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ESTIMATING CARBON—MERCURY BOND IONISATION CONSTANTS FROM PMR SPECTRA OF METHYLMERCURY COMPOUNDS

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Summary

Analysis of $J(^{199}Hg—CH_3)$ spin coupling constants in PMR spectra of CH_3HgX (where X is a carbanion) shows that the affinity of various X groups for the methylmercury cation is linearly dependent on the acidity of the respective CH-acids XH.

There are a great number of reactions in organometallic chemistry whose kinetic, structural, and stereochemical features are best discussed in terms of the $S_E1(N)$ mechanism [1]. The symbol, $S_E1(N)$, denotes that the transition state of the reaction involves a partially ionized carbon—metal bond and the activation of such partial ionization requires assistance of a nucleophilic agent N which may be coordinated with metal atom in the pre-equilibrium or in the rate-determining step of the reaction. With organomercury compounds the $S_E1(N)$ mechanism may be written as follows:

$$\text{R—HgR}' + N \overset{K_m}{\rightleftharpoons} \text{R}^{-+}\overset{N}{\text{Hg}}\text{R}' \xrightarrow[\text{fast}]{E^+} \text{R}E \rightarrow (\text{R}'\text{Hg}N)^+$$

where K_m characterizes the thermodynamic stability of carbanion, R^-, in a system containing the $R'Hg^+$ cation as a carbanion acceptor and nucleophile N (e.g. solvent molecule) as a ligand-assistor:

$$K_m = \frac{(R^-)(R'HgN^+)}{(RHgR')(N)} \; ; \quad -\log K_m = pK_m$$

As pK_m becomes higher the R—Hg bond ionization (i.e. $S_E1(N)$ mechanism) becomes less probable. As a rule, the direct experimental determination of pK_m values is a hard problem because carbanions have extremely high affinities for the mercury cation; the stationary concentration of R^- in $RHgR'$ solutions is practically zero (except for a few organomercury compounds which involve organic groups such as CN which are relatively stable in the anionic form). Instead of unknown pK_m constants we have proposed earlier [1] to use the

TABLE 1

GEMINAL $J(^{199}Hg-CH_3)$ CONSTANTS FOR METHYLMERCURY CH_3HgX COMPOUNDS FOR DIFFERENT X^- ANIONS; pK_m VALUES CHARACTERISING THE AFFINITIES OF X^- FOR CH_3Hg; AND pK_a VALUES OF CH-ACIDS HX ON CRAM'S [3] MSAD SCALE

No.	X	$J(^{199}Hg-CH_3)$ (Hz)	Solvent	Ref	pK_m Found[a]	Calcd.	pK_a
1	C_2H_5	94—96	cyclohexane	4		31.5	42[b]
2	CH_3	100.6	benzene	5		30	40[b]
3	$CH_2=CH$	110	benzene	4		28	36.5[b]
4	CF_3	139	benzene	6		22	26.5[c]
5	$C{\equiv}CH$	143.2	benzene	7		21	25[b]
		150.6	benzene	5			
6	$SHgCH_3$	157	pyridine	5	16.3		
7	CN	176.0	benzene	5	14.2	(14.2)	12[c]
8	SCN	197.5	benzene	7	6.1		
		208	pyridine	5			
9	OH	204	benzene	5	9.5		
10	Br	201.3	benzene	7	6.7		
		212	pyridine	5			
11	Cl	204.3	benzene	7	5.45		
		215.2	pyridine	5			
12	$OCOCH_3$	214.3	benzene	5	ca. 6.3		
13	H_2O	259.6	benzene	5		(ca. —3)	

[a]From Ref. 8. [b]From Ref. 3. [c]From Ref. 9.

constants of acidic ionization (pK_a) of the respective hydrocarbons, RH. We have found [1] a number of examples in organomercury (and organosilicon) chemistry in which correlations exist between the rates of $S_E1(N)$ reactions and acidities of the CH-acids which are conjugated with the carbanions then eliminated at the rate-determining step.

