

# Ionization of Some Aliphatic Alcohol Molecules with Kinetic Energy on Various Surfaces

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This paper describes an experimental study on the influence of kinetic energy of fast aliphatic alcohol molecules on surface ionization (SI), using various refractory metal (Re, Pt, Ir) surfaces. Mass spectrometric measurements were done for various incident kinetic energies, surface materials, and surface temperatures. The SI mass spectra were interpreted in a purely empirical way by means of evidence from previous investigations and then compared to conventional EI techniques. Ionization efficiency ( $\beta$ ) was also studied. We conclude that under hyperthermal surface ionization (HSI) conditions that (a) these alcohol compounds with kinetic energy are efficiently surface-ionized, confirming the HSI mechanism, (b) in general, soft ionization can be obtained where the strong molecular ion  $(M-H)^+$  and a few fragments are generated, (c) the ionization efficiency and mass spectral pattern depend on both surface temperature and the surface material in a complex way, and (d) in the case of *n*-pentanol,  $\beta$  reaches the level of  $10^{-4}$  under the most favorable conditions.

## Introduction

In previous papers,<sup>1</sup> we reported on mass spectrometric studies of the mechanism of hyperthermal surface ionization (HSI). The sample molecules were benzene and toluene. The results confirm that (i) an effect of incident kinetic energy ( $E_k$ ) on surface ionization was deduced, (ii) the mechanism involves conversion of  $E_k$  to chemical reactions and ionization by a collision with a surface, and (iii) the kinetic energies are partially used for surface ionization (SI).

The results of experiments with other molecules may elucidate the mechanism by which dissociative surface ionization occurs. A particularly interesting question is related to phenomenon accompanying the charge-transfer process between an external molecule and a surface if a dissociation reaction on the surface is involved. Aliphatic alcohols are of particular interest with respect to dissociative surface ionization. Little work of this kind work has as yet been done on them, though the dissociative surface ionization denoted as chemically induced hyperthermal surface ionization was studied extensively by Danon and Amirav.<sup>2</sup>

The first SI experiments on these compounds were the studies Fujii et al. made upon thermal energy impact on a ReO solid.<sup>3</sup> Six saturated aliphatic alcohols (methyl, ethyl, propyl, *n*-butyl, *sec*-butyl, and *tert*-butyl alcohols) were studied. These compounds gave no response except for *tert*-butyl alcohol, which forms  $(M-OH)^+$  ions. The measured signals are explained primarily by thermal surface ionization and reflect the fact that tertiary carbons require the smallest amount of energy to be ionized. To the best of our knowledge, no work has as yet been done under conditions in which the alkyl alcohol molecular beams impact a surface with high kinetic energy.

In this study we have investigated some aliphatic alcohols under HSI conditions. In particular, emphasis has been placed on the roles surface materials and temperature played in the dissociation process. The objectives of this study were (i) to identify and interpret the major ions from some aliphatic

alcohols in comparison with conventional EI spectra, (ii) to derive relationships between kinetic energy ( $E_k$ ) and ionic intensity with reference to the principal HSI behavior of benzene and toluene observed previously,<sup>1</sup> and (iii) to demonstrate that surface materials and temperature also affect the magnitude of ionization efficiency.

## Experimental Section

**Instrumentation.** The experimental setup has been reported in detail elsewhere.<sup>1</sup> Briefly, it basically consists of a large main chamber with a supersonic nozzle, a surface and a quadrupole mass spectrometer (QMS) with a sampling interface connected to the diffusion cell.

