Recoil Tritium Excitation of Molecules. Direct Evidence for 1,2-HX Elimination from Ethyl Fluoride and Ethyl Chloride[1]

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Abstract: The gas-phase elimination of HX from excited ethyl chloride and ethyl fluoride has been shown to proceed by a 1,2-elimination mechanism through recoil tritium experiments with the partially deuterated molecules. The ratio of C_2HD_2T to C_2H_2DT is approximately 1.9 from CD_3CH_2X and 1.45 from CH_3CD_2X for either X = F or X = Cl, reflecting a combination of isotopic and position effects in the recoil tritium substitution reactions.

The decomposition of excited ethyl chloride to ethylene and HCl has been described as a unimolecular process in the gas phase, with an activation energy of 60.8 kcal/mole.[3-5] A similar product spectrum obtained from experiments with C_2H_5Br might also originate from reaction 1, but could be initiated by C–Br bond breakage, followed by surface-catalyzed radical reactions.[6,7] Such a chain-reaction mechanism has also been suggested as a possible complicating factor in the ethyl chloride system,[8,9] and the same possibility exists for C_2H_5I, with which reaction 1 is not observed except in the high excitation energy vacuum ultraviolet photolysis experiments.[10,11] The excited C_2H_5F formed by radical combination also eliminates HF with the formation of C_2H_4.[12]

$$C_2H_5X^* \longrightarrow C_2H_4 + HX \tag{1}$$

Two different mechanisms can account for the observed stoichiometry in the ethyl chloride system: (A) 1,2 elimination of H and X from adjacent carbon atoms, with the direct formation of ethylene; and (B) 1,1 elimination of both H and X from the same carbon atom, with the direct formation of the ethylidene radical ($CH_3CH{=}$), and its immediate isomerization to ethylene. A four-centered ring has been used as the model activated complex for this elimination reaction, corresponding to 1,2 elimination.[3-5,13] While this four-centered mechanism has been generally accepted as appropriate for reaction 1, the 1,1 elimination of HX certainly occurs from excited molecules of CH_2X_2,[14-16] and no experimental evidence has existed permitting distinction between mechanisms A and B in the corresponding reaction with ethyl halides. The possibility of complications in the mechanism has seemed even more ready for investigation after the demonstration of the predominantly 1,1 elimination of molecular hydrogen from the vacuum ultraviolet photolysis of CH_3CD_3.[17] As our experiments were being completed, the 1,1 elimination of HF from CF_2HCFH_2 and CD_3CHF_2 has been postulated to explain the experimental observations of Pritchard, *et al.*[18]

The formation of excited molecules through the substitution of energetic tritium atoms for H atoms or other substituents in a molecule has already proven to be a useful approach for the study of the decomposition reactions of excited molecules. The T-for-H substitution reaction in cyclobutane deposits an average of about 5 ev as vibrational energy in the parent molecule, enough to cause a major fraction of the resulting c-$C_4H_7T^*$ to undergo unimolecular decomposition to two molecules of ethylene.[19] Comparable amounts of energy have been shown to be deposited by the same reaction with CH_3Cl,[20] C_2H_5Cl,[21] CH_2Cl_2,[15] CH_2F_2,[16] and other molecules. Studies of the pressure dependence of the T-for-H reaction with C_2H_5Cl have confirmed that C_2H_3T is the product of unimolecular reaction of the excited $C_2H_4TCl^*$ formed in the primary hot reaction.[21] However, these experiments do not furnish any basis for distinguishing between a 1,1 and 1,2 elimination in reaction 1 (neither do they identify the primary mechanism in the pyrolysis, since the absence of a chain mechanism in the 25° "bath" molecules of the recoil experiment does not prove that the chain mechanism is also unimportant at pyrolytic temperatures).

The purpose of the present experiments has been to establish the relative amounts of this decomposition reaction proceeding through 1,1 and 1,2 elimination of HX through the use of partially deuterated ethyl halides. The experimental procedures are based upon the successful resolution of the various $C_2H_xD_{3-x}T$ molecules on a silver nitrate–ethylene glycol gas chromatographic column.[22,23]

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(1) This research was supported by AEC Contract No. AT-(11-1)-34, Agreement No. 126.

