Characterization of Long-Chain Carboxylic Esters with $\text{CH}_3\text{OBOCH}_3^+$ in a Small Fourier-Transform Ion Cyclotron Resonance Mass Spectrometer

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The usefulness of $\text{CH}_3\text{OBOCH}_3^+$ as a chemical ionization reagent was examined by allowing the ion to react with carboxylic esters of various chain lengths in a small Fourier-transform ion cyclotron resonance mass spectrometer equipped with a permanent magnet. $\text{CH}_3\text{OB-OCH}_3^+$ is a strong electrophile and readily abstracts an oxygen-containing group from the carboxylic esters. Long-chain esters exclusively lose the alkoxide moiety to give the acylium ion. The same reaction was observed for saturated, unsaturated, branched and cyclic esters. In each case, the acylium ion reacts further with a neutral ester molecule by proton transfer to yield the protonated ester as a secondary product. This remarkably simple product distribution reveals the molecular weight of the ester, the chain length of its acid moiety, and the degree of unsaturation in the acid and alcohol moieties. © 1996 American Society for Mass Spectrometry (*J Am Soc Mass Spectrom* 1996, 7, 1138–1143)

Long-chain carboxylic esters are becoming increasingly important in many areas of research and industry. For example, they are components of many industrial products, such as cosmetics, lubricants, and flavorings [1]. Furthermore, these compounds are frequently found in fossil fuels and in polluted atmospheres, and therefore play a notable role in environmental studies [1]. Obviously, it is important to be able to readily identify long-chain carboxylic esters.

Mass spectrometry is an ideal tool for the analysis of unknown organic compounds. However, electron ionization mass spectrometry does not provide adequate structural information for unknown long-chain carboxylate esters because the molecular ions frequently are not evident in the spectra and because structurally characteristic fragment ions are often difficult to distinguish from numerous other fragments that also are formed [2]. Similarly, traditional chemical ionization of long-chain carboxylate esters produces several different ions from which structural information, such as chain length, may be difficult to extract [2–8]. Furthermore, the relative abundances of the product ions vary with the chain length of the ester [7]. Collision-activated dissociation (CAD) is generally a useful tool for ion structure determination. However, this method yields complicated spectra for long-chain

carboxylate esters [9], the fragments formed are often the same for esters with different structures [10–12], and the molecular ions have been suggested to isomerize in tandem mass spectrometers after generation and before CAD [13].

The fragment ion $\text{CH}_3\text{OBOCH}_3^+$ (m/z 73) formed upon electron ionization of trimethyl borate was found earlier to be highly reactive toward neutral molecules with oxygen-containing functional groups [14]. The driving force in these reactions is the formation of the strong boron–oxygen bond. The results reported here demonstrate that $\text{CH}_3\text{OBOCH}_3^+$ reacts with long-chain carboxylate esters to give only a few ionic products. These products yield valuable structural information for the esters. Hence, $\text{CH}_3\text{OBOCH}_3^+$ provides an ideal chemical ionization reagent for the mass spectrometric analysis of carboxylate esters.

Experimental Section

All experiments were carried out in a Finnigan FT/MS (Madison, WI) custom-built Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer, which has been described in detail previously [15]. This instrument is comprised of a single cubic cell (approximately 27 cm^3) housed within the bore of a 0.4-T permanent magnet. The vacuum chamber is pumped with an Alcatel (Hingham, MA) 300 L/s diffusion pump to a nominal base pressure of $\leq 2 \times 10^{-9}$ torr. The instrument is controlled with an FTMS 1000 data

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station and a SWIFT module (Finnigan FT/MS).

Experiments were performed with the cell either unscreened or with grounded screens placed directly in front of the trapping plates [15, 16]. The screens consist of 0.001-gauge tungsten wire woven to make a mesh of either 3.1 or 4.3 wires per centimeter in both the x - and the y -directions (the x, y plane is defined as the plane that is perpendicular to the magnetic field lines). The screens decrease the electric field gradients caused by the trapping plates held at 1–3 V [16]. As a result, space-charge effects in the FT-ICR cell are reduced [16].

