

If the racemization of IV involves pyramidal inversion, then there should be no significant difference in the value of ($k_a - k_i$) for compounds IV and V since electron-withdrawing groups have been shown to have no significant effect upon pyramidal inversion rates. The solvolysis of IV should be $\sim 10^3$ times faster than the solvolysis of V. In contrast, if eq 2 best describes the principal pathway for both solvolysis and racemization of IV, then both reactions by this pathway should be very much slower for V than IV. However, V should undergo pyramidal inversion at a rate comparable to the rates of inversion of I and II. The racemization of IV would be ~ 15 times faster than the racemization of V, and pyramidal inversion would represent the principal pathway for racemization of V. The latter type of behavior is observed experimentally. The rate constant for loss of optical activity, k_a , for V at 50° in solvent methanol is $7.0 \times 10^{-6} \text{ sec}^{-1}$. This is very close to the k_a values of $6.5 \times 10^{-6} \text{ sec}^{-1}$ and $6.65 \times 10^{-6} \text{ sec}^{-1}$ for I and II, respectively, under the same conditions. At 90° the rate constant for methanolysis of V is $1.6 \times 10^{-5} \text{ sec}^{-1}$, comparable to the value of $2.45 \times 10^{-5} \text{ sec}^{-1}$ for methanolysis of I at 90° obtained by extrapolation from data at lower temperatures.

We conclude that the principal pathway⁸ for racemization of IV involves the sequence shown in eq 2. If dissociation to a free cation and ethyl methyl sulfide occurred prior to recombination, then a decrease in the rate of solvolysis of IV should be observed on the addition of ethyl methyl sulfide. At 50° , 0.05 M ethyl methyl sulfide has no effect on the rate constant for solvolysis. This observation requires the assignment of an ion-neutral molecule pair structure to the intermediate.

If this interpretation is correct, the racemization of IV represents the first example of the formation of an ion-neutral molecule pair and its return to covalent starting material in which the leaving group is not the same in structure as the solvent.⁹ The formation and recombination of the ion-neutral molecule pair can be viewed as a reaction of the species within a solvent cage.¹⁰

The racemization of IV represents an example of the detection of bond heterolysis and return by racemization of an optically active leaving group. This process was first formally demonstrated^{2,11} in the diastereoisomer interconversion which accompanies solvolysis of α -phenyl- and α -(*p*-methoxyphenyl)ethyl 2,6-dimethylbenzenesulfonates. Another example of this process has been reported by Fava and coworkers¹² in the racemization and rearrangement of optically active benzhydryl *p*-toluenesulfonate.

The racemization of optically active sulfonium and other "onium" salts should be a useful procedure for detecting bond heterolysis and return whenever this reaction is faster than all other processes which can

result in racemization. For the sulfonium salts the formation of racemic starting material will require a simple rotation of the sulfide molecule relative to the carbonium ion within the solvent cage. The degree of rotation will depend on the detailed hybridization of the sulfide. The rotation will not require any further separation of the caged groups and should be energetically very facile. In this case k_1 would be a measure of the rate constant for carbon-sulfur bond heterolysis.

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Ionic Chain Reactions in the Radiation-Sensitized Pyrolysis of Ethanol Vapor

Sir:

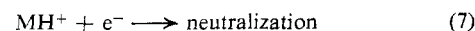
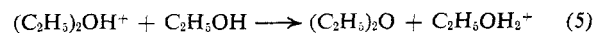
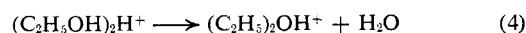
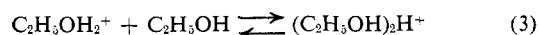
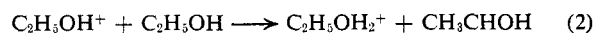
Two new types of ionic chain reaction have been found. They occur during the radiation-sensitized pyrolysis of ethanol vapor at 350° . One chain results in the conversion of ethanol to diethyl ether and water, while the other forms methanol and acetaldehyde from formaldehyde and ethanol.

The samples were irradiated with ^{60}Co γ rays to a dose of $1.3 \times 10^{20} \text{ eV/g}$.



The G values of diethyl ether at t° in ethanol irradiated at a density of 0.66 g/l. are 1.1 (320°), 5.6 (350°), and 15.9 (375°). Water was also formed but its yield was not measured accurately. The yield of ether was unaffected by the presence of propylene (a free radical scavenger) or sulfur hexafluoride (an electron scavenger) but was decreased to $G = 0.3$ at 350° by the presence of 15 mole % of ammonia (a positive ion scavenger).

The proposed mechanism for ether formation is as follows



where MH^+ is any ion.

Charged molecular clusters, such as $(\text{C}_2\text{H}_5\text{OH})_n\text{H}^+$, have been observed in several polar gases by mass spectrometry¹⁻⁴ and by ion cyclotron resonance spectrometry.⁵ Reaction 4 and the equivalent reaction in metha-

(8) Racemization also occurs by pyramidal inversion and by nucleophilic displacement on carbon (eq 1). If the assumption is made that IV undergoes pyramidal inversion with a rate constant identical with that for the inversion of V, then $k_1 = 2.96 \times 10^{-4} \text{ sec}^{-1}$ at 50° over the first 50% reaction; $\sim 46\%$ of the intermediate returns to racemic sulfonium salt.