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Table I

(a) Statistical Expectations from 1,1 and 1,2 Elimination of Hydrogen Halides from Excited Ethyl Halides

Mechanism	Reacting molecule	Recoil T product	Relative yields			
			C_2H_3T	C_2H_2DT	C_2HD_2T	C_2D_3T
1,1 elimination	CH_3CD_2X	CH_2TCD_2X CH_3CDTX	25	75	0	0
$C_2H_5X \rightarrow CH_3CHCH_3CH\colon + HX$	CD_3CH_2X	CD_2TCH_2X CD_3CHTX	0	0	75	25
1,2 elimination	CH_3CD_2X	CH_2TCD_2X CH_3CDTX	0	50	50	0
$C_2H_5X \rightarrow C_2H_4 + HX$	CD_3CH_2X	CD_2TCH_2X CD_3CHTX	0	50	50	0

(b) Effects of Isotopic Impurities in Reacting Molecules upon Statistical Expectations from 1,2 Eliminations.

Mechanism	Reacting molecule	Relative yields			
		C_2H_3T	C_2H_2DT	C_2HD_2T	C_2D_3T
1,2 elimination	CH_3CHDX	63	37	0	0
	CD_2HCH_2X	17	66	17	0
	CH_3CD_2X[a]	1	51	48	0
	CD_3CH_2X[b]	0.3	50.2	49.5	0

[a] Isotopic purity, 98 D atom %. [b] Isotopic purity, 99.5 D atom %.

Experimental Section

The general experimental procedure is the standard one for recoil tritium reactions, involving the formation of energetic T atoms from the reaction $He^3(n,p)T$,[15,16,19–21] and analysis of the radioactive products by radio gas chromatography.[22–24] The neutron irradiations were carried out in the nuclear reactor of the Northrop Space Laboratories in Hawthorne, Calif., utilizing a neutron flux of 10^{12} neutrons/cm^2 sec for 40 min.

A recycling gas chromatographic system was used to extend the column length,[25] and an effective length of 480 ft was obtained from the two matched 120-ft columns of $AgNO_3$–ethylene glycol packed on HMDS-treated Chromosorb P. The four partially deuterated ethylene peaks were separated sufficiently to permit accurate analysis of the relative amounts of each, as illustrated in Figure 1 with the $C_2H_xD_{3-x}T$ molecules from recoil tritium reactions with CD_3CH_2F.

The partially deuterated molecule CH_3CD_2Cl was obtained from International Chemical and Nuclear Corp. and was stated by them to be 98 atom % deuterated. The molecules CD_3CH_2Cl, CH_3CD_2F, and CD_3CH_2F were all kindly given to us by Dr. A. P. Wolf of Brookhaven National Laboratory. The 1,1-*d*$_2$-ethyl fluoride was made from starting material with an isotopic purity of 98 atom % D, while the 2,2,2-*d*$_3$ compounds were made from 99.5 atom D % starting material. We have assumed in each case that the only major isotopic impurity in these molecules is the corresponding molecule with one less deuterium atom in the labeled position: 4% CH_3CHDX in CH_3CD_2X and 1.5% CD_2HCH_2X in CD_3CH_2X. All of the conclusions from these experiments are quite insensitive to other possible minor isotopic impurities.

The relative positions of the various $C_2H_xD_{3-x}T$ molecules were established through internal calibration with a substantial quantity of C_2H_3T.

Results and Discussion

Expected Products from 1,1 and 1,2 Eliminations of HX from Excited Ethyl Halides. The qualitative identification of the various partially deuterated ethylene-*t* molecules is quite sufficient to distinguish between the expectations from 1,1- and 1,2-elimination mechanisms, while quantitative estimates of the yields of these products furnishes additional information about the possible isotopic and positional influences on these relative yields. The qualitative expectations from the two mechanisms are summarized in Table I, as calculated from statistical effects alone, ignoring any isotopic differences in reaction and any differences arising from nonequivalent reactivity of hydrogen atoms in CH_3 and CH_2X groups.