Before trimethyl borate was introduced into the instrument through a pulsed-valve setup that consists of a reservoir attached to two General Valve Corporation (Fairfield, NJ) pulsed valves, the sample was degassed several times by freezing with liquid N_2 , pumping away the air, and allowing the sample to

warm up to room temperature. Trimethyl borate was then pulsed into the instrument at a maximum nominal pressure of 1×10^{-6} torr in the cell as read by an MKS Instruments (Andover, MA) type 290 ion gauge [500 mtorr in the pulsed valve reservoir as read by a Granville-Phillips (Boulder, CO) 275 convection gauge]. The esters were introduced into the cell at a nominal stationary pressure of 5.0×10^{-8} torr by using a custom-built batch inlet system equipped with a Varian variable leak valve (Varian Associates, Walnut Creek, CA).

Electron ionization of trimethyl borate yielded $CH_3OBOCH_3^+$. The emission current (3–8 μA), electron kinetic energy (50–70 eV), and electron beam duration (15–70 ms) were optimized for maximum signal for each experiment. A delay of at least 200 ms preceded the ionization event to ensure that the pressure of the trimethyl borate had reached the maximum

Table 1. Reactions of $CH_3OBOCH_3^+$ with various methyl and ethyl carboxylic acid esters

Ester		Ionic products	Branching ratios of primary products (%)
Methyl acetate	m/z 43	Acylium ion	70
MW 74	m/z 75	Protonated ester	
	m/z 105	$(CH_3O)_2B(HOCH_3)^+$	15
	m/z 147	Adduct	15
Ethyl acetate	m/z 43	Acylium ion	46
MW 88	m/z 89	Protonated ester	
	m/z 119	$(CH_3O)_2B(HOCH_2CH_3)^+$	44
	m/z 133	Loss of ethylene from Adduct	10
Methyl propanoate	m/z 57	Acylium ion	100
MW 88	m/z 89	Protonated ester	
Methyl cyclopropane-carboxylic acid	m/z 69	Acylium ion	100
MW 100	m/z 101	Protonated ester	
Ethyl propanoate	m/z 57	Acylium ion	100
MW 102	m/z 103	Protonated ester	
Methyl 2-methylbutyrate	m/z 85	Acylium ion	100
MW 116	m/z 117	Protonated ester	
Methyl hexanoate	m/z 99	Acylium ion	100
MW 130	m/z 131	Protonated ester	
Ethyl 2-methyl-4-pentenoate	m/z 97	Acylium ion	100
MW 142	m/z 143	Protonated ester	
Ethyl 4-methyl-4-pentenoate	m/z 97	Acylium ion	100
MW 142	m/z 143	Protonated ester	
Ethyl <i>trans</i> -3-hexenoate	m/z 97	Acylium ion	100
MW 142	m/z 143	Protonated ester	
Methyl octanoate	m/z 127	Acylium ion	100
MW 158	m/z 159	Protonated ester	
Ethyl octanoate	m/z 127	Acylium ion	100
MW 172	m/z 173	Protonated ester	
Methyl decanoate	m/z 155	Acylium ion	100
MW 186	m/z 187	Protonated ester	

in the cell before ionization. After ionization, the neutral trimethyl borate was pumped away. The reactant ion $\text{CH}_3\text{OBOCH}_3^+$ was cooled for at least 100 ms by allowing it to collide with the neutral ester present in the cell. This delay also permitted the neutral trimethyl borate to be pumped away. The ion was isolated by ejection of all other ions from the cell through the application of one or several stored-waveform inverse Fourier-transform voltage pulses [17] and/or a sequence of rf sweeps to the excitation plates of the cell. The isolated ion was allowed to react with an ester for a variable period of time.

