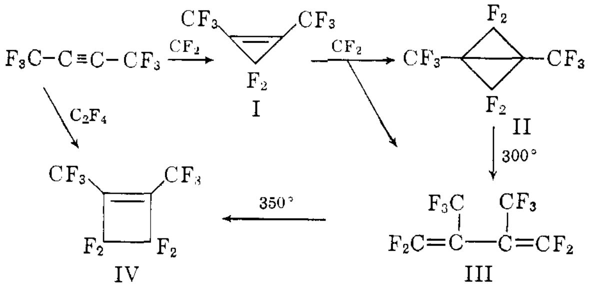

methyl)-3,3-difluorocyclopropene (I), b.p. 11°, m.p. −86°, double bond absorption at 1820 cm.$^{-1}$, mol. wt. (vapor density), observed 212, calcd. for C_5F_8, 212. The cyclopropene I was chlorinated in ultraviolet light to give 1,2-bis(trifluoromethyl)-1,2-dichloro-3,3-difluorocyclopropane as a 1:5 *cis-trans* mixture.

Anal. Calcd. for $C_5Cl_2F_8$: C, 21.20; Cl, 25.08; F, 53.72; mol. wt., 283. Found: C, 21.76; Cl, 24.93; F, 54.09; mol. wt., 287.

The *cis*-dichloro compound, isolated by gas chromatography, has m.p. −72°, 23 mm. vapor pressure at 0° and shows non-equivalent CF_2 fluorines with coupling of 172 c.p.s., characteristic of cyclopropanes.[4,5] The *trans* isomer has m.p. −56°, 27 mm. vapor pressure at 0°, and equivalent *gem* fluorines by n.m.r.

Difluorocarbene adds to the cyclopropene I at 100° in the gas phase to give a 25% yield of 1,3-bis-(trifluoromethyl)-2,2,4,4-tetrafluorobicyclobutane (II), b.p. 39°, m.p. −90°, together with an 8% yield of 2,3-bis-(trifluoromethyl)-1,1,4,4-tetrafluorobutadiene (III), b.p. 52°, m.p. −91°.

Anal. Calcd. for C_6F_{10}: C, 27.48; F, 72.52; mol. wt., 262. Found for II: C, 28.11; F, 72.50; mol. wt., 262. Found for III: C, 27.82; F, 72.30; mol. wt., 263.

No band characteristic of unsaturation appears in the infrared or Raman spectra of the bicyclobutane II. The F^{19} magnetic resonance spectrum of the CF_2 groups of the bicyclobutane in the first approximation is of the type AB[6] with a splitting of 150 c.p.s. In detail, it is A_2B_2[7] further complicated by sevenfold multiplicity due to the equivalent CF_3 groups. The pattern for the CF_3 groups is a triplet of triplets.

The infrared spectrum of the butadiene III shows absorption at 1750 and 1725 cm.$^{-1}$, indicative of two double bonds. The CF_2 fluorines are non-equivalent by n.m.r. with no detectable spin-spin interaction with each other.

At 300° the bicyclobutane II slowly rearranges to the butadiene III (20% conversion, 95% yield in 16 hours). At 350° the butadiene III cyclizes to 1,2-bis-(trifluoromethyl)-3,3,4,4-tetrafluorocyclobutene (IV) (15% conversion, 100% yield in 48 hours). This cyclobutene was prepared independently by the cycloaddition of hexafluoro-2-butyne to tetrafluoroethylene at 230° (3% yield in 4 hours); b.p. 36°, m.p. −66°, absorption at 1715 cm.$^{-1}$, mol. wt., observed, 259. The *gem* fluorines of IV are equivalent by n.m.r. In ultraviolet light, chlorine adds to give the dichloro adduct as a solid *cis-trans* mixture.

Anal. Calcd. for $C_6Cl_2F_{10}$: Cl, 21.32; F, 57.06. Found: Cl, 21.36; F, 56.72.

