Oxidation of Olefinic Compounds in Aqueous Solution by Thallium(III). Evidence for Intermediate Oxythallation Adducts

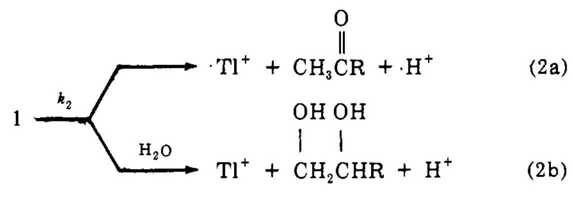
James E. Byrd and Jack Halpern*

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

Abstract: Alkenols were found to react stoichiometrically (1:1) with Tl^{3+} in aqueous perchloric acid to yield the oxidation products indicated in parentheses: 1-propen-3-ol (hydroxyacetone and 1,2,3-propanetriol); 1-buten-4-ol (3-hydroxytetrahydrofuran); 1-penten-4-ol (2-methyl-4-hydroxytetrahydrofuran); 1-penten-5-ol (5-hydroxy-2-pentanone); 1-hexen-6-ol (6-hydroxy-2-hexanone). The results can be accommodated by the oxythallation–dethallation mechanism proposed by earlier workers, namely, $Tl^{3+} + CH_2{=}CHR + H_2O \rightarrow [TlCH_2CH(R)OH]^{2+}$ (**1**) + H^+ followed by **1** $\rightarrow Tl^+$ + oxidation products. Support for this mechanism was provided by (i) comparisons of the rate constants of the first step with the corresponding rate constants of hydroxymercuration of the same compounds, and (ii) the direct spectral detection of some of the intermediate hydroxythallation adducts and the determination of the kinetics of the subsequent dethallation step.

Several workers have previously described the oxidations of olefins by thallium(III) salts.[1–8] In aqueous solution the products of the oxidation of simple olefins are typically 1,2-diols and carbonyls (aldehydes or ketones). The kinetics and products of the oxidation of olefins by thallium(III) perchlorate in aqueous perchloric acid solutions have been interpreted by Henry[5] in terms of the mechanism whose essential features are represented by eq 1 and 2.[9]

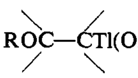
$$Tl^{3+} + CH_2{=}CHR + H_2O \xrightarrow{k_1} [TlCH_2CH(R)OH]^{2+} + H^+ \quad (1)$$



$$\mathbf{1} \xrightarrow{k_2} Tl^+ + CH_3\overset{\overset{\displaystyle O}{\|}}{C}R + H^+ \quad (2a)$$

$$\mathbf{1} \xrightarrow[H_2O]{k_2} Tl^+ + \overset{OH}{\overset{|}{C}}H_2\overset{OH}{\overset{|}{C}}HR + H^+ \quad (2b)$$

Analogous mechanisms, also involving oxythallation adducts, have been invoked for the oxidation of olefins in other solvents notably by thallium(III) acetate in acetic acid.[1–8] Not only could the products of these oxidations be rationalized in terms of their derivation from such intermediate oxythallation adducts but, in several cases, stable oxythallium(III) acetate adducts of the type



have actually been isolated.[2,8] However, while supported by indirect inferences, the intermediacy of oxythallation adducts such as **1** in *acetate-free aqueous solutions* has thus far not been directly demonstrated.

This paper describes detailed kinetic studies of the oxidation of several alkenols by thallium(III) in aqueous perchloric acid solution. These are extensions of earlier related studies by Henry[5] on the corresponding oxidations of simple olefins. Additional evidence for the mechanism depicted by eq 1–2 was sought particularly through the following approaches: (i) comparison of the rates of oxidation by thallium(III) with our previously determined[10] rates of hydroxymercuration (eq 3) for the same series of olefins, and (ii) attempts to detect the intermediate oxythallation adducts directly by monitoring the entire course of reaction spectrally (with a stopped-flow spectrophotometer) rather than following only the initial step of the reaction by uptake of the gaseous olefins as was done in the earlier studies.[5]

$$Hg^{2+} + CH_2{=}CHR + H_2O \xrightarrow{k_3} [HgCH_2CH(R)OH]^+ + H^+ \quad (3)$$

Experimental Section

Materials. The purification of the alkenol substrates, which were also used in our earlier hydroxymercuration studies, has already been described.[10] No impurities were detectable by nmr or glc.

