

A New Method for Surface Ionization of Organic Molecules by Attachment of Alkali Ions in Moderate Electric Fields

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It is shown that polar organic molecules may be ionized at metal surfaces by attachment of alkali ions in moderate electric fields. Lithium salts adsorbed on tungsten surfaces were employed for this method of ionization. The alkali ion attachment results from a surface reaction in the transition region between a thermal and field ionization. The particular advantage of this ionization method lies in the production of very simple mass spectra which contain no decomposition products of ions.

Introduction

Thermally-induced surface ionization of organic molecules is not normally possible since the ionization potential of the molecules is much greater than the work function. Thus a surface ionization would demand such high temperatures that a thermally-induced decomposition of the molecules would set in before ionization. Zandberg and Rasulev^{1–4} used tungsten oxide surfaces, which have a particularly high work function, for ionizing molecules of low ionization potential such as amines. Surface ionization could be observed at temperatures of several hundred °C on oxidized tungsten wires of 18 and 50 μm diameter³, whose work function was determined as 6,7 eV². The field strengths were in the range of 10^3 – 10^4 V/cm as estimated for smooth wire surfaces. The low temperatures of about 100 °C at which surface ionization was already observable in many cases suggest, however, that in addition to the temperatures high local field strengths also play a part in the ionization. Surface regions of high field strengths may result from the oxidation of the tungsten wires by which the surface roughness increases⁵.

The energetic conditions for a surface ionization of organic molecules are considerably more favorable when the ionization is effected by alkali ion attachment. Whereas molecular ion formation demands the ionization energy of the molecule and protonation requires a similarly high energy supply, ionization by alkali ion attachment needs only the energy for releasing the alkali ion and attaching it to the molecule. An ionization method of this kind

can of course only be used with polar molecules, since only these have high affinities for alkali ions. It must also be possible to keep the surface temperature sufficiently low, as defined by the condition $kT \ll$ alkali ion affinity of the molecules, since only under these conditions is it possible to form stable ions which do not immediately decompose into molecule and alkali ion again. Low emitter temperatures are also important in order to prevent a thermally-induced fragmentation of the molecules as far as possible.

The possibility of ionizing polar molecules by alkali ion attachment at the surface of a field ion emitter has recently been demonstrated⁶. In this case salts were adsorbed on the surfaces of conventional carbon field ionization emitters⁷ which have a structure similar to pyrolytic graphite⁸, and the cations of the salts were used for "cationization" of the molecules. The organic molecules either reached the emitter surface from the gas phase or were applied to the emitter with the salts outside the ion source of a mass spectrometer. The investigation showed that an ionization by alkali ion attachment is possible below the threshold field strengths for the formation of M^+ and $(M+H)^+$ ions. However, at these low field strengths emitter temperatures of about 500 °C were necessary to achieve alkali ion attachment⁶.

This paper reports on the possibility of obtaining surface ionization by alkali ion attachment at "smooth" tungsten wire surfaces. The metal surfaces permitted a surface ionization at considerably lower temperatures than were necessary for carbon emitters under otherwise comparable conditions. The salts were here also applied to the emitter wire outside the ion source. Only lithium salts were used for

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ionization since the affinities of polar molecules for lithium ions are considerably larger than for the other alkali ions⁹.

Experimental

A normal 60° magnetic sector mass spectrometer was used for these investigations. The ion source was a conventional field ionization/field desorption source with a vacuum lock for rapid emitter replacement. Instead of the usual carbon emitters, tungsten wires of 10 μm diameter were used. The surfaces of the tungsten wires were not specially treated. Application of the salts to the wire emitters was performed by dipping into concentrated aqueous salt solution. The solvent was then evaporated in the ion source. New wires were used for each measurement. The organic gases were supplied to the ion source via a normal inlet system, and the gas pressure was about 10⁻⁴ torr. Ignoring the roughness of the emitter surfaces the surface field strength was calculated as 2 · 10⁶ V/cm and the temperature of the wire was obtained by extrapolation of calibration curves from pyrometric measurements.

A certain difficulty was due to the short measurement times, during which it was not possible to make an optimal adjustment of the ion optics. To avoid this difficulty the emitter was mounted at right angles to the entrance slit of the mass spectrometer and adjusted geometrically so that no changes were necessary in the settings of the ion optics on exchanging emitters.

Results and Discussion

The mass spectra of the products of a surface ionization of polar molecules using lithium chloride are shown in Figs. 1 and 2. The lithium ion attachment at tungsten required lower surface temperatures than the ionization at the carbon emitters⁶ so long as the field strength remained below the threshold value for the formation of M⁺ or (M + H)⁺ ions. A similar observation was made by Tontegode and Zandberg¹⁰ who observed a smaller ion production when surface ionization of CsCl was carried out at iridium surfaces covered with thick carbon layers than at metal surfaces without carbon deposits.