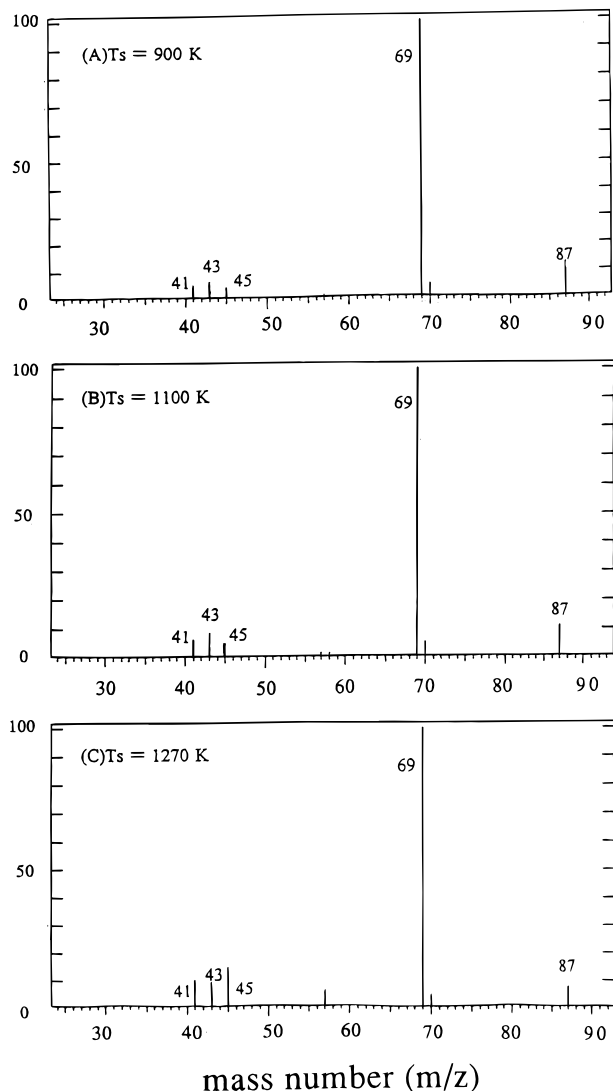
The seeded supersonic free jet can provide neutral molecules over a wide range of kinetic energies on the order of 10 eV. The emitter surface, which is exposed to the supersonic beam of sample molecules, has a face at an angle  $45^\circ$  to the vertical. The surface can be heated electrically, and studies were performed with the ReO-, Pt-, and Ir-foil surface at given temperatures. A quadrupole mass filter (QMS, Anelva Q200) placed normal to the beam axis serves as a detector of ions emitted from the sloped face when it is exposed to the beam. All the ion currents reported in this paper are output from a microchannel plate multiplier with the gain set at 400.

**Samples.** The diffusion cell<sup>4</sup> with a pressure gauge (TC-10, Nagano Keiki, Japan) was in line from the nozzle to a He carrier gas cylinder. The sample molecule to be accelerated was placed in the cell, which was held in a temperature bath. The sample amount was controlled by adjusting the cell temperature to produce an appropriate pressure. Vapor from the sample was swept along through the nozzle and into the vacuum chamber by a stream of carrier gas. All chemicals were purchased from Tokyo Kasei Co., Tokyo and used without further purification.

**Operational Procedure.** To use the available translational energies ( $E_k$ ) to study gas/surface collisions, the free jet is intercepted in an effectively collisionless region. The  $E_k$  could be controlled by varying the nozzle temperature,  $T_n$ . The other experimental variables were the temperature of surface ( $T_s$ ) and the surface material, in addition to  $E_k$ .

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**Figure 1.** Hyperthermal surface ionization mass spectra of *n*-pentanol at surface temperatures,  $T_s$ , 900, 1100, and 1270 K.

