Field Induced Ion Molecule Reactions in Adsorbed Layers Studied by Pulsed Field Desorption

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The formation of ions under field ionization conditions is partly due to ion molecule reactions in adsorbed layers on the emitter surface. In order to study these reactions a pulsed field desorption (PFD) technique was applied, by which ions resulting from these reactions are detected with high relative intensity. The PFD-mass spectra of some small organic molecules are discussed with respect to the principal reaction mechanisms and types of ions formed.

It was found that if reactions involving chemical interaction with the surface are left out of consideration only proton transfer reactions are the primary processes. Desorption products resulting from proton transfer reactions are, for example, $(M+H)^+$, $(2\,M+H)^+$, $(3\,M+H)^+$, $(M+CH_3)^+$ and $(2\,M)^+$ ions in the case of methanol. The formation of complexes preceeding atom rearrangement reactions are suppressed by the high electric field and consequently could not be detected. Secondary reactions of the $(M-H)^{\bullet}$-radical lead to the elimination of H^- from molecules and in certain cases to the formation of addition complexes.

Field induced reactions were found to occur almost adiabatically, i.e. it is not necessary to supply the ionization potential of the proton donor in a proton transfer reaction. Products of reactions with ionization energies above the ionization potential of the molecules involved in the reaction are not observable. To a first approximation the electron transition probability for field reactions seems to be dependent on the energy of formation of the ions and not on the type of reaction.

1. Introduction

Detailed investigations of the ion formation processes occurring in surface reactions during the field ionization of organic molecules have already been described by several authors [1–6]. However, reactions induced by field ionization of molecules in physically adsorbed multilayers without participation of the emitter surface itself have been largely left out of consideration. For instance the reactions of acetone [1]

$$2\,C_3H_6O \xrightarrow{-e} C_3H_5O^{\cdot} + C_3H_6OH^+ \qquad (1)$$

and

$$C_3H_5O^{\cdot} + C_3H_6O \xrightarrow{-e} C_6H_{11}O_2{}^+ \qquad (2)$$

are members of this class of reactions.

The present work is principally concerned with these processes of ion formation in adsorbed layers in which the surface is not chemically active. The types of ions which arise from these reactions and the mechanisms by which they are produced will be described using as examples several small organic molecules with different functional groups. Some general relationships in the desorption kinetics of field ions may be deduced from the results.

Field induced reactions in multilayers are in many respects comparable to Ion Molecule Reactions (IMR) in the gas phase at thermal energies. Thus a further purpose of this work was the evaluation of common features and of the differences between field induced IMR in adsorption layers and IMR in the gas phase. It is particularly interesting here to discover to what extent the results of IMR investigations in the gas phase may be applied to the interpretation of Field Ionization-Mass Spectra (FI-MS) and "Field Desorption-Mass Spectra" [7].

During continuous ionization multilayer adsorption films are largely suppressed in the ionization regions due to the high ionization probabilities of these areas [8]. It is also difficult in this case to distinguish between the various processes of ion generation. For this reason the Pulsed Field Desorption (PFD) method [1, 9, 10] was applied for the investigation of this special class of field reactions as mentioned above. Here ion generation is induced by short field pulses after a period of undisturbed adsorption on the surface producing multilayers.

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The PFD method has the additional advantage that field dissociation of primary ions in the mass spectrometer is less frequently observed[11].

Only graphitized field ion emitters were used in the investigation to avoid the disturbing effect of catalytically active metal emitters.

2. Experimental

Figure 1 shows the ion source for pulsed field desorption schematically. The dc-potential difference between the emitter and the cathode was so adjusted that field ionization was not possible without an additional pulse. Ion production was induced by short (100 nsec) negative high voltage pulses on the cathode. The time between pulses for which adsorption could proceed undisturbed was in the msec range. The current of desorbed ions was analyzed in a magnetic sector field.

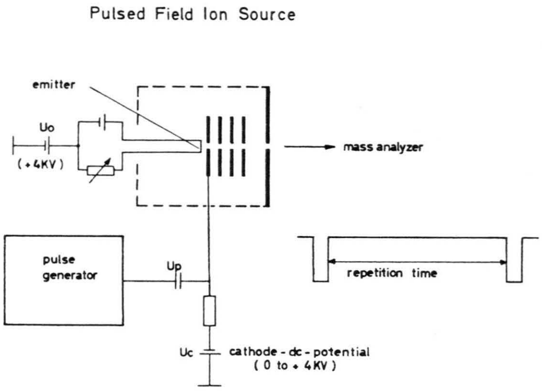


Fig. 1. Schematic representation of a pulsed field ion source.

