Evaluation of the relative Lewis acidities of lanthanoid(III) compounds by tandem mass spectrometry

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The Lewis acidities of five series of lanthanoid(III) compounds are evaluated based on their competitive dissociation observed by tandem mass spectrometry.

The reactivity of lanthanoid compounds is of considerable interest in synthetic organic chemistry and has been studied for the past two decades.[1,2] Although mass spectrometry has been used mainly for organic structure elucidation,[3] tandem mass spectrometry has been applied recently to evaluate the reactivities of organic compounds.[4] Here, we use this method for the investigation of reactivities of lanthanoid compounds.

Trivalent lanthanoid compounds such as $CeCl_3$, $Yb(OTf)_3$ and $Sc(OTf)_3$ are frequently employed as reagents or catalysts, which owing to their high Lewis acidities, interact with carbonyl or imine functionalities in organic compounds.[1,2,5–9] The intrinsic chemical properties of lanthanoid compounds, however, including their reactivity, still remains unclear. A quantitative evaluation of their Lewis acidities is essential for the development of new reagents and catalysts, as well as for a comprehensive understanding of their reactivities. Herein, we report a direct method for the evaluation of the Lewis acidities of lanthanoid compounds by the use of tandem mass spectrometry (MS).[10]

We have observed an extremely reproducible fragmentation of precursor ions derived from a series of lanthanoid(III) triflate complexes, using collision-activated decomposition (CAD) in tandem MS. Moreover, the intensity ratio of the ion due to the loss of the triflate group to that from the loss of a coordinating ligand such as hexamethylphosphoramide (Fig. 1), shows significant differences among the lanthanoid(III) compounds studied. This suggested to us that the stability of these product ions directly reflects the electronic properties of each central element a view strongly supported by recent kinetic studies using MS for thermochemical measurements.[4,11]

A total of 48 compounds consisting of three series of lanthanoid complexes, $M(OTf)_3(hmpa)_4$ (hmpa = hexamethylphosphoramide), $M(OTf)_3(tepo)_4$ (tepo = triethylphosphine oxide) and $M(OTf)_3(tmp)_4$ (tmp = trimethyl phosphate), (M = Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu) were synthesized. The tandem MS measurements were performed with four-sector (EB/EB) equipment, JMS-700T (JEOL), using Xe as the collision gas with a variable collision cell voltage of 0.5–3.0 kV. FAB with NBA as a matrix was used for ionization.

In all hmpa complexes, the fragment ion $[M(OTf)_2(hmpa)_2]^+$ is the base peak. This ion was selected as the parent ion for the
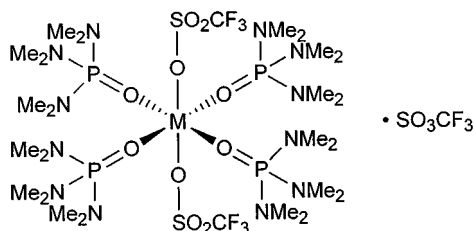
CAD experiments. The FAB MS fragment ion spectrum of $[Er(OTf)_2(hmpa)_2]^+$ is shown in Fig. 2 as a representative example. In this fragment ion spectrum, we focused our attention on $[ErF(OTf)(hmpa)_2]^+$ and $[Er(OTf)_2(hmpa)]^+$, obtained by loss of OTf and hmpa, respectively. The logarithmic ratio of the ion intensities, $\ln\{[MF(OTf)(hmpa)_2]^+/[M(OTf)_2(hmpa)]^+\}$,† show significant differences with M (Fig. 3).

Upon loss of OTf, a fluoride ion remains attached to the central atom. Retention of fluoride has been ascribed to the strong affinity of Ln(III) for fluoride, and it has been previously reported that the thermal decomposition of $Ln(OTf)_3$ affords LnF_3.[12] The overall fragmentation scheme of the complexes studied involves the competitive loss of (OTf − F), and the loss of a ligand connected to the central atom such as hmpa (see Fig. 2). Any difference in the ratio of the two fragment ions reflects the electronic property of the lanthanide in terms of the affinity between the metal and oxygen or fluorine rather than any steric contribution. Observation of a discontinuity at gadolinium (Fig. 4) as a result of its electronic state also supports this theory. The properties of a given lanthanide, *i.e.* its Lewis acidity, can thus be evaluated using tandem MS.
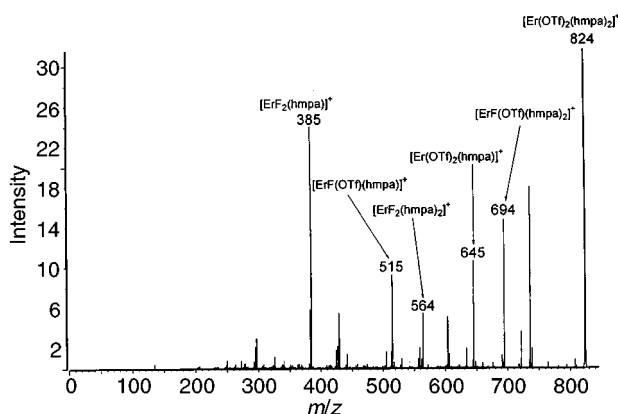