Attachment of Li⁺ to hexanal was observed at temperatures up to about 1000 °C. Surface ionization could be achieved at lower temperatures with LiCl than with Li₂CO₃, LiF, or LiI. The lithium ion attachment ceased when no more Li⁺ ions were available. Under favorable conditions, that is at relatively low temperatures, with LiCl, the current of (M + Li)⁺ ions of hexanal at the detector of the mass spectrometer lay in the order of 10⁻¹⁴ A. These ion currents allowed measurements of some minutes up to an hour duration to be made. Lower ion production was obtained with alcohols — a direct consequence of the lower lithium ion affinity of the alcohols as compared to that of the aldehydes.

At low surface temperatures the mass spectra contain cluster ions (nM + Li)⁺ as can be seen in

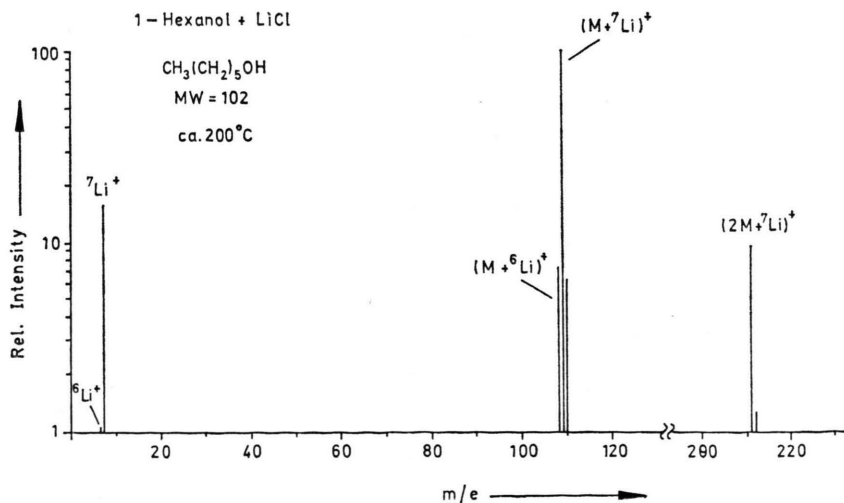


Fig. 1. Mass spectrum of 1-hexanol obtained by surface ionization with LiCl at a 10 μm tungsten wire. The isotopes of lithium are indicated. Surface temperature about 200 °C. Field strength about 2 · 10⁶ V/cm (calculated for a smooth wire surface).

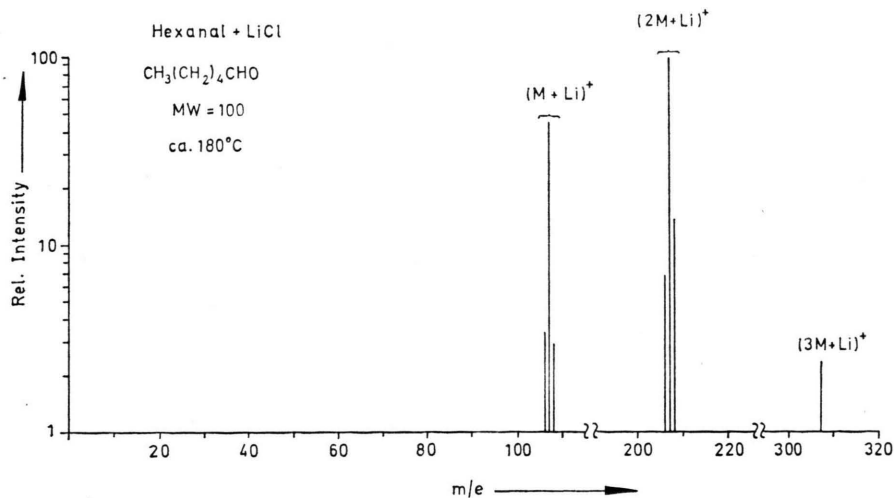
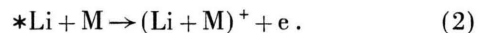
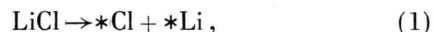


Fig. 2. Mass spectrum of hexanal obtained with LiCl.

