[Contribution from the Department of Chemistry, University of Toronto]

THE KINETICS OF ALKENE OXYMERCURATION

ALAN RODGMAN and GEORGE F WRIGHT

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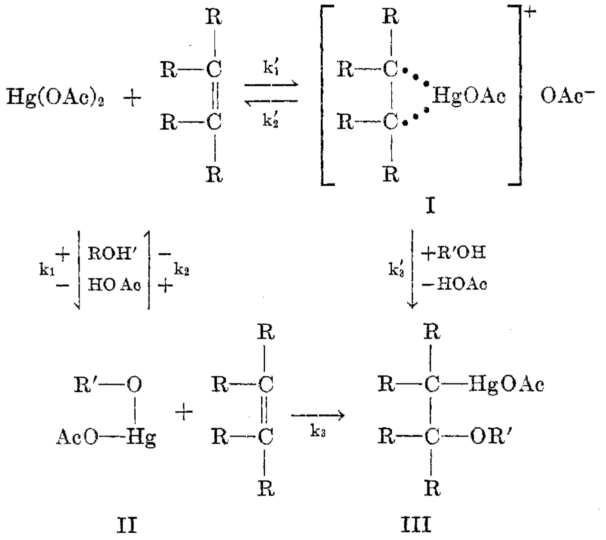
When an alkene is treated with mercuric acetate and an alcohol, the product is that to be expected if the elements of alkoxymercuric acetate were to add to the double bond. When the alkene can exist as *cis* and *trans* forms, each of these geoisomers reacts (*cis* faster than *trans*) to give a characteristic diastereomer uncontaminated with the other (1). Likewise cycloalkenes, where only one geometric isomer is possible, yield only one diastereomeric oxymercurial. The reaction is accelerated by certain peroxides and by boron trifluoride, and is inhibited by electron donors, such as amines, nitriles, and carbonyl compounds. Contrary to an earlier opinion (1) the reactions with mercuric acetate do not arrive at a measurable equilibrium; addition of the other product of the reactions, *i.e.* acetic acid, to the system in which the product is formed does not decompose that product at a rate which can be related to its rate of formation (2). Finally, it is known that mercuric acetate alone will add to some alkenes, but the rate of formation of this alkene-mercuric acetate adduct is so much slower than that of the 2-alkoxyalkylmercuric acetate, that it could not be an intermediate in oxymercuration (3).

Various mechanisms (3–7) have been suggested for the oxymercuration reaction but only two explanations have been detailed sufficiently to merit consideration. These are outlined in Formulation 1.

(1)



Lucas, Hepner, and Winstein (7) consider that the reaction proceeds *via* an "alkenemercurinium" ion (I), while Brook and Wright (3) favor a prior solvolysis of mercuric acetate by the alcohol to give an alkoxymercuric acetate (II), which then adds to the alkene to give the oxymercurial (III).

There are several serious objections to the "alkenemercurinium ion" hypothesis, and these have been outlined in detail by Wright (8). The nonionic mechanism involving coordination of the alkene with alkoxymercuric acetate has been criticized extensively by Chatt (9), but chiefly because of lack of evidence for the existence of the basic salt (II). In the present report we shall present evidence supporting the reality of this species, II.

It has been shown recently (10) that good agreement with observed kinetics is obtained by taking into consideration the acetic acid which is formed during the reaction. Applying this consideration to the reaction wherein the alkene (cyclohexene), mercuric acetate, and the alcohol are separate compounds and assuming the establishment of a steady state for the formation and consumption of alkoxymercuric acetate, one may write for the reactions governed by k_1, k_2, and k_3 (Formulation 1) the following expressions:

$$(2)\quad \frac{d[R'OHgOAc]}{dt} = k_1[Hg(OAc)_2][R'OH] - k_2[R'OHgOAc][HOAc] - k_3[R'OHgOAc][alkene]$$

whence, in the steady state,

$$(3)\quad [R'OHgOAc] = \frac{k_1[Hg(OAc)_2][R'OH]}{k_2[HOAc] + k_3[alkene]}$$

The observed rate may then be expressed

$$(4)\quad \frac{d[oxymercurial]}{dt} = -\frac{d[Hg(OAc)_2]}{dt} = k_3[R'OHgOAc][alkene]$$

$$(5)\quad = \frac{k_1[Hg(OAc)_2][alkene][R'OH]}{\{k_2/k_3\}[HOAc] + [alkene]}$$

In excess of hydroxylated solvent (R'OH), equation 5 becomes

$$(6)\quad \frac{d\,[oxymercurial]}{dt} = \frac{k[Hg(OAc)_2][alkene]}{\{k_2/k_3\}[HOAc] + [alkene]}$$

when k_1 [R'OH] = k.

When the molar quantities of cyclohexene and mercuric acetate are initially equal, the concentration of each may be expressed as "a" at the beginning of the reaction and as "a − x" after a time period *t*. The concentration of acetic acid which is added deliberately is denoted by "b", so that "b + x" is the acetic acid concentration at time *t*. The specific rate constant, k, may then be expressed

$$(7)\quad kt = \frac{k_2}{k_3}(a + b)\left[\frac{1}{a - x} - \frac{1}{a}\right] + \left(1 - \frac{k_2}{k_3}\right)\ln\frac{a}{a - x}.$$

Cyclohexene has been methoxymercurated in a series of experiments wherein acetic acid has been added initially over the concentration range 0 to 2.0×10^{-3} moles per liter.

The analytical method has been described previously (10). The ratio k_2/k_3 has been determined by trial and error to be 2.0 for the methoxymercuration of cyclohexene. It may be seen from Fig. 1 that the plots of kt *vs* t (equation 7) for the several experiments are closely colinear. Essentially the same agreement has been found (Fig. 2) for the ethoxymercuration of cyclohexene where the concentration of additional acetic acid has been varied from 0 to 10 $\times 10^{-3}$ moles per liter. The ratio k_2/k_3 was determined in this instance as 0.9 by the method of trial and error.

