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Determination of branching ratios for the reactions of H_3O^+ with ethylbenzenes as a function of relative kinetic energy

Sohiko Kameyama[a,b], Satoshi Inomata[c,*], Hiroshi Tanimoto[b]

[a] Japan Society for the Promotion of Science, 8 Ichibancho, Chiyoda-ku, Tokyo 102–8472, Japan
[b] Asian Environment Research Group, National Institute for Environmental Studies, 16–2 Onogawa, Tsukuba, Ibaraki 305–8506, Japan
[c] Atmospheric Environment Division, National Institute for Environmental Studies, 16–2 Onogawa, Tsukuba, Ibaraki 305–8506, Japan

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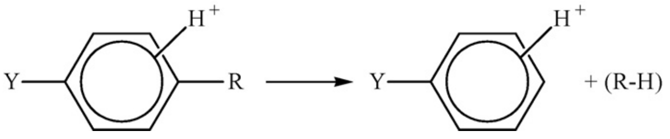
ABSTRACT

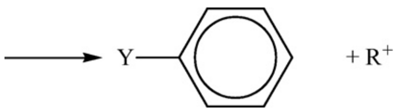
The proton-transfer reactions of H_3O^+ with ethylbenzene and deuterium-labeled ethylbenzenes were systematically investigated by means of proton-transfer reaction mass spectrometry. The branching ratios for the formation of protonated ethylbenzenes and for fragmentation reactions involving elimination of ethylene from the protonated molecules, accompanied by hydrogen migration from the α position or the β position of the ethyl group, were determined as a function of the mean relative center-of-mass kinetic energies of the reactants (K_{cm}). The branching ratio for the intact protonated molecule decreased with increasing relative kinetic energy: the branching ratio decreased from 0.87 at $K_{cm} = 0.19$ eV to 0.05 at $K_{cm} = 0.36$ eV, and in turn the ratio for ethylene elimination increased from 0.13 to 0.95. The branching ratios determined for partially deuterium-labeled ethylbenzenes were consistent with one another as well as with the ratios for unlabeled ethylbenzene. The fraction of H migration from the α position increased with increasing K_{cm} (from 0.13 ± 0.01 at $K_{cm} = 0.19$ eV to 0.24 ± 0.01 at $K_{cm} = 0.36$ eV) and appeared to saturate at ~0.24 at K_{cm} values above 0.28 eV.

1. Introduction

Interest in protonated alkylbenzenes developed with the introduction of chemical ionization mass spectrometry (CI-MS) [1–6]. Munson and Field [2] were the first to apply a methane CI technique to alkylbenzenes. In addition to the formation of protonated alkylbenzenes (MH^+) and cluster ions such as $M{\cdot}C_2H_5{}^+$ and $M{\cdot}C_3H_5{}^+$ ions, Munson and Field observed major fragments arising from the loss of H or alkyl groups from M, from olefin displacement by H^+ or $C_2H_5{}^+$, and, for larger alkyl substituents, from formation of alkyl ions. Hermann and Harrison [3] investigated the dependence of the fragmentation pattern—that is, the competition between olefin elimination (Eq. (1)) and alkyl ion formation (Eq. (2))—on the relative heats of reaction for C_8–C_{11} alkylbenzenes by comparing the mass spectra obtained by means of H_2, N_2/H_2, CO_2/H_2, N_2O/H_2, and CO/H_2 CI-MS:



(1)



(2)

They found that for propylbenzenes and *n*-butylbenzene, olefin elimination (Eq. (1)) increases relative to alkyl ion formation (Eq. (2)) with decreasing protonation exothermicity. They proposed a fragmentation mechanism involving the formation of an incipient alkyl ion solvated by the neutral arene moiety, followed by isomerization to a proton-bound alkene–arene pair, which eventually decomposes by elimination of either the alkene or the arene fragment.

In the olefin elimination reaction (Eq. (1)), a hydrogen atom migrates from the alkyl group to the ring. Isotope-labeling studies are useful for elucidating mass spectrometric fragmentation

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* Corresponding author. Tel.: +81 29 850 2403; fax: +81 29 850 2579.
E-mail addresses: kameyama.sohiko@nies.go.jp (S. Kameyama), ino@nies.go.jp (S. Inomata), tanimoto@nies.go.jp (H. Tanimoto).

