405. *The Preparation and Properties of Some Organomercury Groups.*

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Organomercury groups (RHg) are prepared as cathode deposits on electrolysis of organomercuric chlorides in liquid ammonia. Decomposition temperatures of the groups and decomposition voltages for the electrolyses are measured. Decomposition of the groups in the presence of free-radical detectors suggests the absence of free radicals in the groups. Previous discussions of the chemical character of the groups are reviewed, and their properties described in terms of the Pauling theory of metals. Evidence for the existence of similar organometallic groups is reviewed, and suggestions made for the preparation of possible analogues.

THE term " organomercury group " is used to described the free groups first prepared by Kraus [1] and considered by him to be solid free radicals.[2] Kraus prepared $CH_3{\cdot}Hg$, $C_2H_5{\cdot}Hg$, and n-$C_3H_7{\cdot}Hg$ as black deposition products on the cathode by electrolysis of the corresponding alkylmercuric chlorides in liquid ammonia at temperatures between $-60°$ and $-34°$, platinum wire electrodes being employed. Kraus established that the groups decomposed on warming to " very near ordinary temperatures " according to the equation $2RHg \longrightarrow R_2Hg + Hg$. Attempts to electrolyse the n-pentyl- and n-octyl-mercuric iodides gave, respectively, slight and no indication of the existence of the corresponding organomercury groups. Rice and Evering [3] repeated the preparation of $CH_3{\cdot}Hg$ and observed that the solid would not sublime in a high vacuum at $-20°$ to $-10°$. The substances described by Hein and Mesée [4] are probably the corresponding phenyl- and benzyl-mercury groups: these were prepared by directing the pyrolysis products of benzene and toluene respectively on a stream of mercury vapour condensing on a cold finger, the final products being condensed in a trap cooled in liquid air. The black solids resulting decomposed on warming to room temperature to give mercury and the corresponding diarylmercury. The solids are represented as mercurous aryls and the decomposition expressed as $R_2Hg_2 \longrightarrow R_2Hg + Hg$.

RHg radicals have been postulated as intermediates in the electrolysis of solutions of alkylmercuric compounds,[5, 6] where mercury dialkyls are produced in high ($\geqslant$90%) yields, the reaction being presumably

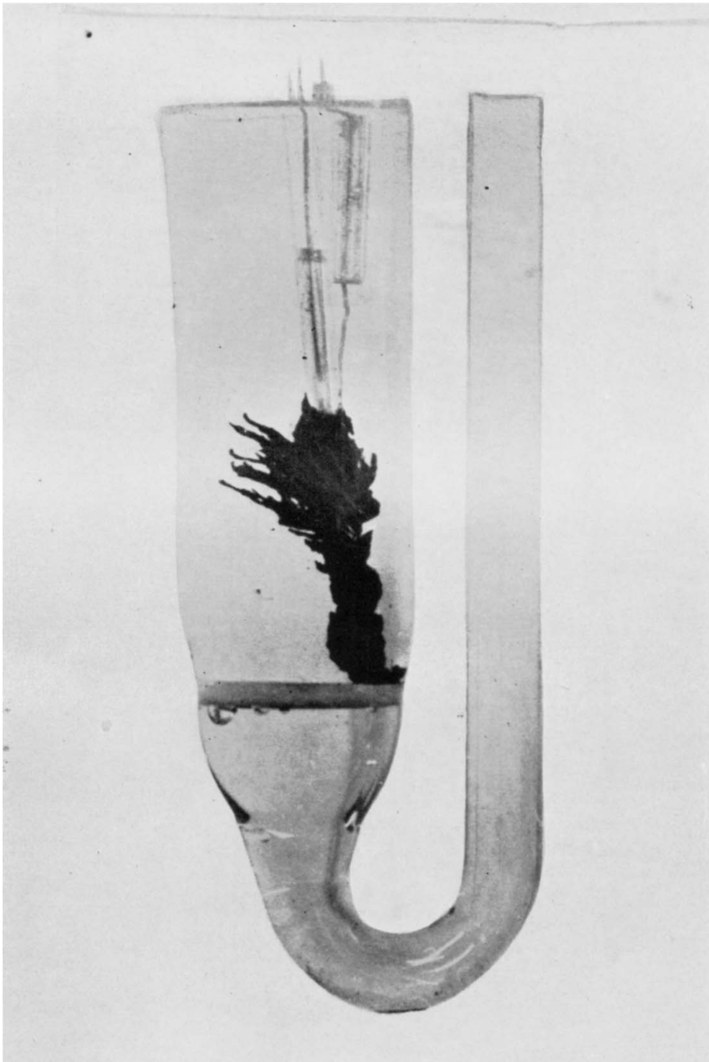
$$2RHg^+ + 2e \longrightarrow 2RHg \longrightarrow R_2Hg + Hg$$