All the spectra shown are the average of at least 50 acquisitions obtained by using chirp detection with an excitation sweep of $54\text{-V}_{\text{p-p}}$ amplitude, 381-kHz bandwidth, and $1.2\text{-kHz}/\mu\text{s}$ sweep rate. The spectra were recorded as 32k data points, subjected to one zero fill before Fourier transformation and background corrected by using a previously described procedure [18]. Plots of $\ln(\text{relative ion abundance})$ as a function of the reaction time were constructed for each reaction to verify that the reactions follow the expected pseudo-first-order kinetics and to identify primary product ions (constant branching ratios at short reaction times).

All the reagents were purchased from Aldrich Chemical Co. (Milwaukee, WI) and were used as received from the manufacturer. The purity of all reagents was verified by gas chromatography and mass spectrometry.

Results and Discussion

The gas-phase reactions of $\text{CH}_3\text{OBOCH}_3^+$ with various methyl and ethyl carboxylate esters (Table 1) were examined in a small Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer based on a 0.4-T permanent magnet. In this mass spectrometer, ion-molecule reactions can be investigated without the complication of interfering reactions that involve the neutral precursor of the reactant ion. This ability was crucial in the present study because $\text{CH}_3\text{OBOCH}_3^+$ reacts quickly with neutral trimethyl borate [mainly to produce an ion of m/z 177 that is likely to have the structure $(\text{CH}_3\text{O})_2\text{B-O}^+(\text{CH}_3)\text{B}(\text{OCH}_3)_2$]. Interference from this reaction was avoided by pulsing trimethyl borate into the cell *prior* to the electron ionization event and by pumping it away immediately after ionization and before examining reactions of $\text{CH}_3\text{OBOCH}_3^+$ (Figure 1a). The reactant ion $\text{CH}_3\text{OBOCH}_3^+$ was isolated by ejection of all other ions from the cell (m/z 73; Figure 1b) and allowed to react with each ester for a variable period of time (for an example, see Figure 1c). The ionic products of the reactions studied are shown in Table 1.

The observed linear decrease of the natural logarithm of the relative abundance of the ion $\text{CH}_3\text{OBOCH}_3^+$ as a function of time (see Figure 2 for an example) indicates that the reactant ion was cooled properly before each reaction (i.e., hot ions that react at

Figure 1. (a) Electron ionization of $(\text{CH}_3\text{O})_3\text{B}$ (MW 104). (b) Isolation of the fragment ion $\text{CH}_3\text{OBOCH}_3^+$ (m/z 73). (c) Reaction of the ion $\text{CH}_3\text{OBOCH}_3^+$ for 1 s with methyl decanoate (MW 186; uncorrected pressure 4.0×10^{-8} torr). The only primary product is the acylium ion (m/z 155).

a faster rate at short reaction times were not observed) and that all the reactions studied follow the expected pseudo-first-order kinetics. Further examination of these rate plots allowed the distinction between primary and secondary reaction products. For example, the ion of m/z 187 in Figure 2 is identified as a secondary product because its relative abundance becomes greater than that of m/z 155 only at longer reaction times.

Reaction of $\text{CH}_3\text{OBOCH}_3^+$ with esters other than the acetates yields the acylium ion as the exclusive primary product (for examples, see Figure 3). Hence, the measurement of the mass-to-charge ratio of the only product ion formed at short reaction times reveals the molecular weight of the acid moiety of the ester. The reaction likely is initiated by attack of $\text{CH}_3\text{OB-OCH}_3^+$ at the alkoxy oxygen of the ester to form a short-lived adduct (the adduct was not observed in most reaction spectra) which decomposes by cleavage

Figure 2. Temporal variation of the ion abundances for the reaction of $\text{CH}_3\text{OBOCH}_3^+$ (m/z 73) with methyl decanoate (MW 186; uncorrected pressure 4.0×10^{-8} torr). The only primary product is the acylium ion (m/z 155). The protonated ester (m/z 187) appears as a secondary product.

of the $\text{C}(\text{O})\text{—O}$ bond to form the acylium ion. This ion transfers a proton to another ester molecule to generate the protonated ester as the only secondary product. Measurement of the mass-to-charge ratio value of the protonated ester formed at longer reaction times indirectly reveals the molecular weight of the ester. All the foregoing information then also reveals the molecular weight of the alcohol moiety.