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mechanisms, and CI-MS studies involving deuterium labeling of the side chain have been performed for primary alkylbenzenes [7–10]. H_2, D_2, CH_4, and CD_4 CI studies of ethyl- and *n*-propylbenzenium ions by Leung and Harrison [7] showed that the migrating hydrogen atoms originate from all positions of the side chain for both compounds but that the ω positions are slightly preferred as donor sites. Leung and Harrison's results also suggested that the fraction of H migration from the α position depends slightly on the relative heats of reaction in the case of ethylbenzene:

$$XH^+ + C_6H_5C_2H_5 \rightarrow (C_6H_5C_2H_5{\cdot}H^+ + X) \rightarrow C_6H_7{}^+ + C_2H_4 + X \quad (3)$$

The heats of reaction (ΔH_r) are −223 and −101 kJ mol^{-1} for X = H_2 and CH_4, respectively [11]. Audier et al. [8] investigated the fraction of H migration by means of H_2O CI, and their results were the same as those obtained by Leung and Harrison using CH_4 CI [7], even though ΔH_r for X = H_2O is +46 kJ mol^{-1} [11]. The similarity between the results by CH_4 CI and H_2O CI is thought to be coincidental [6].

In the present study, we systematically investigated the reactions of H_3O^+ with ethylbenzene and deuterium-labeled ethylbenzenes to determine the dependence of the branching ratios between the formation of protonated ethylbenzenes and the fragmentation reactions on the relative kinetic energies of the reactants, since the isotope labeling studies were performed only at discrete energy levels even for the ethylbenzenium ion, which is a relatively simple alkylbenzenium ion. In addition to the branching ratios for the formation of the protonated molecules and the fragments, the branching ratios for H atom migration from the α and β positions of the ethylbenzenium ion in the fragmentation reactions were determined as a function of the relative kinetic energies by means of deuterium labeling of the ethyl group of ethylbenzene. These data should be useful for elucidating the mechanism of ethylbenzenium ion fragmentation, as well as for determining the energies of intermediates and reaction barriers [9,12]. Note that alkyl ion ($C_2H_5{}^+$) formation has a much higher heat of reaction (ΔH_r = + 116 kJ mol^{-1} [11]) relative to that of the olefin elimination channel (ΔH_r = +46 kJ mol^{-1}), so the olefin elimination channel is the predominant fragmentation reaction for the ethylbenzenium ion [3].

The relative kinetic energy resolved mass spectra for the H_3O^+ + ethylbenzene reaction were obtained by means of proton-transfer reaction mass spectrometry (PTR-MS). PTR-MS is widely used for detecting and quantifying trace volatile organic compounds (VOCs) in the gas phase [13–15]. The proton donor is H_3O^+, which is generated relatively cleanly and simply in the gas-phase discharge without any need for mass pre-selection. The proton-transfer reactions between H_3O^+ and VOCs take place in a drift tube, where a homogeneous electric field of strength *E* is established to suppress the formation of hydronium ion–water clusters, such as $H_3O^+{\cdot}H_2O$. The relative kinetic energies of the reactants are controlled by variation of *E*.

2. Experimental

A commercially available PTR-MS instrument was used (Ionicon Analytik). The PTR-MS instrument, which has been described in detail elsewhere [13–16], consists of a discharge ion source to produce the H_3O^+ ions; a drift tube, in which the proton-transfer reactions between H_3O^+ and VOCs take place; and a quadrupole mass spectrometer (QMS) for the detection of reagent and product ions.

In a hollow cathode discharge ion source, H_3O^+ ions were produced from a pure water vapor flow of 7.8 sccm. The sample air was introduced into the drift tube at a flow rate of approximately 22 sccm; the drift tube pressure was held at 2.1 mbar. Most of the water vapors in the ion source were removed by a pump, but a small fraction of the water escaped into the drift tube. The water vapor concentrations in the drift tube was expected to be ∼10 mmol/mol [16]. The sampling inlet and drift tube were held at 105 °C. The drift tube (9.2 cm long) consisted of stainless steel ring electrodes, separated by Teflon rings for electrical isolation. The ring electrodes were connected to a resistor network, which divided the overall drift voltage (U_{drift}) into a homogeneously increasing voltage and established a homogeneous electric field inside the drift tube. The electric field was applied along the drift tube to avoid substantial formation of cluster ions, $H_3O^+{\cdot}(H_2O)_n$, *n* = 1, 2,. . . [17]:

$$H_3O^+ + H_2O \leftrightarrow H_3O^+{\cdot}H_2O \quad (4)$$

$$H_3O^+{\cdot}(H_2O)_n + H_2O \leftrightarrow H_3O^+{\cdot}(H_2O)_{n+1} \quad (5)$$

