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CLEAVAGE OF (2-HYDROXY- AND 2-ALKOXYCYCLOALKYL)MERCURIC CHLORIDES BY HYDROCHLORIC ACID

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SUMMARY

The kinetics of the cleavage of (*trans*-2-methoxycyclohexyl)-, (*trans*-2-ethoxycyclohexyl)-, (*trans*-2-hydroxycyclohexyl)-, and (*trans*-2-methoxycyclopentyl)mercuric chlorides by hydrochloric acid have been investigated by a conductivity method. The reaction in alcohol/water mixtures were found to be pseudo-second-order. The enthalpies and entropies are discussed in relation to the nature of the organic radical.

A tentative mechanism for the reaction is proposed which involves a rapid and reversible addition of a proton to the (2-alkoxycycloalkyl)mercuric chloride with subsequent formation of the cycloalkene and mercuric chloride.

There have been several studies of the kinetics of cleavage (deoxymercuration) of (2-alkoxycycloalkyl)mercuric halides by mineral acids[1-3], and the topic has been reviewed by Chatt[4] and Zefirov[5]. The cleavage of (*trans*-2-alkoxycycloalkyl)mercuric halide (I) by hydrochloric acid gives the parent cycloalkene (II), alcohol, and the corresponding mercuric halide:

$$\underset{\text{(I)}}{RO\text{-}C_nH_{2n-2}\text{-}HgX} + HX \rightarrow \underset{\text{(II)}}{C_nH_{2n-2}} + ROH + HgX_2 \qquad (1)$$

Wright and coworkers[1,2] investigated this reaction in anhydrous and near anhydrous methanolic solutions and explained their results on the basis of a non-ionic mechanism, in which a molecule of the mineral acid coordinates with the organomercuric halide to form a six-membered "quasi-cyclic" intermediate which then decomposes to give cycloalkene, alcohol and mercuric halide. We believe, however, that their rate data are incorrect because of the use of an inaccurate analytical method for following the reaction (see below).

Kreevoy[6,7] investigated in detail the cleavage of a number of (2-alkoxycycloalkyl)mercuric iodides by perchloric acid both in presence and absence of potassium iodide. He suggested that the features of the cleavage are better explained by an ionic mechanism according to which there is first a rapid and reversible addition of a proton to the alkoxy oxygen with a subsequent formation of alkene and mercuric iodide in the second stage. He used a spectrophotometric method for following the cleavage reaction, a method which could not be applied for studying the cleavage of the corresponding organomercuric chlorides by hydrochloric acid[8].

The purpose of this paper is to describe a convenient and accurate experimental method for following the deoxymercuration of (2-alkoxycycloalkyl)mercuric chlorides by hydrochloric acid, and to present some kinetic data from which a mechanism for the reaction can be established.

EXPERIMENTAL

Organomercury compounds

(*trans*-2-Methoxycyclohexyl)-, (*trans*-2-ethoxycyclohexyl)-, (*trans*-2-hydroxycyclohexyl)-, and (*trans*-2-methoxycyclopentyl)mercury chlorides prepared according to published methods[9,10], were purified by recrystallization from methanol, ethanol, chloroform, and ethanol respectively before use.

Ethyl alcohol

Absolute ethyl alcohol suitable for conductometric purposes was prepared by the method of Lund and Bjerrum[11].

Measurement of rates of reaction with HCl

The most convenient method for following the hydrochloric acid cleavage of organomercury(II) compounds, is by the use of conductivity. This method is applicable provided that (*a*) there is a considerable difference in conductance between the initial and final systems, and (*b*) the change in conductivity is proportional to the progress of reaction. The use of a solvent with a high dielectric constant which is a good solvating medium for the substances used is essential, so 10% (by volume) aqueous ethanolic solutions, with a dielectric constant[12] of ca. 73 and a high solvating capacity for mercuric compounds, was used as a solvent.

The bridge consisted of a variable frequency oscillator capable of applying from 20 to 20000 Hz at a level from 0–10 V, a Jones conductivity bridge type Leeds and Northrup, equipped with compensating condensers, an oscilloscope type OSG41 Radiometer used as a visual detector in the manner described by Fuoss[13]. In general 1000 cycle current was used for the measurements. Four different conductivity cells were used, depending upon the concentration employed. The cells constants ran from 3.79 to 90.61. Bright platinum electrodes were used.

A thermostat operating at temperatures from 10° to 25° was used; the temperature was controlled to an accuracy of ±0.01°.