Stock solutions of thallium(III) perchlorate were prepared by dissolving $Tl(OH)_3$ (which had been precipitated from an aqueous solution of the perchlorate salt with ammonia and washed thoroughly with distilled water) in aqueous perchloric acid. The concentration of thallium(III) was determined by two independent methods which yielded consistent results, namely (i) comparison of the uv spectrum with that reported by Rogers and Waind,[11] and (ii) reduction to thallium(I) with Na_2SO_3 followed by titration with KIO_3.[12] Sodium perchlorate was prepared by neutralizing reagent grade perchloric acid with sodium carbonate and recrystallizing the precipitated salt. Distilled water was used for the preparation of all solutions.

---

(1) R. R. Grinstead, *J. Org. Chem.*, **26**, 238 (1961).

(2) H. J. Kabbe, *Justus Liebigs Ann. Chem.*, **656**, 204 (1962).

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

(4) J. B. Lee and M. J. Price, *Tetrahedron Lett.*, 155 (1962); *Tetrahedron*, 20, 1017 (1964).

(5) P. M. Henry, *J. Amer. Chem. Soc.*, **87**, 990, 4423 (1965); **88**, 1597 (1966); *Advan. Chem. Ser.*, **No.** 70, 126 (1968).

(6) R. J. Ouellette, G. Korkosky, C. Lavin, and S. Williams, *J. Org. Chem.*, **34**, 4104 (1969).

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

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

(9) This representation omits one of the intermediates originally proposed by Henry,[5] *i.e.*, a thallium(III)-olefin π complex, $Tl(CH_2{=}CHR)^{3+}$, which was invoked as the precursor of the σ-bonded oxythallation adduct, **1**. Although such an additional intermediate is not inherently implausible, there is neither specific evidence for it, nor does it influence the features of the mechanism that are relevant in the present context.

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

(11) T. E. Rogers and G. M. Waind, *Trans. Faraday Soc.*, **57**, 1360 (1961).

(12) A. I. Vogel, "A Textbook of Quantitative Analysis," 3rd ed, Wiley, New York, N. Y., 1961.

Table I. Stoichiometry and Products of the Reactions of Tl^{3+} with Various Alkenols

Alkenol	Stoichiometry, [alkenol]/[Tl^{3+}][a]	Oxidation products[b]
1-Propen-3-ol	1.00[c]	25–35% CH_3COCH_2OH; 40–50% $HOCH_2CH(OH)CH_2OH$
1-Buten-4-ol	0.95[d]	3-Hydroxytetrahydrofuran
1-Penten-4-ol	0.95[c]	2-Methyl-4-hydroxytetrahydrofuran
1-Penten-5-ol	0.98[c]	$CH_3COCH_2CH_2CH_2OH$
1-Hexen-6-ol	1.15[c]	
	1.10[d]	$CH_3COCH_2CH_2CH_2CH_2OH$

[a] Estimated accuracy ±0.05. [b] No other products could be detected by nmr or glc. [c] Based on end point of spectral titration. [d] Based on glc determination of unreacted excess alkenol.

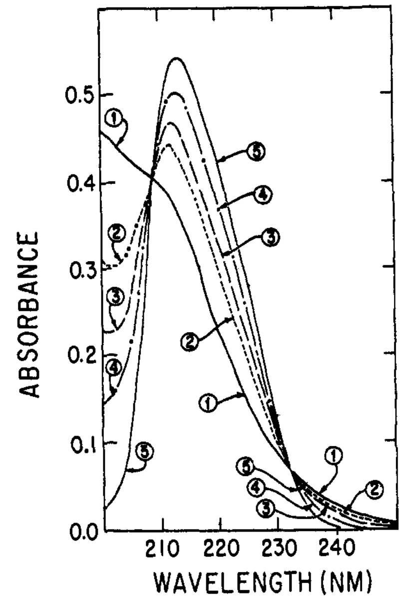


Figure 1. Spectral changes accompanying the incremental addition of 1-buten-4-ol to a 0.1 *M* $HClO_4$ solution initially containing 1.15 × 10^{-4} *M* Tl^{3+}. Concentrations of added 1-buten-4-ol (*M*): **1**, 0.0; **2**, 4.25 × 10^{-5}; **3**, 6.8 × 10^{-5}; **4**, 9.1 × 10^{-5}; **5**, 1.15 × 10^{-4} (1.0-cm light path).

