Oxidation of Olefins by Palladium(II). IV. Effect of Palladium(II) Chloride Concentration on Rate in Aqueous Solution[1a]

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Abstract: The rates of oxidation of ethylene and propylene were measured in the palladium(II) chloride concentration range 0.01–0.2 M and the sodium chloride concentration range 0.2–0.5 M. At an ionic strength of 2 adjusted with $NaClO_4$ and $[HClO_4]$ = 0.2 M, the rate data were accurately fitted by the rate expression: $-d[olefin]/dt = k_1[PdCl_4{}^{2-}][olefin]/[H^+][Cl^-]^2$. This result is in contrast to a previous report by Moiseev and coworkers of a second term of the form, $k_2[PdCl_4{}^{2-}]^2[olefin]/[H^+][Cl^-]^3$, under slightly different reaction conditions than those used in the present work. It is possible that the second-order term found in the previous work resulted from a systematic deviation in the calculation of rate constants from the experimental data.
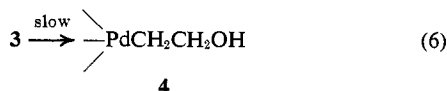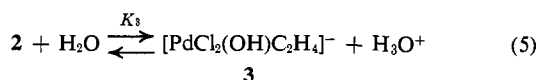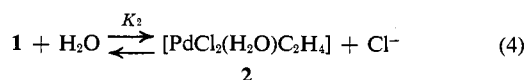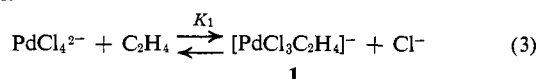
The kinetics of the aqueous oxidation of olefins by palladium(II) chloride has been studied by several

$$PdCl_4{}^{2-} + RCH{=}CHR' + H_2O \longrightarrow$$

$$Pd(0) + R\overset{\overset{\text{O}}{\|}}{C}CH_2R' + 2HCl + 2Cl^- \quad (1)$$
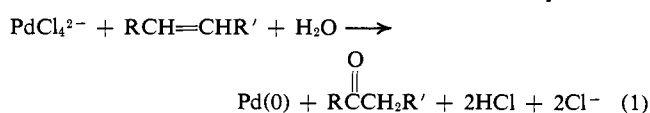
workers[2-9] and there is general agreement that at low Pd(II) concentrations (<0.04 M) the rate equation is given by eq 2.

$$\frac{-d[olefin]}{dt} = \frac{k_1[PdCl_4{}^{2-}][olefin]}{[Cl^-]^2[H^+]} \quad (2)$$

On the basis of the kinetic studies plus other results, the following reaction sequence for the oxidation of ethylene is generally accepted as the mechanism for this oxidation.

$$PdCl_4{}^{2-} + C_2H_4 \underset{K_1}{\rightleftharpoons} [PdCl_3C_2H_4]^- + Cl^- \quad (3)$$
$$\mathbf{1}$$

$$\mathbf{1} + H_2O \underset{K_2}{\rightleftharpoons} [PdCl_2(H_2O)C_2H_4] + Cl^- \quad (4)$$
$$\mathbf{2}$$

$$\mathbf{2} + H_2O \underset{K_3}{\rightleftharpoons} [PdCl_2(OH)C_2H_4]^- + H_3O^+ \quad (5)$$
$$\mathbf{3}$$

$$\mathbf{3} \xoverset{\text{slow}}{\longrightarrow} \diagdown\diagup PdCH_2CH_2OH \quad (6)$$
$$\mathbf{4}$$

$$\mathbf{4} \xoverset{\text{fast}}{\longrightarrow} \text{products} \quad (7)$$

Other olefins are oxidized by analogous mechanisms.

The equilibrium corresponding to eq 3 has been detected and values of K_1 have been determined for several olefins by Moiseev and coworkers[10,11] and the author.[8] Moiseev and coworkers also claimed to have detected the equilibrium corresponding to eq 4 under certain reaction conditions. Equation 2 can thus be written

$$-d[C_2H_4]/dt = k'[\mathbf{1}]/[Cl^-][H^+] \quad (8)$$

where $k'K_1 = k_1$ in eq 2.