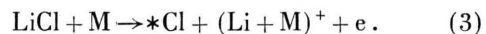
Figs. 1 and 2. These cluster ions disappear at higher temperatures. In the spectrum of Fig. 2, the dimer is even the base peak. This spectrum also contains a further point of interest: there are no Li^+ ions. These ions appear only at higher temperatures. Under the conditions of Fig. 2, the thermal activation of the adsorbate is clearly insufficient to release lithium ions at this temperature. The only way by which lithium can be removed from the surface is by reaction with polar molecules to form $(\text{M} + \text{Li})^+$ ions. This is a result of the energetics of $(\text{M} + \text{Li})^+$ ion formation: the energy required for the formation and desorption of $(\text{M} + \text{Li})^+$ ions is lower than that for the desorption of Li^+ ions by the lithium ion affinity of M. The further energy saving by the formation of dimers is, correspondingly, the reason for the intensity ratio $(\text{M} + \text{Li})^+ / (2\text{M} + \text{Li})^+ < 1$ in the spectrum of Figure 2.

The mechanism of alkali ion attachment makes some further comments necessary. For the case of the thermal surface ionization of alkali halides at high temperatures ($>1000^\circ\text{C}$) and low fields it was found¹¹ that the molecules first dissociate and the thermally-induced desorption of the alkali ions takes place in a second step. It was assumed that such a dissociation of the molecules was also the cause of a desorption ion current observed at about 100°C and field strengths of $7 \cdot 10^6 \text{ V/cm}$ ¹². Since salts were applied to the emitter from aqueous solution under the experimental conditions chosen here it is possible for the LiCl molecules to be adsorbed dissociatively in the form $*\text{Cl}$ and $*\text{Li}$ at room

temperature. It is difficult to determine whether the lithium is adsorbed in a predominantly ionic or predominantly neutral state. If we assume an adsorption in a neutral state the mechanism of surface ionization by lithium chloride would then be:



In contrast to metal surfaces, such a dissociation of lithium chloride at the carbon emitter surfaces is not probable, at least at the low temperatures here under discussion. In order to explain the alkali ion desorption from the carbon emitters it was assumed that radicals and radicalic centers favour the desorption of alkali ions corresponding to the following reaction¹³



This one step mechanism could hold actually also for metal surfaces as dissociation is not always possible. Without any surface interaction the release of Li^+ from LiCl requires an energy of 10,6 eV¹⁴. The formation of $(\text{M} + \text{Li})^+$ ions according to the reactions 2 and 3 requires a considerably lower energy, which is probably a few eV. The thermochemical data necessary for an exact calculation, for instance the lithium ion affinity of hexanal are not available. It has not yet been possible to determine which of the two reaction possibilities predominates at temperatures below 300°C . It is also experimentally difficult to distinguish between the two reaction paths. An indication of a dissociation of the