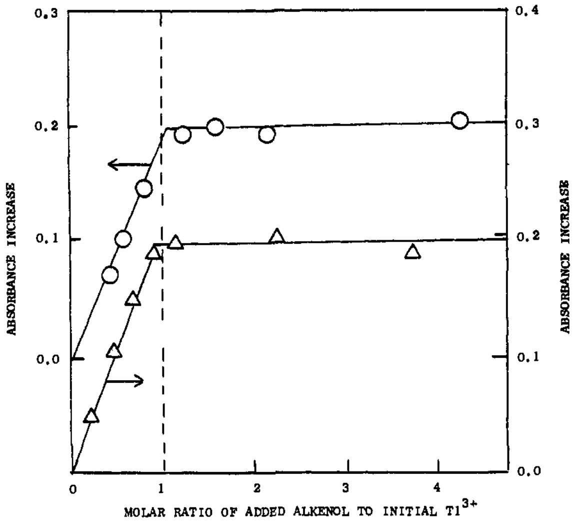


Figure 2. Spectral titrations at 220 nm of 1.15 × 10^{-4} *M* Tl^{3+} solutions with 1-buten-4-ol (○) and 1-hexen-6-ol (△). Plots are displaced for clarity (1.0-cm light path).

Stoichiometry and Products. The stoichiometries of the reactions [*i.e.*, the molar ratio of alkenol and thallium(III) that reacted with each other] were determined by two independent procedures which yielded consistent results, namely (i) the addition of a known amount of (excess) alkenol to a solution containing a known concentration of thallium(III) followed by determination of the unreacted alkenol concentration by glc, and (ii) spectral titrations of dilute solutions (~10^{-4} *M*) of thallium(III) with the alkenols following the final absorbance increase in the 200–220-nm region due to the formation of Tl^+ (λ_{max} 212 nm, ϵ_{max} 4.58 × 10^3).

For purposes of identification and characterization of the oxidation products, reactions were performed with relatively high initial reactant concentrations (~10^{-2} *M* for subsequent glc analysis and ~1 *M* for subsequent nmr analysis). In each case K_2CO_3 was added to the product solution to neutralize the perchloric acid and to precipitate the thallium(I) as Tl_2O and the perchlorate as $KClO_4$. The precipitates were separated by filtration and the solutions analyzed for organic products. Glc determinations on the resulting product solutions were performed with a Varian 661 gas chromatograph equipped with a flame-ionization detector and a 2 ft × $^1/_8$ in. Poropak Q (100–200 mesh) column. Nmr spectra of the product solutions were determined with a Varian A-60 spectrometer using *tert*-butyl alcohol as an internal standard. Since all the oxidation products were known compounds, authentic samples were used to confirm the nmr identifications and to calibrate the glc determinations.

Kinetic Measurements. The kinetics of the reactions were monitored spectrophotometrically in the wavelength range 200–220 nm. The rates of reactions with half-lives of less than 5 sec were determined with a Durrum–Gibson stopped-flow spectrophotometer, while the rates of slower reactions were measured in a Cary 14 spectrophotometer. In each case, the reaction chamber was thermostatted at 25.0 ± 0.2°. The equipment and procedures were identical with those used in our earlier studies on the kinetics of hydroxymercuration and have already been described.[10] The standard conditions for the kinetic experiments, *i.e.*, 25°, 0.1 *M* $HClO_4$ (μ 0.1 *M*), were selected to correspond to those in our earlier experiments on hydroxymercuration[10] and to one set of conditions used by Henry[5] in his Tl^{3+}-oxidation studies, thus making all three sets of data directly comparable with each other.

Results and Discussion

Stoichiometry and Products. Figure 1 depicts the overall spectral changes accompanying the addition of successive increments of 1-buten-4-ol to a given solution of Tl^{3+}. The band at 212 nm, whose intensity increases to a limiting value as the reaction proceeds to completion, is due to the Tl^+ product. The spectra exhibit two well-defined isosbestic points consistent with the assumption of invariant stoichiometry throughout the course of reaction. The results of representative titrations, based on such spectral measurements, are depicted in Figure 2. The end points of such titrations for each of the reactions (as well as of some titrations based on the determination of unreacted alkenol) are listed in Table I, together with the corresponding final oxidation products determined as described earlier. In each case, the overall reaction stoichiometry was found to correspond to a Tl^{3+}:alkenol molar ratio close to 1:1. For 1-propen-3-ol, the oxidation products were a mixture of 1,2,3-propanetriol and hydroxyacetone, corresponding to the typical mixtures of diol and carbonyl products previously obtained by Henry for simple olefins (*e.g.*, 75–85% acetone and 15–25%

