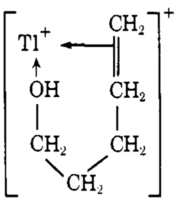
It was confirmed that the role of the 1-penten-5-ol in the dethallation reaction was truly catalytic since the ratio of overall consumption of 1-penten-5-ol in the reaction to the initial Tl^{3+} concentration was always close to 1:1. It was also established that the catalytic effect in question is not exhibited by alcohols in general. Thus, addition of *saturated* alcohols such as methanol or 1-butanol, in concentrations of up to 1 *M*, did not result in significant rate enhancement of the dethallation step. The most probable explanation of the catalytic influence of 1-penten-5-ol is considered to be enhancement of the driving force for reaction 8 due to stabilization of the Tl^+ product ion (relative to the organothallium(III) precursor) by coordination. The tendency for such coordination is presumably enhanced through chelation of the type depicted by **6**, an effect which undoubtedly also contributes to the known exceptionally great stability of the 1-penten-5-ol complex of Ag^+.[16] Direct indications of weak complex formation between Tl^+ and unsaturated alcohols were also provided in separate experiments by the spectral changes (reduction in the absorbance of Tl^+ at 212 nm) that were found to accompany the addition of 1-penten-5-ol (*ca.* 0.3 *M*) to aqueous solutions of Tl^+.[17] Also in accord with this interpretation was our finding that catalysis of the dethallation step by excess substrate was observed only in the case of the alkenols and not in the oxidations of simple olefins such as propylene and isobutene (for which the dethallation step could also be observed) which are expected to be much less effective in stabilizing Tl^+ through coordination.



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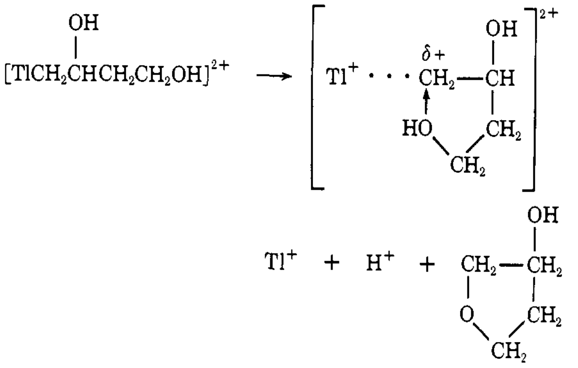
Failure to observe the dethallation step for the class A substrates, *i.e.*, 1-buten-4-ol and 1-penten-4-ol, can reasonably be attributed to enhancement of the rates of dethallation in these cases by neighboring group participation of the type depicted in eq 11. Direct support for this is also provided by the distinctive products of these reactions, *i.e.*, 3-hydroxytetrahydrofuran and 2-methyl-4-hydroxytetrahydrofuran.



(11)

Acknowledgment. Support of this research through grants from the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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[16] C. D. M. Beverwijk, G. J. M. Van der Kerk, A. J. Leusink, and J. G. Noltes, *Organometal. Chem. Rev. Sect. A*, **5**, 215 (1970).

[17] P. Abley and J. Halpern, unpublished results.

Hydroxymercuration and Thallium(III) Oxidation of Cycloalkenes and Methylenecycloalkanes

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Contribution from the Department of Chemistry, The University of Chicago, Chicago, Illinois 60637. *Received August 24, 1972*

Abstract: The kinetics of hydroxymercuration of a series of cycloalkene, 1-methylcycloalkene, and methylenecycloalkane compounds, as well as of their oxidations by thallium(III), were determined in aqueus perchloric acid solution. The rate law for each reaction was similar to that found previously for other olefinic compounds, *i.e.*, $-d[\text{alkene}]/dt = k[M^{n+}][\text{alkene}]$, where $M^{n+} = Hg^{2+}$ or Tl^{3+}. Oxidation by thallium(III) yielded only two products in each case, namely the 1,2-diol and one carbonyl compound (aldehyde or ketone). The carbonyl products of the oxidation of the cyclolakenes were typically ring-contracted aldehydes; of the 1-methylcycloalkenes, ring-contracted ketones; and of the methylenecycloalkanes, ring-expanded cyclo ketones. The nature of the oxidation products, as well as the similarity of rates for the hydroxymercuration and oxidation reactions, provide additional support for an oxidation mechanism involving an oxythallation–dethallation sequence, *i.e.*, $Tl^{3+} + {>}C{=}C{<} + H_2O \rightarrow Tl{>}C{-}C{<}OH^{2+} + H^+$, followed by $Tl{>}C{-}C{<}OH^{2+} \rightarrow Tl^+ +$ oxidation products.

The present paper describes extensions of earlier investigations on the hydroxymercuration[1] and on the thallium(III) oxidation[2-4] of olefinic compounds in aqueous solutions to several additional series of such compounds, namely cycloalkenes, 1-methylcycloal-

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[1] J. Halpern and H. B. Tinker, *J. Amer. Chem. Soc.*, **89**, 6427 (1967).

