Ultraviolet Photoelectron Studies of Dehydration and Dehydrohalogenation Reactions of β-Substituted Alcohols Using H–ZSM-5 and the Formation of Unstable Intermediates

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Dehydration of 1,2-ethanediol and 2-aminoethanol and dehydrohalogenation of 2-chloro- and 2-fluoroethanol over H–ZSM-5 at 200–350 °C was followed under low-pressure (*ca.* 25 mTorr) flow conditions using ultraviolet photoelectron spectroscopy as a direct on-line monitor. This circumvents the necessity of separations since the effluent from the reactor can be monitored immediately after leaving the catalyst bed. Under these conditions all precursors are consumed, leading to the final product acetaldehyde, except in the case of 2-aminoethanol where dehydration gives, in high yield, the unexpected *N*-methyl isomer of methylenimine, an unstable molecule. A postulated mechanism for this result, applicable also to the formation of acetaldehyde in the other β-substituted alcohols, suggests the intermediacy of three-membered cyclic species, namely, ethylenimine and ethylene oxide or their protonated analogs.

Introduction

Zeolites are some of the most important catalysts in the petroleum industry. These porous compounds, crystals of aluminosilicates,[1] are involved in various conversion reactions such as cracking, isomerization, and shape-selective synthesis.[2–7] Even though many of these processes are being used on an industrial scale, the mechanisms of these reactions are not well understood; *e.g.*, conversion of methanol to hydrocarbons (methanol-to-gasoline, MTG) is the subject of intense discussion,[3,8–17] with reaction mechanisms revolving around the involvement of carbenes, oxonium ions, surface-bonded methylide species, free CO, or even free radicals. ZSM-5, a highly siliceous zeolite of intermediate pore size, is of especial interest in this regard because of its high acidity and shape selectivity. Most attention has revolved around the precise details of the conversions, *e.g.*, the formation of the first C–C bond, and the relative merits of Brønsted[18–21] and Lewis acid sites,[22,23] since the proton form of ZSM-5 contains both such sites, the number of which depends on the activation conditions. In addition, the Si/Al ratio and the effect of poisoning of the catalyst are clearly of relevance.[24–26]

Usually studies of the gas-phase products of catalytic reactions are accomplished by means of gas chromatography (GC),[3,24,25] often in combination with mass spectrometry (GC/MS),[8,16] or by FTIR,[23,27] where the final gaseous products of the reactions are identified and quantitated. However, it is also possible to use a direct on-line technique such as ultraviolet photoelectron spectroscopy (UPS) to study the gas-phase products immediately after they exit the catalyst bed. Using this technique, which involves the kinetic energy analysis of photoejected electrons from gas-phase molecules, it is often feasible to study short-lived species which are produced during these gas–solid interactions[28] and which would otherwise react or decompose if they had to traverse a GC column. The presence of unstable species and radicals in the gas phase above a catalyst has recently been demonstrated,[29,30] and in one instance transient radicals have been observed by UPS.[31]

Dehydration reactions of aliphatic alcohols containing two or more carbons usually involve a β elimination process[32,33] and are especially interesting because of the potential formation of higher hydrocarbons. However, addition of substituents such as OH, NH_2, F, or Cl in the C_2 position could modify this process and affect the product distribution. In this study we investigate these circumstances by focusing on reactions of the β-substituted alcohols, 1,2-ethanediol (ethylene glycol), and its isoelectronic analogs, 2-aminoethanol and 2-fluoroethanol (ethylene fluorohydrin), along with 2-chloroethanol (ethylene chlorohydrin), over H–ZSM-5. Of particular interest is the ability of UPS to detect the presence of reactive intermediates.

Experimental Section

All chemicals used in these experiments were purchased from Aldrich. Photoelectron spectra of the starting materials[34,35] and the final products[34,36] were compared with the known literature data. The proton form of ZSM-5 was synthesized hydrothermally by adaption of a literature method.[37] This involved the admixture of 19 g of commercial 30% silica in sodium hydroxide and 17 g of tetrapropylammonium bromide. A 0.27-g sample of sodium aluminate provided the aluminum source. The pH of the solution was adjusted to 8.5 using NaOH, and the mixture was heated inside a stainless steel reaction vessel for 7 days at 160 °C. The filtered and washed product was calcined at 500 °C overnight to remove the organic template. The hydrogen form of ZSM-5 was obtained by refluxing with NH_4Cl, and this was then calcined at 500 °C overnight to produce H–ZSM-5. This synthetic route is identical to that used to prepare a highly siliceous H–ZSM-5 (Si/Al *ca.* 40) with high crystallinity (*ca.* 5 μm) for successful analysis by a combination of XRD[38,39] and ultrahigh-resolution MAS NMR.[39–41] The particular sample synthesized herein was characterized by these techniques with identical XRD and MAS NMR.

