Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 1994, **4(4)**, 146–147
Mendeleev Communications

The Determination of Organomercury Compounds *via* Iododemercuration

Kirill V. Nikitin

Department of Chemistry, M. V. Lomonosov Moscow State University, 119899 Moscow, Russian Federation. Fax: +7 095 939 2679

The conditions for organomercurial quantitative demercuration on a micro-scale and at trace concentrations have been found.

Organomercurial compounds (OMC) are widely used as powerful antiseptics and have become important environmental pollutants, being more dangerous than inorganic mercuric salts[1] (permitted diethylmercury limit 0.0001 mg dm^{-3} for water[2]). Due to lipophility, cell membranes are highly permeable to certain OMC such as methylmercury which interrupts the operation of SH-dependent enzymes.[2] The selective determination of organic and inorganic mercury in natural and industrial samples presents an important analytical task. However, any convenient method of determining OMC, particularly in the presence of excess inorganic mercuric compounds, involves effective chromatography[3,4] whereas a one-pot determination[5] will give rise to aberrations (although the ethylborate method[6] approximates to a correct value). The analysis of individual OMC samples is restricted essentially to mercury assay evaluation.[7,8]

The well-known iododemercuration reaction of organometallic compounds was studied for organomercuric salts RHgX in non-aqueous media,[9] while no iodination could take place for most inorganic mercuric compounds. We found that the salts RHgX undergo quantitative iododemercuration, reaction (1),

$$RHgX + I_2 + 3I^- \rightarrow RI + HgI_4^{2-} + X^- \qquad (1)$$

by action of excess iodine in aqueous solution.

Methyl mercuric halides MeHgX are not active in demercuration,[9] nevertheless, MeHgI at 25 °C in 0.1 M potassium iodide solution and $C_0 = 1 \times 10^{-4}$ M undergoes a dimerization reaction (2),

$$2MeHgI + 2I^- \rightarrow Me_2Hg + HgI_4^{2-} \qquad (2)$$

with HgI_4^{2-} formation (UV absorbance $\lambda_{max} = 323$ nm, $\varepsilon = 1.39 \times 10^4$) within 2 h. The action of air later causes demercuration, reaction (3), taking 90 h.

$$Me_2Hg + O_2 + 2H_2O + 6I^- \rightarrow 2MeI + HgI_4^{2-} + 4OH^- \qquad (3)$$

Furthermore, the aqueous KI stored with admission of air steadily accumulates I_3^- (UV spectrum: $\lambda_{max} = 288$ nm, $\varepsilon = 3.4 \times 10^4$, $\lambda_{max} = 353$ nm, $\varepsilon = 2.22 \times 10^4$). Thus, to accurately accomplish iododemercuration at a low concentration range (10^{-5} M), the air should be removed by argon flow from any vessel or solution used. Even with this precaution a solution of I_2 in 0.1 M KI is not stable enough (Table 1, entries 1,2) and disproportionates to IO_3^-; acidification by HCl up to pH = 2 is required (entry 3).

Table 1 Iodine transformations (starting concentration $C^0_{I_2}$) and iododemercuration of MeHgI (10^{-4}–10^{-6} M) in aqueous 0.1 M KI, 0.01 M HCl under argon.

Entry	C_{MeHgI} taken (M)	$C^0_{I_2}$ (M)	Time /min	T/°C	Starch added	C_{I_2}(M)[a]	C_{I_2}(M)
1	0	2×10^{-5}	5	25	–	2×10^{-5}	0
2[b]	0	2×10^{-5}	10	90	–	0.9×10^{-5}	1.1×10^{-5}
3	0	2×10^{-5}	10	90	–	2×10^{-5}	0
4	0	4×10^{-5}	60	95	+	3.9×10^{-5}	0.1×10^{-5}
5	1.5×10^{-5}	4×10^{-5}	60	25	+	3.9×10^{-5}	0.1×10^{-5}
6	1.5×10^{-5}	4×10^{-5}	60	95	+	2.4×10^{-5}	1.6×10^{-5}
7	0	1×10^{-5}	150	90	+	1×10^{-5}	0
8[c]	0	1×10^{-5}	150	90	+	1×10^{-5}	0
9[c]	2.5×10^{-6}	1×10^{-5}	150	90	+	7.5×10^{-6}	2.5×10^{-6}

[a] The concentration is determined by spectrophotometry. [b] Neutral medium. [c] In the presence of 2.5×10^{-4} M $HgCl_2$.

Table 2 Standardization of RHgX solutions in water and alcohol by iododemercuration–back titration of iodine (0.01 M I_2, 0.1 M KI, 0.5 M AcOH, Ar).

Entry	RHgX	Solvent	C_{taken} (M)	Probe/ml	T/°C	Time/h	C_{found} (M)
1	MeHgI	H_2O	9.92×10^{-4}	10	20	1200	8.8×10^{-4}
2	" "	" "	" "	10	60	10	10.0×10^{-4}
3[a]	" "	" "	" "	10	85	10	8.65×10^{-4}
4[b]	" "	" "	" "	10	85	10	5.6×10^{-4}
5	" "	MeOH	1.28×10^{-2}	1	85	10	1.30×10^{-2}
6[a]	" "	" "	" "	1	85	10	1.18×10^{-2}
7[c]	EtHgBr	MeOH	1.2×10^{-2}	1	85	30	8.65×10^{-3}

[a] Stored for 6 days. [b] Stored for 18 days. [c] Crude sample.