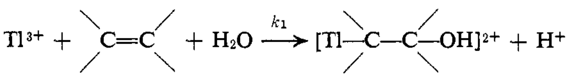
[2] P. M. Henry, *ibid.*, **87**, 990, 4423 (1965); **88**, 1597 (1966).

[3] P. M. Henry, *Advan. Chem. Ser.*, No. **70**, 126 (1968).

[4] J. E. Byrd and J. Halpern, *J. Amer. Chem. Soc.*, **95**, 2586 (1973).

kenes, and methylenecycloalkanes. The objective of these studies was to gain additional insight into the mechanisms and reactivity patterns of these reactions by determining (i) the dependence of the rate of each reaction on the ring size and (ii) the characteristic products of the thallium(III) oxidation reactions. The only earlier studies on the oxidations of *cyclic* olefins by thallium(III) of which we are aware, and which bear directly on the results reported here, are those on the oxidation of cyclohexene by thallium(III) acetate in acetic acid[5,6] and of cyclohexene and cycloheptene by thallium(III) nitrate in methanol.[7] Our own results on the oxidation of 1-methylcyclobutene have also been the subject of a preliminary communication.[8]

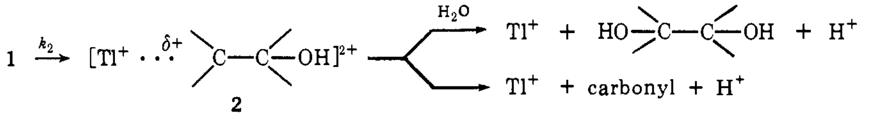
Earlier observations on the oxidation of olefinic compounds in aqueous solution by thallium(III) have generally been interpreted in terms of mechanisms involving the formation of a hydroxythallation adduct (**1**) according to eq 1, followed by dethallation of the



$$Tl^{3+} + \;>C=C<\; + H_2O \xrightarrow{k_1} [Tl-\overset{|}{C}-\overset{|}{C}-OH]^{2+} + H^+ \qquad (1)$$

1

latter (eq 2) to yield an incipient carbonium ion intermediate from which the final oxidation products are derived.[2-8] The nature of the carbonyl product depends upon the parent olefin in accord with the predictions of such a mechanism.

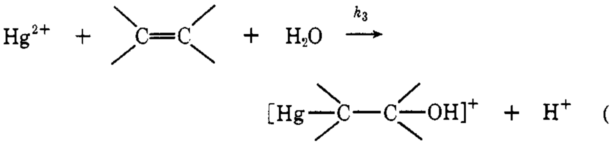


$$1 \xrightarrow{k_2} [Tl^+\cdots\overset{\delta+}{C}-C-OH]^{2+} \xrightarrow{H_2O} Tl^+ + HO-C-C-OH + H^+ \qquad (2a)$$

$$\longrightarrow Tl^+ + \text{carbonyl} + H^+ \qquad (2b)$$

2

Hydroxymercuration reactions have generally been found to follow the simple course depicted by eq 3, to



$$Hg^{2+} + \;>C=C<\; + H_2O \xrightarrow{k_3} [Hg-C-C-OH]^+ + H^+ \qquad (3)$$

3

form β-hydroxyorganomercurials in quantitative yields.[1]

The observations and interpretations encompassed by eq 1-3, when adapted to the distinctive features of the particular substrates which were investigated, also proved to be generally applicable to the results described in this paper.

Experimental Section

Materials. The gaseous alkenes (isobutene and *cis*-2-butene) were Matheson CP grade and were free of impurities detectable by glc (20-ft β,β'-oxydipropionitrile on 60-80 mesh Chromosorb P column). The following alkenes were obtained from Aldrich Chemical Co. (cyclopentene, cyclohexene, cycloheptene, 1-methylcyclopentene, 1-methylcyclohexene, 1-methylcycloheptene, and 2-methyl-2-butene) or from Chemical Samples Co. (methylenecyclobutane, methylenecyclopentane, and methylenecyclohexane). Their purity was confirmed both by nmr analysis and glc, neither of which revealed any detectable impurities. Cyclobutene was prepared by the method of Heisig[9,10] and purified by distillation, bp 0-2° (lit.[9] −1 to −3°). 1-Methylcyclobutene was prepared by the isomerization of methylenecyclobutane[11] and redistilled, bp 41° (lit.[11] 41.3°).

