Available online at www.sciencedirect.com

SCIENCE DIRECT®

International Journal of Mass Spectrometry 229 (2003) 143–149

www.elsevier.com/locate/ijms

Reactions of small hydrocarbons with H_3O^+, O_2^+ and NO^+ ions

Paul F. Wilson, Colin G. Freeman, Murray J. McEwan*

Department of Chemistry, University of Canterbury, P.O. Box 4800, Christchurch 8001, New Zealand

Received 24 February 2003; accepted 2 June 2003

Abstract

We report selected ion flow tube measurements of reaction rate coefficients and branching ratios for the reactions of H_3O^+, O_2^+ and NO^+ with the small hydrocarbons CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_4 (allene and propyne), C_3H_6, *c*-C_3H_6, C_3H_8, C_4H_2, C_4H_8 and *n*,*i*-C_4H_{10}. The relevance of these measurements to quantitative selected ion flow tube mass spectrometry (SIFT-MS) is discussed. An application of the measurements is made to the analysis of the chemical species generated by chemical ionization in the exhaust gases from a petrol combustion engine up to $m/z = 60$. The analysis shows that chemical ionization data are required from more than one precursor ion in order to interpret the data.

Keywords: Chemical ionization of hydrocarbons; Selected ion flow tube (SIFT) mass spectrometry; Ion-molecule rate coefficients

1. Introduction

Chemical ionisation is a method developed in the mid 1960s [1–3] to selectively ionise molecules [4]. Quite a number of different methods for detecting volatile organic chemicals (VOCs) that utilise the principle of chemical ionisation have subsequently been developed. Recently, the technique has been applied to flow tubes. Chemical ionisation by proton transfer has been described by Lindinger et al. [5]. A different variation has been reported by Smith and coworkers [6,7] called selected ion flow tube-mass spectrometry (SIFT-MS), where the chemical ionisation reactions of three different ion precursors (H_3O^+, O_2^+ and NO^+) are utilized. The details and methodology of SIFT-MS have been described extensively by these authors [6,7].

In the SIFT-MS technique, the ion precursor reacts with volatile species in a sample that is admitted via a capillary inlet into the SIFT flow tube. The product ions of the reaction are recorded by the second mass spectrometer. Providing the ion-molecule chemistry of the precursor ions with the VOC is known, the amplitude of the product ion signals from reaction gives a direct measure of the number density of the VOC in the sample mixture [6,7]. We have made several measurements of samples of city air containing small hydrocarbons emitted mainly by motor vehicles, as well as wood and coal burners, utilizing the SIFT-MS technique. Although Spaněl and Smith have reported some reactions of larger aliphatic and aromatic hydrocarbons with H_3O^+, O_2^+ and NO^+ ions [8], a number of the smaller hydrocarbons have not been evaluated under flow tube conditions: particularly those reactions for O_2^+ and NO^+. Although most of the reactions of H_3O^+ with the specified hydrocarbon have been previously determined, the results shown here demonstrate the consistency of our measurements. In order to quantify our measurements of city air, we examine here the kinetics of a series of small hydrocarbons from C_1 through to C_4 with H_3O^+, O_2^+ and NO^+.

We report in this paper the results of an investigation into the ion chemistry of the three precursor ions with C_1 to C_4 hydrocarbons using a selected ion flow tube that has been described previously [9]. For the reactions of H_3O^+, the essential parameter influencing the reaction is the proton affinity (PA) of the hydrocarbon. If the PA (hydrocarbon) > PA H_2O (=691 kJ mol^{-1} [10]), then proton transfer should occur. For the reactions of O_2^+, the essential parameter is the ionisation potential of the hydrocarbon. Only methane has an IP > IP O_2 (=12.071 eV), and thus charge transfer and dissociative charge transfer reactions are to be expected. For NO^+, the essential parameter again is the ionisation potential. The IP of all hydrocarbon molecules in this study are >IP NO (=9.264 eV) with the exception of 2-butene. Therefore, we would not expect rapid reactions to occur between NO^+ and these hydrocarbons.

---

* Corresponding author. Tel.: +64-33-642875; fax: +64-33-642110.
E-mail address: murray.mcewan@canterbury.ac.nz (M.J. McEwan).

1387-3806/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S1387-3806(03)00290-2

2. Experimental

The SIFT instrument at Canterbury has been described previously [9]. The reactions described in this work were carried out using a flow tube reaction length of 50 cm, a tube diameter of 7.3 cm and a SIFT tube pressure of 0.46 Torr of helium carrier gas at 298 K. The O_2^+ and H_3O^+ ions were generated using a microwave discharge to create a helium afterglow (around 0.3 Torr) in the flowing afterglow ion source, into which a stream of moist air was added. The ions formed in the afterglow were then sampled through a nose cone in the flowing afterglow source tube, mass selected by the upstream mass filter and introduced into the SIFT flow tube via a venturi orifice. Rate coefficients and branching ratios were measured in the usual way by observing the semilogarithmic decay of the ion signal with reactant gas flow [9].