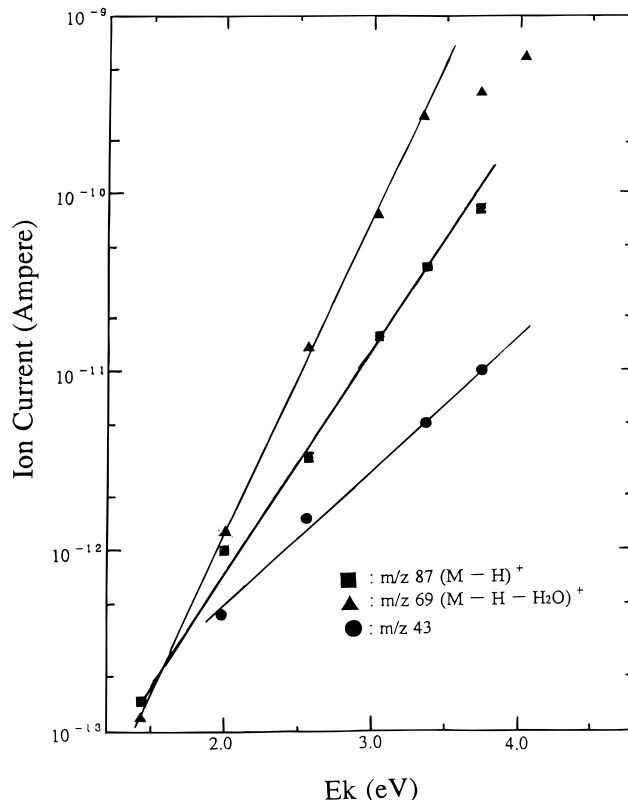
Other instrumental parameters and typical operating conditions were the following:<sup>5</sup> kinetic energy ( $E_k$ ), 0.5–6.8 eV; mass flow rate ( $\nu$ ), 10–100 mL/min; mach disk distance ( $X_m$ ), 50–200 mm; distance between nozzle and skimmer ( $D$ ), 10 mm; nozzle temperature ( $T_n$ )  $\leq$  1000 K; nozzle diameter ( $d$ ), 80  $\mu$ m; stagnation pressure ( $P_o$ ), 1–2 atm; background pressure ( $P_b$ ),  $1.0 \times 10^{-4}$  to  $2 \times 10^{-5}$  Torr.

Blank experiments were performed with all the surfaces by removing the nozzle and fixing a stainless steel pipe. Ionization in these blank experiments could barely be detected for any surface.

## Results and Discussion

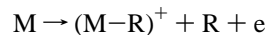
**1. *n*-Pentanol. Mass Spectrum.** When the nozzle was heated to 610  $^{\circ}$ C, the incident energy was calculated to be 3.4 eV. The mass spectral patterns obtained from *n*-pentanol scattered on the ReO surface vary with  $T_s$  (Figure 1).

From these results for *n*-pentanol, we concluded that (i) electron transfer occurs, proving that the kinetic energy contributes to ionization, (ii) the parent ion is missing and the observed  $m/z$  87 ( $M-H$ )<sup>+</sup>, 69 [( $M-H$ )-H<sub>2</sub>O]<sup>+</sup>, 41, 43, and 45 peaks correspond to ions produced by dissociative ionization upon surface collision, and (iii) the heat of the surface was used to break the chemical bonds, since the contribution to dissociative reaction behind the nozzle was negligible.<sup>6</sup>



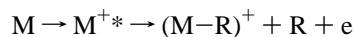
**Figure 2.** Dependence of the  $m/z$  87, 69, and 43 ions yield for *n*-pentanol from the ReO surface at 1100 K on the kinetic energy of the incident molecules.

A possible explanation of the dissociative ionization is as follows. A concerted mechanism is conceivable,



$$AP[(M-R)^+] = IE(M-R) + D[(M-R)-R]$$

where AP, IE, and  $D$  are the appearance potential, ionization energy, and dissociation energy, respectively. According to the calculations, the AP of ( $M-H$ )<sup>+</sup> should be 13.1 eV for methanol. The energies are too high to allow the formation of ions on the surface. Dissociation may occur after ionization:

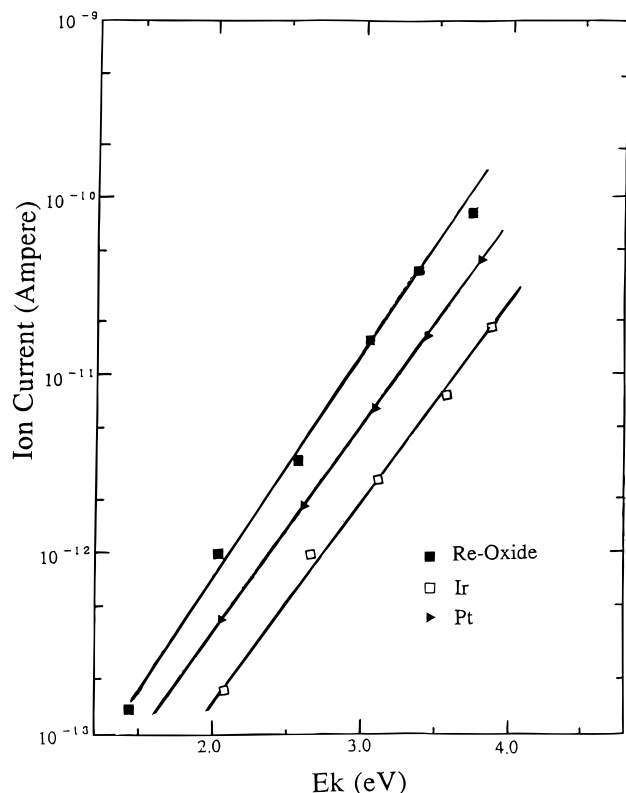


Since even the internal excited energies should be required, this process may be unlikely also.