The preparation and standarization of aqueous solutions of mercury(II) perchlorate and thallium(III) perchlorate have previously been described.[1,4]

Stoichiometry and Products. The stoichiometries of both the hydroxymercuration and oxidation reactions (*i.e.*, the molar ratios of alkene and Hg^{2+} *or* Tl^{3+} that reacted with each other) were determined by spectral titration as described earlier.[1]

For purposes of identification and characterization of the products, a known amount of the alkene was shaken with a 1 *M* $Tl(ClO_4)_3$ or 1 *M* $Hg(ClO_4)_2$ aqueous 0.5-1 *M* $HClO_4$ solution containing an equivalent amount (or slight excess) of the metal ion. The reaction was allowed to proceed to completion, and a relatively concentrated aqueous solution of the product thereby obtained. The organomercurial product ions of the hydroxymercuration reactions were readily identified and their yields quantitatively determined by nmr spectroscopy, using methanol or *tert*-butyl alcohol as an internal standard.

The thallium(III) oxidation reactions typically yielded two products, a 1,2-diol and an aldehyde or ketone. The two products were separated by extracting the product solution (after removing the precipitated $TlClO_4$ by filtration) twice with CCl_4, the carbonyl product being extracted into the organic phase and the diol remaining in the aqueous phase. Each product was then identified and its yield determined by nmr spectroscopy using methanol or *tert*-butyl alcohol as internal standards. The identification and determination of most of the carbonyl products were confirmed by glc (4 ft × 1/8 in. 10% 20M on 60-80 Chromosorb P column).

Kinetic Measurements. The procedures used for the kinetic measurements were identical with those described in our earlier studies on hydroxymercuration[1] and thallium(III) oxidation[4] reactions. Rates of reactions with half-lives shorter than about 5 sec were measured with a Durrum-Gibson stopped-flow spectrophotometer and those of slower reactions with a Cary 14 spectrophotometer. All kinetic measurements were performed at 25.0 ± 0.2° in solutions containing 0.10 *M* $HClO_4$ (μ = 0.1 *M*), *i.e.*, the same conditions as employed in our earlier kinetic measurements,[1,4] thus making all our kinetic data directly comparable.

Results and Discussion

Reaction Stoichiometries. The results of representative spectral titrations on each class of reactions are depicted in Figure 1. As in all previous studies on the hydroxymercuration[1] and thallium(III) oxidations[2-4] of olefinic compounds in aqueous solutions, and in accord with the stoichiometries represented by eq 1-3, such titrations yielded end points close to $[M^{n+}]:[\text{alkene}] = 1:1$ ($M^{n+} = Hg^{2+}$ or Tl^{3+}). The 1:1 stoichiometries of the reactions were also confirmed by the product yield determinations to be reported subsequently.

Products of Hydroxymercuration. In agreement with the results of numerous earlier studies on other olefinic compounds,[1,12] and in accord with the stoichiometry depicted by eq 3, nmr characterization of the product solutions confirmed the formation in each case, in virtually quantitative yield, of the β-hydroxymercurial product of 1,2-trans addition to the C=C bond. Representative products for the three classes of substrates examined, *i.e.*, cyclohexene,[13] 1-methylcyclohexene, and

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(5) C. B. Anderson and S. Winstein, *J. Org. Chem.*, **28**, 605 (1963).

(6) J. B. Lee and M. J. Price, *Tetrahedron*, **20**, 1017 (1964).

(7) A. McKillop, J. D. Hunt, E. C. Taylor, and F. Kienzle, *Tetrahedron Lett.*, 5275 (1970).

(8) J. E. Byrd, L. Cassar, P. E. Eaton, and J. Halpern, *Chem. Commun.*, 40 (1971).

(9) G. B. Heisig, *J. Amer. Chem. Soc.*, **63**, 1698 (1941).

(10) J. L. Ripall and J. M. Conice, *Bull. Soc. Chim. Fr.*, 2755 (1965).

(11) J. Shabtai and E. Gil-Av, *J. Org. Chem.*, **28**, 2893 (1963).

(12) W. Kitching, *Organometal. Chem. Rev.*, **3**, 61 (1968).

(13) The product and yield for the hydroxymercuration of cyclohexene under these conditions have previously been reported.[1]

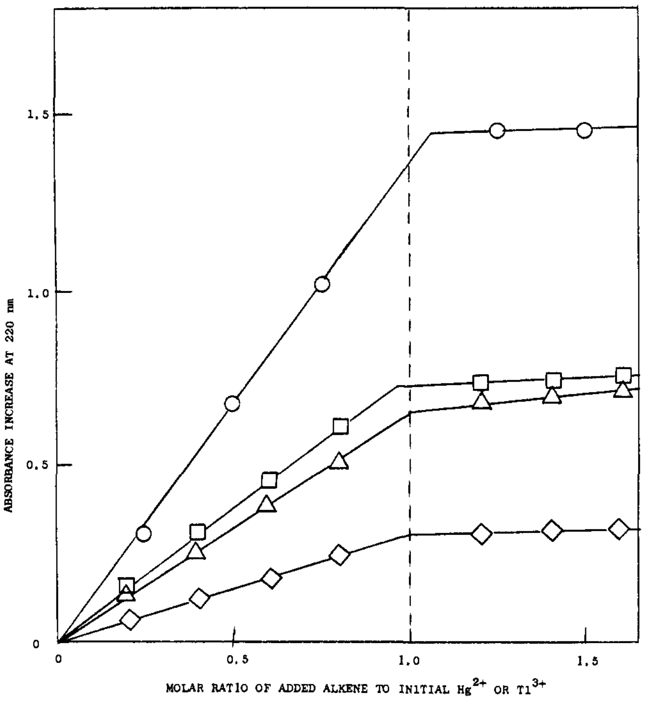
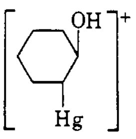


