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REVERSIBILITY OF ALKENE OXYMERCURATION[1]

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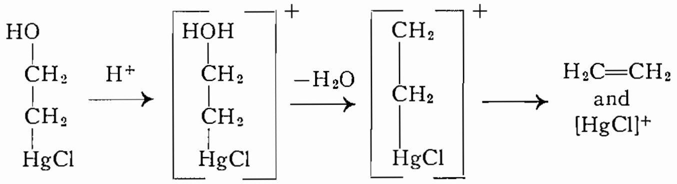
ABSTRACT

It has been shown that deoxymercuration (conversion of an α-oxyorganomercurial to the alkene) is a second-order reaction dependent on concentration of the mercurial and of the deoxymercurating acid. Moreover the rate of deoxymercuration increases with basic strength of the alkoxy substituent in the mercurial. This tendency would indicate that the rate was dependent on the strength of the acid used for deoxymercuration. The supposition has been proved by use of trifluoroacetic acid which decomposes α-2-methoxycyclohexylmercuric trifluoroacetate more slowly than does hydrochloric acid. The trifluoroacetoxymercurial decomposes to the extent of 35% whereas its synthesis is effected in 60% maximum yield from cyclohexene and mercuric trifluoroacetate. A measurable equilibrium is thus attained in this oxymercuration, though not necessarily because of a simple reversible reaction.

Whitmore has suggested that the conversion of alkaneoxymercurials to alkenes is dependent on the hydrogen ion concentration of the system (14). In terms of the decomposition of β-hydroxyethylmercuric chloride this may be expressed as follows:



$$\mathrm{HO{-}CH_2{-}CH_2{-}HgCl} \xrightarrow{H^+} \left[\mathrm{HOH{-}CH_2{-}CH_2{-}HgCl}\right]^+ \xrightarrow{-H_2O} \left[\mathrm{CH_2{-}CH_2{-}HgCl}\right]^+ \longrightarrow \mathrm{H_2C{=}CH_2}\ \text{and}\ [\mathrm{HgCl}]^+$$

This opinion is at variance with that of Sand and Breest (11), who effected a conductimetric study in which this oxymercurial was treated with hydrochloric acid. They described the reaction as one of measurable equilibrium,

$$\mathrm{HOCH_2CH_2HgCl + HCl} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{CH_2{=}CH_2 + HgCl_2 + H_2O},$$

from which the constant may be derived:

$$K = k_1/k_2 = [\mathrm{H^+}]\,[\mathrm{Cl^-}]\,[\mathrm{HOCH_2CH_2HgCl}]/[\mathrm{HgCl_2}][\mathrm{CH_2{=}CH_2}]$$

where $k_1 = 1.21-1.34\times10^{-7}/p$ and $k_2 = 2.81\times10^{-7}/p$. In these constants p is the solubility of ethylene in the system at 1 mm. pressure.

This expression may be questioned from several aspects. First it implies a measurable equilibrium which has not been observed in unbuffered systems of alkenes and mercuric chloride. Secondly the participation of trichloromercurate and tetrachloromercurate ions is not so significant as Sand and Breest thought them to be (6). Actually the experimental method is not sufficiently definitive in consideration of the conclusions which were drawn (1).

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In order to test the rate dependence specified by Sand and Breest we have examined the system of alkoxycyclohexylmercuric halides in methanolic hydrogen chloride using the colorimetric analysis for inorganic mercury which has been described previously (2). First we have examined the reaction of mercuric chloride with cyclohexene in anhydrous methanol and find (Fig. 1) that even if the slight diminution in mercuric chloride could be attributed to the reaction of oxymercuration it would be so slow and so slight that it might be ignored during kinetic treatment of the deoxymercuration. Secondly we have decomposed near-anhydrous methanolic solutions of α-2-methoxycyclohexylmercuric chloride (1.0×10^{-3} mole/liter) by treatment with hydrogen chloride and find the reaction to be first order in respect of oxymercurial and first order in respect of the acid. Thus at an acid concentration of 0.5×10^{-3} mole/liter (80% of reaction) the rate constant is 0.65 liter mole^{-1} sec.$^{-1}$. At 1.0×10^{-3} mole/liter of acid (75% investigated) the constant is 0.64 liter mole^{-1} sec.$^{-1}$ while at 2.0×10^{-3} mole/liter of hydrogen chloride (90% investigated) the constant is 0.63 liter mole^{-1} sec.$^{-1}$. Moreover it may be seen in Table I that the second-order decomposition is unaffected by inclusion either of sodium chloride or of mercuric chloride. Therefore the decomposition of this oxymercurial seems not to be dependent on the anion, either as chloride ion or as tetrachloromercurate ion.

