Appearance Energies and Calculated Partial Mass Spectra of (2,3-), (2,4-) and (2,5-) Dimethylaniline Isomers

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The ionization and appearance energies for the molecular and fragment ions, respectively, of the three dimethylaniline isomers are reported. Breakdown graphs have been constructed expressing the energy dependence of the fragmentation of the isomeric molecular ions covering the internal energy range from threshold to approximately 10 eV. The kinetic shift and the critical energy for the fragments $(M\text{-}H)^+$ and $(M\text{-}CH_3)^+$ ions are also calculated.

Introduction

Appearance energy (A) determinations allow for the evaluation of critical energies (E^0) and heats of formation of ions [1]. One of the significant sources of errors in measurements of A is the kinetic shift [2, 3]. Several authors tried to quantify A's free of any kinetic shift by measuring metastable ions for different reactions in the field free regions (FFR) [4 – 7] of a mass spectrometer.

A more precise test of the quasi equilibrium theory (QET) [8] is possible by calculating the ion abundances at different electron energies (breakdown graph) and compare calculated and experimental values [9 – 11]. The breakdown graphs provide detailed information on the fragmentation channels of the molecular ion and the competition between these channels as a function of the internal energy of the molecular ion [12, 13]. As such they provide more detailed information than electron impact (EI) mass spectra, which sum the breakdown graphs over an unknown internal energy distribution; also they are better than metastable ion abundances which provide information only on the energy fragmentation channels.

The aim of this investigation is to study the effect of the position of the methyl groups on the ionization (I) and A values obtained from the three isomers. This also includes a check of the applicability of the QET for calculating the partial mass spectra of large molecules.

Experimental

The measurements were made with a Varian MAT-CH5 double focusing mass spectrometer of the reversed Nier-Johnson geometry. The ion source used was the conventional EI ion source, designed so that it can be operated by an electron energy varying between 4.5 and 29.5 eV. For the standard normal operation the ionizing electron energy was 70 eV. The filament current was set at 2.6 A during the operation while the electron emission current was fixed at 15 μA and the ion accelerating voltage was at 3 kV. The I's and A's were measured by the method of semi-log plots [5, 14], except that A for the loss of CH_2 in 2,5-dimethylaniline was measured by the vanishing current method. The electron energy scale was calibrated with benzene ($I = 9.25$ eV) [15] for the measurement of molecular and fragment ions. The ionization efficiency (IE)-curves were recorded several times and gave reproducible values of I and A within ± 0.05 eV and ± 0.10 eV, respectively. The solutions of the integral for molecular and fragment ions were computed by a programable calculator HP 97.

Results and Discussions

Ionization and Appearance Energies

Figure 1 shows semi-log plots of IE curves for the three isomers, namely for the molecular M^+ ions formed in the ion source and for the fragments $(M\text{-}H)^+$ and $(M\text{-}CH_3)^+$ ions formed in both ion source and second FFR. Data for ions formed in the ion source and in the 2nd FFR are limited to 0.01% and 0.09%, respectively, due to the low detection sensitivity.

The extrapolation of the linear parts of the IE curves for the isomers give the I's of M^+ ions and

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A's of $(M\text{-}H)^+$ and $(M\text{-}CH_3)^+$ ions, see Table 1. The I's are in agreement with those reported [16]. Within experimental error, the I's of the molecular ions of the three isomers are equal. The lower values of the I's of the dimethylaniline isomers are due to the NH_2 group which has an electron-donating character. Also, no appreciable difference is observed in the A's in both regions for the reactions in 2,3- and 2,4-dimethylaniline isomers, except for the loss of CH_3 from the molecular ions in the ion source, which is greater in 2,4- than in 2,3-dimethylaniline isomers. On the other hand, in the case of 2,5-dimethylaniline the A's for the loss of H and CH_3 from molecular ions show notably higher differences from their counterparts in 2,3- and 2,4-dimethylanilines. Therefore, one might expect that 2,3- and 2,4-dimethylaniline reactions proceed from the same transition state configuration, which is different in the case of 2,5-dimethylaniline.