Multilayer adsorption was observed with polar substances at room temperatures and at pressures of several 10^{-4} torr used in the ion source. Capillary condensation in potential troughs of the surface must also be taken into account here.

A multilayer adsorption is favoured by field compression[12], i. e. at a pressure p_0 in the field free space in the ion source the pressure p at the surface of the emitter is given by $p = p_0 \exp\{\frac{1}{2}\,\alpha\,F_{\mathrm{dc}}^2 + \mu\,F_{\mathrm{dc}}\}/k\,T$ where F_{dc} is the electric field at the emitter surface corresponding to the emitter cathode dc-voltage applied during the pulse free adsorption time. α is the polarizability and μ the permanent dipole moment of the molecules. Field compression is small at the relatively small dc-fields used ($\lesssim 0.1$ V/Å). For the substances investigated the compression factor p/p_0 was mostly below 10, however, the micromorphology of the surfaces of the activated emitter had the decicive influence on the coverage of the emitter surface with multi-adsorption layers.

A second ion source which allowed the possibility of cooling the emitter to liquid nitrogen temperature was used for the measurements of non-polar substances. The ionization probability at the emission centers on the tips of the microneedles was less than unity during one pulse. The repetition time of about 0.7 msec used was sufficient for the multi-adsorption layer to be rebuilt.

The residual partial pressure of water was normally less than 10^{-6} torr neglecting the unavoidable water traces in some substances. The influence of the water which has a field chemistry of its own[2] could be checked by looking for the appearance of H_3O^+-ions.

Most of the PFD-MS were made under standard conditions; unless otherwise stated. The emitter-cathode dc-voltage was −3 kV and the voltage pulses on the cathode were of −6 kV amplitude, 100 nsec length and repetition rate of 1.5 kcps. Although the relative importance of the reactions in multi-adsorption layers rises in comparison to the formation of molecular ions at smaller frequencies the absolute ion intensity of the ion currents and the dynamic sensitivity range decrease.

The field ion emitters were 10 μm tungsten wires activated with benzonitrile at high temperature[13]. Some of the emitters were also treated with water in order to increase the surface roughness and thus to promote a coverage with multilayers.

3. Analysis of the PFD-MS of Several Organic Molecules

Methane

Figure 2 shows the PFD-MS of methane at an emitter temperature of about 110 °K. The methane spectrum exhibits only the three peaks shown in

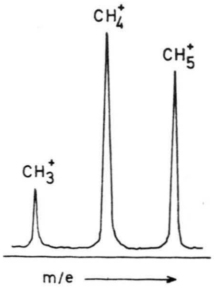


Fig. 2. PFD-MS of methane. (Emitter cathode dc-potential: −4 kV; pulses: −7 kV/100 nsec; frequency: 1,5 kcps; emitter: 10 μm W-emitter activated with benzonitrile at 1200 °C.)

Figure 2. The noise level was about 2% of the CH_5^+-ion current. Since no H_3O^+-peak was observed in the spectrum an involvement of water which has a higher proton affinity than methane in the protonation of the latter can be ruled out. The formation of the CH_5^+-ions can be ascribed to a field induced proton transfer reaction in the methane adsorption layers:

$$2\,CH_4 \xrightarrow{-e} CH_3^{\cdot} + CH_5^+ \tag{3}$$

In this case and also in that of other protonation reactions it was not possible to decide whether the transfer of the proton takes place in a secondary step after field ionization of the molecule, or whether the proton transfer and the electron transition occur simultaneously. Only in the latter case can the activation energy for such a field reaction be smaller than the ionization potential of the proton donor. Investigations of IMR of methane in the gas phase have shown that the transfer of the proton in the reaction

$$CH_4^+ + CH_4 \rightarrow CH_3^{\cdot} + CH_5^+ \tag{4}$$

can also take place for the methane ions in the ground state[14]. It follows thus that the energy necessary for the formation of CH_5^+-ions according to (3) cannot be larger than the adiabatic ionization energy of methane.

The formation of the CH_3^+-ions in the spectrum of Fig. 2 cannot be adequately explained as a field ionization of the $CH_3^{\cdot}$ radical left over from reaction (3), since a value of the intensity ratio $CH_3^+/CH_5^+ > 1$ was also obtained at somewhat higher emitter temperatures under PFD conditions. The source of the CH_3^+-ions with methane and in general of the $(M\text{-}H)^+$-ions with paraffins is probably the following reaction

$$M \xrightarrow{-e} {*H} + (M-H)^+ \tag{5}$$

($*$ is a radicalic center of the surface). As would be expected from this a very much larger value of the ratio $(M-H)^+/M^+$ for paraffins is observed at metal oxide surfaces[15] so that the $(M-H)^+$-ions seen with field ionization at organic emitters probably also arise via a surface interaction. The energy necessary for the formation of $(M-H)^+$-ions according to (5) decreases as the hydrogen binding energy at the surface increases. This formation energy can be considerably more than 1 eV less than the ionization potential of the undissociated molecule.

