230. *Organomercury Groups. Part III.*[1] *Compounds* $(RHg)_n$ *Containing Active sec-Butyl and Groups containing Five, Six, or Seven Carbon Atoms.*

By B. H. M. BILLINGE and B. G. GOWENLOCK.

The organomercury groups, $(RHg)_n$, are studied where R = active sec-butyl, sec-butyl, n-pentyl, isopentyl, n-hexyl, n-heptyl, *p*-tolyl, and cyclohexyl. Where possible, decomposition temperatures of the solids are investigated. It is shown that the decomposition results in destruction of the optical activity. Conclusions concerning the structure of the solids are drawn.

IN previous papers [1,2] on organomercury groups, in which the work of Kraus [3] was extended, we proposed the annexed structure for these labile solids, suggesting that it would explain the electrical conductivity, the absence of free radicals or unpaired electrons, and the decomposition to mercury and dialkyl(or diaryl)mercury. It was further suggested that the size of the group, R, modified the stability, *e.g.*, that the inability to prepare benzylmercury [2] and octylmercury [3] was due to the distortion of the RHg lattice by the bulky

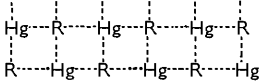
---

[1] Part II, Gowenlock, Jones, and Ovenall, *J.*, 1958, 535.

[2] Gowenlock and Trotman, *J.*, 1957, 2114.

[3] Kraus, *J. Amer. Chem. Soc.*, 1913, **35**, 1732.

organic moiety. Further to test this theory, it is necessary to prepare further organomercury groups where R contains 5, 6, or 7 carbon atoms, and thereby to attempt to correlate both size and normal covalent-bonding character with the decomposition temperatures of the solids. An investigation of the stereochemical character of the decomposition is also desirable as the proposed structure does not enable us to distinguish whether the functional groups, R, are spherically symmetrical or whether they rotate to engage in bonding with neighbouring mercury atoms during the decomposition. It is the purpose of this paper to study these questions and to see if the structures previously proposed[2] can be distinguished from that of Coates,[4] namely $(RHg)^+$ aggregates with electrons in a conduction band.



EXPERIMENTAL

The organomercury halides were prepared by standard methods; dialkylmercury reacted with ethanolic mercuric chloride, the Grignard reagent (from RCl in tetrahydrofuran[5]) was treated with mercuric chloride, or iodine was added to di-*p*-tolylmercury. A sample of active sec-butylmercuric bromide was provided by Mr. F. G. Thorpe and Sir Christopher Ingold: it was made by Charman, Hughes, and Ingold's method[6] and had $[\alpha]_D^{20}$ $-15{\cdot}0°$ (*c* 5 in acetone), *i.e.*, about 60% of the maximum rotation. The general experimental method was as previously described.[2] An attempt was made to measure the solid-state electrical conductance of methyl- and n-butyl-mercury by inserting the cathode of the electrolysis cell into a hypodermic syringe, which contained two probe-wires sealed into the capillary at a separation of about one inch. Insufficient yields of cathode deposit, and secondary electrolysis at the probe-wires, caused this attempt to be abandoned.

The decomposition voltages of the solutions are given in the Table. That for *p*-tolylmercury iodide decreased throughout a run, being 2 v after 3 hr.

Decomposition voltages of saturated solutions of RHgX in liquid ammonia at −78°.

R	Bu^s	Active Bu^s	n-C_5H_{11}	$Bu^t{\cdot}CH_2$	n-C_6H_{13}	n-C_7H_{15}	Cyclohexyl	*p*-Tolyl
Decomp. voltage (v)	2·0	1·8	2·2	2·5	3·0	4·2	2·4	13·6
X	Cl	Br	Cl	Cl	Cl	Cl	Cl	I

The properties of the cathode deposits were:

Bu^s: Black deposit, grows in tree-like fashion; initially adheres firmly to the cathode but on further electrolysis falls from the wire; decomposes rapidly at about −37°.

n-C_5H_{11}: Little indication of formation of RHg (cf. Kraus[3]). At first a misty blue-black colloidal precipitate appears in vicinity of cathode, which gradually becomes brown and pervades the whole solution.

CH_2Bu^t: Similar to the n-isomer; a few black particles are formed at the cathode.

n-C_6H_{13}: A light brown deposit adheres to cathode but appears to decompose completely at −30°.

n-C_7H_{15}: Slight dulling of the cathode surface.

Cyclohexyl: Large black tree-like deposit, similar to that from Bu^s; decomposes at −20°.

p-Tolyl: Thin black flaky film at the cathode; iodine at the anode. Both deposits fall on to the internal sinter and the decomposition temperature is impossible to detect.

