NOTES

A Mass Spectrometric Study of Aluminum Chloride

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The mass spectra of aluminum halides have already been reported on by Porter and Zeller.[1] According to them, the presence of a trimer of aluminum chloride is indicated, and the mean bond-strength between aluminum and chlorine is larger than that between aluminum and bromine. In the present report, the effect of several additives on aluminum chloride was investigated with a mass spectrometer of the high-resolution type (Hitachi RMU-7HR), the effect was investigated in relation to the work reported previously[2-4] on the reaction intermediate of the catalytic polymerization of sublimated aluminum chloride.

Experimental

The tube used for storing sublimated aluminum chloride[2-4] was connected at the sampling part of the mass spectrometer. The aluminum chloride was then sublimated again by heating it into the sampling part and by leading it into the ion source of the mass spectrometer.

In the cases of samples containing hydrogen chloride or deuterium chloride, aluminum chloride was introduced into the storing tube, and the vapor of the compound to be added was introduced into the storing tube through gaseous substances.

In the cases of samples containing water or deuterium oxide, the aluminum chloride tube was heated after the addition of water or deuterium oxide, so as to collect volatile substances only, and thus preventing non-volatile substances from being introduced into the mass spectrometer. The indentification of the ions was very easy because of the presence of the chlorine isotopes, ^{35}Cl and ^{37}Cl, in the ratio of 3 : 1.

Results and Discussion

From the spectra thus obtained, the corresponding peaks of the Al^+(m), Cl^+(m), $AlCl^+$(m), $AlCl_2^+$(v. s.), $AlCl_3^+$(s), $Al_2Cl_5^+$(s) and $Al_2Cl_6^+$ (v. w.) ions were identified, the maximum peak being that of the $AlCl_2^+$ ion. Besides, HCl^+ could be observed as a result of the reaction of aluminum chloride with a small quantity of water in the spectrometer. A peak corresponding to that of the $Al_3Cl_8^+$(w) ion appeared in the measurement of aluminum chloride alone, as had been reported previously.[1] A peak corresponding to that of the $Al_3Cl_9^+$(v. w)[1] ion could also be identified in the measurement of aluminum chloride with deuterium oxide added.

The present results agree well qualitatively with those of Porter and Zeller,[1] but the pattern coefficient does not agree very well with theirs. Moreover, several small peaks were observed in the regions near $m/e=171$(w) and 303(v. w.), they were assigned to the D_2AlCl_4, $HDAlCl_4$, H_2AlCl_4, HAl_2Cl_7 and DAl_2Cl_7 ions, as Tables 1 and 2 show. Of course, they are produced by the reaction of aluminum chloride with additives and water in the mass spectrometer, and by the exchange reaction of hydrogen with deuterium.

When water or hydrogen chloride was added to aluminum chloride, the peaks in the regions near $m/e=171$ and 303 were very weak and the pattern coefficient in the presence of water or hydrogen chloride was smaller than that when deuterium oxide was added. The peaks of $m/e=167$ and $m/e=168$, which could be ascribed to the $AlCl_4^+$ and $HAlCl_4^+$ ions respectively, did not appear even if they did exist. When deuterium oxide was added to aluminum chloride, the corresponding peak of $DAlCl_4^+$ did not appear either.

Therefore, the peaks in the regions near m/e;171 seem to be H_2AlCl_4, D_2AlCl_4, and $HDAlCl_4$, while the very weak peak at $m/e=169$ is interpreted as being H_2AlCl_4 by means of the small pattern coefficient when water or hydrogen chloride is added.

When deuterium oxide or deuterium chloride was added to aluminum chloride, the peak of the $Al_2Cl_7^+$ ion ($m/e=299$) was not observed, but small peaks of the $HAl_2Cl_7^+$ ion ($m/e=300$) and the $DAl_2Cl_7^+$ ion ($m/e=300$) appeared. The pattern coefficient of these ions can be interpreted

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1) R. F. Porter and E. E. Zeller, *J. Chem. Phys.*, **33**, 858 (1960).
2) K. Hirota and T. Imanaka, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **84**, 960 (1963).
3) T. Imanaka and K. Hirota, *ibid.*, **85**, 359 (1965).
4) T. Imanaka and K. Kishimoto, *ibid.*, **85**, 819 (1964).

TABLE 1. PARTIAL MASS SPECTRA OF ALUMINUM CHLORIDE ADDED BY SEVERAL ADDITIVES

m/e	Experimental values D_2O	Relative height assumed as $AlCl_4$ *etc.*	Possible ions
167	4	75($AlCl_4$)	$AlCl_4$
168	1		$HAlCl_4$
169	2	100($AlCl_3Cl^*$)	$DAlCl_4$, H_2AlCl_4
170	20		$HDAlCl_4$
171	100	50($AlCl_2Cl_2^*$)	D_2AlCl_4, $H_2AlCl_3Cl^*$
172	14		$HDAlCl_3Cl^*$
173	70	11($AlClCl_3^*$)	$D_2AlCl_3Cl^*$, $H_2AlCl_2Cl_2^*$
174	8		$HDAlCl_2Cl_2^*$
175	19	1($AlCl_4^*$)	$D_2AlCl_2Cl_2^*$, $H_2AlClCl_3^*$

$Cl^* = {}^{37}Cl$

Pattern Coefficient: $AlCl_2$ (maximum peak, $m/e=97$)$=100$
$AlCl_2Cl^*$ (D_2O, $m/e=171$)$=8$

Numerical values are relative ones.

vs, very strong; s, strong; m, medium; w, weak; vw, very weak

TABLE 2. PARTIAL MASS SPECTRA OF ALUMINUM CHLORIDE ADDED BY SEVERAL ADDITIVES

m/e	Experimental values D_2O	Experimental values DCl	Relative height assumed as $Al_2Cl_7^+$ *etc.*	Possible ions
299	0	0	43(Al_2Cl_7)	Al_2Cl_7
300	12			HAl_2Cl_7
301	64	62	100($Al_2Cl_6Cl^*$)	DAl_2Cl_7
302	24			$HAl_2Cl_6Cl^*$
303	100	100	100($Al_2Cl_5Cl_2^*$)	$DAl_2Cl_6Cl^*$
304	19			$HAl_2Cl_5Cl_2^*$
305	64	55	56($Al_2Cl_4Cl_3^*$)	$DAl_2Cl_5Cl_2^*$
306	10			$HAl_2Cl_4Cl_3^*$
307	24	14	19($Al_2Cl_3Cl_4^*$)	$DAl_2Cl_4Cl_3^*$

$Cl^* = {}^{37}Cl$

Pattern Coefficient: $AlCl_2$ (maximum peak)$=100$
$Al_2Cl_5Cl_2^*$ (D_2O, $m/e=303$)$=1.6$
$Al_2Cl_5Cl_2^*$ (DCl, $m/e=303$)$=0.03$

Numerical values are relative ones.

by means of the existence of the $HAl_2Cl_7^+$ and $DAl_2Cl_7^+$ ions. Thus, small quantities of H_2AlCl_4-type ions (H_2AlCl_4, $HDAlCl_4$, and D_2AlCl_4) and HAl_2Cl_7-type ions (HAl_2Cl_7 and DAl_2Cl_7) are expected to exist in the ion source. This fact suggests that not only the molecules of the HAl_2Cl_7 type, but also those of the H_2AlCl_4 type are present in the vapor phase. The presence of HAl_2Cl_7-type species, proposed in our previous paper,[3] is thus supported by these experimental results.

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