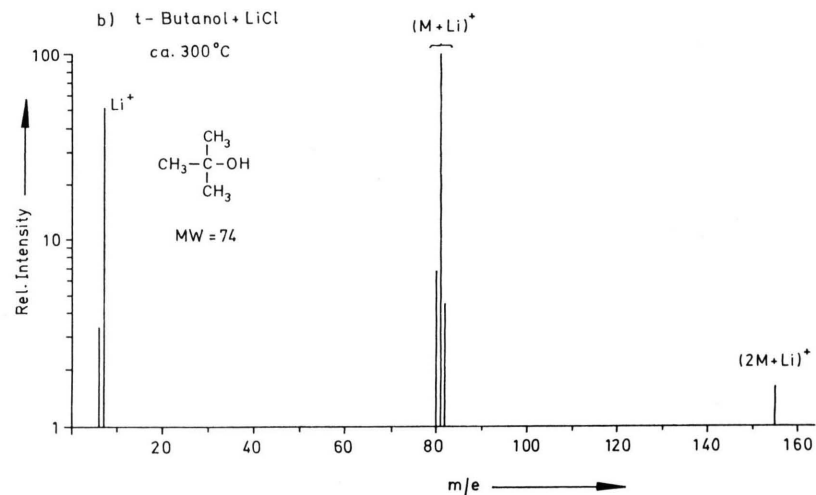
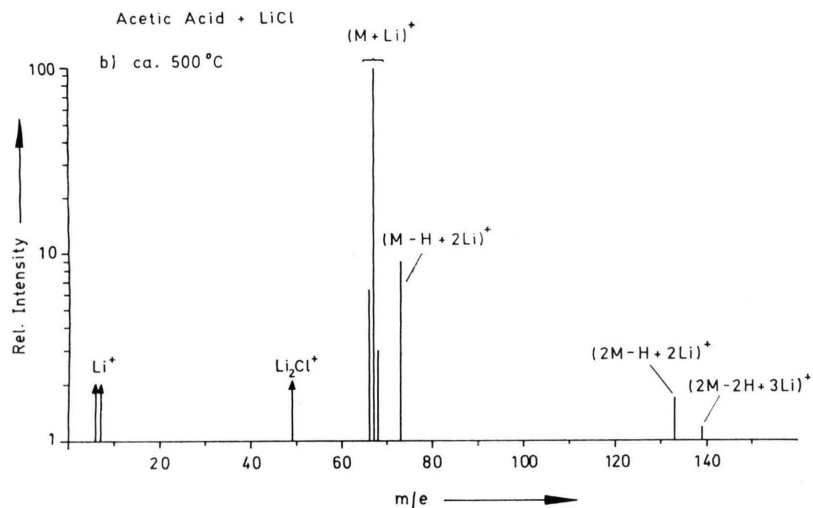
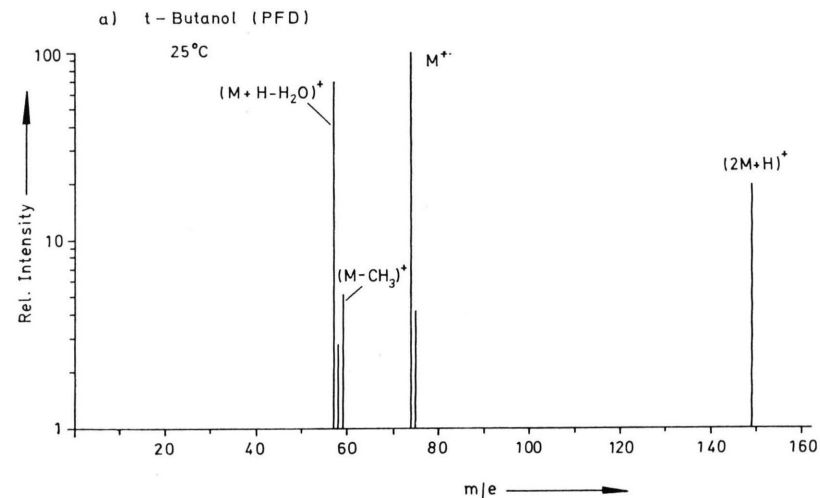
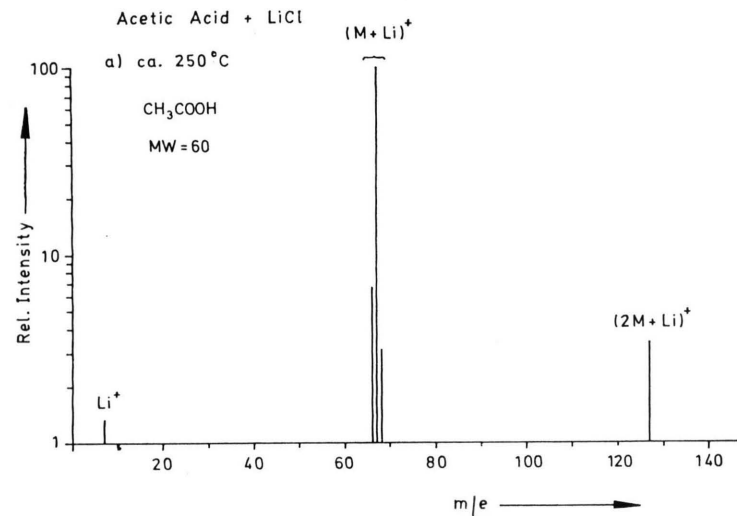


Fig. 3. Mass spectrum of acetic acid obtained with LiCl (a) at low and (b) at high emitter temperature. In (b) the Li^+ and Li_2Cl^+ peaks are indicated by arrows.

Fig. 4. Mass spectra of tert. butanol obtained (a) by pulsed field desorption¹⁵ and (b) by surface ionization with LiCl. A conventional carbon emitter was used in (a) and a $10 \mu m$ W wire in (b).

salts at the surface prior to the cationization reaction was obtained from the investigation of the surface ionization of acetic acid with lithium chloride. Whereas at low temperatures only $(M+Li)^+$ and $(2M+Li)^+$ ions were formed (see Fig. 3 a), at higher emitter temperatures new peaks appeared in the mass spectrum (Figure 3 b). These peaks indicated an exchange of the acidic H atom of acetic acid for a lithium atom from LiCl. A possible explanation for such an exchange reaction is a dissociative adsorption of LiCl. However, it has to be considered that ion formation may also occur on small salt crystals present at the wire surface.