Two minor problems were experienced with the generation of the ions O_2^+ and NO^+. It was not possible to generate either of these ions *completely* free from small amounts of excited ions. We observed that a fraction of the O_2^+ ions produced in this way were excited ions, O_2^{+*}, since they reacted with CH_4 to produce very small amounts of product ions other than CH_2OOH^+. The chemistry of this reaction has been well studied by Ferguson and coworkers [10–14]. It is known that significant amounts of metastable O_2^+ (a $^4\Pi_u$) ions are made from Penning ionisation of metastable helium atoms. These O_2^+ (a $^4\Pi_u$) metastables are efficiently removed by reaction with N_2 and O_2 [15,16]. By adjusting the flow rate of moist air into the flowing afterglow, the fraction of excited O_2^{+*} was kept to less than a few percent. The NO^+ used in this work was produced by adding a stream of N_2O to the helium flowing afterglow. Evidence of small amounts of excited NO^{+*} species was seen in the detection of product ions of reactions that were endothermic from ground state NO^+. Again, appreciable amounts of metastable NO^+ (a $^3\Sigma$) are formed by Penning ionisation from metastable helium atoms. These metastable ions are reactive with N_2 and O_2 [15,16] and were kept to a few percent by adding small amounts of moist air to the flow tube.

3. Results and discussion

Summaries of the reactions that have been investigated in this work are presented in Table 1 (H_3O^+ reactions), Table 2 (O_2^+ reactions) and Table 3 (NO^+ reactions).

3.1. H_3O^+ reactions

As noted in Section 1, the key parameter for determining the reactivity of H_3O^+ with small hydrocarbon ions is the PA of the hydrocarbon. All hydrocarbons having a PA > PA

Table 1
Reactions of H_3O^+ with the given hydrocarbon

Neutral	PA (kJ mol^{-1})	Products	Branching ratio	Observed rate[a,b]	Previous measurements
CH_4	543.5	n.r.	–	<0.001 (1.3)	
C_2H_6	596.3	n.r.	–	<0.001 (1.5)	
C_2H_4	680.5	$C_2H_4{\cdot}H_3O^+$	0.20	0.063 (1.4)	0.063[c,d], 0.084[e], 0.078[f]
		$C_2H_5^+ + H_2O$	0.80		
C_2H_2	641.4	$C_2H_2{\cdot}H_3O^+$	1.0	0.011 (1.3)	8×10^{-28}[g], 0.011[d,h]
C_3H_8	625.7	No reaction	–	<0.001 (1.6)	n.r.[d]
C_3H_6 (propene)	751.6	$C_3H_7^+ + H_2O$	1.0	1.5 (1.7)	1.5[i,j]
c-C_3H_6	750.3	$C_3H_7^+ + H_2O$	1.0	1.3 (1.5)	1.6[d], 1.5l[k]
C_3H_4 (propyne)	748	$C_3H_5^+ + H_2O$	1.0	1.7 (1.9)	1.1[l], 1.8[d]
C_3H_4 (allene)	775.3	$C_3H_5^+ + H_2O$	1.0	1.4 (1.6)	1.4[d]
C_4H_2 (diacetylene)	737.2	$C_4H_3^+ + H_2O$	1.0	1.6 (1.8)	
n-C_4H_{10}		$C_4H_{10}{\cdot}H_3O^+$	0.70	0.003 (1.8)	n.r.[m], <0.003[d]
		$C_4H_9^+ + H_2O + H_2$	0.30		
i-C_4H_{10}	677.8	$C_4H_{10}{\cdot}H_3O^+$	0.55	0.0042 (1.8)	n.r.[m], <0.004[d]
		$C_4H_9^+ + H_2O + H_2$	0.45		
C_4H_8 (2-butene)	747	$C_4H_9^+ + H_2O$	1.0	1.6 (1.8)	1.6[d]

n.r., no reaction.

[a] The rate coefficient is listed in units of 10^{-9} cm^3 s^{-1}.

[b] The calculated collision rate coefficients (in units of 10^{-9} cm^3 s^{-1}) are shown in parenthesis.

[c] Ref. [17].

[d] Ref. [18].

[e] Ref. [19].

[f] Ref. [20].

[g] Ref. [21] measured for the three body reaction in cm^6 s^{-1} units.

[h] Ref. [22].

[i] Ref. [23].

[j] Ref. [24].

[k] Ref. [25].

[l] Ref. [26].

[m] Ref. [8].