Under the conditions of these experiments all the products and reactants except hydrochloric acid contribute insignificantly to the conductance, so if we define λ_0 as the specific conductance at time zero and λ_∞ as the specific conductance at time infinity, then $\lambda_0-\lambda_\infty$ is equivalent to the complete path length of the reaction. The assumption is made that any distance along this path $\lambda_0-\lambda_t$ is proportional to the amount of reaction that has taken place at time *t*.

The fraction *x*, of the (2-alkoxycycloalkyl)mercury chloride decomposed by hydrochloric acid can then be expressed as $x=(\lambda_0-\lambda_t)/(\lambda_0-\lambda_\infty)$ where λ=cell constant/*R*, *R* being the resistance of the solution.

Conductances at zero time were obtained by measuring the conductances of the corresponding solutions containing the same concentration of hydrochloric acid but no mercurial. They were essentially equal to those values obtained by extrapolating the first few readings of the kinetic solutions back to zero time. Infinity readings were obtained in the majority of cases by allowing the reaction to proceed untill the resistance became constant. In a few cases they were obtained by immersing the cell after about 75% of the reaction path length in a hot water bath (ca. 50°) for about 30 min, after which the resistance readings became constant. The infinity readings were similar in both cases.

Kinetic runs

Suitable aliquots of stock solution of the (2-alkoxycycloalkyl)mercury chloride in absolute ethanol at the thermostat temperature were added to solutions of hydrochloric acid at the same temperature and of appropriate concentration up to 3.1×10^{-3} M (and at least 4 times that of organomercury compound). The final kinetic solution contained 10% by volume of ethanol and the concentration of the organomercury compound was 4.4×10^{-4} M. The reaction rates were measured at four different temperatures, *viz.* 10, 15, 20, and 25° for every acid concentration.

Second order plots were good for over 75% of the reaction. The rate constants were calculated from slopes of the plots of $\log[(B/A)\cdot(A-X)/(B-X)]$ *vs.* time, where A and B are the initial concentrations of hydrochloric acid and organomercury compound respectively in the kinetic medium.

RESULTS AND DISCUSSION

The reactions were found to be pseudo-second-order overall, and typical plots are shown in Fig. 1. The rate constants are given in Table 1, for the cleavage of (*trans*-2-methoxycyclohexyl)- (III), (*trans*-2-ethoxycyclohexyl)- (IV), (*trans*-2-hydroxycyclohexyl)- (V), and (*trans*-2-methoxycyclopentyl)mercuric chloride (VI) at 10, 15, 20, and 25° and various acid strengths. Inspection of this Table reveals that the reaction rates

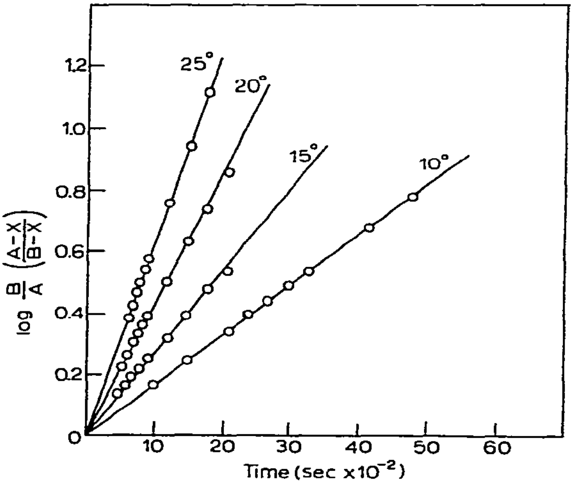

Fig. 1. Pseudo-second-order plots for deoxymercuration of (*trans*-2-hydroxycyclohexyl)mercuric chloride. Initial [RHgCl] 4.438×10^{-4} M; Initial [HCl] 19.971×10^{-4} M.

TABLE 1

REACTION RATES BETWEEN (*trans*-2-ALKOXYCYCLOALKYL)MERCURIC CHLORIDES (RHgCl) AND HYDROCHLORIC ACID AT VARIOUS ACID CONCENTRATIONS AND TEMPERATURES

