The decreases in k' are so small they are difficult to assign to any specific cause. They probably result from a combination of steric and electronic effects, and studies would have to be carried out with olefins with the same steric requirements but different values of σ before the two effects can be separated. The higher value of k' for *trans*-2-butene over that for *cis*-2-butene is unexpected, but appears to be real.

The changes in K_1 for the various olefins are qualitatively the same as those reported for π-complex formation with Ag(I).[15] Quantitatively, the differences between the various olefins are smaller for Pd(II). However, again, the differences between the two metal ions are small and the contributions of steric and electronic effects cannot be easily separated.

Experimental Section

All reagents, stock solutions, and kinetic procedures have been described previously.[1,12] The data are not as precise as those obtained with ethylene because of faster olefin hydrolysis and the smaller values of K_1, which caused the measurement of K_1 to be less accurate.

Corrections for hydration of the olefin were made by the procedure described for ethylene,[1] but for substituted ethylenes this side reaction was much more serious than it was for ethylene. Chloride concentrations above 0.3 M were not used since, at higher chloride concentrations, the hydration of the olefin was faster than the oxidation, and accurate rate constants for the oxidation could not be obtained.

An attempt was made to study the oxidation of the substituted ethylene at lower chloride ion concentration than that used in the study of the ethylene oxidation. The use of these lower chloride ion concentrations was possible in principle, since the rate of oxidation of the substituted ethylenes was somewhat slower than the rate for ethylene itself and therefore provided an opportunity to extend the range of chloride ion concentrations studied, and to increase the accuracy of the values of K_1. Of course, at lower chloride ion concentrations, the determination of K_1 is more accurate since the olefin uptake due to olefin π-complex formation is greater than at higher chloride concentrations. However, at chloride ion concentrations of less than about 0.08 M, the value of K_1, calculated on the basis of the equilibrium represented by eq 2, does not remain constant but drifts to smaller values. Thus, at 0.04 M [Cl$^-$], the value of K_1 for propylene is about one-half that obtained at higher chloride ion concentrations. The rate of the over-all reaction is slower than would be expected if the value of k' is calculated on the basis of the value of K_1 ion Table I. If the experimental value of K_1 is used, the value of k' calculated is usually higher than the value given in Table I.

Because of these experimental complications, the value of [Cl$^-$] was varied only for 0.1 to 0.3 M. The value of [H$^+$] was varied from 0.05 to 0.2 M. Higher acid concentrations were not used because of the hydrolysis side reaction.

Acknowledgment. The author gratefully acknowledges helpful discussion with Dr. H. G. Tennent and Professors H. Taube and S. Winstein. The author also acknowledges the assistance of Mr. John Jackson and Mr. Alan Jones with experimental work.

---

[15] M. A. Muks and F. T. Weiss, *J. Am. Chem. Soc.*, **84**, 4697 (1962).

Kinetics of the Thallic Ion Oxidation of Olefins. III. The Oxidation in Aqueous Acetic Acid[1]

Patrick M. Henry

Contribution from the Research Center, Hercules Powder Company, Wilmington, Delaware 19899. *Received October 2, 1965*

Abstract: The rates of oxidation of ethylene, propylene, and all four butenes to mixtures of glycols and carbonyl products by $Tl(OAc)_3$ in aqueous acetic acid were measured at various free acetate ion concentrations. By pH measurements, the values of K_3 and K_4 corresponding to the equilibria

$$Tl(OAc)_2^+ + OAc^- \overset{K_3}{\rightleftharpoons} Tl(OAc)_3 \qquad Tl(OAc)_3 + OAc^- \overset{K_4}{\rightleftharpoons} Tl(OAc)_4^-$$

were determined for this system. By comparing rates at the various acetate ion concentrations with the distribution of the thallium(III) species, as calculated from the values of K_3 and K_4, $Tl(OAc)_2^+$ was found to be the only important reactive species over a wide range of acetate ion concentrations. At very low acetate ion concentrations, the oxidation by Tl^{+3} and $Tl(OAc)^{+2}$ probably becomes appreciable, but $Tl(OAc)_3$ and $Tl(OAc)_4^-$ are relatively unreactive. The effect of olefin structure on rate and distribution of products is very similar to that found earlier for the oxidation by thallic ion in aqueous perchloric acid. This similarity indicates that Tl^{+3} and $Tl(OAc)_2^+$ are almost equivalent in their reactivity toward olefins despite the difference in charge, a result explained by strong solvation of Tl^{+3} in aqueous solution.

Thallic acetate in acetic acid oxidizes olefins to 1,1- and 1,2-diacetates as well as to allylic oxidation products.[2-4] The reactive species has been postulated[3] to be $Tl(OAc)_2^+$, but there is no experimental confirmation of this assumption. Thallic acetate in aqueous acetic acid has been reported[5] to be unreactive, presumably because of complexing of thallic ion by acetate. However, we have found that addition of strong acid to aqueous thallic acetate accelerates the oxidation of olefins, no doubt by proton removal of acetate groups from the coordination sphere of the thallic ion to give a thallic species of higher reactivity.