Electrolysis of Active sec-Butylmercuric Bromide.—Several electrolyses were conducted in order to have a sufficient quantity of the product by means of the cycle $R°HgBr \longrightarrow (RHg)_n \longrightarrow R_2Hg + Hg \xrightarrow{HgBr_2} RHgBr$ (the degree sign denotes optical activity; cf. ref. 6); 0·1586 g. of sec-butylmercuric bromide was collected in this way; its rotation in acetone (22·5 ml.) was 0·01°; as the error in reading the polarimeter is 0·02°, it follows that all optical activity is destroyed. In the course of the electrolysis the majority of the organomercuric halide is not electrolysed, and a sample of sec-butylmercuric bromide recovered from the ammonia solution

---

[4] Coates, *Quart. Rev.*, 1950, **4**, 217; "Organo-Metallic Compounds," Methuen, London, 1960, p. 78.

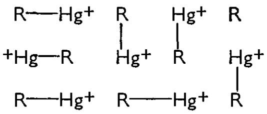
[5] Dessy, Reynolds, and Jaffe, *J. Org. Chem.*, 1958, **23**, 1217.

[6] Charman, Hughes, and Ingold, *J.*, 1959, 2523, 2530.

filtered from the electrolysis products showed unaltered activity, proving that dissolution of the compound does not alter its optical activity.

DISCUSSION

The major difference between our previous theory of the structure of the groups [1,2] and that of Coates [4] is that the latter invokes the existence of covalent bonding R–Hg$^+$, whereas we suggested delocalization of electrons throughout the lattice and the essential equivalence of all Hg $\cdots$ C " bonds ". The drop in stability on passing from the normal to the secondary alkyl could plausibly be associated either with weakening of the Hg–C bond or with distortion of the lattice and greater instability caused by the increased bulk. Size alone cannot explain the considerable difference in stability according to whether R is benzyl or *p*-tolyl, and this result supports Coates's structure. The loss of optical activity on decomposition of the organomercury group is compatible with the assumption of delocalised electrons and completely equivalent " half bonds " throughout the lattice. On decomposition to R_2Hg and metal, we expect no preference for any orientation and a completely random, racemised product will result. If we picture the Coates structure as annexed, then on decomposition only one half of the discrete R–Hg bonds will be broken and re-formed. Therefore, if there are active groups R present, half of these must retain their optical activity. The other half may undergo three possible changes: (*a*) the activity may be retained with resultant formation of R°–Hg–R°, which on reaction with mercuric bromide will give [6] 2R°HgBr and thus the activity of the final compound will be the same as that of the starting material; (*b*) the new bond may be completely racemised, giving R°–Hg–R, and the final bromide will have an optical rotation that is half that of the starting material; or (*c*) the new bond may be completely inverted and an internally compensated molecule °R–Hg–R$^{-°}$ formed, leading to two salts of opposite rotation, R°HgBr and R$^{-°}$HgBr, and thus absence of optical activity. The only way in which the Coates structure can account for the observations is by mechanism (*c*). If we accept this we imply that, in the decomposition, rotation of the radical R is impossible and that the reaction takes place only along the line of centres C $\cdots$ Hg $\cdots$ C, one carbon being covalently bonded to mercury.



It thus appears that both suggestions for the structure of organomercury groups are incomplete. Neither explains all the experimental observations: but a combination of the two structures may explain them in the following way. If we assume that, in the temperature range where the groups are stable, the Coates structure is the stable form, then the electrical conductance results, electron-spin-resonance results, and the apparent existence of some degree of discrete Hg–C covalent bonding have a rational basis. Then as the temperature increases, the conduction electrons return to Hg$^+$ and the solid then has the structure proposed by Gowenlock and Trotman. Decomposition to R_2Hg and metal then ensues with complete racemisation.

In conclusion, we note that destruction of optical activity which we have observed is unusual for organomercury compounds; it suggests that investigation of other electrochemical and chemical reductions of R°HgBr should be undertaken, *e.g.*, electrolysis in a variety of solvents at temperatures ranging from 20° to 80° (cf. Maynard and Howard,[7] and Melnikov and Rokitskaya [8]), or reaction with sodium stannite, potassium iodide, or potassium thiocyanate.[4] In such cases the formation of the dialkylmercury takes place without intermediate formation of an organomercury group.

One of us (B. H. M. B.) acknowledges a grant from British Nylon Spinners Ltd. We thank Mr. F. G. Thorpe and Sir Christopher Ingold for supplying active sec-butylmercuric bromide.

UNIVERSITY OF BIRMINGHAM. [*Received, November* 10*th*, 1961.]

---

[7] Maynard and Howard, *J.*, 1923, **123**, 760.

[8] Melnikov and Rokitskaya, *J. Gen. Chem.* (*U.S.S.R.*), 1937, **7**, 2596.