We are indebted to Prof. D. J. LeRoy for suggesting to us the method of checking approximately the trial and error values for the ratio k_2/k_3. If a known amount of acetic acid is added to a reaction which is already underway, a comparison may be made of the rate of reaction before and after this event. The following equality is valid if the concentration of acetic acid just before the event is [HOAc] and afterwards is [HOAc]′

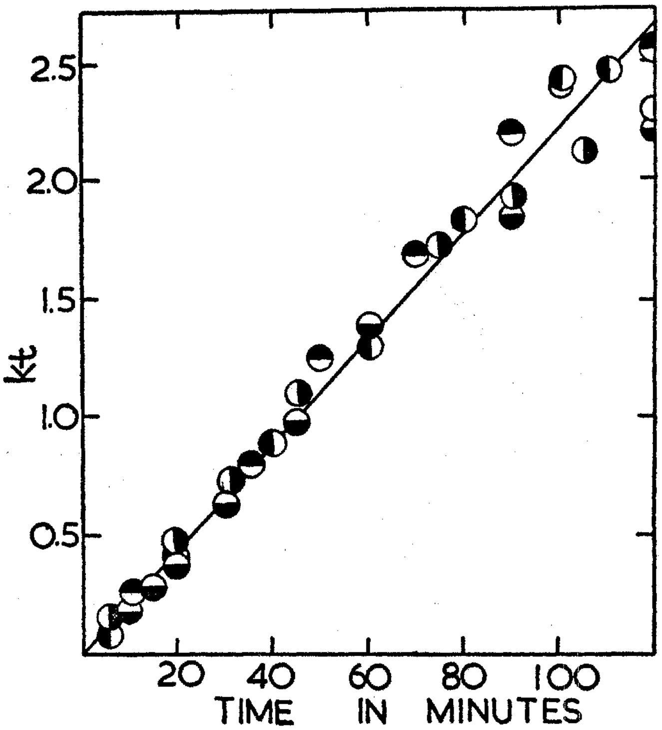


FIG. 1. THE REACTION BETWEEN MERCURIC ACETATE (1.0 $\times 10^{-3}$ Moles/Liter), CYCLOHEXENE (1.0 $\times 10^{-3}$ Moles/Liter), AND METHANOL IN METHANOL WITH ADDED ACETIC ACID AT 25.0 ± 0.1°. Legend: Acetic acid ◒ none; ◓ 0.5 $\times 10^{-3}$ moles/liter; ◑ 1.0 $\times 10^{-3}$ moles/liter; ◐ 2.0 $\times 10^{-3}$ moles/liter.

$$\frac{\left(\dfrac{d\,[\text{oxymercurial}]}{dt}\right)_{[\text{HOAc}]}}{\left(\dfrac{d\ \text{oxymercurial}}{dt}\right)_{[\text{HOAc}]'}} = \frac{\dfrac{k[\text{Hg(OAc)}_2][\text{alkene}]}{\{k_2/k_3\}[\text{HOAc}] + [\text{alkene}]}}{\dfrac{k[\text{Hg(OAc)}_2][\text{alkene}]}{\{k_2/k_3\}[\text{HOAc}]' + [\text{alkene}]}} \tag{8}$$

Since only k_2/k_3 is unknown, then at time t, when acetic acid is added, the comparison gives:

$$\text{Ratio of slopes} = \frac{\{k_2/k_3\}[\mathrm{HOAc}]' + [\mathrm{alkene}]}{\{k_2/k_3\}[\mathrm{HOAc}] + [\mathrm{alkene}]} \tag{9}$$

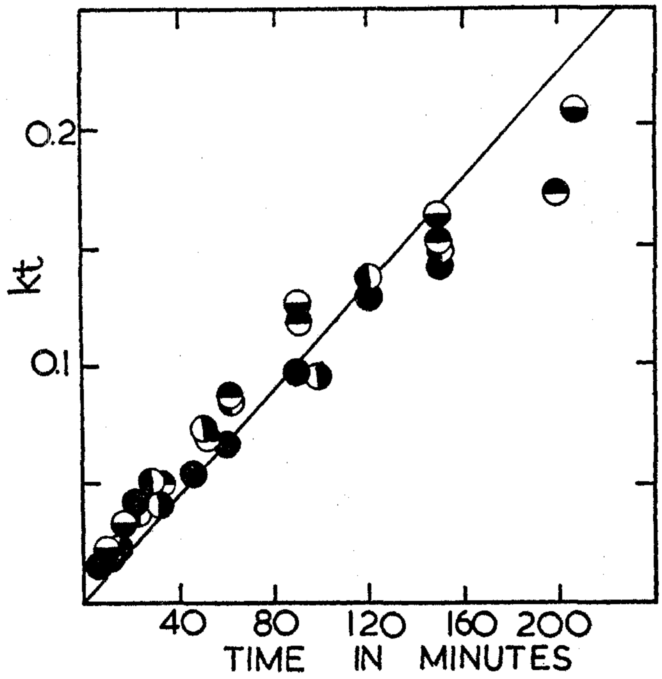


FIG. 2. THE REACTION BETWEEN MERCURIC ACETATE (2.5 × 10^{-3} Moles/Liter), CYCLOHEXENE (2.5 × 10^{-3} Moles/Liter) AND ETHANOL IN ETHANOL WITH ADDED ACETIC ACID AT 25.0 ± 0.1°. Legend: Acetic acid ● none; ◓ 1.25 × 10^{-3} moles/liter; ◐ 2.5 × 10^{-3} moles/liter; ◑ 5.0 × 10^{-3} moles/liter; ◒ 10.0 × 10^{-3} moles/liter.