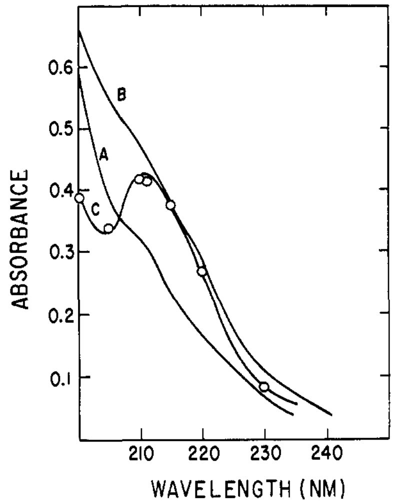


Figure 3. Spectral changes accompanying the reaction of 6.0 × 10^{-5} M Tl^{3+} with an excess (1.2 × 10^{-3} M) of 1-hexen-6-ol: (A) initial spectrum (*i.e.*, sum of spectra of 6.0 × 10^{-5} M Tl^{3+} and 1.2 × 10^{-3} M 1-hexen-6-ol); (B) spectrum immediately (*ca.* 1 min) after mixing; (C) final spectrum (after 3 hr). The points ○ correspond to the spectrum of a synthetic solution of the composition predicted for the final reaction solution (*i.e.*, 6.0 × 10^{-5} M Tl^+, 6.0 × 10^{-5} M 6-hydroxy-2-hexanone, and 1.14 × 10^{-3} M 1-hexen-6-ol in 0.1 M $HClO_4$).

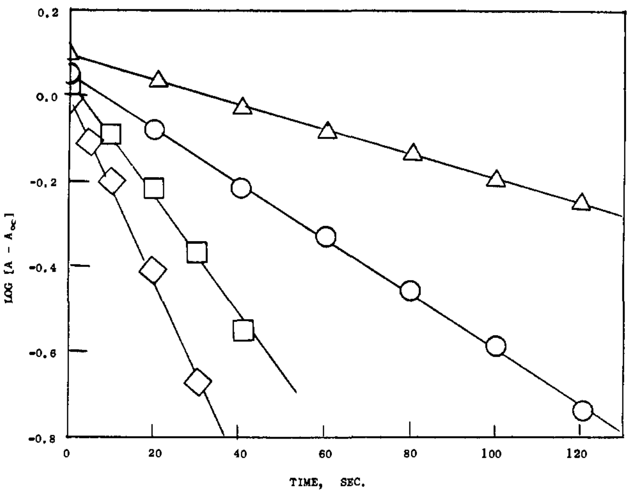


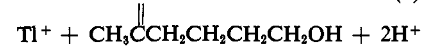
Figure 4. Pseudo-first-order rate plots for the reaction of 5.0 × 10^{-5} M Tl^{3+} with 1-buten-4-ol. Initial [1-buten-4-ol] (M): △, 5.0 × 10^{-4}; ○, 1.0 × 10^{-3}; □, 2.0 × 10^{-3}; ◇ 3.0 × 10^{-3} M. A and A_∞ are the absorbance at time t and the final absorbance, respectively, at 205 nm (5.0-cm light path).

1,2-dihydroxypropane for propylene).[5] In the case of each of the higher alkenols only one oxidation product was obtained, the nature and significance of which will be discussed below.

Spectral Changes. The several reactions that were examined exhibited two distinct patterns of spectral changes, designated below as classes A and B, respectively.

Class A: 1-Buten-4-ol and 1-Penten-4-ol. In the cases of these two substrates, the spectral changes accompanying the reactions revealed no evidence for intermediates. The successive spectra of the solutions, as reaction proceeded, resembled those depicted in Figure 1, exhibiting well-defined isosbestic features and indicating that formation of the final products (whose known spectra agreed with the observed final spectra of the reaction solutions) is essentially coincident with the consumption of the reactants. Accumulation of intermediates in these cases apparently is insignificant.

Class B: 1-Propen-3-ol, 1-Penten-5-ol, and 1-Hexen-6-ol. For these three substrates the spectral behavior was distinctly different. In each of these cases, mixing a solution of the alkenol with a solution of Tl^{3+} resulted in a rapid initial absorbance *increase* in the 200–250-nm region, followed by a slower absorbance *decrease* in the 200–215-nm region.[13] The behavior characteristic of these systems is depicted in Figure 3 for the reaction of 1-hexen-6-ol with Tl^{3+}. The final spectrum (curve C) is identical with that of a synthetic solution containing the predicted mixture of products (6.0 × 10^{-5} M each of Tl^+ and of 6-hydroxy-2-hexanone) and unreacted alkenol, thus confirming the *overall* stoichiometry corresponding to eq 4.



$$Tl^{3+} + CH_2{=}CHCH_2CH_2CH_2CH_2OH + H_2O \longrightarrow Tl^+ + CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_2OH + 2H^+ \qquad (4)$$

The intermediate spectral features of these reactions are clearly associated with the formation and decay of reaction intermediates. It is reasonable to identify these intermediates with the oxythallation adducts (*i.e.*, **1**) of the mechanistic scheme depicted by eq 1–2. This interpretation will be adopted at the outset, used as a basis for interpretation of the kinetic results, and ultimately reinforced by additional supporting evidence.