Ethane

No $(M+H)^+$-ions were observed in the PFD-MS of ethane even with cooled emitters. Apart from the molecular ion peak the spectrum exhibited only an $(M-H)^+$-peak of low intensity (several %).

Ethane undergoes no field induced proton transfer reactions. Investigations of the IMR of ethane in the gas phase[16, 17] showed correspondingly that at thermal energies no proton transfer reaction analogous to (4) exists for ethane without additional excitation energy. The proton transfer between an ethane ion and an ethane molecule is an endothermic reaction[18] at 25 kcal $mole^{-1}$.

The PFD-MS of the higher paraffins also contain only M^+ and $(M-H)^+$-ions and their monomolecular decomposition products. The absence of proton transfer reactions may be explained thermochemically as in the case of ethane.

A pecularity of the ethane spectrum is that no evidence of a $(C_2H_6)_2^+$-ion or its decomposition products was discovered despite the multilayer adsorption at temperatures <200 °K and the small energy transfer during field ionization. However, this dimeric cluster ion is formed at relatively high yields by IMR in the gas phase at pressures in the torr range and temperatures up to 400 °K[19, 20].

Ethylene

The PFD-MS of ethylene was also taken with a cooled emitter. Apart from the molecular ion ($\equiv 100$) the spectrum exhibits only the protonated molecule ($\cong 40$) and an H_3O^+-peak ($\cong 10$). In the case of ethylene there is a possibility of field induced ionic adsorption of the molecules at the emitter surface[21]. The H_3O^+ and the $C_2H_5^+$-ions are typical products of reactions with surface ions e. g.

$$*C_2H_4^+ + C_2H_4 \rightarrow *C_2H_3 + C_2H_5^+ \,. \tag{6}$$

Such reactions involving surface ions are discussed in more detail elsewhere[3, 6].

In the gas phase the proton transfer between an ethylene molecular ion and an ethylene molecule is an endothermic reaction[22] at 18 kcal $mole^{-1}$, thus under field ionization conditions there is no proton transfer reaction analogous to (4) in the case of ethylene. Protonation of ethylene molecules occurs exclusively by chemical interaction with the emitter surface e. g. by reaction (6).

None of the reaction products of IMR in the gas phase for instance $(C_2H_4)_2^+$-ions and their exothermic decomposition products, $C_3H_5^+$ and $C_4H_7^+$-ions, could be observed in the PFD-MS of ethylene.

Methanol and Ethanol

High $(M+H)^+$- and $(2M+H)^+$-ion currents (Fig. 3) resulting from the reactions

$$2\,ROH \xrightarrow{-e} RO^{\cdot} + ROH_2^+ \qquad (7)$$

$$3\,ROH \xrightarrow{-e} RO^{\cdot} + (ROH)_2H^+ \qquad (8)$$

are typical for alcohols. Dahmen[23] observed an isotope effect in these reactions where hydrogen was substituted by deuterium in the OH-group. This suggests the participation of the tunnel effect in theses protonation reactions. A $(3M+H)^+$-ion is also observed with methanol (Figure 3 a).

The $C_2H_5^+$-peak in the ethanol spectrum (Fig. 3 b) may be attributed to a field dissociation of the $(M+H)^+$-ion. The $(M+H-H_2O)^+$-peak in alcohol spectra grows with increasing field strength and increasing length of the alkyl group.

An $(M+C_2H_5)^+$-peak in the ethanol spectrum corresponds at somewhat lower intensity to the $(M+CH_3)^+$-ion peak in the methanol spectrum. Such $(M+R)^+$-ions could no longer be detected in the PFD-MS of propanol and the higher alcohols. The absence of a CH_3^+-peak in the methanol spectrum eliminates the possibility that $(M+CH_3)^+$-ions are produced by an addition reaction of desorbing CH_3^+-ions with methanol molecules.

It is known that $(CH_3OH)_2H^+$ and $(C_2H_5OH)_2H^+$-ions decompose thermically or by collision as follows[24, 25]:

$$(2M+H)^+ \rightarrow (M+R)^+ + H_2O\,. \qquad (9)$$

The conclusion that under FI conditions a $(2M+H)^+$-ion is formed at first from which a R_2OH^+-ion splits off by field dissociation cannot be drawn from Eq. (9) since this fails to explain firstly the high activation energy of 27 kcal mole^{-1} measured for ethanol[25] and secondly that the ratio $(M+R)^+/(2M+H)^+$ is only large at low desorption field strength. It is more probable that the precursor of the $(M+R)^+$-ions desorbed from the emitter surface is a trimolecular complex from which the product ion arises by straight-forward rearrangement.

$$3\,M \xrightarrow{-e} (M-H)^{\cdot} + H_2O + (M+R)^+\,. \qquad (10)$$

This mechanism for the field induced formation of $(M+R)^+$-ions differs considerably from that observed in the gas phase (9).

