathrm{C_2H_6}} \geq 2$ kcal/mole) or to the likelihood that a substantial portion of ethane molecules entering reaction 2 are converted to methane *via* the sequence 11, 11d, etc. Assuming the latter to be the case

$$\mathrm{d(C_2H_5D)/d}t = k_2(\mathrm{D\cdot})(\mathrm{C_2H_6}) \times \left[\frac{k_{17}(\mathrm{D_2}) + (k_{11}/k_{11}')k_{11a}(\mathrm{D\cdot})}{k_{17}(\mathrm{D_2}) + (k_{11}/k_{11}')(k_{11a} + k_{11b} + k_{11d})(\mathrm{D\cdot})}\right]$$

$G(\mathrm{C_2H_5D}) = Ck_2(\mathrm{C_2H_6})[G_1/(2k_{10}(\mathrm{M})I)]^{1/2}$, where C represents the term in brackets and is assumed to be independent of temperature. Thus we assign E_{obsd} to $E_2 = 6.5 \pm 0.5$ kcal/mole, the activation energy for $\mathrm{D\cdot + C_2H_6 \rightarrow HD + C_2H_5\cdot}$ at 25 to 125°. This value is virtually identical with that of Berlie and LeRoy (6.8 ± 0.4)[20] and is consistent with Wijnen and Steacie's rather gross estimate for the reverse reaction (12 ± 1)[26] and estimates of $\Delta H°$ for the over-all reaction (−6 kcal/mole).[24]

Interpretation of the 150 to 200° data of either system must be strongly qualified, because ionic reactions must be assumed to have contributed to some extent to the product yields in the absence of NH_3. Subject to this important qualification, which is difficult to evaluate quantitatively, we assume that atomic and free-radical steps are predominant at 150 to 200° in both unscavenged systems and that the applicable steady-state relations are $\mathrm{d(D\cdot)/d}t = G_1I + k_8(\mathrm{R})(\mathrm{D_2}) - k_2(\mathrm{D})(\mathrm{RH}) = 0$, and $\mathrm{d(R)/d}t = k_2(\mathrm{D\cdot})\cdot(\mathrm{RH}) - k_8(\mathrm{R})(\mathrm{D_2}) - ak_9(\mathrm{R})^2 = 0$, where (R) represents the total methyl or ethyl radical concentration in the CH_4 and C_2H_6 systems, respectively, and a is a constant approximately equal to 2. Since, $\mathrm{d(R_1D)/d}t = bk_8\cdot(\mathrm{R})(\mathrm{D_2})$, where b is the fraction of the total deuterated methane or ethane yield from the abstraction sequence represented by CH_3D (b = 0.84, 150–200°) or C_2H_5D (b = 1.0, 150–220°), $G(\mathrm{R_1D}) = bk_8(\mathrm{D_2})[G_1/ak_9I]^{1/2}$. Thus, we assign an activation energy of 12.0 ± 0.7 kcal/mole to the step $\mathrm{CH_3\cdot + D_2 \rightarrow CH_3D + D\cdot}$ and an activation energy of 13.5 ± 1 kcal/mole to the step $\mathrm{C_2H_5\cdot + D_2 \rightarrow C_2H_5D + D\cdot}$ in the temperature ranges investigated. These estimates agree as well as might be expected with previously published estimates of 11.8 ± 0.4[23] and approximately 12,[26] and are nicely consistent with our assigned values for the respective $\mathrm{D\cdot + RH}$ steps.

TD-D$_2$/Xe-CH$_4$ System. Since Maschke and Lampe[9] have suggested that Xe is an effective ion scavenger in irradiated D_2-CH_4 mixtures at Xe concentrations considerably greater than that which we have found to be relatively ineffective (Table II), we have investigated the effects of temperature and CH_4 concentration in irradiated Xe-CH_4-D_2 mixtures similar to theirs; 100-ev yields of deuterated methanes and of ethane for

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Table VI. 100-Ev Yields of Products in Irradiated D_2–CH_4–Xe Mixtures[a]