More recently studies of the oxidation of ethylene, propylene, and 1-butene at higher Pd(II) concentrations indicated a higher order term in [Pd(II)]. The complete rate expression[12] over a wide range of [Pd(II)] and [Cl$^-$] was suggested to be

$$w = \frac{-d[olefin]}{dt} = k_1\frac{[PdCl_4{}^{2-}][olefin]}{[H^+][Cl^-]^2} + k_2\frac{[PdCl_4{}^{2-}]^2[olefin]}{[H^+][Cl^-]^3} \quad (9)$$

Using ethylene as an example the rate expression was interpreted in terms of a second route shown in eq 10–12 (eq 3–5 are believed to be common to both routes).

An alternate proposal[12] is that a reactive binuclear complex, $Pd_2Cl_6{}^{2-}$, is formed which is more reactive than $PdCl_4{}^{2-}$.

A study of the isomerization of olefins in aqueous solution gave similar kinetics which were also interpreted in terms of Pd(I) species such as those shown in eq 12.[13]
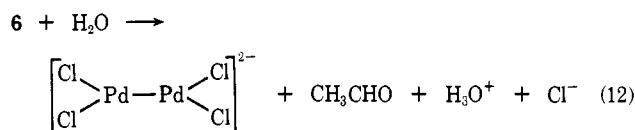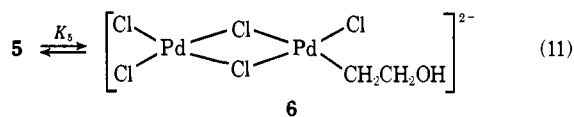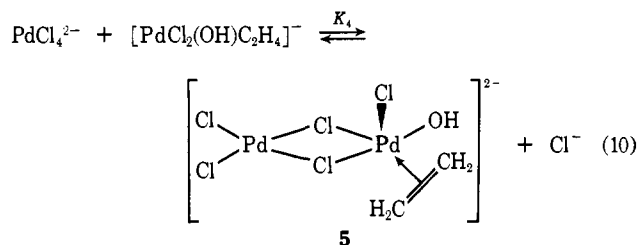
Whatever the mechanism, the finding of the second term in the rate expression is of considerable importance in Pd(II) chemistry since it indicates reaction paths, not previously suspected, which could influence mechanistic

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$$PdCl_4{}^{2-} + [PdCl_2(OH)C_2H_4]^- \overset{K_4}{\rightleftharpoons}$$

$$5 \quad (10)$$

$$5 \overset{K_5}{\rightleftharpoons}$$

$$6 \quad (11)$$

$$6 + H_2O \longrightarrow$$

$$+ CH_3CHO + H_3O^+ + Cl^- \quad (12)$$

interpretation in all Pd(II) chemistry. Thus it seems worthwhile to check these results by a different experimental procedure.

The interpretation of experimental data by any experimental method is complicated by the fact that the value of K_1 in eq 3 is large enough that appreciable amounts of 1 are formed under most experimental conditions.

Moiseev and coworkers[3] used an experimental procedure which did not involve a gas phase and used quinone to reoxidize the Pd(0) to Pd(II) while the author uses experimental procedures which do involve a gas phase. Errors in the values of K_1 assumed for the equilibrium of eq 3 will affect the calculated values of the rate constant in eq 2 or 8 in quite a different manner for the two experimental procedures.

Results

All rates were measured at 25° using creased flask reactors[8] and gas burets to measure the rate of olefin uptake. To prevent complications resulting from formation of Pd(0) during the course of a run, quinone was used to reoxidize the Pd(0) to Pd(II). All runs were 0.2 M in HClO$_4$ and the ionic strength was adjusted to 2 with NaClO$_4$. The data for ethylene are summarized in Table I. Values of π-complex concentration, [1], and uncomplexed chloride, [Cl$^-$], are readily calculated from the amounts of Na$_2$PdCl$_4$ and NaCl added assuming K_1 for eq 3 is 17.4.[8a]

Similar data for propylene are given in Table II assuming a value of 14.5 for the propylene π-complex formation constant.[8b]

