J. Am. Chem. Soc. 1980, 102, 6881-6882

Chemical/Field Ionization. Effect of Chemically Bonded Surface Groups in Field Ionization Mass Spectrometry

Sir:

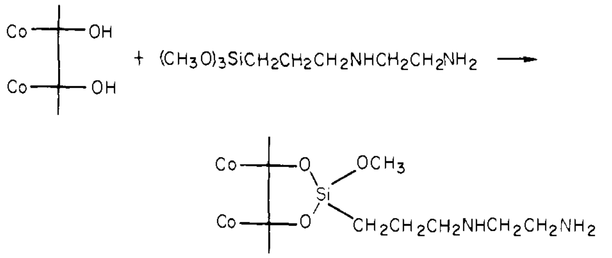
Previously we have reported the selective altering of surface reactivity in field desorption mass spectrometry by physically coating emitter surfaces.[1-3] We now report a striking change in reactivity due to chemical bonding of a functional group to the surface.

Because the oxidized surface layer of a metal surface can be silanized,[4] and because the modified surface then has profoundly modified chemical characteristics, we chose to coat functionalized silanes on cobalt emitters,[5] after an activation procedure which involves heating the emitters in a strong electric field gradient in a vacuum.[5]

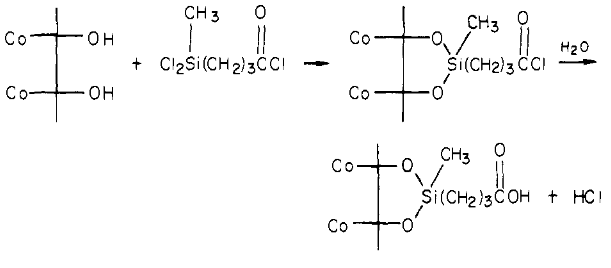
ESCA spectra of unactivated and activated cobalt emitters give binding energies of 782.9 and 783.8 eV, respectively, for cobalt. This indicates[6] that the surface cobalt is in a highly oxidized state. Transmission electron microscopy studies support this and show the bulk of the unactivated emitter to be composed of cobalt oxide; even after activation, cobalt oxide is still present.[7] Because of this information, it was reasonable that silanes could be chemically bonded to surface hydroxyl groups. We have studied surface modifications which we expected to act as Brønsted acids and bases toward adsorbed species. Ligon recently documented[8] surface modification of emitters by coating with polyphosphoric acid.[9] We note that our observations could be extended to provide a protonating surface for all functionally substituted molecules which at the same time should cause less acid-catalyzed decomposition of applied samples.

Emitter surfaces were first modified with an aminosilane, $(CH_3O)_3SiCH_2CH_2CH_2NHCH_2CH_2NH_2$, chosen because the silanization process could be confirmed with ESCA Si, Ni, and Co spectra taken of silanized and unsilanized dendrites.

Optimal silanization takes place when activated cobalt emitters, previously dried in a 190 °C oven for 30 min, are immersed in a continually stirred 5% aminosilane/dry (Na) toluene solution at ambient temperature (eq 1[10]). Emitters so treated gave a field ionization (FI) molecular ion intensity at *m/z* 103 for benzonitrile comparable to that from unsilanized emitters. No peaks corresponding to any fragments of silane surface products were detected in the FI mass spectra. ESCA spectra showed the silane still present on the emitter surface after exposure to FI conditions for at least 15 min.


(1)