TABLE I

EXPERIMENTAL DETERMINATION OF RATIO k_2/k_3 AT 25.0 ± 0.1°

RO	$[Hg(OAc)_2]$ = $[C_6H_{10}]$ moles/liter	[HOAc] ADDED		$\frac{dx}{dt}$ [HOAc]	$\frac{dx}{dt}$ [HOAc]′	k_2/k_3
		moles/liter	at t, min.			
CH_3O	0.0010	0.001	25	0.94	0.36	2.15
CH_3O	.0010	.002	12	0.90	0.30	1.78
C_2H_5O	.0025	.0025	10	1.58	0.83	0.90
C_2H_5O	.0025	.005	11	1.00	0.35	0.94

Table I shows such a test of the values of the ratio k_2/k_3 for the methoxymercuration and ethoxymercuration of cyclohexene.

It may be seen that the averages of these values closely approximate to the 2.0 and 0.9 obtained by trial and error.

It has been shown previously (10) that 1,2-dimethoxyethane may be employed as a non-reacting solvent in alkoxymercuration of dimethylheptenol, since the solubility of mercuric acetate (0.01 moles per liter at 25.0°) is well within the concentration limits to which the colorimetric analysis is applicable. The usefulness of this innovation could not at that time be entirely realized since the alcohol function, being intrinsic in the dimethylheptenol, could not be varied for kinetic studies in respect of the alkene. This restriction does not apply to the components, cyclohexene, mercuric acetate, and methanol, ethanol, or water in 1,2-dimethoxyethane. Since the reaction products from the etherous medium are identical with those obtained when the alcohols or water comprise the reaction medium, the rate of their formation in 1,2-dimethoxyethane may be, and now has been studied.

The concentrations of equimolar amounts of cyclohexene and mercuric acetate in 1,2-dimethoxyethane may be designated as "a", initially, and as "a − x" at time t. In the same sense the concentration of the alcohol may be designated as "c" and "c − x". Then from equation 5, the specific rate constant k_1 may be expressed as

$$k_1t = \frac{k_2}{2k_3}a\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right] + \left(1 - \frac{k_2}{k_3}\right)\left[\frac{1}{a-x} - \frac{1}{a}\right] \tag{10}$$

when $a = c$, and

$$k_1t = \frac{k_2a}{k_3(c-a)}\left[\left(\frac{1}{a-x} - \frac{1}{a}\right) - \frac{1}{c-a}\ln\frac{a(c-x)}{c(a-x)}\right] + \frac{(1 - k_2/k_3)}{c-a}\ln\frac{a(c-x)}{c(a-x)} \tag{11}$$

when $a \neq c$. It may be expected that the ratio k_2/k_3 will necessarily be similar to that found when the alcohol rather than 1,2-dimethoxyethane comprises the reaction medium.

When the amount of methanol is varied from 4.0 to 20.0 × 10^{-3} moles per liter in respect of cyclohexene and mercuric acetate (each 4.0 × 10^{-3} moles per liter) in 1,2-dimethoxyethane, the plot of k_1t *vs.* t (Fig. 3) is consistent with equations 10 and 11 when $k_2/k_3 = 2.0$. The same agreement (Fig. 4) is found when the ethanol concentration is varied from 1.0 to 5.0 × 10^{-2} moles per liter in respect of cyclohexene and mercuric acetate (each 1.0 × 10^{-2} moles per liter) in 1,2-dimethoxyethane. The value of 0.9 for k_2/k_3, which was obtained by trial and error in experiments employing ethanol alone as the medium, is also found to be applicable to the experiments in 1,2-dimethoxyethane.

The direct dependence of oxymercuration rate on the concentration of the alcohol may thus be demonstrated experimentally but it does not seem wise to attempt to differentiate the alternative mechanisms of Formulation 1 on this basis. It may be seen (eq. 5) that the rate according to the basic mercuric salt mechanism is directly proportional to the concentration of the alcohol, but this simple dependence is not realized in the rate expression (eq. 12) describing the alkenemercurinium ion mechanism.

$$\frac{d\,[\text{oxymercurial}]}{dt} = \frac{k_1'[\text{Hg(OAc)}_2][\text{alkene}][\text{R'OH}]}{\{k_2'/k_3'\}[\text{OAc}^-] + [\text{R'OH}]} \tag{12}$$

However inspection of equations 5 and 12 shows that the rate should be strongly dependent on the extent to which acetic acid is ionized in the system. Mercuric acetate, a salt of a weak acid and base, is known to solvolyze in hydroxylic media (Formulation 1, k_1/k_2). The addition of acetic acid reduces this solvolysis and would be expected to retard the rate of oxymercuration. On the other hand one might expect that oxymercuration by an ionic mechanism would be accelerated by nominal amounts of acetic acid, which would prevent solvolysis and thus increase the ion population. A series of methoxymercurations of cyclohexene has been carried out with the inclusion of 0.5 to 2 equivalents of acetic acid. When the rates are plotted as simple second-order constants neglecting the acetic acid, it