Figure 1. Spectral titrations at 220 nm (1-cm path length): ○, 2.0×10^{-4} M Hg^{2+} with methylenecyclobutane; △, 1.0×10^{-4} M Hg^{2+} with 1-methylcycloheptene; □, 4.2×10^{-4} M Tl^{3+} with methylenecyclohexane; ◇, 1.6×10^{-4} M Tl^{3+} with cyclohexene.

methylenecyclohexane, are depicted by **4**, **5**, and **6**, respectively.



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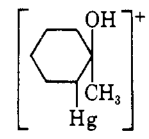

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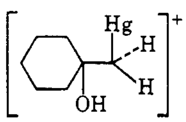

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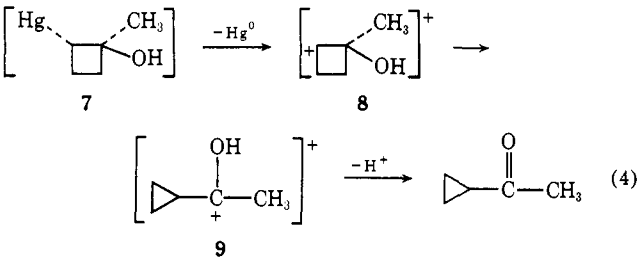
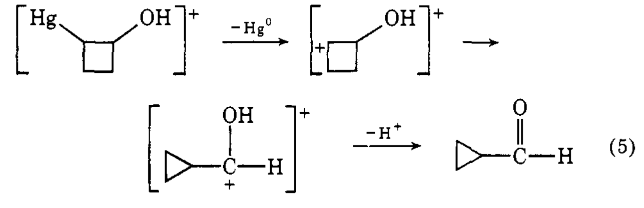
With one notable exception previously described,[8] the hydroxymercurial product ions appeared to be indefinitely stable in solution following the reactions. The exception was the hydroxymercuration product (**7**) of 1-methylcyclobutene. This ion was stable for about 1 hr in the typical reaction medium, *i.e.*, 0.1 M HClO$_4$, but on prolonged standing underwent decomposition, presumably through the sequence of steps depicted by eq 4 (which parallels the corresponding oxidation of the same alkene by Tl^{3+}) to form cyclopropyl methyl ketone in essentially quantitative yield.



The driving force for this reaction, which apparently is sufficient to induce heterolysis of the mercury–carbon bond despite the inefficiency of Hg^0 as a leaving group, is presumably the well-known[14] stabilization of the resulting incipient cyclobutyl carbonium ion by rearrangement to the cyclopropylcarbinyl ion (**9**). The latter is further stabilized in this case by the methyl and hydroxyl substituents. In more strongly acid solution ($\geqslant$ 1 M HClO$_4$) the decomposition of **7**, in accord with eq 4, was virtually instantaneous, and when Hg^{2+} was allowed to react with 1-methylcyclobutene under these conditions, the intermediate formation of the oxymercuration adduct (**7**) in the overall oxidation to cyclopropyl methyl ketone could no longer be detected. The hydroxymercuration adduct of cyclobutene itself was considerably more stable, although decomposition to cyclopropanecarboxaldehyde, presumably in accord with eq 5, was still observed to occur slowly, especially in strongly acidic solutions. The driving force for heterolysis of the mercury–carbon bond in this case is presumably lower by virtue of the absence of methyl stabilization of the cyclopropylcarbinyl ion. No evidence of similar instability was detected for the hydroxymercuration adducts of the higher cycloalkenes and 1-methylcycloalkenes, nor for any of the methylenecycloalkanes.



Products of Oxidation by Thallium(III). For each alkene only two products of oxidation could be detected, the combined yields of which were always virtually quantitative. The two products were (i) the 1,2-diol and (ii) *a single* carbonyl product (aldehyde or ketone), the nature of which depended upon the alkene. Tables I, II, and III list the carbonyl products together with the yields of both oxidation products, for the three classes of substrates examined, *i.e.*, cycloalkenes, 1-methylcycloalkenes, and methylenecycloalkanes. In each case, a representative *acyclic* compound (*i.e.*, *cis*-2-butene, 2-methyl-2-butene, and isobutene, respectively) is included for comparison.

