CHEMISTRY LETTERS, pp. 733-736, 1974. Published by the Chemical Society of Japan

ION-MOLECULE REACTIONS BETWEEN THALLIUM(I) AND VARIOUS LIGANDS: FORMATION OF 1:1 COMPLEXES IN GAS PHASE

Hiroaki NAKAYAMA, Chiho NISHIJIMA and
Satoshi TACHIYASHIKI
Kagawa Nutrition College, Sakadomachi, Saitama 350-02

Gas phase reactions of thallium(I) cation with several ligands were investigated by the use of hexafluoroacetylacetonato-thallium(I) as a precursor of the ion. 1:1 complex formation with thallium(I) was observed.

The present paper reports the detection of TlL^+ type complexes in a gas phase where L is amine, phosphine, arsine and bismuthine derivatives or an aromatic hydrocarbon, with the aid of mass spectrometers.

Our interest lies in the comparison of the ligands in their reactivity to Tl^+ ion and also in the detection of new thallium(I) complexes not found in a liquid phase so far. Mass spectrometry has advantages in the investigation of unstable metal complexes without isolating products.

But in general, the experimental study of complex forming reaction between free metal cations and ligand molecules is difficult because of the difficulty to supply metal ions in sufficient amounts at reasonably low temperature where the ligands do not decompose. These obstacles were overcome by the use of the volatile precursor, hexafluoroacetylacetonato-complex, for Tl^+ ion. Eight ligands, triphenylbismuthine, triphenylarsine, triphenylphosphine, 1,10-phenanthroline, 2,2'-bipyridine, 4,4'-bipyridine, p-phenylenediamine and phenanthrene were subjected to study.

The 1:1 mixture of a ligand and hexafluoroacetylacetonatothallium(I), Tlhfa, prepared by the Hartman's method1) was ground in an agate mortar and inserted directly to the source chamber of a JEOL JMS-D10C or a JEOL JMS-07-S high resolution mass spectrometer2) with the direct inlet system.

In the case of all the ligands except p-phenylenediamine3), the formation of TlL^+ ions was confirmed in more than two runs4) (see Table 1.). The conditions of bombardment vary with complexes; for instance, triphenylphosphinethallium(I) complex cation was observed when the vapor phase mixture was bombarded with 30eV energy. It was, however, more preferable to bombard with 75eV in order to observe 4,4'-bipyridinethallium(I) cation.

Since the complex formation in a solid phase before vaporization was not noticed5) and Tl^+ was the predominant species in the mass spectrogram of hexafluoroacetylacetonatothallium(I)6), it is likely that the reaction proceeds in a

Table 1. Some examples of mass spectra of 1:1 mixtures of hexafluoroacetylacetonatothallium(I) with various ligands.

ligand molecule (L)		Tlhfa$^+$	Tl$^+$	L$^+$	TlL$^+$	a)	b)
triphenylbismuthine	m/e	412	205	440	645		
I		100*	out	0.80	0.74	60°C	30V
I		100*	out	1.08	0.70	40	75
triphenylarsine	m/e	412	205	306	511		
I		100	out	1635*	2.33	40	30
I		100	out	1440*	0.98	-	-
triphenylphosphine$^{c)}$	m/e	412	205	262	467		
I		100	out	214	10.7	90	30
I		100	5750*	6000	-	90	75
I		100	out	174*	2.9	50	30
1,10-phenanthroline	m/e	412	205	180	385		
I		100	1900	30300*	55.6	90	75
I		100	1920*	1170*	18.6	50	75
2,2'-bipyridine	m/e	412	205	156	361		
I		100	4540	8200*	9.1	60	75
I		100	4260*	2210	5.9	70	75
4,4'-bipyridine	m/e	412	205	156	361		
I		100	1423*	19920*	5.6	70	75
I		100	out	1337*	1.96	70	75
p-phenylenediamine	m/e	412	205	108	313		
I		100	2680	29700*	-	70	75
I		100	out	2670*	-	60	75
phenanthrene	m/e	412	205	178	383		
I		100	2161	2260*	58.2	-	30
I		100	1868	18804*	11.4	-	75

a). source filament temperature.

b). electron accelerating voltage.