A consecutive process is therefore more likely. A surface dissociative reaction product is formed followed by surface ionization of the scattered dissociated species. The observed ion peak can be explained in this way and its structure is most probably the one whose corresponding fragment neutral possesses a lower IE.

**Effect of Kinetic Energy.** The ion yield at  $m/z$  87, 69, and 43 was studied as a function of incident energy for *n*-pentanol to demonstrate the effect of translational energy with the ReO surface temperature held constant at 1100 K.

The HSI ions were enhanced exponentially with an increase in kinetic energy ( $E_k$ ) with a deviation from this exponential trend at higher energies (Figure 2). The  $m/z$  87 ionic yield increases by 3 orders of magnitude when  $E_k$  was increased from 0.5 to 4 eV. The trend is the same as that reported for many molecules studied by Amirav's group<sup>7–9</sup> and our group.<sup>1</sup> The threshold energy and energy dependence suggest a mechanism of energy transfer upon ionization. The internal energy of the



**Figure 3.** Dependence of the  $m/z$  87 ion yield for  $n$ -pentanol from the three surfaces (ReO, Pt, and Ir) at 1100 K on the kinetic energy of the incident molecules.

**TABLE 1: Effect of Surface Material on HSI Mass Spectra: Dependence of Ionization Threshold ( $E_{th}$ ),<sup>a</sup> Mass Spectral Pattern, Sensitivity (C/g), and Ionization Efficiency ( $\beta$ )<sup>b</sup> on the Surface Material**

surface material	$E_{th}$ ( $\varphi$ , eV) <sup>d</sup>	mass spectral pattern <sup>c</sup> (%)	sensitivity (C/g)	ionization efficiency ( $\beta$ )
ReO (6.4)	1.3	69(100), 87(11), 43(8), 41(6), 45(5)	1.2	$1.1 \times 10^{-3}$
Pt (5.65)	1.5	69(100), 87(21), 41(9), 45(7), 43(7)	$1.8 \times 10^{-2}$	$1.6 \times 10^{-5}$
Ir (5.27)	1.8	69(100), 87(13), 43(48), 41(12), 45(3)	$1.9 \times 10^{-2}$	$1.7 \times 10^{-5}$

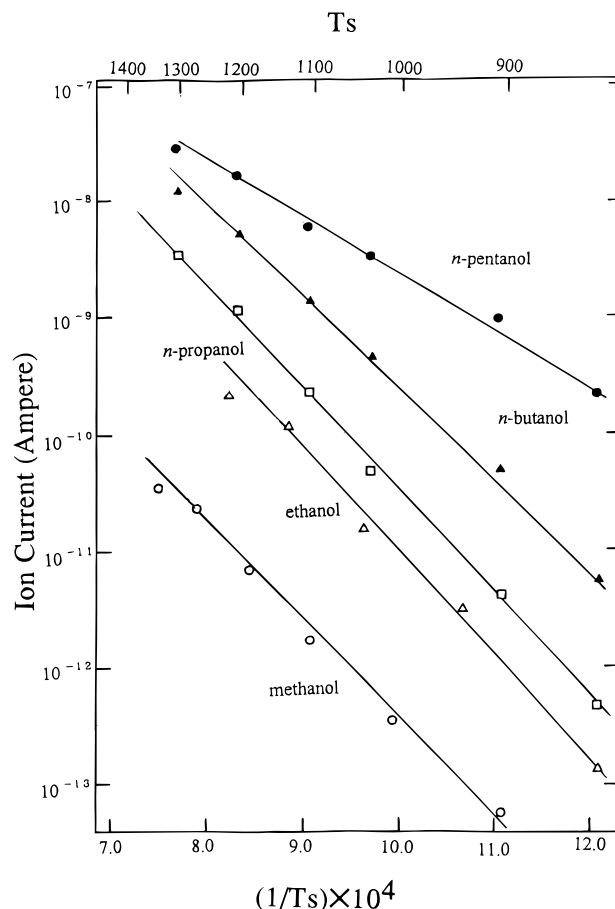
<sup>a</sup> Defined as  $E_{th}$  giving an ion current of  $10^{-13}$  A (detectable ion current of the present system). Refer to Figure 3.  $T_s = 1100$  K.