Table 2
Reactions of O_2^+ with the given hydrocarbon

Neutral	IP (eV)	Products	Branching ratio	Observed rate[a,b]	Previous measurements
CH_4	12.61	$CH_3O_2^+ + H$	1.0	0.005 (1.2)	0.0052[c], 0.005[d], 0.0063[e]
C_2H_6	11.52	$C_2H_6^+ + O_2$	0.30	1.1 (1.3)	1.2[f]
		$C_2H_5^+ + O_2 + H$	0.55		
		$C_2H_4^+ + O_2 + H_2$	0.15		
C_2H_4	10.51	$C_2H_4^+ + O_2$	1.0	1.0 (1.2)	0.68[g]
C_2H_2	11.40	$C_2H_2^+ + O_2$	1.0	1.1 (1.1)	
C_3H_8	10.94	$C_3H_8^+ + O_2$	0.30	1.4 (1.3)	1.4[f]
		$C_3H_7^+ + O_2 + H$	0.35		
		$C_2H_5^+ + O_2 + CH_3$	0.05		
		$C_2H_4^+ + O_2 + CH_4$	0.25		
C_3H_6 (propene)	9.73	$C_3H_6^+ + O_2$	1.0	1.3 (1.4)	
c-C_3H_6	9.86	$C_3H_6^+ + O_2$	0.95	1.3 (1.3)	0.9[h]
		$C_3H_5^+ + O_2 + H$	0.05		
C_3H_4 (propyne)	10.36	$C_3H_4^+ + O_2$	1.0	1.6 (1.6)	
C_3H_4 (allene)	9.69	$C_3H_4^+ + O_2$	1.0	1.3 (1.4)	
C_4H_2 (diacetylene)	10.17	$C_4H_2^+ + O_2$	1.0	1.4 (1.5)	
n-C_4H_{10}	10.57	$C_4H_{10}^+ + O_2$	0.25	1.4 (1.5)	2.0[f], 1.5[i]
		$C_4H_9^+ + O_2 + H$	0.05		
		$C_3H_7^+ + O_2 + CH_3$	0.65		
		$C_3H_6^+ + O_2 + CH_4$	0.05		
i-C_4H_{10}	10.68	$C_3H_7^+ + O_2 + CH_3$	0.45	1.5 (1.5)	1.5[i]
		$C_3H_6^+ + O_2 + CH_4$	0.55		
C_4H_8 (2-butene)	9.13	$C_4H_8^+ + O_2$	0.50	1.4 (1.5)	
		$C_3H_5^+ + O_2 + CH_3$	0.50		

[a] The rate coefficient is listed in units of 10^{-9} cm^3 s^{-1}.
[b] The calculated collision rate coefficient (in units of 10^{-9} cm^3 s^{-1}) are shown in parenthesis.
[c] Ref. [12].
[d] Ref. [11].
[e] Ref. [27].
[f] Ref. [28].
[g] Ref. [29].
[h] Ref. [30].
[i] Ref. [8].

Table 3
Reactions of NO^+ (IP = 9.264 eV) with the given hydrocarbon

Neutral	IP (eV)	Products	Branching ratio	Observed rate[a,b]	Previous measurements
CH_4	12.61	n.r.	–	<0.001 (1.2)	
C_2H_6	11.52	n.r.	–	<0.001 (1.3)	
C_2H_4	10.51	$C_2H_4{\cdot}NO^+$	1.0	<0.001 (1.3)	
C_2H_2	11.40	$C_2H_2{\cdot}NO^+$	1.0	<0.001 (1.2)	
C_3H_8	10.94	$C_3H_7^+ + HNO$	1.0	~0.001 (1.4)	<0.0001[c]
C_3H_6 (propene)	9.73	$C_3H_6{\cdot}NO^+$	1.0	0.063 (1.5)	
c-C_3H_6	9.86	$C_3H_6^+ + NO$	1.0	0.045 (1.3)	<0.05[d]
C_3H_4 (propyne)	10.36	$C_3H_4{\cdot}NO^+$	1.0	0.063 (1.6)	
C_3H_4 (allene)	9.69	$C_3H_4{\cdot}NO^+$	0.9	0.025 (1.4)	
		$C_3H_3^+ + HNO$	0.1		
C_4H_2 (diacetylene)	10.17	$C_4H_2{\cdot}NO^+$	1.0	0.1 (1.5)	
n-C_4H_{10}	10.57	$C_4H_9^+ + HNO$	1.0	~0.002 (1.5)	<0.002[c], n.r.[e]
i-C_4H_{10}	10.68	$C_4H_9^+ + HNO$	1.0	1.0 (1.5)	0.46[c], 0.9[e], 0.81[f,g]
C_4H_8 (2-butene)	9.13	$C_4H_8^+ + NO$	1.0	1.3 (1.5)	1.3[h], 1.4[i]

n.r., no reaction.
[a] The rate coefficient is listed in units of 10^{-9} cm^3 s^{-1}.
[b] The calculated collision rate coefficients (in units of 10^{-9} cm^3 s^{-1}) are shown in parenthesis.
[c] Ref. [31].
[d] Ref. [30].
[e] Ref. [8].
[f] Ref. [32].
[g] Ref. [33].
[h] Ref. [34].
[i] Ref. [35].

