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C−F Bond Cleavage by Mass-Selected Free Radicals at Fluorinated Self-Assembled Monolayer Surfaces

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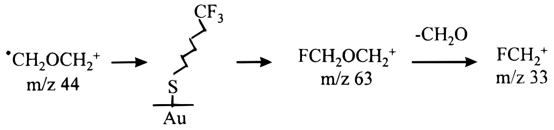
Reactions of gas-phase free radicals with surfaces occur in various technological processes. These include plasma etching,[1] deposition of thin films,[2,3] enhanced surface adhesion,[4] and plasma-enhanced chemical vapor deposition.[5] Plasma technology used in semiconductor and polymer processing is typical of the state of the science in many of these areas in that it is empirically based and there is limited information on the underlying processes. Even the chemical identity of key reactive species is often unknown.[6] Tandem mass spectrometry has been used for more than a decade to study the reactions of ions of defined structure and translational energy with well-characterized surfaces.[7] We now extend this approach to examine free radical/surface reactivity. We use charged radicals (distonic ions[8]) and fluorinated self-assembled monolayer (F-SAM) surfaces to show that C−F bonds can be cleaved by chemical reactions with carbon-centered radicals at low collision energy. The activation of C−F bonds is one of the most challenging problems in chemistry[9] and several investigators are exploring gaseous ion reagents for this purpose.[7a,10]

The charged radicals $^{\bullet}CH_2OCH_2^+$ (**1**) and $^{\bullet}CH_2CH_2OCH_2^+$ (**2a**) (and the deuterated form $^{\bullet}CD_2CD_2OCD_2^+$ (**2b**)) were generated by 70 eV EI upon 1,3-dioxalane, 1,4-dioxane, and d_8-1,4-dioxane, respectively. Gas-phase studies show that $^{\bullet}CH_2CH_2OCH_2^+$ can abstract $CH_3S^{\bullet}$ from CH_3SSCH_3,[11] and $^{\bullet}CH_2OCH_2^+$ can abstract methylene from ketene.[12] The corresponding ions $CH_3CH_2OCH_2^+$ and $CH_3OCH_2^+$ do not react in these ways, indicating that the distonic ion chemistry is dominated by the radical center.[13,14] Because distonic ions are also distonic radicals, they can be used to explore the surface reactivity of free radicals. The effects of collision energy are then conveniently investigated by mass spectrometry and the reactions of α- and β-distonic ions with F-SAM surfaces[15] were studied with these objectives.

Collision of the radical $^{\bullet}CH_2OCH_2^+$ with the F-SAM surface[16] at very low energy (18 eV) yields only two products, CH_2F^+(*m/z* 33) and $FCH_2OCH_2^+$(*m/z* 63). The latter product, even though present in very low abundance, is clearly indicative of a free radical abstraction reaction. The radical/surface reaction involves C−F bond cleavage in the surface-bound fluorocarbon chain, formation of a new bond between the fluorine atom and the projectile, and loss of formaldehyde (1).



(1)

The collision energy dependence (Table 1) shows that the relative abundance of CH_2F^+ gradually increases with collision energy, and at still higher energy (>28 eV) it is accompanied by fragmentation to CHF^+. The total reaction yield[17] ranges from 1% to 10%. Even though CHO^+ is the major product of surface-induced dissociation,[18] neither $FCHO^{+\bullet}$ nor its reaction products are detected.

To confirm that the reactivity of $^{\bullet}CH_2OCH_2^+$ is associated with the radical site, the closed-shell methoxymethyl cation $CH_3OCH_2^+$ was reacted with the F-SAM surface (Table 1). This cation showed considerably lower reactivity toward the fluorocarbon surface and no CH_2F^+ was observed at collision energies <30 eV. Only at higher collision energies (30−60 eV) did $CH_3OCH_2^+$ react with the fluorocarbon and form CH_2F^+ (*m/z* 33), although with a low relative abundance much lower compared to $^{\bullet}CH_2OCH_2^+$. Gas-phase studies indicate that $CH_3OCH_2^+$ can transfer CH_3^+ to nucleophiles with accompanying loss of stable neutral CH_2O.[19] The formation of C−F bond cleavage products at low collision energies with use of distonic ions, in contrast to the behavior of the closed-shell cation, $CH_3OCH_2^+$, indicates that the radical site plays an essential role in the activation of highly inert C−F bonds.

