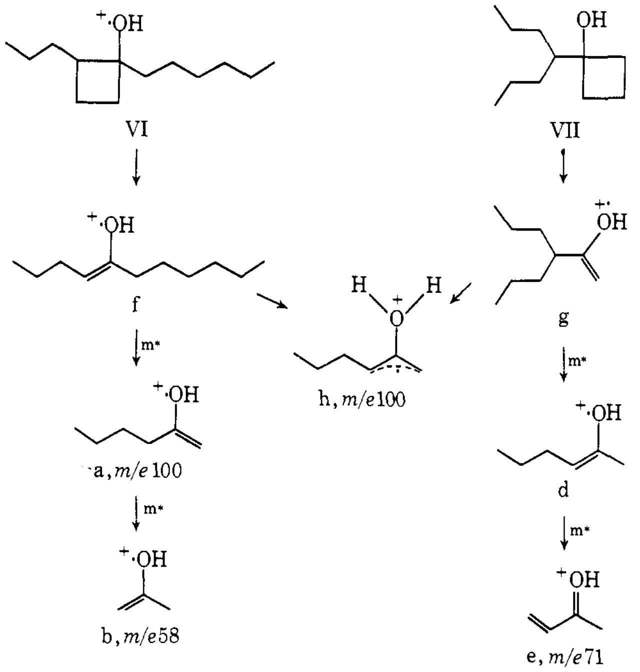
mentations occur more rapidly than interconversion of the two ions. It should therefore be possible to utilize these reactions to differentiate between the two possible mechanisms of the double McLafferty rearrangement (*cf.* Scheme I).

Elimination of ethylene from 1-hexyl-2-propylcyclobutanol (VI)[8,14] forms the enol ion f. Elimination of ethylene from 1-(4′-heptyl)cyclobutanol (VII)[8,15] generates the enol ion g. If the second step of the double McLafferty rearrangement proceeds with hydrogen transfer to the enolic oxygen, fragmentation of ions f and g generates an identical ion h, *m/e* 100. To the extent that the double McLafferty rearrangement occurs *via* this pathway, the *m/e* 100 ions should fragment identically. The alternative mechanism, hydrogen transfer to the carbon–carbon double bond, generates two isomeric *m/e* 100 ions, a and d. As has already been demonstrated, a fragments to give *m/e* 58 (eq 6), and d fragments to give *m/e* 71 (eq 8). In fact, it is the latter fragmentations which are observed. An intense peak is observed at *m/e* 71 (C_4H_7O by high resolution) in the mass spectrum of 1-(4′-heptyl)cyclobutanol, while the *m/e* 58 peak is of negligible intensity (71/58 = 8.5). Conversely, the *m/e* 58 peak predominates in the mass spectrum of 1-hexyl-2-propylcyclobutanol (71/58 = 0.7).[16] It can therefore be concluded that the predominant mechanism of the double McLafferty rearrangement among the high energy–short lived ions observed in the conventional mass spectrum involves transfer of hydrogen to the carbon–carbon double bond. The apparent invariance of mechanism among these ions, those observed in the icr spectrometer, and those fragmenting in the metastable regions lends credence to the validity of these latter techniques as probes into the behavior of ions fragmenting in the source region of the mass spectrometer. In addition, these observations demonstrate that cyclobutanols have wide utility in the study of mechanistic and structural problems relating to enolic ions.

