BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (11), 3387—3388 (1975)

Proton Transfer Reactions in Oxygen-Containing Molecules and Ammonia Mixtures

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(Received April 19, 1975)

Synopsis. Ion-molecule reactions leading to the formation of NH_4^+ in a number of mixtures of oxygen-containing molecules and ammonia have been studied using pulsed-source mass spectrometry. Some unique features in the reactivities of $C_2H_4O^+$ and CHO^+ ions from ethylene oxide have been found.

The gas-phase ion chemistry of oxygen-containing molecules has been investigated by several investigators.[1-4] Blair and Harrison[1] have recently reported that the $C_2H_4O^+$ ion initially formed by electron impact of ethylene oxide is unreactive but undergoes a collisional modification to a more reactive species which shows a different reactivity from that of the $C_2H_4O^+$ ion from acetaldehyde. They have pointed out two possibilities: the difference arises from structural effects or from energy effects.

In this paper we report the rate constants of proton transfer reactions from the prominent ions in the mass spectra of oxygen-containing molecules including acetaldehyde and ethylene oxide to ammonia as a common neutral molecule. The results offer additional evidence for the unique features of ionic species from ethylene oxide. The rate constants of the hydrogen atom transfer reactions from oxygen-containing molecules to ammonia ion were also determined.

Experimental

The experiments were performed on a Hitachi-RMU5 mass spectrometer fitted with a pulsed ion source as described previously.[4]

Acetaldehyde prepared from paraldehyde, commercial dimethyl ether, and methanol were purified by vacuum distillation. The purities of these samples were more than 99%. Ethylene oxide and ammonia purchased from Takachiho Kagaku Co., Ltd., in research grade purity of 99.9% were used without further purification. The rate constants of the ion-molecule reactions studied were calibrated with reference to the reported rate constant, $k=1.22\times10^{-9}$ cm^{3}mol^{-1} s^{-1}, for the reaction $CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$.[5]

Results and Discussion

As a preliminary to the study of the proton transfer reactions in mixtures containing ammonia, the reactions forming NH_4^+ ion in pure ammonia were investigated at 12—25 eV electron energies. NH_3^+, NH_2^+, and NH^+ were observed as the primary ions. However, as has been suggested by Derwish and co-workers,[6] NH^+ was not a reactant ion for forming NH_4^+ with ammonia. The rate constants of proton transfer reactions of NH_3^+ and NH_2^+ ions were determined from the analysis of $I_{NH_2^+}/I_{NH_3^+}$ *vs* delay time plots. The results obtained are given in Table 1 and are in agreement with those reported by Harrison and co-workers,[5] except for Reaction 2. It should be pointed out here that impact electron energies higher than 12 eV were employed for all the experiments, since k_1 varies with the energy of the impact electron below 12 eV.[7]

In the mixtures of an oxygen-containing molecule and ammonia, the significant primary ions, omitting the ions from ammonia, are as follows: $CH_3OCH_3^+$, $CH_3OCH_2^+$, $C_2H_3O^+$, and CHO^+ for dimethyl ether, $C_2H_4O^+$, $C_2H_3O^+$, and CHO^+ for acetaldehyde and ethylene oxide, and CH_4O^+, CH_3O^+, and CHO^+ for methanol. Table 1 shows the possible reactions leading to the formation of an NH_4^+ ion in each system.

The secondary ion current of NH_4^+ ($m/e=18$) can be generally described for the dimethyl ether–ammonia system by

$$I_{18} = \left\{k_1I_{17}+k_2I_{16}+k_3I_{46}+k_4I_{45}+k_5I_{43}+k_6I_{29} + k_7I_{17}\frac{[CH_3OCH_3]}{[NH_3]}\right\}[NH_3]t + C_1$$