Acetate esters differ from the other esters in that they yield other products in addition to the acylium ion and the protonated ester. $\text{CH}_3\text{OBOCH}_3^+$ abstracts methanol from methyl acetate and ethanol from ethyl acetate to yield protonated trimethyl borate and protonated ethyl dimethyl borate, respectively, by the loss of ketene (Scheme Ia). Ethyl acetate also loses ethylene from the collision complex with $\text{CH}_3\text{OBOCH}_3^+$ to form an acetic acid-dimethoxyborocation adduct (Scheme Ic). The same products were observed for ethyl acetate in *prior* work conducted by using a different instrument—a dual-cell 3.0-T FT-ICR mass spectrometer [14].

The absence of protonated trimethyl borate and protonated ethyl dimethyl borate in the reaction spectra of the longer-chain esters indicates that for these esters, loss of ketene from the adduct cannot effectively compete with the acylium ion formation. Hence, we propose that, in contrast to a mechanism presented

Figure 3. Reaction of $\text{CH}_3\text{OBOCH}_3^+$ (m/z 73) (a) for 500 ms with methyl octanoate (MW 158; uncorrected pressure 4.0×10^{-8} torr), (b) for 1 s with methyl hexanoate (MW 130; uncorrected pressure 4.5×10^{-8} torr), and (c) 2.5 s with ethyl octanoate (MW 172; uncorrected pressure 4.0×10^{-8} torr). The only observed primary products are the acylium ions (m/z 127, 99, and 127, respectively). The protonated esters appear as secondary products (m/z 159, 131, and 173, respectively).

earlier for ethyl acetate [14], the acylium ion formation generally occurs by a simple C—O bond cleavage in the adduct formed upon addition of the alkoxy oxygen of the ester to $\text{CH}_3\text{OBOCH}_3^+$ (as illustrated for ethyl acetate in Scheme Ia). Loss of ketene (to form protonated trimethyl or ethyl dimethyl borate) requires proton transfer from the initially generated acylium ion to the borate ester before decomposition of the complex (Scheme Ib). Hence, the simple C—O bond cleavage dominates if the complex is hot, that is, if the formation of the acylium ion is highly exothermic.

The exothermicity of the acylium ion formation increases drastically with the size of the acid moiety of the ester [14, 19, 20]. For example, the exothermicity associated with the formation of the acylium ion is estimated to be 1.4–2.4 kcal/mol for the simple acetates ($\Delta H_{rxn}[\text{CH}_3\text{COOCH}_3 + \text{CH}_3\text{OBOCH}_3^+ \rightarrow$