<sup>b</sup> Sensitivity and ionization efficiency were taken under the most favorable conditions (see section 4 in the text). <sup>c</sup> For  $E_k = 3.4$  eV and  $T_s = 1100$  K. <sup>d</sup>  $\varphi$  (eV); work function from the literature.<sup>11</sup>

fast molecules may increase because of the increased nozzle temperature. But this effect has not been considered because of the rapid and drastic decrease in gas temperature<sup>5</sup> in a region of the free jet expansion.

Interesting is that the kinetic energy dependence of these ions and their threshold energies differ from each other. No plausible explanation for these differences has yet been offered. However,  $E_k$  is also associated with thermal dissociation on surfaces; superthermal molecules take dissociation energy directly from their kinetic energy.

**Effect of Surface Material.** The energy dependence of HSI from various surfaces was studied by measuring the mass spectra for an  $n$ -pentanol beam striking Pt, Ir, and ReO foil surfaces with the surface temperature kept constant at 1100 K. The ionic signals at  $m/z$  87 depend on the nature of the surface (Figure 3); with the same  $n$ -pentanol energy at 3.4 eV, the yield increases in the order Ir < Pt < ReO. The energy dependency



**Figure 4.** Arrhenius plot of  $(M-H)^+$  ion intensity versus reciprocal surface temperature at a constant kinetic energy of 3.4 eV. The lines relate to  $CH_3OH$ ,  $C_2H_5OH$ ,  $n-C_3H_7OH$ ,  $n-C_4H_9OH$ , and  $n-C_5H_{11}OH$ , respectively.

curves also suggest differences in thresholds at around 1.5, 1.8, and 1.3 eV for Pt, Ir, and ReO, respectively, which appear to depend on the nature of the surface. However, the curve slopes from these surfaces are similar over the tested energy range, suggesting that the kinetic energy dependence of the  $n$ -pentanol dissociation to  $(M-H)$  is almost the same.

We believe that the wide variations in threshold energy ( $E_{th}$ ) and ionization efficiency ( $\beta$ ) could be related<sup>10,11</sup> to the work function<sup>12</sup>  $\psi$  of the surface, since  $\psi$  is always an important factor for surface ionization (Table 1). In fact,  $E_{th}$  decreases with increasing  $\psi$  of the surface.

Presumably the surface can influence the chemical reaction on the surface and, hence, contribute to the spectrum in some way (see Table 1).

**2. Effect of Surface Temperature.** We drew an Arrhenius plot of the logarithm of ionization probability versus reciprocal surface temperature for 5  $n$ -alcohols (Figure 4). The surface temperature,  $T_s$ , was raised from 820 to 1310 K. The nozzle temperature was constant at 900 K for these experiments. The experimental points fall on a straight line whose slope corresponds to an activation energy ( $E_a$ , heats of vaporization) of 1.63, 1.67, 1.82, 1.59, and 0.9 eV for the  $C_1$ – $C_5$   $n$ -alcohols, respectively.

It is tempting to compare the above results with the following equation modifying the Saha–Langmuir equation, which defines variations in surface ion formation with changing surface temperature ( $T_s$ ):

$$\alpha \approx \exp[(\gamma E_k + \varphi - IE)/(kT_s)] \quad (1)$$

**TABLE 2: Apparent  $\gamma$  Calculated for Ionization of Various Fast  $n$ -Alcohol Molecules ( $C_1$ – $C_5$ ); Units = eV**

observed molecule	activation energy (Ea) <sup>a</sup>	ionization energy <sup>b</sup> (IE)	kinetic energy (Ek)	$\gamma$
CH <sub>3</sub> O <sup>+</sup>	1.63	8.6	1.56	0.37
C <sub>2</sub> H <sub>5</sub> O <sup>+</sup>	1.67	9.11	1.94	0.54
C <sub>3</sub> H <sub>7</sub> O <sup>+</sup>	1.82	9.2	2.07	0.47
C <sub>4</sub> H <sub>9</sub> O <sup>+</sup>	1.59	9.22	2.54	0.48
C <sub>5</sub> H <sub>11</sub> O <sup>+</sup>	0.90	not available	2.58	?