The experimental setup is shown in Figure 1. The H–ZSM-5 powder (typical loading 1 g) was loosely distributed among Pyrex glass wool inside the Pyrex reaction tube of the microreactor (20-cm × 8-mm i.d.). This was mounted directly to the inlet of a fast pumping photoelectron spectrometer and surrounded by a small tube furnace. Prior to each run, the catalyst was heated at 375 °C under vacuum (10^{-6} Torr) for 5 h to remove water and other adsorbed species. The amount of gaseous feed was controlled by the inlet valves and the pumping speed across the ionization chamber; typical pressures in the reaction zone were 10–50 mTorr.

It should be noted that the focus of this work is not in quantitating the yields of products, although this can be done with knowledge of the photoionization cross sections and analyzer transmission function, but in demonstrating the viability of the photoelectron technique for monitoring directly the effluent coming off the catalyst. The distance between the catalyst and the photoionization point was 15 cm; with the pumping speed

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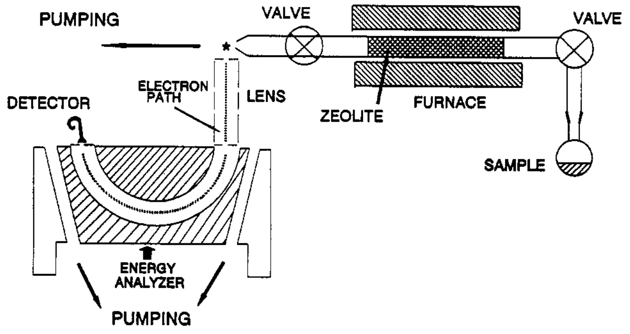


Figure 1. Schematic of the photoelectron apparatus used for following the reactions of β-substituted alcohols over H-ZSM-5. The asterisk represents the photoionization point. The photoelectron part of the apparatus is maintained under high vacuum (not shown).

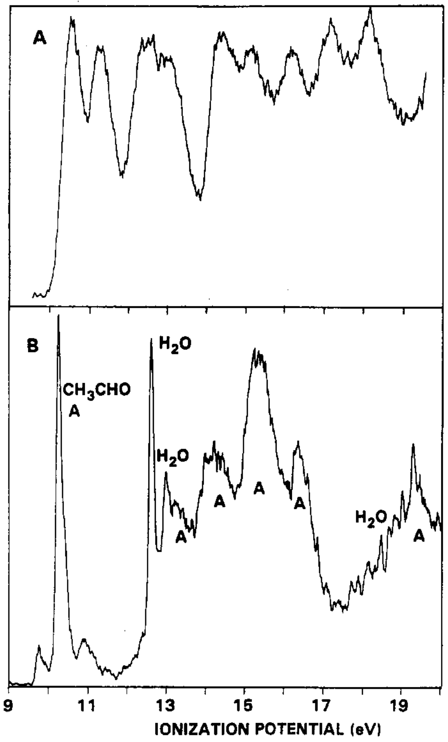


Figure 2. (A) He I photoelectron spectrum of ethylene glycol, $HOCH_2CH_2OH$. (B) He I photoelectron spectrum of the reaction products of $HOCH_2CH_2OH$ passed over H-ZSM-5 at 350 °C. The principal products are CH_3CHO (labeled A) and H_2O. The weak peaks at 9.7 and 10.9 eV are possibly small amounts of vinyl alcohol and an unknown species, respectively.

used (1600 L/s), we estimate that species with lifetimes as short as 50 μs can be observed.