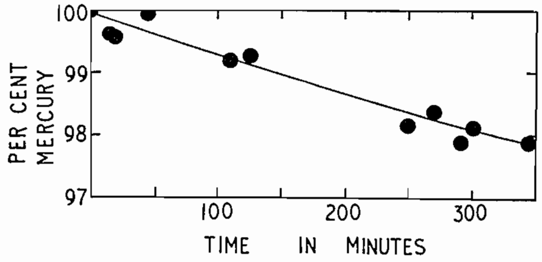


FIG. 1.

TABLE I

DECOMPOSITION OF α-2-METHOXYCYCLOHEXYLMERCURIC CHLORIDE BY HYDROGEN CHLORIDE (BOTH 1.0×10^{-3} MOLE/LITER) IN ANHYDROUS METHANOL AT 25° WITH ADDED SODIUM CHLORIDE AND MERCURIC CHLORIDE

Reagent added		% Reaction investigated	k, liter mole^{-1} sec.$^{-1}$
Reagent	Mole/liter		
None	—	—	0.64
NaCl	1.0×10^{-3}	72	0.64
NaCl	2.0×10^{-3}	70	0.65
NaCl	3.0×10^{-3}	75	0.66
$HgCl_2$	1.0×10^{-3}	72	0.63
$HgCl_2$	2.0×10^{-3}	70	0.64
$HgCl_2$	3.0×10^{-3}	70	0.66

This result does not support the opinion of Chatt (5), who disagrees with Whitmore's implication that deoxymercuration is dependent on acid strength. Chatt claims that nitric and sulphuric acids do not decompose halogen-free mercurials but this statement is not in accord with fact. For example α-2-methoxycyclohexylmercuric acetate is converted to cyclohexene either by cold nitric or by hot acetic acid (3). However, more definitive evidence is provided by the dependence of deoxymercuration rate upon the basicity of the ether function in the oxymercurial.

This dependence of deoxymercuration rate upon the electron-donating propensity of the ether function is shown in Fig. 2 and listed in Table II. This series of α-2-oxycyclohexylmercuric halides has been treated with hydrogen chloride in near-anhydrous methanol, and then the systems have been analyzed by the colorimetric analytical method (6). This method probably gives high results for the most rapid of these reactions (the deoxymercuration of 2-hydroxycyclohexylmercuric chloride) because of incomplete extraction by chloroform of the hydroxyorganomercurial. This analytical failure, shown in Fig. 2 as a variation in slope of the second-order rate with respect to time, serves in a sense to support the reliability of the other slopes of Fig. 2 and the recorded rate constants of Table II.