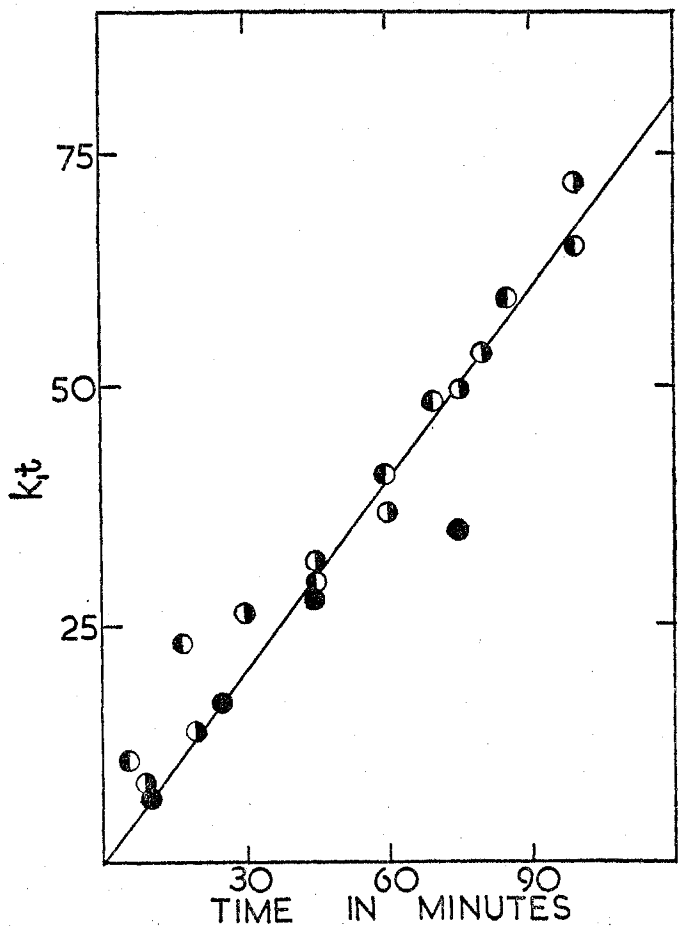


FIG. 3. THE METHOXYMERCURATION OF CYCLOHEXENE (4.0×10^{-3} Moles/Liter) WITH MERCURIC ACETATE (4.0×10^{-3} Moles/Liter) IN 1,2-DIMETHOXYETHANE AT 25.0 ± 0.1°. Legend: Methanol ● 4.0×10^{-3} moles/liter; ◑ 12.0×10^{-3} moles/liter; ◐ 20.0×10^{-3} moles/liter.

may be seen (Fig. 5) that retardation is proportional to the concentration of acetic acid. These results indicate that solvolysis and not ionization is the dominant factor in methoxymercuration.

The introduction of sodium acetate rather than acetic acid to the methoxymercuration system would seem to contradict this opinion. If the reaction were ionic, as shown in Formulation 1, the rate ought to be retarded by addition of acetate ion. On the other hand the rate ought to be little-changed or else slightly accelerated by sodium acetate if the oxymercuration involves the solvolysis product II. It may be seen (Fig. 5) that inclusion of sodium acetate retards the rate slightly more than does acetic acid. However another experiment shows that the retardation by added sodium acetate cannot be interpreted in favor of the

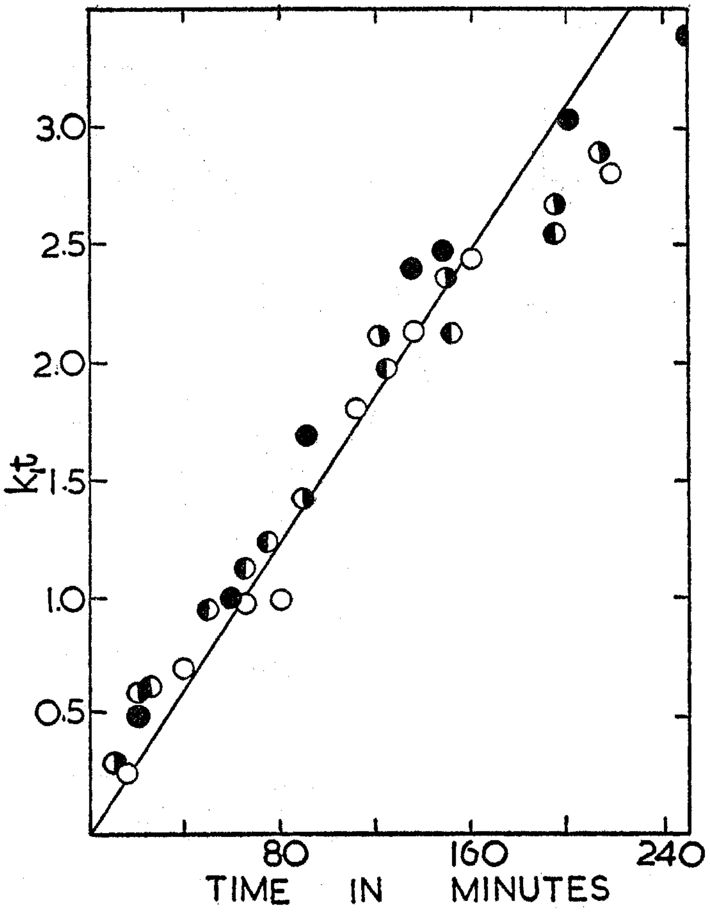


Fig. 4. The Ethoxymercuration of Cyclohexene (1.0×10^{-2} Moles/Liter) with Mercuric Acetate (1.0×10^{-2} Moles/Liter) in 1,2-Dimethoxyethane at 25.0 ± 0.1°. Legend: Ethanol ● 1.0×10^{-2} moles/liter; ○ 1.5×10^{-2} moles/liter; ◐ 3.0×10^{-2} moles/liter; ◑ 5.0×10^{-2} moles/liter.

ionic mechanism. When sodium acetate is added to a suspension of mercuric acetate in an amount of methanol insufficient for solution of the single salt, then both salts are dissolved rapidly and completely. Presumably disodium tetracetoxymercurate is formed, since complete evaporation of a solution which should have this composition leaves a residue showing an x-ray diffraction pattern which is distinctive from that of sodium acetate or mercuric acetate. On the other hand, evaporation of a solution from which monosodium triacetoxymercurate might be formed gives only a non-crystalline gum as residue. Parenthetically it may be inferred that the tetracetoxymercurate ion is not involved in the oxymercuration reaction.