---

[1] Paper II: P. M. Henry, *J. Am. Chem. Soc.*, **87**, 4423 (1965).

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

[3] H. J. Kabbe, *Ann.*, **656**, 204 (1962).

[4] J. B. Lee and M. J. Price, *Tetrahedron Letters*, **24**, 1155 (1962).

[5] R. R. Grinstead, *J. Org. Chem.*, **26**, 238 (1961).

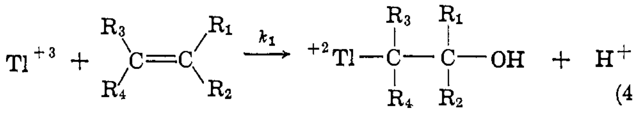
$$\mathrm{Tl(OAc)}_n{}^{(3-n)+} + \mathrm{H}^+ \overset{K_n}{\rightleftharpoons} \mathrm{Tl(OAc)}_{n-1}{}^{(4-n)+} + \mathrm{HOAC} \quad (1)$$

$$\mathrm{Tl(OAc)}_{n-1}{}^{(4-n)+} + \mathrm{H}^+ \overset{K_{n-1}}{\rightleftharpoons} \mathrm{Tl(OAc)}_{n-2}{}^{(5-n)+} + \mathrm{HOAc} \quad (2)$$

$$\mathrm{Tl(OAc)}^{+2} + \mathrm{H}^+ \overset{K_1}{\rightleftharpoons} \mathrm{Tl}^{+3} + \mathrm{HOAc} \quad (3)$$

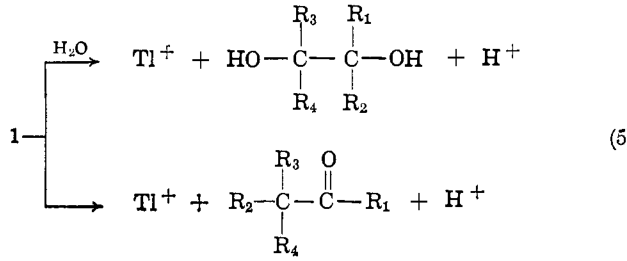
Since the hydrogen ion concentration can be conveniently measured in aqueous solution, the equilibrium constants can in principle be determined and the concentration of the various thallium(III) species in the solution calculated. This paper describes the use of this information, together with rate data on the oxidation of olefins, to define the reactive species.

In aqueous perchloric acid the kinetics, and the effect of structure on rate, were interpreted according to the following mechanism[1] (R_n = CH_3, C_2H_5, or H)



1

(4)



(5)

in which k_1 is the rate-determining step. The products obtained indicated that for ethylene, propylene, and all the butenes, except isobutene, **1** decomposed either by attack of water on the thallium–carbon bond to form glycol or by hydride shift simultaneous with the departure of Tl(I) to form the carbonyl compound. With the adduct (**1**) from isobutene, decomposition occurred by neighboring hydroxyl participation.

Results

All equilibrium and rate measurements were made at 25°. Table I lists a sample of the data used to calculate the values of K_3 and K_4. The solutions are characterized by three known quantities: the total acid concentration, $[H_t]$, equal to $[H^+]$ + [HOAc]; the total acetate concentration, $[OAc_t]$, equal to $[OAc^-]$ + [HOAc] + $\sum_0^n n[\mathrm{Tl(OAc)}]_n$; and the total thallium(III) concentration, [Tl(III)], equal to $\sum_0^n[\mathrm{Tl(OAc)}_n]$. The hydrogen ion concentration was measured and the acetate ion concentration calculated using a K_a of 2.95×10^{-5} for acetic acid at this ionic strength. The average coordination number, $\bar{n}$, equal to

$$\sum_0^n n[\mathrm{Tl(OAc)}_n]/\sum_0^n[\mathrm{Tl(OAc)}_n]$$

was then calculated from these data in the usual fashion.[6]

Table I. Values of $\bar{n}$ at Various Acetate Ion Concentrations[a]

$[H_t]$, M	$[OAc_t]$, M	$[H^+]$, M	$[OAc^-]$,[b] $M \times 10^3$	$\bar{n}$	K_a of HOAc[c]
1.196	1.285	0.151	0.20	2.53	
1.148	1.335	0.071	0.45	2.71	
1.049	1.285	0.039	0.77	2.89	
1.150	1.435	0.025	1.3	3.25	
1.000	1.310	0.0078	3.8	3.31	
1.000	1.360	0.0025	12	3.69	
1.000	1.485	0.000295	100[c]	4.00	2.95×10^{-5}
1.000	1.685	0.000099	300[c]	4.00	2.96×10^{-5}

[a] [Tl(III)] = 0.1 M; [$NaClO_4$] = 0.5 M; [HOAc] = 1.0 to 1.15 M. [b] Calculated assuming the K_a of acetic acid is 2.95×10^{-5}. [c] Calculated assuming the maximum n is 4.