<sup>a</sup> Calculated from Arrhenius plot (see Figure 4). <sup>b</sup> From the literature.<sup>17</sup>

**TABLE 3: HSI Mass Spectra of  $n$ -Alcohols ( $C_1$ – $C_5$ )<sup>a</sup> in Comparison with Electron Ionization Mass Spectra**

compounds (M, <sup>c</sup> IE <sup>d</sup> )	ion species	rel int	EI spectrum <sup>b</sup> (%)
methanol (32, 10.9)	(M–H) <sup>+</sup> <sup>e</sup>	100	31(100), 32(79), 29(39), 28(32)
	(M–3H) <sup>+</sup>	11	15(12), 30(7)
ethanol (46, 10.5)	(M–H) <sup>+</sup>	100	31(100), 45(44), 27(20), 29(19)
	(M–3H) <sup>+</sup>	5	46(19), 43(8), 15(8), 26(6)
<i>n</i> -propanol (60, 10.2)	(M–H) <sup>+</sup>	100	31(100), 27(19), 29(18), 59(11)
	<i>m/z</i> 43	6	42(9), 60(7), 41(7), 28(7)
	(M–3H) <sup>+</sup>	3	
<i>n</i> -butanol (74, 10.0)	(M–H) <sup>+</sup>	100	56(100), 31(88), 41(54), 43(48)
	(M–H–H <sub>2</sub> O) <sup>+</sup>	15	27(31), 42(26), 29(21), 55(14)
	<i>m/z</i> 41	6	
	<i>m/z</i> 43	4	
<i>n</i> -pentanol (88, 10.0)	(M–H–H <sub>2</sub> O) <sup>+</sup>	100	42(100), 55(76), 70(63), 41(58)
	(M–H) <sup>+</sup>	48	31(45), 29(42), 43(33), 57(28)
	<i>m/z</i> 43	19	
	<i>m/z</i> 41	7	

<sup>a</sup> For Ts = 1100 K and Ek = 2.0 eV. <sup>b</sup> EI mass spectra from the literature.<sup>15</sup> <sup>c</sup> M, nominal mass number <sup>d</sup> IE, ionization energy.<sup>17</sup> <sup>e</sup> The italicized *m/z* appears in both the HSI and EI mass spectra.

where  $\gamma$  is the ratio of the energy used effectively for ionization to the total kinetic energy Ek. Consequently,

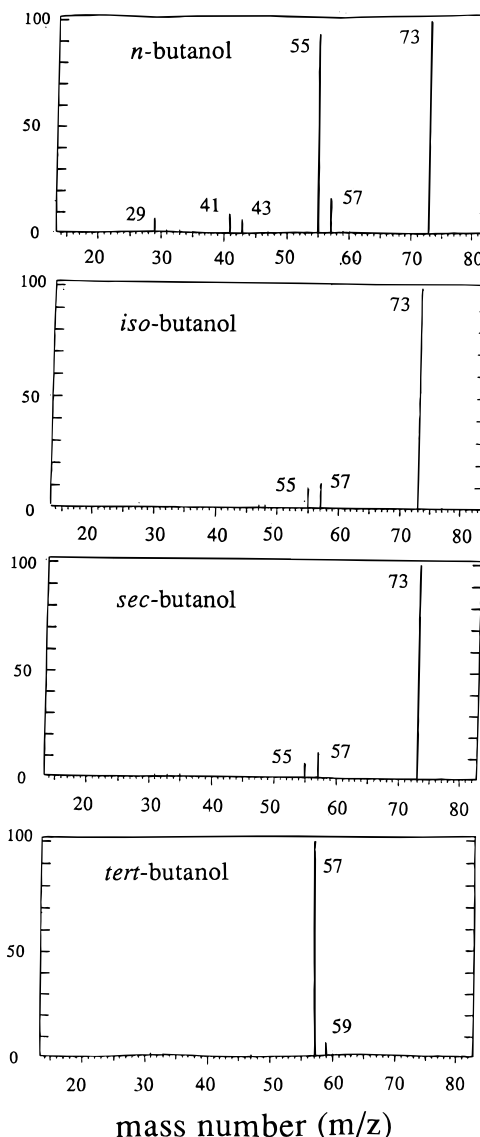
$$-Ea = \gamma Ek + \varphi - IE \quad (2)$$