Under PFD conditions $(2M)^+$-ions were detected only with methanol. They can also be observed with ethanol under continuous FI conditions. It was even possible to observe a ratio $(2M)^+/(2M+H)^+ > 1$ for methanol and water[2]. To the best of the authors knowledge $(2M)^+$-ions of alcohols have not previously been observed during investigations of IMR in the gas phase. Since the proton transfer between alcohols is a strongly exothermic reaction with zero activation energy, the $(2M)^+$-ions must have the structure

$$[(M+H)^+(M-H)^{\cdot}]\,.$$

Goldenfeld and Korostyshevsky[26] showed by deuteration experiments that the $(M-H)^+$-ions in the FI-MS of alcohols on Pt possess only the structure $R'CHOH^+$, i. e. that a field ionization of the $RO^{\cdot}$ radical remaining on the surface after proton transfer reactions is not probable. The assumption of a field dissociation of the weaker $\alpha-C-H$ bond in order to explain the $(M-H)^+$-peaks in the spectrum can be dismissed for PFD-conditions because of the low desorption field strength. A much more probable reaction for the production of $(M-H)^+$-ions is

$$RO^{\cdot} + ROH \xrightarrow{-e} ROH + R'CHOH^+ \qquad (11)$$

where the difference between the $O-H$ and $C-H$ bond energies favours the reaction. Accordingly the large $C_7H_{15}^+$-peak observed in the PFD-MS of a mixture of methanol and n-heptane (Fig. 4) results from the reaction

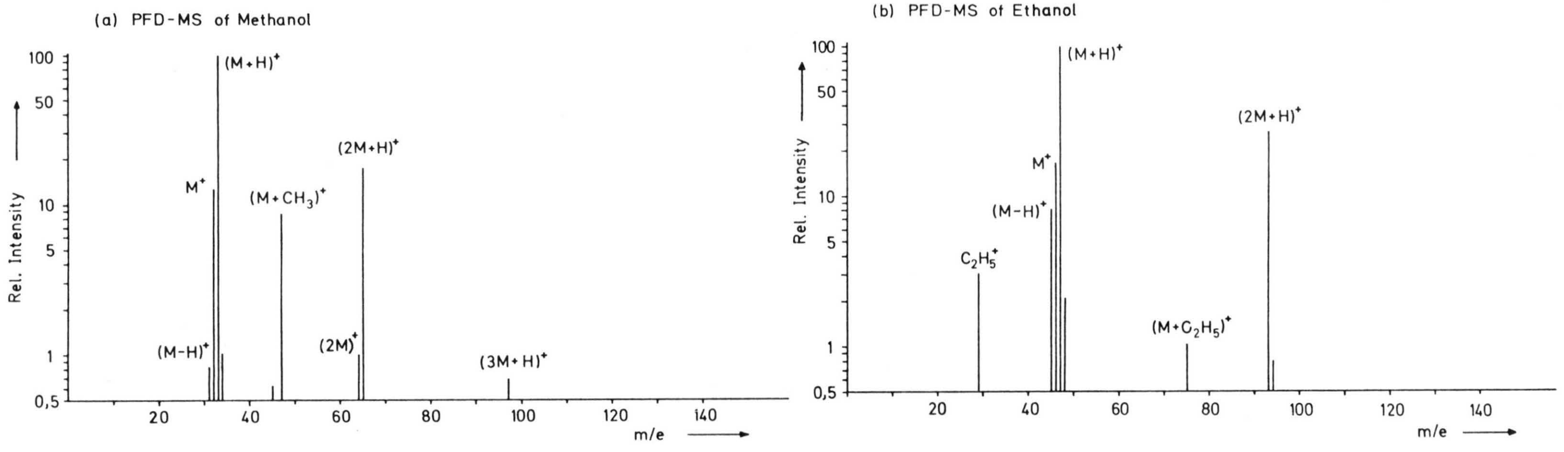
$$CH_3O^{\cdot} + C_7H_{16} \xrightarrow{-e} CH_3OH + Q_7H_{15}^+\,. \qquad (12)$$

In the absence of methanol the ratio $C_7H_{15}^+/C_7H_{16}^+$ was less than 10%. Since the ratio $(M-H)^+/(M+H)^+$ for the FI of alcohols can be greater than unity under certain conditions[27] it is possible to conclude that a reaction analogous to (5) contributes to the formation of $(M-H)^+$-ions.

