1340 © *1982 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.,* ***55,*** *1340—1343 (1982)* [Vol. 55, No. 5

A Temperature-dependent Desorption Process of Molecular Ions in Field Desorption Mass Spectrometry

Hiroaki Shiraishi,* Akira Otsuki, and Keiichiro Fuwa
Department of Chemistry and Physics, National Institute for Environmental Studies, Yatabe, Ibaraki 305

(Received April 17, 1981)

A temperature dependent desorption process of molecular ions operating in field desorption mass spectrometry (FDMS) was examined by means of measurements of desorption rates using cholesterol, stearic acid, and poly(oxyethylene) nonylphenyl ether. The desorption of ions formed under high electric field followed the first order kinetics. The desorption rate constants were measured at several emitter currents, and apparent activation energies for the desorption of molecular ions were calculated. A mass transfer process operating in FDMS is discussed.

Field desorption mass spectrometry (FDMS) has been successfully applied for various qualitative and quantitative analyses of organic compounds in many kinds of samples during the last several years.[1] In this technique, an activated emitter of 10 μm diameter tungsten wire covered with carbon microneedles is commonly employed in order to attain the high electric field essential to the ionization. The desorption of ions from the emitter is often assisted with heating by passing current through the emitter. Thus, the emitter temperature can strongly influence the FD mass spectra which are obtained.

Several types of emitter current programmers have been developed to control the emitter temperature.[2–4] Further detailed study for the temperature dependence of FD mass spectra is needed by use of these programmers in order to understand the picture of the FD process. A simple model for sample supply to activation sites of a tip emitter by field-enhanced surface diffusion from large reservoirs of adsorbed molecules on the shank of the tip has been proposed by Beckey *et al.*[5] in order to explain the results from angular distribution studies, and was supported by Cocke *et al.*[6] But, Holland *et al.* reported that the electric field has little effect on mass transfer from the activated emitter and proposed a model for the FD process which was later argued against by Beckey and Röllgen.[8] The uncertainty in the picture of the processes operaing in conventional FDMS may arise from the use of an activated emitter with many activated points under different field strengths and different temperatures.

This paper describes the temperature dependence of the field desorption process of molecular ions and the effect of high electric field on mass transfer operating in conventional FDMS.

Experimental

Mass spectrometry was performed on a JEOL JMS O1-SG double focusing mass spectrometer with a combined field desorption/field ionization/ electron impact ion source, connected to JMS-2000 mass data analysis system (Japan Electric and Optics Laboratory). The FD emitter used was 10 μm tungsten wire with carbon needles grown at high temperature.[9] An anode potential of 10 kV and cathode potential of −3 kV were applied. Emitter current was controlled by use of a modified emitter current programmer. The emitter was loaded with samples from a stock solution (1 μg/μl) using a dipping technique. Sample loading by dipping resulted in more reproducible determination of the desorption rate constants than that by microsyringe technique. Initial focusing was done on acetone introduced *via* the batch inlet, and finally using an FD ion of a sample at room temperature. A profile of FD ion current was measured by single ion monitoring. Ion current was integrated for every 0.2 s and stored in a computer. The mass chromatogram of poly(oxyethylene) nonylphenyl ether was measured by repetitive magnet scanning at an interval of 10 s. After measurement of each sample, the emitter current was increased to 60 mA in order to clean the emitter.

The emitter current-emitter temperature relationship was obtained in the following manner. An emitter was introduced into an electrically heated air bath, and its resistance was measured by means of an LCR meter (Yokokawa, Hewlett-Packard; model 4216A). Then the same emitter was introduced in an ion source and heated by passing direct current through it; the applied potential was measured by means of a voltmeter. Resistance was calculated according to the equation R=V/I.

All chemicals supplied by Wako Pure Chemical Industries, Ldt. were used without further purification.

Results and Discussion

Generation of many types of ions, such as molecular ion(M^+), protonated and cationated molecular ion ($(M+H)^+$, $(M+\text{cation})^+$), cluster ion $(nM+H)^+$, multiple charged ion (M^{n+}, $(M+nH)^{n+}$), and fragment ion, make it difficult to investigate the mechanism of ion formation and desorption in FDMS. In order to simplify the mechanism of ion formation and desorption, typical samples, which give only molecular ions in their FD mass spectra, were used in the present study.

