

Gas phase elimination of methyl group from acetophenones within the range of 10^{-11} to 10^{-6} second

A I HELAL

Physics Department, Atomic Energy Authority, Cairo, Egypt

MS received 28 July 1983

Abstract. The field ionization of acetophenone, *p*-methyl and *p*-chloroacetophenones on a $5\ \mu\text{m}$ activated wire yields an abundant peak at parent minus CH_3 group. Variations of the reaction rate as a function of the decomposition times of the elimination reaction in the range 10^{-11} - 10^{-6} sec are studied. Remarkable changes in the reaction rate according to the type of the substituent are noticed.

Keywords. Field ionization; acetophenone; reaction rate.

1. Introduction

Field ionization (FI) mass spectrometry is well suited to study the kinetics of fast unimolecular decomposition processes of organic ions in the gas phase (Beckey 1971, 1977; Van der Greef 1980; Zahran and Helal 1983; Johnstone 1972). It is possible to distinguish between fast and slow decomposition reactions in the wide range 10^{-14} to 10^{-6} sec. This is due to the extremely large potential gradient in front of the field emitter.

If a wire emitter is used, normal fragment ions are formed at the surface and near the emitter surface within a time range of 5×10^{-14} - 3×10^{-11} sec. Ions formed later in the gas phase appear as tails of strongly broadened mass lines. These ions are attributed to decompositions between 3×10^{-11} and 10^{-8} sec (fast metastable ions).

The reaction time of the decomposing ion can be calculated from the observed mass displacement (Beckey 1971, 1977). The average reaction rate constants $\bar{K}(t)$ can be evaluated as recommended by Beckey (1971, 1977) from the following equation:

$$\bar{K}(t) = I_m(t)/I_M \Delta t, \quad (1)$$

where $I_m(t)$ is the fragment ion intensity at time t , I_M is the molecular ion intensity at Δt is the time interval in which decompositions give a contribution to $I_m(t)$.

If there are no focusing lenses, fragment ions formed within 10^{-8} - 3×10^{-6} sec are called metastable ions. These ions are observed at an apparent mass number $m^* = m^2/M$, where m is the mass of the fragment ion and M is the mass of the molecular ion.

If the lens voltage is varied, a new group of metastable peaks appears which is similar in shape to the normal metastable peak group. The numbers of this group are termed "metastable plateau peaks". The apparent masses of these peaks lie between the normal metastable mass at lens voltage zero and the actual mass of the fragment ion at maximum lens voltage.

Beckey (1971, 1977) discussed in detail the method of measuring the distribution of

the average rate constant in the time range available from the fast metastable peak and the metastable plateau peaks.

According to the quasi-equilibrium theory of the mass spectra the reaction rate for a certain reaction can be expressed in a simple way:

$$K = \nu[(E - C_0)/E]^{n-1}, \quad (2)$$

where ν is the frequency factor, E is the energy absorbed, C_0 is the critical energy necessary for dissociation and n is the number of free oscillators in the molecular ion.

This simple rate equation can be used to discuss the fragmentation of organic molecules in a general sense. One would expect that greater the energy transferred during ionization *i.e.* as $((E - C_0)/E)$ increases, the faster is the decomposition of the ion. Therefore for two alternative fragmentations of an ion having similar frequency factors the rates are proportional to the activation energies.

The purpose of the present study is to determine the changes in the average rates of the elimination of methyl radical by FI of *p*-methylacetophenone, *p*-chloroacetophenone and acetophenone, in the gas phase and to learn about the substituent effect on the reaction rate. An acceptor group like Cl and a donor group like CH₃ are selected as substituents to compare their effect relative to acetophenone.

2. Experimental

A mass spectrometer (Atlas CH4) equipped with a special field ion source was used. A 5 μm tungsten wire activated with benzonitrile (Migahed and Beckey 1971) was used as field anode. The counter electrode was placed at a distance of 0.15 cm from the field anode. The focusing system contained a cylinder used as a retarding electrode (plateau electrode) of 1 cm length. The plateau electrode was raised to a variable voltage causing a variation in the metastable ion residence times on the plateau and consequently in the arrival time of the ions at the field-free region.