It has been suggested that a partial measurement of the kinetic shift, the excess energy required for observation of mass spectrometric fragmentation, can be obtained from the difference between the A's of metastable and normal fragment ions [5, 17]. Accordingly, it is clear from Table 1 that the partial shifts for the loss of H and CH_3 from 2,3-, 2,4- and 2,5-dimethylaniline are (0.45 eV and 0.25 eV), (0.67 eV and 0.68 eV) and (0.59 eV and 0.68 eV), respectively. These values provide a lower limit for the kinetic shift operative in ion source reactions.

Table 1. Ionization and appearance energies of dimethylaniline isomers.

Compound	M^+	$(M\text{-}H)^+$		$(M\text{-}CH_3)^+$	
	I (eV)	A (eV)			
		Ion source	2nd FFR	Ion source	2nd FFR
2,3-dimethylaniline	7.45	10.9	10.45	10.1	9.85
2,4-dimethylaniline	7.38	11.0	10.33	10.6	9.92
2,5-dimethylaniline	7.59	12.58	11.99	11.31	11.19

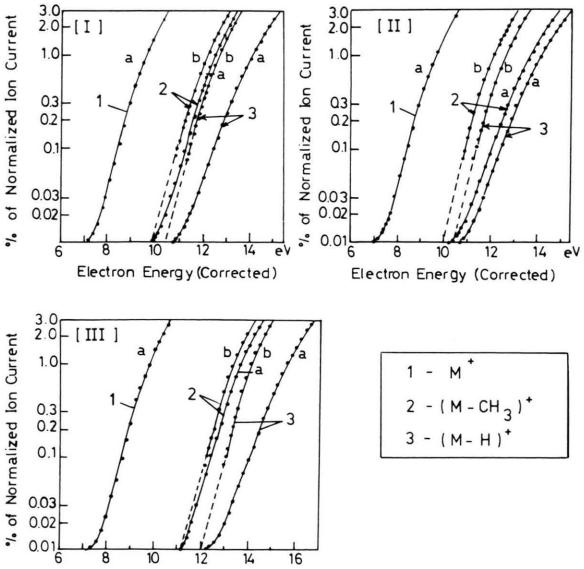

Fig. 1. Semi-log plots of ionization efficiency curves for molecular ions M^+ and fragment ions $(M\text{-}CH_3)^+$ and $(M\text{-}H)^+$. I: 2,3-dimethylaniline; II: 2,4-dimethylaniline; III: 2,5-dimethylaniline. a) Ions formed in ion source; b) ions formed in 2nd FFR.

The experimental E^0 [6] with minimum kinetic shift (A in 2nd FFR-I) led to the values (3 eV and 2.95 eV and 4.4 eV) for the loss of H and (2.4 eV and 2.54 eV and 3.6 eV) for the loss of CH_3 in 2,3-, 2,4- and 2,5-dimethylaniline, respectively. These large values of E^0 indicate the formation of thermodynamically reactive fragment ions which can decompose significantly further [11]. It is clear that the E^0 data above are nearly equal in 2,3- and 2,4-dimethylaniline but differ from their counterparts in 2,5-dimethylaniline. Also, it is interesting to notice that the direct cleavage of C−H bond requires a higher critical energy than C−C bond cleavage for every compound in the three isomers.

It is evident that the kinetic shifts reach considerable values for the reactions studied in the three aniline isomers as a result of the high E^0's of these processes.

Partial Mass Spectra

The reactions studied are the loss of H and CH_3 from the three isomers 2,3-, 2,4- and 2,5-dimethylaniline, in addition to the loss of CH_2 which is present only in the case of 2,5-dimethylaniline. For this purpose a calculation was carried out on the basis of the model proposed by Heller et al. [10], using the experimental I's and E^0's. Since no mtastable transition is assigned to the loss of CH_2 in 2,5-dimethylaniline, E^0 was calculated – using A as measured by the vanishing current method for the