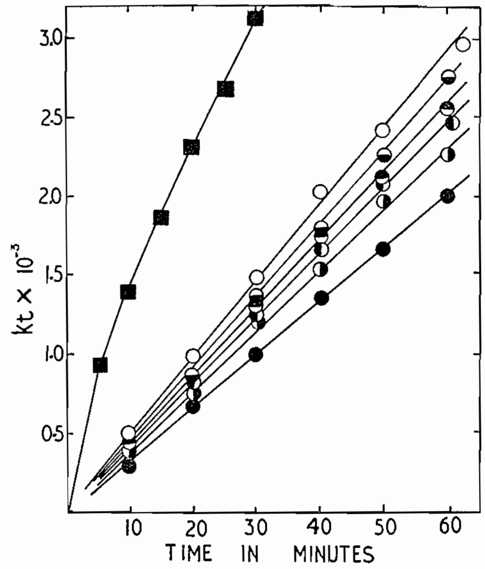


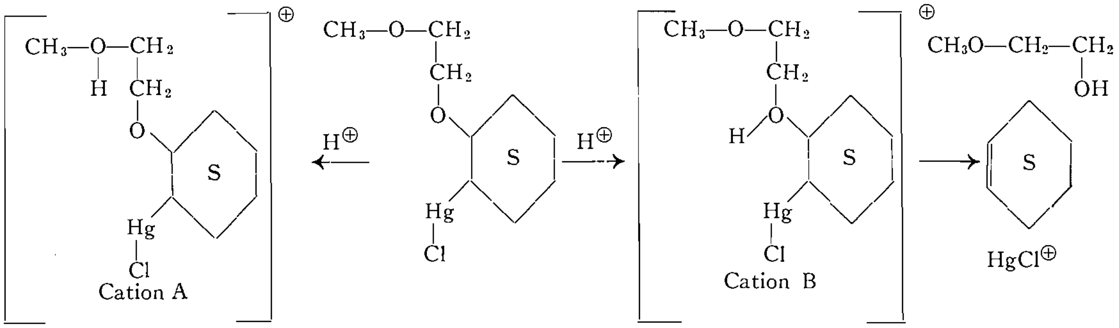
FIG. 2.

TABLE II

DECOMPOSITION OF α-2-ALKOXYCYCLOHEXYLMERCURIC CHLORIDE, $ROC_6H_{10}HgCl$ (1.0×10^{-1} MOLE/LITER), BY HYDROGEN CHLORIDE IN METHANOL AT 25° C.

Symbol, Fig. 2	R	HCl, mole/liter $\times 10^{-3}$	k, liter mole^{-1} sec.$^{-1}$
●	$CH_3O—C_2H_4—$	0.5	0.56
●	$CH_3O—C_2H_4—$	1.0	0.56
●	$CH_3O—C_2H_4—$	2.0	0.54
◑	Me	1.0	0.64
◐	Et	1.0	0.68
◓	Pr	1.0	0.71
◒	iso-Pr	1.0	0.75
○	*t*-Bu	1.0	0.81
■	H	1.0	*ca.* 1.0

The monoethers of Table II are arranged in order of increasing rate constant for the deoxymercuration reaction. But this is the same order of basicity (co-ordinative electron donation) which is characteristic of the parent alcohols corresponding to these alkoxy substituents. In view of this correlation the methoxyethyl analogue (top, Table II) might seem to behave anomalously in its slow deoxymercuration because such vicinal polyethers are known to be strongly co-ordinative. One must presume in this instance that co-ordination of the deoxymercurating agent with the ultimate ether–oxygen (Cation A) is ineffective toward the scission from which the alkene is formed. This diversion of co-ordination may be expressed in Whitmore's terms:



It must be assumed in this formulation of reaction that decomposition of the effective ion (Cation B) is very fast and that the rate is that of co-ordination of hydrogen ion with the oxymercurial. It is obvious that this description of the second-order rate does not depend upon ionic species but could as well involve co-ordination of molecular acid with an oxymercurial. The likelihood of a molecular reaction will be discussed in a forthcoming publication. In the present report the ionic mechanism will be considered in relationship to the acid strength of the decomposing reagent.

Unfortunately there is still insufficient knowledge of acid dissociations in non-aqueous media. However, one may assume that trifluoroacetic acid, which seems to have an acid strength comparable with hydrochloric acid in water, will be about half as strong in near-anhydrous methanol. This assumption is made by reference to the evaluation of acid strength of trifluoroacetic acid in 70% acetone–water (8).

Deoxymercuration occurs when α-2-methoxycyclohexylmercuric trifluoroacetate is prepared from the analogous chloromercurial by treatment with silver trifluoroacetate and then is treated in methanol with trifluoroacetic acid. Kinetic analyses of this reaction, recorded in Table III, show that the initial rate is much slower (compare with Table II) than that observed when the chloromercurial is deoxymercurated by use of hydrogen chloride. Therefore it would appear that the strength of the acid is significant to the rate of deoxymercuration.

TABLE III

DECOMPOSITION OF α-2-METHOXYCYCLOHEXYLMERCURIC TRIFLUOROACETATE BY TRIFLUOROACETIC ACID (BOTH 4×10^{-3} MOLE/LITER) IN METHANOL AT 25° C.