The products of reaction can all be readily rationalized in terms of the general mechanistic scheme depicted by eq 1–2, comprising an oxythallation step followed by dethallation through heterolysis of the thallium–carbon bond. Since Tl$^+$ is a much better leaving group than Hg^0, such heterolysis is strongly favored for the oxythallation adducts, compared with the corresponding oxymercurials.

The carbonyl products of oxidation of the cycloalkenes and 1-methylcycloalkenes are, typically, ring-contracted aldehydes and ketones. These parallel the corresponding products of oxidation of cyclobutene and 1-methylcyclobutene by mercury(II), and presumably arise through similar mechanisms, for example, those depicted by eq 6 and 7, respectively. The formation of ring-contracted carbonyl products has previously been reported also for the oxidations of certain cycloalkenes by thallium(III) acetate in acetic acid[5,6] and by thallium(III) nitrate in methanol.[7]

The notable exception to this pattern is cyclopentene whose oxidation yields cyclopentanone instead of cyclobutanecarboxaldehyde. In this case, ring contraction is apparently opposed by the introduction of sufficient

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(14) M. S. Silver, M. C. Caserio, H. E. Rice, and J. D. Roberts, *J. Amer. Chem. Soc.*, 83, 3671 (1961).

Table I. Results for Cycloalkenes

Alkene	Carbonyl product	Product yields, %[a]		Rate constants, M^{-1} sec^{-1}	
		Carbonyl	1,2-Diol	k_1	k_3
cis-2-Butene	$CH_3COCH_2CH_3$	(65–80)[b]	(<0.5)[b]	11.7	5.8×10^3 [c]
Cyclobutene	Cyclopropanecarboxaldehyde	75–85[d]	*e*	3.1	3.5×10^3
Cyclopentene	Cyclopentanone	21–27	72–75	6.0	3.8×10^3
Cyclohexene	Cyclopentanecarboxaldehyde	85–87	10–11	7.1	5.0×10^3 [c]
Cycloheptene	Cyclohexanecarboxaldehyde	81–83	9–11	1.0	0.9×10^3

[a] Range of yields reported for each compound are actual results of duplicate determinations. [b] Data from ref 3. [c] Data from ref 1. [d] Low yield in this case believed to reflect losses due to volatility of compound. [e] Not detected.

Table II. Results for 1-Methylcycloalkenes

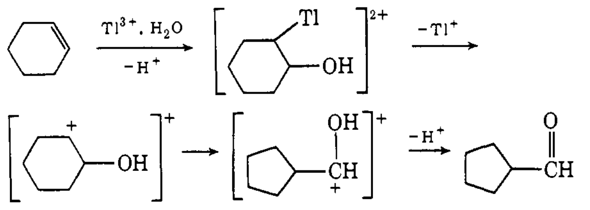
Alkene	$RCOCH_3$ product R =	Product yields, %[a]		Rate constants, M^{-1} sec^{-1}	
		Carbonyl	1,2-Diol	k_1	k_3
2-Methyl-2-butene	Isopropyl	80	20	29	1.9×10^4
1-Methylcyclobutene	Cyclopropyl	88–92	*b*	68	4.2×10^4
1-Methylcyclopentene	Cyclobutyl	16–24	76–79	44	2.1×10^4
1-Methylcyclohexene	Cyclopentyl	41–47	52–56	15	1.9×10^4
1-Methylcycloheptene	Cyclohexyl	86–92	5–10	5	3.7×10^3

[a] Range of yields reported for each compound are actual results of duplicate determinations. [b] Not detected.

Table III. Results for Methylenecycloalkanes

Alkene	Carbonyl product	Product yields, %[a]		Rate constants, M^{-1} sec^{-1}	
		Carbonyl	1,2-Diol	k_1	k_3
Isobutene	Isobutyraldehyde	(35–45)[b]	(55–65)[b]	6.3×10^3	$>10^6$ [c]
Methylenecyclobutane	Cyclopentanone	77–81	15–18	1.4×10^3	$>2 \times 10^6$ [c]
Methylenecyclopentane	Cyclohexanone	78–82	10–20	2.4×10^4	$>2 \times 10^6$ [c]
Methylenecyclohexane	Cycloheptanone	30–34	63–71	8.3×10^3	*Ca.* 10^6

[a] Ranges of yields reported for each compound are actual results of duplicate determinations. [b] Data from ref 3. [c] Too fast to measure; lower limits based on assumption that half-life is shorter than mixing time of stopped-flow experiment, *i.e.*, *ca.* 2 msec.



