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A Study of the Reactions of H_3O^+, NO^+ and $O_2^{+\cdot}$ Ions with Nine Alkoxy Alcohols

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Abstract Following a selected ion flow tube mass spectrometry (SIFT-MS), analysis of the headspace of a commercial available nail polish remover pad in which γ-butyrolactone (GBL) and 2-butoxy-1-ethanol were found to be the major volatiles, a study of the reactions of H_3O^+, NO^+ and $O_2^{+\cdot}$ ions with nine alkoxy alcohols ($R_1—O—R_2OH$) was carried out using selected ion flow tube(SIFT) at a carrier gas (helium) pressure of 9.3×10^1 Pa. Experiments were also performed at various carrier gas pressures (4×10^1-1.1×10^2 Pa) for some reactions and under moist air condition. The number and distribution of the hydrates for the product ions were used to identify their structures and to investigate reaction mechanisms. The H_3O^+ reactions proceed *via* nascent ion-molecule complex $(H_3O^+\cdot M)^*$, then produce $R_1—O—R_2OH.H^+$, $(R_1—O—R_2)^+$, $HOR_2OH.H^+$ and $R_2{=}O.H^+$ ions through various channels. Similarly, *via* a nascent complex $(NO^+\cdot M)^*$, $NO^+\cdot M$, $(M—H)^+$ and $(M—ROH)^+$ ions were produced in the NO^+ reactions. The collisions between the nascent complexes $(H_3O^+\cdot M)^*$ and $(NO^+\cdot M)^*$ with a third body (He, N_2 and O_2 etc) have influence on the product ion distributions. The $O_2^{+\cdot}$ reactions produce mainly dissociative product ions and it is uncertain whether they proceed *via* the nascent ion-molecule complex $(O_2^{+\cdot}\cdot M)^*$. This study provides rate coefficients and product ions in the SIFT-MS database for the analysis of these compounds in normal and humid air samples. It will be further utilised into addiction and drug abuse, respiratory medicine and other research areas using SIFT-MS.

Keywords SIFT; SIFT-MS; Mechanism; Nascent ion-molecule complex; Volatile; Biomarker

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1 Introduction

Alkoxy alcohols ($R_1—O—R_2OH$) have both —C—O—C— and —OH functional groups in their structures. Nine of them are included in this study:

2-Methoxyethanol(ME, $CH_3OCH_2CH_2OH$),

2-Ethoxyethanol(EE, $CH_3CH_2OCH_2CH_2OH$),

1-Methoxy-2-propanol(MP, $CH_3OCH_2CH(CH_3)OH$),

3-Methoxy-1-butanol (MB, $CH_3OCH(CH_3)(CH_2)_2OH$),

2-Propoxyethanol(PE, $CH_3(CH_2)_2OCH_2CH_2OH$),

2-Isopropoxyethanol(IPE, $(CH_3)_2CHOCH_2CH_2OH$),

3-Ethoxy-1-propanol(EP, $CH_3CH_2O(CH_2)_3OH$),

2-Butoxy-1-ethanol(BE, $CH_3(CH_2)_3O(CH_2)_2OH$),

1-Propoxy-2-propanol(PP, $CH_3(CH_2)_2OCH_2CH(CH_3)OH$).

Some of them, ME, EE, MP, PE and BE belong to a family of glycol ether compounds which are widely used as industrial solvents due to their physical properties and chemical characteristics. They can enter human body *via* inhalation of their vapours in the air and can rapidly absorbed into the body through skin contact. Some of them have adverse effects on human reproductive systems; damage red blood cells and the bone marrow; intoxicate nervous system and cause irritation to eyes, skin, nose and throat. In rats, it has been

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shown that the majority of the inhaled BE was eliminated in the urine and a small proportion (5%-8%) of the retained BE was exhaled as CO_2 and most (greater than 80%) of the BE derived material in blood was in the plasma[1]. Further, EE, ME and BE were found to be extremely accumulated as long as only very low levels of ethanol are present in blood[2]. This is important in the metabolic pathways since alcohol, as one of the most popular consumer products, is not only commonly involved with addiction and drug abuses[3], but also a common metabolite produced by bacteria that can colonised in the body[4].

Chemical ionisation methods involving "soft ionization" of gases[5] coupled with mass spectrometry, such as the proton transfer reaction mass spectrometry (PTR-MS)[6] and negative ions used in chemical ionisation mass spectrometry (CIMS)[7] are very useful in detecting gaseous compounds and studying reaction mechanisms.

