244. *An Estimation of the Effective Electronegativities of Some Fluoroalkyl Groups.*

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The ionization constants of heptafluoroisopropyl-, 1,2,2,2-tetrafluoroethyl-, and 2,2,2-trifluoroethyl-mercuric hydroxide, chloride, bromide, and iodide have been determined in aqueous solution using a potentiometric method. These results, along with other data, have been used to estimate effective electronegativities of the C_2F_5, $(CF_3)_2CF$, $CF_3CF_2CF_2$, CF_3CHF, and CF_3CH_2 groups. The nature of the substances isolated in the attempted preparation of fluoroalkylmercuric hydroxides by the action of aqueous silver oxide slurries on the corresponding halide is discussed.

THE ionization constants of the perfluoro-methyl-, -ethyl-, and -propyl-mercuric hydroxides are markedly smaller [1] than those of the corresponding alkylmercuric hydroxides, in accord with predictions [2] based on conductivity data. This decrease is expected because the relatively large electron-withdrawing effect of a fluoroalkyl group imparts a more positive character to the mercury atom than does an alkyl group and causes the electron-rich oxygen atom to be more strongly polarized in the fluoroalkyl compounds. The observed differences in the properties of trifluoromethylmercury(II) salts or bistrifluoromethylmercury and the corresponding methylmercury compounds, *e.g.*, the formation of co-ordination complexes,[3,4] the conductivity of their aqueous solutions,[2] and their solubility,[2] can be accounted for on this basis.

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[1] Powell and Lagowski, *J.*, 1962, 2047.

[2] Emeléus and Haszeldine, *J.*, 1949, 2948, 2953.

[3] Emeléus and Lagowski, *J.*, 1959, 1497.

[4] (*a*) Powell and Lagowski, *J.*, 1963, 2484; (*b*) Barbieri, Giustiniani, Praglia, and Roncucci, *J. Inorg. Nuclear Chem.*, 1964, **26**, 203.

The physical and chemical properties of the fluoroalkylmercurials and of the higher homologues of the perfluoroalkylmercurials suggest that these compounds resemble bistrifluoromethylmercury more closely than they do the alkylmercurials, but information on the partially fluorinated compounds is meagre. Neither conductivity nor quantitative solubility data have been reported for fluoroalkylmercurials other than for bistrifluoromethylmercury. Co-ordination compounds of $(C_2F_5)_2Hg$, $[(CF_3)_2CF]_2Hg$, $(CF_3CFH)_2Hg$, and $(CF_3CH_2)_2Hg$ with a series of neutral donor ligands have been detected in solution.[4a]

We report here the preparation and characterization of a series of perfluoro- and fluoroalkylmercuric hydroxides as well as the ionization constants of these hydroxides and the corresponding halides.

EXPERIMENTAL

Materials.—Perfluoroisopropyl-, 1,2,2,2-tetrafluoroethyl-, and 2,2,2-trifluoroethyl-mercuric chloride were prepared, in hydrogen fluoride, by allowing equimolar quantities of mercuric chloride and fluoride to react at elevated temperatures with a slight deficiency of the olefin (Table 1). These reactions were carried out in a stainless steel autoclave under autogenous pressure. Whereas the perfluoro-olefins had to be added to the heated vessel in small increments to retard undesirable side-reactions (polymerization), the entire amount of the partially fluorinated olefins could be added initially. A similar preparation has been described for perfluoroisopropylmercuric chloride.[5] The fluoroalkylmercuric chlorides were isolated by evaporating the excess of hydrogen fluoride and subliming the residual solid *in vacuo*; repeated sublimation was required to effect purification. The structures of these compounds were confirmed by infrared and nuclear magnetic resonance (n.m.r.) spectroscopy.

TABLE 1.

Preparation and characterization of some fluoroalkylmercuric chlorides and hydroxides.