Initial [RHgCl] 4.37×10^{-3} *M*; Cell constant 17.023

R	10^4 *M* [HCl]	*k* (l·mole^{-1}·sec^{-1})			
		10°	15°	20°	25°
$CH_3OC_6H_{10}$	22.188	0.069±0.02	0.119±0.042	0.209±0.006	0.297±0.008
	26.625	0.070±0.02	0.131±0.025	0.216±0.037	0.353±0.03
	28.80	0.078±0.02	0.136±0.02	0.227±0.02	0.377±0.01
$C_2H_5OC_6H_{10}$	22.189	0.074±0.01	0.129±0.028	0.222±0.002	0.366±0.01
	26.622	0.076±0.01	0.136±0.020	0.236±0.02	0.370±0.03
	28.89	0.082±0.03	0.140±0.014	0.268±0.04	0.391±0.04
	31.059	0.094±0.01	0.161±0.014	0.247±0.028	–
HOC_6H_{10}	19.97	0.208±0.03	0.34 ±0.04	0.614±0.02	0.64 ±0.03
	22.188	0.22 ±0.04	0.335±0.03	0.63 ±0.02	0.74 ±0.02
	24.407	0.233±0.03	0.368±0.024	0.652±0.02	0.907±0.03
$CH_3OC_5H_8$	24.407	0.158±0.026	0.263±0.03	0.456±0.004	0.666±0.05
	26.627	0.153±0.024	0.276±0.03	0.469±0.015	0.639±0.06

increase appreciably with increasing hydrochloric acid concentration over the narrow range studied.

Similar effects were reported by Wright and co-workers[2] who studied the deoxymercuration of a number of (2-alkoxycycloalkyl)mercuric chlorides by hydrochloric acid in anhydrous methanolic solutions, but their rate constants are rather unreliable because of the use of an inaccurate method for analysing the mixtures of mercury(II) and (2-alkoxycycloalkyl)mercury(II) ions in the kinetic solutions. Wright's method was based on the separation of organomercury halide from mercuric halide prior to the determination of the latter. Thus an aliquot of the kinetic solution was first diluted with water and then mixed with excess 0.1 *N* hydrochloric acid. (*trans*-2-Alkoxycycloalkyl)mercuric chloride was said to be completely separated from mercuric chloride by solvent extracting it into chloroform. Mercuric chloride which was thought to be left entirely in the aqueous phase was determined spectrophotometrically by dithizone. The inaccuracies in this procedure may be attributed to: (*a*) Addition of excess 0.1 *N* hydrochloric acid to kinetic solutions prior to separation of (2-alkoxycycloalkyl)mercuric chloride, which would cause further cleavage and raise the concentration of mercury(II) ions; perhaps because of this Wright's rates were always higher than the correct values. (*b*) Mercury(II) halides are also known to be extracted to some extent into chloroform, the degree of extraction increasing in the order: chloride < bromide < iodide; thus clean separation of mercury(II) halides from the corresponding (2-alkoxycycloalkyl)mercury(II) halides* via extraction with chloroform is difficult. Any (2-alkoxycycloalkyl)mercuric ions extracted into the

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* The problem of determination of mixtures of mercury(II) and organomercury(II) ions has always been encountered in following both deoxymercuration and mercuration processes. The conductivity method used in the present study is believed to be both accurate and convenient. Another method, based on the stoichiometrically different reactions of dithizone with mercury(II) and organomercury(II) ions has been described elsewhere[8].

chloroform will interfere with the spectrophotometric determination of mercury(II) by dithizone.

The inaccuracy of Wright's reaction rates was also confirmed by repeating one of his experiments and measuring the rate constant of the deoxymercuration of (*trans*-2-methoxycyclohexyl)mercuric chloride by hydrochloric acid in 96% (by volume) methyl alcohol at 25°. The initial concentrations of hydrochloric acid and organomercurial were adjusted to those used by Wright[2], namely, 1×10^{-3} *M*. The rate constant was found to be $0.0341 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$, a value 20 times smaller than that reported by Wright.

Chloride ion appears to be essential for the reaction, since the cleavage was extremely slow when perchloric acid was used in place of hydrochloric acid. Cleavage occurred immediately when sodium chloride was added to the kinetic solution containing perchloric acid. The effect of chloride ion concentration on the rate of cleavage of (*trans*-2-hydroxycyclohexyl)mercuric chloride is shown in Table 2. The rate was found to be almost independent of chloride ion concentration when this was low (< ca. 0.006 *M*) but to increase appreciably on further increase of the chloride ion concentration; the reaction remained second-order within a run. The effect of chloride ion was not detected by Wright, possibly because of his inaccurate analytical method.

TABLE 2

EFFECT OF SODIUM CHLORIDE ON THE RATE OF CLEAVAGE OF (*trans*-2-HYDROXYCYCLOHEXYL)MERCURIC CHLORIDE BY HYDROCHLORIC ACID IN 10% AQUEOUS ETHANOLIC SOLUTIONS
Initial [RHgCl] 4.438×10^{-4} *M*; Initial [HCl] 17.751×10^{-4} *M*

[NaCl] *M*	*k* ($\text{l} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$)	[NaCl] *M*	*k* ($\text{l} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$)
0.000	0.63	0.010	0.73
0.002	0.63	0.020	1.07
0.004	0.64	0.040	1.73
0.006	0.65		

Active participation of chloride ions most probably involves coordination with mercury(II) ion to form highly stable anionic mercuric chloride complexes, $HgCl_3^-$ and $HgCl_4^{2-}$. Formation of organomercuric anionic complexes, *i.e.* $RHgCl_2^-$ and $RHgCl_3^{2-}$, is unlikely for if such complexes exist they would have very low stability constants[14,15].