The remarkable stability of ions formed by alkali ion attachment in comparison to molecular ions has already been pointed out⁶. For instance, while the molecular ions of hexanol and hexanal desintegrate very easily by hydrogen rearrangement and simple bond rupture as the electron impact and field ionization mass spectra show, such a fragmentation does not take place for the $(M+Li)^+$ ions. Similarly the stability of $(M+Li)^+$ ions is often considerably higher than that of the corresponding $(M+H)^+$ ions. This is shown in Fig. 4 for tertiary butanol. Figure 4 a shows a pulsed field desorption (PFD) mass spectrum of t-butanol. In pulsed field desorption the ionization takes place during short high field-pulses after periods of undisturbed adsorption of the molecules of the order of milliseconds (see Ref. 15). Under these conditions a particularly gentle protonation takes place, that is only a small amount of energy is transferred to the $(M+H)^+$ ions¹⁵. Nevertheless Fig. 4 a shows an almost quan-

titative decomposition of the $(M+H)^+$ ions into $(CH_3)_3C^+$ ions by elimination of water. Such a decomposition is difficult only in the case of dimers. In contrast to the $(M+H)^+$ ions there is no fragmentation of the $(M+Li)^+$ ions of t-butanol, as the spectrum of Fig. 4 b shows. The cause of the stability of these ions is the localization of charge at the alkali ion — a consequence of the low ionization potential of alkali atoms — since any fragmentation, for instance in the form of an elimination of LiOH, would demand a charge shift. An excessively high inner energy of the ions can only lead to a dissociation of $(M+Li)^+$ into M and Li^+ .

Figure 5 shows, using D-glucose as an example, that a surface ionization by lithium ion attachment is also possible and yields simple spectra when the substance is applied to the tungsten wire simultaneously with the LiCl from an aqueous solution outside the ion source of the mass spectrometer and the ionization is then induced inside the ion source by heating the emitter. This technique, well known in field desorption mass spectrometry⁷ is, however, only advantageous when a desorption temperature can be chosen which is low enough to avoid a thermal fragmentation before ionization.

The $(M-H_2O+Li)^+$ peak in the spectrum results from a thermal decomposition of M by elimination of water and the subsequent ionization of the decomposition product $(M-H_2O)$ by lithium ion attachment. As expected the spectrum contains no decomposition products of the $(M+Li)^+$ ion.

It can be seen that the sensitivity of this ionization method for the detection of thermal decomposi-

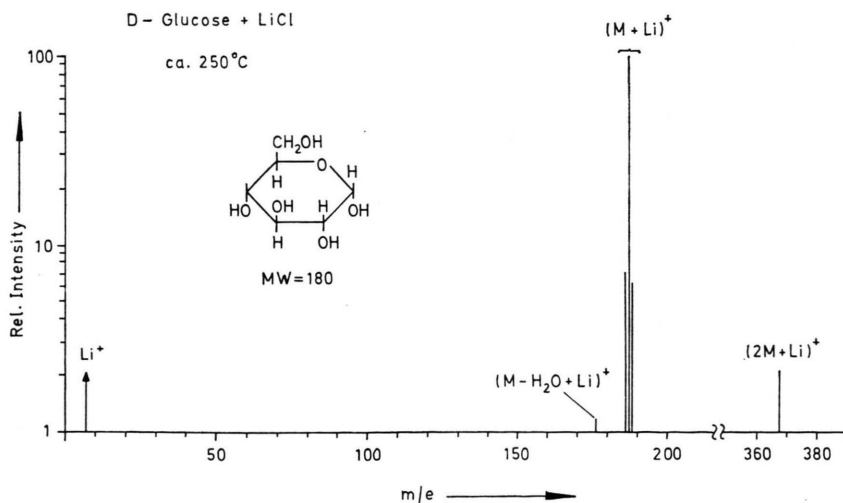


Fig. 5. Mass spectrum of D-glucose obtained with LiCl; LiCl and D-glucose were supplied to the emitter surface from aqueous solution. The Li^+ peak is indicated by an arrow.

tion products is relatively low. This probably results from the fact that a thermal fragmentation usually only sets in at higher temperatures at which the probability of capture of an alkali ion is already greatly decreased.

Conclusion

It has been shown with the aid of several examples that polar organic molecules can be ionized at metal surfaces by attachment of alkali ions. In the case of the system lithium chloride/tungsten the process required temperatures of about 200 °C at a field strength in the order of some 10^6 V/cm. The cause

of the alkali ion attachment is a surface reaction whose mechanism still requires more precise investigation. The particular advantage of this new ionization method lies in the generation of ions which do not fragment further, excepting the splitting off of alkali ions. This ionization method is correspondingly also of analytical interest for the determination of molecular weight and analysis of mixtures where no fragmentation is desired.

Acknowledgement

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