When the emitter current was kept constant during the measurement, the intensity of molecular ions was observed to decrease exponentially with time, as shown in Fig. 1. If the desorption process of ions formed under high electric field follows the following equation at a constant temperature:

$$C_t = C_0\,\mathrm{e}^{-kt},$$

C_t: Amount of neutral material to be ionized (or ions) remaining on the emitter at time t.
C_0: Initial amount of neutral material to be ionized (or ions) remaining on the emitter at time, 0.
k: First order rate constant (desorption rate constant).

a plot $\log[C_t]$ against time should give a linear relation.

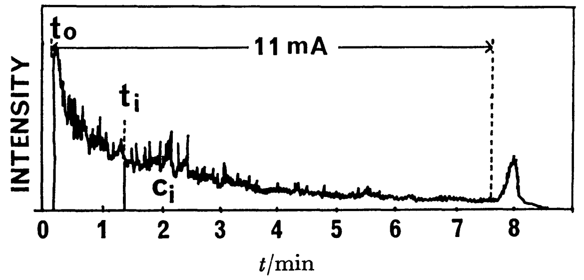

Fig. 1. Ion current profile for molecular ion of cholesterol (*m*/*z* 386) at 11 mA followed by linear increase in emitter current.

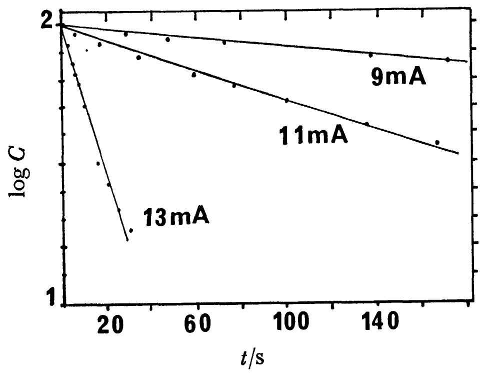

Fig. 2. log[C_t]-time plot for molecular ion of cholesterol (*m*/*z* 386) at 9, 11, and 13 mA.

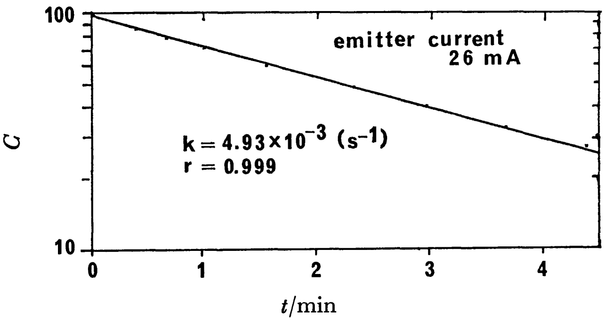

Fig. 3. log[C_t]-time plot for lithium ion attached molecular ion of lithium iodide (Li_2I^+, *m*/*z* 141) at 26 mA.

Table 1. First order rate constants *k* for desorption of molecular ions of poly(oxyethylene) nonylphenyl ether

m/*z*	8 mA	10 mA	11 mA
396	6.11×10^{-3}	1.73×10^{-2}	5.37×10^{-2}
440	3.69×10^{-3}	8.11×10^{-3}	1.88×16^{-2}
484	2.66×10^{-3}	5.79×10^{-3}	1.00×10^{-2}