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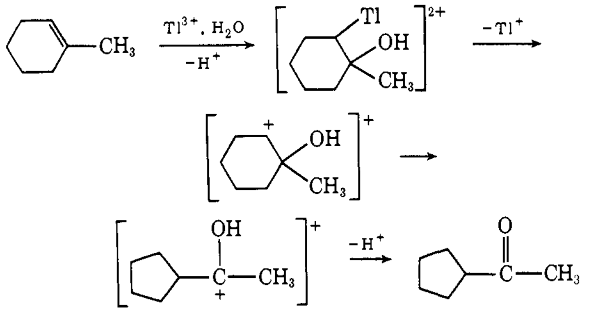
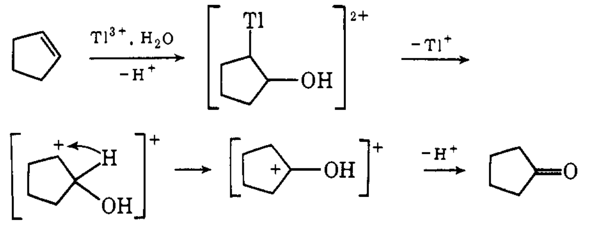


(7)

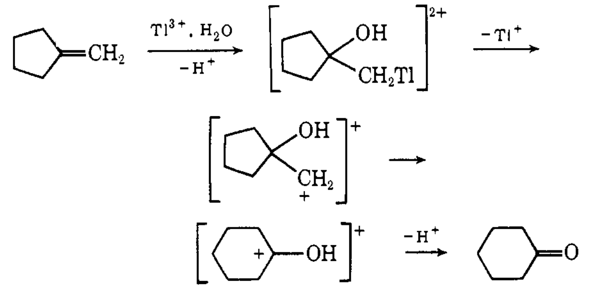
strain in going from a five- to a four-membered ring, so that an alternative mode of carbonium ion stabilization, namely a 1,2-hydride shift according to eq 8, becomes more favorable. This also corresponds to the predominant mode of formation of carbonyl products in the oxidation of acyclic alkenes (for example *cis*-2-butene to methyl ethyl ketone).[2]



(8)

In contrast to this behavior of cyclopentene, 1-methylcyclopentene *does* yield the ring-contracted carbonyl product, *i.e.*, methyl cyclobutyl ketone. In this case, the additional stabilization of the ring-contracted carbonium ion by the methyl substituent (*cf.* eq 4 and 5 or 6 and 7) apparently is sufficient to overcome the strain energy associated with the formation of the cyclobutyl ring and to cause ring contraction to be favored over the alternative modes of rearrangement of the incipient carbonium ion formed by dethallation.

The methylenecycloalkanes also yielded distinctive carbonyl oxidation products, namely the corresponding *ring-expanded* cyclo ketones. The formation of these can be readily rationalized in terms of the same mechanistic framework through a sequence of steps such as that depicted by eq 9. Indeed, a very considerable driving force for the rearrangement of the incipient primary carbonium ion product of dethallation to the ring-expanded secondary oxo carbonium ion would be anticipated in these cases.



(9)

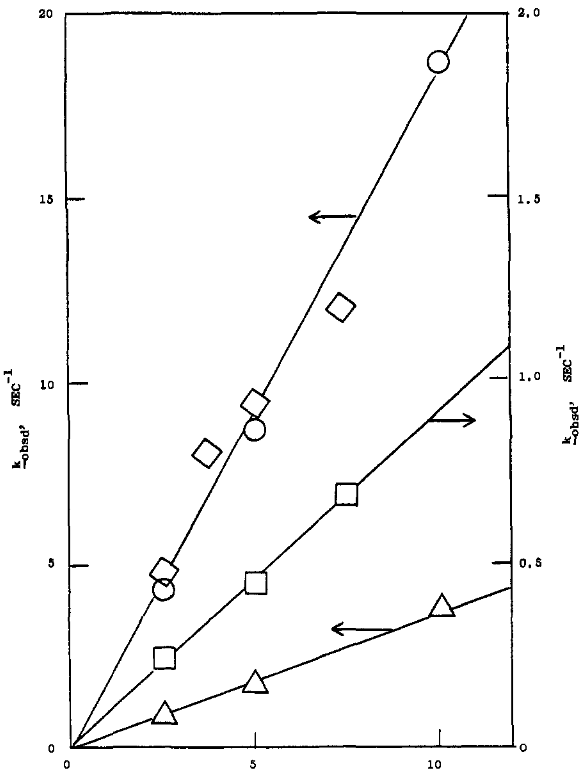


Figure 2. Dependence of k_{obsd} for hydroxymercuration on the alkene concentration: ○, 2-methyl-2-butene; ◇, 1-methylcyclohexene; □, cycloheptene; △, cyclobutene.