The estimates of Table I indicate that two of the four $C_2H_xD_{3-x}T$ molecules are expected in substantial yield from each partially deuterated ethyl halide by either mechanism, while the other two are expected to be entirely absent. Furthermore, the same pair of molecules, C_2H_2DT and C_2HD_2T, is anticipated from the 1,2-elimination reaction with either parent molecule, while the 1,1-elimination reaction will produce different pairs from CH_3CD_2X and CD_3CH_2X.

Qualitative observation of the experimental results tabulated in Table II indicates that only two major peaks are found in each case, and that they are always the pair characteristic of the 1,2-elimination mechanism. The qualitative conclusion can be immediately drawn that the main mechanism of elimination of HX from excited $C_2H_5X^*$ molecules in these experiments is through the formation of HX from substituents on different carbon atoms, with the direct formation of ethylene. An estimate of the magnitude of possible minor contribution from the 1,1-elimination mechanism requires consideration of the quantitative aspects of the experiments.

Table II includes results from both ethyl fluoride and ethyl chloride as reacting molecules, with the latter tested both in the presence and absence of O_2 scavenger molecules. The quantitative data indicate that the relative yields of the various $C_2H_xD_{3-x}$ molecules vary with the location of the deuterium atoms in the original ethyl halide, but that these yields are essentially unaffected by the change from F to Cl in the halide or by the presence of a scavenger molecule in substantial concentration.

Contributions from Isotopic Impurities and from the T-for-X Reaction. Two additional contributing factors can affect interpretations of the qualitative presence of the different $C_2H_xD_{3-x}$ molecules: (a) isotopic impurities in the original partially deuterated molecules; and (b) decomposition of excited ethane-*t* formed by the energetic substitution of T for Cl or F.[21] The replacement of Cl or F by T is roughly equally probable with

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Table II. Relative Yields of Ethylene-*t* Molecules from Recoil Tritium Reactions with Ethyl Halides[a]

Parent molecule	CH_3CD_2F		CH_3CD_2Cl	CD_3CH_2F		CD_3CH_2Cl
	Gas Pressure, cm					
Parent	12.1	19.0	19.7	14.0	9.5	6.3
He^3	2.5	2.1	2.1	2.3	2.4	2.4
O_2	9.9	5.8	...	5.3	5.2	...
	Relative Yields of Ethylene-*t* Molecules					
$C_2H_xD_{1-x}T$						
C_2H_3T	0.05 ± 0.02	0.05 ± 0.02	0.07 ± 0.02	0.06 ± 0.02	0.08 ± 0.02	0.13 ± 0.02
C_2H_2DT	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)
C_2HD_2T	1.45 ± 0.05	1.47 ± 0.05	1.5 ± 0.1	1.90 ± 0.05	1.95 ± 0.05	1.78 ± 0.05
C_2D_3T	$\leq$0.03	$\leq$0.03	<0.01	0.07 ± 0.05	$\leq$0.05	0.07 ± 0.03

[a] Errors are estimated accuracy of individual experiments reflecting chiefly the resolution of the radio gas chromatography.

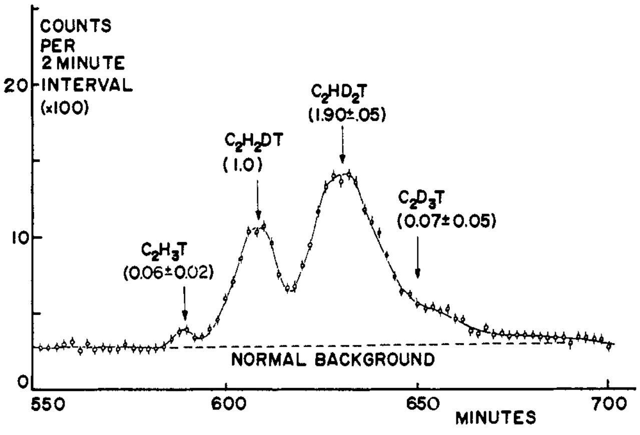

Figure 1. Relative yields of $C_2H_xD_{3-x}T$ molecules from T* + CD_3CH_2F (O_2 present).

