

A Softness Scale for Ligands and Organomercurials Determined by Bromine Nuclear Magnetic Resonance Relaxation

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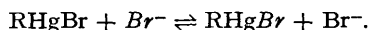
Summary Bromine n.m.r. relaxation measurements give the relative stability constants for organomercurials with various ligands and are used to define a softness scale.

MEASUREMENT of nuclear magnetic spin-lattice relaxation times of solutions of organomercuribromides (RHgBr) pro-

vides a convenient and rapid method for determining the relative stability constants of organomercuriations with a variety of competing ligands. The magnitudes of the stability constants can be used to order both ligands and mercurials on a softness scale for Lewis acids and bases. The technique is particularly useful because CH_3Hg^+ has

been recommended as a reference cation for a ligand softness scale.¹

Baldeschweiler has shown² that halogen nuclei exchange rapidly between aquated halide ions and organomercurihalide. For the organomercuribromide system the reaction is



In the limits of 'extreme narrowing' and 'fast exchange' the average spin-lattice relaxation time, \bar{T}_1 , of an aqueous

The ⁷⁹Br spin-lattice relaxation times, which appear in equation (1), were found to have the following values: $T_1(\text{Br})$ 420 μs ; $T_1(\text{RHgBr})$ 153, 64, 42 ns for $\text{RHgBr} = \text{ME}$, BEN , CIN , respectively. The applicability of the 'extreme narrowing' limit was demonstrated by the equality of \bar{T}_1 and \bar{T}_2 (spin-spin relaxation time), for all mercurials. In the 'fast exchange' limit it can be shown³ that $T_1(\text{RHg}^{79}\text{Br})/T_1(\text{RHg}^{81}\text{Br}) = (Q^{81}/Q^{79})^2 = 1.42$, where Q^{81} is the electric quadrupole moment for ⁸¹Br. This value, within experimental error, was found for all mercurials.

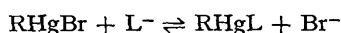
Ligands	Bromomercuricinnamic acid			Bromomercuribenzoic acid		Methylmercuric bromide	
	[KLN]/mol dm ⁻³	[CIN] = 1.5 × 10 ⁻⁴ mol dm ⁻³	K	[BEN] = 2.5 × 10 ⁻⁴ mol dm ⁻³	K	[ME] = 2.5 × 10 ⁻⁴ mol dm ⁻³	K
I ⁻	0.25	3.37 ± 0.06	10.5 ± 0.6	3.19 ± 0.17	15.2 ± 3.1	3.17 ± 0.09	4.4 ± 0.3
Br ⁻	—	6.00 ± 0.23	1.0	6.24 ± 0.19	1.0	4.01 ± 0.09	1.0
Cl ⁻	3.0	3.86 ± 0.25	0.48 ± 0.05	4.46 ± 0.14	0.29 ± 0.01	3.09 ± 0.07	0.44 ± 0.05
OAc ⁻	3.0	5.22 ± 0.22	0.09 ± 0.04	5.31 ± 0.28	0.11 ± 0.03	3.44 ± 0.10	0.18 ± 0.02
SCN ⁻	3.0	4.46 ± 0.38	0.25 ± 0.07	5.09 ± 0.28	0.14 ± 0.04	3.42 ± 0.13	0.19 ± 0.03
CN ⁻	0.25	3.08 ± 0.11	16.6 ± 3.3	2.55 ± 0.05	86.6 ± 15.0	2.91 ± 0.17	8.5 ± 2.4

solution containing RHgBr and Br^- in equilibrium is given by equation (1).³

$$[\text{Br}]_{\text{total}}/\bar{T}_1 = [\text{Br}^-]/T_1(\text{Br}) + [\text{RHgBr}]/T_1(\text{RHgBr}) \quad (1)$$

Square brackets indicate concentration and $T_1(\text{Br})$ and $T_1(\text{RHgBr})$ are the relaxation times of the bromine nuclei in Br^- and RHgBr respectively.

\bar{T}_1' , the average relaxation time for an equilibrate containing RHgBr , Br^- , and a second ligand L^- , is longer than \bar{T}_1 the relaxation time in the absence of any competing ligand because the concentration of RHgBr is lower. The equilibrium stability constant, K , for the reaction



is given by equation (2).

$$K = [\text{RHgL}][\text{Br}^-]/[\text{RHgBr}][\text{L}^-] \quad (2)$$

Assuming that, under the conditions of the experiments, $[\text{Br}]_{\text{total}} \gg [\text{RHgBr}]$, equation (3) follows from equations (1) and (2).

$$K = (\bar{T}_1 - \bar{T}_1')[\text{Br}^-]/\{\bar{T}_1 - T_1(\text{Br})\}[\text{L}^-] \quad (3)$$

⁷⁹Br and ⁸¹Br spin lattice relaxation times were measured by the standard 90°- τ -90° pulse sequence. Data for ⁷⁹Br, which are summarized in the Table, were obtained for the organomercurials: bromomercuricinnamic acid, CIN, bromomercuribenzoic acid, BEN, methyl mercuribromide, ME; and the ligands: I⁻, Br⁻, Cl⁻, OAc⁻, SCN⁻, CN⁻. All measurements were made in solutions of 1 mol (KBr) dm⁻³.

An order of softness amongst the ligands, which is similar to that found by electrochemical methods,^{1,4} may be derived using the stability constants found for a particular mercurial:



The reversal of order of Cl⁻ and SCN⁻ on the two scales may be due to a contribution, in the n.m.r. method, from a third, weakly bound ligand at mercury. Bjerrum⁵ has reported solubility data for ME in the presence of SCN⁻ which suggest that a trivalent species is formed, but trivalent species were not formed with Cl⁻ or Br⁻.

Organomercurials are relatively soft therefore differences between them are best resolved by the stability constants of the bromide derivatives in the presence of a softer, competing ligand such as CN⁻. The order of softness was found to be $\text{BEN} > \text{CIN} > \text{ME}$.

As the relative softness of organomercurials can readily be determined by this novel n.m.r. technique the contribution of the organic group to the thermodynamic stability of the mercury-bromide bond can conveniently be studied. This *trans* effect at mercury may partially be understood in terms of bond hybridisation type and meso-meric interactions.

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