Table I. Rates of Oxidation of Ethylene at Various Na$_2$PdCl$_4$ and NaCl Concentrations[a]

[Na$_2$-PdCl$_4$], M	[NaCl], M	[1],[b] $M \times 10^3$	[Cl$^-$],[b] M	k_{obsd}, M sec^{-1} $\times$ 10^5	k',[c] M^2 sec^{-1} $\times$ 10^4
0.01	0.2	1.9	0.202	1.07	2.26
0.05	0.2	9.3	0.209	4.81	2.15
0.10	0.2	18	0.218	9.53	2.3
0.20	0.2	34	0.234	14.9	2.05
0.01	0.3	1.3	0.301	0.436	1.98
0.05	0.3	6.5	0.306	2.48	2.34
0.10	0.3	13.0	0.313	3.79	1.82
0.20	0.3	25.0	0.325	8.4	2.19
0.01	0.4	0.89	0.401	0.311	2.79
0.05	0.4	5.1	0.405	1.70	2.70
0.10	0.4	10.0	0.410	3.22	2.63
0.20	0.4	20.0	0.420	6.11	2.57
0.01	0.5	0.86	0.501	0.244	2.83
0.05	0.5	4.3	0.504	1.1	2.58
0.10	0.5	8.4	0.508	2.09	2.53
0.20	0.5	17.2	0.517	3.79	2.20

[a] All runs at 25° under 1 atm of ethylene pressure. [b] Calculated assuming K_1 for eq 3 = 17.4, and [C$_2$H$_4$] = 2.7 × 10^{-3} M. [Cl$^-$] = uncomplexed chloride. [c] $k' = k_{obsd}(0.2)[Cl^-]/[1]$.

Table II. Rates of Oxidation of Propylene at Various Na$_2$PdCl$_4$ and NaCl Concentrations[a]

[Na-PdCl$_4$], M	[NaCl], M	[1'],[b] $M \times 10^3$	[Cl$^-$],[b] M	k_{obsd}, M sec^{-1} $\times$ 10^5	k',[c] M^2 sec^{-1} $\times$ 10^4
0.01	0.2	1.6	0.202	0.576[d]	1.44
0.05	0.2	7.7	0.208	2.61	1.41
0.10	0.2	15.0	0.215	4.83	1.39
0.20	0.2	28.5	0.229	10.7	1.72
0.01	0.3	1.1	0.301	0.478[d]	2.57
0.05	0.3	5.5	0.306	1.41	1.56
0.10	0.3	10.9	0.311	2.22	1.27
0.20	0.3	21.1	0.321	4.65	1.41
0.01	0.4	0.87	0.401	0.155[d]	1.43
0.05	0.4	4.4	0.404	0.753	1.40
0.10	0.4	8.7	0.409	1.88	1.76
0.20	0.4	16.7	0.417	2.95	1.47
0.01	0.5	0.76	0.501	0.166[d]	2.15
0.05	0.5	3.5	0.504	0.527	1.51
0.10	0.5	7.0	0.507	1.09	1.58
0.20	0.5	13.8	0.514	2.08	1.55

[a] All runs at 25° under 1 atm of propylene pressure. [b] [1] is corresponding π complex if in eq 3 propylene replaces ethylene. These values calculated assuming K_1 = 14.5 for propylene equilibrium and [C$_3$H$_6$] = 2.62 × 10^{-3} M. [Cl$^-$] = uncomplexed chloride. [c] $k' = k_{obsd}(0.2)[Cl^-]/[1]$. [d] Rate adjusted for a side reaction which consumed propylene but was not Pd(II) catalyzed. Thus, these values are less accurate than the others.

To determine if diffusional effects were important, some runs were made using one-half the ordinary volume of reaction mixture; rates were unaffected.

