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## Oxidation of Olefins by Palladium(II). II. Effect of Structure on Rate in Aqueous Solution[1]

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*Contribution from the Research Center, Hercules Powder Company, Wilmington, Delaware 19899.* *Received November 24, 1965*

**Abstract:** The kinetics of the oxidation of propylene to acetone and of *cis*- and *trans*-2-butene and 1-butene to methyl ethyl ketone were found to be identical with the kinetics previously found for ethylene, *i.e.*, $-\mathrm{d}[\text{olefin}]/\mathrm{d}t = k'K_1[PdCl_4^{-2}][\text{olefin}]/[Cl^-]^2[H^+]$, where $K_1$ is the equilibrium constant for $\pi$-complex formation between the olefin and palladium(II) chloride in water. The change in $k'$ with olefin structure was in the order ethylene > *trans*-2-butene ≅ propylene > *cis*-2-butene ≅ 1-butene, but the total range is only a factor of 6. Such a small change indicates that there is little carbonium ion character in the transition state for oxypalladation, the rate-determining step in the oxidation. The mechanism of oxypalladation is compared with that for oxymercuration and oxythallation. The trend of $K_1$ with olefin structure was ethylene > propylene > 1-butene > *cis*-2-butene > *trans*-2-butene. This is the same order previously found for $\pi$-complex formation with Ag(I).

The rate expression for the aqueous palladium(II) chloride oxidation of ethylene to acetaldehyde is[1]

$$\frac{-\mathrm{d}[C_2H_4]}{\mathrm{d}t} = \frac{k'K_1[PdCl_4^{-2}][C_2H_4]}{[Cl^-]^2[H^+]} \qquad (1)$$

where $K_1$ is the equilibrium constant for the formation of a palladium(II)–ethylene $\pi$ complex.

$$PdCl_4^{-2} + C_2H_4 \overset{K_1}{\rightleftharpoons} \underset{\text{I}}{(PdCl_3C_2H_4)^-} + Cl^- \qquad (2)$$

The deuterium isotope effects indicated that this rate expression was best fitted by a mechanism in which the rate-determining step is the insertion of ethylene into a Pd–OH bond to give an oxypalladation adduct, the decomposition of the adduct to acetaldehyde being fast.

This paper describes a study of the effect of olefin structure on $k'$, knowledge of which should provide insight into the nature of the insertion reaction.

The kinetics of the oxidation of propylene to acetone have been reported.[2] However, no values of $K_1$ were determined, so the effect of olefin structure on $\pi$-complex formation was not separated from the effect of olefin structure on the decomposition of the $\pi$ complex.

### Results

The high-efficiency gas–liquid mixing reactor used previously to study the ethylene oxidation[1] was employed in this study. As with ethylene, a very rapid initial olefin absorption took place, followed by a slower olefin absorption. The initial olefin uptake was greater than that required to saturate the solution with gas. Assuming this net initial uptake resulted from an equilibrium analogous to that represented by eq 2, values of $K_1$ which remained constant with changing $[Cl^-]$ could be calculated for all the olefin studies. The initial isobutene uptake was, within experimental error, the same as the solubility, so no values of $K_1$ could be calculated for this olefin. All rate measurements were made at 25°.

By varying $[Cl^-]$ and $[H^+]$ the form of the rate expression for the slower olefin uptake, which resulted in the deposition of palladium metal, was shown to be identical with that found for ethylene (eq 1). The values of $K_1$ and $k'$ are listed in Table I. The value for ethylene is included for comparison. Isobutene is not included, since $K_1$ was too small to be measured and thus $k'$

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[1] Paper I: P. M. Henry, *J. Am. Chem. Soc.*, **86**, 3246 (1964).

[2] T. Dozono and T. Shiba, *Bull. Japan Petrol. Inst.*, **5**, 8 (1963).

could not be calculated. Moreover, because of the slowness of the oxidation and the complication of hydration, the over-all kinetic expression for the isobutene oxidation was not determined. Thus, it may be different from that found for the other olefins (eq 1).[3]

Table I. Values of $K_1$ and $k'$[a]

| Olefin | $K_1$[b] | $k'$,[c] $M^2$ sec$^{-1}$ $\times 10^5$ | Olefin solubility, m$M$ |
|---|---|---|---|
| Ethylene | 17.4 | 20.3 | 2.67 |
| Propylene | 14.5 ± 1.5 | 6.5 ± 0.09 | 2.62 |
| *cis*-2-Butene | 8.7 ± 0.5 | 3.5 ± 0.4 | 3.92 |
| *trans*-2-Butene | 4.5 ± 0.5 | 7.5 ± 0.9 | 3.74 |
| 1-Butene | 11.2 ± 1.1 | 3.5 ± 0.4 | 2.59 |

[a] $\mu$ = 2.0 (adjusted with $NaClO_4$). [b] Average of at least four runs. [c] Average of at least eight runs.

