2. The rate of thermal decomposition of mixtures \((\text{NH}_2)_2\text{COH}\)\(\text{ClO}_4\)\(-\text{(NH}_2)_2\text{CO}\) in a melt is significantly higher than that of the pure compound, owing to the crucial role of preliminary dissociation into the initial base and acid.

LITERATURE CITED


A MASS–SPECTROMETRIC INVESTIGATION OF NITROGEN TRIFLUORIDE
BY THE ELECTRON SHOCK METHOD

A. V. Dudin, A. V. Baluev, and L. N. Gorokhov

Ionization of \(\text{NF}_3\) molecules with formation of positive ions (PI) was investigated in [1–4]. Information on ionization of \(\text{NF}_3\) with formation of negative ions (NI) is both scanty and conflicting [1, 5, 6]. Reese and Dibeler [1] detected \(\text{F}^-\) and \(\text{F}_2^-\) ions with appearance potentials (AP) close to zero; Thynne [5] also recorded the \(\text{NF}^-\) ion, but there is no information on the behavior of the ionization efficiency curves (IEC) during electron dissociative capture near the threshold energy values. Harland and Franklin [6] detected the \(\text{NF}_2^-\) ion and measured the AP of \(\text{F}^-\), \(\text{F}_2^-\), and \(\text{NF}_2^-\) ions.

Our aim is to obtain fuller information on formation of NI in gaseous \(\text{NF}_3\) under the influence of electron shock (ES) and to measure the appearance potentials of PI and the initial kinetic energies of the ions.

EXPERIMENTAL

The work was performed on a redesigned MKh-1303 mass spectrometer. Volatile fluorides were introduced into the ion source via a stainless-steel admission system. The ion source had a liquid-nitrogen-cooled jacket. The measurement apparatus and procedure were described in [7]. The \(\text{NF}_3\) specimen was freed of highly volatile impurities at liquid-nitrogen temperature and from the less volatile ones at \(-140^\circ\text{C}\).

DISCUSSION OF RESULTS

The mass spectrum of PI, recorded at an ionizing electron energy of 70 eV, practically coincided with that given in [1] and contained the following ions (the relative intensities are given in parentheses): \(\text{NF}_3^+\) (62.5), \(\text{NF}_2^+\) (100.0), \(\text{NF}^+\) (31.2), \(\text{F}^+\) (1.4), \(\text{N}^+\) (2.0). In contrast to the IEC for the standard (the \(\text{CO}^+\) ion from CO) and for \(\text{N}^+\) and \(\text{NF}_3^+\) ions, in certain cases the IEC for \(\text{NF}^+\) and \(\text{NF}_2^+\) have elongated initial sectors of weak intensity (Figs. 1 and 2). Cooling of the ion source jacket with liquid nitrogen greatly reduces the intensity of the initial sectors, that of \(\text{NF}^+\) being virtually eliminated (see Fig. 1). It seems that the initial sectors of the IEC are due to ionization of the \(\text{NF}_2\) and \(\text{NF}\) free radicals, formed on the hot cathode of the ion source and in the hot zone adjoining the cathode.

Fig. 1. Ionization efficiency curves with formation of positive ions. Here and in Figs. 2 and 3 the ion current is in arbitrary units.

Fig. 2. Ionization efficiency curves with formation of positive ions.

In the determination of the AP of the ions from the IEC, we deducted the contribution of processes which lead to the appearance of the initial sectors. The intensity of the initial sector was linearly extrapolated to high electron energies (the dashed line in Fig. 2).

From Table 1 we see that our values of the AP for PI agree with the more accurate results of photoionization measurements in [3]. The ES method often leads to values somewhat higher than the photoionization data. Previously [7], we estimated the overall error of AP measurement as 0.2 eV. Table 1 shows that the systematic overestimation of the measured AP for PI in this investigation is less than 0.1 eV. Taking account of reproducibility errors, the overall error can be estimated as ±0.15 eV or ±3 kcal/mole, except in the case of the N⁺ ion, for which it is ±5 kcal/mole (owing to the low intensity).

Using the deviation method [9] we measured the initial (i.e., before acceleration of the ion source by the electric fields) kinetic energies of the fragment ions. The distribution maxima for the kinetic energies correspond to the following values: NF₂⁺ (0.04±0.01 eV), NF⁺ (0.04±0.01 eV), N⁺ (0.10±0.02 eV). The measurements were performed at electron energies 5 eV higher than the threshold values. The initial kinetic energy of the ions must be taken into account in calculations of the bond splitting energies from the AP of the ions (see below). In the calculation we must use the initial energy of the fragments at the threshold value of the ionizing electron energy, which is less than the overall energy of the fragments at the distribution maximum. In the formation of NF₂⁺ the overall kinetic energy of the fragments can be unambiguously calculated from the kinetic energy of NF₂⁺ by means of

<table>
<thead>
<tr>
<th>Ions</th>
<th>Process</th>
<th>Potential difference, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>auto [8]</td>
<td>data [3]†</td>
</tr>
<tr>
<td>NF₃⁺</td>
<td>NF₃⁺→NF₃⁺+2e⁻</td>
<td>13.10±0.06</td>
</tr>
<tr>
<td></td>
<td>NF₃⁺→NF₃⁺+F⁺+2e⁻</td>
<td>14.14±0.06</td>
</tr>
<tr>
<td>NF⁺</td>
<td>NF⁺→NF⁺+F⁺+2e⁻</td>
<td>17.64±0.08</td>
</tr>
<tr>
<td>N⁺</td>
<td>NF⁺→N⁺+3F⁺+2e⁻</td>
<td>25.1±0.2</td>
</tr>
</tbody>
</table>

*The ± sign is followed by the values of the 95% confidence interval.
†Photoionization method.