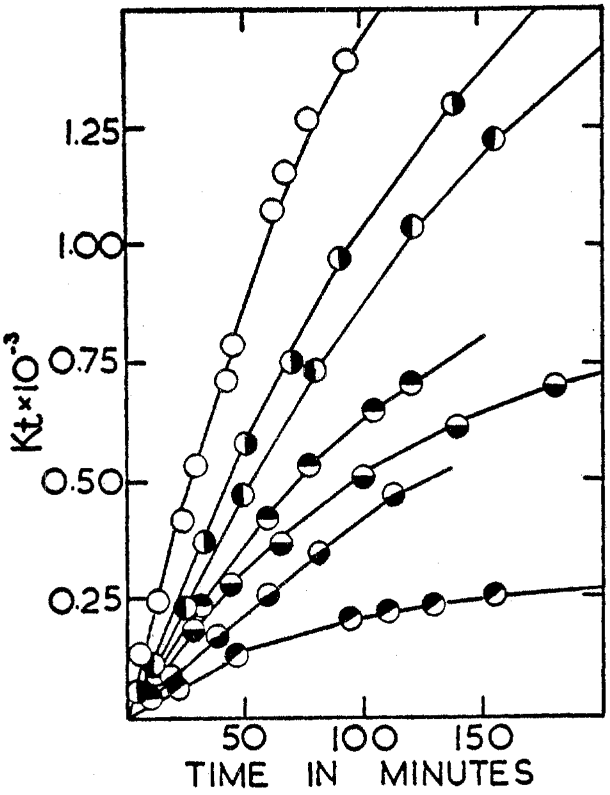


FIG. 5. THE REACTION BETWEEN MERCURIC ACETATE (1.0 × 10^{-3} MOLES/LITER), CYCLOHEXENE (1.0 × 10^{-3} MOLES/LITER) AND METHANOL IN METHANOL WITH ADDED ACETIC ACID OR SODIUM ACETATE AT 25.0 ± 0.1°. Legend: Acetic acid ○ none; ◑ 0.5 × 10^{-3} moles/liter; ◓ 1.0 × 10^{-3} moles/liter; ◔ 2.0 × 10^{-3} moles/liter. Sodium acetate ○ none; ◐ 0.5 × 10^{-3} moles/liter; ◒ 1.0 × 10^{-3} moles/liter; ◕ 2.0 × 10^{-3} moles/liter.

Since the formation of the tetracetoxymercurate ion prevents a test of the mechanism by the addition of acetate ion, we have tried, alternatively to decrease the ion population and to increase solvolysis by depriving the system of acetic acid. According to Formulation 1 this ought to accelerate the reaction if it involves the solvolysis product II, but should decelerate it if an ionic species is involved. The removal of acetic acid has been accomplished by use of methoxyethanol. Since this alcohol has a higher boiling point than that of acetic acid, part of this acid may be removed by vacuum-distillation of a solution of mercuric acetate in the alcohol, so as to shift the equilibrium (eq. 13) toward the right.

(13) $CH_3OCH_2CH_2OH + Hg(OAc)_2 \rightleftharpoons CH_3OCH_2CH_2OHgOAc + HOAc$

According to our analysis of the distillate we have removed as much as 12% of the acetic acid by rapid distillation to complete dryness of a dilute solution. The residue, which is free from peroxide and mercurous acetate, may then be dissolved in 1,2-dimethoxyethane (approx. 0.01 m.p.l. of mercuric salt at 25°)

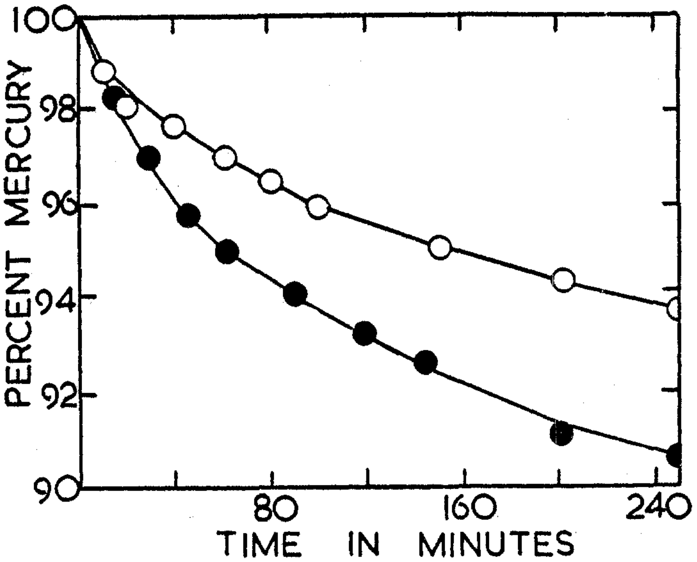


FIG. 6. THE METHOXYETHOXYMERCURATION OF CYCLOHEXENE (1.0×10^{-2} Moles/Liter) WITH MERCURIC ACETATE (1.0×10^{-2} Moles/Liter) IN 1,2-DIMETHOXYETHANE AT 25.0 ± 0.1°. Legend: 2-Methoxyethanol ○ 1.0×10^{-2} moles/liter; ● 3.0×10^{-2} moles/liter.

The formation of 2-methoxyethoxycyclohexylmercuric acetate proceeds as satisfactorily in 1,2-dimethoxyethane containing one equivalent of 2-methoxyethanol as it does in this alcohol alone. The rates of reaction with cyclohexene and methoxyethanol at several concentrations of ordinary mercuric acetate in dimethoxyethane are shown in Fig. 6. In contrast are shown in Fig. 7 the reaction rates when solutions containing 5% (Curve B) and 12% (Curve C) of the basic 2-methoxyethoxymercuric acetate (VI) are treated with equivalent amounts of cyclohexene. It may be seen that these rates are initially faster than those shown in Fig. 6, involving ordinary mercuric acetate at higher concentrations. As would be expected, Curves B and C (Fig. 7) assume the slope of Curve A [cyclohexene and mercuric acetate alone in dimethoxyethane (3)] when approximately 5% and 12% respectively of the total mercury has been consumed. This consumption has been shown to involve the addition of methoxyethoxymercuric acetate (VI) to cyclohexene, since a 58% yield of 2-(2-methoxyethoxy)cyclohexylmercuric chloride (VIII) was isolated from the reaction mixture depicted by Curve C, Fig. 7.