Mercurial	Yield (%)	M. p.[a]	Found[b] (%) Hg	Cl	equiv.	Formula	Calc. (%) Hg	Cl	equiv.
$(CF_3)_2CF{\cdot}HgCl$ [c]	18	76—77° [d]	48·76	8·20	—	C_3ClF_7Hg	49·52	8·75	—
$CF_3CFH{\cdot}HgCl$ [e]	33	68·5—70	59·38	10·73	—	C_2HClF_4Hg	59·51	10·52	—
$CF_3CF_2{\cdot}HgCl$ [e]	47	111—112	63·72	11·31	—	C_2ClF_5Hg	62·87	11·11	—
$(CF_3)_2CF{\cdot}HgOH$	65 [f]	280	51·77	—	384	C_3HF_7HgO	51·88	—	387
$CF_3CFH{\cdot}HgOH$	50 [f]	205—208	61·99	—	315	$C_2H_2F_4HgO$	62·98	—	319
$CF_3CH_2{\cdot}HgOH$	30 [f]	138—141 [g]	67·52	—	306	$C_2H_3F_3HgO$	66·72	—	301

[a] All m. p.'s obtained in sealed capillaries. [b] Average of replicate determinations. [c] Reaction temperature, 100°. [d] Lit.,[5] m. p. 77·7—78·1°. [e] Reaction temperature, 80—90°. [f] Calculated from the weight of fluoroalkylmercuric halide taken. [g] Melted at 78—85°, then solidified and remelted at 138—141°.

The action of moist silver oxide on solutions (ethanol–water, 75 : 25) of the fluoroalkylmercuric chlorides yielded the corresponding hydroxides (Table 1) which were purified by sublimation *in vacuo*.[1,2] Infrared and proton n.m.r. spectral data support the structures of these compounds, except that less than stoicheiometric amounts of hydroxyl protons were observed for all samples.

The mercurials were decomposed with aqueous sodium sulphide (50%) for analysis, care being taken to prevent volatilization of the mercurial during hydrolysis. Mercury was determined either by electrolytic deposition at a silver electrode (from aqueous sodium sulphide at 25—50 ma./cm.^{2}) or as $[(C_6H_5)_4As]_2HgCl_4$. Electrolytic determination of mercury on standard samples gave consistently low values (0·25—0·5%), but no attempt was made to correct the values reported in Table 1.

Infrared spectra were determined with a Beckman IR-7 recording spectrometer as Nujol mulls and as CCl_4 solutions in the 200—700 and 600—4000 cm.$^{-1}$ regions, respectively.

Ionization Constants.—The ionization constants (Table 2) for the fluoroalkylmercuric hydroxides and the corresponding halides were determined at 25·0 ± 0·2° from potentiometric titration data.[1] The concentration of mercurial employed (2×10^{-4} to 2×10^{-3}M) was below the solubility limits of the hydroxides and halides in all cases.

[5] Miller and Freedman, *J. Amer. Chem. Soc.*, 1963, **85**, 180.

TABLE 2.

p*K* Values for fluoroalkyl- and alkyl-mercuric hydroxides and halides at 25°.

	OH	Cl	Br	I	Ref.
$(CF_3)_2CF{\cdot}Hg$	10·64 ± 0·12	5·84 ± 0·11	7·62 ± 0·03	9·88 ± 0·03	—
$CF_3CHF{\cdot}Hg$	10·28 ± 0·05	5·55 ± 0·11	7·22 ± 0·03	9·06 ± 0·03	—
$CF_3CH_2{\cdot}Hg$	10·20 ± 0·05	5·58 ± 0·11	7·18 ± 0·03	8·98 ± 0·03	—
$CF_3{\cdot}Hg$	10·77	—	—	9·64	1
$C_2F_5{\cdot}Hg$	10·58	—	—	9·66	1
$CF_3CF_2CF_2{\cdot}Hg$	10·50	—	—	9·96	1
$CH_3{\cdot}Hg$	9·51	—	—	8·70	6
$C_6H_5{\cdot}Hg$	10·00	—	—	—	6