With the same procedure, the carboxylic acid chloride functionality[11] was attached to an activated cobalt emitter surface (eq 2[12]) then hydrolyzed to the carboxylic acid by immersion in water for 5 min at ambient temperature.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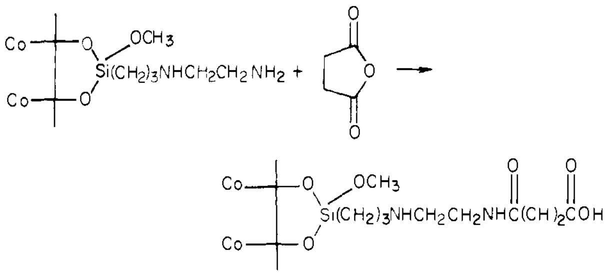
With this emitter, only the usual ion current due to the molecular ion, M^+, of benzonitrile at *m/z* 103 was observed until the heating current reached 20 mA. Remarkably, the only peak then observed was *m/z* 104 $(M + 1)^+$ of benzonitrile. Indeed, many compounds with a wide range of functional groups—amine, nitrile, ketone, aldehyde, carboxylic acid, ether, alcohol, nitrile, olefin, aromatic ring, iodo, and chloro—and zero-field proton affinities[13] from 218 to 168 kcal/mol gave $(M + 1)^+$ peaks.

Saturated compounds ionized with these emitters produced $(M - 1)^+$ ions by hydride abstraction rather than protonated molecules; thus, isobutane produced an *m/z* 57 peak (100%), plus *m/z* 58 (10%) and 59 (10%), decane an *m/z* 141 peak (100%), and cyclohexane an *m/z* 83 peak (100%) (*m/z* 84, 10%).

In order to confirm that the source of protons was indeed the surface carboxyl proton and not merely the byproduct HCl trapped in the silane matrix, an alternative synthesis was designed which produced no acidic byproducts. This synthesis made use of the previously described aminosilane emitters. The aminosilane emitter was immersed in a saturated solution of succinic anhydride in dry toluene at ambient temperature for 5 min (eq 3). Of the emitters so prepared, 80% had sensitivity equal to uncoated emitters, a greater success rate than for eq 2. The protonation results were identical with those described for the earlier emitters.


(3)

Further confirmation of the carboxyl proton as the source of protonation was gained from the following observations. Other kinds of bonded silane emitters without acidic groups, but with only alkyl groups, alkyl halides, or alcohols, do not protonate amines after immersion in aqueous HCl. Immersion of carboxylic acid surface emitters in dilute aqueous NH_4OH for 5 s caused protonation to cease; immersion of these nonprotonating emitters then in dilute aqueous HCl for 5 s caused the emitter to protonate as before. When the carboxylic acid emitter was dipped into D_2O for 30 min to exchange the carboxyl H, $(M + 2)^+$ ions were observed as $(M + 1)^+$ ions had been previously.

The onset of protonation is determined by a threshold heating current of about 20 mA. This value varies slightly from emitter

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[9] Polyphosphoric acid surfaces protonate even alkanes in the high electric field at the emitter surface.[8]

[10] Equations 1 and 2 are illustrative; they do not imply a uniform attachment of the silane by two bonds, nor the absence of polymer due to reaction with adsorbed water.

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[12] Prolonged hydrolysis time or heating is critical to provide an adequate number of carboxylic acid groups; these conditions are our experimental minimum for a 20% success rate.

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to emitter as length, amount, density, and morphology of the cobalt dendrites vary slightly.

The influence of an electric field gradient on the position of chemical equilibrium has been treated by several workers.[14-16] Application of an appropriate model[14] to this example adequately predicts the protonation of molecules of low basicity by carboxylic acids in a strong electric field in our observations; this will be amplified in the full paper.

We propose the study of the attachment of surface groups to other kinds[17-20] of field desorption emitters. Goals of such work could be the protection of the sample against decomposition by native surface groups, and altering spectra in a predictable manner, as we have demonstrated here.

Acknowledgment. We thank Dr. Jerome Lenhard for the ESCA spectra.

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Received June 30, 1980

Temporary Negative Ions of Methyl-Substituted Ethylenes: Trends in the Electron Affinities, Ionization Potentials, and Excitation Energies

Sir:

Many investigations have addressed the effect of alkyl groups on various properties of unsaturated hydrocarbons. Although the π ionization potentials and the π → π* excitation energies are known for the methyl-substituted ethylenes, a complete set of accurate electron affinities (EA) is not available. To this end, we have employed electron transmission spectroscopy (ETS)[1,2] to study the ground-state negative ions of the methyl-substituted ethylenes. We then combine the resulting electron affinities with existing ionization potential (IP) data to explore the relationship between the lowest singlet and triplet π → π* excitation energies and the quantity IP − EA. A similar investigation[3] carried out on the fluoroethylenes revealed an approximately linear dependence of the triplet energies on IP − EA. For the singlet state, only the symmetrically substituted compounds displayed this behavior, with the asymmetrically substituted compounds falling well below the line. If this behavior is indeed the result of symmetry differences, similar trends would be expected upon methyl substitution even though methyl groups and fluorine atoms have very different inductive and mesomeric properties.