In further demonstration of the structure, the bicyclobutane II reacts in the dark at 200° to add chlorine across the diagonal bond.

Anal. Calcd. for $C_6Cl_2F_{10}$: C, 21.62; Cl, 21.32; F, 57.06. Found: C, 21.37; Cl, 21.65; F, 57.04.

F^{19} magnetic resonance shows this to be a *cis-trans* mixture, different from the 1,2 isomers derived from the cyclobutene. The *cis* 1,3 isomer has non-equivalent CF_2 fluorines with coupling constants of 211 c.p.s. characteristic of cyclobutanes.[4] The *trans* 1,3 isomer shows equivalent *gem* fluorines as expected.

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THE XENON RADIOSENSITIZED EXCHANGE OF DEUTERIUM ATOMS WITH METHANE

Sir:

In a recent paper[1] describing studies of the deuterium-methane exchange initiated by tritium β-rays, the absence of the abstraction reaction (1) was reported. This surprising conclusion is contradictory to what recently has been

$$D + CH_4 \longrightarrow HD + CH_3 \qquad (1)$$

thought to be a well-established reaction[2-4] and is based mainly on the observations that no ethane was detected and that the only initial exchange product was CH_3D. With evidence against (1), these authors[1] propose that the exchange proceeds *via* a non-abstraction mechanism (other than a high activation energy inversion[5]), *viz.*

$$D + CH_4 \longrightarrow CH_3D + H \qquad (2)$$

$$H + D_2 \longrightarrow HD + D \qquad (3)$$

Moreover, temperature dependence studies of this exchange system[1] were found to be inconsistent with the results of Berlie and Leroy,[2] who found E_1 = 4.5 kcal./mole and a steric factor of the order of 10^{-5}.

In studies of the xenon radio-sensitized deuterium-methane exchange at room temperature we have obtained evidence consistent with LeRoy's contention[3] that (1) occurs at room temperature and above. Furthermore, our results are in accord with the low values of E_1 and P_1 found by Berlie and LeRoy,[2] with Whittle and Steacie's estimate[6] of E_1 = 7.8 kcal./mole and $P_1 \sim 10^{-3}$ to

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10^{-4}, and are consistent with the older values[7-10] of E_1 of 11-13 kcal./mole found by the assumption that $P_1 = 0.1$.

In our studies we have irradiated 3:3:1 mixtures of Xe-D_2-CH_4 at a total pressure of 350 mm. with 2.5 mev. electrons from the Van de Graaff accelerator at the Mellon Institute. Under these conditions xenon absorbs 84% and deuterium 9% of the total dose.[11] Doses were calculated using pertinent energy loss data[11]; the absorption rate by xenon in all experiments was 8.5×10^{14} e.v./cm.^{3}-sec. In all experiments conversions were less than 8% and all products were analyzed with a Bendix Model 14-101 time-of-flight mass spectrometer.

In Table I are shown G' values for all products found, the G' referring to energy absorbed solely by xenon. There are two principal conclusions to be drawn from Table I. Firstly, G'(HD) is nearly five times $G'(CH_3D)$ whereas exchange *via* (2) and (3) requires equality of these values. Secondly, ethanes (d_0–d_5) are formed in significant amounts, suggesting the presence of methyl and deuterated methyl radicals in our system.

TABLE I

100-ELECTRON VOLT YIELDS OF OBSERVED PRODUCTS

Component	HD	CH_3D	CH_2D_2	CHD_3	CD_4	C_2H_6
G'	4.8	1.0	0.39	0.19	0.11	0.043
Component	C_2H_5D	$C_2H_4D_2$	$C_2H_3D_3$	$C_2H_2D_4$	C_2HD_5	
G'	0.13	0.13	0.11	0.044	0.021	

TABLE II

RELATIVE FORMATION RATES OF CH_3D AND CH_2D_2

Dose (e.v./cm.^{3}) $\times 10^{-17}$	$(CH_3D)/(CH_2D_2)$	Dose (e.v./cm.^{3}) $\times 10^{-17}$	$(CH_3D)/(CH_2D_2)$
3.1	1.6	12.7	1.7
5.1	2.0	12.7	2.5
7.6	1.6	15.3	1.7
10.2	1.8		