Similarly, RHg radicals have been postulated as intermediates in the polarographic reduction of some organic and organomercuric halides.[7, 8, 9]

EXPERIMENTAL

Compounds RHgCl (R = Me, Et, Pr^n, Pr^i, Bu^n, Ph, $PhCH_2$, *trans*-Cl·CH:CH·) were prepared by standard methods.[10, 11] A run was carried out by first saturating liquid ammonia with the mercurial at $-78°$. The solution was then displaced into the glass reaction vessel containing an internal sintered-glass filter after the design of Fowles and Pollard,[12] the reaction

1 Kraus, *J. Amer. Chem. Soc.*, 1913, **35**, 1732.
2 *Idem*, *Rec. Trav. chim.*, 1923, **42**, 588.
3 Rice and Evering, *J. Amer. Chem. Soc.*, 1934, **56**, 2105.
4 Hein and Mesée, *Ber.*, 1943, **76**, 430.
5 Maynard and Howard, *J.*, 1923, 760.
6 Melnikov and Rokitskaya, *J. Gen. Chem., U.S.S.R.*, 1937, **7**, 2596.
7 Benesch and Benesch, *J. Amer. Chem. Soc.*, 1951, **73**, 3391; *J. Phys. Chem.*, 1952, **56**, 648.
8 Colichman and Maffei, *J. Amer. Chem. Soc.*, 1952, **74**, 2744.
9 Oldham, Ph.D. Thesis, Manchester, 1952, cited by Pritchard, *Chem. Rev.*, 1953, **52**, 529.
10 Krause and von Grosse, " Die Chemie der metall-organischen Verbindungen," Borntraeger, Berlin, 1937, p. 129.
11 Freidlina and Nesmeyanov, *Compt. rend. Acad. Sci. U.R.S.S.*, 1940, **26**, 60.
12 Fowles and Pollard, *J.*, 1953, 2588.



Cathode deposit of n-*butylmercury group formed on electrolysis of* Bu^nHgCl *in liquid ammonia at* $-78°$.

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vessel being cooled to $-78°$ by solid CO_2–acetone. All operations were carried out with exclusion of air and moisture. Two platinum wire electrodes mounted in the centre of the reaction vessel were employed and the solutions were electrolysed at $-78°$, a potential difference of about 4—6 v being used for most cases; the current passed was 2—10 mA. A deposit, usually black, formed rapidly at the cathods, and a stream of bubbles (presumably chlorine) appeared at the anode. The anode was attacked by the gas liberated thereat, and this necessitated renewal of the electrode after about four runs. In every case, deposition of the solid was accelerated visibly by continued electrolysis. The length of runs varied from 2 to 4 hr. and on completion the solid was filtered off and washed with liquid ammonia or cold ($-78°$) methanol. The deposit was then continuously pumped under high vacuum to remove traces of ammonia or methanol: in practice, it proved difficult to produce a pressure lower than 0·01 mm. Hg. The decomposition voltage for each electrolysis was measured; the results are in Table 1. The values were reproducible and were unaltered on substitution of a silver-coated cathode.

TABLE 1. *Decomposition voltages of saturated solutions of* RHgCl *in liquid ammonia at* $-78°$.

R	Me	Et	Pr^n	Pr^i	Bu^n	Ph	$PhCH_2$	Cl·CH:CH·
Decomp. voltage (v)	1·2	1·4	1·75	1·5	1·8	37[a]	-----[b]	0·9[c]

[a] Slowly decreased throughout run, 8v after 3½ hr., 2v after 5 hr.
[b] Considerable fluctuations of current accompanying decomposition of product made determination impossible.
[c] White crystals deposited in solution, mercury deposited at cathode.

The approximate decomposition temperatures of the groups were determined by rapid removal of the groups from the sintered disc to a tube containing ethanol at $-78°$. The tube and contents were allowed to warm slowly to room temperature and the temperature at which the solid changed rapidly to give mercury globules was determined by means of a pentane thermometer. In no case did the solid melt before decomposition; results are in Table 2.