The values of $K_1$ and $k'$ remained constant for reaction mixtures in which $[Cl^-] > 0.1\ M$. At lower concentrations the values of $K$ and $k'$ drifted appreciably toward lower values. This variation probably results from the formation of $\pi$-complex dimers. A change in the rate law has been reported for the oxidation of ethylene with aqueous palladium(II) chloride at low chloride ion concentrations.[5]

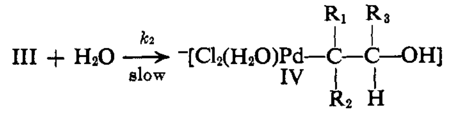
No determination of oxidation products was made, since propylene has been reported to give acetone as the main product and the butenes have been reported to give methyl ethyl ketone as the main product.[4]

## Discussion

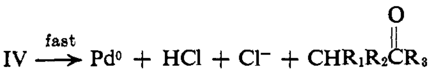
Based on arguments presented previously, the mechanism proposed for the oxidation is given by eq 3 to 6 ($R = H, CH_3$, or $C_2H_5$).

$$\mathrm{I} + H_2O \overset{K_2}{\rightleftharpoons} \underset{\mathrm{II}}{[PdCl_2(H_2O)olefin]} + Cl^- \qquad (3)$$

$$\mathrm{II} + H_2O \overset{K_3}{\rightleftharpoons} \underset{\mathrm{III}}{[PdCl_2(OH)olefin]^-} + H_3O^+ \qquad (4)$$



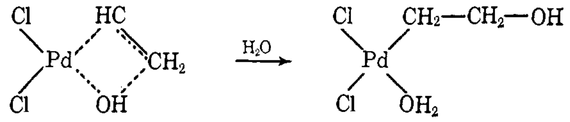
$$\mathrm{III} + H_2O \xrightarrow[\text{slow}]{k_2} {}^-[Cl_2(H_2O)\underset{\mathrm{IV}}{Pd}—\underset{R_2}{\overset{R_1}{C}}—\underset{H}{\overset{R_3}{C}}—OH] \qquad (5)$$



$$\mathrm{IV} \xrightarrow{\text{fast}} Pd^0 + HCl + Cl^- + CHR_1R_2\overset{\overset{O}{\|}}{C}R_3 \qquad (6)$$

Since the differences in $\pi$-complex formation ($K_1$) are separated out in obtaining $k'$, the effect of structure on rate must be operative in eq 3, 4, and 5. Certainly, olefin structure would not be expected to have any large effect on $K_2$ or $K_3$. In any case, the inductive effects would tend to cancel out since the species dissociating from the complex are of different charges in eq 3 and 4 and the effects on $K_2$ and $K_3$ would be of opposite signs. Thus, any large effect of olefin structure on rate would be reflected by changes in $k_2$.

The actual effect of olefin structure on rate shown in Table I is small, so the fact that a large acceleration of rate is not observed with increasing substitution means that the insertion reaction has little carbonium ion character in the transition state. This result is consistent with a concerted nonpolar four-center addition for the rate-determining oxypalladation step of the oxidation.



An oxymetallation adduct intermediate has also been suggested as an intermediate in the thallic ion oxidation of olefins,[6-8] and kinetic evidence[8] indicates its formation is the rate-determining step. Thus, since the formation of the oxypalladation adduct is the rate-determining step of the oxidation of olefins by Pd(II), we can compare the mechanism of oxythallation and oxypalladation with oxymercuration in which stable adducts are formed.[9]

The rate law for oxymercuration[10] and oxythallation[8] contains no term involving proton inhibition, as does oxypalladation, so the kinetic expression for these first two oxymetallations is[11]

$$\frac{d[C_2H_4]}{dt} = k_2[M^{+n}][C_2H_4]$$

Moreover the effect of olefin structure on these two reactions is quite different from that found for oxypalladation. Oxythallation is greatly accelerated by substitution on the vinyl carbons, propylene reacting at about 150 times the rate of ethylene and isobutene at about 1000 times the rate of propylene.[12] Oxymercuration has the same qualitative effect of structure or rate as oxythallation[13] implying that the mechanisms of these two oxymetallations are similar, a result which is not surprising since the two metal ions are isoelectronic.

Therefore, while oxymercuration and oxythallation apparently take place by rearrangement of a metal–olefin $\pi$ complex to an incipient carbonium ion, which then reacts with water, oxypalladation occurs by insertion of the olefin moiety of a metal–$\pi$ complex into a Pd–OH bond. These differences in mechanism may reflect either stronger $\pi$-complex formation with palladium(II) or else the higher positive charge on the metal ion in oxymercuration and oxythallation.

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(3) Even if the values of $K_1$ and $k'$ were determined, the data would be difficult to interpret since isobutene does not give the same products (ketones) as the other olefins studied.[4] Therefore the mechanism of isobutene oxidation may differ from that proposed for the oxidation of the olefins in Table I.

(4) J. Smidt, *et al.*, *Angew. Chem.*, **71**, 176 (1959).

(5) M. N. Vargaftik, I. I. Moiseev, and Ya. K. Sirkin, *Dokl. Akad. Nauk SSSR*, **147**, 399 (1962).

(6) H. J. Kabbe, *Ann.*, **656**, 204 (1962).

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

(8) P. M. Henry, *J. Am. Chem. Soc.*, **87**, 990 (1965).

(9) J. Chatt, *Chem. Rev.*, **48**, 7 (1951).

(10) P. Brandt and O. Plum, *Acta Chem. Scand.*, **7**, 97 (1953).

(11) Oxythallation or oxymercuration does not occur in an aqueous chloride solution because of complexing of the metal ion by $Cl^-$. On the other hand, the Pd(II) oxidation is studied in a chloride-containing system because, in a chloride-free system, the oxidation is very fast. Thus, the three reactions are not being compared under exactly the same conditions.

(12) P. M. Henry, *J. Am. Chem. Soc.*, **87**, 4423 (1965).

(13) In a previous paper,[12] the author erroneously assumed, on the basis of rate measurements with propylene in strongly complexing media,[14] that the rate of oxymercuration is insensitive to olefin structure. Professors J. Halpern and M. Kreevoy have kindly informed the author that they have data indicating that in strong acid solution oxymercuration qualitatively has the same effect of structure on rate as oxythallation.

(14) E. R. Allen, J. Cartlidge, M. M. Taylor, and C. F. H. Tipper, *J. Phys. Chem.*, **63**, 1442 (1959).

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 $\sigma$ 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 $\pi$-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 $\pi$-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.

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

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

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*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).