Selected ion flow tube mass spectrometry (SIFT-MS)[8] was developed from selected ion flow tube technique[9] in combination with chemical ionisation. It allows the identification and accurate quantification of a wide range of volatile organic compounds (VOCs) and some inorganic compounds using precursor ions (H_3O^+, NO^+ and $O_2^{+\cdot}$)[8]. Real time analyses of ambient air, single exhalations of breath, and the headspace above liquids such as urine, blood, cell cultures, bacterial culture and oil, can be achieved[3, 4, 8-16]. Combined with flowing afterglow mass spectrometry (FA-MS), it has been used to study the metabolism of ethanol in the body[17].

Recently, SIFT-MS has been applied into addiction research[3]. The headspace vapour of a commercially available GBL sample (acetone free nail polish remover pad), which is used as a source of GBL by drug users, was analysed by SIFT-MS[3]. Notably, high quantities of 2-butoxy-1-ethanol as well as GBL were detected in the vapour[3]. This has prompted us to investigate the ion chemistry of GBL[16], 2-butoxyl-ethanol and other compounds in the same family studied in this paper. This will provide the required rate coefficients and product ions for the analysis of these compounds in normal and humid air samples using SIFT-MS, also give an opportunity to investigate the ion molecule reaction mechanisms of H_3O^+, NO^+ and $O_2^{+\cdot}$ with these compounds.

2 Experimental

Using SIFT technique to obtain rate coefficients and product ion distributions of ion-molecule reactions has been described previously in details[8, 9]. The collisional rate coefficients (k_c) were calculated using the parameterised trajectory formulation[18]. The polarisabilities: 8, 10, 12 and 14 ($\times 10^{-24}$ cm^3) for C3, C4, C5 and C6 alkoxy alcohols and their dipole moment: 1.6 Debye were estimated from data of similar compounds[19]. Experiments were carried out at a helium carrier gas pressure of 9.3×10^1 Pa at room temperature (296 to 300 K) under three conditions: (i) helium/dry air; (ii) laboratory air (relative humidity ~ 1.5% by volume); and (iii) humid air (relative humidity ~ 6%)[8, 15]. Three-body association rate coefficients, k_{3b}, (unit: 10^{-28} cm^6 · s^{-1}) for formation of hydrates from the product ions can be obtained[8, 20]. Experiments were also performed at various flow tube pressures between 4×10^1-1.1×10^2 Pa. These can provide valuable information and understanding of the ion chemistry reaction mechanisms[20]. All compounds (> 97%) were obtained from Sigma Aldrich. The instrument used was the SIFT-MS Mk1 machine at Keele[20].

3 Results and Discussion

3.1 General Comments

These reactions all proceed at the calculated collisional rates[18], i.e. (2.8±0.1), (2.3±0.1) and (2.3±0.1) × 10^{-9} cm^3 · s^{-1} for the H_3O^+, NO^+ and $O_2^{+\cdot}$ reactions. The product ion distributions are listed in Table 1.

3.2 H_3O^+ Reactions

In general, the alkoxy compounds react with H_3O^+ *via* nascent ion-molecule complex $(H_3O^+ \cdot R_1{-}O{-}R_2OH)^*$ then produce $R_1{-}O{-}R_2OH \cdot H^+$, $(R_1{-}O{-}R_2)^+$, $(R_2{=}O \cdot H)^+$ and $HOR_2OH_2^+$ ions through various channels after collisions with a third body as proposed in Scheme 1.

In channel (1a), $R_1{-}O{-}R_2{-}OH \cdot H^+$ is produced. There are two possibilities of the locations of the proton, one is at the oxygen atom on the C—O—C structure, as in the reaction of ethers[21]; the other is on the —OH group as in the reaction of alcohols[20, 22]. Therefore, in the $(H_3O^+ \cdot M)^*$ ion-molecule complex the H_3O^+ ion can interact with the alkoxy alcohol at either the C—O—C or the C—OH group, and the complex will further go into reaction channels (1a, 1b, 1c, 1d) after collisions with a third body as we have seen in a previous experiment[20]. In channel (1a) a H_2O molecule was lost from the complex and $R_1{-}O{-}R_2{-}OH \cdot H^+$ is produced as the final product.