TABLE 2. *Decomposition temperatures of organomercury groups.*

R	Me	Et	Pr^n	Pr^i	Bu^n	Ph	$PhCH_2$
Decomp. temp.	$-10°$ to $-15°$	$-15°$ to 0°	$-5°$	$-25°$	$-5°$	$-20°$ to 0°[a]	-----[b]

[a] Solid changes only slightly in appearance on decomposition.
[b] Some decomposition occurs at $-78°$.

When some of the *iso*propylmercury group was allowed to warm in air whilst attached to the cathode it decomposed with a loud cracking sound.

The groups varied in appearance; the methyl and ethyl groups were black flaky deposits which could be readily detached from the cathode by tapping the vessel or rotating the electrode. The deposits fell from the cathode at short intervals during electrolysis. The *iso*propyl group was very similar in appearance to the methyl and ethyl analogues, but adhered more strongly to the cathode. The *n*-propyl group was a black deposit with a reddish-brown tinge, thin layers being purple: it was softer than the methyl, ethyl, and *iso*propyl analogues, adhered to the cathode, and grew in a tree-like manner. The *n*-butyl group was black, with a reddish-brown tinge which became more intense as electrolysis proceeded: it adhered firmly to the cathode and grew in a tree-like manner (see Plate). The phenyl and benzyl groups were black and dark grey respectively, and the latter adhered firmly to the cathode.

Reactions of the Groups.—Neither the methyl nor the ethyl group changed when kept in the presence of 10 mm. of nitric oxide at $-78°$ for 12 hr. On gradual warming to room temperature, followed by cooling to $-78°$, there was no change in pressure, indicating that nitric oxide had not been consumed. Ultraviolet spectrophotometric examination of the decomposition products in ethanol solution gave $\lambda_{max.}$ 210 mμ, characteristic of mercury compounds,[13] with no evidence of formation of nitrosoalkanes.[14]

Decomposition of the methylmercury group by warming to room temperature, followed by cooling to $-78°$ and measurement of the pressure (McLeod gauge) gave no pressure rise, indicating absence of volatile hydrocarbons and ammonia in the decomposition products. The

[13] Gowenlock and Trotman, *J.*, 1955, 1454.
[14] *Idem, ibid.*, p. 4190.

decomposition products of the phenylmercury group when dissolved in ethanol had ultraviolet absorptions characteristic of diphenylmercury,[13] the low intensity of absorption in the 245—250 mμ region indicating very little formation, if any, of diphenyl, which has $\lambda_{max.}$ (in EtOH) 248 mμ, log ε 4·21.

Electrolysis of methylmercuric chloride in the presence of styrene, prolonged contact of the methylmercury group with styrene in liquid ammonia at −45°, and warming the methylmercury group to room temperature in the presence of an ethanolic solution of styrene produced no polystyrene.

An acetone solution of diphenylpicrylhydrazyl gave no observable colour change at −78° during 12 hr. with the ethylmercury group or on warming the group to room temperature. The relative proportions were approximately 1 mole of diphenylpicrylhydrazyl to 100 " moles " of EtHg.

Discussion

The decomposition voltages observed by us are of the same order as those reported by Evans, Lee, and Lee [15] for ethereal solutions of Grignard reagents, which are the only analogous determinations reported in the literature. For Grignard reagents, the variation of decomposition voltage with increase in size of the alkyl group is irregular. The cathodic deposition of mercury and the precipitation of white needles during the electrolysis of *trans*-2-chlorovinylmercuric chloride suggest the occurrence of the reaction

$$2Cl\cdot CH{:}CH\cdot HgCl \longrightarrow HgCl_2 + Hg(Cl\cdot CH{:}CH)_2 \downarrow$$

which can occur in chloroform solution impregnated with gaseous ammonia.[11] Confirmation of this explanation, which implies that electrolysis is confined to the soluble mercuric chloride, is provided by the close agreement of the observed decomposition voltage with that recorded by Groening and Cady [16] for liquid ammonia solutions of mercuric chloride (0·85 v).