the replacement of H, per atom of each,[21] so that the primary ethane-*t* yield should be about 0.2 ± 0.1 times the ethyl halide-*t* yield. However, we assume that the contributions from this source are relatively insignificant since the relative yield of ethylene-*t* is smaller by approximately a factor of 20 following T for H in ethane than in ethyl chloride or ethyl fluoride;[23] the ethyl-*t* halide and ethylene-*t* yields are approximately equal for the samples listed in Table II. (The substitution of T for X can, and probably does, leave a different average amount of energy on the product molecule from the substitution of T for H, but the indications are that the difference is unlikely to be large enough to make ethylene-*t* from ethane-*t* more than a 5% fraction of the total ethylene-*t* formed in ethyl halide systems.[20,21])

The chief isotopic impurity in 1,1-d_2-ethyl halides is presumed to be 1-d_1-ethyl halide, while that in the 2,2,2-d_3-ethyl halides is assumed to be 2,2-d_2-ethyl halide, in amounts corresponding to 4 and 1.5% for the quoted 98 and 99.5 atom % D in the parent molecules used for these experiments. The chief interpretative consequence of 4% CH_3CHDX in CH_3CD_2X is that a small yield of C_2H_3T (see Table II) is not necessarily evidence for a small contribution from the 1,1-elimination mechanism, but could be the consequence of reactions with the isotopic impurity, as shown in Table Ib.

A similar calculation for the 1,2 mechanism with CD_3CH_2X also leads to the expectation of a small yield of C_2H_3T; it does *not* predict any formation of C_2D_3T, which is shown in Table Ia to be a characteristic product of the 1,1-elimination mechanism with CD_3CH_2X. An estimate of the maximum contribution from the 1,1 mechanism can be made through measurement of the yield of C_2D_3T from CD_3CH_2X, but depends experimentally upon the relatively inaccurate resolution of a small peak of C_2D_3T in the tailing region of the preceding large peak of C_2HD_2T (see Figure 1). Even with still better peak resolution than now available, the measured yield of C_2D_3T could not be accurately converted into an estimate of the fractional yield of the 1,1 mechanism without precise corrections for (a) the small yield of ethylene-*t* from the decomposition of ethane-*t* and (b) consideration of the isotopic and position effects outlined below which determine the relative magnitudes of the various yields from each mechanism.

The measured yields of C_2H_3T from CH_3CD_2X are very similar to the magnitude anticipated from the isotopic impurity molecules and indicate a maximum contribution from the 1,1 mechanism to the total elimination of HX of at most 2 or 3%. Similarly, the yield of C_2D_3T from CD_3CH_2X indicates at most a very small contribution from the 1,1 mechanism, even without the correction for ethane-*t* decomposition. Consequently, we reach the general conclusion that, in our experiments, the elimination of HX from excited ethyl halides occurs in more than 97% of the decomposing molecules by a 1,2 mechanism, with no positive evidence ($\leq$3%) for any contribution at all from the 1,1 mechanism.

Factors Affecting the Quantitative Yields of the Isotopic $C_2H_xD_{3-x}T$ Molecules. The qualitative identification of C_2H_2DT and C_2HD_2T as the only prominent ethylene-*t* molecules is sufficient to demonstrate that the 1,2-elimination mechanism is the only important one operating in this system. However, the yields of these two molecules, as shown in Table II, are not equal, as suggested in Table I from statistical factors alone. A complex set of additional factors is involved in any attempt at quantitative explanation of the experimental observation that the ratio (*R*) of C_2HD_2T/C_2H_2DT substantially exceeds unity in every case. Noting that the values of *R* in Table II are (a) greater than unity, and (b) not the same for CH_3CD_2X and CD_3CH_2X, these factors can be conveniently classified into two general groups: those which tend to change *R* from unity in the same direction for both CH_3CD_2X and CD_3CH_2X, and those which tend to raise *R* for one and lower it for the other. The first three factors listed below are in the former category, and the last three affect the values of *R* from the isotopic ethyl halides in opposite directions: (1) isotopic differences in the relative yields of the T-for-H and T-for-D substitution reactions; (2) isotopic differences in the deposition of excitation energy during the substitution of T for H and T for D; (3) isotopic differences in the rates of decomposition of molecules possessing equal excitation energies; (4) isotopic rate effects in the relative amounts of the isotopic hydrogen halides eliminated from excited molecules, *i.e.*, HX *vs.* DX *vs.* TX; (5) position differences in the relative yields of T for H in CH_3 and CH_2X; and (6) position differences in the excitation energy deposited in the T-for-H reaction in CH_3 and CH_2X.