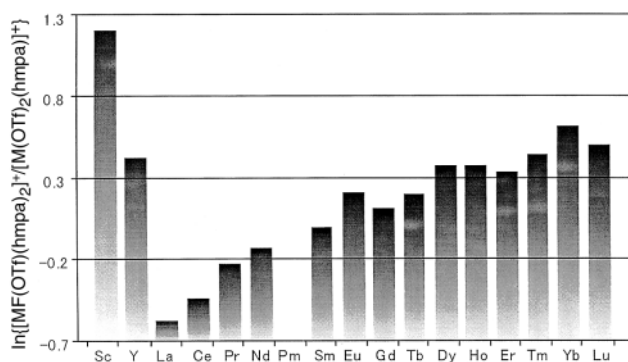**Fig. 2** MS/MS spectrum of $[Er(OTf)_2(hmpa)_2]^+$ (m/z = 824).

Fig. 3 MS/MS ion peak ratio, $\ln\{[MF(OTf)(hmpa)_2]^+/[M(OTf)_2(hmpa)]^+\}$.
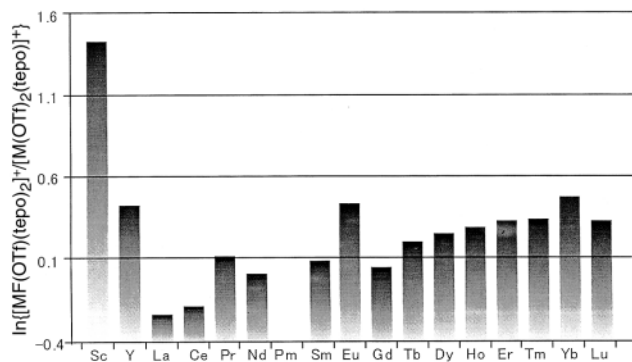

Fig. 1 Chemical structure of $M(OTf)_3(hmpa)_4$.

Fig. 4 MS/MS ion peak ratio, $\ln\{[\text{MF(OTf)(tepo)}_2]^+/[\text{M(OTf)}_2(\text{tepo})]^+\}$.

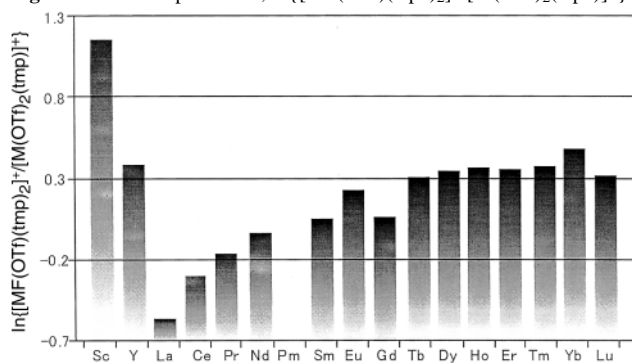**Fig. 5** MS/MS ion peak ratio, $\ln\{[\text{MF(OTf)(tmp)}_2]^+/[\text{M(OTf)}_2(\text{tmp})]^+\}$.

Two other series of rare earth complexes, $\text{M(OTf)}_3(\text{tepo})_4$ and $\text{M(OTf)}_3(\text{tmp})_4$, exhibit similar results. The corresponding intensity ratios for $\ln\{[\text{MF(OTf)(tepo)}_2]^+/[\text{M(OTf)}_2(\text{tepo})]^+\}$ obtained from $[\text{M(OTf)}_2(\text{tepo})_2]^+$ as the parent ion, and for $\ln\{[\text{MF(OTf)(tmp)}_2]^+/[\text{M(OTf)}_2(\text{tmp})]^+\}$ from $[\text{M(OTf)}_2(\text{tmp})_2]^+$ are illustrated in Fig. 4 and 5, respectively.

