# THE REACTION OF AQUEOUS POTASSIUM CHLOROACETATE WITH MERCURIC OXIDE*

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In 1899, Hofmann[1] reported a reaction in which mercuric oxide dissolved in a hot aqueous solution of potassium chloroacetate to yield a crystalline product formulated as the double salt (I): The product gives an immediate quantitative precipitate of mercuric oxide with sodium hydroxide, and with dilute hydrochloric acid yields mercuric chloride and glycollic acid. These reactions are not consistent with the above formulation.

$$\text{KCl.ClHg–}\underset{\underset{\text{Cl}}{|}}{\overset{\overset{\text{H}}{|}}{\text{C}}}\text{–COOK}$$
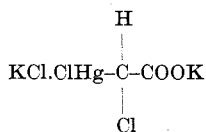
(I)

Under the reaction conditions chloroacetate is hydrolysed to glycollate. Indeed two-thirds of the chlorine in (I) must have originated in this way. Furthermore Hofmann's method of analysis, treatment with silver nitrate solution, would estimate "ionic chloride" only unless the carbon-bound chlorine was labile.

Clearly any product would be expected to arise from glycollate not chloroacetate. In addition Hofmann's formulation bears no relationship to the analyses of our preparations.

In several preparations we always obtained crystalline material but with substantially different analyses (see Table 1). The crystal appearance, the same for all preparations, differs from that usually observed for alkyl mercury salts, for mercuric salts, and for potassium chloride. Microscopic examination suggests the product is homogeneous and not a mixture of crystals.

The proton magnetic resonance spectrum in D_2O solution consists of a single peak at $6\cdot35\tau$ corresponding to the carbon-bound protons of glycollate and a peak due to HOD arising from exchangeable protons. No resonance is observed arising from the $^1\text{H-C-}^{199}\text{Hg}$ system although clearly evident in the spectra of authentic organomercury compounds.[2,3] We conclude from this that there is no carbon-bound mercury, as indicated by the reactions of the compound, and that in fact no mercuration has occurred.

An aqueous solution of the product immediately yields a white precipitate of an ethylenediamine complex of mercury(II) on treatment with 10% aqueous ethylenediamine. This complex does not show infrared absorption associated with glycollate but its infrared spectrum is indistinguishable from that of the authentic mercuric chloride–ethylenediamine complex. Methyl mercury salts do not react in this way with ethylenediamine.

[1] Hofmann, K. A., *Ber. dtsch. chem. Ges.*, 1899, **32**, 880.

[2] Dessy, R. E., Flautt, T. J., Jaffé, H. H., and Reynolds, G. F., *J. Chem. Phys.*, 1959, **30**, 1422.

[3] Wells, P. R., and Kitching, W., unpublished data 1963.

The infrared spectra were essentially identical for all samples. The absorptions observed at 3400 cm^{-1} (free OH); at 2880 and 2840 cm^{-1} (in phase and out of phase CH$_2$ stretching vibrations); at 1350 and 1600 cm^{-1} (symmetric and antisymmetric $-CO_2^-$ vibrations); and at 1440 cm^{-1} (CH$_2$ deformation) are consistent with glycollate as the only infrared active species in the region scanned (4000 to 700 cm^{-1}).

For samples 1 and 2 the C : H ratios are approximately 2 : 3 so that the organic material can be completely accounted for as potassium glycollate (C$_2$H$_3$O$_3$K). The Cl : Hg ratio is always greater than 2 : 1 (2·3, 2·6, and 2·6 for samples 1, 2, and 3 respectively) reaching a maximum of 3 : 1 for sample 4 and Hofmann's product. Mercury can thus be accounted for completely as HgCl$_2$. The remainder is KCl and the various samples have the composition:

Sample 1   HgCl$_2$·0·2–0·25KCl·3C$_2$H$_3$O$_3$K

Sample 2   HgCl$_2$·0·6–0·7 KCl·3C$_2$H$_3$O$_3$K

Sample 3   HgCl$_2$·KCl·2·5C$_2$H$_3$O$_3$K

Sample 4   HgCl$_2$·KCl·C$_2$H$_3$O$_3$K

Aqueous solutions containing HgCl$_2$, KCl, and HOCH$_2$CO$_2$K in these proportions have ultraviolet spectra identical in the range 218–230 mμ as the solutions of

TABLE 1

PERCENTAGE ANALYSES

| Sample	C	H	Hg	Cl	K
1*	11·54	1·58	31·6	12·6	—
2†	10·88	1·61	29·3	14·2‡ 14·0§	20·5
3	—	—	31·5	17·1	—
4	—	—	45·4	25·3	—
Hofmann reports	5·87	0·5	45·5	23·85	17·2

* C and H sample 1 by Mr. J. Kriauciunas.

† C, H, and K sample 2 by C.S.I.R.O. Microanalytical Laboratory.

‡ "Ionic" chloride.

§ Total chloride, following alkali carbonate fusion.

the appropriate samples. A mixture of HgCl$_2$, KCl, and HOCH$_2$CO$_2$K dissolved in ethanol yielded the characteristic crystals having an identical infrared spectrum with that of the above samples. Clearly the reactions involved are the hydrolysis of chloroacetate,

$$2ClCH_2CO_2^- + 2H_2O \rightarrow 2HOCH_2CO_2^- + 2HCl$$
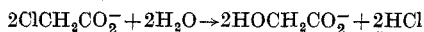
followed by dissolution of the mercuric oxide in the acid produced,

$$HgO + 2HCl \rightarrow 2HgCl_2 + H_2O$$
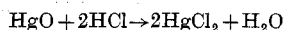
This is in agreement with the observed stoicheiometry whereby 0·094 mole of HgO are dissolved by 0·2 mole of potassium chloroacetate.

It is hoped that structural determinations can be carried out upon this crystalline material.