I. relative intensities normalized to ^{205}Tlhfa in a run of mass spectrum.

out. scale out.

* values estimated on the intensity of the peaks of the ions containing isotopes.

c). A JEOL JMS-07-S mass spectrometer was employed in the measurements for triphenylphosphine ligand, while a JEOL JMS-D100 mass spectrometer was employed for other ligands.

gas phase as ion-molecule reactions (1), (2).

$$\mathrm{Tlhfa} \dashrightarrow \mathrm{Tlhfa}^{\ddagger} \dashrightarrow \mathrm{Tl}^+ + \mathrm{hfa}^{\bullet} \qquad (1)$$

$$\mathrm{Tl}^+ + \mathrm{L} \dashrightarrow \mathrm{TlL}^+ \qquad (2)$$

Direct evidences for the formation of 1:1 complexes of thallium(I) with triphenylbismuthine, triphenylarsine, triphenylphosphine, phenanthrene, 4,4'-bipyridine, 2,2'-bipyridine and 1,10-phenanthroline were obtained. No thallium(I) complexes with bismuth, arsenic nor phosphorus ligands has been isolated from a liquid phase so far. The 1:2 complexes of the last two ligands with thallium(I) have been reported[7]. No evidences of the presence of 1:2 nor 2:1 complexes was obtained in the present experiments.

The intensity ratio of TlL^+ to Tl^+, $I_{\mathrm{TlL}^+}/I_{\mathrm{Tl}^+}$, represents the concentration ratio, $[\mathrm{TlL}^+]/[\mathrm{Tl}^+]$. A plot of log $I_{\mathrm{TlL}^+}/I_{\mathrm{Tl}^+}$ vs. the reciprocal of the source filament temperature in the case of 1,10-phenanthroline ligand is shown in Fig. 1. The formation of the complex is favored at higher temperatures and the plot is approximately linear. This temperature dependence is attributable to those of the vapor pressure of the ligand and of the reaction rate constant. The slope may be the sum of the activation energy of the ion-molecule reaction and the sublimation enthalpy change of 1,10-phenanthroline. The measurements of