The oxophilicity of lanthanoids was also observed by the measurement of the competitive loss of OTf and tepo from $[\text{M(OTf)}_2(\text{tepo})_4]^+$ to give $[\text{M(OTf)}_2(\text{tepo})_3]^+$ or $[\text{M(OTf)}_2(\text{tepo})_2]^+$. The values of $\ln\{[\text{M(OTf)}_2(\text{tepo})_3]^+/[\text{M(OTf)}_2(\text{tepo})_2]^+\}$ for the lanthanoid(III) metals were as follows Sc: 1.55, Y: 1.45, La: 1.40, Ce: 1.42, Pr: 1.42, Nd: 1.40, Sm: 1.43, Eu: 1.45, Gd: 1.41, Tb: 1.43, Dy: 1.46, Ho: 1.42, Er: 1.43, Tm: 1.45, Yb: 1.52, Lu: 1.42. Additionally, pure oxophilicity was estimated using $[\text{MCl}_2(\text{tepo})_3]^+$ in which the effect of fluorine is not involved and the values of $\ln\{[\text{MCl}_2(\text{tepo})_2]^+/[\text{MCl}_2(\text{tepo})]^+\}$ were as follows: Sc: 2.37, Y: 1.87, La: 1.36, Ce: 1.37, Pr: 1.41, Nd: 1.49, Sm: 1.68, Eu: nd., Gd: 1.72, Tb: 1.76, Dy: 1.80, Ho: 1.84, Er: 1.87, Tm: 1.91, Yb: 2.09, Lu: 1.97.

The data presented in Figs. 3–5 and above, clearly demonstrate that Sc has the largest quotient followed by Yb.[13]† This is consistent with the exceptionally high catalytic activity of both Sc(III) and Yb(III) compounds in many Lewis acid-promoted reactions. Identical results were derived from experiments for complexes of other ligands such as dimethylsulfoxide and dimethylpropyleneurea. The high Lewis acidity of Sc(III) and Yb(III) is mainly ascribed to their small ionic radii. The higher acidity of Yb(III) relative to Lu(III) may originate from an incomplete number of electrons (thirteen) in the 4f orbital which has a tendency to become filled (f^{14}) which renders Yb(III) more electron-attractive than Lu(III). Other important observations of lanthanoid(III) behavior such as the gadolinium break and tetrad effects are also observed in these results.

In summary, using tandem mass spectrometry we have successfully evaluated the relative Lewis acidities of lanthanoid(III) compounds. The application of this methodology to other related compounds is in progress.

Notes and references

† The ratio of the rate constant k_1 (OTf loss) and k_2 (ligand loss) can be determined from the abundance of two product ions, $[\text{MF(OTf)(ligand)}_2]^+$ and $[\text{M(OTf)}_2(\text{ligand})]^+$. Therefore, $\ln(k_1/k_2)$ gives a measure of the affinity for each central atom. See ref. 4, pp. 378–381.

‡ These facts are consistent with the data obtained from X-ray crystallographic analysis of a series of hmpa-coordinated lanthanoid triflates. The Sc and Yb complexes show relatively long P–O bond lengths towards hmpa. It is reasonable to consider that such P–O bond elongations are due to the relatively strong Lewis acidity of Sc^{3+} and Yb^{3+}.

1 G. A. Molander, in *Comprehensive Organic Synthesis*, ed. B.M. Trost, Pergamon, Oxford, 1991, vol. 1, ch. 1.9.
2 T. Imamoto, *Lanthanides in Organic Synthesis*, Academic Press, London, 1994.
3 E. De Hoffmann, J. Charette and V. Stroobant, *Mass Spectrometry; Principles and Applications*, John Wiley, New York, 1996.
4 R. G. Cooks and P. S. H. Wong, *Acc. Chem. Res.*, 1998, **31**, 378.
5 T. Imamoto, in *Comprehensive Organic Synthesis*, ed. B. M. Trost, Pergamon, Oxford, 1991, vol. 1, ch. 1.8.
6 S. Kobayashi, *Synlett*, 1994, 689.
7 S. Kobayashi, *Pure Appl. Chem.*, 1988, **70**, 1019.
8 A. Sella and J. G. Brennan, *Organometallics.*, 1998, **26**, 28.
9 S. Kobayashi, *Eur. J. Org. Chem.*, 1999, **1**, 15.
10 K. L. Busch, G. L. Glish and S. A. McLuckey, *Mass Spectrometry/Mass Spectrometry: Techniques and Applications of Tandem Mass Spectrometry*, VCH, New York, 1988.
11 R. G. Cooks, J. S. Patrick, T. Kotiaho and S. A. McLuckey, *Mass Spectrom. Rev.*, 1994, **13**, 278.
12 N. Yanagihara, S. Nakamura and M. Nakayama, *Chem. Lett.*, 1995, 555.
13 T. Imamoto, M. Nishiura, Y. Yamanoi, H. Tsuruta and K. Yamaguchi, *Chem. Lett.*, 1996, 875.

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