The He I (58.4 nm, 21.22 eV) fast pumping photoelectron spectrometer used in these experiments is based on a 180° hemispherical energy analyzer,[42] with control and data acquisition *via* a PC/XT, thus permitting mathematical manipulation of collected spectra. This is particularly useful when mixtures are obtained, giving the capability for subtracting out the spectra of simple known molecules. Spectra are calibrated with the known IPs of MeI, CO, HCl, and H_2O. Resolution was 50 meV during the experiments.

Results

Figures 2–5 are representative spectra of the starting materials and the final products. Dehydration of ethylene glycol over H-ZSM-5 at 350 °C produced acetaldehyde as the dominant product (Figure 2). Dehydration of 2-aminoethanol produced *N*-methylmethylenimine as the major, and unexpected, product at 350 °C (Figure 3). The UPS of this unstable molecule has been previously obtained from direct thermolysis of the ring trimer.[36] Figures 4 and 5 show that the Cl- and F-halogenated ethanols do not undergo a straightforward dehydration reaction, but instead dehydrohalogenation takes place at 250 °C leading to the formation of acetaldehyde and HCl and HF, respectively. In the case of FCH_2CH_2OH the dehydrohalogenation reaction is not so clean, with H_2O (12.62 eV), HF (16.05 eV), and SiF_4 (strongest band at 17.5 eV) all being seen in varying amounts depending on the pumping speed. The SiF_4 presumably arises from the reaction of HF with the Si component of the catalyst.

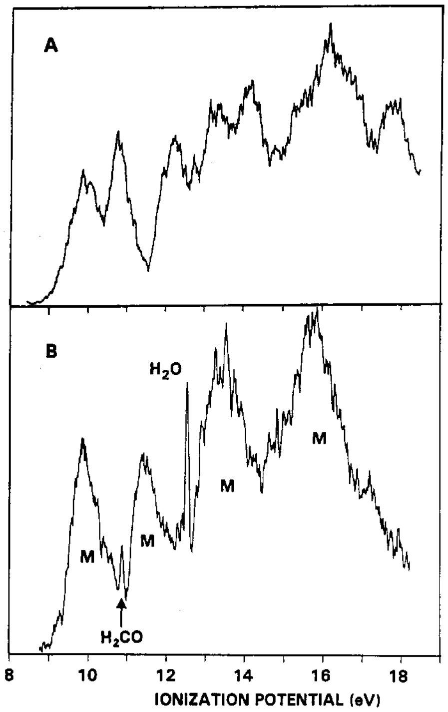


Figure 3. (A) He I photoelectron spectrum of 2-aminoethanol, $H_2NCH_2CH_2OH$. (B) He I photoelectron spectrum of the reaction products of $H_2NCH_2CH_2OH$ passed over H-ZSM-5 at 350 °C. The principal products are *N*-methylmethylenimine, $CH_3N{=}CH_2$ (labeled M) and H_2O. A trace of H_2CO is noted.

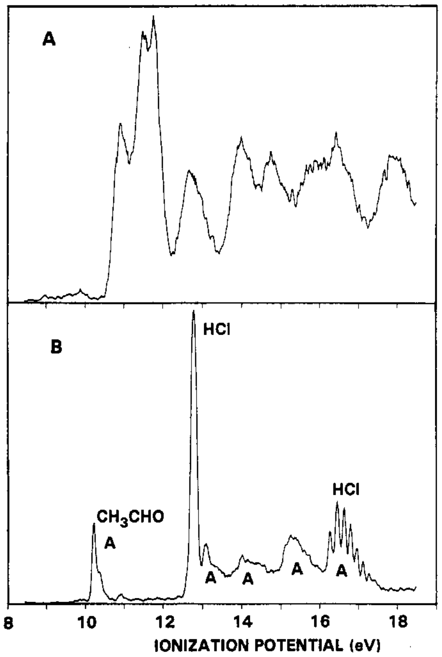


Figure 4. (A) He I photoelectron spectrum of 2-chloroethanol, $ClCH_2CH_2OH$. (B) He I photoelectron spectrum of the reaction products of $ClCH_2CH_2OH$ passed over H-ZSM-5 at 250 °C. The principal products are CH_3CHO (labeled A) and HCl.