Values of 2.09×10^2 for K_4 and 3.62×10^3 for K_3 were calculated from the values of $\bar{n}$ at various acetate ion concentrations by the method of Rossotti and Rossotti.[7] The various data points were averaged by least squares with a computer. In the range of these measurements, $\mathrm{Tl(OAc)}_4^-$ must be the most highly coordinated species since at higher $[OAc_t]/[H_t]$ the K_a of acetic acid, calculated from the pH measurements and assuming all acetate ion except that required to form $\mathrm{Tl(OAc)}_4^-$ is free acetate, remains constant. The K_a determined from these measurements is very close to that expected at this ionic strength.[8]

Almost all the kinetics runs were carried out at a constant olefin pressure of 1 atm. Rates were measured by gas uptake. Plotting the data as first-order reactions, presuming the decrease in thallic ion concentration is proportional to the olefin uptake, gave linear plots indicating that the reaction is first order in thallic ion. The expected[9] first-order dependence on olefin was confirmed by running two reactions at less than atmospheric pressure. Isobutene was used for this purpose since the rates were in a convenient range for measurement. The complete rate expression is thus

$$d[\mathrm{Tl(III)}]/dt = k'[\mathrm{Tl(III)}][\mathrm{olefin}]$$

To cover conveniently a wide range of acetate ion concentrations, ethylene, propylene, and isobutene were used to determine the effect of reaction mixture composition on the rate of olefin oxidation. The rate data are given in Tables II–IV. Also included are the distributions of $\mathrm{Tl(OAc)}_4^-$, $\mathrm{Tl(OAc)}_3$, and $\mathrm{Tl(OAc)}_2^+$ calculated from the values of K_3 and K_4 assuming that these are the only species present under these conditions.

A plot of k' *vs.* $\mathrm{Tl(OAc)}_2^+$ for the oxidation of ethylene is shown in Figure 1, and values of k' plus the concentration of the various Tl(III) species for several runs are given in Table II.

The data in Table II indicate that the value of k' bears no relationship to $[\mathrm{Tl(OAc)}_3]$ or $[\mathrm{Tl(OAc)}_4^-]$. Thus, in runs 4 to 13, the value of k'_{exptl} decreases by a factor of 10 while the value of $\mathrm{Tl(OAc)}_3$ *increases* by a factor of over 3, and the value of $\mathrm{Tl(OAc)}_4^-$ *increases* by a factor of over 27. However, there is a linear relationship between $\mathrm{Tl(OAc)}_2^+$ and k'. This linear relationship is

---

(6) J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants. Part I. Organic Ligands," The Chemical Society, London, 1958, p viii.

(7) F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, **9**, 1166 (1955).

(8) H. S. Harned and F. C. Hickey, *J. Am. Chem. Soc.*, **59**, 1284, 2303 (1937).

(9) P. M. Henry, *ibid.*, **87**, 990 (1965).

Table II. Data for the Oxidation of Ethylene[a]

Run no.	$[H_t]$, M	$[OAc_t]$, M	[Tl(III)], M	k'_{exptl}[b] $\times 10^2$	k'_{calcd}[b,c] $\times 10^2$	$\frac{[Tl(OAc)_2^+]}{[Tl(III)]}$	$\frac{[Tl(OAc)_3]}{[Tl(III)]}$	$\frac{[Tl(OAc)_4^-]}{[Tl(III)]}$	$[OAc^-]$,[d] M
1	0.40	0.050	0.050	28.0	...	...	...	...	...
2	0.48	0.080	0.040	13.3	3.02	1.00	<0.001	<0.001	1.09×10^{-7}
3	1.500	1.057	0.019	3.02	2.48	0.82	0.18	<0.01	6.09×10^{-5}
4	1.400	1.057	0.019	2.78	2.39	0.79	0.21	<0.01	7.67×10^{-5}
5	1.300	1.057	0.019	2.15	2.21	0.73	0.27	<0.01	1.03×10^{-4}
10	1.147	1.285	0.094	1.45	1.42	0.47	0.50	0.03	2.98×10^{-4}
13	1.15	1.435	0.094	0.27	0.26	0.087	0.64	0.273	2.04×10^{-3}

[a] Ionic strength adjusted to 0.5 with $NaClO_4$; ethylene pressure of 1 atm. [b] M^{-1} sec^{-1}; ethylene solubility is 4.2×10^{-3} M. [c] Calculated assuming $Tl(OAc)_2^+$ is the reactive species and k_c' is 3.02×10^{-2} M^{-1} sec^{-1}. [d] Calculated from values of K_3, K_4, and K_a.

