Inorganica Chimica Acta, *147* (1988) 131–133

Ligand Basicities from Reactions with Nd[$(CF_3CO)_2CH]_3\cdot$THF

GREGORY R. CHOPPIN and KEMIN YAO*

Department of Chemistry, Florida State University, Tallahassee, Fla., 32306-3006, U.S.A.

(Received January 22, 1988)

Abstract

Proton NMR spectroscopy has been used to obtain the equilibrium constants for the reaction in $CDCl_3$ solvent:

$$\mathrm{Nd[(CF_3CO)_2CH]_3\cdot THF + B \rightleftharpoons Nd[(CF_3CO)_2CH]_3\cdot B + THF}$$

where B represents neutral bases with oxygen or nitrogen donors. The ΔG of reaction is well correlated with the Gutmann donor number of the bases. For the oxygen bases, ΔG correlates with Drago's E_B parameter but not the C_B parameter; for the nitrogen bases, the reverse was obtained (*i.e.*, correlation with the C_B but not the E_B).

Introduction

A method of preparation of ternary lanthanide compounds with hexafluoroacetone and tetrahydrofuran was described earlier [1]. The compounds dissolve well in chloroform. The ability of Nd(III) to induce large pseudo-contact shifts in hydrogen resonances has been employed to study the reaction in which the THF adduct in Nd[$(CF_3CO)_2CH]_3\cdot$THF is displaced by other basic adducts. These reactions are rapid and reversible, so the shift of the THF protons can be used to calculate equilibrium constants for the reactions. These constants provide a measure of the relative basicities of the adducts.

Experimental

Reagents

Nd[$(CF_3CO)_2CH]_3\cdot$THF was prepared and analyzed as described in ref. 1. The bases were reagent or spectral grade and used with no further purification after drying over molecular sieves. $CDCl_3$(99.8 atom % D) from Aldrich was used as the solvent.

NMR Experiments

The solutions for NMR study were normally 0.005 M Nd[$(CF_3CO)_2CH]_3\cdot$THF and 0.005 M base. The assignment of the resonance peaks of the protons in the Nd[$(CF_3CO)_2CH]_3\cdot$THF were made from spectra of solutions of the Nd compound and dimethylsulfoxide in $CDCl_3$ in which the molar ratio of the Nd complex to DMSO varied from 1:0.33 to 1:1.3. The ^1H shifts were measured at ambient temperature on the 270 MHz Bruker spectrometer with pulsed Fourier transform of the NMR of the Chemistry Department at Florida State University. The shifts were measured relative to the internal standard tetramethylsilane, TMS.

Results and Discussion

The shift values relative to TMS were −0.71 ppm and −2.84 ppm for the α-CH_2 and β-CH_2 protons of free THF in $CDCl_3$ solution. In the Nd[$(CF_3CO)_2CH]_3\cdot$THF complex in solution the shift values are 3.75 ppm (α) and 1.85 ppm (β). No resonance lines were observed for water in any of the solutions. In solutions of Nd[$(CF_3CO)_2CH]_3\cdot$THF + base, single, narrow but shifted resonance peaks were observed for the α and the β group protons of the THF indicating that the exchange of THF between free and bound species was rapid on the NMR time scale.

The reaction with base, B, is

$$\mathrm{Nd[(CF_3CO)_2CH]_3\cdot THF + B \rightleftharpoons Nd[(CF_3CO)_2CH]_3\cdot B + THF} \qquad (1)$$

The measured shift is the sum of the limiting shifts of the free and bound THF weighted by the fraction of THF in each form; *i.e.*,

$$\delta_{\mathrm{obs}} = \delta_f^{\circ} X_f + \delta_b^{\circ} X_b = \delta_f^{\circ} X_f + \delta_b^{\circ}(1 - X_f) \qquad (2)$$

where δ_i° are the limiting shifts for the free (f) and bound (b) species and X_i, their mole fractions. When the reactants have the same initial concentrations, the equilibrium constant can be calculated with eqn. (2) as follows:

---

*On leave from the Department of Chemistry, Zhejiang University, Hangzhou, China.

0020-1693/88/$3.50

$$X_f = (\delta_{obs} - \delta_b^0)/(\delta_f^0 - \delta_b^0) \qquad (3)$$

and

$$K_{eq} = X_f^2/(1 - X_f)^2 \qquad (4)$$

The shifts of the α-CH_2 protons were used to calculate the values of K_{eq} for the reaction of the different bases. From duplicate NMR experiments, the error of the values of log K_{eq} for reaction (1) was about ±0.1. The values of K_{eq} and the corresponding ΔG are listed in Table I.