Scheme 1

$$H_3O^+ + R_1{-}O{-}R_2{-}OH + X \rightarrow (H_3O^+ \cdot R_1{-}O{-}R_2{-}OH)^* + X$$

$$\rightarrow R_1{-}O{-}R_2{-}OH \cdot H^+ + H_2O + X \quad (1a)$$

$$\rightarrow (R_1{-}O{-}R_2)^+ + 2H_2O + X \quad (1b)$$

$$\rightarrow HO{-}R_2{-}OH \cdot H^+ + R_1OH + X \quad (1c)$$

$$\rightarrow R_2{=}O \cdot H^+ + R_1OH + H_2O + X \quad (1d)$$

X= He, N_2, O_2 etc.

In channel (1b), the —OH group is lost from the mole-

cules and two water molecules are produced. This is very common in the reaction of alcohols[22].

In channel (1c), $HO—R_2—OH.H^+$ ions were produced. This ion can only be produced through the interaction of H_3O^+ with the compounds at the structure of $R_1—O—R_2$ *via* a nascent $(H_3O^+.R_1—O—R_2—OH)^*$ ion-molecule complex. Notably, this type of the product ion was produced in the reactions of three of the four alkoxy ethanols. Its fraction in the final product yields increases with the number of carbons in the alkoxy group with 2-methoxyethanol, which has the lowest number of carbon atoms, the only exception which does not produce this type of product. The mechanism of this channel could also be used to explain some reactions of ethers[21]. e.g. $C_3H_7OH_2^+$ was produced in the reaction of $C_3H_7OC_3H_7$ with H_3O^+ and the neutral product was proposed to be $C_3H_6+H_2O$ (exothermic by ~ 12 kcal·mol^{-1}). Using the mechanism proposed in channel (1c) the neutral product ion is C_3H_7OH (exothermic by ~ 20 kcal·mol^{-1}) and fewer steps will be involved to produce the final products.

In channel (1d), $R_2=O.H^+$ ions are produced. There are two possible structures for the $(ROH)^+$ ion: one is the carbonium cation which has the charge on the end carbon of R; the other has the charge on hydrogen atom on the $>C=O.H^+$ structure which is like the protonated aldehyde or ketones. As can be seen from 2-emthoxyethanol, 1-methoxypropanol, 3-ethoxy-1-propnaol and 1-propoxy-2-propanol reactions, the later structure should be the product ion since it has multiple water clusters like a protonated aldehyde or ketones when there is moisture around[8, 15], whereas carbonium cation do not form water cluster easily under the present SIFT-MS experimental conditions[23]. There are two possible pathways to produce this product: one is firstly by breaking up of the bond between the $R_1O—$ and the $—R_2OH$ group, then produces $R_2=O.H^+$ through isomerisation; the other is through the product ions in channel (1c), $(HO—R_2—OH_2)^+$, which like protonated diols that are known to be able to further lose a H_2O molecule to produce $R=O.H^+$ ions[24]. Notably, channels (1c) and (1d) rarely exist together in the reactions between H_3O^+ and these compounds with 2-ethoxyethanol the only exception.

The influence of the third body (He, N_2 and O_2) has been studied by varying the flow tube pressure under the helium/dry air condition. In Fig. 1, it can be seen that at low pressure, $C_3H_8O_2H^+$ (m/z 77) dominates, the other two product ions $C_3H_7O^+$ (m/z 59) and $C_2H_5O^+$ (m/z 45) were elevated with the increased flow tube pressure. This observation agrees with phenomenon seen in a recent experiment on the propanol isomers[20] in which the reactions firstly proceed through a nascent ion-molecule complex $(H_3O^+.M)^*$, then with further collisions with a third body, the production of MH^+, fragment ions like $[M—OH]^+$ and other product ions are promoted[20].

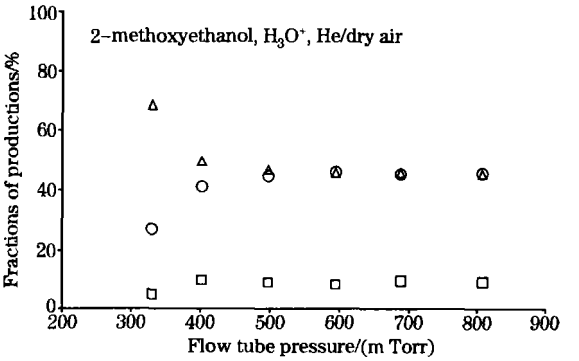

Fig. 1　The product ion distributions (□- m/z 45, ○- m/z 59, △- m/z 77) for the reaction of H_3O^+ with 2-methoxyethanol at various flow tube pressures

3.3　NO^+ Reactions

NO^+ reacts with alkoxy alcohols through channels as proposed in Scheme 2.