These correlations are relevant only in the case when there is a direct relationship between pK_m and pK_a values; this is not obvious a priori because the proton is a hard whereas the mercury (or alkylmercury) cation a soft Lewis acid. In the present paper, however, it is shown that such proportionality indeed exists.

When Scheffold was studying a number of complexes of the methylmercury cation with different anions X^- by NMR he discovered [2] that the magnitudes of spin coupling constants, $J(^{199}Hg-CH_3)$ are linearly dependent

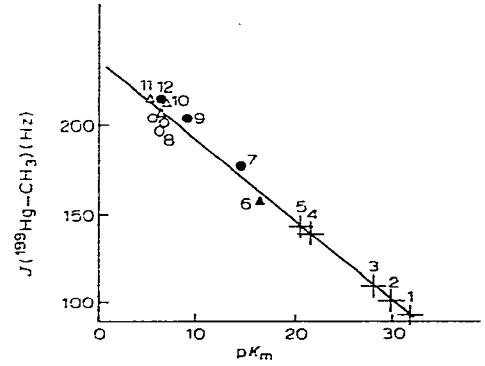

Fig. 1. Dependence of $J(^{199}Hg-CH_3)$ for CH_3HgX upon pK_m. Numbers refer to Table 1.

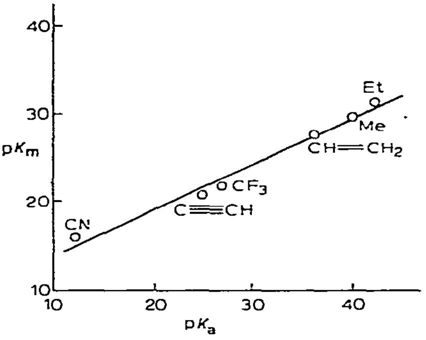

Fig. 2. The plot of pK_m vs. pK_a for carbanions.

on the logarithms of stability constants (i.e. pK_m) of the complexes CH_3HgX. Hence NMR spectra of CH_3HgX are useful for judging the relative strength (in the thermodynamic sense) of bonds between CH_3Hg^+ and various X^- anions. A linear dependence was also found between the $J(^{199}Hg—CH_3)$ constants and relative reactivities of X^- in S_N2 type reactions at a saturated carbon atom [2]. It is very noticeable that Scheffold's correlation embraces a wide range of anions with different donor atoms such as O, S, N, Cl, Br, and C (CN^- anion).The latter is especially important. Using this observation we may attempt to estimate the stability constants of methylmercury complexes with a number of carbanions, including alkyl anions.

In Table 1 the values of spin coupling constants, $J(^{199}Hg—CH_3)$, are given for different CH_3HgX compounds in which X varies from an ethyl anion to a neutral water molecule. The constants are taken from refs. 5 - 7; they were obtained in benzene solutions. Alongside, Table 1 contains the values of J obtained in pyridine; the absolute values of the constants depend on the solvent nature, as expected. The plot J vs. pK_m (the latter quantity determined in water solutions [8]) is drawn in Fig. 1, which shows that a linear dependence does exist between these two parameters. By extrapolation of the plot to small values of J (the sign of the constants does not change across the series [7]) we can estimate the pK_m values for carbanions $HC{\equiv}C^-$, CF_3^-, $H_2C{=}CH^-$, CH_3^- and $C_2H_5^-$. The pK_m values so obtained (Table 1) show that ionization constants of C—Hg bonds are very low for alkylmercury compounds and therefore the unimolecular mechanism for alkyl—mercury bond fission is extremely improbable.

The plot in Fig. 2 shows a good linear dependence of pK_m values upon the acidic ionisation constants (Table 1) of the respective hydrocarbons. This dependence may be described by the equation $pK_m = 0.6\ pK_a + \text{const.}$

Thus, the correlation between the rates of $S_E1(N)$ reactions of organomercury compounds and the basicities of the respective carbanions is reasonable.

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