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METHYLMERCURIC HALIDE—HALIDE COMPLEXATION IN ETHANOL SOLUTION

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Summary

The formation constants for $CH_3HgCl_2^-$ at 26°C (0 31 l/mole), and for $CH_3HgBr_2^-$ at 26°C (0 94 l/mole) and at 60°C (0 70 l/mole) in ethanol solution have been determined from the variation of Hg NMR chemical shift (by INDOR) with composition of methylmercuric halide—lithium halide solutions These data have been employed in a reexamination of the 'one-anion" and "two anion" catalysed reactions of mercuric bromide with alkylmercuric bromides

Introduction

In a most important series of papers [1-6] Hughes, Ingold and their co-workers established the stereochemical and kinetic features of substitution in simple alkylmercurials by simple mercury electrophiles Their mechanistic interpretation is in dispute [7], but the main thrust of the counter argument concerning the application of the concept of microscopic reversibility has been shown to be erroneous [8] Whatever the subsequent interpretation, the experimental findings are of great importance, in particular the observation in some cases of catalysis by halide ions The interpretation of this catalysis and its analysis into individual rate steps is hampered by absence of formation constant data for the species involved appropriate to the conditions of the reactions

Various methods are available for the determination of formation constants, e g conductivity and polarography, but these are difficult for non aqueous systems and we concluded that the variation of ^{199}Hg NMR chemical shift of the methylmercuric halide in solutions containing lithium halide at concentrations

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comparable with those of the kinetic studies would be the most appropriate method of investigation

Experimental

Methylmercuric chloride and bromide were purified as described previously [9] AR grade lithium salts were used without further purification Ethanol was absolute GR (Merck)

^{199}Hg NMR spectra were obtained in the INDOR mode by irradiation of the high field component of the methyl group doublet in the proton spectrum [10]. The PS-100 spectrometer was operated in the frequency sweep mode with the field locked at the solvent CH_2 group for methylmercuric chloride, the solvent OH-group for methylmercuric bromide at 26°C and the solvent CH_3-group for the studies at 60°C These lock positions were dictated by the complex nature of the spectrum of the solvent ($^{13}CH_3CH_2OH$ and $CH_3{}^{12}CH_2OH$ are present at concentrations of ca 2 mol/l, which is twice that of the methylmercuric halide and considerably greater than $CH_3{}^{199}HgX$) The irradiation frequency was derived from a Rohde and Schwarz BNB4444803 Synthesizer swept by a ramp voltage from a Hewlett—Packard HP 3304A unit and monitored by a Hewlett—Packard HP 5244L Counter with an eight digit read-out Dimethylmercury in a capillary was used as an external reference in the first (without added lithium halide) and the last (maximum lithium halide) measurements of each series

TABLE 1

^{199}Hg CHEMICAL SHIFTS METHYLMERCURIC CHLORIDE IN ETHANOL (26° C)

	$[CH_3HgCl]$ (mol/l)	[LiCl] (mol/l)	ν_2 (Hz)	ν_3 (Hz)	δ (ppm)
Ref (in expt. no 1)			17909280		
1	0 0998	0 000	17894430	17894221	0 00
2	0 0991	0 0387	17894464	17894255	1 90
3	0 0988	0 0712	17894491	17894282	3 40$_5$
4	0 0907	0 0970	17894507	17894299	4 33
5	0 0989	0 1330	17894538	17894331	6 08$_5$
6	0 0987	0 1651	17894564	17894356	7 51
7	0 0986	0 1941	17894585	17894376	8 65$_5$
8	0 0973	0 2265	17894613	17894404	10 22
9	0 0978	0 2639	17894636	17894428	11 53
10	0 0983	0 2873	17894658	17894446	12 66
11	0 0979	0 3245	17894679	17894470	13 89
12	0 0979	0 3856	17894724	17894513	16 39
13	0 0976	0 4503	17894764	17894555	18 87
14	0 0973	0 5106	17894806	17894597	20 83
15	0 0974	0 5648	17894844	17894633	23 26
16	0 0967	0 6394	17894890	17894679	25 64
Ref. (in expt. no 16)			17909280		

Results

Results of methylmercuric chloride and bromide are given in Tables 1 and 2 respectively The reference resonance occurs at the same frequency in each case for the lithium halide free and maximum solutions However it is at different frequencies for the three sets of experiments due to the different locked fields The frequency for the reference at a field strength corresponding to tetramethylsilane at 100 000 MHz is 17910771 (±4) Hz McFarlane [11] reports 17910670 Hz for a neat sample

