SHORT COMMUNICATION

On the Dissociation of Ethanol Molecular Ions Formed by Charge-Exchange-Collisions with Positive Ions

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Recently, Koch and Lindholm1) studied the ions produced from ethanol molecule by use of a double mass spectrometer; the ions were formed by charge-exchange-collisions with several positive ions in the collector of the first spectrometer.

A theoretically interesting point in their research is the fact that two maxima were found in the curve of relative intensities of main fragments 45 and 31 vs. the internal energy of ethanol molecular ions formed. Such a result cannot be expected by the usual statistical theory2) which should give only one maximum. This finding, therefore, is necessitated for the theory to explain the discrepancy by introducing some factors in it, though the relative intensities for many substances can be reproduced with success.

However, the above discrepancy may be explained, if it is assumed that an electronically excited state is also taken into consideration besides the ground state of the ethanol ion. In actual calculation the following dissociation scheme was adopted, extending Friedman's mechanism3).

\[
\text{Excited state} \quad \text{IP}=10.4 \text{ eV.} \\
\text{Ground state} \quad \text{IP}=11.6 \text{ eV.}
\]

The total amount of the j-th ion will thus be given by the sum of the corresponding ions of both states: 0.62 \( I_j \) (ground state) + 0.38 \( I_j \) (excited state).

Adopting the frequency factors and activation energies cited in Table 1, the relative abundance of the ions was calculated. The results on the fragments 45 and 31, i.e. \( \text{C}_2\text{H}_5\text{OH}^+ \) and \( \text{CH}_3\text{OH}^+ \), as well as on the parent ion are shown in Fig. 1, where the relative abundance after \( 10^{-5} \) sec. is plotted against the internal energy of ethanol molecular ions formed. From these curves it may be seen also that the second discrepancy which Koch and Lindholm pointed out is disap-
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Fig. 1. Excess internal energy vs. relative intensities of ions.
\[ C_2H_5OH^+, C_2H_4OH^+, CH_2OH^+, \text{ theor. value.} \]

peared; e.g. the observed steep uprising of the fragment ion 45 at about 0.2 – 0.4 eV above the appearance potential can be reproduced. This is due to the assumption that the numbers of the internal degrees of freedom in the excited and ground states are one-third and one-fifth, respectively, to the numbers theoretically expected. Such an assumption of the effective internal degrees of freedom may be reasonable if Chupka's research on photodissociation\(^4\) is considered.

Details of the calculation including the comparison of the calculated relative intensities with the observed will be reported in Nippon Kagaku Zasshi (J. Chem. Soc. Japan).

In short Koch and Lindholm's result can be explained by the ordinary statistical theory if an electronically excited state is introduced into the dissociation scheme.

References