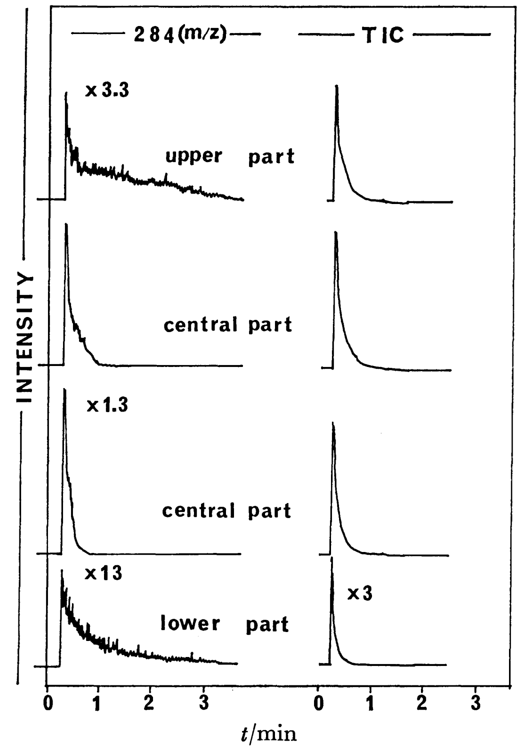

Fig. 4. Influnce of *axial* focus on ion current profile for molecular ion of stearic acid (*m*/*z* 284) at 10 mA. TIC (total ion current).

Figures 2 and 3 show log[C_t]-time plots for molecular ions of cholesterol at three different emitter currents and lithium-ion-attached molecular ion of lithium iodide (*m*/*z* 141) at 26 mA in emitter current, respectively. These results indicate that the desorption process of ions from the activated emitter at high electric field follows the first order kinetics. Table 1 shows first order rate constants for desorption of poly(oxyethylene) nonylphenyl ether containing different degrees of polymerization of ethylene oxide, calculated from each slope in the log[C_t]-time plots. Rate constants of lower molecular weight components have larger values than those of higher molecular weight components, and rate constants of each component are larger at higher emitter current than at lower emitter current. These results are consistent with the fact that fractional desorption occurs during increase in emitter current when a mixture is analyzed, permiting the analysis of a mixture under controlled conditions of emitter current.4)

It was concluded from these results that desorption of ions formed under high electric field can be expressed as a first order reaction. Therefore, it is suggested that not only qualitative but also quantitative discussion about the fractional desorption should be done by use of desorption rate constants for each compound. However, it should be mentioned that these values given in Table 1 are relative because of uncertainty of the temperature gradient along the emitter wire and also along the carbon needles under the conditions used. Fugure 4 presents the evidence which suggests that a temperature gradient may be present in an activated emitter with 5 mm separation between the two supporting poles even if the emitter current is kept constant. In a Mattauch-Herzog type mass spectrometer, accelerated ions are focused by radial and axial foucs lens on the ion detector, but all widths of ion beam band desorbed from the 5 mm long emitter cannot be simultaneously focussed on the ion detector. Thus, one part of the ion beam band, usually the central part, is focussed on the ion detector by adjusting the axial foucs lens.

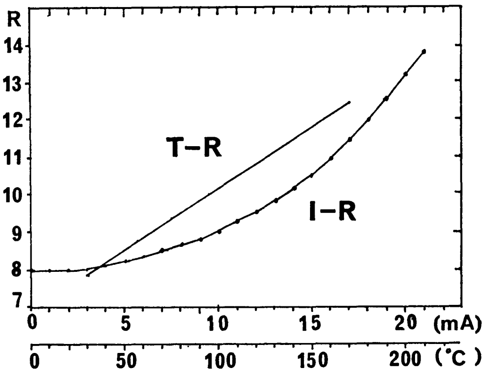

Fig. 5. Relations between emitter temperature and emitter resistance, and between emitter current and emitter resistance.

In Fig. 4, the molecular ion beam band of stearic acid was roughly divided into four parts: upper quarter, two central quarters, and lower quarter. Although similar profiles of the total ion current in each quarter were observed in every measurement, desorption profiles of the molecular ions from the two central parts of the emitter were different from the other two and the initial ion intensities were also much higher than those in the other two. These data would mean that there exists a temperature gradient on the activated emitter, and that the upper and lower parts near the two supporting poles were at a lower temperature than in the two central parts.