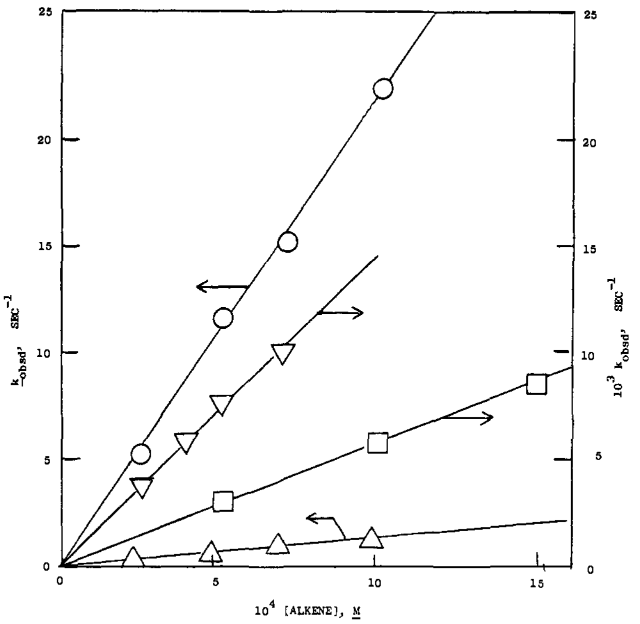
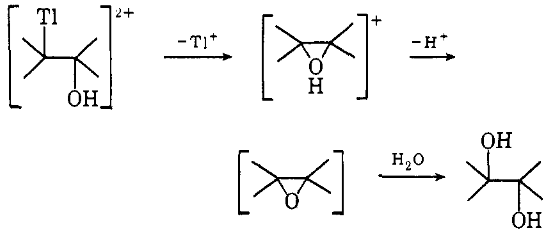


Figure 3. Dependence of k_{obsd} for the oxidation of alkenes by Tl^{3+} on the alkene concentration: ○, methylenecyclopentane; ▽, 1-methylcyclohexene; □, cyclopentene; △, methylenecyclobutane.

In view of the several alternative rearrangement pathways that are open to the intermediates in most of these reactions (*e.g.*, 1,2-hydride, carbon, and hydroxyl shifts) it is remarkable that, in each of the reactions reported here as well as those examined previously,[2,7] only one such rearrangement pathway contributes significantly and only one carbonyl product is formed. Whatever the reasons for this selectivity, it clearly enhances the synthetic utility of thallium(III) as an oxidant for olefins.[7]

The present results add little to our understanding of the detailed mechanism of formation of the 1,2-diols which are among the characteristic products of the oxidation of olefinic compounds by thallium(III) in aqueous solution. By comparison with authentic samples of both isomers, we have established that the 1,2-cyclohexanediol product of the oxidation of cyclohexene in our experiments is exclusively the trans isomer.[15] This is consistent with, but not overwhelmingly strong evidence for, the suggestion[16] of neighboring hydroxyl participation in these reactions through mechanisms such as that depicted by eq 10. Support for this suggestion is provided by the actual formation of epoxides (in yields exceeding 70%) in the oxidations of propene and isobutene by thallium(III) in relatively nonnucleophilic media such as 70% (v/v) tetrahydrofuran, 20% water, and 10% acetic acid.[16] However, the possible roles of such neighboring hydroxyl participation in the corresponding formation of diols in aqueous solution remains uncertain.[17]



(10)

Kinetics. Since the kinetics of both the hydroxymercuration and thallium(III) oxidation reactions of all the alkenes encompassed by the present study were identical with those already reported for other olefinic substrates,[1-4] an extensive description is unnecessary. All the reactions exhibited the usual second-order kinetics according to the rate law of eq 11 (where M^{n+} =

$$-d[M^{n+}]/dt = -d[\text{alkene}]/dt = k_i[M^{n+}][\text{alkene}] \quad (11)$$

Hg^{2+} or Tl^{3+}). Since all the experiments were conducted with the alkene in substantial excess over the metal ion, the observed kinetics were pseudo first order in accord with eq 12, where k_i = k_1 for Tl^{3+} and k_3 for Hg^{2+}.

$$-d \ln [M^{n+}]/dt = k_{obsd} = k_i[\text{alkene}] \quad (12)$$

The kinetic measurements typically encompassed the initial composition ranges 2.5×10^{-5} to 1×10^{-4} M Hg^{2+} or Tl^{3+} and 2.5×10^{-4} to 2×10^{-3} M alkene. All kinetic experiments were performed at 25.0° in 0.1 M $HClO_4$ ($\mu = 0.1$).

The measurements yielded good pseudo-first-order kinetic plots similar to those of our earlier studies,[1,4] from the slopes of which values of k_{obsd} were determined. Representative plots of k_{obsd} *vs.* [alkene] for the hydroxymercuration and for the thallium(III) oxidation reactions are depicted in Figures 2 and 3, respectively, and serve to confirm the kinetic dependence of eq 12.

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[15] A similar result for the oxidation of 3-*tert*-butylcyclohexene by thallium(III) sulfate was recently reported by C. Freppel, F. Favier, J.-C. Richer, and M. Zador, *Can. J. Chem.*, **49**, 2586 (1971).

[16] W. Kruse and T. M. Bednarski, *J. Org. Chem.*, **36**, 1154 (1971).

