

382. *Ionization Constants of Some Perfluoroalkylmercuric Hydroxides and Halides.*

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The ionization constants of trifluoromethyl-, pentafluoroethyl-, and heptafluoro-n-propyl-mercuric hydroxide, chloride, bromide, and iodide have been determined in aqueous solution by a potentiometric method. The results are discussed with respect to the effective electronegativity of the perfluoroalkyl group. Attempts to titrate aqueous solutions of perfluoroalkylmercuric hydroxides prepared *in situ* by the action of moist silver oxide on the perfluoroalkylmercuric iodides indicated an abnormally high solubility of silver oxide in these systems.

THE properties of the metal atom in alkyl-metal compounds are markedly affected by substituting fluorine for hydrogen atoms; this has been attributed to the relatively high electron-withdrawing character of the perfluoroalkyl groups. The effective electronegativity of the trifluoromethyl group has been estimated at 3.3 on the Pauling scale.¹ In the series alkyl-, fluoroalkyl-, and perfluoroalkyl-metal compounds it appears that the properties of the metal atom should vary with the degree of fluorination of the alkyl group. As part of a general investigation of the inductive effect of fluoroalkyl groups on the electronic environments of metal atoms, we have determined the ionization constants of some perfluoroalkylmercuric hydroxides and halides. These were chosen since they are relatively easy to prepare, purify, and manipulate and are soluble in water, without decomposition, giving weakly conducting solutions.

EXPERIMENTAL

Materials.—Trifluoromethyl-, pentafluoroethyl-, and heptafluoro-n-propyl-mercuric iodide were prepared by the action of the appropriate perfluoroalkyl iodide on mercury^{2,3} and converted into the corresponding hydroxides. Aqueous solutions of the hydroxides were obtained by either metathesis of a freshly prepared aqueous suspension of silver oxide and the perfluoroalkylmercuric iodide^{2,4} or an anion-exchange reaction (Dowex 12K resin in the hydroxide form). Evaporating the filtrate from the metathesis *in vacuo* at room temperature, and then subliming the residue *in vacuo* gave yields (25—40%) of the hydroxides (see Table) somewhat

¹ Lagowski, *Quart. Rev.*, 1959, **13**, 233.

² Emeléus and Haszeldine, *J.*, 1949, 2948.

³ Lagowski, Ph.D. Diss., Cambridge, 1959.

⁴ Banus, Emeléus, and Haszeldine, *J.*, 1950, 3041.

lower than those in the literature, probably owing to presence of bis(perfluoroalkyl)mercury in the iodides used. The difficulties encountered in isolating heptafluoro-*n*-propylmercuric hydroxide from large-scale preparations were partially overcome by using methanol rather than water as solvent.

Compound	Equiv. wt.		M. p.	
	obs.	calc.	obs.	lit.
CF ₃ ·HgOH	281	286.6	259—260°	—
C ₂ F ₅ ·HgOH	334	336.6	222—225 (sealed tube)	220—225 (sealed tube)
C ₃ F ₇ ·HgOH	380	386.6	229—230 (sealed tube)	—

Preparation of solid perfluoroalkylmercuric hydroxides by the ion-exchange method⁵ was not satisfactory. Appreciable quantities of the mercurials could not be removed from the resin, although the eluates gave titration curves similar to those obtained with solutions prepared from pure samples of the hydroxides. Evaporation of the eluates yielded solids from which no identifiable compounds could be sublimed. Several days after use, the ion-exchange resins became black.

Apparatus.—A Leeds and Northrup model 7664 pH meter was calibrated with either a Beckman certified pH 7 buffer or a Parstains pH 7.7 buffer; a Leeds and Northrup glass/calomel electrode system was used in following the titration of the perfluoroalkylmercuric hydroxides with perchloric acid. Titration of the perfluoroalkylmercuric hydroxides with hydrohalogen acid afforded ionization constants of the corresponding halides, these titrations being followed by measuring the potential difference of a glass/silver–silver chloride electrode pair. Silver halide electrodes were prepared by depositing silver halide electrolytically on to finely etched silver wire from a solution of hydrohalogen acid.⁶ Values of E^0 for the various glass/silver–silver halide and glass/calomel electrode pairs were obtained from the intercept, determined by the method of least squares, of a plot of the potential difference between the electrodes against the pH of solutions containing varying concentrations of the appropriate hydrohalogen acid or perchloric acid. Titrations were conducted in a cell at $25.0^\circ \pm 0.2^\circ$.

DISCUSSION

The high solubility of the perfluoroalkylmercuric hydroxides in most solvents, coupled with their volatility, made their isolation difficult; pure solid samples were eventually prepared in low yield by the action of an aqueous suspension of silver oxide on resublimed perfluoroalkylmercuric iodides. Because the yields were low and the supply of starting materials was limited, an attempt was made to titrate aqueous solutions of these compounds prepared by the silver oxide method. These solutions gave normal titration curves; however, they became cloudy when titrated with hydrohalogen acids, as did those titrated with perchloric acid if potassium chloride was later added (see below). The precipitate formed on addition of hydrochloric acid to aqueous solutions of heptafluoro-*n*-propylmercuric hydroxide, prepared by the silver oxide method, was identified (*X*-ray) as silver chloride; analysis of these solutions showed the presence of much more silver than can be accounted for by the solubility of silver oxide in water. These results appear to be compatible with the observation⁷ that perfluoroalkylmercurials form complex ions of the types $R_F Hg X_3^{2-}$ and $(R_F)_2 Hg X_2^{2-}$ (R_F = perfluoroalkyl, X = halogen) and suggest that similar complexes containing hydroxyl ions are formed. The nature of the interaction of silver oxide with perfluoroalkylmercurials in aqueous solution is being investigated further.