Since the average emitter temperature is one of the most important factors in the desorption process of ionization under high electric field, we tried to estimate the emitter temperature inside the ion source by a different way from that used in earlier papers on the estimation of emitter temperature.[10,11] Figure 5 shows a typical example of relations between emitter temperature and emitter resistance, and between emitter current and emitter resistance of 10 μm tungsten wire 5 mm long with carbon needles 20—30 μm in length. In this emitter, when the emitter current was adjusted to 9 mA, the emitter temperature was estimated to be about 65 °C with 9 Ω. The resistivity of tungsten varies as a function of temperature following the equation

$$R = R_0(1+\alpha\Delta T),$$

where $\alpha=0.0047\ \mathrm{K}^{-1}$ is the temperature coefficient of resistivity. For the activated emitter, the tungsten wire is partially converted to tungsten carbide whose temperature coefficient of resistivity is $0.0049\ \mathrm{K}^{-1}$.[12] The calculated coefficients of the activated emitters were in the range of about 0.0047 to 0.0050. The result indicated that each emitter has slightly different relations depending upon the length and number of carbon microneedles. Thus, the relations given in Fig. 5 may be used as a relative measure of the emitter temperature for the other emitters.

Using these relations, the apparent activation energy for desorption of ions formed under high electric field was obtained. Figure 6 shows an example of the Arrhenius plots (log k vs. $1/T$) for cholesterol and stearic acid. Apparent activation energies for the desorption of molecular ions of cholesterol and stearic acid at high electric field were calculated from the slopes to be 30 and 55 kcal/mol, respectively. The apparent activation energy obtained in the present study is not equivalent to that in field desorption, but may mean that required for an overall process of field desorption including migration of sample molecules to activation sites of carbon microneedles. Theoretically, the activation energy required for FD of ions under high electric field should be smaller than that for desorption of neutral molecules under no electric field.[13] These calculated values were apparently lower than the ionization potentials of both compounds, suggesting the importance of the electric field.

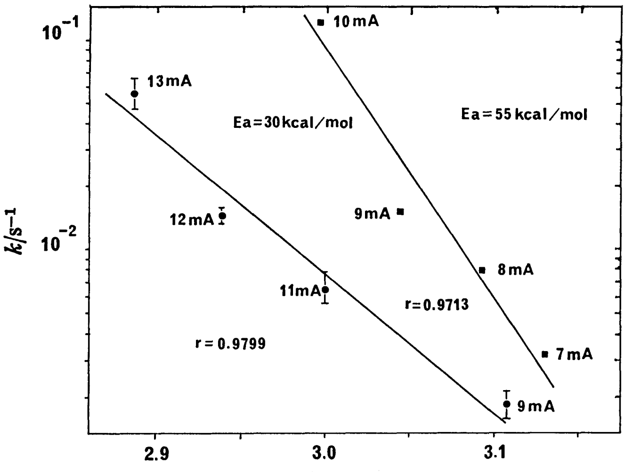

Fig. 6. $\log k - 1/T$ plot for desorption of molecular ions of cholesterol (●) and stearic acid (■).

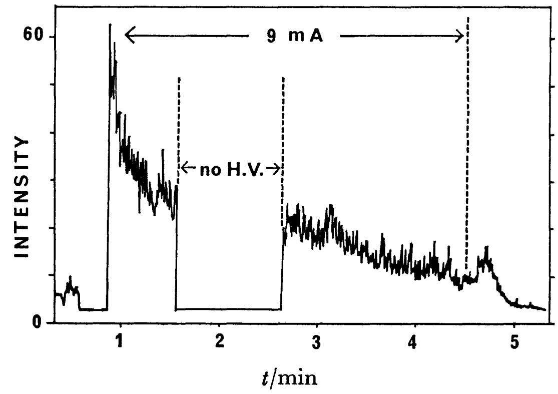

Fig. 7. Mass chromatogram of molecular ion of stearic acid measured at 9 mA followed by linear increase. High electric field was turned off for 1.5 to 2.7 min in the time course of measurement.