While experimental data are available about the magnitude of some of these effects, it is not available for all, and we thus have insufficient information for a precise quantitative explanation of the different values of R. The yields of the primary substitution process have been shown to favor T for H over T for D by a factor of 1.3 in several molecular systems.[23] If this value is assumed for both CH_3 and CH_2X groups, then the corresponding values of R would be 1.3 from both CH_3CD_2X and CD_3CH_2X. Similarly, the deposition of a larger amount of energy in the substitution of T for H than in T for D would increase the fraction of the former molecules which would decompose, and therefore would also tend to increase R for both molecules. No information is yet available concerning the magnitude, or even the direction, of such an isotope effect in recoil tritium systems.

The third factor presumably tends to reduce R for both molecules, since the excited molecule left after substitution of T for H contains one more D and one less H atom than its counterpart after T-for-D substitution, and the rate of decomposition of excited molecules is about 20–30% faster per H (or D) atom in the molecule.[26] However, this effect should only be significant for the relatively small fraction of excited molecules with excitation energies corresponding to lifetimes in the range of 10^{-9} sec; for the much more excited molecules which decompose almost completely, and for the less excited molecules which do not decompose appreciably for either isotopic variant, the isotopic difference in rates does not produce a significant difference in product yield. From the observed pressure dependence of yields in other systems,[19,21] we conclude that this factor averaged over the entire distribution of excitation energies would tend to reduce R for both molecules by 2 or 3% and can be neglected as an important consideration in the explanations.

The experimental values of R from CH_3CD_2X and CD_3CH_2X average about 1.7, while a combination of the effects of factors 1 and 3 can readily account for an average value of R of 1.3. If these estimates are substantially correct, then the difference between 1.3 and 1.7 would indicate greater average energy deposition following the replacement of H by T than of D by T.

The values of R for CH_3CD_2X and CD_3CH_2X of 1.45 and 1.9, respectively, require an additional contribution from factors such as 4 to 6 to account for the inequality. The difference in R values could be explained by preferential elimination of the heavier isotopic molecule, $k_{TX} > k_{DX} > k_{HX}$, by higher primary yields in CH_2X than in CH_3, and/or by greater deposition of excitation energy following substitution in CH_2X than in CH_3. If the relative rates of elimination of hydrogen halide were, for example, $k_{TX} = 1.7$, $k_{DX} = 1.4$, and $k_{HX} = 1.0$, the value of R for CH_3CD_2X would be decreased from the statistical unity to 0.54, while R for CD_3CH_2X would be increased to 1.07. No information is available about the direction or magnitude of isotope effects in the elimination of hydrogen halides from excited alkyl halides, but the average "position" effect of about 15% [$= (1.9/1.45)^{1/2}$] can obviously be explained in its entirety by relatively small isotopic differences in the direction of preferential elimination of the hydrogen halides containing the heavier isotopes of hydrogen. Experimental observation of the preferential elimination of RD over RH (R = CH_3 or CD_3) from $CH_3CH_2CD_2CD_3$ during vacuum ultraviolet photolysis[27] provides a possible precedent for the suggestion that TX may be eliminated in preference to HX or DX.[28]

Acknowledgment. We especially thank Dr. A. P. Wolf of Brookhaven National Laboratory for the gift of several partially deuterated ethyl halides synthesized in his laboratory.

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