The frequencies of the central pair (ν_2 and ν_3) of the ^{199}Hg quartet are listed The mean of these is the mercury chemical shift from which the lithium halide induced changes, δ, are obtained The difference between each pair is $^2J(^1H-^{199}Hg)$ and were found to be 209 ± 1, 205 ± 1 and 206 ± 1 5 Hz for the three sets of experiments, essentially as observed in the proton spectra

Presuming no dissociation or association in the absence of added lithium halide, the chemical shift given by experiment 1 is that of the methylmercuric halide (δ_0) Then

Ethanol, 26°	CH_3HgCl	276 6 ppm to high field of $(CH_3)_2Hg$ (ext)
Ethanol, 26°	CH_3HgBr	380 1 ppm to high field of $(CH_3)_2Hg$ (ext)
Ethanol, 60°	CH_3HgBr	380 6 ppm to high field of $(CH_3)_2Hg$ (ext)

For the equilibrium

TABLE 2

^{199}Hg CHEMICAL SHIFTS METHYLMERCURIC BROMIDE IN ETHANOL

	$[CH_3HgBr]$ (mol/l)	[LiBr] (mol/l)	26 C			60°C		
			ν_2 (Hz)	ν_3 (Hz)	δ (ppm)	ν_2 (Hz)	ν_3 (Hz)	δ (ppm)
Ref (in expt no 1)			17909243			17909314		
1	0 0641	0 0000	17892538	17892333	0 00	17892599	17892395	0 00
2	0 0635	0 0468	17892584	17892380	6 93	17892640	17892435	6 06
3	0 0636	0 0670	17892649	17892444	9 47	17892696	17892492	8 32
4	0 0635	0 0997	17892725	17892519	13 12	17892762	17892558	11 49
5	0 0632	0 1374	17892794	17892590	17 36	17892829	17892620	15 20
6	0 0630	0 1722	17892865	17892659	21 32	17892884	17892681	18 80
7	0 0626	0 2138	17892908	17892703	25 89	17892927	17892721	22 03
8	0 0626	0 2407	17892957	17892752	27 62	17892980	17892774	24 33
9	0 0624	0 2727	17893008	17892804	30 40	17893026	17892822	27 32
10	0 0622	0 3050	17893059	17892852	33 22	17893068	17892863	29 94
11	0 0619	0 3385	17893151	17892944	35 97	17893160	17892954	32 26
12	0 0617	0 3997	17893230	17893029	41 52	17893241	17893034	37 31
13	0 0610	0 4739	17893307	17893102	45 87	17893309	17893102	41 84
14	0 0607	0 5312	17893378	17893172	49 75	17893384	17893176	45 66
15	0 0603	0 5953	17893443	17893239	53 76	17893452	17893243	49 75
Ref (in expt. no 15)			17909243			17909314		

$$CH_3HgX + X^- \overset{K_f}{\rightleftharpoons} CH_3HgX_2^-$$

$$a - x \qquad b - x \qquad x$$

$$x = K_f(a - x)(b - x) \approx K_f b(a - x)$$

If $b \gg a$ and/or K_f is small

Only one mercury resonance and one methyl group proton resonance are observable so that the reactions involved in the equilibrium are rapid on the NMR time scale These resonances occur at the weighted average of those of the components of the equilibrium Hence

$$\delta + \delta_0 = \delta_0(a - x)/a + \delta_x x/a$$

$$\delta = K_f b(\delta_x - \delta_0)/(1 + K_f b)$$

Where δ_x is the chemical shift for $CH_3HgX_2^-$

$$\delta^{-1} = (\delta_x - \delta_0)^{-1} + K_f^{-1}(\delta_x - \delta_0)^{-1}b^{-1}$$

which gives by least squares analysis

Ethanol, 26° CH_3HgCl $\delta^{-1} = 0\ 0066(\pm\ 0007) + 0\ 0210(\pm\ 0001)b^{-1}$
Experiments 5 16

Ethanol, 26° CH_3HgBr $\delta^{-1} = 0\ 0067(\pm\ 0001) + 0\ 0071(\pm\ 0000)b^{-1}$
Experiments 7 15

Ethanol, 60° CH_3HgBr $\delta^{-1} = 0\ 0059(\pm 0\ 0002) + 0\ 0084(\pm\ 0001)b^{-1}$
Experiments 7-15

For the excluded data b is not substantially greater than a, and there are deviations from the above linear relationships quantitatively as expected