Channel (2a) only exists in the reactions of 2-methoxyethanol. This type of reaction is known to proceed *via* nascent ion-molecule complex $(NO^+.M)^*$ and facilitated by further collisions with a third body[8, 15, 25]. As expected, the fraction from this channel increased when the lab air is introduced into the flow tube, see Table 1.

Scheme 2

$$NO^+ + R_1—O—R_2—OH + X \rightarrow$$

$$(NO^+.R_1—O—R_2—OH)^* + X \rightarrow NO^+.M + X \quad (2a)$$

$$\rightarrow (M—H)^+ + HNO + X \quad (2b)$$

$$\rightarrow (M—ROH)^+ + (R'ONO) + X \quad (2c)$$

$M = R_1—O—R_2—OH$; X = He, N_2, O_2 etc.

Channel (2b) is the major channel and exists in the reactions of all nine compounds. The hydride ion H^- could be abstracted from either the carbon on the C—O—C structure or from the carbon on the C—OH structure. Under moist air conditions, the former product ions (carbonium ions) will not form water cluster ions but the latter (which could be rearranged into $>C=O.H^+$ [20]) will form water cluster. Therefore, in the reactions of 2-methoxyethanol, 1-methoxy-2-propanol and 3-ethoxy-1-propnanol, $(M—H)^+$ product ions form significant water clusters and could be formed by abstracting H^- from the carbon on C—OH. The $(M—H)^+$ in the reactions of five other alkoxy alcohols are mostly dominated by the carbonium ions while in case of 2-ethoxyethanol, it is possible that both type of ions exist. For details see Table 1.

Channel (2c) exists in the reaction of 3-methoxy-1-butanol in which —ROH group is connected to a secondary carbon

in the carbon chain, and finally results in the breaking up of the bond between this secondary carbon and the —ROH group. The minor product ions in 2-butoxy-1-ethanol and 2-methoxyethanol are also produced *via* this channel. For details see Table 1.

Table 1 The product ion distributions (rounded to the nearest 5%) from the H_3O^+ and NO^+ reactions. The estimated absolute and relative errors are ±25% and ±15%, respectively

Molecule	H_3O^+ product	p: m: d(: t)[a]	k_{3b}/(10^{-28} cm^6·s^{-1})	NO^+ product	p: m: d	k_{3b}/(10^{-28} cm^6·s^{-1})
ME	$C_3H_8O_2H^+$ (45)	5: 75: 20	33.3	$C_3H_7O_2^+$ (95)[d]	20: 25: 55	24.4
IE= 10.13 eV[27]	$C_3H_7O^+$ (45)	90: 10: 0	< 1.6	$NO^+ C_3H_8O_2$ (5)[d]		
	$C_2H_5O^+$ (10)	55: 25: 20(: 0[c])	5.9			
EE	$C_4H_{10}O_2H^+$ (55)	15: 80: 5	22.6	$C_4H_9O_2^+$ (100)	90: 10: 0[c]	< 1.3
IE= 9.6~9.97 eV[27]	$C_4H_9O^+$ (30)	100: 0: 0	< 0.1			
	$C_2H_7O_2^+$ (10)[b] $C_2H_5O^+$ (5)[b]					
MP	$C_4H_9O^+$ (90)	100: 0: 0	< 0.1	$C_4H_9O_2^+$ (100)	75: 20: 5	2.4
IE= 9.6 or 9.96 eV[27]	$C_3H_7O^+$ (5)	25: 15: 25(: 35)	13.7			
	$C_4H_{10}O_2H^+$ (5)	10: 90: 0[c]	23.4			
MB	$C_5H_{12}O_2H^+$ (75)	95: 5: 0	< 0.6	$C_5H_{11}O_2^+$ (85)[e]	100: 0[c]: 0	< 0.1
	$C_5H_{11}O^+$ (25)[b]			$C_3H_7O^+$ (15)[e]	95: 5: 0	< 0.5
PE	$C_5H_{12}O_2H^+$ (55)	20: 75: 5	17.7	$C_5H_{11}O_2^+$ (100)	95: 5: 0[c]	< 0.5
	$C_2H_7O_2^+$ (40)	10: 25: 65	26.1			
	$C_5H_{11}O^+$ (5)[b]					
IPE	$C_2H_7O_2^+$ (90)	5: 25: 70	47.0	$C_5H_{11}O_2^+$ (100)	95: 5: 0[c]	< 0.8
	$C_5H_{12}O_2H^+$ (10)	55: 40: 5	6.0			
EP	$C_5H_{12}O_2H^+$ (80)	95: 5: 0	< 0.9	$C_5H_{11}O_2^+$ (100)	65: 35: 0[c]	5.6
	$C_5H_{11}O^+$ (15)[b]					
	$C_3H_7O^+$ (5)	20: 70: 10	< 1.6			
BE	$C_2H_7O_2^+$ (40)	5: 15: 75(: 5)	56.1	$C_6H_{13}O_2^+$ (85)	100: 0: 0	< 0.5
	$C_6H_{14}O_2H^+$ (60)	30: 70	17.6	$C_2H_5O^+$ (5) $C_2H_5O_2^+$ (5)		
				$C_4H_9O^+$ (5)		
PP	$C_6H_{13}O^+$ (50)	100: 0: 0	< 0.1	$C_3H_7O^+$ (5)		
	$C_3H_7O^+$ (30)	0[c]: 70: 30	62.5	$C_6H_{13}O_2$ (95)	100: 0[c]: 0	< 0.2
	$C_6H_{14}O_2H^+$ (20)	65: 35: 0	4.3			