TABLE 3

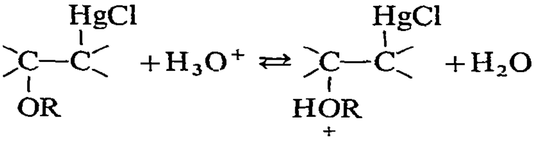
THERMODYNAMIC TERMS OF THE CLEAVAGE OF (*trans*-2-ALKOXYCYCLOALKYL)MERCURIC CHLORIDES (RHgCl) BY HYDROCHLORIC ACID

R	Temp. range (°C)	No. of expts.	ΔH^* (kcal/mole)	$-\Delta S^*$ (e.u.)
HOC_6H_{10}	10–25	12	5.18 ± 0.06	42.4 ± 0.7
$CH_3OC_6H_{10}$	10–25	12	7.49 ± 0.06	36.3 ± 0.4
$C_2H_5OC_6H_{10}$	10–25	17	6.80 ± 0.017	38.5 ± 0.8
$CH_3OC_5H_8$	10–25	8	6.42 ± 0.09	38.6 ± 0.4

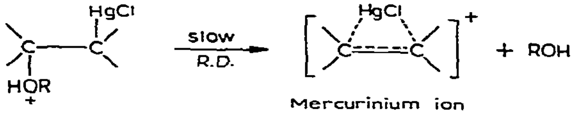
Inspection of Table 3 shows that the nature of the alkoxy group R in the organomercuric compounds has a marked effect[16] upon the enthalpies of activation ΔH^*, and entropies of activation ΔS^*. This can be attributed to the increasing basicity of the oxygen atom in the alkoxy group in the order: $OH > C_2H_5O > CH_3O$.

That (VI) is more readily deoxymercurated by hydrochloric acid then (III) may be attributed to the greater flexibility of cyclopentyl than of the cyclohexyl ring; (VI) will give more negative entropies of activation than (III), in accord with the rule that a loss in internal freedom accompanies the formation of a polar transition state[17] from a relatively non-polar starting state. The starting state for (III) can assume a "perfect" conformation with all bonds staggered and all bond angles tetrahedral. The transition state for (VI) cannot nor the starting state for (III) assume such conformation.

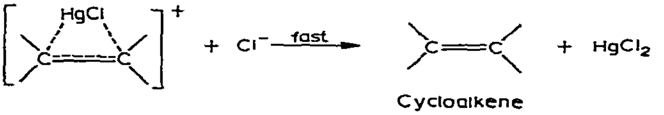
Our results may be explained by proposing that deoxymercuration of the (2-alkoxycycloalkyl)mercuric chlorides by hydrochloric acid involves firstly a rapid and reversible addition of a proton to the alkoxy oxygen with the subsequent formation of a mercurinium ion as an intermediate which may be expressed as follows:



$$\underset{OR}{\overset{}{\gt C}}-\overset{HgCl}{C}\lt + H_3O^+ \rightleftharpoons \underset{\overset{+}{HOR}}{\gt C}-\overset{HgCl}{C}\lt + H_2O \qquad (3)$$



(4)



(5)

Similar mechanism was suggested by Kreevoy[7] in describing the deoxymercuration of (2-methoxyethyl)mercuric iodide by perchloric acid in presence of iodide ions.

The mercurinium ion can be regarded essentially as a π-complex[6], in which the 6 sp hybrid orbitals of the mercury atom overlap with the two 2 p orbitals of the carbon atom, forming a pseudoaromatic structure. Additional stabilization is also possible with the participation of the $5d$ electrons of the mercury and the antibonding π-orbitals of the alkene.

The increase in the rate of deoxymercuration with increasing the basicity of the oxygen atom of the alkoxy group in the organomercurial is in accord with the mechanism since it involves protonation at the oxygen.

The effect of chloride ion on the cleavage of (2-alkoxycycloalkyl)mercuric chlorides by hydrochloric acid may be attributed to the fact that reaction (5) occurs rapidly only in the presence of chloride ion. Similar effects of halide ions on the cleavage of C–Hg bond in both organomercuric halides RHgX and diorganomercury compounds R_2Hg have also been reported[18,19]

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