Further evidence for the reactivity of carbon radicals toward the fluorocarbon surface comes from reactions of the homologous β-distonic ion $^{\bullet}C_2H_4OCH_2^+$ (*m/z m/z* 58) (**2a**) and its deuterated form $^{\bullet}C_2D_4OCD_2^+$ (*m/z* 64) (**2b**). Exactly as expected, collisions

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Table 1. Relative Abundance of Ion/Surface Reaction and Other Products of $^{\bullet}CH_2OCH_2^+$ and $CH_3OCH_2^+$ Collision at an F-SAM Surface as a Function of Collision Energy

projectile	mass-to-charge ratio														
$^{\bullet}CH_2OCH_2^+$	14	15	16	26	27	29	30	31	32	33	42	43	44	63	69
18 eV	7.7	8.4	6.5	0.2	0.1	56.2	0.3	0.4	0.0	0.7	1.5	6.5	11.1	0.1	0.0
23 eV	24.3	20.2	4.8	0.2	0.6	37.9	0.8	0.9	0.0	2.0	1.7	3.6	3.1	0.0	0.0
28 eV	28.7	22.7	3.1	0.5	0.5	32.2	1.5	1.7	0.1	3.1	1.8	2.6	1.0	0.0	0.1
38 eV	33.3	20.6	1.0	1.0	0.8	30.7	1.4	2.4	0.4	5.0	1.4	0.6	0.2	0.0	0.4
48 eV	32.3	12.2	0.4	3.7	1.6	28.7	0.7	5.3	2.2	7.9	0.7	0.3	0.5	0.0	2.4
58 eV	32.8	10.2	0.5	3.8	2.7	27.2	0.8	5.5	2.1	8.3	0.9	0.4	0.6	0.0	4.8

projectile	mass-to-charge ratio											
$^{\bullet}CH_3OCH_2^+$	14	15	17	27	29	30	31	33	42	43	45	69
18 eV		18.3	1.1		28.0						52.6	
23 eV		61.0	1.0	0.4	21.5						16.0	
38 eV	2.1	70.5		0.5	23.5	0.8	0.5	0.8	0.3	0.2	0.4	0.3

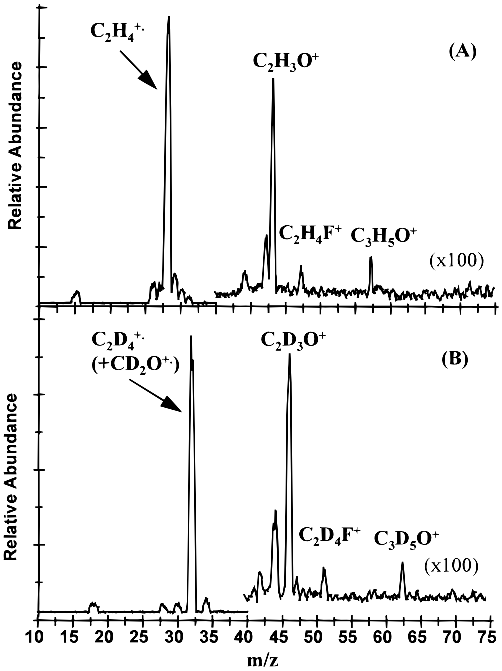

Figure 1. Product ion spectra recorded for collisions of (A) $^{\bullet}CH_4OCH_2^+$ and (B) $^{\bullet}C_2D_4OCD_2^+$ with an F-SAM surface at 20 eV.

of the distonic ion **2a** and **2b** with the F-SAM surface lead to the radical/surface reaction products $C_2H_4F^+$ (*m/z* 47) (Figure 1(A)) and $C_2D_4F^+$ (*m/z* 51) (Figure 1(**B**)), respectively. The F-abstraction product corresponding to the intact projectile ion was not observed.

There are several important features of Figure 1: (i) the radical site of the β-distonic ions reacts with the F-SAM surface to form F-atom transfer products $C_2H_4F^+$ and $C_2D_4F^+$; (ii) no CH_2F^+ and $CHF^{+\bullet}$ (or CD_2F^+ and $CDF^{+\bullet}$ for **2b**) are detected, a result that strongly suggests that the charge site in the β-distonic molecule is not responsible for the reaction; and (iii) the chemical sputtering products[20] from the F-SAM surface, $C_nF_m^+$, are almost absent at an energy where the ion/surface reaction product is clearly evident. This last observation confirms that charge exchange between the projectile and F-SAM surface is not involved in the fluorine atom abstraction reaction. The result is consistent with the body of data on gas-phase ion/molecule reactions which show that distonic ions preferentially undergo radical addition reactions.[12]

The abundance of $C_2H_4F^+$ increases with collision energy, but gradually diminishes at high collision energy (>30 eV) where the vibrationally excited ion $C_2H_4F^+$ fragments further to ions *m/z* 46 and 45 by loss of one or two H atoms. Correspondingly, the deuterated form $C_2D_4F^+$ yields the ions *m/z* 49 and 47. At high collision energy (>30 eV), the distonic ions **2a** and **2b** also yield CH_2F^+ (*m/z* 33) and CD_2F^+ (*m/z* 35), respectively, presumably as the products of ionic rather than radical reactions of the chosen distonic ions.

This investigation of the charged-radical/surface reactions demonstrates that tandem mass spectrometry can be used to probe free radical/surface reactivity with mass-selected and energy-resolved projectiles.[21] The results show that translationally energetic free radicals react readily with fluorocarbon surfaces by net F-atom transfer. The demonstrated high reactivity of the α-distonic ion over the conventional cation demands an important role for the radical site. The observation of the scattered $C_2H_4F^+$ ion in reactive collisions of β-distonic ions confirms the radical/surface reaction mechanism.

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