Figure 1 shows the potential distributions in the source. The effect of temperature on

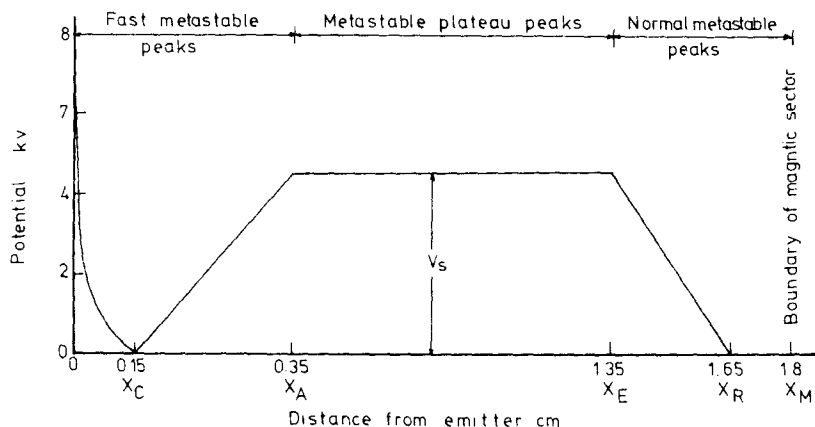
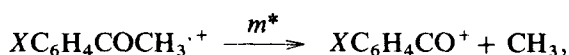


Figure 1. Potential distribution in a field ionization source with retarding electrode (X-axis: distance of electrodes from the field anode, C = counter electrode, A and E are the limits of the retarding electrode and R is the entrance slit of the first field free region).

the mass spectrum could be observed by varying the anode temperature using a direct current passing through the anode.

3. Results and discussion

The mass spectra of acetophenone, *p*-chloro and *p*-methyl acetophenones show an intense molecular ion peak which is taken as a base peak and very little fragment peaks. Elimination of CH₃ group from the molecular ions is considered as a gas phase reaction after field ionization according to the reaction:



where $X = Cl, H$ and CH_3 . This reaction is associated with the corresponding metastable peaks.

The fragment ion $(M-CH_3)^+$ is formed as a result of the C–C rupture, the bond adjacent to CO group *i.e.* it is a single bond cleavage. Helal and Zahran (1982) showed

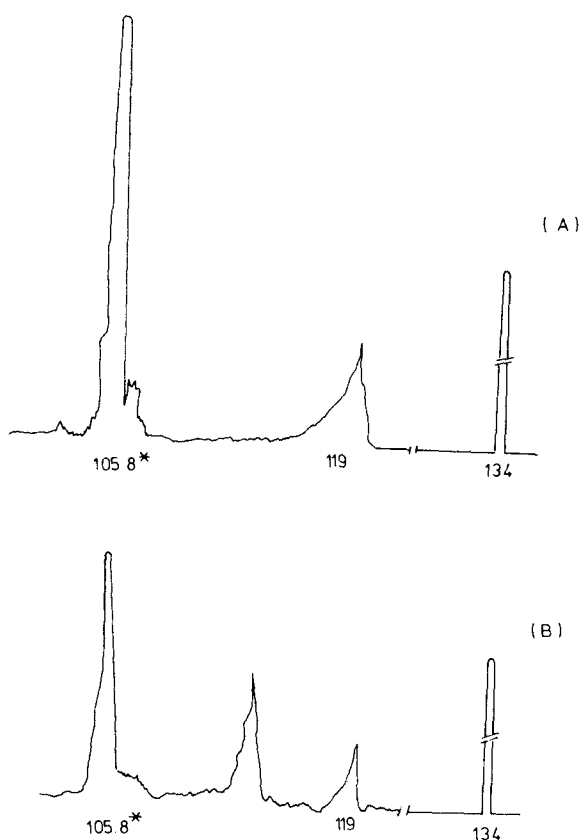


Figure 2. Part of the field ionization mass spectrum of *p*-methyl acetophenone: A-lens voltage = 0 kV, B lens voltage = 4 kV.

that the energy ΔE necessary to remove a methyl group in acetophenone from the parent ion differs from one compound to another. It is clear that the order of increase of ΔE is from *p*-chloro acetophenone to *p*-methyl acetophenone. The reaction rates may behave similar to that for the energy removal of CH_3 radical in the three molecules. The fragment ion $(\text{M}-\text{CH}_3)^+$ is formed near the emitter surface within a time range of 5×10^{-14} – 3×10^{-11} sec. Ions formed later in the gas phase and appearing as tails are attributed to decompositions between 3×10^{-11} and 10^{-8} sec, while the associated metastable ions are formed within 10^{-8} and 3×10^{-6} sec.