DISCUSSION

Fluoroalkylmercuric Hydroxides.—The action of moist silver oxide on a fluoroalkylmercuric chloride followed by sublimation of the reaction product apparently yields the oxide $(R_FHg)_2O$ or a mixture of the oxide and hydroxide, rather than the pure hydroxide (R_FHgOH) (R_F = perfluoroalkyl). The infrared and n.m.r. spectra of these compounds show disproportionately small contributions from hydroxyl groups. The melting points of the substances prepared by this method are somewhat higher than would be expected for the pure hydroxides. In addition the behaviour of some of these compounds upon heating, *i.e.*, melting followed by solidification then remelting, suggests that water is lost by the hydroxide to form the oxide. These compounds dissolve slowly in water (2—3 days for some samples) to give solutions containing a substance with the theoretical equivalent weight of the hydroxide; this behaviour is consistent with the slow hydration of the oxide to produce the hydroxide prior to solution. The melting point of heptafluoroisopropylmercuric hydroxide obtained in this investigation is similar to that reported for bisheptafluoroisopropylmercuric oxide prepared [6] by the action of water on bisheptafluoroisopropylmercury. The ready loss of water is not unexpected since " methylmercuric hydroxide " exists as either the oxide or an equimolar mixture of the oxide and hydroxide, depending on the method of preparation,[7] and the isomeric trifluoromethylphenylmercuric hydroxides have been shown to be admixed with the corresponding oxides.[8]

Ionization Constants.—The ionization constants obtained for the heptafluoroisopropyl-, 1,2,2,2-tetrafluoroethyl-, and 2,2,2-trifluoroethyl-mercuric salts are in accord with the constants previously reported for trifluoromethyl-, pentafluoroethyl-, and methyl-mercuric salts,[1,9] and are in the order which would be predicted on the basis of the relative inductive effect of the fluoroalkyl groups. Agreement between the results of titrations on different samples of the same mercurial was satisfactory except for heptafluoroisopropylmercuric hydroxide, in which case the somewhat larger deviations can probably be attributed to contamination by carbon dioxide absorbed during its slow dissolution (2—3 days). Both the chloride ionization constants and the Hg–Cl stretching frequencies of the fluoroalkylmercuric chlorides are relatively insensitive to the nature of the organic moiety; similar behaviour of the chloride ionization constants was noted [1] for methyl- and trifluoromethylmercuric chloride.

Effective Electronegativities of Some Fluoroalkyl Groups.—The variation in certain physical and chemical properties, such as the relative reactivities of molecules containing the groups in question, and the magnitude of a characteristic group frequency have been used to estimate effective electronegativities of organic moieties. Recently, the method used to calculate orbital electronegativities has been extended to group electronegativities.[10] It has been suggested that the best experimental method for evaluating electronegativities

[6] Aldrich, Howard, Linn, Middleton, and Sharkey, *J. Org. Chem.*, 1963, **28**, 184.
[7] Grdenić and Zado, *J.*, 1962, 521.
[8] Maung Tin Maung, M.Sc. Thesis, The University of Texas, 1963.
[9] Waugh, Walton, and Laswick, *J. Phys. Chem.*, 1955, **59**, 395.
[10] Hinze, Whitehead, and Jaffé, *J. Amer. Chem. Soc.*, 1963, **85**, 148.

is the variation in the frequency of certain characteristic vibrational modes of a series of suitable compounds, provided other factors do not contribute to the frequency shifts.[11]

The effective electronegativities of the fluoroalkyl groups studied were estimated from the ionization constants of the fluoroalkylmercuric hydroxides and chlorides, as well as from the Hg–O and Hg–Cl stretching frequencies. Steric and resonance effects should be negligible in the organomercurials because of a linear C–Hg–X (X = O, I) arrangement and the improbability of double-bonding between the mercury and saturated carbon atoms. A linear relationship exists between the effective electronegativities, χ, of the CF_3, C_6H_5, and CH_3 groups and either pK_b for the corresponding mercuric hydroxides (equation 1) or pK_i for the mercuric iodides (equation 2).

$$\chi = -8{\cdot}5 + 1{\cdot}10\ \mathrm{p}K_b \qquad (1)$$

$$\chi = 9{\cdot}77 + 1{\cdot}35\ \mathrm{p}K_i \qquad (2)$$

Equations (1) and (2) were obtained using the ionization constants in Table 2 and the following electronegativities: CF_3, 3·3;[12] C_6H_5, 2·4;[13] and CH_3, 2·0.[13] These equations and the data in Table 2 were then used to estimate the effective electronegativities given in Table 3.

TABLE 3.

The effective electronegativities of some fluoroalkyl groups.