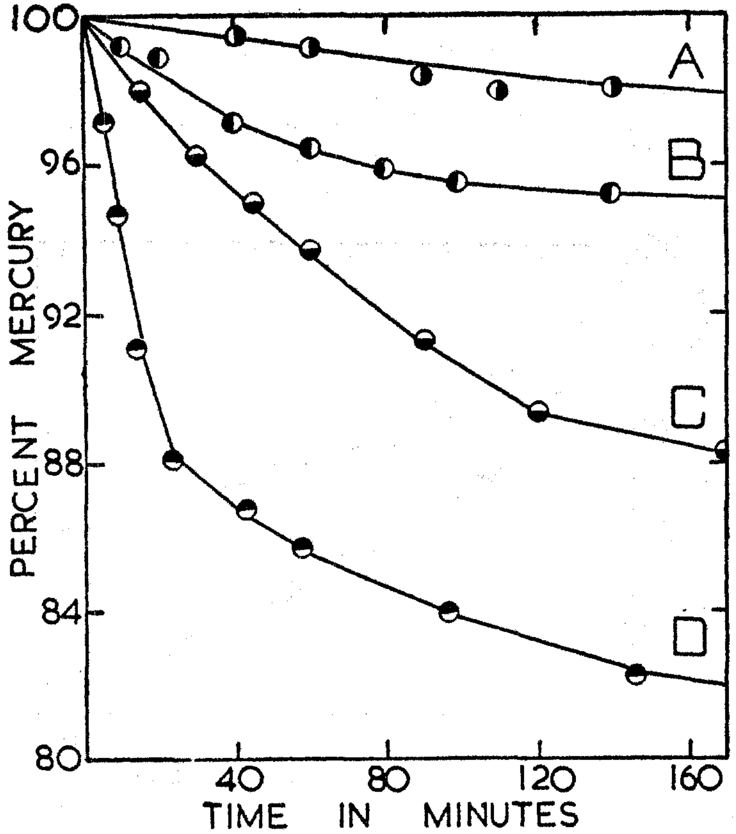
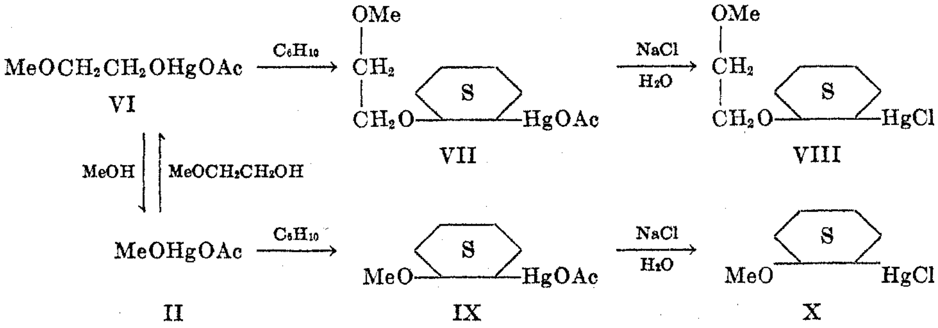


FIG. 7. THE METHOXYETHOXYMERCURATION OF CYCLOHEXENE WITH 2-METHOXYETHOXYMERCURIC ACETATE IN 1,2-DIMETHOXYETHANE AT 25.0 ± 0.1°.
Legend:

SYMBOL	MERCURIC ACETATE Moles/liter	CYCLOHEXENE Moles/liter	2-METHOXYETHOXYMERCURIC ACETATE Moles/liter	METHANOL Moles/liter
◑	1.0×10^{-2}	1.0×10^{-2}	—	—
◐	1.1×10^{-2}	0.59×10^{-3}	0.59×10^{-3}	—
◒	1.1×10^{-2}	1.46×10^{-3}	1.46×10^{-3}	—
◓	1.1×10^{-2}	2.91×10^{-3}	1.46×10^{-3}	1.46×10^{-3}

Thus it seems apparent that oxymercuration proceeds by a mechanism involving solvolysis rather than ionization of the mercuric salt. In order to show that the acceleration of oxymercuration rate is not specific to methoxyethanol, we report an experiment in which methanol is added in molar equivalence with the 12% deficiency of acetic acid to a dimethoxyethane solution such as that used in determining Curve C. When cyclohexene is added in equivalence with the sum of the methoxyethanol and methanol present, the rate of reaction is represented by Curve D, Fig. 7. The initial rate is more rapid than that of a comparable methoxymercuration in which all of the acetic acid contributed by mercuric acetate is present. Subsequently the slope of Curve D resembles the initial portions of Curves B and C. This non-uniform consumption might be expected if the equilibrium VI ⇆ II were attained rapidly, because of the great difference (0.29 *vs.* 0.025) in the rate of formation of methoxy- (IX) *versus* methoxyethoxy- (VII) cyclohexylmercuric acetate. This difference in rate has been demonstrated further by treatment of cyclohexene and mercuric acetate with a 1:1 molar medium comprising methanol and 2-methoxyethanol. Upon completion and treatment with aqueous sodium chloride an 89 % yield of 2-methoxycyclohexylmercuric chloride (X) is obtained.



Since addition of acetic acid retards oxymercuration while removal of it accelerates the reaction we believe that a solvolytic rather than ionic process is involved. Because of the stereospecificity in oxymercuration of geometric isomers it is necessary to assume either a coordination complex such as that of an alkoxymercuric acetate with an alkene, or else a coordinative ion such as the "alkene-mercurinium ion". However reliable evidence for existence of this ion has never been presented (11), and the present experiments indicate that it could not be operative in oxymercuration. On the other hand the present results are in accord with the behavior expected if a basic mercuric salt were to add directly to the alkene. The objections on steric grounds which have been advanced (9) against this latter mechanism may be valid on the basis of existing factual evidence concerning the reaction. However such objections cannot be satisfied by the "alkene-mercurinium ion" hypothesis when it is applied to oxymercurations of substances like stilbene and α-terpineol. Therefore there would seem to be no advantage in further consideration of this "alkenemercurinium ion" hypothesis.