TABLE 1. RATE CONSTANTS OF ION-MOLECULE REACTIONS IN PURE AMMONIA AND OXYGEN-CONTAINING MOLECULE-AMMONIA MIXTURES

	Reaction	Rate constant, $k\times10^{10}$ (cm^3 mol^{-1} s^{-1})
	NH_3	
1	$NH_3^+ + NH_3 \longrightarrow NH_4^+ + NH_2$	10.7(10.0[a])
2	$NH_2^+ + NH_3 \longrightarrow NH_4^+ + NH$	7.99(6.5[a])
	$CH_3OCH_3-NH_3$ mixture	
3	$C_2H_6O^+ + NH_3 \longrightarrow NH_4^+ + C_2H_5O$	8.43
4	$C_2H_5O^+ + NH_3 \longrightarrow NH_4^+ + C_2H_4O$	4.73
5	$C_2H_3O^+ + NH_3 \longrightarrow NH_4^+ + C_2H_2O$	<0.5
6	$CHO^+ + NH_3 \longrightarrow NH_4^+ + CO$	11.2
7	$NH_3^+ + C_2H_6O \longrightarrow NH_4^+ + C_2H_5O$	9.37
	$CH_3CHO-NH_3$ mixture	
8	$C_2H_4O^+ + NH_3 \longrightarrow NH_4^+ + C_2H_3O$	12.0
9	$C_2H_3O^+ + NH_3 \longrightarrow NH_4^+ + C_2H_2O$	<0.5
10	$CHO^+ + NH_3 \longrightarrow NH_4^+ + CO$	11.1
11	$NH_3^+ + C_2H_4O \longrightarrow NH_4^+ + C_2H_3O$	4.37
	$C_2H_4O-NH_3$ mixture	
12	$C_2H_4O^+ + NH_3 \longrightarrow NH_4^+ + C_2H_3O$	<0.1
13	$C_2H_3O^+ + NH_3 \longrightarrow NH_4^+ + C_2H_2O$	<0.1
14	$CHO^+ + NH_3 \longrightarrow NH_4^+ + CO$	1.8
15	$NH_3^+ + C_2H_4O \longrightarrow NH_4^+ + C_2H_3O$	5.46
	CH_3OH-NH_3 mixture	
16	$CH_4O^+ + NH_3 \longrightarrow NH_4^+ + CH_3O$	34.0
17	$CH_3O^+ + NH_3 \longrightarrow NH_4^+ + CH_2O$	8.57
18	$CHO^+ + NH_3 \longrightarrow NH_4^+ + CO$	10.4
19	$NH_3^+ + CH_4O \longrightarrow NH_4^+ + CH_3O$	9.00

a) From Ref. 5).

where k_i is the rate constant for reaction (i), I_M the intensity of ion ($m/e=M$), [NH_3] and [CH_3OCH_3] are the concentrations of the reactant molecules, t is the delay time, and C_1 is a constant. Similar relations consisting of several reactions shown in Table 1 can be applied to the other systems investigated. By analysis of the results obtained under various impact electron energies and mixing ratios of reactant molecules, the rate constants of the reactions leading to the formation of NH_4^+ were determined and are shown in Table 1.

The rate constants for a proton transfer reaction from the parent ions to ammonia are strongly dependent on ion species: highest for methanol, lowest ($<1\times10^{-11}$ $cm^3mol^{-1}s^{-1}$) for ethylene oxide. Taking into account our experimental conditions, in which the reaction time did not exceed 2 μs, the very low reactivity of the $C_2H_4O^+$ ion from ethylene oxide is in agreement with the result observed for initially formed $C_2H_4O^+$[1] prior to the collisional modification. Another interesting result is that the CHO^+ ions derived from dimethyl ether, acetaldehyde, and methanol show a high reactivity of about 11×10^{-10} $cm^3mol^{-1}s^{-1}$, while the CHO^+ ion from ethylene oxide is less reactive. Since the proton transfer processes of CHO^+ and $C_2H_4O^+$ ions from ethylene oxide and acetaldehyde to ammonia are all quite exothermic, a simple thermochemical consideration cannot explain the low reactivities of CHO^+ and $C_2H_4O^+$ ions derived from ethylene oxide.

The fragment ions $CH_3OCH_2^+$ and CH_3O^+ react with significant rates to give NH_4^+ ion, while the $C_2H_3O^+$ ions are unreactive.

The rate constants for the hydrogen atom transfer reaction from oxygen-containing molecules to ammonia ion are less specific compared with those of the proton transfer reactions.

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