Discussion

The value of k' does not appear to show any systematic variation with Pd(II) concentration as would be expected if the complete rate expression were given by eq 9. However, before reaching any conclusions it must be determined if the variations expected are outside of the variation of rate constants resulting from experimental error. Moiseev and coworkers[12] studied their kinetics at 25° at an ionic strength adjusted to 3.0 with LiClO$_4$. They found k_1 to be 1.13 × 10^{-3} M^2 sec^{-1} and k_2 to be 3.9 × 10^{-3} M^2 sec^{-1}. Under the present reaction conditions, k_1 (= $k'K_1$) was 3.8 × 10^{-3} M^2 sec^{-1}. Assuming the ratio of k_1/k_2 is the same for both reaction conditions the value of k_2 under the reaction conditions of this paper would be 1.31 × 10^{-2} M^2 sec^{-1}. Using these values of k_1 and k_2 we can calculate expected values of k_{obsd} under the present reaction conditions assuming eq 9 is operative. Results at [NaCl] = 0.2 and 0.5 M are listed in Table III. Also included are the calculated values of k_{obsd} if k_2 did not change with reaction conditions and thus has the value 3.9 × 10^{-3} M^2 sec^{-1}.

In the case of propylene the reported[12] value of k_1 was 3.45 × 10^{-4} M^2 sec^{-1} and k_2 was 2.52 × 10^{-3} M^2 sec^{-1}. The corresponding value of k_1 in this work is

Table III. Comparison of Experimental and Calculated Values of k_{obsd} for the Ethylene Oxidation[a]

[Na₂PdCl₄], M	[NaCl], M	Exptl k_{obsd}, M sec⁻¹ × 10⁵	($k_2 = 1.31$ × 10⁻² M^2 sec⁻¹/calcd k_{obsd}), M sec⁻¹ × 10⁵	($k_2 = 3.9$ × 10⁻³ M^2 sec⁻¹/calcd k_{obsd}), M sec⁻¹ × 10⁵
0.01	0.2	1.07	1.15	1.05
0.05	0.2	4.8	7.9	5.7
0.1	0.2	9.5	20.2	12.8
0.2	0.2	14.9	52.9	26.6
0.01	0.5	0.24	0.20	0.19
0.05	0.5	1.1	1.3	1.0
0.1	0.5	2.1	2.9	2.1
0.2	0.5	3.8	7.6	4.7

[a] Values calculated assuming rate expression of eq 9 and k_1 = 3.8 × 10⁻³ M^2 sec⁻¹. [PdCl₄²⁻] = [Na₂PdCl₄] − [1]; [H⁺] = 0.2 M. [C₂H₄] = 2.67 × 10⁻³ M and [Cl⁻] is obtained from Table II.

2.05 × 10⁻³ M^2 sec⁻¹. Once again assuming that either k_2 changes in the same fashion as k_1 or does not change in going from the reaction conditions of Moiseev and coworkers to those of this work, values of k_{obsd} can be calculated. Results of [NaCl] = 0.2 and 0.5 M are listed in Table IV. The first assumption gives k_2 a value of 1.5 × 10⁻² M^2 sec⁻¹.

Table IV. Comparison of Experimental and Calculated Values of k_{obsd} for the Propylene Oxidation[a]

[Na₂PdCl₄], M	[NaCl], M	Exptl k_{obsd}, M sec⁻¹ × 10⁵	($k_2 = 1.5$ × 10⁻² M^2 sec⁻¹/calcd k_{obsd}), M sec⁻¹ × 10⁵	($k_2 = 2.52$ × 10⁻³ M^2 sec⁻¹/calcd k_{obsd}), M sec⁻¹ × 10⁵
0.01	0.2	0.58	0.73	0.59
0.05	0.2	2.6	6.5	3.3
0.10	0.2	4.8	19.3	7.4
0.20	0.2	10.7	57.0	17.1
0.01	0.5	0.17	0.11	0.10
0.05	0.5	0.53	0.83	0.55
0.10	0.5	1.09	2.3	1.19
0.20	0.5	2.1	6.8	2.7

[a] Values calculated assuming rate expression eq 9 and K_1 = 2.05 × 10⁻³ M^2 sec⁻¹. [PdCl²⁻] = [Na₂PdCl₄] − [1]; [H⁺] = 0.2 M; [C₃H₆] = 2.62 × 10⁻³ M and [Cl⁻] is obtained from Table II.