Diethylether

The $(M+H)^+$-peak in the PFD-MS of diethylether (Fig. 5 a) suggests the proton transfer reaction

$$2\,(C_2H_5)_2O \xrightarrow{-e} C_2H_4OC_2H_5^{\cdot} + (C_2H_5)_2OH^+\,. \qquad (13)$$



(a) (b)

Fig. 3. PFD-MS of methanol (a) and ethanol (b).

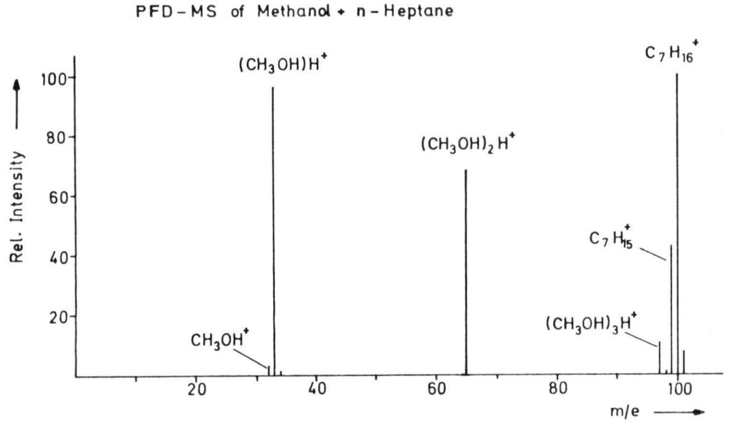


Fig. 4. PFD-MS of a mixture of methanol and n-heptane.