A new group of metastable peaks appears when the lens voltage is changed. Figure 2 shows a part of the mass spectrum of *p*-methyl acetophenone at zero lens voltage where there are no plateau peaks and at 4 kV where these peaks are of considerable intensity.

The average rate constants are measured for the elimination of the CH_3 group from acetophenone, *p*-methyl and *p*-chloroacetophenones as shown in figure 3 in the range 10^{-11} to 10^{-6} sec by the combination of the rates of the ions collected as fast metastable peaks and ions collected as plateau peaks. It is remarkable that the points originating from the two techniques fit together. This result implies the continuous distribution of the individual rate constants, which is in agreement with the statistical theory of the mass spectra.

It is clear from figure 3 that the order of increase of the average rates is from *p*-methyl acetophenone to *p*-chloroacetophenone, which is in agreement with the order of increase of energy.

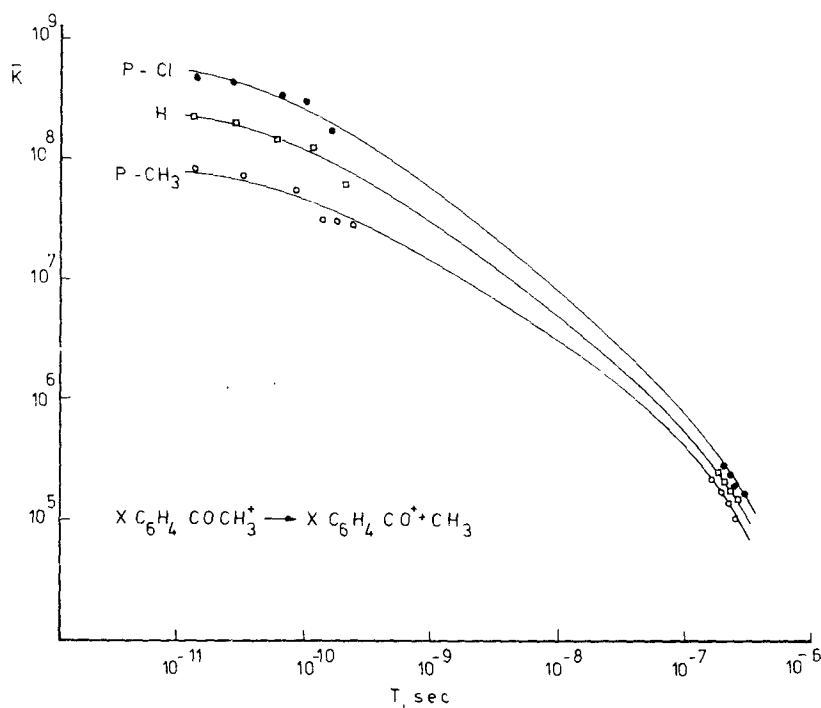


Figure 3. Average rate constants for the decomposition of acetophenone, *p*-methyl acetophenone and *p*-chloroacetophenone as a function of the ion residence time.

The dependence of the average rate constants upon the internal energy can also be obtained from the dependence of the reaction rate curves on temperature. Figure 4 shows that the relative intensity of the fragment ion $(\text{M}-\text{CH}_3)^+$ increases continuously with temperature. This can be understood according to the quasi-equilibrium theory, as the rate constant for a certain decomposition reaction is a function of the total energy transferred to the molecular ion and increase in thermal energy increases the rate of dissociation and consequently the fragment intensity.

Figure 5 shows that the curve of the average rate constant at high temperature is in general parallel to the curve obtained at room temperature but is shifted towards higher rates. This is in agreement with the statistical theory according to which the rate constants should be strongly dependent of the internal energy transferred to the molecule.