Table III. Data for the Oxidation of Propylene[a]

Run no.	$[H_t]$, M	$[OAc_t]$, M	[Tl(III)], M	k'_{exptl}[b]	k'_{calcd}[b,c]	$\frac{[Tl(OAc)_2^+]}{[Tl(III)]}$	$\frac{[Tl(OAc)_3]}{[Tl(III)]}$	$\frac{[Tl(OAc)_4^-]}{[Tl(III)]}$	$[OAc^-]$,[d] M
16	1.15	1.138	0.045	2.0	2.41	0.52	0.45	0.03	2.38×10^{-4}
17	1.05	1.069	0.023	1.26	1.29	0.275	0.640	0.085	6.42×10^{-4}
18	1.025	1.069	0.023	0.71	0.77	0.164	0.675	0.161	1.14×10^{-3}
19	1.000	1.069	0.023	0.31	0.27	0.055	0.588	0.357	2.94×10^{-3}
20	1.000	1.094	0.023	0.064	0.052	0.007	0.275	0.718	1.16×10^{-2}
21	1.000	1.119	0.023	0.023	0.025	0.0012	0.131	0.868	3.0×10^{-2}
22	1.000	1.144	0.023	0.015	0.022	0.0004	0.09	0.91	5.4×10^{-2}

[a] Ionic strength adjusted to 0.5 with $NaClO_4$; propylene pressure of 1 atm. [b] M^{-1} sec^{-1}; propylene solubility is 4.4×10^{-3} M. [c] Calculated from the formula $k'_{calcd} = 0.02 + 4.6([Tl(OAc)_2^+]/[Tl(III)])$. [d] Calculated from values of K_3, K_4, and K_a.

Table IV. Data for the Oxidation of Isobutene[a]

Run no.	$[H_t]$, M	$[OAc_t]$, M	[Tl(III)], M	k'_{exptl}[b]	k'_{calcd}[b,c]	$\frac{[Tl(OAc)_2^+]}{[Tl(III)]}$	$\frac{[Tl(OAc)_3]}{[Tl(III)]}$	$\frac{[Tl(OAc)_4^-]}{[Tl(III)]}$	$[OAc^-]$,[d] M
23	1.000	1.276	0.0092	1.4	1.38	1.60×10^{-4}	0.052	0.948	0.091
24	1.000	1.130	0.018	0.94	0.98	1.035×10^{-4}	0.042	0.958	0.112
25	1.000	1.160	0.018	0.73	0.72	6.54×10^{-5}	0.033	0.967	0.142
26	1.000	1.240	0.018	0.46	0.45	2.67×10^{-5}	0.008	0.992	0.222
27	1.000	1.440	0.018	0.31	0.31	7.5×10^{-6}	0.001	0.999	0.422
28	0.300	0.430	0.018	0.93	0.98	1.035×10^{-4}	0.042	0.9587	0.112
29	0.300	0.460	0.018	0.71	0.72	6.54×10^{-5}	0.033	0.967	0.142
30	0.300	0.540	0.018	0.46	0.45	2.67×10^{-5}	0.008	0.992	0.222
31	0.300	0.740	0.018	0.28	0.31	7.5×10^{-6}	0.001	0.999	0.422

[a] Ionic strength adjusted to 0.5 M with $NaClO_4$; isobutene pressure is 1 atm. [b] M^{-1} sec^{-1}; isobutene solubility is 4.7×10^{-3} M. [c] Calculated from the formula $k'_{calcd} = 0.26 + 7 \times 10^3([Tl(OAc)_2^+]/[Tl(III)])$. [d] Calculated from values of K_3, K_4, and K_a.

demonstrated by Figure 1 in which all but runs 1 and 2 are plotted. The slope of this line is equal to the value of k_c', the value of k' if all the thallic ion is present as $[Tl(OAc)_2^+]$. This value is 3.02×10^{-2} M^{-1} sec^{-1}. The values of k' calculated from this value of k_c' are also given in Table II.

The data for the oxidation of propylene are given in Table III. Once again a linear relationship between k' and $[Tl(OAc)_2^+]/[Tl(III)]$ is found, but no relationship with $[Tl(OAc)_3]$ or $[Tl(OAc)_4^-]$ (*i.e.*, in going from run 16 to 19, k' decreases but $[Tl(OAc)_3]$ and $[Tl(OAc)_4^-]$ increase). However, in this case, the plot of $[Tl(OAc)_2^+]/[Tl(III)]$ has a positive intercept at $[Tl(OAc)_2^+]/[Tl(III)] = 0$. The value of the intercept is 2.0×10^{-2} M^{-1} sec^{-1}, and the value of the slope or k_c' is 4.6 M^{-1} sec^{-1}.

The data for the oxidation of isobutene is given in Table IV. The relationship between k' and $[Tl(OAc)_2^+]$ is still present, but the value of the intercept at $[Tl(OAc)_2^+]/[Tl(III)] = 0$ is higher than that found with propylene. The value of the intercept is 0.26 M^{-1} sec^{-1} and k_c' is 7×10^3 M^{-1} sec^{-1}.