Scheme I



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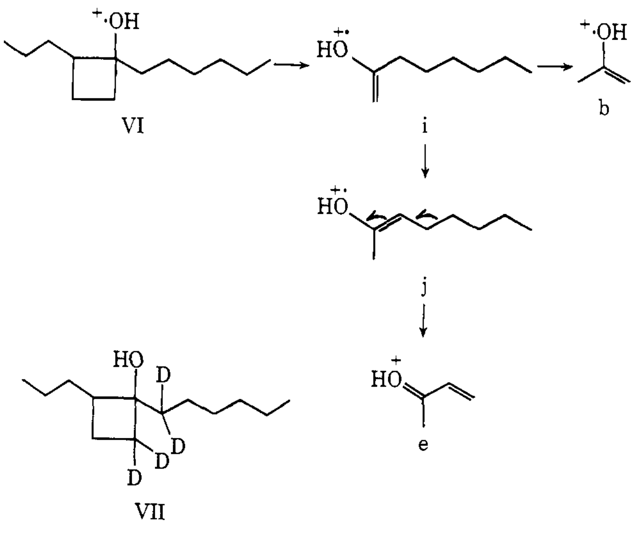
[14] Obtained by photolysis of 7-tridecanone in pentane using 2537-Å light. Two stereoisomers with nearly identical mass spectral behavior were isolated.

[15] Obtained by reaction of the Grignard reagent prepared from 4-bromoheptane and magnesium with cyclobutanone.

[16] A competing reaction sequence also produces peaks at *m/e* 58 (VI → i → b) and 71 (probably VI → i → j → e). Since it was desired



to exclude these processes from consideration, the labeled alcohol VII was prepared; the number quoted here represents the ratio of the sum o the intensities of *m/e* 71, 72, and 73 to the intensity of *m/e* 60 in the mass spectrum of this compound.

Experimental Evidence for Statistical Randomization of Hydrogen Atoms in the Ethyl Cation[1]

Sir:

Recently there has been considerable interest in the problem of hydrogen migration in the ethyl cation.[2] Theoretical calculations have led to the conclusion that the bridged structure represents the transition state (activated complex) involved in the 1,2 hydride shift.[2c,d] Although several calculations have shown the bridged structure to be nearly 10 kcal/mol less stable than the classical ion,[2c,e] some recent improved theoretical treatments[2f,g] suggest that the energy of the bridged configuration is slightly less than that of the classical ion. Assuming the latter, the energy barrier for H atom migration in $CH_3CH_2^+$ may be quite low and one would expect complete statistical

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[1] This work was supported in part by the U. S. Atomic Energy Commission.

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Table I Evidence for Statistical Scrambling Based on the H^- (D^-) Transfer Reaction: $C_2D_3H_2^+$ ($C_2D_2H_3^+$) + RH (RD) → $C_2D_3H_3$ + R^+

Precursor	Ionization	Neutral reactant,[a] RH or RD	Total pressure, Torr	Neutral product % distribution[b] CD_2HCDH_2	CD_3CH_3
CD_3CH_2I	11.6–11.8-eV photon	i-C_4H_{10}, c-C_5H_{10}	4–20	89 ± 4	11 ± 4 (a)
	^{60}Co-γ	i-C_4H_{10}, $(CH_3)_4C$	100–1000	90 ± 2	10 ± 2 (b)
CH_3CD_2I	11.6–11.8-eV photon	i-C_4D_{10}	10	91 ± 4	9 ± 4 (a)
	^{60}Co-γ	i-C_4D_{10}	300–800	90 ± 3	10 ± 3 (a)
CD_3CH_2Br	11.6–11.8-eV photon	$(CH_3)_4C$	5	92 ± 4	8 ± 4 (c)
	^{60}Co-γ	c-C_5H_{10}, $(CH_3)_4C$	300	90 ± 2	10 ± 2 (a)
$CD_3CH_2CD_3$[c]	^{60}Co-γ	$(CH_3)_4C$, c-C_4H_8	700	90 ± 6	10 ± 6 (c)

[a] The ratio RH(RD)/precursor varies from 2 to 20. [b] Maximum error limits in fractional yield determination are based on five (a), ten (b), and two (c) experiments. [c] The fractional composition of the $C_2D_3H_3$ (CD_2HCDH_2, 70%; CD_3CH_3, 30%) obtained in earlier radiolysis experiments of pure $CH_3CD_2CH_3$ [P. Ausloos and S. G. Lias, *J. Chem. Phys.*, **36**, 3163 (1962)] represents a less accurate picture of the degree of scrambling of the $C_2D_2H_3^+$ ions. It was shown in a later study (ref 6) that the HD^- transfer reaction, $C_2D_2H_2^+ + CH_3CD_2CH_3 \rightarrow C_2D_3H_3 + C_2H_5D^+$, contributes to the formation of $C_2D_3H_3$.