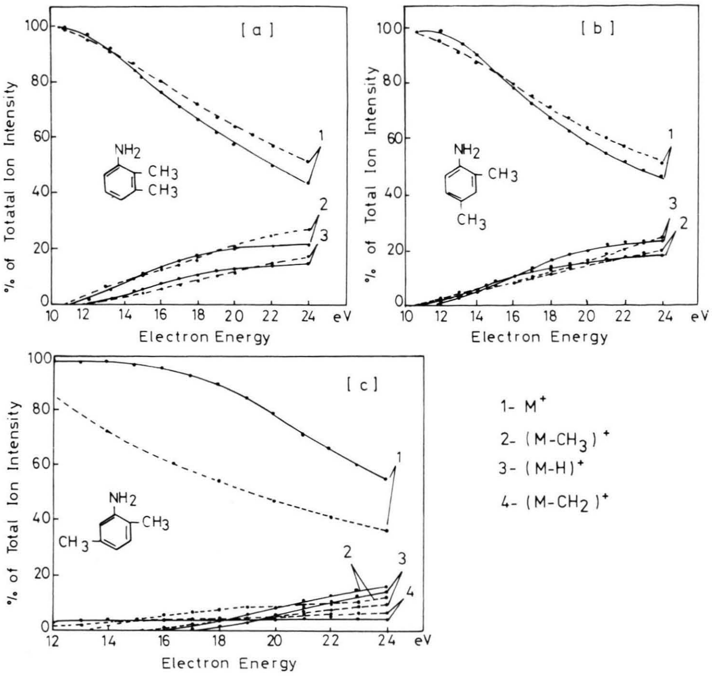

Fig. 2. Plot of ion intensity vs. electron energy for a) 2,3-dimethylaniline, b) 2,4-dimethylaniline and c) 2,5-dimethylaniline; solid lines: experimental; dashed lines: calculated.

$(M\text{-}CH_2)^+$ ion formed in the ion source – and found to be 0.45 eV. In addition, the frequency factors for the loss of H and CH_3 are $64 \times 10^{13}\,s^{-1}$ and $4 \times 10^{13}\,s^{-1}$, while for the loss of CH_2 ($1 \times 10^6\,s^{-1}$) is taken as adjusted parameter. The results are summarized in Figure 2.

2,3-Dimethylaniline

The abundance of the $(M\text{-}H)^+$ and $(M\text{-}CH_3)^+$ ions shows that a dramatic increase with electron energy increase occurs with the latter more than the former. A good agreement is obtained between experimental and calculated curves.

2,4-Dimethylaniline

The mass spectra of this compound show that below an electron energy of about 16 eV the intensities of both the $(M\text{-}H)^+$ and $(M\text{-}CH_3)^+$ ions are nearly equal while at higher energies the $(M\text{-}H)^+$ ions are more aboundant than the $(M\text{-}CH_3)^+$ ions. Again a good agreement is obtined.

2,5-Dimethylaniline

The abundance of the $(M\text{-}CH_2)^+$ ion shows a slight variation with electron energy which characterizes a rearrangement reaction. It has been observed that the yield of the $(M\text{-}CH_2)^+$ ion at energies lower than 18 eV is higher than that of the $(M\text{-}CH_3)^+$ ion, while at energies higher than 18 eV the intensity of the $(M\text{-}CH_3)^+$ ion is greater. A calculation using only the frequency factor ($10^6\,s^{-1}$) for CH_2 loss as adjustable parameter gives rise to a moderate fit with the observed spectra. We can presently offer no explanation for the poor agreement in the case of 2,5-dimethylaniline except that it may partially reflect experimental errors in the determination of A of the $(M\text{-}CH_2)^+$ ion.

It is evident that the process with the lower E^0 and tighter transition state (rearrangement) predominates at low internal energies, while, the process with higher E^0 and looser transition state (direct cleavage) predominates at higher internal energies. This result is in agreement with that reported previously [18, 19].

In conclusion we can say that the energy dependence can be used to differentiate between rearrangement reactions and direct bond cleavages. The agreement achieved between the observed and calculated breakdown graphs helps to emphasize that the QET is applicable for calculations of the partial mass spectra of large molecules. In general, from I and A values and breakdown graphs it is believed that the internal energy distributions for 2,3- and 2,4-dimethylaniline molecular ions are identical and that isomerization can occur. This is different from the case of 2,5-dimethylaniline.

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