It is not clear from the data in Table IV that k' does not have a linear relationship with $Tl(OAc)_3$ ($[Tl(OAc)_4^-]$ is still rising while k' is dropping). However, if a plot of k' *vs.* $[Tl(OAc)_3]/[Tl(OAc)_4^-]$ is made for runs 23 to 27, the plot shows considerable curvature.

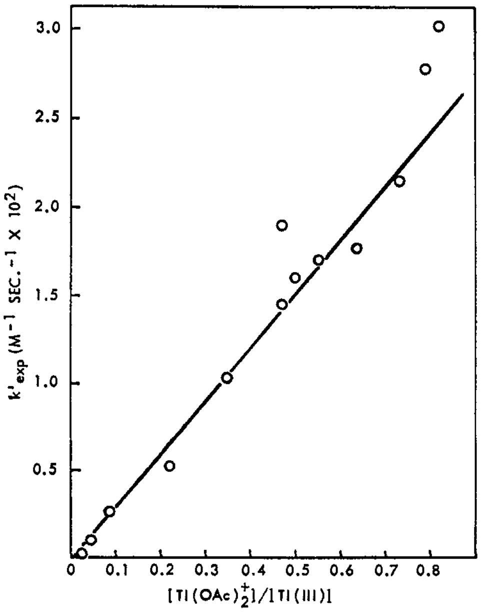


Figure 1. Plot of k' *vs.* $[Tl(OAc)_2^+]/[Tl(III)]$ for ethylene.

Table V. Relative Rates of Oxidation of Several Substituted Ethylenes

Olefin	k'^a	$[H_t]$, M	$[OAc_t]$, M	[Tl(III)], M	$\frac{[Tl(OAc)_2^+]}{[Tl(III)]}$	$k_c'^a$	Rel value of k'^a
Ethylene	...	...	...	...	...	0.0302	1
Propylene	...	...	...	...	...	4.60	152
1-Butene	0.78	1.025	1.069	0.023	0.164	4.75	157
cis-2-Butene	0.495	1.05	1.069	0.023	0.275	1.80	60
trans-2-Butene	0.291	1.05	1.069	0.023	0.275	1.06	35
Isobutene	...	...	...	...	...	7×10^3	2.3×10^5

[a] $M^{-1}\,sec^{-1}$.

On the other hand, the plot of $[Tl(OAc)_2^+]/[Tl(OAc)_4^-]$ is linear. This is demonstrated by the close agreement of k'_{exptl} and k'_{calcd} when the relationship $k'_{calcd} = 0.26 + 7 \times 10^3[Tl(OAc)_2^+]/[Tl(III)]$ is used.

The effect of acetic acid concentration on rate was tested by running several isobutene oxidations at two different acid concentrations. The runs with excess acetate were chosen because varying the acetic acid concentration did not significantly change the acetate ion concentration. Thus in Table IV, runs 23 to 27, the acetic acid concentration is 1.0 M, while in runs 28 to 31 it is 0.3 M.

To determine the effect of structure on k_c' the rates of oxidation were measured for 1-butene and *cis*- and *trans*-2-butene under one set of reaction conditions, and the value of k_c' was calculated from the $[Tl(OAc)_2^+]/[Tl(III)]$ ratio for that reaction mixture. Data are given in Table V with the values of k_c' for ethylene, propylene, and isobutene for comparison.

The yields of carbonyl and glycol products for each of the olefins under one set of reaction conditions are given in Table VI. The initial glycol products were shown to be the free glycol rather than acetate esters of the glycol. This distribution of products between glycol and carbonyl products for each olefin is almost identical with that found previously for the oxidation in strong acid.

Table VI. Product Distribution for the Thallic Ion Oxidation of Various Olefins[a]

Olefin	Carbonyl product	Carbonyl product, %	Glycol product,[b] %
Ethylene	Acetaldehyde	45	55
Propylene	Acetone	81	17
1-Butene	Methyl ethyl ketone	75	16
cis-2-Butene	Methyl ethyl ketone	85–90	<0.5
trans-2-Butene	Methy ethyl ketone	85–90	<0.5
Isobutene	Isobutyraldehyde	37	52

[a] $[H_t] = 1.000$ M; $[OAc_t] = 0.942$ M; $[Tl(III)] = 0.114$ M. [b] Glycol product is always that expected from 1,2 addition to a double bond.