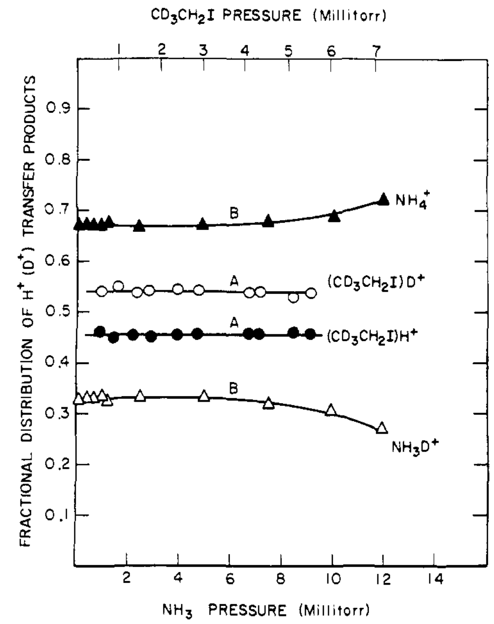

Figure 1. Isotopic distribution of H^+ (D^+) transfer products obtained in the reaction of partially labeled ethyl cations. Curves A: fractional yields of $(CD_3CH_2I)H^+$ and $(CD_3CH_2I)D^+$ obtained from the reaction of $C_2D_3H_2^+$ ions from CD_3CH_2I with CD_3CH_2I as a function of CD_3CH_2I pressure in the reaction chamber (NBS). Curves B: fractional yields of NH_4^- and NH_3D^+ obtained from the reaction of $C_2H_3D_2^+$ ions from $CH_3CD_2CH_3$ with NH_3 as a function of NH_3 pressure in the collision chamber (ARL).

scrambling in ions such as $C_2D_3H_2^+$ and $C_2D_2H_3^+$ with low internal energy content. In this communication we wish to report conclusive experimental evidence for the randomization of H and D atoms in $C_2D_3H_2^+$ and $C_2H_3D_2^+$ obtained as unimolecular decomposition products of $CD_3CH_2I^+$, $CH_3CD_2I^+$, $CD_3CH_2Br^+$, $CD_3CH_2CD_3^+$, $CH_3CD_2CH_3^+$, and $CD_3CH_2CH_2CD_3^+$, at reactant gas pressures ranging from 10^{-5} to 1000 Torr. Photon absorption (11.6–11.8 eV), electron impact, and ^{60}Co-γ radiation have been used for production of ethyl cations. Two experimental approaches, kinetic mass spectrometry and chemical end-product analysis, have been applied to this problem.