The quantities pertaining to the equilibria are

Ethanol, 26° CH_3HgCl $K_f = 0\ 313 \pm 0\ 032$ l/mole, $\delta_x - \delta_0 = 153 \pm 15$ ppm
$CH_3HgCl_2^-$ 124 ppm to high field of $(CH_3)_2Hg$ (ext)

Ethanol, 26° CH_3HgBr $K_f = 0\ 938 \pm 0\ 014$ l/mole, $\delta_x - \delta_0 = 149 \pm 2$ ppm
$CH_3HgBr_2^-$ 231 ppm to high field of $(CH_3)_2Hg$(ext)

Ethanol, 60° CH_3HgBr $K_f = 0\ 702 \pm 0\ 016$ l/mole, $\delta_x - \delta_0 = 170 \pm 6$ ppm
$CH_3HgBr_2^-$ 211 ppm to high field of $(CH_3)_2Hg$ (ext)

Discussion

Although no results have been reported for non aqueous solutions, the behaviour of mercuric halides in aqueous solutions has been thoroughly studied and there is some information concerning methylmercuric halides (Table 3)

TABLE 3

DISSOCIATION AND ASSOCIATION IN AQUEOUS SOLUTIONS

$HgCl_2 \rightleftharpoons ClHg^+ + Cl^-$	$K_d = 5 \times 10^{-7}$ mol/l [12]
$HgBr_2 \rightleftharpoons BrHg^+ + Cl^-$	$K_d = 5 \times 10^{-9}$ mol/l [12]
$HgCl_2 + Cl^- \rightleftharpoons HgCl_3^-$	$K_f = 9$ mol/l [12]
$HgCl_3^- + Cl^- \rightleftharpoons HgCl_4^{2-}$	$K_f = 1 \times 10^2$ mol/l [12]
$HgBr_2 + Br^- \rightleftharpoons HgBr_3^-$	$K_f = 2 \times 10^2$ mol/l [12]
$HgBr_3^- + Br^- \rightleftharpoons HgBr_4^{2-}$	$K_f = 1 \times 10^4$ mol/l [12]
$CH_3HgCl \rightleftharpoons CH_3Hg^+ + Cl^-$	$K_d = 6 \times 10^{-6}$ mol/l [13]
$CH_3HgBr \rightleftharpoons CH_3Hg^+ + Br^-$	$K_d = 4 \times 10^{-7}$ mol/l [13]

[12, 13] It would be anticipated that for non aqueous solutions, particularly those in which solvation of the halide is poor, the already unfavourable dissociations will have smaller K_d values but the association reactions will be favoured as is the case for the silver halide complexes (Table 4) [14]

Lithium bromide suppresses the rate of reaction of mercuric bromide with bis(2-butyl)mercury in acetone solution such that the kinetic data can be fitted to an expression corresponding to the removal of an amount of mercuric bromide equivalent to the added lithium bromide, i e essentially complete complexation and negligible electrophilicity for $HgBr_3^-$ [2] From the data for all three species initially 4×10^{-3} mol/l in acetone solution (25°C) one may deduce that $K_1 \approx 1\ 5 \times 10^5$ for

$$HgBr_2 + Br^- \rightleftharpoons HgBr_3^- \ (K_1)$$

$$HgBr_3 + Br^- \rightleftharpoons HgBr_4^{2-} \ (K_2)$$

and that K_2 is not significant

For ethanol solution (35°) there are no indications of significant complexation in the reaction of 2-butylmercuric bromide with bis(2-butyl)mercury although there is a modest, positive salt effect for which lithium bromide is almost as effective as lithium perchlorate and four times as effective as lithium nitrate [3]

The salt effect of lithium nitrate on the reaction of methylmercuric bromide and mercuric bromide (ethanol, 100°C) is somewhat larger than in the above case [4], but the effect of lithium bromide (ethanol, 60°C) is dramatic [5] The behaviour is ascribed to catalysis and is observed beyond two equivalents of lithium bromide so that both 'one-anion ' and "two-anion" catalysis is involved

In addition to the uncatalysed reaction

TABLE 4

SILVER HALIDE/HALIDE COMPLEXATION [a]

		Water	Methanol	Acetonitrile
$AgCl + Cl^- \rightleftharpoons AgCl_2^-$	$K_f =$	$2\ 5 \times 10^5$	8×10^7	$2\ 5 \times 10^{13}$ mol/l
$AgBr + Br^- \rightleftharpoons AgBr_2$		4×10^7	4×10^{10}	5×10^{13} mol/l