Using ETS, one can determine the energies of anion states lying above the ground state of the neutral molecule from the positions of resonances, i.e., rapidly varying structures, in the electron-scattering cross section. The electron transmission spectra of ethylene and the methyl-substituted ethylenes are presented in Figure 1. The structure which occurs in the 1–2-eV region of the ethylene spectrum has been assigned[4] to the temporary anion formed by the capture of an electron into the b_{2g} (π*) orbital. The corresponding features in the spectra of the methyl derivatives, which are only slightly shifted from that of ethylene, can likewise be associated with the capture of electrons into the low-lying π* orbitals. The vertical EAs determined from the transmission spectra are summarized along with the IPs and the neutral excitation energies in Table I. Electron affinities obtained by other workers with the trapped electron method (TEM)[5] are also listed.

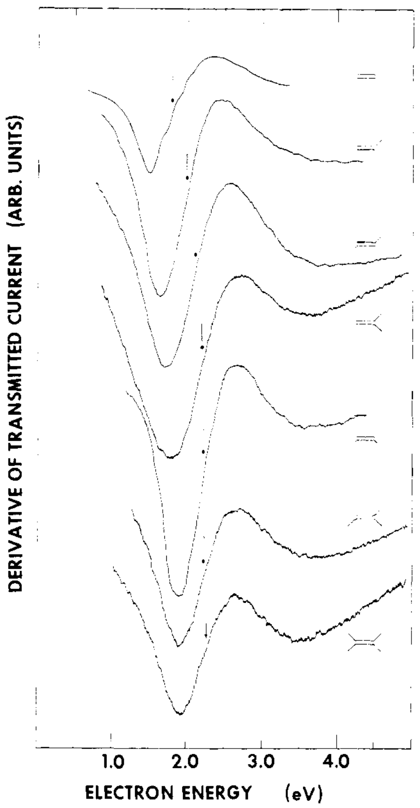

Figure 1. The derivative with respect to energy of electron current transmitted through ethylene and the methyl-substituted ethylenes as a function of impact energy. The arrows indicate the midpoints between the extrema of the derivative. These energies are taken as the vertical attachment energies, that is, the negatives of the vertical electron affinities. Faint undulations in the lower curves are due to a N_2 impurity.

Table I. Vertical Ionization Potentials, Electron Affinities, and Rydberg, Singlet, and Triplet Transition Energies (eV)

compd	IP[a]	EA[b] (ETS)	EA[c] (TEM)	EA[d] (TEM)	T[e]	S[f]	R[f]
ethylene	10.515	−1.78	−1.87	−1.8	4.32	7.58	7.15
propene	9.744	−1.99	−2.2		4.28	7.15	6.72
isobutylene	9.239	−2.19			4.22	6.68	6.19
cis-2-butene	9.124	−2.22	−2.3	−2.3	4.21	7.10	6.03
trans-2-butene	9.122	−2.10	−2.4	−2.2	4.24	6.97	6.09
trimethyl-ethylene	8.682	−2.24			4.16	6.75	5.74
tetramethyl-ethylene	8.271	−2.27		−2.0	4.10	6.61	5.40

[a] Reference 9. [b] This study. [c] Reference 13. [d] Reference 14. [e] Reference 11. [f] Reference 12.

The weak undulations appearing in the ethylene spectrum have been assigned[6] to ν_2, the C–C stretching mode. Fine structure due to nuclear motion is not seen in the transmission spectra of the substituted ethylenes. This indicates that methyl substitution

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