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) provides a convenient and rapid method for determining the relative stability constants of organomercuri-cations 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 shown[2] that halogen nuclei exchange rapidly between aquated halide ions and organomercurihalide. For the organomercuribromide system the reaction is

$$\mathrm{RHgBr} + \mathit{Br}^- \rightleftharpoons \mathrm{RHg}\mathit{Br} + \mathrm{Br}^-.$$

In the limits of 'extreme narrowing' and 'fast exchange' the average spin-lattice relaxation time, $\bar{T}_1$, of an aqueous solution containing RHgBr and Br^- in equilibrium is given by equation (1).[3]

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

Ligands		Bromomercuricinnamic acid		Bromomercuricbenzoic acid		Methylmercuric bromide	
		$[\mathrm{CIN}] = 1{\cdot}5 \times 10^{-4}$ mol dm^{-3}		$[\mathrm{BEN}] = 2{\cdot}5 \times 10^{-4}$ mol dm^{-3}		$[\mathrm{ME}] = 2{\cdot}5 \times 10^{-4}$ mol dm^{-3}	
L^-	[KL]/mol dm^{-3}	ms/$\bar{T}_1$	K	ms/$\bar{T}_1$	K	ms/$\bar{T}_1$	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

Square brackets indicate concentration and $T_1(\mathrm{Br})$ and $T_1(\mathrm{RHgBr})$ 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

$$\mathrm{RHgBr} + \mathrm{L}^- \rightleftharpoons \mathrm{RHgL} + \mathrm{Br}^-$$

is given by equation (2).

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

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

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

^{79}Br and ^{81}Br spin lattice relaxation times were measured by the standard 90°–τ–90° pulse sequence. Data for ^{79}Br, 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}.

The ^{79}Br spin-lattice relaxation times, which appear in equation (1), were found to have the following values: $T_1(\mathrm{Br})$ 420 μs; $T_1(\mathrm{RHgBr})$ 153, 64, 42 ns for RHgBr = 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 shown[3] that $T_1(\mathrm{RHg^{79}Br})/T_1(\mathrm{RHg^{81}Br}) = (Q^{81}/Q^{79})^2 = 1{\cdot}42$, where Q^{81} is the electric quadrupole moment for ^{81}Br. This value, within experimental error, was found for all mercurials.

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:

$$\mathrm{CN}^- > \mathrm{I}^- > \mathrm{Br}^- > \mathrm{Cl}^- > \mathrm{SCN}^- > \mathrm{OAc}^-.$$

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. Bjerrum[5] 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 BEN > CIN > 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 mesomeric interactions

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