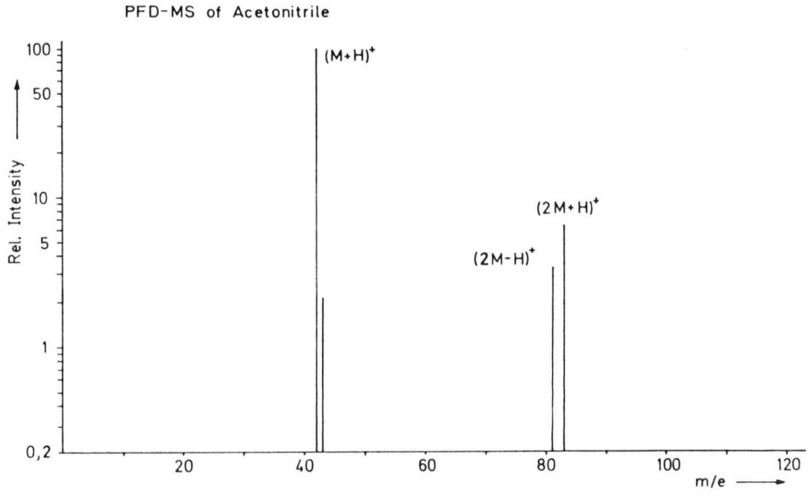
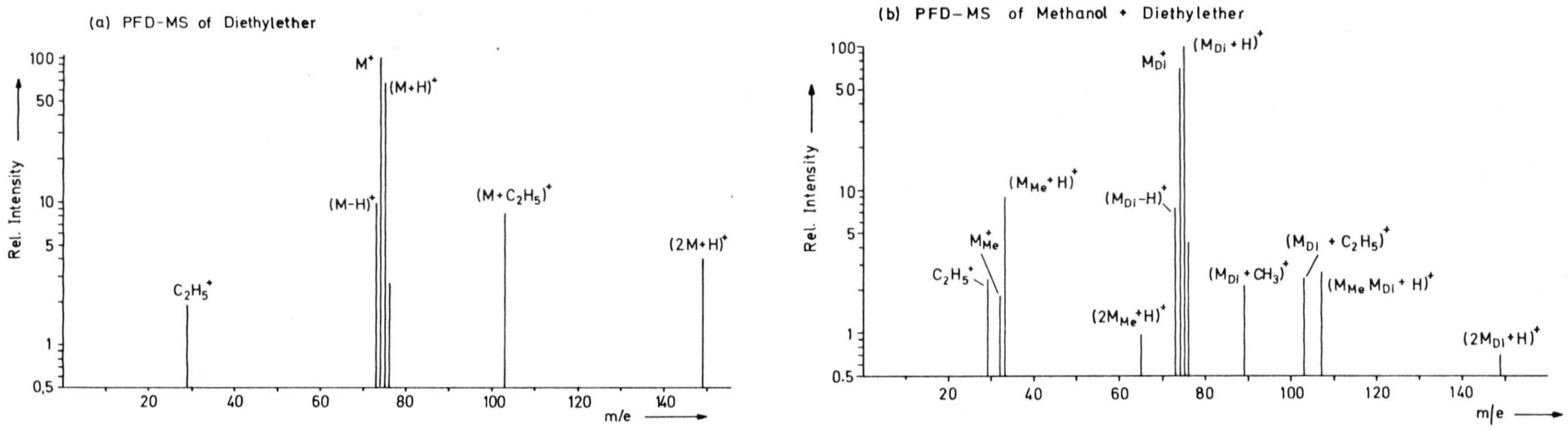
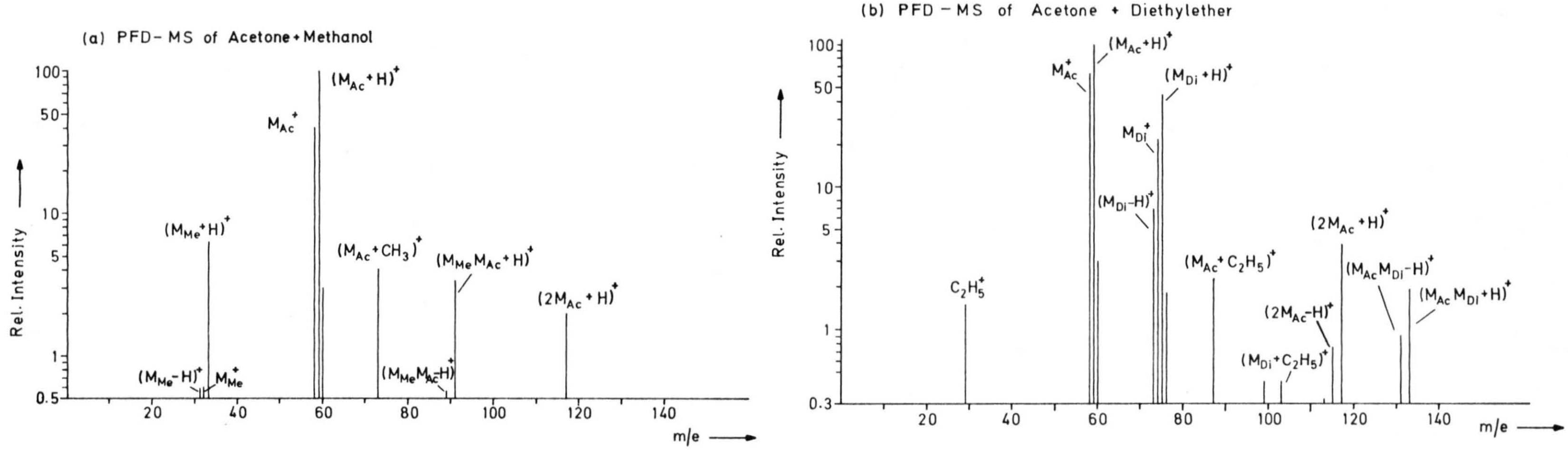


Fig. 7. PFD-MS of acetonitrile.



(a) (b)

Fig. 5. PFD-MS of diethylether (a), and a mixture of methanol and diethylether (b).



(a) (b)

Fig. 6. PFD-MS of mixtures of acetone and methanol (a), and acetone and diethylether (b).

The proton transfer is less exothermic for the IMR of diethylether than for the alcohols so that a smaller ratio $(M+H)^+/M^+$ is obtained in Fig. 5 a than in Figure 3. This ratio is once more larger for a mixture with methanol (Fig. 5 b) since protonation of diethylether by methanol can take place.

Analogously to (10) the $(C_2H_5)_3O^+$ cluster ions (Fig. 5 a) are formed by the reaction

$$3\,(C_2H_5)_2O \xrightarrow{-e} C_2H_4OC_2H_5 + C_2H_5OH + (C_2H_5)_3O^+ \,. \tag{14}$$

The $(C_2H_5)_2OCH_3{}^+$-ions in the spectrum of Fig. 5 b are produced in a similar fashion.

A field ionization of the $(M-H)^{\cdot}$ radicals left on the surface after the reaction (13) and (14) should contribute to the $(M-H)^+$-peak of the spectrum in Fig. 5 a as well as reaction (5), since the ionization potential of $(M-H)^{\cdot}$ is smaller than that of diethylether and these ions in contrast to the $RO^{\cdot}$ radicals of the alcohols do not have the ability to react with M for energetic reasons.