Kinetics of the First Reaction (Hydroxythallation). For the class A substrates (1-buten-4-ol and 1-penten-4-ol), no reaction intermediates were detectable, and therefore in these cases a single rate law describes the overall reaction. These reactions exhibited second-order kinetics corresponding to the rate law defined by eq 5 which is identical with that previously reported by

$$-d[Tl^{3+}]/dt = -d[\text{alkenol}]/dt = k_1[Tl^{3+}][\text{alkenol}] \qquad (5)$$

Henry[5] for the oxidation of simple olefins by Tl^{3+} (monitored by olefin uptake).

The range of initial conditions encompassed by the kinetic measurements was 5 × 10^{-5}–1 × 10^{-4} M Tl^{3+}, 5 × 10^{-4}–1 × 10^{-2} M alkenol, 0.1 M $HClO_4$ (μ = 0.1), 25.0°. The alkenol was always in sufficient excess over Tl^{3+} so that the observed kinetics were pseudo first order (eq 6). Typical pseudo-first-order plots, from the slopes of which values of k_{obsd} were determined, are depicted in Figure 4. The first-order dependence on the alkenol concentration is demonstrated by the linear plots of k_{obsd} *vs.* [alkenol] which are depicted in Figure 5 and which are in accord with eq 6. The values of

$$-d \ln [Tl^{3+}]/dt = k_{obsd} = k_1[\text{alkenol}] \qquad (6)$$

k_1 determined from the slopes of these plots are listed in Table II.

For the class B substrates (1-propen-3-ol, 1-penten-5-ol, and 1-hexen-6-ol) the kinetic behavior was complicated by the successive occurrence of the two separate reactions (oxythallation and dethallation, respectively).

---

[13] Simple alkenes such as ethylene, propylene, and isobutene, whose oxidations have previously been studied by Henry,[5] were found to exhibit qualitatively similar behavior. However, our own studies were restricted to alkenols because the limited solubilities of the simple alkenes introduced obstacles to their quantitative investigation.

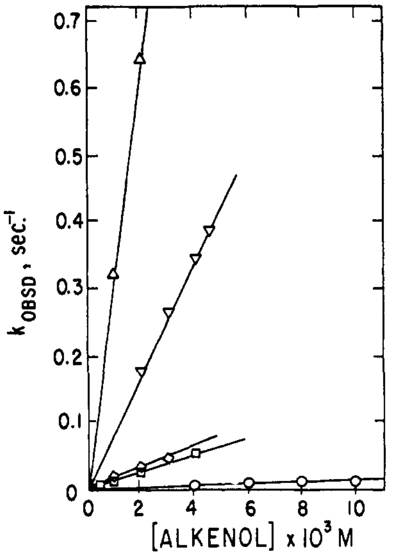


Figure 5. Dependence of k_{obsd} on the alkenol concentration: △, 1-penten-5-ol; ▽, 1-hexen-6-ol; ◇, 1-buten-4-ol; □, 1-penten-4-ol; ○, 1-propen-3-ol.

Table II. Values of k_1 at 25° [a]

Alkenol	k_1, M^{-1} sec^{-1}
1-Propen-3-ol	1.21 ± 0.03
1-Buten-4-ol	15.0 ± 0.5
1-Penten-4-ol	12.2 ± 0.6
1-Penten-5-ol	317 ± 8
1-Hexen-6-ol	86 ± 2

[a] Based on kinetic measurements encompassing the initial composition ranges: 5×10^{-5}–1×10^{-4} *M* Tl^{3+}; 5×10^{-4}–1×10^{-2} *M* alkenol; 0.10 *M* $HClO_4$ ($\mu = 0.1$ *M*).