Time, min.	$C_9H_{13}F_3HgO_3$, mole/liter	k, liter mole^{-1} sec.$^{-1}$
0	4.00	—
10	3.68	0.037
20	3.44	0.034
30	3.23	0.033
60	3.08	0.021
90	2.80	0.019
120	2.56	0.012
150	2.62	0.0125

It may be seen in Table III that the rate constant calculated for a unidirectional second-order reaction decays rapidly with respect to time. Indeed the constancy of organomercurial after 120 minutes indicates that an equilibrium has been reached after 35% has been consumed. Confirmation of this equilibrium state is established by treatment of cyclohexene in methanol with mercuric trifluoroacetate. The exact amount of α-2-methoxycyclohexylmercuric trifluoroacetate that is produced in this manner has been found by treatment of the system with aqueous sodium chloride. The chloromercurial isolated in this manner does not exceed a 60 mole per cent yield.

The demonstration of this equilibrium specifies the reaction of mercuric trifluoroacetate with cyclohexene in methanol as intermediate between the virtual non-reactivity of mercuric chloride and the essentially quantitative conversion by methanolic mercuric acetate. These differences conform with the probable differences in acid strength.

It would be easy to conclude from these results that the equilibrium demonstrated for the cyclohexene – mercuric trifluoroacetate – methanol system (and by analogy for all oxymercurations) was the result of a simple reaction like Whitmore's deoxymercuration of β-hydroxyethylmercuric salt in which complete reversibility existed. This conclusion would not be supported by experiment. For example boron fluoride catalyzes oxymercuration but not deoxymercuration (12). Also the oxymercurations now known seem not to be acid catalyzed (9) as we have found deoxymercuration of α-2-methoxycyclohexanemercuric salts to be. In brief these examples show that oxymercuration must be more complex than can be explained as a reversal of Whitmore's deoxymercuration mechanisms.

EXPERIMENTAL*

α-2-Isopropoxycyclohexylmercuric Chloride

To a solution of 3.18 g. (0.01 mole) of mercuric acetate in 30 ml. of propanol-2 was added 0.90 g. (0.011 mole) of cyclohexene. After 3 hours, filtration into 25 ml. of 5% aqueous sodium chloride at 0° C. precipitated 3.05 g. (80%) of the isopropoxymercurial, m.p. 90.5–91.5° C. Crystallization from absolute ethanol (20 ml./g.) raised the melting point to 94.8–95.5° C. Calc. for $C_9H_{17}ClHgO$: C, 28.7; H, 4.52; Hg, 53.2. Found: C, 28.4; H, 4.68; Hg, 52.2.

α-2-Alkoxycyclohexylmercuric Halides Used in Kinetic Studies

These oxymercurials, prepared by standard procedures, were purified to melt as shown in Table IV.

TABLE IV

MELTING POINTS OF 2-ALKOXYCYCLOHEXYLMERCURIC HALIDES, $ROC_6H_{10}HgX$

Diastereomer	R	X	M.p., ° C.	Reference
α	Me	Cl	115.2–116.0	(17)
β	Me	Cl	114.1–114.5	(10)
α	Et	Cl	60.8– 61.5	(3)
α	Pr	Cl	57.5– 58.5	(9)
α	*t*-Bu	Cl	115.0–116.0	(3)
α	$MeOC_2H_4$	Cl	121.5–122.5	(9)
α	H	Cl	153.0–153.6	(3)
α	Me	Br	114.0–114.5	(10)
α	Me	I	81.4– 82.0	(4)

**Melting points have been corrected against reliable standards (16). X-Ray diffraction data have been obtained with* Cu K_α (Ni *filtered) radiation at d spacings in* Å *at visual relative intensities* I/I_1.