a. Mass Spectrometric Results. The proton (deuteron) transfer reactions $C_2X_5^+ + M \rightarrow C_2X_4 + MX^+$, where $C_2X_5^+$ is $C_2D_3H_2^+$ or $C_2D_2H_3^+$ from various sources and M is a suitable proton (deuteron) acceptor, have been investigated in both the NBS photoionization mass spectrometer[3a] (11.6–11.8-eV photons, thermal kinetic energies, 298°K) and the ARL tandem instrument[3b] (70-eV electrons, 298 and 425°K, kinetic energies of 0.3 ± 0.3 eV and 1.2 ± 0.3 eV). At NBS, the specific reactions investigated were of the type $C_2D_3H_2^+ + CD_3CH_2I \rightarrow (CD_3CH_2I)H^+$ or $(CD_3CH_2I)D^+$ + ethylene ($\Delta H = -15$ kcal/mol)[4] which are quantitative for ethyl cations produced *via* photoionization of CD_3CH_2I or CH_3CD_2I. Typical NBS data found for CD_3CH_2I, given as the fractional distribution of the $(CD_3CH_2I)H^+$ and $(CD_3CH_2I)D^+$ products as a function of CD_3CH_2I pressure in the reaction chamber, are given in Figure 1. In each iodide >95% of the ethyl cations have reacted at a pressure of ~5 mTorr ($k = 1.0 \pm 0.2 \times 10^{-9}$ cm^3/(mol sec)). The only other primary ion present, the parent ethyl iodide ion, reacts only to give $(C_2X_5I)_2^+$ and $(C_2X_5)_2I^+$. At ARL mass and energy selected beams of ethyl cations resulting from 70-eV electron-impact ionization of $CD_3CH_2CD_3$, $CH_3CD_2CH_3$, and $CD_3CH_2CH_2CD_3$ were separately impacted on NH_3. The specific reaction monitored, which is also quantitative for ethyl cations, was of the type $C_2D_3H_2^+ + NH_3 \rightarrow NH_4^+$ (NH_3D^+) + ethylene ($\Delta H = -47$ kcal/mol). ARL data for $C_2D_2H_3^+$ ions from $CH_3CD_2CH_3$ reacting with NH_3 are also given in Figure 1 as a function of NH_3 pressure in the collision chamber. The apparent fractional decrease in the probability for D^+ transfer at higher pressures of NH_3 is due to the exchange reaction $NH_3D^+ + NH_3 \rightarrow NH_4^+ + NH_2D$, which occurs prior to removal of NH_3D^+ from the reaction zone. The extrapolated "zero pressure" distributions for any system were found to be equivalent at 298 and 425°K and at kinetic energies of 0.3 ± 0.3 and 1.2 ± 0.3 eV. The combined results from both laboratories, given as the fractional yields of the H^+ and D^+ transfer products from the various sources of ethyl cations, are as follows: $C_2D_3H_2^+$ (CD_3CH_2I), $D^+ = 0.55$, $H^+ = 0.45$; $C_2D_3H_2^+$ ($CD_3CH_2CD_3$), $D^+ = 0.59$, $H^+ = 0.41$; $C_2D_3H_2^+$ ($CD_3CH_2CH_2CD_3$), $D^+ = 0.57$, $H^+ = 0.43$; $C_2H_3D_2^+$ (CH_3CD_2I), $D^+ = 0.28$, $H^+ = 0.72$; $C_2H_3D_2^+$ ($CH_3CD_2CH_3$), $D^+ = 0.33$,

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H^+ = 0.67. These overall distributions obviously indicate extensive randomization in the ethyl ion. This conclusion is in disagreement with that of a recent ICR study[2h] in which it was reported that D^+ transfer occurred quantitatively in the reaction of $C_2D_3H_2^+$ from $(CD_3CH_2)_2NNO$ with the parent molecule. It is probable that the interpretation of the latter experiment was complicated by the large number of potential D^+ donors, including the parent ion and fragment ions other than $C_2D_3H_2^+$.[5]