The two reactions were, however, sufficiently well resolved to permit the rates of each to be determined separately. The first reaction, corresponding to the consumption of Tl^{3+} and alkenol (but, in these cases to the formation of the intermediate **1** rather than of the final products), could be monitored readily by the absorbance *increase* at *ca.* 205 nm (see Figure 3). The kinetics were found to be identical with those of the earlier reactions and conformed accurately to eq 5 and 6. Typical oscillograms depicting these reactions, together with the corresponding pseudo-first-order plots, are depicted in Figure 6.[14] The values of k_{obsd} derived from the slopes of such plots are plotted together with the corresponding data for the other reactions in Figure 5. Values of k_1 for all the reactions are listed in Table II.

Reactivity Patterns for k_1. Support for the interpretation that has been adopted for the step whose rate is determined by k_1, *i.e.*, *that it corresponds to the oxythallation reaction described by eq 1*, is provided by an examination of the dependence of k_1 on olefin structure and a comparison of this dependence with the corresponding reactivity pattern for the analogous hydroxymercuration reaction (eq 3). Such a comparison, for all the substrates for which applicable data are available, is depicted in Figure 7 in the form of plots of log *k* (for $CH_2{=}CHR$) *vs.* Taft's σ^* for R. The plot for

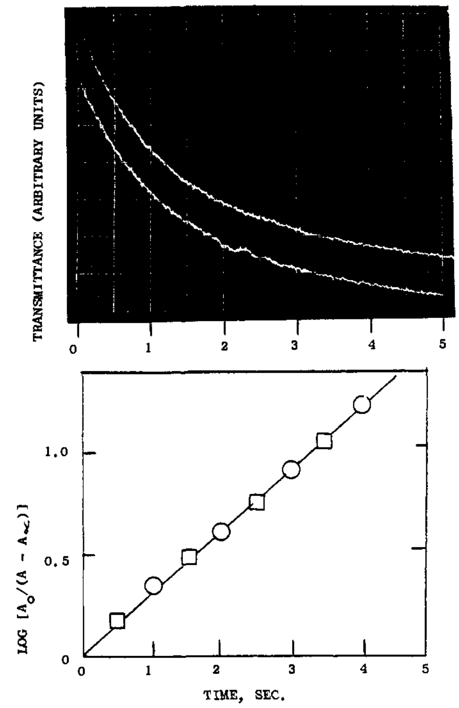


Figure 6. Duplicate stopped-flow oscillograms (displaced for clarity) and corresponding pseudo-first-order plots for the first stage of reaction (oxythallation) of 1.0×10^{-4} *M* Tl^{3+} with 2.5×10^{-3} *M* 1-penten-5-ol: ○, upper trace; □, lower trace.

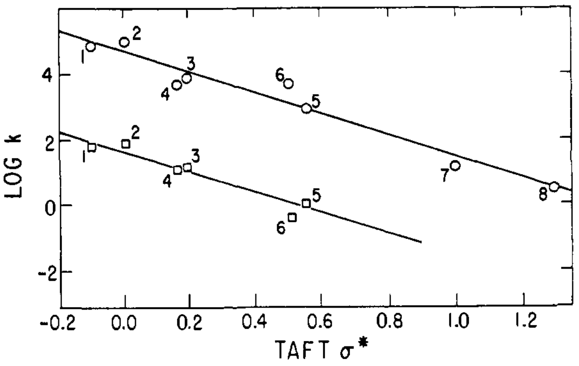


Figure 7. Taft plots for the rate constants of hydroxythallation, k_1 (□), and of hydroxymercuration, k_3 (○), of various olefinic compounds, $CH_2{=}CHR$: **1**, 1-butene; **2**, propene: **3**, 1-buten-4-ol; **4**, 1-penten-4-ol; **5**, 1-propen-3-ol; **6**, ethylene; **7**, allyl chloride; **8**, allyl cyanide. Values of the hydroxymercuration rate constants and of σ^* are from ref 10. Values of k_1 for ethylene, propene, and 1-butene are from ref 5; other values of k_1 from this work.

k_1 (*i.e.*, for the reactions of Tl^{3+}) includes not only several values from the present study but also the applicable values for ethylene, propylene, and 1-butene previously determined by Henry.[5,15]

The similarity of the reactivity patterns for the two reactions (corresponding to $\rho^* \sim -3.2$ in each case) lends support to the suggestion that they correspond to the closely related hydroxythallation and hydroxymercuration processes depicted by eq 1 and 3, respectively. The reactivity pattern for hydroxymercuration has previously been interpreted[10] in terms of a

---

(14) In the several experiments where interference from the second reaction set in before the first one went essentially to completion, reliable values of k_1 could still be obtained by treating the initial kinetic data by the Guggenheim method.