H_2O (=691 kJ mol^{-1}) exhibited a rapid proton transfer reaction at close to the collision rate. These hydrocarbons include propene, *c*-propane, propyne, allene, diacetylene and 2-butene. The small acyclic alkanes have low proton affinities and are all unreactive with H_3O^+ except for slow association in the case of the butanes that occurred in conjunction with formation of the stable *t*-butyl ion. We have found that association often occurs when proton transfer is close to thermoneutral or is endothermic. The rates of these association reactions appear to increase with the complexity of the hydrocarbon and can become equal the collision rate [8]:

$$H_3O^+ + i\text{-}C_4H_{10} \rightarrow C_4H_9^+ + H_2O + H_2 \quad (0.55), \quad \Delta H^\circ = -39.0\,\text{kJ mol}^{-1} \tag{1a}$$

$$\rightarrow C_4H_{10} \cdot H_3O^+ \quad (0.45) \tag{1b}$$

$$k = 4.2 \times 10^{-12}\,\text{cm}^3\,\text{s}^{-1}$$

Similarly ethene, for which proton transfer is about 10 kJ mol^{-1} endothermic, has a branching ratio of 20% to association. The remaining 80% is endothermic proton transfer. These results are similar to those reported in earlier studies [15–19].

With ethyne the adduct was the only product observed. All the larger unsaturated hydrocarbons, reacted with H_3O^+ via a rapid proton transfer channel to yield the protonated hydrocarbon ion and H_2O.

3.2. O_2^+ reactions

3.2.1. Acyclic and cyclic alkanes

The reaction of O_2^+ (generated by addition of moist air to a flowing afterglow) with methane, although very slow at room temperature, has been closely studied by Ferguson and coworkers in several laboratories [10–15]. The $CH_3O_2^+$ product of the reaction is known to have the structure of the hydroperoxy radical [11]. Channel 2b is exothermic by 288.6 kJ mol^{-1} and a small channel yielding this product could not be excluded from our results as the issue is clouded somewhat by very small amounts of CH_3^+ (formed by O_2^{+*} on CH_4) which reacted at the collision rate with CH_4 to make $C_2H_5^+$. We conclude that it is the $CH_3^+ + CH_4$ secondary process that is responsible for most, or all, of the product signal at $m/z = 29$:

$$O_2^+ + CH_4 \rightarrow CH_2OOH^+ + H, \quad \Delta H^\circ = -102.6\,\text{kJ mol}^{-1} \tag{2a}$$

$$\rightarrow (HCO^+ + H_2O + H), \quad \Delta H^\circ = -288.6\,\text{kJ mol}^{-1} \tag{2b}$$

The reactions with the larger alkanes are all rapid with charge transfer and dissociative charge transfer reactions as the major channels. Whereas only charge transfer was reported in one earlier study of the O_2^+ reaction with ethane and propane [28], we found that dissociative charge transfer accounted for ∼70% of all reactive collisions for both of these alkanes:

$$O_2^+ + C_2H_6 \rightarrow C_2H_6^+ + O_2 \quad (0.30), \quad \Delta H^\circ = -53\,\text{kJ mol}^{-1} \tag{3a}$$

$$\rightarrow C_2H_5^+ + HO_2 \quad (0.55), \quad \Delta H^\circ = -169\,\text{kJ mol}^{-1} \tag{3b}$$

$$\rightarrow C_2H_4^+ + O_2 + H_2 \quad (0.15), \quad \Delta H^\circ = -14\,\text{kJ mol}^{-1} \tag{3c}$$

$$k = 1.1 \times 10^{-9}\,\text{cm}^3\,\text{s}^{-1}$$

The neutral product leaving the complex in reaction (3b) has been shown as HO_2 and not $H + O_2$ as the reaction for the $H + O_2$ products is endothermic by 38 kJ mol^{-1}.

Similarly, the reaction with propane also yielded multiple channels:

$$O_2^+ + C_3H_8 \rightarrow C_3H_8^+ + O_2 \quad (0.30), \quad \Delta H^\circ = -109\,\text{kJ mol}^{-1} \tag{4a}$$

$$\rightarrow C_3H_7^+ + O_2 + H \quad (0.35), \quad \Delta H^\circ = -44\,\text{kJ mol}^{-1} \tag{4b}$$

$$\rightarrow C_2H_5^+ + O_2 + CH_3 \quad (0.05), \quad \Delta H^\circ = -13\,\text{kJ mol}^{-1} \tag{4c}$$

$$\rightarrow C_2H_4^+ + O_2 + CH_4 \quad (0.25), \quad \Delta H^\circ = -44\,\text{kJ mol}^{-1} \tag{4d}$$

$$k = 1.4 \times 10^{-9}\,\text{cm}^3\,\text{s}^{-1}$$

The rate coefficients observed for the butanes were in reasonable agreement with an earlier measurement [28]. The product distributions found here were similar to those reported by Spaněl and Smith who used a flow tube [8], but quite different from Matsuoka and Ikezoe who used X-ray pulse ionization and an ion trap in which they estimated non-dissociative charge transfer as 84% with a 15% channel to $C_3H_7^+$ [28]:

$$O_2^+ + n\text{-}C_4H_{10} \rightarrow C_4H_{10}^+ + O_2 \quad (0.25), \quad \Delta H^\circ = -153\,\text{kJ mol}^{-1} \tag{5a}$$

$$\rightarrow C_4H_9^+ + O_2 + H \quad (0.05), \quad \Delta H^\circ = -127\,\text{kJ mol}^{-1} \tag{5b}$$

$$\rightarrow C_3H_7^+ + O_2 + CH_3 \quad (0.65), \quad \Delta H^\circ = -11\,\text{kJ mol}^{-1} \tag{5c}$$

$$\rightarrow C_3H_6^+ + O_2 + CH_4 \quad (0.05), \quad \Delta H^\circ = -154\,\text{kJ mol}^{-1} \tag{5d}$$

$$k = 1.4 \times 10^{-9}\,\text{cm}^3\,\text{s}^{-1}$$

The only cyclic alkane studied was *c*-propane and again the results were similar to those reported by Spaněl and Smith [30] with rapid charge transfer being the dominant channel.

3.2.2. *Alkenes*

The reactions with O_2^+ are all fast, occurring at close to the collision rate. For ethene and propene, only non-dissociative charge transfer reactions were found but larger alkenes such as 2-butene exhibited dissociative charge transfer channels consistent with one other study of O_2^+ reactions of larger alkenes [8]:

$$O_2^+ + 2\text{-}C_4H_8 \rightarrow C_4H_8^+ + O_2 \quad (0.50), \quad \Delta H^\circ = -287\,\text{kJ mol}^{-1} \qquad (6a)$$

$$\rightarrow C_3H_5^+ + O_2 + CH_3 \quad (0.50), \quad \Delta H^\circ = -65\,\text{kJ mol}^{-1} \qquad (6b)$$

$$k = 1.4 \times 10^{-9}\,\text{cm}^3\,\text{s}^{-1}$$

3.2.3. *Alkynes*

The reactions of O_2^+ with the small alkynes (up to C_4) were similar to the alkenes in that they underwent fast non-dissociative charge transfer reactions.

3.3. *NO^+ reactions*

As noted earlier, the ionization potentials of almost all of the small hydrocarbons used in this work are larger than that of NO (IP = 9.264 eV) and consequently the reactivity was low for all hydrocarbons with the one exception of 2-butene. The reactivity of NO^+ when it occurred, was found to involve three mechanisms. Simple association (7a), charge transfer (7b), and hydride ion transfer (7c) although other mechanisms have been suggested for some organic halides and alcohols [32]:

$$NO^+ + MH \rightarrow NO \cdot MH^+ \qquad (7a)$$

$$\rightarrow MH^+ + NO \qquad (7b)$$

$$\rightarrow M^+ + HNO \qquad (7c)$$

The reactions with the C_1, C_2 and C_3 hydrocarbons were all slow, and only the reactions with *i*-butane and 2-butene proceeded at a significant fraction of the collision rate. As Table 3 shows, there is good agreement between these results and the few reactions that have been reported previously. The very slow reaction between NO^+ and propane is consistent with the reaction endothermicity of $\Delta H = 18.8\,\text{kJ mol}^{-1}$ assuming that the $C_3H_7^+$ ion product has the isopropyl structure. In contrast, *c*-propane has a lower IP and exhibits a faster reaction although its rate coefficient remains considerably less than the collision rate coefficient. We have assumed that ring opening occurs in the process of charge transfer and that the product ion has the propene structure:

$$NO^+ + c\text{-}C_3H_6 \rightarrow C_3H_6^+ + NO \quad (1.0), \quad \Delta H^\circ = 11.9\,\text{kJ mol}^{-1} \qquad (8)$$

There is an interesting distinction between the reactions of *n*- and *i*-butane. The reaction for *i*-butane (2-methyl propane) occurs at close to the collision rate whereas the reaction for *n*-butane is scarcely reactive:

$$NO^+ + i\text{-}C_4H_{10} \rightarrow C_4H_9^+ + HNO, \quad \Delta H^\circ = -55.9\,\text{kJ mol}^{-1} \qquad (9)$$

$$k = 1.0 \times 10^{-9}\,\text{cm}^3\,\text{s}^{-1}$$

$$NO^+ + n\text{-}C_4H_{10} \rightarrow C_4H_9^+ + HNO, \quad \Delta H^\circ = -63.8\,\text{kJ mol}^{-1} \qquad (10)$$

$$k \sim 2 \times 10^{-12}\,\text{cm}^3\,\text{s}^{-1}$$

The *t*-butyl structure has been assumed for $C_4H_9^+$. Clearly there is a barrier to reaction operating in the *n*-butane reaction that is absent in *i*-butane and that is presumably related to the ease of isomerisation to the $C_4H_9^+$ ion.