a) p= product; m, d, t= mono-, di- and tri-hydrates; b) The hydrates for these ions are uncertain; c) Fractions < 2%; d) In moist air, the fraction of NO^+ M increased to 15%; e) The hydride ion transfer product $C_5H_{11}O_2^+$ increases to 95% under lab air condition.

Notably, in the 2-methoxy-1-butanol reaction with NO^+, where both channels (2b) and (2c) exist, the fractions of the product ion from hydride ion transfer channel (2b) increases when lab air is introduced into the flow tube (see Table 1), indicating that components of air facilitates the hydride ion transfer channel. Combined with reactions in 2-methoxyethanol when both association product ion and the hydride transfer product ions are formed, these results provide evidence that the carrier gas and the components of air are involved in this reaction *via* the nascent ion-molecule complex $(NO^+ \cdot M)^*$ as proposed in Scheme 2.

The general mechanism of this reaction: firstly a nascent complex $(NO^+ \cdot M)^*$ was formed then product ions were formed *via* various channels after further collisions with a third body: could be applied to other similar reactions: e.g. in the H_2ONO^+ reaction with toluene (C_7H_8)[25] where the only product ion is the parent cation $C_7H_8^+$ but the direct charge transfer reaction was shown to be endothermic by 0.28 eV[25]. It was proposed that this was due to excited state ions, and the components of air (N_2 and O_2 etc) were used to quench them but with little effect[25]. In fact this could mean that either the components of air do not quench the excited state ions efficiently or there were little excited state ions present in the system and other reaction mechanism exists. By employing the mechanism proposed in this study, the H_2ONO^+ reaction with toluene will firstly form an ion-molecule complex $(H_2ONO^+ \cdot C_7H_8)^*$, then undergoes further collisions with a third body, since the mean centre-of-mass energy of the complex ion/He (or components in air) is typically ~ 1-2 eV[25], which could provides extra energy for the reaction to go through the charge transfer channel exothermically.

3.4 $O_2^+ \cdot$ Reactions

$O_2^+ \cdot$ reactions with alkoxy alcohols (see Table 2). result mostly in various dissociative product ions involving breaking the C—O—C, C—OH and C—C bonds in the structures

Hydride ion transfer and charge transfer product ions are usually in minor fractions. Whether this reaction proceeds *via* the nascent ion-molecule complex ($O_2^+ \cdot . M$) is still uncertain.