Model calculations were made using eq 2 on the assumption<sup>13,14</sup> that  $\varphi = 6.4$  eV for the ReO surface. The apparent  $\gamma$  values calculated for ionization of the fast  $n$ -alcohol molecules ranged from 0.37 to 0.54 (Table 2), in good agreement with the values previously reported for benzene and toluene, 0.4 and 0.37 eV, respectively.

Strictly speaking, eq 2 does not consider the energy of the desorption process that must be involved in the activation step. If this term is taken into account,  $\gamma$  increases. We conclude that the kinetic energies are partially used for ionization.

**3. Characteristics of HSI Mass Spectral Pattern.** We measured the mass spectra of five  $n$ -alcohol compounds ( $C_1$ – $C_5$ ) of interest under the studied HSI conditions. The samples were introduced directly from the glass holder in the diffusion cell. The HSI spectra were compared to conventional EI spectra from the literature<sup>15</sup> (Table 3).

An important point common to all spectra observed throughout this work is that the HSI mass spectra exhibit the (M–H)<sup>+</sup> molecular ions with a few small peaks in the low mass range, which are basically different from those of EI. No similarities exist between the HSI and EI mass spectra. It is also clear that



**Figure 5.** HSI mass spectra of *n*-, iso-, *sec*-, and *tert*-butyl alcohol. Experimental conditions are Ts = 1100 K and Ek = 2.7 eV.

HSI yields large molecular (M–H)<sup>+</sup> ions for all of the examined alcohols, while EI does not yield any intense ions in the molecular region for the higher alcohols (*n*-butanol and *n*-pentanol).

The HSI spectra are characterized by thermal dissociation on the emitter surface, which is followed by surface ionization of thermally dissociated products. Therefore, extensive thermal dissociation takes place on the hotter emitter surface. Our approach to structural interpretation of the HSIMS signals is based on this mechanism.

We measured the HSI mass spectra of the butanol isomers to study the dependence of mass spectral pattern on structure. The HSI mass spectra of *n*-, iso-, *sec*-, and *tert*-butyl alcohols (Figure 5) illustrate that the difference is clearly indicated in HSI. A dissociative surface reaction on a hot emitter results in the loss of hydrogen atoms; consequently, a major peak was observed at (M–H)<sup>+</sup>. Some other signals at *m/z* 57 and 55 can be reasonably assigned to [(M–OH)]<sup>+</sup> and [(M–H<sub>3</sub>O)]<sup>+</sup>, respectively. The expected ionization of the thermally dissociated species is clearly present. Again, abundant ionic species at *m/z* 73 [(M–H)]<sup>+</sup>, 71 (M–3H)<sup>+</sup>, 57 [(M–OH)]<sup>+</sup>, and 55 [(M–H<sub>3</sub>O)]<sup>+</sup> appear. The signals at (M–OH)<sup>+</sup> from *tert*-butyl alcohol correspond to OH losses of the side chain. It is also