In Table II are shown ratios of the amounts of CH_3D and CH_2D_2 formed over a five-fold variation in dose. Within some scatter (due to water background corrections in the analyses) this ratio is constant over the dose range investigated. Similar constant ratios at a higher dose level and over a narrower range were observed for CHD_3, CD_4 and the ethanes. Thus the conclusion seems inescapable that these products are formed simultaneously, which is not possible if the exchange goes *via* (2) and (3).

Pratt and Wolfgang[12] have reported that xenon effectively scavenges ionic reactants in the tritium-methane exchange, and it is very probable, therefore, that in our system all ionic paths leading to exchange are inhibited. Since energetic considerations indicate all reactions of XeD^+ other than neutralization are endothermic by at least 8 kcal./mole, it seems very likely that ionization of xenon and deuterium leads only to deuterium atoms through formation and neutralization of XeD^+.[13-15] If ionic processes are thus suppressed we can most reasonably reconcile our results with the formation of methyl radicals *via* (1). The most reasonable mechanism[16,17] (following D-atom formation and (1)) then is

$$D + CH_3 \longrightarrow CH_3D^* \qquad (4)$$

$$CH_3D^* + M \longrightarrow CH_3D + M \qquad (5)$$

$$CH_3D^* \longrightarrow CH_2D + H \qquad (6)$$

$$H + D_2 \longrightarrow HD + D \qquad (3)$$

$$D + D + M \longrightarrow D_2 + M \qquad (7)$$

$$CH_2D + D \longrightarrow CH_2D_2^* \text{ (etc.)} \qquad (8)$$

$$CH_mD_n + CH_xD_y \longrightarrow C_2H_{m+x}D_{n+y} \qquad (9)$$

Use of this mechanism to interpret our rate data permits an estimate of the collision yield of (1). Since methane is consumed only in (1) we can write

$$-d(CH_4)/dt = k_1(D)(CH_4) \qquad (10)$$

and calculate the left-hand side from the observed rates of product formation (note from Table I that an excellent material balance is obtained). Assuming a steady state for deuterium atoms and two deuterium atoms formed per ion we can write

$$\frac{2Q_{Xe}}{W_{Xe}} + \frac{2Q_{D_2}}{W_{D_2}} = \frac{d(HD)}{dt} + 2k_7(D)^2(M) \qquad (11)$$

where Q is the dose rate and W is the average energy expended per ion formed.[18] Deuterium atom formation by primary excitation is neglected in this estimate. From measured formation rates, calculated dose rates and the reported value of 2.8×10^{-32} (cc.)^2/molecule^2-sec. for k_7,[19] (10) and (11) lead to the values (D) = 7.9×10^{12} atoms/cm.^{3} and $k_1 = 1.8 \times 10^{-18}$ cm.^{3}-molecule^{-1} sec.$^{-1}$. If a collision diameter of 2.6 Å. is assumed we are led to a collision yield of 4.5×10^{-9}. This value is consistent with the results of Berlie and LeRoy[2] and Whittle and Steacie.[6] If, as usually done in the older work,[7-10] a steric factor of 0.1 is assumed a value of 10.1 kcal./mole for E_1 is obtained which is in reasonable accord with the 11-13 kcal./mole reported. This consistency with other work lends support to our choice of mechanism, although it is contradictory to the results of Firestone, *et al.*[1]

Our results can be reconciled with those of Firestone, *et al.*,[1] if one assumes a high rate of formation of excited xenon atoms which react almost exclusively with methane to form CH_3 and H. However, in view of the 3:1 ratio of deuterium to methane and their relative quenching cross-sections for Cd($^3P_1$), Hg($^3P_1$) and Na(^2P) atoms,[20] this seems unlikely.

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