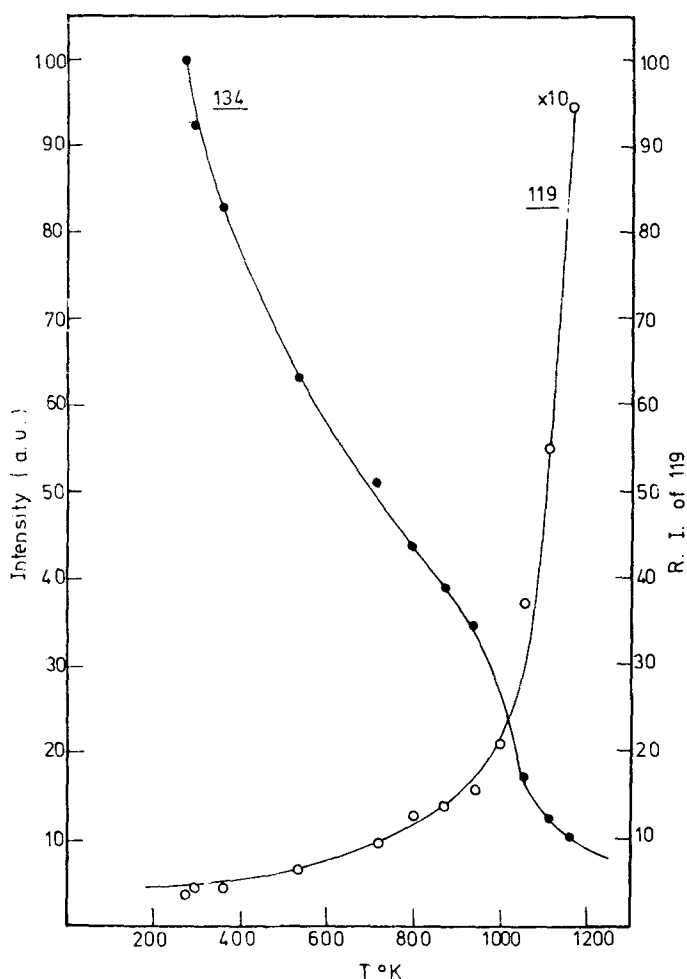


Figure 4. Variation of the ion intensities in *p*-methylacetophenone with field anode temperature (134 = parent ion and 119 = $(\text{M}-\text{CH}_3)^+$ ion).

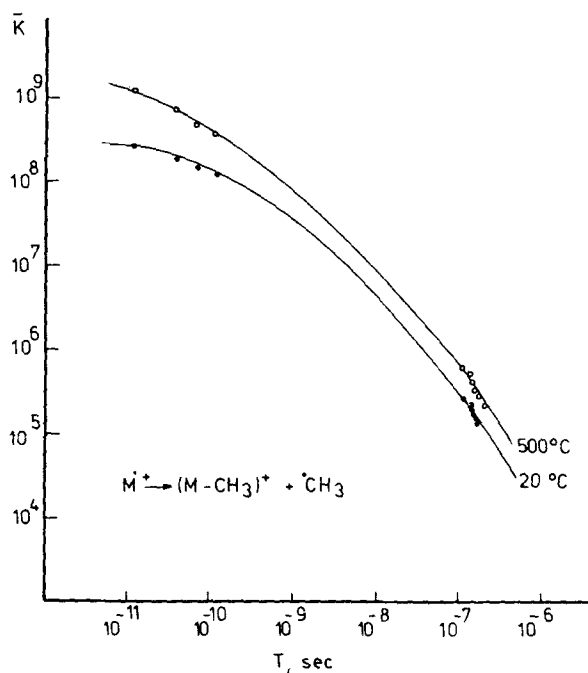


Figure 5. Average rate constants for decomposition of *p*-methyl acetophenone as a function of the ion residence time at two temperatures.

References

- Beckey H D 1971 *Field ionization mass spectrometry* (Oxford: Pergamon Press)
- Beckey H D 1977 *Principles of field ionization and field desorption mass spectrometry* (Oxford: Pergamon Press)
- Helal A I and Zahran N F 1982 *Indian J. Phys.* **B56** 205
- Johnstone R A W 1972 *Mass spectrometry for organic chemists* (Cambridge: Cambridge University Press)
- Migahed M D and Beckey H D 1971 *Int. J. Mass Spectrom. Ion. Phys.* **7** 1
- Van der Greef 1980 *Field ionization and field desorption mass spectrometry* Ph.D. thesis, Amsterdam University
- Zahran N F and Helal A I 1983 *Org. Mass Spectrom.* **18** 212