EXPERIMENTAL

Melting points have been corrected against reliable standards. X-ray diffraction patterns were prepared, using CuK_α (Nickel-filtered) radiation, and are expressed as relative intensities $[I/I_1]$ for spacings in Å.

Alkoxymercuration in 1,2-dimethoxyethane. A suspension of 3.18 g. (0.01 mole) of mercuric acetate in 15.0 ml. of 1,2-dimethoxyethane was treated with 0.82 g. (0.01 mole) of cyclohexene and the amount of alcohol shown in Table II. Upon completion of the reaction, the solution was filtered into 50 ml. of 3% aqueous sodium chloride. The chloromercurials were removed by filtration and were crystallized from absolute ethanol.

2-n-Propoxycyclohexylmercuric chloride. To a suspension of 3.18 g. (0.01 mole) of mercuric acetate in 25.0 ml. of anhydrous propanol-1 was added 0.85 g. (0.0105 mole) of cyclohexene. The mixture was agitated at 20–25° for 24 hours but the mercuric acetate had dissolved after 2 hours. Filtration into 60 ml. of 2.5% aqueous sodium chloride gave a semi-solid oil which solidified completely when it was chilled. This solid, filtered off and washed with 15 ml. each of water and absolute ethanol, weighed 2.68 g. (71%), m.p. 56–58°. Recrystallization from absolute ethanol (15 ml. per g.) raised the melting point to 58.5–59.5°.

Anal. Calc'd for $C_9H_{17}ClHgO$: C, 28.7; H, 4.52; Hg, 53.2.
Found: C, 28.6; H, 4.57; Hg, 52.2.

Cyclohexene oxymercuration in 1:1 methanol 2-methoxyethanol. To a solution of 4.77 g. (0.015 mole) of mercuric acetate in 100 ml. of 1:1 methanol and 2-methoxyethanol was added 1.23 g. (0.015 mole) of cyclohexene. After 30 minutes, one-half of the solution was filtered into 100 ml. of 3% aqueous sodium chloride at 0°. The suspension was extracted with chloroform. Evaporation of this solution left a residue (2.67 g.) which was crystallized from hot absolute ethanol, 2.35 g. (90%), m.p. 113.5–114.3°. This was identified as 2-methoxycyclohexylmercuric chloride.

TABLE II

THE ALKOXYMERCURATION OF CYCLOHEXENE

ALCOHOL, R	ROH Moles	ALKOXYMERCURIAL	
		Yield, %	M.P., °C.
CH_3	0.025	80	113.5–114.5
C_2H_5	.022	79	61.0– 61.8
$CH_3OCH_2CH_2$	.025	60	122.4–123.6

2-Methoxyethanol and mercuric acetate. A solution of 2.3902 g. (0.0075 mole) of mercuric acetate in 250 ml. of anhydrous 2-methoxyethanol was prepared under nitrogen and distilled rapidly at 7–17°/0.05 mm. The distillate was received at Dry Ice temperature. The residue was treated repeatedly under nitrogen with seven 250-ml. lots and one 175-ml. lot of 2-methoxyethanol, each of which was distilled in the same way. The distillate was analyzed as follows: A 25.0-ml. aliquot was diluted to 100 ml. with distilled water and titrated with 0.004559 *N* aqueous sodium hydroxide with phenolphthalein as the indicator. The blank was determined as 0.14 ml. of alkali for 100 ml. of an aqueous solution containing 25 ml. of 2-methoxyethanol and this blank was deducted from the titrations to give values as follows:

Distillation Numbers	1	2	3	4	5	6	7	8	9
ml. of Alkali	3.18	2.96	2.71	2.32	2.25	2.14	2.02	1.85	0.81

The total moles of acetic acid is therefore

$$(19.43 \times 10 + 0.81 \times 7)\ 0.004559/1000 = 0.000913$$

or 12.2% as calculated on the amount of mercuric acetate used. The residue, which should thus contain 12% of methoxyethoxymercuric acetate and 88% of mercuric acetate, was kept at 0.05 mm. and 25° for 16 hours prior to use in kinetic experiments in order to ensure complete removal of 2-methoxyethanol. The residue gave a negative peroxide test with titanous chloride and a negative test for mercurous salt with alkali. The distillate tested negatively for aldehydes. Treatment of 1.80 g. of mercuric acetate with four 250-ml. lots of 1,2-dimethoxyethane in the manner described with methoxyethanol gave titration values identical with the blank.

A portion of the distillate (700 ml.) was neutralized with 0.1 *N* sodium hydroxide and then vacuum-distilled to dryness. The residue was dissolved in 2 ml. of 50% sulfuric acid, and this solution was distilled. The distillate (0.5 ml.) was diluted to 1 ml. with water, and then tested with the lanthanum nitrate-iodine reagent (12) and with uranyl formate (13). In both instances a definite test for acetic acid was obtained.

The mixture of 12% of 2-methoxyethoxymerucric acetate and 88% of mercuric acetate (1.0 g.) in 15.0 ml. of 1,2-dimethoxyethane was treated with 0.08 g. of cyclohexene. After 30 minutes, the reaction system was treated with 40 ml. of 4% aqueous sodium chloride. The 2-(2-methoxyethoxy)cyclohexylmercuric chloride weighed 0.13 g. (90%), m.p. 120–122°. This product was crystallized from absolute ethanol (20 ml. per g.), 0.10 g., m.p. 122.2–123°.

Anal. Calc'd for $C_9H_{17}ClHgO_2$: C, 27.5; H, 4.33; Hg, 51.1.
Found: C, 27.4; H, 4.40; Hg, 50.5.