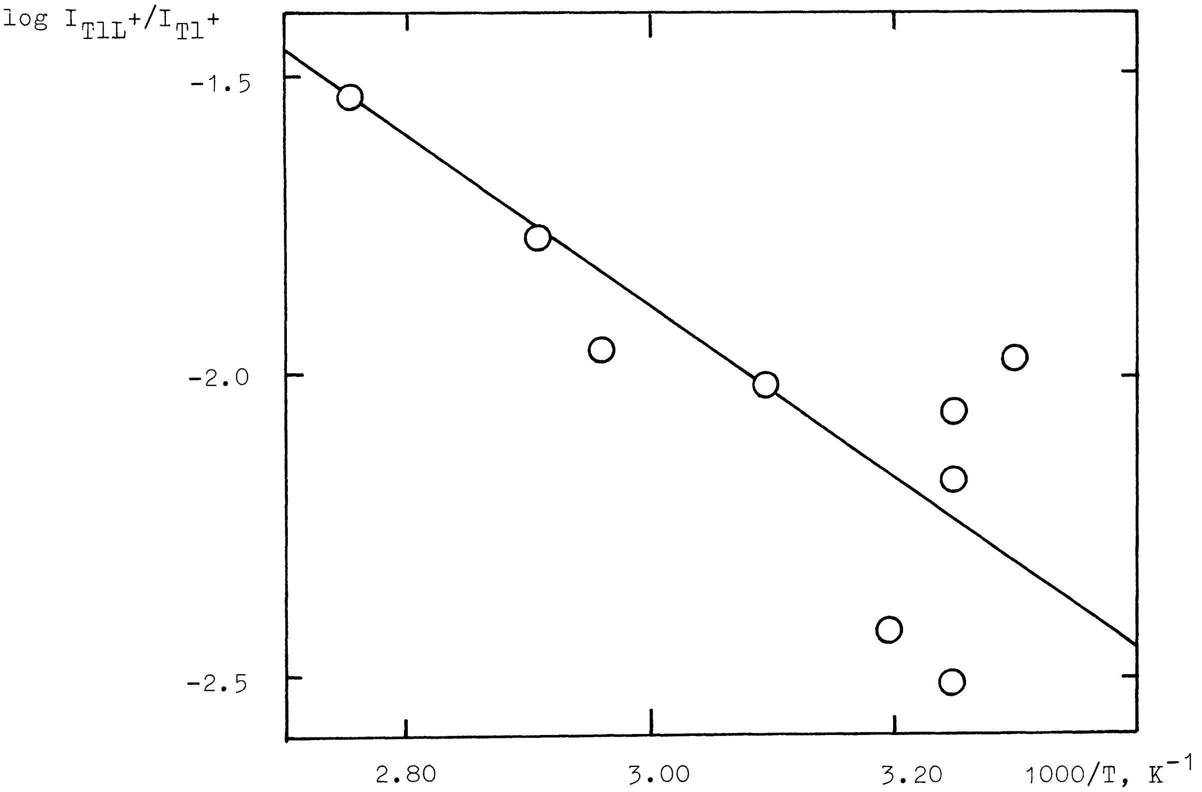

Fig. 1. Temperature dependence of the intensity ratio $I_{\mathrm{TlL}^+}/I_{\mathrm{Tl}^+}$ in the mass spectrogram of 1:1 mixture of Tlhfa and L for 1,10-phenanthroline.

the vapor pressure of the ligand molecules in the source chamber will be a future subject of studying the complex formation reactions in more quantitative way by estimating their relative cross sections like a recent report$^{8)}$, in which the reactions between (cyclopentadienyl)nitrosylnickel complex cation and various ligands were discussed.

ACKNOWLEDGEMENT: The authors wish to express their hearty thanks to Prof. Hiroo Inokuchi and Prof. Yukiyoshi Sasaki of the University of Tokyo for their kind interest in this work.

REFERENCES

1) F. A. Hartman, P. L. Jacoby and A. Wojciki, Inorg. Synth., 12 81 (1970).
2) We are indebted to Mr. M. Shino, Mr. Y. Shirai, Mr. K. Matsuura, Mr. H. Ishijima and Mr. M. Suzuki of Japan Electron Optics Laboratory Co., Ltd. for their aid in the mass spectrometric measurements.
3) Two interpretations may be considerable; one is that p-phenylenediamine has too small cross section with Tl^+ ion to be observed, and the other is that electron transfer from p-phenylenediamine to Tl^+ ion resulted in the formation of thallium atom and $L^{\dagger}$ ion.
4) Abundance ratio of thallium isotopes was successfully used to identify TlL^+, Tl^+ and $Tlhfa^{\dagger}$ peaks and to distinguish $TlBi(C_6H_5)_3^+$ and $Tl_2(OC)hfa^+$ having the same m/e values of 645. The only peaks observed, which were assigned to the ions containing a thallium atom and were absent in the mass spectrum of hexafluoroacetylacetonatothallium(I), were those of TlL^+ ions in the present experiments.
5) The infrared spectra of the mixtures of hexafluoroacetylacetonatothallium(I) and 2,2'-bipyridine are representable as the overlapping of the spectra of the two components, even for the sample kept at 70°C for 10 minutes and for that left for 10 months after mixed at room temperature. The infrared spectra were recorded with a Hitachi EPI-S2 spectrometer for the samples in the nujol mulls.
6) H. Nakayama, unpublished work. Metastable peaks relating to the reaction process (1) were observed in the mass spectrum of acetylacetonatothallium(I). So postulating the process (1) for hexafluoroacetylacetonatothallium(I) is reasonable. Peaks of the fragment ions other than Tl^+ were less intensive than that of the parent ion in the mass spectrum of hexafluoroacetylacetonatothallium(I).
7) literatures cited in a review, A. G. Lee, Coord. Chem. Reviews, 8 289 (1972).
8) J. Mueller and W. Goll, Chem. Ber., 106 1129 (1973).

(Received April 30, 1974)