(15) Since Henry's kinetic measurements were based on olefin uptake,[5] they correspond to the first step of the overall reaction (*i.e.*, the k_1 step) and do not depend on whether the initial reaction leads to the accumulation of the intermediate oxythallation adduct or immediately to the formation of the final products.

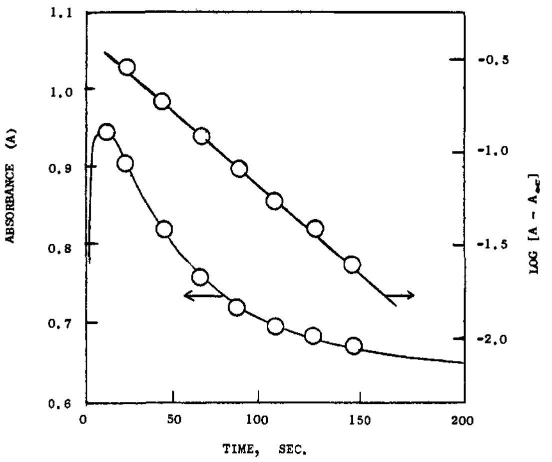
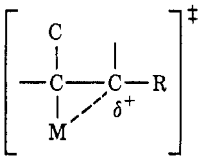


Figure 8. Rate plots (monitored at 205 nm) for the second stage of reaction (dethallation) of 5.0 × 10^{-5} Tl^{3+} with 1.0 × 10^{-3} *M* 1-penten-5-ol (1.0 cm light path).

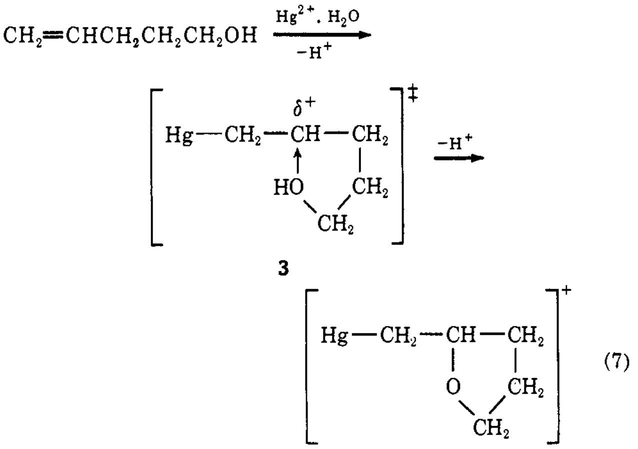
transition state (2) involving a high degree of positive



2 (M = Hg^{2+} or Tl^{3+})

charge localization (*approaching* carbonium ion character) on the carbon atom adjacent to the substituent R. The present results support a similar conclusion with respect to oxythallation.

The anomalously high rates of oxymercuration of 1-penten-5-ol and 1-penten-6-ol (the former being immeasureably fast even by stopped-flow) found in our earlier study[10] were interpreted in terms of cyclic transition states such as 3, stabilized by neighboring OH group participation. This interpretation was also in accord with the formation of cyclic ethers such as 4, instead of the usual hydroxymercurials, as the products of oxymercuration in aqueous solution (eq 7). The



3

4

(7)

strikingly high values of k_1 for these two alkenols (Table II) and the order of the rates (1-penten-5-ol > 1-hexen-6-ol) suggest that similar neighboring group stabilization effects operate in the case of oxythallation. In this context, the absence of formation of cyclic ether products during oxidation of these alkenols by thallium(III) is somewhat surprising and may reflect rearrangements during the dethallation step.

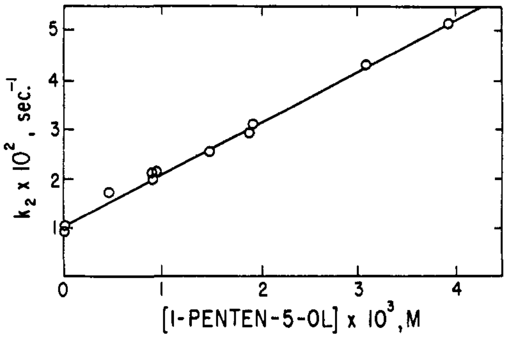
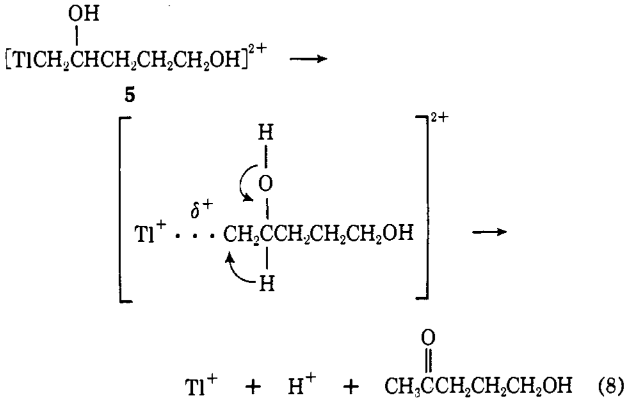


Figure 9. Dependence of k_2 for the reaction of Tl^{3+} with 1-penten-5-ol on the concentration of 1-penten-5-ol.