Table 3 Quantitative iododemercuration of organomercurials (1 ml MeOH, 3 ml 0.01 M I_2 in CCl_4, 0.5 mmol NaI, 2.5 mmol AcOH, 10 min).

Entry	RHgX	Taken/mmol	T/°C	Found RHgX/mmol
1	MeHgI	0.0846	60	0.0845
2	EtHgBr	0.0927	60	0.0925
3	PhHgCl	0.227	60	0.228
4	*p*-MeC_6H_4HgBr	0.1053	60	0.1055
5	*p*-$C_8H_{17}NHC_6H_4HgOAc$	0.108	50	0.109

The course of MeHgI demercuration, reaction (4),

$$MeHgI + I_3^- + I^- \rightarrow HgI_4^{2-} + MeI \qquad (4)$$

was followed by UV photometry at I_3^- absorbance wavelength. Since HgI_4^{2-} produced disrupts the observation of UV absorbance, the residual I_2 has been incorporated into a starch complex ($\lambda_{max} = 588$ nm, $\varepsilon = 2.5 \times 10^4$) to avoid overlapping. The adduct absorbance is recorded referring to 0.1 M potassium iodide solution from which I_2 and any form of Hg are excluded (Table 1, entries 4–9).

The iododemercuration reaction for I_3^- and MeHgI concentrations of about 10^{-5} M appears to be fairly slow at 25 °C (Table 1, entry 5), but at 95 °C (the reaction vessel kept in boiling water) it runs quantitatively with a satisfactory rate (entry 6). Notably, for the reaction to be conducted precisely the reaction volume should be isolated thoroughly to avoid I_2 and Me_2Hg escape. A ground-in stopper equipped with a screw-clamp is suitable for isolation of 10–30 ml reaction volume, while at a lower scale sealed glass tubes are preferable. With a sufficiently long reaction time, 2.5×10^{-6} M MeHgI in a 2 ml sample (1.00 cm cell), could be determined in the presence of a 100-fold excess of 2.5×10^{-4} M $HgCl_2$ (Table 1, entries 7–9), while any non-resolution technique is likely to fail.

The determination of RHgX in the 10^{-3} M concentration range is available through iododemercuration followed by iodine excess back-titration with thiosulfate. The iododemercuration proceeds in an acidic medium at elevated temperature, while under ambient conditions demercuration is too slow (Table 2, entry 1). Iododemercuration back-titration allowed us to check solutions of MeHgI and EtHgBr in water and methanol (Table 2). Ethanol turns out to be a poor solvent, since some impurities react with I_2. It is also possible to measure the decrease in MeHgI concentration in the solution being kept (Table 2, entries 2–6) as easily as to state the effective content of EtHgBr in a crude sample (entry 7) containing a good deal of $HgBr_2$.

The determination of organic mercury assay through demercuration in a neat sample of RHgX is easy to conduct in methanol when a tetrachloromethane solution of I_2 is used and nucleophilic assistance by NaI is applied (Table 3) as follows. A portion of about 0.03–0.06 g ($1–2 \times 10^{-4}$ mol) of individual OMC was placed into a round-bottomed flask, equipped with a magnetic stirrer, then 1 ml of methanol, 0.1 g of $NaI \cdot H_2O$ (0.54 mmol), 3.00 ml of 0.100 M I_2 solution in CCl_4 and 0.15 ml of AcOH were added. The flask was warmed with a clasped ground stopper for 10 min, chilled at 10–15 °C and excess iodine was titrated by 0.005 mol dm^{-3} aqueous thiosulfate solution. The mole quantity of OMC was calculated from the difference between the blank experiment. For various OMC, of both alkyl (Table 3, entries 1,2) and substituted aryl (entries 3–5) kind, accurate results for RHgX determination and good "taken-found" correlation may be achieved provided a tight isolation of reaction volume takes place during demercuration.

The method proposed is suitable for the analysis of solutions or extracts with OMC content no less than 0.5 mg dm^{-3} regardless of inorganic mercuric salts. Moreover, it is of value for C–Hg bond determination in industrial or laboratory samples, and it also gives a method of determining various

$$R{-}MX + HgCl_2 \rightarrow R{-}HgCl + MXCl \qquad (5)$$

organometallic compounds (*e.g.* R–MX) *via* the conversion reaction (5) to organomercurials.

References

1 *Mercury Contamination in Man and his Environment*, International Atomic Energy Agency, Vienna, 1972.
2 *Organicheskie Soedineniya Rtuti (Organic Compounds of Mercury)*, ed. N. F. Ismerov, The International Proposal Centre for the State Committee of Science and Technology, Moscow, 1989 (in Russian).
3 I. S. Krull, *Analyst*, 1986, **111**, 345.
4 G. Decadt, W. Baeyens, D. Bradley and L. Goeyenes, *Anal. Chem.*, 1985, **57**, 2788.
5 C. E. Oda and J. D. Ingle, *Anal. Chem.*, 1981, **53**, 2305.
6 S. Rapsomanikis and P. J. Craig, *Anal. Chim. Acta*, 1991, **248**, 563.
7 J. Medinella, F. Ales and F. G. Sanchez, *Talanta*, 1986, **33**, 329.
8 L. Mazor, *Methods of Organic Analysis*, Akademiai Kiado, Budapest, 1983.
9 O. A. Reutov and I. P. Beletskaya, *Reaction Mechanisms of Organometallic Compounds*, North-Holland Publishing Co., Amsterdam, 1968.

Received: Moscow, 8th December 1993
Cambridge, 1st February 1994; Com. 3/007316E