The fact that the desorption process follows the first order kinetics gives us the opportunity to investigate the role of high electric field for the desorption process. Figure 7 shows the mass chromatogram of molecular ions of stearic acid measured at 9 mA, followed by a linear increase. When the high electric field was turned off for 1.5 to 2.7 min in the time course of measurement, the molecular ion intensity was observed to become zero. Figure 8 shows the

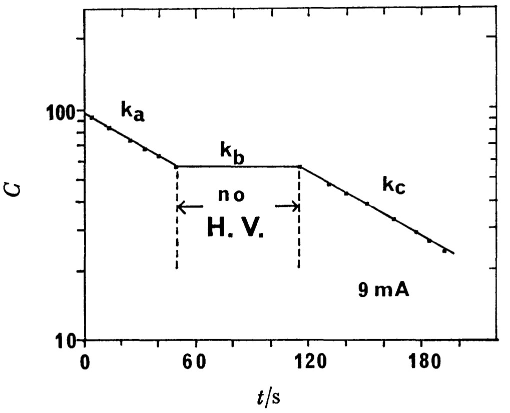

Fig. 8. log[C_t]-time plot for molecular ion of stearic acid, assuming that desorption of stearic acid did not occur under low electric field.

log [C_t]-time plot, assuming that desorption of stearic acid from the emitter under low electric field did not occur. As shown in Fig. 8, the desorption rate constant in the first stage was equal to that in the third stage when the high electric potentials were again applied. This result means that desorption of stearic acid under low electric field did not occur at 9 mA.

The same kind of experiment was carried out using cholesterol at 8 mA. It was found that the desorption rate of cholesterol under low electric field was nearly equal to that under high electric field. This result suggests that the desorption rate of cholesterol was little affected by the electric field. Similar field-independent desorption was reported by Holland *et al.*[7] and was explained on the basis of field ionization processes by Beckey and Röllgen, assuming the sample molecules to be evaporated before ionization takes place.[8] This means that the calculated apparent activation energy for desorption of cholesterol (30 kcal/mol) is mainly due to the heat of desorption of neutral molecules of cholesterol. Although there is no report on the heat of adsorption of stearic acid on the activated carbon surface, the fact that stearic acid was not desorbed at 9 mA under low field suggests that stearic acid having a carboxy group may be more strongly adsorbed on an emitter surface than cholesterol having a hydroxy group.

In conclusion, the present study indicated that desorption of ions formed under high electric field follows the first order kinetics, and that the desorption rate is temperature dependent.

References

1) H. D. Beckey, "Principle of Field Ionization and Field Desorption Mass Spectrometry," Pergamon Press, Oxford (1977).

2) H. R. Schulten and H. D. Beckey, *Cancer Treat. Rep.*, **60**, 501 (1976).

3) J. W. Maine, B. Soltmann, J. F. Holland, N. D. Young, J. N. Gerber, and C. C. Sweeley, *Anal. Chem.*, **48**, 427 (1976).

4) H. Shiraishi, A. Otsuki, and K. Fuwa, *Bull. Chem. Soc. Jpn.*, **52**, 2903 (1979).

5) H. D. Beckey, J. Dahmen, and H. Knöppel, *Z. Naturforsch., Teil A*, **21**, 141 (1966).

6) D. L. Cocke, G. Abent, and J. H. Block, *Int. J. Mass Spectrom. Ion Phys.*, **24**, 271 (1977).

7) J. F. Holland, B. Soltmann, and C. C. Sweeley, *Biomed. Mass Spectrom.* **3**, 340 (1976).

8) H. D. Beckey and F. W. Röllgen, *Org. Mass Spectrom.*, **14**, 188 (1979).

9) H. D. Beckey, E. Hilt, and H.-R. Schulten, *J. Phys. E: Sci. Instr.*, **6**, 1043 (1973).

10) H. U. Winkler and B. Linden, *Org. Mass Spectrom.*, **11**, 327 (1976).

11) D. Kümmler and H.-R. Schulten, *Org. Mass Spectrom.*, **10**, 813 (1975).

12) S. N. L'vov, M. I. Lesnaya, I. M. Vinitskii, and V. Ya Naumenko, *High Temp. (Engl. Transl.)*, **10**, 1196 (1972).

13) R. Gomer, *J. Chem. Phys.*, **31**, 341 (1959).