The ionization constants reported here for perfluoroalkylmercuric hydroxides were determined by titrating aqueous solutions of the appropriate hydroxide in $\sim 0.001M$ -solution (100 ml.) with perchloric acid. As in the titration of alkylmercuric hydroxides with perchloric acid,⁵ addition of potassium chloride (1–2 g.) to the perfluoroalkylmercuric hydroxide solution before the equivalence point had been reached was necessary

⁵ Waugh, Walton, and Laswick, *J. Phys. Chem.*, 1955, **59**, 395.

⁶ Brown, *J. Amer. Chem. Soc.*, 1934, **56**, 646.

⁷ Emeléus and Lagowski, *J.*, 1959, 1497.

to obtain the characteristic break in the titration curve. This suggests that perfluoroalkylmercuric chlorides are weakly ionized in aqueous solution. It is assumed that, under the conditions used, there is no association between perfluoroalkylmercuric and perchlorate ions. At the half-neutralization point the concentrations of the perfluoroalkylmercuric ion, $[R_F \cdot Hg^+]$, and un-ionized perfluoroalkylmercuric hydroxide, $[R_F \cdot HgOH]$, are related by the expression $[R_F \cdot HgOH] = [R_F \cdot Hg^+] + 2[H^+]$. Since the hydrolysis of the perfluoroalkylmercuric ion cannot be neglected under the conditions employed, the ionization constant, K_b , for the equilibrium $R_F \cdot HgOH \rightleftharpoons R_F \cdot Hg^+ + OH^-$ was calculated from the expression $K_b = (a - [H^+])[OH^-]/(a + [H^+])$, where a represents one-half of the formal concentration of the perfluoroalkylmercuric hydroxide titrated and the remaining symbols have their usual significance. No attempt was made to apply corrections for activities. The results of these titrations are shown in the Table. The ionization constant, K , for the reaction $R_F \cdot HgX \rightleftharpoons R_F \cdot Hg^+ + X^-$ ($X = Cl, Br, \text{ or } I$; $R_F = CF_3, C_2F_5, \text{ or } C_3F_7$) was calculated from the expression $\log K = (E - E^0)/0.05915 + pK_w + \log K_b$, where E is the potential difference at half-neutralization, E^0 is the standard E.M.F. of the cell with hydrohalogen acid at unit activity, and K_w is the ion product of water. Here the concentration of halide ions arising from the ionization of the perfluoroalkylmercuric halide is assumed to be negligible, an approximation that was found to be valid, within the experimental error of the apparatus, when the titration was followed simultaneously with a glass/calomel electrode combination and a silver-silver halide/calomel electrode pair (the halide ion concentration at half-neutralization was calculated from the expression $E = E^0 + 0.05915 \log [X^-]$, where E is the potential of the silver-silver halide/calomel electrode pair at half-neutralization, and E^0 is the standard potential of this electrode pair). The pK values obtained for the perfluoroalkylmercuric halides are summarized in the Table.

pK values for perfluoroalkylmercuric and alkylmercuric ⁵ hydroxides and halides at 25°.

	OH	Cl	Br	I
$CF_3 \cdot Hg$	10.76 ± 0.01	5.78 ± 0.04	7.24 ± 0.02	9.63 ± 0.05
$C_2F_5 \cdot Hg$	10.58 ± 0.03	5.64 ± 0.03	7.16 ± 0.02	9.66 ± 0.04
$C_3F_7 \cdot Hg$	10.50 ± 0.03	5.56 ± 0.05	7.16 ± 0.02	9.96 ± 0.02
$CH_3 \cdot Hg$	9.51	5.46	6.70	8.7
$C_2H_5 \cdot Hg$	9.10	—	—	—

Comparison of the perfluoroalkylmercuric hydroxide and halide ionization constants with those for the corresponding alkylmercurials ⁵ (Table) indicates that the fully fluorinated derivatives are less ionized, as would be expected from the relatively high effective electronegativity of the perfluoroalkyl group.¹ It is perhaps surprising that the effect of the perfluoroalkyl group is not more pronounced in view of the fact that the mercury atom in perfluoroalkylmercurials but not in alkylmercurials forms co-ordinate covalent bonds with halide donors.⁷ There is little difference between the ionization constants of the pentafluoroethylmercurials and the corresponding heptafluoro-*n*-propylmercurials, suggesting that the relative inductive effects of the pentafluoroethyl and heptafluoro-*n*-propyl moieties are approximately the same (cf. the carbonyl stretching frequency in perfluoroacyl halides¹). The lower ionization constants of trifluoromethyl- than of pentafluoroethyl- or heptafluoropropyl-mercurials are attributed to a slight decrease in the inductive effects of the longer-chain perfluoroalkyl groups. Formalistically, the pentafluoroethyl group can be derived from the trifluoromethyl group by replacement of a fluorine atom in the latter with a less electronegative trifluoromethyl group, so that the relative electronegativity of the pentafluoroethyl group, and of heavier perfluoroalkyl groups, should be less than that of the trifluoromethyl group.

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