In the drift tube, trace gases such as VOCs in the sample air were ionized by proton-transfer reactions. A fraction of the reagent ion, H_3O^+, and the product ions was extracted through a small orifice into the QMS. The ions were detected by a secondary electron multiplier operated in the ion pulse counting mode. The mass dependence of the transmission efficiency of the QMS was calibrated by the manufacturer.

Ethylbenzene vapor was prepared by injecting a liquid sample into a 5-l Pyrex glass vessel [18], and mass spectra were obtained at six values of *E*/*N* (108, 119, 130, 140, 151, and 162 Td; 1 Td = 10^{-17} cm^2 V molecule^{-1}), where *E* is the electric field strength (V cm^{-1}) and *N* is the buffer gas number density (molecule cm^{-3}). A small amount of each sample (0.1 μl) was injected into the vessel and diluted with air from a zero-air supply (Model 111, Thermo Environmental Instruments Inc.), resulting in a sample mixture of approximately 2 parts per million by volume (ppmv). Data were recorded using the PTR-MS instrument's scan mode from *m*/*z* 21 to 125 with 0.5 s Da^{-1} and were averaged for five mass spectra at each *E*/*N* ratio.

The count rate of the reagent ion, H_3O^+, calculated from the count rate at *m*/*z* 21 ($H_3{}^{18}O^+$) multiplied by 500, was in the range (4–6) × 10^6 cps. The ratios of the ion intensity of $H_3O^+{\cdot}H_2O$ (*m*/*z* 37) to that of H_3O^+ were 0.03 at *E*/*N* = 108 Td and 0.0004 at *E*/*N* = 162 Td; that is, the intensity ratio strongly depended on the *E*/*N* ratio. The ratio of the ion intensity of $O_2{}^+$ (*m*/*z* 32), which was probably generated by back diffusion of air from the drift tube to the ion source, to that of H_3O^+ was 0.03–0.05. The ion count rates of the product ions totaled (4–12) × 10^3 normalized counts per second (ncps) normalized to an H_3O^+ intensity of 10^6 cps, which is within the linear dynamic range of the PTR-MS instrument.

The stated purities of the chemicals used were as follows: ethylbenzene, >98.0% ($C_6H_5CH_2CH_3$; Wako Pure Chemicals); ethylbenzene-d_{10}, 99.0 at.% D ($C_6H_5CD_2CD_3$; Acros Organics); ethyl-β,β,β-d_3-benzene, 96.1 at.% D ($C_6H_5CH_2CD_3$; C/D/N Isotopes); ethyl-α,α-d_2-benzene, 99.1 at.% D ($C_6H_5CD_2CH_3$; C/D/N Isotopes); and ethyl-α,α-d_2-benzene-d_5, 99.3 at.% D ($C_6D_5CD_2CH_3$; C/D/N Isotopes).

3. Results and discussion

PTR mass spectra of ethylbenzenes obtained at *E*/*N* = 108 Td are shown in Fig. 1, and the ion intensities of the product ions are summarized in Table 1. In the spectra, ion signals at *m*/*z* 32 ($O_2{}^+$) and *m*/*z* 37 ($H_3O^+{\cdot}H_2O$) are masked because they were largely scattered by the subtraction of the background mass spectrum.

In the mass spectrum of $C_6H_5CH_2CH_3$ (Fig. 1a), the peak of the protonated $C_6H_5CH_2CH_3$ ion (*m*/*z* 107) was the most intense. The peaks at *m*/*z* 79, 91, and 106, were assigned to $C_6H_7{}^+$, $C_7H_7{}^+$, and $C_6H_5CH_2CH_3{}^+$, respectively. The relative intensity of the signal at *m*/*z* 79 to that at *m*/*z* 107 was 0.15, whereas the relative intensities