[a] Ref 14

$$\mathrm{CH_3HgBr + HgBr_2} \xrightarrow{k_2^0} \qquad (1)$$

two reactions could be responsible for the "one-anion" catalysis, i e

$$\mathrm{CH_3HgBr + HgBr_3^-} \xrightarrow{k_A} \qquad (1A)$$

$$\mathrm{CH_3HgBr_2^- + HgBr_2} \xrightarrow{k_B} \qquad (1B)$$

and three for the "two anion" catalysis, i e

$$\mathrm{CH_3HgBr + HgBr_4^{2-}} \xrightarrow{k_C} \qquad (1C)$$

$$\mathrm{CH_3HgBr_2^- + HgBr_3^-} \xrightarrow{k_D} \qquad (1D)$$

$$\mathrm{CH_3HgBr_3^{2-} + HgBr_2} \xrightarrow{k_E} \qquad (1E)$$

and within each set these are kinetically indistinguishable Thus

$$k_A[\mathrm{CH_3HgBr}][\mathrm{HgBr_3^-}] + k_B[\mathrm{CH_3HgBr_2^-}][\mathrm{HgBr_2}] = \left(\frac{k_1 k_A}{K_f} + k_B\right)[\mathrm{CH_3HgBr_2^-}][\mathrm{HgBr_2}] \qquad (2)$$

and

$$k_C[\mathrm{CH_3HgBr}][\mathrm{HgBr_4^{2-}}] + k_D[\mathrm{CH_3HgBr_2^-}][\mathrm{HgBr_3^-}] + k_E[\mathrm{CH_3HgBr_3^{2-}}][\mathrm{HgBr_2}] = \left(\frac{k_2 k_C}{K_f} + k_D + \frac{K'_f k_E}{K_1}\right)[\mathrm{CH_3HgBr_2^-}][\mathrm{HgBr_3^-}] \qquad (3)$$

(K'_f is the formation constant of $\mathrm{CH_3HgBr_3^{2-}}$)

Assuming, as indicated from studies of related reactions, that K_1 is substantial and $K_1 \gg K_2$, $K_f \gg K'_f$, then for $[\mathrm{LiBr}]_s < [\mathrm{HgBr_2}]_s$, where the subscript 's' indicates stoichiometric concentration, (cf [5])

"One-anion" catalysis

$$k_{obs} = \mathrm{Rate}/[\mathrm{CH_3HgBr}]_s[\mathrm{HgBr_2}]_s \simeq k_2^0 + \left(\frac{k'_B K_f}{K_1} - k_2^0\right)\frac{[\mathrm{LiBr}]_s}{[\mathrm{HgBr_2}]_s} + \frac{k'_D K_f [\mathrm{LiBr}]_s^2}{K_1([\mathrm{HgBr_2}]_s - [\mathrm{LiBr}]_s)} \qquad (4)$$

where $k'_B = k_B + k_A K_1/K_f$

$k'_D = k_D + k_E K'_f/K_1 + k_C K_2/K_f$

and for $[\mathrm{LiBr}]_s > [\mathrm{HgBr_2}]_s$

"Two anion" catalysis

$$k_{obs} \simeq \frac{k_2^0}{K_1([\mathrm{LiBr}]_s - [\mathrm{HgBr_2}]_s)} + \frac{k'_B K_f}{K_1} + k'_D K_f([\mathrm{LiBr}]_s - [\mathrm{HgBr_2}]_s) \qquad (5)$$

Only four k_{obs} values were reported for the "one-anion" region and only two of these were employed in the graphical presentation of the catalysis [5] The latter correspond to

$$\frac{(k'_B K_f - k_2^0)}{K_1} = 3\ 0 \times 10^{-4}\ \mathrm{l\ mol^{-1}\ s^{-1}},\ k_2^0 = 2\ 5 \times 10^{-5}\ \mathrm{l\ mol^{-1}\ s^{-1}}$$

and the former, for higher concentrations, to

$$\frac{(k'_B K_f - k_2^0)}{K_1} = 2\ 7 \times 10^{-4}\ \mathrm{l\ mol^{-1}\ s^{-1}},\ k_2^0 = 13\ 8 \times 10^{-5}\ \mathrm{l\ mol^{-1}\ s^{-1}}$$

The discrepancy between these values of k_2^0 and that observed, $0\ 5 \times 10^{-5}\ \mathrm{l\ mol^{-1}\ s^{-1}}$ for the uncatalysed reaction is larger than could be accounted for by salt effect alone However a salt effect somewhat larger than that observed for lithium nitrate with a contribution from the third term of eqn 4 will reproduce the observed data if

$$k'_B K_f/K_1 \approx 3\ 3 \times 10^{-4}\ \mathrm{l\ mol^{-1}\ s^{-1}},\ k'_D K_f/K_1 \approx 3 \times 10^{-5}\ \mathrm{l\ mol^{-1}\ s^{-1}}$$