4. Application to monitoring of small atmospheric hydrocarbons by SIFT-MS

The suitability of a precursor ion for analysis of a particular analyte depends on both the rate and the number of product channels of the reaction between the two. Ideally a precursor ion will react rapidly (at or near the collision rate) with the analyte neutral to yield a single ion product that does not react further in the conditions of the flow tube. Since all the precursor and product channels of a given analyte must be monitored to obtain a quantitative measurement of the analyte concentration, the fewer active species that must be counted, the more straightforward is the analysis.

In the case of most volatile organic compounds, especially those with hetero-atoms, H_3O^+ is a natural choice for a precursor since it reacts rapidly by proton transfer to yield only one primary product. However, the use of H_3O^+ can lead to complications where the analyte gas stream is wet since water clusters form and these clusters complicate the analysis through switching reactions [36]. Further, as the data in Table 1 shows, for small hydrocarbons H_3O^+ is not an attractive choice as a precursor ion since it reacts only very slowly with the small saturated species and quite slowly with the smaller unsaturated species ethene, and ethyne.

O_2^+ satisfies the primary criterion for suitability as a precursor agent for *small* hydrocarbons as it reacts rapidly with all the hydrocarbon species except methane. Even the reaction with methane proceeds at a measurable rate however. A further advantage of O_2^+ as a precursor ion is that the additional complication of water cluster formation experienced with H_3O^+ is absent. (Compare Fig. 1A and B). Although small signals of water cluster ions are present in the O_2^+ mass spectrum, their amounts do not complicate the analysis. This advantage is however somewhat offset in the case of saturated hydrocarbons by the tendency of O_2^+ to produce dissociative ionisation, causing the collision complex

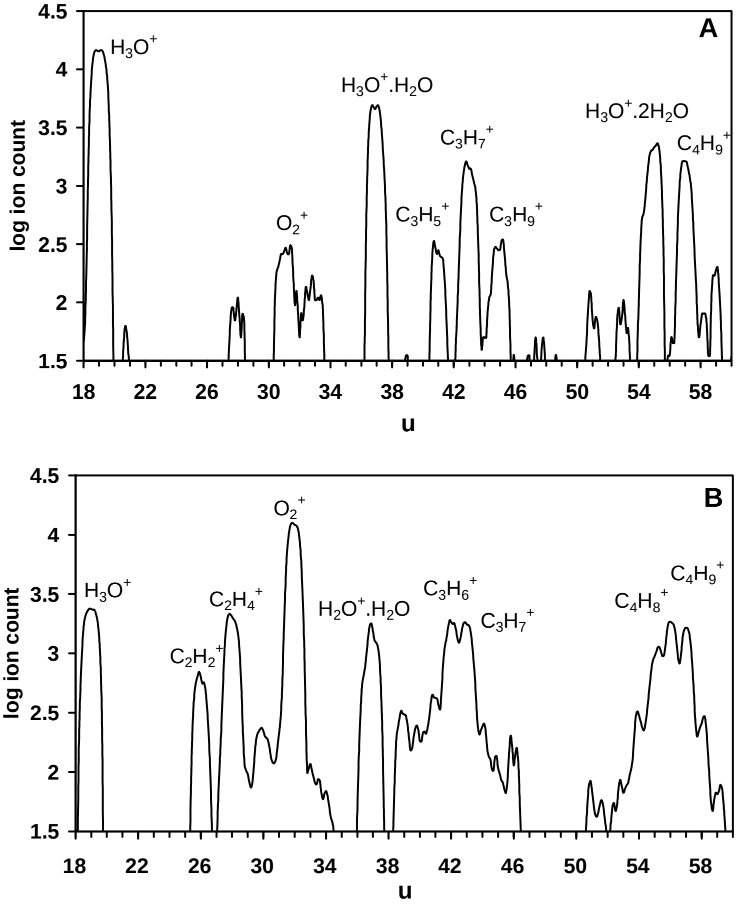

Fig. 1. The chemical ionisation spectra of the exhaust gases from a petrol combustion engine shortly after start-up are shown up to $m/z = 60$. (A) The mass spectrum for H_3O^+ and (B) the mass spectrum for O_2^+.

to fragment via a number of different channels. Not surprisingly certain stable hydrocarbon cations are favoured in these fragmentation processes. For example, $C_3H_7^+$ is formed from the dissociative charge transfer of O_2^+ with the three small hydrocarbons, propane, *n*-butane and *i*-butane. This tendency for several different analytes to yield common product ions complicates the analysis of hydrocarbon mixtures.

NO^+, the third precursor ion used was generally unreactive with the hydrocarbon neutrals in this study as previously discussed. The only reactions of NO^+ that proceeded at a significant fraction of the collision rate were the hydride ion transfer reaction with *i*-butane and the charge transfer reaction with 2-butene. With C_1 and C_2 hydrocarbons no reaction rate could be measured, and with the C_3 hydrocarbons the rates were less than 10% of the collision rate. Although NO^+ has an advantage in that the reactions of water clusters do not complicate the kinetic analysis of trace components in ambient (moist) air, the slow rates of its reactions with the small hydrocarbons studied here rule NO^+ out as a precursor ion for the analysis of hydrocarbon mixtures.