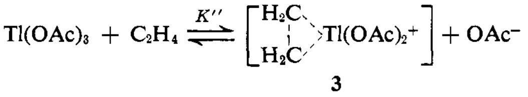
Discussion

Reactive Species. The linear relationship between k' and $[Tl(OAc)_2^+]/[Tl(III)]$ shown in Figure 1 and Tables II–IV would seem to indicate that $Tl(OAc)_2^+$ is the only important reactant in the region where this linear relationship exists. However, this dependence of the rate on the acetate ion concentration could also be explained by two other reaction schemes. The first is represented by

$$Tl(OAc)^{+2} + C_2H_4 + H_2O + OAc^- \overset{K'}{\rightleftharpoons} \underset{\mathbf{2}}{^+AcOTl{-}CH_2{-}CH_2{-}OH} + HOAc \qquad (6)$$

$$\mathbf{2} \xrightarrow[\text{slow}]{k} \text{products} \qquad (7)$$

and the second by



$$Tl(OAc)_3 + C_2H_4 \overset{K''}{\rightleftharpoons} \left[\begin{matrix} H_2C \\ H_2C \end{matrix} \rangle Tl(OAc)_2^+\right] + OAc^- \qquad (8)$$

3

$$\mathbf{3} \xrightarrow[\text{slow}]{k} \text{products} \qquad (9)$$

The rate expression for the first possibility is

$$\text{rate} = k\frac{K'[Tl(OAc)^{+2}][OAc^-][C_2H_4]}{[HOAc]} \qquad (10)$$

This reaction path can be rejected because it predicts a first-order inhibition by [HOAc]. This inhibition is not observed (in Table IV, compare runs 24–27 with runs 28–31).

If the π complex (**3**) is an intermediate which is formed reversibly, there is, of course, no way to distinguish kinetically whether it is formed from ethylene and $Tl(OAc)_2^+$ by loss of water; from ethylene and $Tl(OAc)_3$ by loss of acetate ion; or even from $Tl(OAc)^{+2}$, ethylene, and acetate ion, since all these species are in equilibrium.

We can say that the composition of the activated complex is one ethylene, one Tl(III), and two acetate ions. This kinetic result requires that an intermediate such as **2** is not reversibly formed. However, as discussed previously,[2] the product distribution plus other evidence strongly suggests that an oxythallation adduct (**2**) is involved in the reaction sequence. Therefore, the reaction scheme must be analogous to that proposed in the strong acid system (eq 4 and 5) where Tl^{+3} is replaced by $Tl(OAc)_2^+$ and the intermediate (**1**) contains 0–2 acetate groups attached to the thallium(III).

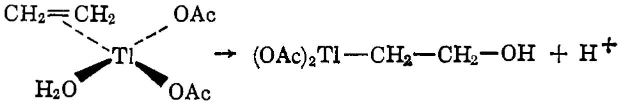
Although the path involving $Tl(OAc)_2^+$ is certainly the most important over most of the range of acetate concentrations used in this study, the positive intercepts for isobutene and propylene, and the deviation of Figure 1 from linearity at lower acetate ion concentrations, indicate that the oxidation by species other than $Tl(OAc)_2^+$ is important at either end of the range of $[OAc^-]$ used in this study. The positive intercepts indicate a reaction which is independent of acetate ion concentration. Therefore, the reactant must be $Tl(OAc)_4^-$, or, alternately, $Tl(OAc)_3$ reacting with ethylene and/or acetate ion.

$$Tl(OAc)_3 + C_2H_4 + OAc^- \longrightarrow (OAc)_3Tl{-}CH_2{-}CH_2{-}OAc \qquad (11)$$

The ratio of rates for this acetate-independent reaction for isobutene and propylene is only 13 while the ratio of k_c' for these two olefins shown in Table V is *ca.* 2000. This indicates that the acetate-independent reaction has much less carbonium ion character in the transition state than the acetate-dependent reaction. This result is not surprising since the acetate-independent reaction involves neutral or negatively charged species. The reaction under these conditions is currently under investigation.

The deviation of Figure 1 from linearity at low acetate ion concentration no doubt results from the oxidation by more reactive Tl^{+3} and $Tl(OAc)^{+2}$ species. In fact, this deviation could very well have been expected at higher acetate ion concentrations. Thus, the value of $K_1K_2K_3K_4$ (β_4) has been estimated to be 2×10^{15}.[10] From the value of K_3K_4 determined from this work, K_1K_2 can be estimated to be 3×10^9. If we assume $K_1/K_2 = K_2/K_3 = K_3/K_4$, we obtain a value of 7×10^4 for K_2, 1.4×10^6 for K_1, and thus a value of *ca.* 10^{10} for K_1K_2. Assuming k_c' for $Tl(OAc)^{+2}$ is $28 \times 10^{-2}\ M^{-1}\ sec^{-1}$ (the value at $[OAc^-]/[Tl(III)] = 1$), the deviation from linearity becomes serious ($k'_{exptl}/k'_{calcd} = 1.25$) at $[OAc^-] = 5 \times 10^{-4}$. Actually the deviation becomes obvious at $[OAc^-] = 7 \times 10^{-5}$. Either k_c' for $Tl(OAc)^{+2}$ is lower or K_2 is higher. It would be interesting to determine K_1 and K_2 so the reactivity of $Tl(OAc)^{+2}$ can be measured.