Run no.	Mole % CH_4	$G(CH_3D)$	$G(CH_2D_2)$	$G(CHD_3)$	$G(CD_4)$	G(ethane)
			At 25°			
2b	1.54	1.00	0.14	0.11		
3b	3.06	0.62	0.25	0.10	0.06	
2a	6.2	0.43	0.21	0.09	0.05	0.076
5b	8.64	0.73	0.28	0.08	0.02	
3a	11.8	0.38	0.17	0.09	0.05	0.073
7b	15.9	0.39	0.32	0.10	0.03	0.087
			At −78°			
1b	1.54	0.36	0.18	0.11	0.07	<0.0
4b	3.6	0.75	0.19	0.10	0.05	
1a	6.2	0.65	0.30	0.22		
6b	8.6	1.55	0.32	0.03	<0.0	<0.0
8b	15.9	2.03	<0.0	<0.0		<0.0

[a] The a series experiments were performed at dose rate = 1.22×10^{13} ev/cc sec, and the b series experiments were performed at dose rate = 0.617×10^{13} ev/cc sec.

TD-D_2 (1:100)/Xe (50–58%)-CH_4 (1.5–16%) at 25 and −78° are presented in Table VI.

We observe that (1) ethane, propane, butane, and all deuterated methanes are formed initially at 25°, whereas, at −78° deuterated methanes are the only significant products, with CH_3D overwhelmingly predominant at higher CH_4 concentrations; (2) the higher hydrocarbons are destroyed at −78° at all CH_4 concentrations, whereas, the 100-ev yields of the more highly deuterated methanes are negative only above 6.2 mole % CH_4; (3) CH_3D yields are strongly dependent upon the CH_4 concentration at both 25 and −78°, but the proportionality is direct at −78° and inverse at 25°. On the basis of these observations it is apparent that Xe is incapable of inhibiting ionic reactions at Xe/CH_4 ratios in the range 40:1 to 4:1. It is also apparent that the proton–deuteron transfer sequence and other ionic reactions are responsible for the majority of products in these mixtures and that $XeD^+ + CH_4 \rightarrow CH_4D^+ + Xe$ cannot be ignored. It is not unlikely that Maschke and Lampe were correct in their assumption that the abstraction sequence is significant at the roughly 100-fold higher dose rates employed in their experiments at 25°, but ionic contributions must, if possible, be taken into account in the quantitative interpretation of their results.

Acknowledgment. The authors are grateful for support of this work by the U. S. Atomic Energy Commission (Contract AT(11-1)-1116).

Kinetics and Mechanism of the Gas Phase Reaction between Iodine and Formaldehyde and the Carbon–Hydrogen Bond Strength in Formaldehyde[1a]

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Abstract: The gas phase reaction of iodine with formaldehyde has been investigated spectrophotometrically in the temperature range 180–300°. The reaction is very clean, giving CO and HI as the only products except at very high conversions at the lowest temperatures, when a little CH_3I is formed as a side product. A reaction mechanism is presented in the text. Kinetic measurements over a wide range of initial conditions indicate that the rate-determining step is $I\cdot + CH_2O \rightarrow \cdot CHO + HI$, and $\log k_4 = 10.92 - 17.43/\theta$, where $\theta = 2.303RT$ in kcal/mole. Further measurements of the inhibiting effect of HI on the reaction suggest that the back activation energy for step 4 is 1.5 kcal/mole. This difference in forward and back activation energies establishes a bond strength of $DH°_{298}$(H–CHO) = 87.0 kcal/mole. The value implies a dative π-bond energy in carbon monoxide of 68.5 ± 2 kcal/mole, in good agreement with other estimates.

Detailed studies of the kinetics of gas phase reactions of iodine with a variety of hydrocarbons have proved extremely fruitful in providing reliable values for many bond dissociation energies[2] and radical resonance energies.[3] Much of this work has been made possible by the development of a highly sensitive spectrophotometric technique,[2,3] which permits detection of as little as 10^{-3} torr of iodine and organic iodides in these systems.

Recently this work has been extended to reactions of iodine with oxygen-containing compounds.[4a] It has been shown that, as is the case with hydrocarbons, the reaction proceeds through the rate-determining step

$$I\cdot + RH \longrightarrow R\cdot + HI$$

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[1] (a) This investigation was supported in part by Public Health Service Research Grant AP-00353-02 from the Air Pollution Division, Public Health Service. (b) Research Associate. Address correspondence to the Department of Chemistry, Reading University, Reading, Berkshire, England.

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