Acetone

The reactions of acetone have already been discussed in detail elsewhere[1]. Because of the possibility of the production of surface ions with acetone the peaks at *m/e* 73 (Fig. 6 a) and 87 (Fig. 6 b) in the PFD-MS of mixtures of methanol and diethylether with acetone can result from two reactions. For instance in the case of methanol the reaction

$$2\,CH_3OH + (CH_3)_2CO \xrightarrow{-e} CH_3O^{\cdot} + H_2O + (CH_3)_2COCH_3{}^+ \tag{15}$$

may be expected in analogy with reaction (10). For methanol there is also a possibility of a reaction with acetone surface ions resulting also in $(CH_3)_2COCH_3{}^+$-ions[3]

$$*OC(CH_3)_2OCH_3 \xrightarrow{-e} *O + (CH_3)_2COCH_3{}^+ \,. \tag{16}$$

It is not possible to distinguish between (15) and (16) by deuteration. Reaction (15) should predominate under PFD conditions.

It was possible to determine the structure of the ions of masses 89 in Fig. 6 a and 131 in Fig. 6 b by deuteration. From these experiments it can be concluded that in both cases the hydrogen atom is absent in acetone: *m/e* 89: $CH_3COCH_2\overset{+}{O}HCH_3$ and *m/e* 131 $CH_3COCH_2\overset{+}{O}(C_2H_5)_2$. Here we are concerned with products of addition reactions of the acetonyl radical with methanol and diethylether

$$CH_3COCH_2{}^{\cdot} + CH_3OH \xrightarrow{-e} CH_3COCH_2OHCH_3{}^+ \,. \tag{17}$$

The binding energy released should reduce the necessary ion formation energy.

Acetonitrile

The PFD-MS of acetonitrile (Fig. 7) exhibits a curiosity which is not observed elsewhere. No M^+-ion is found in the spectrum. The noise level was approximately 0.1% of the $(M+H)^+$-peak. Obviously this is a result of both the high ionization potential of acetonitrile (12.2 eV)[28] and the large energy release ΔE in the IMR

$$CH_3CN^+ + CH_3CN \rightarrow CH_2CN^{\cdot} + CH_3CNH^+ + \Delta E \,. \tag{18}$$

According to thermochemical calculations ΔE should be more than 4 eV[28]. The absence of an M^+-peak in Fig. 7 can be taken as direct evidence that field induced proton transfer reactions are approximately adiabatic and that the ionization potential of the proton donor does not necessarily need to be supplied. A very large value of the ratio $(M+H)^+/M^+$ was also observed in the PFD-MS of formic and acetic acid. The $(2M-H)^+$-ion in Fig. 7 corresponds to the $(2M-H)^+$ acetone ion and it is also known from ion cyclotron resonance investigations of the IMR of acetonitrile[29]. $(CH_3OH + CH_3CN + CH_3)^+$-ions are also found in the PFD-MS of a mixture of acetonitrile and methanol.

The analysis of the PFD-MS of some other small organic molecules with different functional groups (amines, nitriles, esters, acids, etc.) resulted in no further points of interest concerning the mechanisms of field induced reactions in adsorption layers discussed here.

4. Field Induced Reactions in Adsorption Layers

If the consideration of reactions in adsorbed multilayers is restricted to those in which the emitter surface itself is not active, then the only primary processes are proton transfer reactions. The term proton transfer reaction as applied to field induced processes includes the concept that the ionization process together with the transfer of the proton is a concerted process and not a consecutive reaction. The desorption products of proton transfer reactions are in the case of ethanol $(M+H)^+$, $(2M+H)^+$, $(M+C_2H_5)^+$ and $C_2H_5^+$-ions. Higher order associations are observed only rarely.

Proton transfer reactions are only observed under FI conditions when the proton affinity (PA) of M and $(M-H)^\cdot$ satisfy the following condition

$$PA(M) - PA(M-H)^\cdot \geqq 0 \qquad (19)$$

i. e. the energy necessary for protonating molecules must not be larger than that for their ionization. This restriction leads in the case of the paraffins to a difference in the field induced reactivity between methane and the higher paraffins. No influence of the external field on (19) has yet been detected.

If the proton donor and proton acceptor are different, instead of (19) the following relationship should be applicable

$$IP(M_a) - IP(M_d) + PA(M_a) - PA(M_d - H)^\cdot \geqq 0 \qquad (20)$$

where $IP(M_a)$ and $IP(M_d)$ are the ionization potentials of M_a and M_d respectively. A direct experimental verification of this condition is difficult since it is not easy to distinguish between the proton donor and proton acceptor in adsorption layers. However, indirect evidence for (20) may be obtained from the ethylene protonation reaction (6). According to (19) proton transfer reactions between ethylene ions and ethylene molecules in adsorption layers are energetically impossible. However, the protonation reaction (6) involves a surface interaction so that we may write $PA({*}C_2H_3) \cong PA(C_2H_4)$ and $IP({*}C_2H_3^\cdot) < IP(C_2H_4)$ and thus the condition (20) is fulfilled in a modified form.