The reactivity of $Tl(OAc)_3$, although probably higher than that of $Tl(OAc)_4^-$, cannot be more than about 0.05 that of $Tl(OAc)_2^+$, for, if it were any higher, the agreement between k'_{exptl} and k'_{calcd} in Tables II–IV would not be as good as it is. The reason for this difference may well be the large difference in electrophilic power between $Tl(OAc)_2^+$ and $Tl(OAc)_3$. However, the composition of the activated complex would be also consistent with the rate-determining step being the addition of ethylene to the thallium(III)–water in **4**.



4

This insertion would be analogous to that proposed for the oxidation of ethylene by Pd(II) in aqueous solution. In the latter case, ethylene inserts between Pd(II) and a hydroxyl oxygen.[11]

Comparison of the Reactivity of Tl^{+3} and $Tl(OAc)_2^+$. Perhaps the most significant result of this study is the finding that $Tl(OAc)_2^+$ is so similar to Tl^{+3} in reactivity. Despite the difference in charge, Tl^{+3} (at low salt concentrations[9]) is only 18 times more reactive than $Tl(OAc)_2^+$. This result, no doubt, attests to the strong solvation of Tl^{+3} by water. Retardation of rate by solvation explains the strong acceleration of rate of oxidation of ethylene obtained by lowering water activity.[9] Thus, the neutralization of charge by OAc^- in $Tl(OAc)_2^+$ as compared with Tl^{+3} is almost compensated for by the lowering of hydration energy of the ion.

Effect of Olefin Structure on Rate. The effect of olefin structure on k_c', shown in Table V, is almost identical with that previously found in strong acid solution.[1] This similarity is perhaps the most dramatic demonstration of the effect of ionic hydration on rate since it means Tl^{+3} and $Tl(OAc)_2^+$ have about the same amount of carbonium ion character in the transition state despite the difference in charge.

Effect of Olefin Structure on Product Distribution. Also surprising is the close similarity of the distribution of products for the oxidation of the various olefins by $Tl(OAc)_2^+$ shown in Table VI and that previously found for the oxidation by Tl^{+3}.[1] Different leaving groups would be expected to give different distributions of products. This suggests that the acetate groups ionize from II before decomposition so that the leaving groups are identical.

$$^{+(2-n)}(OAc)_nTl{-}CH_2{-}CH_2{-}OH \overset{K}{\rightleftharpoons} nOAc^- + \underset{\mathbf{1}}{^{+2}Tl{-}CH_2{-}CH_2{-}OH} \quad (12)$$

$$\mathbf{1} \xrightarrow{\text{fast}} \text{products}$$

This scheme has been found to be operative for the decomposition of mercury(II) alkyls,[12] and it is known that acetate ions stabilize thallium(III)–oxythallation adducts.[3,13]

The product yields were determined at low free acetate ion concentrations because the reduction of thallic ion is more rapid than at high $[OAc^-]$. Problems of secondary oxidation of the original products by unreacted thallic ion were thus avoided. However, another reason for using low $[OAc^-]$ is that at high $[OAc^-]$ the initial product distribution is somewhat different from that at low $[OAc^-]$. There is evidence that this difference results from formation of stable oxythallation adducts. As mentioned previously, the high $[OAc^-]$ reaction is being investigated.

The methyl ethyl ketone yields reported in Table VI for *cis*- and *trans*-2-butene are higher than those previously found in the strong acid system. The lack of glycol product in both systems implies that methyl ethyl ketone is the only primary product from these olefins in both systems, but, in aqueous acetic acid, secondary oxidation is not as serious as in strong aqueous acid.

Experimental Section

Reagents. Thallic acetate was prepared by dissolving thallic oxide (Fairmount Chemical Co.) in hot acetic acid, filtering hot to remove insolubles, and cooling to precipitate the acetate. Analysis of stock solutions has been described previously.[9] Gases were Phillips Petroleum Co. pure grade. All other chemicals were of reagent grade.

Identification of Products. Since all the products had been identified previously in strong aqueous acid, vapor phase chromatography retention time was used to confirm that the products in aqueous acetic acid were the same as in strong acid solution. The monoacetates and diacetates of the glycols were prepared, and a 12-ft Ucon 75 h column, which separated the glycols from the acetate esters for all the glycols, was used to demonstrate that the initial products were the free glycols.

Analysis of Reaction Mixtures. The analysis of reaction mixtures has been described.[1,9]

Kinetic Runs. The procedures for measuring the rates have been described.[1,11] For isobutene a correction was made for the hydration of isobutene. This correction was made by measuring the rate of isobutene uptake of solutions containing all the ingredients

---

[10] Reference 6, p 4.

[11] P. M. Henry, *J. Am. Chem. Soc.*, **86**, 3246 (1964).

[12] F. R. Jensen and R. J. Ouellette, *ibid.*, **83**, 4476 (1961).

[13] K. C. Pande and S. Winstein, *Tetrahedron Letters*, No. **46**, 3933 (1964).