Method	C_2F_5	$(CF_3)_2CF$	$CF_3CF_2CF_2$	CF_3CHF	CF_3CH_2
ν (H–X)	3·3	3·1	—	—	—
ν (Hg–O)	3·2	3·6	2·4	3·0	2·8
pK_b	—	3·2	3·0	2·8	2·7
pK_i	—	3·6	3·5	2·6	2·5

A linear relationship (equation 3) was observed between the Hg–O stretching frequency,

$$\chi = -9{\cdot}3 + 0{\cdot}0259\ \nu(\text{Hg–O}) \qquad (3)$$

ν(Hg–O), (Table 4) and the effective electronegativities, χ, of the organic moiety for CF_3HgOH, C_6H_5HgOH, and CH_3HgOH. Considerable broadening of the Hg–O stretching mode is observed for these compounds, arising presumably from either solid-state interactions such as hydrogen-bonding or the presence of two species, *i.e.*, RHgOH and $(RHg)_2O$. The magnitude of the error introduced in equation (3) because of broadening does not, however, significantly affect the estimated group electronegativities (Table 3). A similar linear relationship was observed for the Hg–Cl stretching frequencies (Table 4), but was not satisfactory for estimating group electronegativities because of the short range of values for ν(Hg–Cl) (315—341 cm.$^{-1}$) and the error in determining the position of these bands (±2·5 cm.$^{-1}$).

TABLE 4.

Infrared stretching frequencies (cm.$^{-1}$) for Hg–O and Hg–Cl in fluoroalkylmercuric hydroxides and chlorides.

	CF_3	C_2F_5	$CF_3CF_2CF_2$	$(CF_3)_2CF$	CF_3CHF	CF_3CH_2	C_6H_5	CH_3
ν (Hg–O) ...	488	475	497	449	474	468	457	429
ν (Hg–Cl) ...	335	330	335	341	337	335	317	315

The mass-corrected H–X stretching frequency of the hydrogen halides and of H–CF_3 is a linear function of the electronegativity, χ, of X (equation 4),[11] where the electronegativities

$$\chi = -1{\cdot}19 + (2{\cdot}20 \times 10^{-3})\nu(\text{H–X}) \qquad (4)$$

of F, Cl, Br, I, and CF_3 are taken as 4·0, 3·0, 2·8, 2·5,[14] and 3·3,[12] respectively. This relationship cannot be used for species having more than one hydrogen atom on the carbon

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[11] Bellamy, " The Infra-red Spectra of Complex Molecules," Wiley, New York, 1958, pp. 377—409.

[12] Lagowski, *Quart. Rev.*, 1959, **13**, 233.

[13] Bell, Heisler, Tannenbaum, and Goldenson, *J. Amer. Chem. Soc.*, 1954, **76**, 5185.

[14] Pauling, " The Nature of the Chemical Bond," 3rd edn., Cornell University Press, Ithaca, New York, 1960.

atom because of mixing of the H–X modes. Thus, only the electronegativities of the perfluoroethyl and perfluoroisopropyl moieties could be estimated from equation (4) and the appropriate value of ν(H–X) 3008 and 2980 cm.$^{-1}$, respectively.[15]

The values estimated for the electronegativities of the various fluoroalkyl groups using different methods (Table 3) are in satisfactory agreement considering the qualitative nature of the electronegativity concept. For a given method the effective group electronegativities fall in the order expected on the basis of the inductive effects of the fluoroalkyl groups, except for the values found for the perfluoroisopropyl group from ν(Hg–O) which, by previous arguments,[1] might have been expected to be less than that for the trifluoromethyl group; this discrepancy could be due to a solid-state effect of a bulky group. The electronegativity of the 2,2,2-trifluoroethyl group might have been expected to be more than 0·1 unit below that of the 1,2,2,2-tetrafluoroethyl group, but it is in agreement with the observation that the fluoroalkylmercurials resemble bistrifluoromethylmercury more closely than dimethylmercury. The linear relationship observed between the effective electronegativities of fluoroalkyl groups and the pK_b's of the organomercuric hydroxides indicates, as had been previously postulated,[1] that the variation in the ionization constants of these hydroxides is due to the inductive effect of the organic group.

The bond electronegativities calculated[10] for the trifluoromethyl (3·3) and 2,2,2-trifluoroethyl group (2·4) are in surprisingly good agreement with the experimental values obtained in this and in a previous[1] investigation, in view of the very different approaches employed.

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[15] (*a*) Nielson and Howard, *J. Chem. Phys.*, 1955, **23**, 329; (*b*) Powell and Lagowski, unpublished results.