[17] Hydroxyl group migration is clearly implicated in the formation of isobutyraldehyde as one of the products of the oxidation of isobutene by thallium(III) in aqueous solution.[3] However, this is a case in which the usually preferred 1,2-hydride shift is precluded.

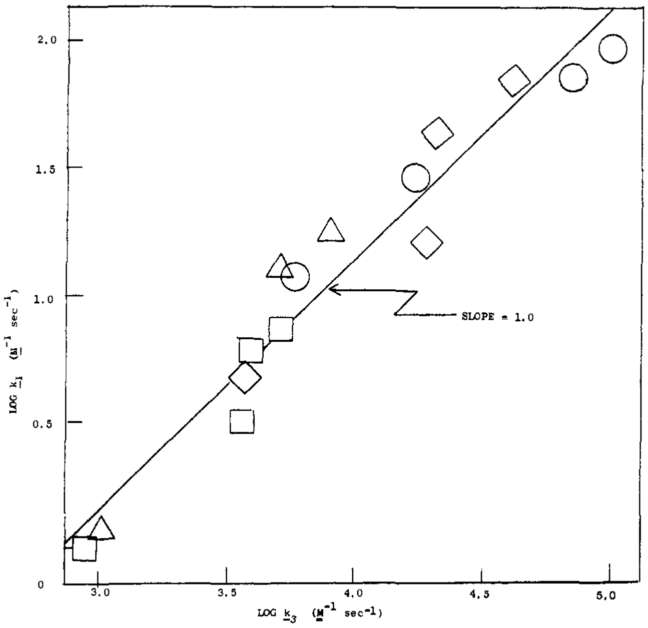


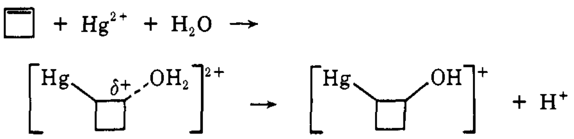
Figure 4. Relation between the rate constants for hydroxythallation (k_1) and hydroxymercuration (k_3): ○, alkenes (based on data from this work and from ref 1 and 3); △, alkenols (based on data from ref 1 and 4); □, cycloalkenes; ◇, 1-methylcycloalkenes.

Values of k_1 and k_3, computed from the slopes of such plots, are listed in Tables I-III.

For most of the alkenes encompassed by this study, the dethallation reactions (eq 2) were sufficiently rapid that the oxythallation adducts (**1**) could not be detected spectrally and formation of the final products was essentially coincident with the consumption of reactants. However, in several cases, just as in some of the systems previously described,[4] the two steps of the reaction were sufficiently well separated that the oxythallation adduct could be detected spectrally (*cf.* Figure 3 of ref 4) and both k_1 and k_2 could be measured. Such measurements yielded k_2 values of 0.41, 0.086, and 0.053 sec^{-1} for methylenecyclopentane, methylenecyclohexane, and isobutene, respectively.

Reactivity Patterns. One of the features revealed by the data in Tables I–III is the relative insensitivity of the rates of both oxymercuration and oxythallation to ring size. For each class of alkenes, the values of k_1 and k_3 are constant to within about one order of magnitude and lie in the same ranges as the corresponding values for the acyclic compounds of the same structure. Thus, for the 1-methylcycloalkenes, $5 < k_1 < 68\ M^{-1}$ sec^{-1}, compared with 29 M^{-1} sec^{-1} for 2-methyl-2-butene (Table II).

Of particular interest is the absence of evidence of markedly enhanced reactivity for the four-membered ring compound of any of the series. Such rate enhancement might have been anticipated in view of the relief of strain which is generally associated with saturation of the cyclobutene ring and which gives rise to the expectation of enhanced reactivity for electrophilic addition to cyclobutenes.[18] In the case of these reactions, however, such relief of strain is presumably offset by the corresponding strain of the cyclobutyl carbonium ion-like transition states through which the oxymetalation reactions are believed to proceed, as exemplified by eq 13.[1,14]



(13)

Another striking feature of the kinetic data in Tables I–III is the relatively constant ratio of the rate constants for corresponding hydroxymercuration and hydroxythallation reactions (*i.e.*, $k_3/k_{-1} \sim 10^3$). This is demonstrated by Figure 4 which compares k_3 and k_1 not only for the reactions described in this paper, but for all other reactions for which applicable data are available from earlier studies.[1,2,4] With the single exception of ethylene which, for reasons that are unclear, lies well below the plot of Figure 4 (just outside the range of the figure), the large number of data points for a variety of compounds (simple alkenes, cycloalkenes, alkenols, etc.) all fall close to a single linear plot of log k_1 *vs.* log k_3, of unit slope. This reinforces the conclusions that (i) the initial step in the oxidation of olefinic compounds by thallium(III) is indeed the formation of an oxythallation adduct, and (ii) oxymercuration and oxythallation proceed through closely related mechanisms and transition states.

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[18] T. G. Traylor, *Accounts Chem. Res.*, **2**, 152 (1969).