b. Isotopic Analysis of Ethane Produced in the H^- (D^-) Transfer to $C_2D_3H_2^+$ and $C_2D_2H_3^+$. The ethyl ions from various sources (first column of Table I) have been produced in the presence of the H^- and D^- donors given in column 3 of Table I. If all $C_2D_3H_2^+$ retain the structure indicated by the precursor only CD_3CH_3 will be formed in the reaction $C_2D_3H_2^+ + RH \rightarrow CD_3CH_3 + R^+$ ($k \sim 10^{-9}$ cc/(mol sec)).[6] If, however, the D and H atoms in $C_2D_3H_2^+$ are completely scrambled, 90% of the $C_2D_3H_2^+$ should react with RH to yield CD_2HCDH_2. The same holds for $C_2D_2H_3^+$ ions accepting a D^- entity from a deuterated reactant (RD). The position of the deuterium atoms was established by analysis of the ethane fraction on a high-resolution mass spectrometer using verified standard mass spectral cracking patterns for CD_3CDH_2, CD_2HCD_2H, CD_3CH_3, and CD_2HCDH_2, which were run on the same instrument. The latter were in consistent agreement with those reported by Bell and Kistiakowski.[7] A complete detailed analysis of the data as well as the interpretation of other facets relating to the photolysis and radiolysis of alkyl halides would require an inordinate amount of space and will be presented later.[8] The distributions given in the last column represent that of the ethane-d_3 product formed in the H^- (D^-) transfer reaction within the indicated error limits. All thermal free radicals were removed by O_2 or NO and a small unscavengeable contribution from "hot" ethyl radicals abstracting[9] a H (D) atom has been taken into account. In the 11.6–11.8-eV CD_3CH_2I–RH photolysis experiments the reaction $CD_3CH_2^* + RH \rightarrow CD_3CH_3 + R$ accounts for 5% of the ethane fraction under conditions ($RH/CD_3CH_2I > 5$) where over 90% of the $C_2D_3H_2^+$ ions are intercepted by RH. From the limiting value of ethane observed at high RH concentrations, it is estimated that at 11.6–11.8 eV (pressure, 5 Torr), 20% of the photons absorbed by ethyl iodide result in the formation of ethyl cations ($\Phi(C_2H_5^+) = 0.2$). In the photolysis of pure ethyl iodide the quantum yield of ethane which can be ascribed to hot ethyl radicals is 0.011, 0.009, and 0.004 at 8.4, 10, and 11.6–11.8 eV, respectively. In contrast with the 11.6–11.8-eV photolysis, no increase of Φ(ethane) is noted when RH is added to CD_3CH_2I–NO (1 : 001) mixtures at photon energies (8.4–10.0 eV) below the threshold for $C_2D_3H_2^+$ formation (appearance potential = 10.6 eV). In the radiolysis of ethyl iodide (pressure, 200–500 Torr) the *G* value of hot ethyl radicals and of ethyl cations is 0.08 and 1.2, respectively. As expected in both the photolysis and radiolysis, the ethane-d_3 produced by thermal as well as by hot CD_3CH_2 radical reactions consists exclusively of CD_3CH_3.

The proton transfer (Figure 1) and the hydride transfer (Table I) results taken together can only be accounted for by a statistical scrambling of the hydrogen atoms in the ethyl cation irrespective of its structure. Furthermore, the fact that at pressure up to 1000 Torr of reactant gas (RH or RD) the H and D atoms in the ethyl cation are statistically scrambled shows that 1,2 hydride shift occurs with a high rate constant ($k > 10^{10}$ sec^{-1}). Of particular importance is the observation that the $C_2D_3H_2^+$ formed (appearance potential = 11.4 eV) in the photoionization of CD_3CH_2Br is statistically scrambled. It follows that, in agreement with recent calculations,[2a,f,i] the energy barrier of a 1,2 hydride shift in the ethyl cation must be less than about 5 kcal/mol. This is in agreement with the observation that an energy barrier of not more than 6 kcal/mol can be attributed to the 2,3 hydride shift in 2-butyl cations formed in SbF_5–HSO_3[2j] or SO_2ClF–SbF_5.[2k]

The present results do not throw any light as to the structure of the $C_2X_5^+$ ion at the time of reaction. Also, it should be emphasized that the present study does not exclude the existence of unscrambled ethyl cations at the shorter reaction times encountered in condensed phase systems.

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Rates of Exchange of Acetic Acid Molecules at the Amide Hydrogen-Bond Acceptor Site of Aniline Bases

Sir:

Recent work has established that there is a relationship between hydrogen-bond acceptor strength and base strength only for bases of closely related structure.[1,2] Equilibrium constants for hydrogen-bond formation then increase slowly with K_B, the slope of the linear free-energy correlations being about 0.2.[1] We now wish to report some results concerning the *kinetics* of hydrogen bonding for a number of meta- and para-substituted anilines. Basicity and hydrogen bond strength should be well correlated in this series.

Using methods described previously,[3–5] we have obtained rate constants (k_H) for the exchange of acetic acid molecules at the $-NH_2$: hydrogen-bond acceptor

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