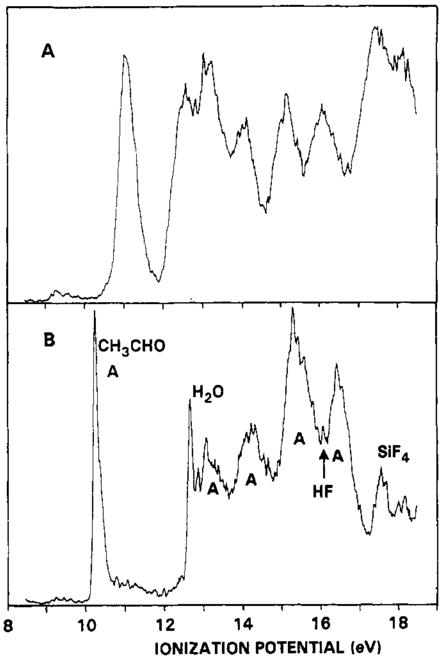


Figure 5. (A) He I photoelectron spectrum of 2-fluoroethanol, FCH_2CH_2OH. (B) He I photoelectron spectrum of the reaction products of FCH_2CH_2OH passed over H-ZSM-5 at 250 °C. The principal products are CH_3CHO (labeled A) and H_2O with traces of SiF_4 and HF, the relative yields depending upon pumping speed (see text).

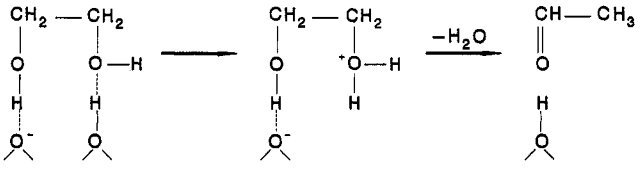
TABLE 1: Expected and Observed Products from Dehydration Reactions of β-Substituted Alcohols

	expected product	observed product
CH_2OH CH_2OH $\xrightarrow[-H_2O]{}$	$[CH_2{=}CHOH]$	CH_3CHO
CH_2OH CH_2NH_2 $\xrightarrow[-H_2O]{}$	$[CH_2{=}CHNH_2]$	$CH_3N{=}CH_2$
CH_2OH CH_2Cl $\xrightarrow[-H_2O]{}$	$[CH_2{=}CHCl]$	$CH_3CHO + HCl$
CH_2OH CH_2F $\xrightarrow[-H_2O]{}$	$[CH_2{=}CHF]$	$CH_3CHO + HF$

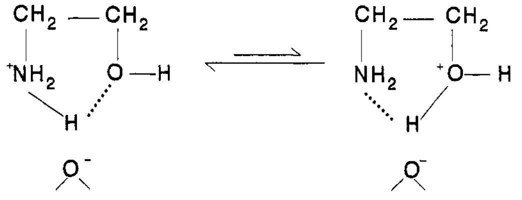
The temperature required for this dehydrohalogenation was some 100 °C lower than that required for dehydration of the diol and amino alcohol. The remarkable aspect of all of these processes is that they lead to essentially a single product, other than H_2O in the gas phase.

Discussion

SCHEME 1



SCHEME 2



SCHEME 3

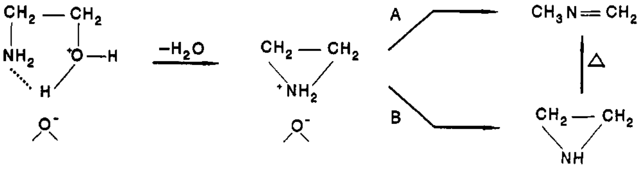


Table 1 shows the products expected from straightforward dehydration reactions, together with the actual observed dehydration and dehalogenation products. Previous work on the dehydration products of ethylene glycol over modernite and other catalysts at intermediate pressures (1 atm) and moderate temperatures (>370 °C)[43–45] concurs with our reactions over H-ZSM-5 at low pressures (*ca.* 25 mTorr) and 350 °C. Acetaldehyde is produced as the major product, although upon careful inspection a weak peak at 9.7 eV may be attributable to the intermediate vinyl alcohol.[46,47] This species has been observed as the noncatalyzed product of ethylene glycol dehydration at 1000 °C, this route having been used to obtain the microwave spectrum.[48] It should be noted that vinyl alcohol ketonizes to acetaldehyde, a process catalyzed by water.[49] We have no evidence for the formation of 1,4-dioxane, a product observed in *inter*molecular dehydration reactions of ethylene glycol.[45] Mechanisms previously proposed for formation of acetaldehyde[43] include a unimolecular scheme involving a dual site (Scheme 1), where both equivalent OH groups attach to the surface, either through a hydrogen atom to a lattice oxygen anion or through hydrogen bonding to a surface hydroxyl group. Even though such a protonation at a Brønsted site and subsequent H_2O elimination could explain dehydration of ethylene glycol, it fails to provide a satisfactory explanation for the reaction of 2-aminoethanol over H-ZSM-5. An analogous dehydration of $H_2NCH_2CH_2OH$ involving a dual-site mechanism would lead to *C*-methylmethylenimine, $HN{=}CHCH_3$. A process involving the intermediacy of the transient vinylamine molecule, $H_2NCH{=}CH_2$ (Table 1), not observed experimentally, would also involve rearrangement to the *C*-methylmethylenimine. The observed final product is, however, *N*-methylmethylenimine, $CH_3N{=}CH_2$.