**TABLE 4: Sensitivity (C/g) of Alcohol Compounds Studied and Ionization Efficiency ( $\beta$ )<sup>a</sup>**

alcohols	sensitivity (C/g)	$\beta'$ <sup>b</sup>	$\beta$
methanol	$1.55 \times 10^{-7}$	$5.2 \times 10^{-11}$	$5.2 \times 10^{-7}$
ethanol	$6.96 \times 10^{-7}$	$3.3 \times 10^{-10}$	$3.3 \times 10^{-6}$
<i>n</i> -propanol	$2.94 \times 10^{-6}$	$1.8 \times 10^{-9}$	$1.8 \times 10^{-5}$
2-propanol	$1.62 \times 10^{-5}$	$1.0 \times 10^{-8}$	$1.0 \times 10^{-4}$
<i>n</i> -butanol	$4.78 \times 10^{-6}$	$3.7 \times 10^{-9}$	$3.7 \times 10^{-5}$
isobutanol	$9.57 \times 10^{-6}$	$7.3 \times 10^{-9}$	$7.3 \times 10^{-5}$
2-butanol	$1.53 \times 10^{-5}$	$1.2 \times 10^{-8}$	$1.2 \times 10^{-4}$
<i>tert</i> -butyl alcohol	$1.62 \times 10^{-5}$	$1.2 \times 10^{-8}$	$1.2 \times 10^{-4}$
<i>n</i> -pentanol	$1.24 \times 10^{-5}$	$1.1 \times 10^{-8}$	$1.1 \times 10^{-4}$

<sup>a</sup>  $\beta$ , the ionization efficiency on the surface under the most favorable conditions.  $T_s = 1100$  K and  $T_n = 1000$  K, which is a maximum nozzle temperature at which the nozzle is reasonably durable. <sup>b</sup>  $\beta'$ , the number ratio of the ions reaching the Faraday-cup detector of the QMS to the sample molecule flux from the nozzle assembly.

possible that the ions at 57 are formed by protonation of M and subsequent removal of H<sub>2</sub>O.

**4. Ionization Efficiency  $\beta$ .** Before conducting a study of ionization efficiency, the ionic current measured by the QMS was investigated as a function of surface bias potential. The surface bias potential is directly related to sensitivity (C/s). Sensitivity is defined as measured currents of ions (C/s) reaching the detector of the QMS against the sample molecule flux (g/s) from the nozzle assembly. The optimum bias potential giving the maximum signal is about around 30 V but depends somewhat on the experimental procedures and conditions.

Next we have considered the ionization efficiency,  $\beta$ , of the HSI method, using the apparent ionization efficiency,  $\beta'$ , which is defined as the number ratio of the ions reaching the Faraday-cup detector of the QMS to the sample molecule flux from the nozzle assembly.  $\beta'$  can be calculated from the sensitivity (C/g); we assumed from the instrumental conditions that  $\beta' = 10^{-4}\beta$ . The details have been described in a previous paper.<sup>1</sup>

Table 4 lists the sensitivity and  $\beta$  values for the alcohols studied. In comparison with electron ionization, HSI produced greater output ionic currents for *n*-pentanol by a factor of 35. It should be noted that although the electron impact (EI) ionization mass spectrum was optimized, our comparisons were limited to the few EI sources we used. Nevertheless, the HSI sensitivity seems good. Hence, HSI seems to have greater potential than EI for use in the routine analysis of alcohols in chemical laboratories, which require sensitive, selective, and rapid positive identification and determination capabilities.

$\beta$  reached the level of  $10^{-4}$  under the most favorable conditions, depending on molecular species. The intensity trend clearly demonstrates that alkyl alcohols with higher carbon number are higher in sensitivity and, hence, ionization efficiency. This trend is as expected, since the heavier alcohol

molecules obtain more kinetic energy from the supersonic free jet.

## Concluding Remarks

This was the first HSIMS study for the characterization of some alcohols. The results suggest further possibilities and limitations of the HSI technique. The main conclusions are (a) the HSI mechanism of the dissociated ionization works on alcohols, (b) the ionization efficiency depends, in some way, on the nature of molecules and surfaces, and (c) the kinetic energies are used partially for ionization. The value of  $\gamma$  (the ratio of the energy used effectively for ionization to the total kinetic energy,  $E_k$ ) is between 0.37 and 0.54 for the alcohols studied.

There are several principal advantages expected with the use of HSI techniques. HSI produces a few specific ions in abundance, and hence, use of HSI with MS and GC/MS can result in new opportunities in the field of analytical chemistry.<sup>16</sup> Owing to increased sensitivity, improved detection capability is achieved. GC/HSIMS facilitates identification of compounds with certainty as a complement to conventional EI. GC/HSIMS may also facilitate detection of a large number of chemicals when an extensive HSI mass spectral library has been established.

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