Kraus's original observations [1] are confirmed and extended, except that the reddish liquid observed when the ethylmercury group melts (and predicted for the *n*-propylmercury group) was never observed by us. In particular, we have confirmed Kraus's observation that alcoholic solutions of organomercuric halides can be similarly electrolysed at low temperatures to yield the organomercury groups. However, the solubility of the halides is much lower, the decomposition voltages are higher (about 7 v for MeHgCl), and much larger potential differences are necessary (about 100 v) to yield the organomercury groups in any quantity. We have also confirmed that the groups decompose slowly at about −50; such decomposition rendered impossible attempts to measure the resistance of the solid groups and its temperature dependence. The predominant decomposition reaction of the groups is

$$2HgR \longrightarrow Hg + HgR_2$$

and our failure to detect R radicals or R–R products suggests that the reactions

$$HgR \longrightarrow Hg + R\cdot;\ R\cdot + R\cdot \longrightarrow R{-}R$$

can participate to a small extent only.

The organomercury groups can be considered to be (*a*) free radicals, RHg·, (*b*) amalgams of mercury with organic free radicals R·, (*c*) organomercurous compounds R·Hg·HgR, or (*d*) organic " metals." Each of these hypotheses can be evaluated in the light of the experimental evidence.

If the groups are free radicals, it seems likely that they would react with either nitric oxide or diphenylpicrylhydrazyl, or initiate the polymerization of styrene. It is also known that solid free radicals that have no resonance stabilization decompose at temperatures much lower than −20°, *e.g.*, the nitrogen- and sulphur-containing radicals

[15] Evans, Lee, and Lee, *J. Amer. Chem. Soc.*, 1935, **57**, 489.
[16] Groening and Cady, *J. Phys. Chem.*, 1926, **30**, 1597.

listed by Rice [17] which decompose between $-195°$ and $-125°$. A further argument against the free-radical hypothesis is given by the fact that D(Hg–H) is approximately equal to $D(Hg-CH_3)$,[18] yet the solid of composition HgH decomposes into mercury and hydrogen between $-125°$ and $-100°$.[19] This observation suggests that whereas the HgH solid may be a free radical, the organomercury group has a non-radical character.

If the groups are 1 : 1 amalgams of mercury and free radicals, it would be expected that further addition of mercury would cause further amalgamation; such behaviour has not been observed by either Kraus [1] or us. The polarographic reduction of RHg^+ at room temperature gives RHg· radicals [7, 8, 9] with resultant dissolution of the radicals in the mercury drop

$$RHg\cdot + Hg \longrightarrow R \text{ (solution in Hg)}$$

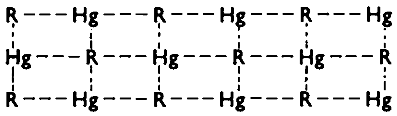
The marked difference in behaviour of the organomercury groups suggests that they are neither radicals nor amalgams. In addition the failure to yield R–R on decomposition suggests that R is not free from bonding of some type with the mercury. The groups are obviously different from the tetramethylammonium amalgam which yields free methyl radicals [20] on decomposition above 0°.

Hein and Mesée [4] implied that the groups were organomercurous compounds R·Hg·HgR, and the close analogy between the decomposition of the groups and inorganic mercurous compounds makes such a hypothesis plausible. It is known that the decomposition temperatures of mercurous halides decrease from chlorine to iodine (*i.e.*, with increase in covalent character) and the presumably covalent mercurous alkyls should have an even lower decomposition temperature. Molten mercurous chloride is red-brown [21] and thus exhibits a similar colour to the *n*-propyl- and the *n*-butyl-mercury groups. It can be further argued that, although mercuric alkyls are undissociated into ions and concentration of mercurous ions will therefore also be negligible ($[Hg_2^{2+}]/[Hg^{2+}] = 116$ in presence of metallic mercury [22]), the disproportionation reaction $Hg_2^{2+} \longrightarrow Hg + Hg^{2+}$ by which the decomposition must occur is considerably retarded by the low temperature, and that the decomposition temperature represents the threshold at which this can occur. However, it seems unlikely that a covalent mercurous bond could exist,[22] and to attribute a large ionic character to a mercurous–carbon bond would be contrary to expectation. A very approximate estimate of the Hg–Hg bond length in "mercurous methyl" can be obtained from a plot of known Hg–Hg bond lengths in mercurous halides [23] against the electronegativity of the halide; [24] extrapolation to zero electronegativity at 3·3 Å (bond length [25] in Hg_2) produces an Hg–Hg distance of 2·75—2·90 Å at electronegativity 2·0—2·1 (cf. Pritchard [9]). This distance corresponds to the expected value for a covalent Hg–Hg bond. The most conclusive argument against the identification of the groups with a mercurous alkyl structure lies in the high electrical conductivity of the solid groups compared with the very high resistances of solid inorganic mercurous compounds.[26]