To demonstrate the applicability of the SIFT-MS technique to the monitoring of small hydrocarbons in air, we refer to Fig. 1A and B that examine the exhaust gases from a petrol combustion engine. This engine was sampled shortly after a cold start up and did not contain a catalytic converter. A similar analysis of larger hydrocarbons has been presented by Smith et al. who sampled the exhaust gases of a warm engine containing a catalytic converter [37]. The two spectra shown exhibit the product ions from H_3O^+ in Fig. 1A and O_2^+ in Fig. 1B from the *same* gas sample, stored in a mylar bag. In each case the analyser mass spectrometer was scanned up to $m/z = 60$. The concentrations of hydrocarbons in the sample were above the limit for quantitative analysis using the capillary in our instrument. Nevertheless, the superior diagnostics of O_2^+ over H_3O^+ are clearly seen in that the signals from $C_2H_2^+$ (26) and $C_2H_4^+$ (28) present in Fig. 1B and that arise from fast charge transfer reactions of O_2^+, are absent in Fig. 1A because the corresponding reactions of H_3O^+ with the hydrocarbon are much slower. What is also worth noting is that the O_2^+ spectrum in Fig. 1B shows the presence of both 2-butene in the mixture from the $C_4H_8^+$ signal at $m/z = 56$ and the butanes at $m/z = 57$. In contrast, H_3O^+ cannot distinguish between these species as the product of both hydrocarbons with H_3O^+ in Fig. 1A is $C_4H_9^+$ at $m/z = 57$. Similarly the O_2^+ precursor distinguishes between *c*-propane and other hydrocarbons as it produces a $C_3H_6^+$ signal at $m/z = 44$ whereas H_3O^+ reacts with cyclopropane to give only a $C_3H_7^+$ signal at $m/z = 43$. What is also evident from a comparison of the two spectra is the presence of acetaldehyde seen in Fig. 1A as a signal at $m/z = 45$ ($C_2H_5O^+$) and in Fig. 1B as a contributor to the signals at $m/z = 43$ ($C_2H_3O^+$) and 44 ($C_2H_4O^+$). Acetaldehyde is a species known to arise from the combustion of petroleum products [38,39]. The levels of hydrocarbons from the exhaust in the bag were at the ppm level and were sufficiently high to cause some minor secondary chemical processing, but these levels were insufficient to alter the conclusions drawn.

5. Conclusions

The reaction rate coefficients and branching ratios for the ions H_3O^+, O_2^+ and NO^+ with a series of C_1–C_4 hydrocarbon ions have been measured using the SIFT technique. The reactions are observed to follow predictable pathways with H_3O^+ exhibiting proton transfer and association reactions, O_2^+ charge transfer and dissociative charge transfer reactions and NO^+ being largely unreactive with C_1–C_3 hydrocarbons. An unusual feature of the reactions of NO^+ with the butanes is that the isomeric butanes are easily distinguished by their reactions: *n*-butane reacts very slowly whereas *i*-butane exhibits a rapid reaction that occurs at a substantial fraction of the collision rate. The application of these measurements via chemical ionisation to analysing the composition of vehicle exhaust emissions, showed O_2^+ to be more useful at identifying small hydrocarbons than either H_3O^+ or NO^+. These findings are consistent with the ion chemistry reported in this study. It is also evident that for complex mixtures, analysis by a single precursor ion is not sufficient for identification of the analytes present.

Acknowledgements

We thank the Marsden Fund for their financial support of this work. PFW also thanks the Marsden Fund for the award of a postdoctoral fellowship.