Table VII. Oxidation of Isobutene at Different Pressures

Pressure, cm	$[H_t]$, M	$[OAc_t]$, M	[Tl(III)], M	k'_{exptl}, M^{-1} sec^{-1}	k'_{calcd}, M^{-1} sec^{-1}	$\frac{[Tl(OAc)_2^+]}{[Tl(III)]}$
401	1.01	1.140	0.0019	0.83	0.83	7.8×10^{-5}
212	1.01	1.140	0.0019	0.89	0.83	7.8×10^{-5}

of reaction mixtures except the thallic ion. For ethylene and propylene this side reaction was insignificant. Determination of olefin solubilities has been described.[11] The order in olefin was determined only for isobutene since the reaction in strong acid solution had previously been demonstrated to be first order in olefin.[1,9] A constant volume reactor[11] was used for these measurements. The rate was measured by change in pressure. Since the concentration of Tl(III) was small (*ca.* 10^{-3} M), the change in pressure was small compared to the total pressure, so the pressure was assumed to be constant and the data were plotted as a first-order reaction. The second-order rate constant was then calculated from the solubility at that pressure. Data on the two runs at lower pressures are given in Table VII.

Measurement of Equilibrium Constants. The pH of the solutions was measured with a Beckman pH meter. Readings tended to drift with time, probably because of diffusion of chloride ion from the saturated calomel electrode into the solution. Thus, the first reading on a freshly prepared solution was taken as the correct pH reading.

Acknowledgment. The author gratefully acknowledges helpful discussions with Dr. H. G. Tennent and Professors M. Kilpatrick and S. Winstein. The author is also grateful for the assistance of Mr. John Jackson with experimental work and Mr. K. Horowitz of the Mathematics Group at the Hercules Research Center for writing the program for the computer calculations.

Electron Donor–Acceptor Interactions of Molecular Iodine with Olefins

R. J. Cvetanović,[1] F. J. Duncan,[2] W. E. Falconer,[3] and W. A. Sunder[3]

Joint Contribution from Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey, and Division of Applied Chemistry, National Research Council of Canada, Ottawa, Canada. *Received September 15, 1965*

Abstract: A study of the interactions of olefins and related hydrocarbons with molecular iodine has been made using a gas–solid chromatographic technique. Relative equilibrium constants for olefin–iodine complexes have been determined and are compared with the corresponding equilibrium constants for silver nitrate–olefin complexes. A pronounced inverse secondary deuterium istope effect on complex formation has been observed.

Molecular iodine interacts with molecules containing π-electron systems to form weakly bonded association products which can be described as electron donor–acceptor complexes.[4,5] Such complexes are characterized by strong absorption bands in the ultraviolet, commonly called "charge-transfer bands." According to the theory of Mulliken and co-workers,[6–8] the charge-transfer absorption maximum, λ_{max}, is a function of the vertical ionization potential of the donor, I_D^V, the vertical electron affinity of the acceptor, E_A^V (1.7 ev for iodine),[9] and the interaction and resonance energy differences between ground and dative states of the complex. The binding energies of molecular compounds are small relative to $I_D^V - E_A^V$, and therefore λ_{max} itself does not provide a suitable measure of complex stability. So far, the extinction coefficients or integrated intensities have not been accurately measured and correlated with the thermodynamic equilibrium constant for complex formation.

Complexing equilibrium constants were first obtained from spectrophotometric data by Benesi and Hildebrand[10] from measurements of extinction coefficients for solutions of varying donor and acceptor concentrations in an "inert" solvent. Haymann[11] has recently discussed the reliability of spectrophotometric methods in comparison with the partition method. Neither method has been broadly applied to complexes of iodine with the simpler olefins.

Equilibrium constants have been determined for Ag^+–olefin complexes in ethylene glycol solution using gas chromatographic methods.[12–14] Solid 1,3,5-trinitrobenzene–olefin complexes have also been investigated chromatographically,[15] and, although equilib-

---

(1) National Research Council.

(2) National Research Council Postdoctoral Fellow, 1961–1963.

(3) Bell Telephone Laboratories.

(4) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961.

(5) L. J. Andrews and R. M. Keefer, *Advan. Inorg. Chem. Radiochem.*, 3, 91 (1961).

(6) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

(7) R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

(8) L. E. Orgel and R. S. Mulliken, *J. Am. Chem. Soc.*, **79**, 4839 (1957).

(9) W. B. Person, *J. Chem. Phys.*, **38**, 109 (1963).

(10) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

(11) H. J. G. Haymann, *J. Chem. Phys.*, **37**, 2290 (1962).

(12) M. A. Muhs and F. T. Weiss, *J. Am. Chem. Soc.*, **84**, 4697 (1962).

(13) E. Gil-Av and J. Herling, *J. Phys. Chem.*, **66**, 1208 (1962).

(14) R. J. Cvetanović, F. J. Duncan, W. E. Falconer, and R. S. Irwin, *J. Am. Chem. Soc.*, **87**, 1827 (1965).