The results with ethylene indicate that even at high chloride the second reaction path would be detected if k_2 = 1.31 × 10⁻² M^2 sec⁻¹. If k_2 = 3.9 × 10⁻³ this path would still be outside experimental variation at [Na₂PdCl₄] = 0.2 M and [NaCl] = 0.2 M. The difference between calculated and observed k_{obsd} values are even larger for propylene because of the larger spread between k_1 and k_2. Also the experimental variation in the propylene runs is less than with ethylene.

Differences in methods of measuring values of the equilibrium and rate constants between the two systems could explain the discrepancy. The author previously measured values of K_1 under the reaction conditions using a high efficiency gas–liquid mixer. The gas uptake was measured using a gas buret. In this system the gas uptake due to solubility and complex formation *via* eq 3 could be measured before any appreciable reaction could take place. Moiseev and coworkers measured equilibrium constants at acid and chloride concentrations higher than those normally used to study the

kinetics of the olefin oxidation. Under these conditions the olefin oxidation was slow enough to permit determination of equilibrium constants without the side reaction of olefin oxidation. Olefin uptake was also measured by gas burets.

The kinetics measurements of Moiseev and coworkers were carried out in the absence of a gas phase using quinone to reoxidize the Pd(0) back to Pd(II). The amount of olefin oxidized was determined by the amount of hydroquinone formed as measured by the potential of the quinone–hydroquinone couple. The Pd(II) concentration range was the same as in the present work. The olefin concentration range used was 3 × 10⁻³–2 × 10⁻⁵ M.

As mentioned previously, rates of olefin oxidation in the present work measured by olefin concentrations were those of a saturated solution at 1 atm olefin pressure (*ca.* 10⁻³ M) gas uptake using gas burets.

Since the system of Moiseev and coworkers did not contain a gas phase it was not subject to mass transfer control effects. The present system is subject to the rate of oxidation being limited by the transfer of olefin from gas to liquid phase. In fact, under some reaction conditions, it was necessary to use a high efficiency gas–liquid agitator to avoid this complication. This one experimental complication which could result in k_2 not being detected in the present work is mass transfer control of the olefin uptake which would cancel out any increase in rate resulting from the k_2 term. However, this is a very unlikely possibility for several reasons. First altering the volume of the reaction mixture did not affect the rate as would be expected for a mass transfer controlled reaction. Second, rates much faster than those measured in this study have previously[14] been measured by the same technique. Third, it would indeed be fortuitous if mass transfer effects almost exactly canceled out increases in rate for the k_2 term for two different olefins for all the runs in Tables I and II.

There appear to be no other major experimental differences between the present work and that of Moiseev and coworkers which could explain the failure of the present work to detect the k_2 term. Thus, although one difference between our present work and previous work is the use of quinone to reoxidize the Pd(0) to Pd(II), Moiseev and coworkers also used quinone and the agreement in rates between the two methods of measurement at low Pd(II) is satisfactory. In addition, the k' for ethylene in this work is almost exactly the same as in our previous work not employing quinone.[8a] The value of k' for propylene is somewhat higher than found previously[8b] but, at the low Pd(II) concentrations used in the prior work, the rate of propylene oxidation is difficult to obtain accurately because of the side reaction of hydration of the propylene. Thus, the present value should be the more accurate one.

Moiseev and coworkers[3b] also corrected for dissociation of PdCl₁²⁻ into PdCl₃(H₂O)⁻ and Cl⁻ but even at the lowest [Cl⁻] and highest Na₂PdCl₁, this is a minor correction.

Thus, it appears that for some unknown reason either k_2 is considerably lower than the reaction conditions of this work than under the conditions of Moiseev and coworkers or else the k_2 term in Moiseev's work arose from some systematic deviation in the calculation

(14) P. M. Henry, *J. Amer. Chem. Soc.*, **87**, 990 (1965).

of k_1 in eq 2 from the experimental rate constant. The author believes that the latter answer is a very likely possibility.

In calculating the values of k_1 and k_2 in eq 9, the concentrations of all the reactants except the free olefin concentration, [olefin], are known accurately because they do not differ significantly from the quantities added. However, the value of [olefin] must be calculated from the total olefin concentration, [olefin]$_\Sigma$, using eq 3.[3] Errors in K_1 would thus give errors[15] in calculated values of [olefin].