Table 2　The product ion distributions (rounded to the nearest 5%) from the $O_2^+ \cdot$ reactions

Molecule	$O_2^+ \cdot$ product
ME	$C_2H_5O^+$ (90) $C_3H_6O^+ \cdot$ (5) $C_3H_8O_2^+ \cdot$ (5)
EE	$C_3H_7O^+$ (85) $C_4H_8O^+ \cdot$ (15)
MP	$C_2H_5O^+$ (65) $C_2H_7O^+$ (35)
MB	$C_3H_7O^+$ (90) $C_2H_3O^+$ (5) $C_4H_9O_2^+$ (5)
PE	$C_4H_9O^+$ (85) $C_3H_7^+$ (10) $C_2H_5O^+$ (5)
IPE	$C_4H_9O^+$ (55) $C_4H_9O_2^+$ (25) $C_3H_7^+$ (15) $C_3H_7O^+$ (5)
EP	$C_3H_6O^+ \cdot$ (30) $C_3H_7O^+$ (20)
	$C_4H_7O^+$ (20) $C_3H_7O_2^+$ (15) $C_2H_5O^+$ (10) $C_5H_{10}O^+ \cdot$ (5)
BE	$C_5H_{11}O^+$ (50) $C_4H_9O^+$ (10)
	$C_4H_7O^+$ (5) $C_4H_8^+$ (30) $C_4H_8^+ \cdot$ (5)
PP	$C_4H_9O^+$ (65) $C_2H_5O^+$ (30) $C_4H_8O^+ \cdot$ (5) $C_3H_7^+$ (5)

4　Concluding Remarks

The H_3O^+ and NO^+ reactions proceed *via* nascent ion-molecule complex ions $(H_3O^+ . M)^*$ and $(NO^+ . M)^*$ then after further collisions with a third body (e.g. He, N_2 and O_2), which provide some extra energy (1-2 eV under various conditions) for the reactions, to produce ions *via* various channels. This reaction mechanism could be applied to other similar reactions such as H_2ONO^+ reaction with toluene in which the parent cation is observed as the only product but the direct charge transfer channel is endothermic by 0.28 eV[25] and H_3O^+ with dipropyl ether[21]. Whether this mechanism applied to the reactions between H_3O^+ and NO^+ and other compounds still needs further study. The $O_2^+ \cdot$ reaction with these compounds produce mainly dissociative product ions and it is uncertain whether they proceed *via* the nascent ion-molecule complex $(O_2^+ \cdot . M)^*$.

The results from this study will be further applied into research fields such as addiction where 4-butoxy-1-ethanol and GBL from commercial available nail polish remover pad are known to be ingested together by drug abusers[3]; respiratory medicine where there is a case that the breath from a patient, who is not drug abuser, smells like the nail polish remover pad due to yet unknown reasons[26] and other areas. These evidences show[2, 3, 26] that compound like 4-butoxy-1-ethanol could be used as a potential biomarker for monitoring misuse of and exposure to industrial and commercial solvents and their metabolism and effects in human being.

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H_3O^+, NO^+ 和 $O_2^{\pm\cdot}$ 离子同九种烷氧基醇化合物反应的研究

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摘 要 在用选择离子流动管质谱(SIFT-MS)分析常用指甲油清洗垫发现大量 4-丁酸内脂(γ-butyrolactone, GBL)和 2-丁氧基乙醇(2-butoxy-1-ethanol)等挥发性气体后, 运用选择离子流动管(SIFT)对 H_3O^+, NO^+ 和 $O_2^{\pm\cdot}$ 离子同九种烷氧基醇化合物(R_1—O—R_2OH)之间的反应进行了研究。获得了这些反应在潮湿空气条件下进行的情况, 并运用产物离子水合物的种类和分布来确认产物离子的结构和反应机理。还研究了在不同载气压力下进行的反应。结果表明, 这些化合物同 H_3O^+ 和 NO^+ 的反应都是先生成初生态离子-分子络合物, $(H_3O^+\cdot M)^*$ 和 $(NO^+\cdot M)^*$, 然后经不同反应渠道生成各种离子产物。这些初生态络合物同反应体系中存在的气体分子(如氮气, 氮气和氧气分子)的碰撞对最终离子产物的形成和分布也有影响。这些化合物同 $O_2^{\pm\cdot}$ 反应会生成各种离解碎片离子, 但不能确定这些离子是否经由初生态络合物 $(O_2^{\pm\cdot}\cdot M)^*$ 生成。该项研究提供了用 SIFT-MS 在空气和潮湿气体中分析这些化合物所需的反应速率常数和离子产物等动力学数据, 并将进一步应用到药物成瘾及滥用和呼吸道疾病的诊断和分析等领域。

主题词 SIFT; SIFT-MS; 反应机理; 初生态离子-分子络合物; 挥发性气体; 生物标志物
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