Gutmann [2] has proposed the concept of 'donor number' to measure the basicity of species. The scale of donor numbers (DN) of adduct bases is based on the enthalpy of reaction, ΔH, of the donor base with $SbCl_5$ in 1,2-dichloroethane solvent. The $Nd[(CF_3CO)_2CH]_3 \cdot THF$ was insufficiently soluble to use this solvent but the relative DN scale should remain the same in $CDCl_3$ solvent. If we assume that the entropy change for reaction (1) is essentially constant for all the bases in Table I, $\Delta G \propto \Delta H$ and ΔG of reaction (1) should correlate with the DN of the bases. This correlation is shown in Fig. 1. The values of DN from ref. 2 are given in units of kcal mol^{-1} so the units of ΔG in Table I are also in kcal mol^{-1} for consistency. The correlation coefficient of the least squares fit is 0.94. From this plot estimates can be made for the missing DN of Table I: dimethylsulfate, 0.3; trifluoroethanol, 11; pyrrole, 8; aniline, 17; diethylamine, 49 (in kcal mol^{-1} and based on the reaction with $SbCl_5$ in 1,2-dichloroethane). Kramer *et al.* [3], have shown in an earlier study of ^1H NMR spectral shifts using $UO_2[(CF_3CO)_2CH]_2 \cdot THF$ in chloroform with some of these bases that the ΔG of reaction correlated with the Gutmann DN values.

TABLE I. Equilibrium Constants, Free Energy Values for the Reaction of $Nd[(CF_3CO)_2CH]_3 \cdot THF$ + Base

Base	log K_{eq}	$-\Delta G$[a]	DN[b]
(a) Oxygen bases			
Dimethyl sulfate	−3.94	−5.37	
Trifluoroethanol	−2.65	−3.61	
Diethyl ether	−1.98	−2.70	19.2
Acetone	−1.67	−2.28	17.0
Methanol	−1.43	−1.95	(19.0)
Dimethyl acetamide	−1.14	−1.56	27.8
Dimethyl sulfoxide	−0.36	−0.49	29.8
Tetramethylurea	−0.36	−0.49	(31.0)
Dimethyl formamide	−0.35	−0.48	26.6
Hexamethylphosphoramide	0.26	+0.36	38.8
(b) Nitrogen bases			
Pyrrole	−2.96	−4.04	
Acetonitrile	−2.57	−3.50	14.1
Aniline	−1.98	−2.70	
Pyridine	−0.21	−0.29	33.1
Diethylamine	1.65	+2.25	
Piperidine	1.69	+2.30	(51.0)

[a] kcal mol^{-1}. [b] Donor Numbers from Table 2.1 and (in parentheses) Table 2.2 from ref. 1.

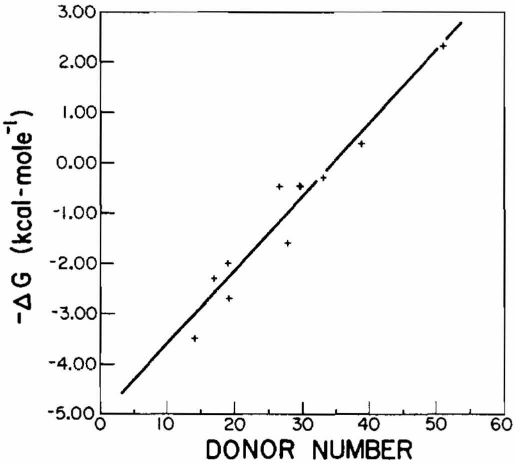

Fig. 1. Plot of $-\Delta G$ for the reaction of eqn. (1) with the Gutmann donor number of the bases (see Table I).

The values of ΔG in Table I were also tested with Drago's E_B and C_B parameters [4] for these bases. In this treatment, the E parameters are associated with the electrostatic part of the acid–base interaction while the C parameters reflect the covalent part. For the oxygen donor bases, a linear fit of $-\Delta G$ and E_B was obtained with a correlation coefficient of 0.86. No correlation between $-\Delta G$ and C_B exists (R^2 = 0.35) for the oxygen donor bases. The situation was reversed for the nitrogen donor bases with a good fit (R^2 = 0.996) between the $-\Delta G$ and C_B values but no fit (R^2 = 0.34) with the E_B values. The predominantly ionic character of lanthanide–oxygen donor interactions is a well recognized feature of lanthanide chemistry [5]. The pattern of correlations may be reflecting an increased covalency in the Nd–N(base) interactions than in that of the Nd–O(base) interactions. It has been proposed [6] that lanthanide–nitrogen donor bonding possesses more covalent character than does lanthanide–oxygen donor bonding.

Acknowledgement

This research was supported by a contract with the U.S. D.O.E.–O.B.E.S. Division of Chemical Sciences.

References

1 K. Yao and G. R. Choppin, *Inorg. Chim. Acta, 122,* L13 (1986).

2 V. Gutmann, 'The Donor–Acceptor Approach to Molecular Interactions', Plenum, New York, 1980.
3 G. M. Kramer, E. T. Maas and M. B. Dines, *Inorg. Chem., 20,* 1415, 1418 (1981).
4 R. S. Drago, *Struct. Bonding (Berlin), 15,* 73 (1973).
5 G. R. Choppin, *J. Less-Common Met., 93,* 323 (1983).
6 C. Musikas, in G. Choppin, J. Navratil and W. Schultz (eds.), 'Proceedings of the Intern. Sym. on Actinide/Lanthanide Separations', World Science Publishers, Philadelphia, Pa., 1985, p. 19.