Preparation of Mercuric Trifluoroacetate

Mercuric trifluoroacetate was prepared by solution of 10.83 g. (0.05 mole) of mercuric oxide in 10 ml. (0.147 mole) of trifluoroacetic acid. After the initial evolution of heat a further 5-ml. portion of trifluoroacetic acid was added, and the whole was heated on the steam bath until solution was almost complete. The hot suspension was filtered through sintered glass and chilled to 0° C. The white crystals were filtered off and vacuum dried, 10.9 g. (53%), m.p. 164–168° C. with softening at 158° C. The X-ray diffraction pattern was: [20] 10.00; [18] 10.64; [16] 15.49, 13.71; [14] 4.90; [12] 7.82, 4.18; [10] 4.07, 3.40, 3.15; [8] 4.48, 3.53; [6] 5.27, 3.91, 2.98, 2.66, 2.28; [4] 6.91, 3.76, 2.93, 2.36, 2.23, 2.03; [2] 6.44, 5.49, 4.76, 3.33, 2.77, 2.00, 1.96, 1.93; [1] 7.49, 5.71, 2.59, 2.48. Calc. for $Hg(CF_3COO)_2$: Hg, 47.0. Found: Hg, 46.8, 46.7.

Trifluoroacetoxymercuration of Cyclohexene

A solution of 1.07 g. (0.0025 mole) of mercuric trifluoroacetate in 10 ml. of pure methanol was let stand 1 hour, then 0.25 ml. (0.0025 mole) of pure cyclohexene was added. Reaction was terminated by dilution into aqueous sodium chloride. The yield of α-2-methoxycyclohexylmercuric chloride was determined by solution of the precipitate in chloroform and evaporation of this solution under reduced pressure. After a 3-minute reaction time the product weighed 0.38 g. (44%) while a 60-minute reaction time increased this yield to 58%. In both instances the product melted at 114–115° C.; a mixture melting point was not lowered. The yield was not appreciably increased by longer reaction time.

α-2-Methoxycyclohexylmercuric Trifluoroacetate

To a solution of 2.21 g. (0.01 mole) of silver trifluoroacetate (X-ray diffraction: [20] 3.62; [18] 6.41, 6.06; [12] 2.56, 2.32; [10] 3.01, 2.69; [8] 3.32, 2.29; [6] 2.60, 2.51, 2.41; [2] 3.50, 3.15, 2.15; [1] 2.10) in 25 ml. of distilled water was added 3.40 g. (0.0097 mole) of α-2-methoxycyclohexylmercuric chloride; the resulting suspension was agitated at 20° C. for an hour. The precipitated silver chloride was removed by filtration, and washed with water, ethanol, and ether. It weighed 1.43 g. (101%).

The combined filtrates were distilled under reduced pressure, leaving a gummy solid (4.17 g., 97%, m.p. 63–75° C.). This gum was dissolved in warm ethanol (60° C., 2.5 ml./g.) containing 0.3 g. of Norit, then filtered. The filtrate, diluted with 35 ml. of petroleum ether (b.p. 60–70° C.), gave a granular solid upon seeding, wt. 2.58 g., m.p. 73.8–74.8° C. Recrystallization from hot ethanol–petroleum ether (1:9) without seeding gave 1.55 g., m.p. 128–129° C. Solution of 0.1 g. of this compound, m.p. 128° C., in ethanol, followed by dilution with the same petroleum ether (b.p. 60–70° C.) and with addition of the seeds, m.p. 73° C., gave 0.08 g., m.p. 73.8–74.5° C. Calc. for $C_9H_{13}F_3O_3Hg$: Hg, 47.1. Found: Hg, 47.6. Treatment of 0.42 g. (0.001 mole) of this mercurial in ethanolic solution with aqueous sodium chloride gave 0.30 g. (85%) of α-2-methoxycyclohexylmercuric chloride, m.p. 114.2–115.0° C.

Kinetic measurements were made at $25.0° \pm 0.1°$ C. The methanol was purified under nitrogen by Lund and Bjerrum's method (7) and was free from peroxide ($TiCl_3$ test) and aldehyde (Schiff test). Solutions of hydrogen chloride in methanol were prepared from hydrogen chloride which had been dried by passage through sulphuric acid. The trifluoroacetic acid was purified by distillation while the diphenylthiocarbazone (dithizone) was prepared by the method of Winkler (15, 13). The kinetic procedure and apparatus was essentially that reported previously (2, 9).

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