2-Aminoethanol in the gas phase is a hydrogen-bonded species, and protonation may best be viewed as a single-site process, involving a cyclic intramolecular complex (Scheme 2).

From the proton affinities of nitrogen and oxygen the left-hand side of Scheme 2 should predominate. Such intermolecular species have a precedence in mass spectroscopic studies[50,51] where the final result can be either deamination or dehydration, the latter being thermodynamically favored. The unexpected generation of *N*-methylmethylenimine suggests the formation of a cyclic imine, ethylenimine (aziridene), or its protonated form (Scheme 3). Whether the protonated intermediate can lead to a ring opening (path A) or whether the nascent ethylenimine itself is thermolyzed (path B) is a matter of conjecture. What is known is that catalytic dehydration of $H_2NCH_2CH_2OH$ is particularly suitable for the commercial production of ethylenimine,[52] and in the laboratory such a cyclodehydration using diethoxytriphenylphosphorane leads to a 91% yield of ethylenimine.[53] Ring opening of ethylenimine is acid catalyzed, although it is also to be noted that the direct gas-phase pyrolysis products of ethylenimine[54] have identified *N*-methylmethylenimine as the major product (>80%) and *C*-methylmethylenimine as the minor product (<20%).

This notion of cyclic intermediates is possibly also germane to the halohydrins, which both give CH_3CHO and HX (X = Cl, F) as products. Dehydrochlorination reactions of 2-chloroethanol in solution are known to produce ethylene oxide, this being one of the oldest synthetic routes to this important chemical.[55] As it turns out, reactions involving the three-membered ring compound ethylene oxide over acid catalysts have been studied extensively,[7,56,57] with isomerization of ethylene oxide to acetaldehyde occurring at 200–300 °C following breakage of a C–O bond. Such an intermediacy of ethylene oxide or its protonated form in the present reactions would therefore account for the production of acetaldehyde, the major product in both dehydrohalogenation reactions. It is feasible that these intermediates are also involved in the ethylene glycol dehydration.

It is important to notice that any intermediates must be formed, to a certain extent, inside the zeolite cavities and may not leave unreacted. Thus, although vinyl alcohol has a lifetime measured in minutes at low pressure,[48] it was not observed in any great yield and vinylamine was not seen at all. This is in contrast to reactions on nonporous catalysts where gaseous, and very short-lived, intermediates can be observed.[29–31] We do however have in this case clear formation of the *N*-methyl isomer of methylenimine, itself an unstable molecule.

Conclusions

The zeolite-catalyzed reactions involved in this work point to the usefulness of a real-time technique like UPS for detecting the species directly exiting the catalysis bed. It is unlikely, for example, that *N*-methylmethylenimine would survive a GC column. In the situations described herein, it has been inferred from the product distributions that the thermolysis of β-substituted alcohols over H–ZSM-5 possibly proceeds *via* three-membered ring intermediates bound to sites in the zeolite. This conjecture, which involves known chemistry of ethylenimine and ethylene oxide, is consistent with the known products arising from thermolysis of such ring species. Clarification of this mechanism would be helped by *in-situ* studies of the species in the zeolite, *e.g.*, by FTIR[58] or NMR,[59] combined with the use of deuterium labeling. Further work would also involve the use of a nonporous catalyst, where intermediates may be encouraged to leave the catalyst surface and be more readily detected in the gas phase.

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