$\text{CH}_3\text{CO}^+ + \text{B}(\text{OCH}_3)_3 = -2.4$ kcal/mol; $\Delta H_{r,n}[\text{CH}_3\text{COOCH}_2\text{CH}_3 + \text{CH}_3\text{OBOCH}_3^+ \rightarrow \text{CH}_3\text{CO}^+ + (\text{CH}_3\text{O})_2\text{B}(\text{OCH}_2\text{CH}_3)] = -1.4$ kcal/mol), but 11.4–12.4 kcal/mol for the simple propanoates ($\Delta H_{r,n}[\text{CH}_3\text{CH}_2\text{COOCH}_3 + \text{CH}_3\text{OBOCH}_3^+ \rightarrow \text{CH}_3\text{CH}_2\text{CO}^+ + \text{B}(\text{OCH}_3)_3] = -12.4$ kcal/mol; $\Delta H_{r,n}[\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + \text{CH}_3\text{OBOCH}_3^+ \rightarrow \text{CH}_3\text{CH}_2\text{CO}^+ + (\text{CH}_3\text{O})_2\text{B}(\text{OCH}_2\text{CH}_3)] = -11.4$ kcal/mol). Hence, esters with acyl chains of three or more carbons are not expected to generate protonated alkyl dimethyl borate, in spite of the fact that also ketene loss becomes more exothermic as the acyl chain length of the ester increases ($\Delta H_{r,n}[\text{CH}_3\text{COOCH}_3 + \text{CH}_3\text{OBOCH}_3^+ \rightarrow \text{CH}_2\text{CO} + (\text{CH}_3\text{O})_2\text{B}(\text{HOCH}_3)^+] = -1.1$ kcal/mol; $\Delta H_{r,n}[\text{CH}_3\text{COOCH}_2\text{CH}_3 + \text{CH}_3\text{OBOCH}_3^+ \rightarrow \text{CH}_2\text{CO} + (\text{CH}_3\text{O})_2\text{B}(\text{HOCH}_2\text{CH}_3)^+] = -3.8$ kcal/mol; $\Delta H_{r,n}[\text{CH}_3\text{CH}_2\text{COOCH}_3 + \text{CH}_3\text{OBOCH}_3^+ \rightarrow \text{CH}_3\text{CHCO} + (\text{CH}_3\text{O})_2\text{B}(\text{HOCH}_3)^+] = -9.7$ kcal/mol; $\Delta H_{r,n}[\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + \text{CH}_3\text{OBOCH}_3^+ \rightarrow \text{CH}_3\text{CHCO} + (\text{CH}_3\text{O})_2\text{B}(\text{HOCH}_2\text{CH}_3)^+] = -12.4$ kcal/mol). The preceding numbers show that the formation of the acylium ion is nearly thermoneutral for the acetate esters. Hence, the complex formed upon this reaction has a longer lifetime than in the case of the long-chain esters. This lifetime is long enough for some of the acylium ions to transfer a proton to the neutral borate and to form protonated trimethyl or ethyl dimethyl borate (Scheme Ib).

Ethyl acetate alone loses ethylene from the adduct with $\text{CH}_3\text{OBOCH}_3^+$ to form an acetic acid–dimethoxyborocation complex (Scheme Ic). This is the only observed reaction that takes place via the thermodynamically favored adduct of $\text{CH}_3\text{OBOCH}_3^+$ and the ester carbonyl oxygen rather than the alkoxy oxygen (which

leads to formation of the acylium ion). For methyl esters, this more stable adduct has no thermodynamically accessible exit channels except dissociation back to the reactants. Hence, methyl acetate, for example, cannot undergo reactions via the more stable adduct. For the ethyl esters, cleavage of ethylene can occur, but this requires rearrangement via a tight transition state. This process must be too slow to compete with the acylium ion formation when the latter reaction is highly exothermic, as is the case for esters other than the acetates.

Conclusions

Ionization of long-chain carboxylate esters with $\text{CH}_3\text{OBOCH}_3^+$ results in remarkably simple but structurally informative mass spectra. The product distributions consist of only one primary product ion—the acylium ion—and only one secondary product ion—the protonated ester—regardless of unsaturation or branching present in the acyl chain of the ester. The chain lengths of the acid and alcohol moieties, the degree of unsaturation in each, and the molecular weight of the ester can be derived from the mass-to-charge ratios of the two product ions. However, the nature and location of unsaturation and branching points cannot be resolved from these data alone. In spite of this limitation, the use of $\text{CH}_3\text{OBOCH}_3^+$ provides a promising new chemical ionization method for the mass spectrometric analysis of long-chain carboxylate esters. The analysis is readily carried out in a simple permanent magnet-based Fourier-transform ion cyclotron resonance mass spectrometer.

Scheme I

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