There is sufficient data within the 'two-anion" region for analysis by means of eqn 5, which gives a good performance with the first term negligible and

$$k'_B K_f/K_1 \approx 3\ 5 \times 10^{-4}\ \mathrm{l\ mol^{-1}\ s^{-1}},\ k'_D K_f \approx 5\ 5 \times 10^{-3}\ \mathrm{l^2\ mol^{-2}\ s^{-1}}$$

These results indicate that $K_1 \approx 1\ 8 \times 10^2\ \mathrm{l\ mol^{-1}}$ and that $k'_B/k'_D \approx 12$ With the value of K_f found in the present studies $k'_B \approx 8\ 5 \times 10^{-2}\ \mathrm{l\ mol^{-1}\ s^{-1}}$, to be compared with $k_2^0 = 5 \times 10^{-6}\ \mathrm{l\ mol^{-1}\ s^{-1}}$, and $k'_D \approx 8 \times 10^{-3}\ \mathrm{l\ mol^{-1}\ s^{-1}}$

Similar studies are reported for the uncatalysed reactions of ethylmercuric bromide (100° and 73°C) and the catalysed reaction of neopentylmercuric bromide (100°C) [6] In the latter case the "one-anion" region is fitted by

$$k_{obs} = 4 \times 10^{-5} + 2\ 9 \times 10^{-4}\ [\mathrm{LiBr}]_s/[\mathrm{HgBr_2}]_s\ \mathrm{l\ mol^{-1}\ s^{-1}}$$

and the "two anion" region by

$$k_{obs} = 3\ 1 \times 10^{-4} + 1\ 2 \times 10^{-3}\ ([\mathrm{LiBr}]_s - [\mathrm{HgBr_2}]_s)\ \mathrm{l\ mol^{-1}\ s^{-1}}$$

Correcting for the value of $k'_D K_f[\mathrm{LiBr}]_s/K_1([\mathrm{HgBr_2}]_s - [\mathrm{LiBr}]_s)$ yields $k_2^0 \approx 3 \times 10^{-5}\ \mathrm{l\ mol^{-1}\ s^{-1}}$, which will include any salt effect enhancement, $k'_B K_f/K_1 \approx 3 \times 10^{-4}\ \mathrm{l\ mol^{-1}\ s^{-1}}$ and $k'_D K_f \approx 1\ 2 \times 10^{-3}\ \mathrm{l^2\ mol^{-2}\ s^{-1}}$ Taking $K_1 \approx 1\ 5 \times 10^2\ \mathrm{l\ mol^{-1}}$ at 100°C yields $k'_B K_f \approx 4\ 5 \times 10^{-2}\ \mathrm{l^2\ mol^{-2}\ s^{-1}}$ and $k'_B/k'_D \approx 40$

As a general mechanistic principle, where a number of experimentally indistinguishable steps may be postulated, only the minimum required to account for the observed behaviour should be retained In the case of "one-anion" catalysis reaction 1A is rejected on the grounds that all precedents indicate $HgBr_3^-$ has negligible electrophilic character relative to $HgBr_2$, i e $k_2^0 > k_A$, whereas it is readily appreciated that $CH_3HgBr_2^-$ is a superior substrate to CH_3HgBr, i e $k_B > k_2^0$ Thus k'_B may be identified with k_B

Reaction 1C may be excluded from consideration in the case of "two anion' catalysis since $HgBr_4^{2-}$ can have no electrophilic power Reaction 1D could be significant if $CH_3HgBr_2^-$ were sufficiently reactive to bring out any weak electrophilicity in $HgBr_3^-$ Comparing k'_B and k'_D shows that if this were so $HgBr_2$ would only be about one power of ten more reactive than $HgBr_3^-$ This does not seem to be the case for ' one anion" catalysis nor where catalysis is absent However such a reactivity ratio is reported in the case of 2 pyridinomethylpentacarbonylmanganese [15] On the other hand one might then anticipate a smaller difference between $HgBr_2$ and $HgBr_3^-$ towards $CH_3HgBr_3^{2-}$ leading to a significant "three anion" catalysis The data do not appear to require such a term The "two anion" process is thus most reasonably identified as reaction 1E, i e $k'_D = k_E K'_i / K_i$

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