Kinetic measurements. The analytical procedure for the determination of mercury with dithizone was the same as that reported previously (10). All measurements were carried out at 25.0 ± 0.1°. The alcohols were purified under a nitrogen atmosphere by the method of Lund and Bjerrum (14). These alcohols were peroxide-free (titanous chloride) and also aldehyde-free (2,4-dinitrophenylhydrazine reagent and Schiff's reagent). The 1,2-dimethoxyethane, purified by refluxing and distillation from sodium under nitrogen, was anhydrous and peroxide-free according to tests with benzophenone and sodium. The mercuric acetate was vacuum-dried after crystallization from acetic acid. It was completely soluble in the alcohols and in 1,2-dimethoxyethane. The cyclohexene was peroxide-free according to tests with potassium iodide and titanous chloride.

The kinetic studies with the mixture of 12% of 2-methoxyethoxymercuric acetate and 88% of mercuric acetate required a modified procedure. A sample of the mixture (approximately 0.10 g.) was transferred rapidly to a tared 10.0-ml. volumetric flask and its weight was determined accurately. A solution of 10 ml. with 1,2-dimethoxyethane was then prepared. One ml. of this solution, diluted to 20 ml. with 1,2-dimethoxyethane, was used in the kinetic experiments. An equivalent amount of peroxide-free cyclohexene, based on the amount of 2-methoxyethoxymercuric acetate, was added from a standard solution in 1,2-dimethoxyethane, and the final volume was quickly adjusted to 25.0 ml. with 1,2-dimethoxyethane.

Sodium acetate and mercuric acetate. When 1.0 g. (0.00315 mole) of mercuric acetate was suspended in 5.0 ml. of anhydrous methanol and agitated for 30 minutes, only two-thirds of the salt dissolved. The amount of solution occurred within 5 minutes. Addition of 0.52 g. (0.0063 mole) of anhydrous sodium acetate caused complete solution of the remaining mercuric acetate within 10 seconds. Evaporation of the solvent gave a colorless, crystalline solid. This material appeared homogeneous upon microscopic crystallization. In the absence of a satisfactory melting point it was characterized by its x-ray diffraction pattern: [10] 8.57, 8.42; [8] 12.27, 9.93; [4] 5.15, 4.69, 3.28, 1.98; [3] 3.60, 3.10, 2.90, 2.71; [2] 6.91, 6.41, 6.19; [1] 7.76, 6.06 5.87, 4.77, 4.29, 4.19, 4.02, 3.80, 3.55, 3.36, 3.17, 3.03, 2.92, 2.79, 2.67, 2.59, 2.54, 2.51, 2.49, 2.39, 2.31, 2.29, 2.25, 2.20, 2.19, 2.15, 2.12, 2.05, 1.87, 1.81, 1.76, 1.72; [0.5] 4.01.

The diffraction pattern of anhydrous sodium acetate was also determined; [10] 4.13; [7] 3.88; [6] 3.70, 2.97; [5] 3.55, 3.37, 3.25, 2.86; [4] 9.01, 2.62; [3] 5.12, 4.52, 2.48, 2.05, 1.92, 1.75; [2] 4.84, 2.75, 2.11, 1.64; [1] 2.16, 1.85.

Finally in order to show dissimilarity, the diffraction pattern of mercuric acetate was determined: [10] 5.68, 2.95; [9] 3.66; [8] 4.29, 4.06, 3.40; [7] 2.17, 2.01; [6] 3.20; [5] 9.40; [4] 2.36, 1.84, 1.78; [3] 1.87, 1.73, 1.47; [2] 2.74, 2.54, 1.57, 1.40; [1] 1.63, 1.35, 1.30.

Variation in cyclohexene-mercuric acetate ratio in methanol. When the concentration of mercuric acetate in methanol was varied from 1.0 to 2.0 × 10^{-3} moles per liter with respect to that of cyclohexene (1.0 × 10^{-3} m.p.l.) the initial rate of methoxymercuration was almost directly proportional to the mercuric salt concentration, thus eliminating the possibility that intermediate formation of mercuri-*bis*-2-methoxycyclohexane is involved.

Acceleration of cyclohexene oxymercuration by benzoyl peroxide. When equivalent amounts (1.0×10^{-3} m.p.l.) of cyclohexene and mercuric acetate in methanol were included with 0.05 to 0.50×10^{-3} m.p.l. of benzoyl peroxide at 25.0 ± 0.1°, the initial rate was dependent on the amount of this catalyst. After 100 minutes the rate decayed until it was slightly slower than that of the uncatalyzed reaction, as might be expected since mercurous salt was precipitated. Essentially the same initial acceleration with subsequent decay of rate was observed with the otherwise comparable ethoxymercuration.

Oxymercuration rates in several alcohols. The initial rates of oxymercuration of cyclohexene have been determined in propanol-1 and in methoxyethanol. In Table III these are compared with the observed rates in methanol and ethanol, and with the approximate rate in water (3). The three alkanols behave in direct dependence with their dielectric constants, but methoxyethanol and water are anomalous in this respect.

TABLE III

COMPARISON OF DIELECTRIC CONSTANTS WITH INITIAL RATES OF OXYMERCURATION OF CYCLOHEXENE AT 25°

MEDIUM	DIELECTRIC CONSTANT	CONC'N OF MERCURIC ACETATE AND OF CYCLOHEXENE moles/liter	INITIAL RATE liters moles^{-1} sec^{-1}	REF.
Water	83.2	0.025	$0.29 > k > 0.022$	(15)
Methanol	31.5	.001	.29	(16)
2-Methoxyethanol	15.95	.0025	.025	(15)
Ethanol	24.3	.0025	.022	(16)
Propanol-1	20.1	.004	.004	(16)

SUMMARY

1. Kinetic studies on the methoxymercuration of cyclohexene have taken into account the retarding effect of acetic acid. This retardation over a range of concentrations is not compatible with that expected if an "alkenemercurinium ion" were formed from mercuric acetate, a salt of a weak acid and base, and the alkene.

2. Kinetic studies on the methoxyethoxymercuration of cyclohexene show that the reaction is accelerated by removal of acetic acid. This removal should cause formation of the alkoxymercuric acetate which has been postulated as the intermediate according to the nonionic coordination mechanism of oxymercuration.

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