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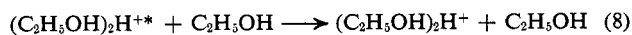
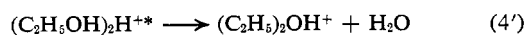
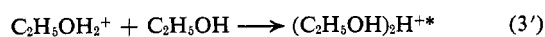
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nol have also been observed to occur at low gas pressures (10^{-6} – 10^{-1} torr).³⁻⁵ It was suggested that reaction 4 involved excited ions and was in competition with collisional stabilization of the protonated dimer.^{3,5}

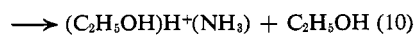


In the present system the pressures are sufficiently high (10^2 – 10^3 torr) that essentially all of the initially formed dimers would be thermally equilibrated with the medium. Reaction 4 therefore represents the normal pyrolysis of the ionic species.

It may be shown by steady-state kinetics treatment that if the dimer $(\text{C}_2\text{H}_5\text{OH})_2\text{H}^+$ were the main identity of MH^+ in the neutralization reaction 7, then ether formation should be 0.5 order. On the other hand, if the trimer were the main identity of MH^+ in reaction 7, ether formation should be -0.5 order. Experimentally, at 350° the order of the ether formation reaction was 0.7 at 100 torr and -0.5 at 1000 torr. This means that the average "solvation number" of the protons shifted from about two to three as the ethanol pressure increased from 100 to 1000 torr.

The activation energy of ether formation in the low-pressure region corresponds to $(E_4 - \frac{1}{2}E_7)$, and in the high-pressure region it corresponds to $(E_4 - \Delta H_6 - \frac{1}{2}E_7)$. The value of E_7 may be assumed to be zero. That of ΔH_6 is unknown, but as an approximation it may be taken as equal to that of the analogous reaction in water vapor, which is -22 kcal/mole.⁶ This estimate is based upon information about the clustering of methanol and water molecules about protons in the gas phase.⁷ Thus, $E_4 \leq E_4(\text{ether}) \leq E_4 + 22$ kcal/mole. At an ethanol concentration of 0.66 g/l. (570 torr at 350° , which is intermediate between the high- and low-pressure regions), the activation energy of the ether formation is 30 kcal/mole. Thus, $30 > E_4 > 8$ kcal/mole. However, reaction 4 is about 19 kcal/mole endothermic, so one may conclude that $30 > E_4 > 19$ kcal/mole.

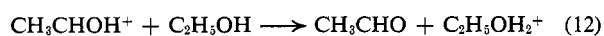
Ammonia inhibits ether formation, probably through reactions such as



The proton affinity of ammonia (209 ± 7 kcal/mole⁸) is greater than that of ethanol (193 ± 8 kcal/mole⁹).

$\text{H}_2\text{CO} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{OH} + \text{CH}_3\text{CHO}$

During the radiolysis of ethanol vapor (0.66 g/l., 375°), methanol was formed with a G value of 50. Mechanistic considerations indicated that the important reactions were (11) and (12). One or more ethanol molecules



might be clustered about the positive ions in reactions 11 and 12, but they should have little effect on the ener-

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getics of the reactions because the "solvation" energy of $\text{C}_2\text{H}_5\text{OH}_2^+$ should be approximately equal to that of CH_3CHOH^+ .

Support for the proposed reactions 11 and 12 was obtained by irradiating a sample that contained 5 mole % of formaldehyde. The increases in the G values of methanol and acetaldehyde were 563 and 521, respectively, and corresponded to the conversion of 70% of the formaldehyde in the sample. The somewhat smaller increase in the acetaldehyde yield was interpreted in terms of secondary decomposition of that compound.

Reaction 11 is analogous to the reaction of alkane ions with olefins.¹⁰

The study of these ionic chain reactions is continuing.

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Lysozyme Catalysis. Evidence for a Carbonium Ion Intermediate and Participation of Glutamic Acid 35¹

Sir:

A mechanism of action of lysozyme has been put forward by Phillips, *et al.*^{2a} A central part of this proposal is formation of a glycosyl carbonium ion in a reaction in which glutamic acid 35 participates as an acid catalyst and aspartic acid 52 stabilizes the developing ion. Since studies of model systems^{2b} have demonstrated that glycoside cleavage can be either general or specific acid catalyzed and proceed through either a covalent or a carbonium ion intermediate, it is particularly necessary to examine the chemistry of the enzymic reaction. The following data suggest that lysozyme catalysis does involve general acid catalyzed formation of a carbonium ion.

Since lysozyme catalyzes glycosyl transfer³⁻⁵ as well as glycoside hydrolysis, there must be an intermediate that can partition between reaction with water (hydrolysis) and some other acceptor (transfer). A change in transfer rate that results from a change in acceptor chemistry should reflect the nature of the glycosyl enzyme and its path of reaction. There should be less difficulty understanding data of this kind than that derived from studies of the over-all process, in which nonproductive binding of substrate causes severe kinetic complications.³

In a typical transfer experiment, tri-NAG⁶ was hydrolyzed by lysozyme in the presence of a small amount of radioactive acceptor (of specific activity sufficient to compete with the solvent, yet not perturb the system, *i.e.*, an acceptor concentration of less than 5%). The

(1) This work was supported by Research Grant GB-6446 from the National Science Foundation.

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(6) Abbreviations: NAG, N-acetylglucosamine; tri-NAG, β -(1,4)-linked trisaccharide of NAG.