Secondary reactions of free $(M-H)^\cdot$ radicals can lead according to (11) and (12) to the elimination of H from M and thus to the desorption of $(M-H)^+$-ions. The field induced elimination of hydrogen from M should be the subject of a similar condition to that imposed on proton transfer reactions, as (19) and (20).

Addition reactions of $(M-H)^\cdot$ radicals are only observed for unsaturated polar molecules under PFD-conditions.

5. Desorption Kinetics

The high $(M+H)^+$ intensity and absence of M^+ in the PFD-MS of acetonitrile (Fig. 7) not only substantiate the statement that the ionization potential of acetonitrile is not supplied during proton transfer reactions, but shows also that the electron transition probability (tunneling prob.) is larger in the formation of $(M+H)^+$. This means that the electron transition probability D mainly depends on the adiabatic ionization potential IP, or in other words on the energy which must be supplied for the formation of an ion without activation. When the ionization potentials of two ion types differ then with $IP_1 < IP_2$ we have also $D(IP_1) > D'(IP_2)$ where the function D and D' describe different electron rearrangement processes. This relationship is not only valid for protonation reactions but also for other ion forming reactions, e. g. addition reactions etc., and in many cases explains the intensity distribution of the ions of a spectrum.

6. The Specificity of Field Induced IMR in Adsorbed Layers as Compared with IMR in the Gas Phase

Ion formation by field reactions in adsorption layers may often be ascribed to IMR, similar to those observed in the gas phase. Leaving aside once more the reactions involving a chemical interaction with the surface of the emitters, field induced reactions in adsorption layers represent an intermediate stage between gas phase reactions and IMR in liquids. The characteristics of field reactions in adsorption layers as compared to IMR in the gas phase are as follows.

1. All the ions formed are immediately removed from the reaction zone because of the steep potential gradient at the emitter surface. Secondary reactions can only involve neutral products of the primary reactions.

2. The ionization potential of one of the reaction partners does not necessarily need to be supplied in order to form the products. Field reactions take place mostly without activation energy.

3. The products of field induced IMR are only generated by an electron rearrangement in a previously formed molecular complex, i. e. by simple bond rearrangement. There is no evidence for a complex formation, for instance hydrogen scrambling etc. This feature is a consequence of the particularly rapid relaxation of the excitation energy necessary for complex formation at the surface and in adsorption layers [11].

4. Despite a low emitter temperature (<200 °K) and the possibility of the relaxation of the excitation energy resulting from the ionization process no M_2^+-ions could be found with ethane and ethylene. However, M_2^+-ions of these molecules can be formed by IMR in the gas phase and stabilized by collision deactivation at pressures in the torr range. The reason for the absence of corresponding M_2^+-peaks in the FI spectrum is to be found in the high field strength (>0.1 V/Å) at the emitter surface at which a bond between M and M^+ can no longer be formed. In the case of ethane and ethylene the binding energy between M^+ and M results from polarization forces and is therefore very small ($\cong 0.1$ eV). Therefore the superimposition of the high electric field causes the minimum of the binding energy to disappear. This explains why the production of short lived M_2^+ complexes as precursor of atom rearrangement reactions cannot be expected in a high electric field. The number of possible reactions is therefore smaller in a high electric field than under field free conditions. Association of molecules is only observed under FI conditions when the binding energy between the ion and the neutral molecule is at least of the order of magnitude of that of a hydrogen bond as for instance with alcocols.

7. Conclusion

The mechanistic, energetic and kinetic aspects of field induced ion formation in adsorption layers have been discussed using small organic molecules as examples. The PFD-MS consists principally of products of protonation reactions. Exothermic IMR in the gas phase correspond to the field induced proton transfer reactions in adsorbed multilayers. However, the reaction products are not always the same for both cases. The special condition of IMR in adsorption layers lead to desorption, e. g. in the case of methanol of $(M+CH_3)^+$-ions which do not occur as exothermic reaction products of bimolecular proton transfer reactions in the gas phase. The formation of complexes preceeding rearrangement reactions is inhibited by the rapid relaxation of excitation energy in the adsorbed layers [11] and by the external high electric field. This eliminates possible reaction channels which one is led to expect from the observation of certain exothermic IMR in the gas phase.

It is hoped that the results of this investigation lead to a better interpretation of mass spectra taken with the "field desorption technique" [7], since ion formation occurs also preferably by reactions in adsorbed layers. However, reactions involving chemical surface interactions play a more important role with this method than under PFD conditions.

Acknowledgement

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