The displacement of the two Taft plots in Figure 7 corresponds to a relatively constant ratio of the rate constants of hydroxymercuration and hydroxythallation, *i.e.*, $k_3/k_1 \approx 10^3$. Since the oxymetalation step is presumably accompanied by some desolvation of the metal ion, the higher solvation energy of Tl^{3+} (relative to the dipositive Hg^{2+} ion) would be expected to contribute to the observed reactivity order, *i.e.*, $k_3 > k_1$.

Kinetics of the Second Reaction (Dethallation). The second stage of reaction which, according to the interpretation that we have adopted, corresponds to the dethallation step and formation of the final oxidation products, was examined in greatest detail for 1-penten-5-ol. For this substrate the proposed dethallation step, following the interpretations of Henry[5] and other previous workers, can be represented as



5

(8)

In accord with the spectra depicted in Figure 3 (curves B and C), reaction 8 could be conveniently followed by monitoring the accompanying decrease in absorbance due to the oxythallation intermediate 5 in the 205-nm region (where the final product, Tl^+, exhibits an absorption minimum). The resulting kinetics were pseudo first order according to eq 9, as illustrated by

$$-d[\mathbf{5}]/dt = d[Tl^+]/dt = k_2[\mathbf{5}] \qquad (9)$$

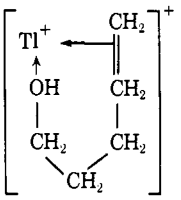
the rate plots in Figure 8.

An unexpected result was the finding that reaction 8 was catalyzed by excess 1-penten-5-ol. The form of the catalysis is depicted in Figure 9 which reveals contributions to reaction 8 both from uncatalyzed and catalytic pathways, in accord with eq 10, where k_2^0 =

$$k_2 = k_2^0 + k_2'[CH_2{=}CHCH_2CH_2CH_2OH] \qquad (10)$$

1.0 × 10^{-2} sec^{-1} and k_2' = 10.8 M^{-1} sec^{-1}.

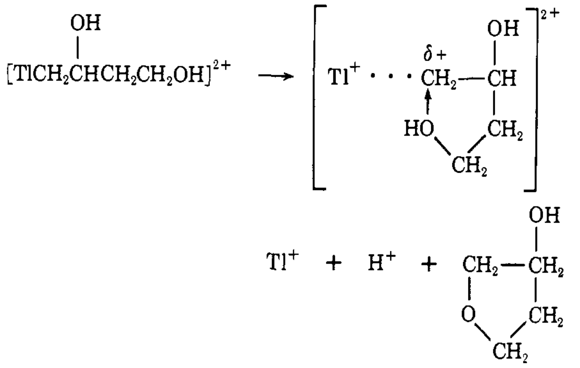
It was confirmed that the role of the 1-penten-5-ol in the dethallation reaction was truly catalytic since the ratio of overall consumption of 1-penten-5-ol in the reaction to the initial Tl^{3+} concentration was always close to 1:1. It was also established that the catalytic effect in question is not 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



6

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.

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.

---

(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

Peter Abley, James E. Byrd, and Jack Halpern*

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.*, $-\mathrm{d}[\text{alkene}]/\mathrm{d}t = k[\mathrm{M}^{n+}][\text{alkene}]$, where $\mathrm{M}^{n+} = \mathrm{Hg}^{2+}$ 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.*, $\mathrm{Tl}^{3+} + {>}\mathrm{C}{=}\mathrm{C}{<} + \mathrm{H_2O} \rightarrow \mathrm{Tl}{>}\mathrm{C}{-}\mathrm{C}{<}\mathrm{OH}^{2+} + \mathrm{H}^+$, followed by $\mathrm{Tl}{>}\mathrm{C}{-}\mathrm{C}{<}\mathrm{OH}^{2+} \rightarrow \mathrm{Tl}^+ +$ 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-

---

(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).