Kraus implied that the groups were metallic and contained delocalised free electrons; Coates [27] has elaborated this view, considering the groups to be $R-Hg^+$ ions in a metallic lattice, together with the equivalent number of "free" electrons, *i.e.*, an *organic metal.* The electrical properties of the groups necessitate such an approach, or treatment in terms

[17] Rice, *J. Chem. Phys.*, 1956, **24**, 1259.
[18] Gowenlock, Polanyi, and Warhurst, *Proc. Roy. Soc.*, 1953, *A*, **219**, 270.
[19] Geib and Harteck, *Chem. Ber.*, 1932, **65**, 1550.
[20] Porter, *J.*, 1954, 760.
[21] Klemm and Biltz, *Z. anorg. Chem.*, 1926, **152**, 225.
[22] Sidgwick, "The Chemical Elements and their Compounds," Oxford Univ. Press, 1950, p. 292.
[23] Grdenić and Djordjević, *J.*, 1956, 1316.
[24] Pauling, "The Nature of the Chemical Bond," Cornell University Press, New York, 1940, p. 64.
[25] Syrkin and Dyatkina, "Structure of Molecules and the Chemical Bond," Butterworths, London, 1950, p. 151.
[26] Gowenlock and Trotman, unpublished observations.
[27] Coates, *Quart. Reviews*, 1950, **4**, 217; "Organo-Metallic Compounds," Methuen, London, 1956, p. 47.

of a theory of metals. The existence of an electron-pair bond and a free electron in R:Hg· suggests the possibility of resonance on the pattern of the Pauling theory of metals (ref. 24, p. 401). We can represent the group structure diagrammatically as in (I), each mercury atom being bonded to six organic groups R, the electrons being delocalised throughout the solid. Thus we have a distorted mercury lattice. At low temperatures the structure is reasonably stable, but as the temperature increases, the lattice vibrations become more intense and an HgR_2 molecule is formed as two energetic R groups converge simultaneously and collinearly on the opposite sides of a mercury atom, localisation of electrons resulting. R–R formation is improbable as all R groups are separated from one another by mercury atoms. Such a hypothesis implies that stability of the group depends on the size of R. Thus the relatively small hydrogen atom can diffuse through the mercury rhombohedral lattice, and so the HgH group will possess low thermal stability. When R is large, it can no longer be accommodated by the lattice and hence thermal stability is low. Our observations for R = $PhCH_2$, and those of Kraus [1] for R = *n*-pentyl and *n*-octyl again confirm this hypothesis. We are of the opinion that this approach to the structure of the organomercury groups accords better with the experimental observations than the other suggestions we have examined.



(I)

It is possible that other organometallic groups occur. Hein and Eissner's [28] "chromium polyphenyls" are similar to the organomercury groups in their method of preparation, but have recently been shown to possess ferrocene-type structures.[29] Other possible analogues are the "trimethyltin radical" [30] and dimethylgallium.[31] However, the former is identical with hexamethyldistannane, and the latter reacts rapidly with ammonia. Possible analogues must possess the same capacity for limited distortion of the metal lattice, and probably have an alkyl : metal ratio of 1 : 1. Investigation of the reduction of RZnX, RCdX (as yet unknown), $RAuX_2$, $RTlX_2$, $RPbX_3$, and their analogues (X = halogen) in suitable media at low temperatures is necessary. The zinc and cadmium metallic lattices and interatomic distances are sufficiently similar to the mercury lattice to make preparation of their organometallic groups possible; also the decomposition of these groups would parallel the mercury case. It is possible that the greater thermal stability of RZn and RCd radicals than of RHg radicals [estimated on the assumption that $D(CH_3{-}M) \simeq D(H{-}M)$[18, 32]] implies that the second stage in the reaction sequence

$$RM^+ + e \longrightarrow RM \text{ (radical)} \longrightarrow (RM)_n \text{ (group)}$$

is less likely to occur. In this case, the organomercury groups may well be unique.

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[28] Hein and Eissner, *Ber.*, 1926, **59**, 362.
[29] Cotton, *Chem. Rev.*, 1955, **55**, 551; Fischer and Seus, *Chem. Ber.*, 1956, **89**, 1809.
[30] Kraus and Sessions, *J. Amer. Chem. Soc.*, 1925, **47**, 2361.
[31] Kraus and Toonder, *ibid.*, 1933, **55**, 3547.
[32] Gaydon, "Dissociation Energies," Chapman and Hall, London, 1953, chapter 12.