References

[1] M.S.B. Munson, F.H. Field, J. Am. Chem. Soc. 88 (1966) 2621.
[2] M.S.B. Munson, F.H. Field, J. Am. Chem. Soc. 88 (1966) 4337.
[3] M.S.B. Munson, F.H. Field, J. Am. Chem. Soc. 89 (1967) 1047.
[4] A.G Harrison, Chemical Ionisation Mass Spectrometry, 2nd ed., CRC Press, Boca Raton, FL, 1992.
[5] W. Lindinger, A. Hansel, A. Jordan, Int. J. Mass Spectrom. Ion Process. 173 (1998) 191.
[6] P. Španěl, D. Smith, Med. Biol. Eng. Comput. 34 (1996) 409.
[7] D. Smith, P. Španěl, SIFT applications in mass spectrometry, in: J. Lindon, G. Tranter, J. Holmes (Eds.), Encyclopedia of Spectroscopy and Spectrometry, Mass Spectrometry, Academic Press, London, 1999, p. 2092.
[8] P. Španěl, D. Smith, Int. J Mass Spectrom. Ion Process. 181 (1998) 1.
[9] D.B. Milligan, D.A. Fairley, C.G. Freeman, M.J. McEwan, Int. J. Mass Spectrom. 202 (2000) 351.
[10] E.E. Ferguson, in: P. Ausloos, S.G. Lias (Eds.), Structure, Reactivity and Thermochemistry of Ions, D. Reidel Publ. Co., 1987, p. 81.
[11] J.M. Van Doren, S.E. Barlow, C.H. DePuy, V.M. Bierbaum, I. Dotan, E.E. Ferguson, J. Phys. Chem. 90 (1986) 2772.
[12] S.E. Barlow, J.M. Van Doren, C.H. DePuy, V.M. Bierbaum, I. Dotan, E.E. Ferguson, N.G. Adams, D. Smith, B.R. Rowe, J.B. Marquette, G. Dupeyrat, M. Durup-Ferguson, J. Chem. Phys. 85 (1986) 3851.
[13] H. Bohringer, M. Durup-Ferguson, D.W. Fahey, F.C. Fehsenfeld, E.E. Ferguson, J. Chem. Phys. 79 (1983) 4201.
[14] M. Durup-Ferguson, H. Bohringer, D.W. Fahey, F.C. Fehsenfeld, E.E. Ferguson, J. Chem. Phys. 81 (1984) 2657.
[15] W. Lindinger, D.L. Albritton, M. McFarland, F.C. Fehsenfeld, A.L. Schmeltekopf, E.E. Ferguson, J. Chem. Phys. 62 (1975) 4101.
[16] J. Glosik, A.B. Rakshit, N.D. Twiddy, N.G. Adams, D. Smith, J. Phys. B. Atom. Mol. Phys. 11 (1978) 3365.
[17] D.K. Bohme, G.I. Mackay, J. Am. Chem. Soc. 103 (1981) 2173.
[18] D.B. Milligan, P.F. Wilson, C.G. Freeman, M. Meot-Ner, M.J. McEwan, J. Phys. Chem. A 106 (2002) 9745.
[19] D.A. Fairley, G.B.I. Scott, C.G. Freeman, R.G.A.R. Maclagan, M.J. McEwan, J. Phys. Chem. A 101 (1997) 2848.
[20] K.K. Matthews, N.G. Adams, N.D. Fisher, J. Phys. Chem. A 101 (1997) 2841.
[21] E. Herbst, D. Smith, N.G. Adams, B.J. McIntosh, J. Chem. Soc. Faraday Trans. 2 (85) (1989) 1655.
[22] D.A. Fairley, G.B.I. Scott, C.G. Freeman, R.G.A.R. Maclagan, M.J. McEwan, J. Chem. Soc. Faraday Trans. 92 (1996) 1305.
[23] D.K. Bohme, G.I. Mackay, S.D. Tanner, J. Am. Chem. Soc. 101 (1979) 3724.
[24] G.I. Mackay, M.H. Lien, A.C. Hopkinson, D.K. Bohme, Can. J. Chem. 56 (1978) 131.
[25] P. Španěl, D. Smith, Int. J. Mass Spectrom. Ion Process. 145 (1995) 177.
[26] S. Dheandhanoo, L. Forte, A. Fox, D.K. Bohme, Can. J. Chem. 64 (1986) 641.
[27] N.G. Adams, D. Smith, J.F. Paulson, J. Chem. Phys. 72 (1980) 288.
[28] S. Matsuoka, Y. Ikezoe, J. Phys. Chem. 92 (1988) 1126.
[29] A.B. Rakshit, Int. J. Mass Spectrom. Ion Process. 69 (1986) 45.
[30] P. Španěl, D. Smith, J. Chem. Phys. 104 (1996) 1893.
[31] S.K. Searles, L.W. Sieck, J. Chem. Phys. 53 (1970) 794.
[32] A.D. Williamson, J.L. Beauchamp, J. Am. Chem. Soc. 97 (1975) 5714.
[33] S.G. Lias, J.R. Eyler, P. Ausloos, Int. J. Mass Spectrom. Ion Phys. 19 (1976) 219.
[34] C.G. Beggs, C.H. Kuo, T. Wyttenbach, P.R. Kemper, M.T. Bowers, Int. J. Mass Spectrom. Ion Process. 100 (1990) 397.
[35] A.J. Midey, S. Williams, A.A. Viggiano, J. Phys. Chem. A 105 (2001) 1574.
[36] P. Španěl, D. Smith, Rapid Commun. Mass Spectrom. 14 (2000) 1898.
[37] D. Smith, P. Cheng, P. Španěl, Rapid Commun. Mass Spectrom. 16 (2002) 1124.
[38] R. Guichert, Sci. Total Environ. 205 (1997) 201.
[39] B. Zielinska, J.C. Sagebiel, G. Harshfield, A.W. Gertler, W.R. Pierson, Atmos. Environ. 30 (1996) 2269.