To determine what type of systematic deviation would give eq 9, assume eq 2 is the correct rate expression. Thus since the rate w is known accurately, we have

$$w = k_1 \frac{[PdCl_4{}^{2-}][olefin]_A}{[H^+][Cl]^2} + k_2 \frac{[PdCl_4{}^{2-}]^2[olefin]_A}{[H^+][Cl]^3} = \frac{k_1[PdCl_4{}^{2-}][olefin]}{[H^+][Cl]^2} \quad (13)$$

where [olefin]$_A$ is the incorrect apparent value of the olefin concentration calculated using an incorrect value of K_1. Dividing the equation by the right-hand side and rearranging gives eq 14. The type of sys-

$$\frac{[olefin]}{[olefin]_A} = 1 + \frac{k_1[PdCl_4{}^{2-}]}{k_2[Cl^-]} \quad (14)$$

tematic deviation on the right hand of eq 14 in the ratio of [olefin]/[olefin]$_A$ would then lead to an apparent rate expression of the form of eq 9. An error in K_1 in eq 3 could lead to this type of deviation as demonstrated by the following line of reasoning. The equilibrium expression for this equation is shown in eq 15. Re-

$$K_1 = \frac{[PdCl_3(olefin)^-][Cl^-]}{[olefin][PdCl_4{}^{2-}]} = \frac{[PdCl_3(olefin)^-][Cl^-]}{([olefin]_\Sigma - [PdCl_3(olefin)^-])[PdCl_4{}^{2-}]} \quad (15)$$

arranging gives eq 16. [Olefin] is then obtained as

$$[PdCl_3(olefin)^-] = \frac{K_1[olefin]_\Sigma[PdCl_4{}^{2-}]}{[Cl^-] + K_1[PdCl_4{}^{2-}]} \quad (16)$$

shown in eq 17.

$$[olefin] = [olefin]_\Sigma - [PdCl_3(olefin)^-] = [olefin]_\Sigma \left(\frac{1}{1 + \frac{K_1[PdCl_4{}^{2-}]}{[Cl^-]}} \right) \quad (17)$$

Now assume a correct equilibrium constant, K_1, to give [olefin] and an apparent equilibrium constant, K_1', to give an apparent olefin concentration, [olefin]$_A$. Thus if we divide eq 17 by a similar equation containing

(15) The concentration of $PdCl_4{}^{2-}$ is considerably higher than [olefin] so complex formation does not appreciably affect its concentration.

$$\frac{[olefin]}{[olefin]_A} = \frac{1 + K_1'[PdCl_4{}^{2-}]/[Cl^-]}{1 + K_1[PdCl_4{}^{2-}]/[Cl^-]} \quad (18)$$

[olefin]$_A$ and K_1', we obtain, after rearranging, eq 18. If K_1' is made equal to $K + \Delta K$ where ΔK is the difference between K_1' and K_1, we obtain eq 19. If $1 \gg K_1[PdCl_4{}^{2-}]/[Cl^-]$, eq 19 reduces exactly to eq 14.

$$\frac{[olefin]}{[olefin]_A} = 1 + \frac{\Delta K[PdCl_4{}^{2-}]/[Cl^-]}{1 + K_1[PdCl_4{}^{2-}]/[Cl^-]} \quad (19)$$

Actually $K_1[PdCl_4{}^{2-}]/[Cl^-] \geqq 1$ under the experimental conditions so eq 14 will not be followed exactly. However, the important point is that the error will still increase with [PdCl$_4^-$] and decrease with [Cl$^-$] so that error in K_1 will tend to suggest a rate expression of the form of eq 9. Any attempt at more detailed analysis of their data does not seem justified since the exact value of K_1 used to calculate [olefin] was not given.[12] A further complication is that under their conditions K_2 in eq 4 was found to have a detectable value and presumably this equilibria was taken into account in calculating [olefin]. Finally, errors in K_1 may be suspected since K_1 was not measured under the reaction conditions.

The present work may suffer also from errors in K_1. However, these will not be systematic errors since the reaction mixture was, at all times, saturated with the olefin. Thus, although one experimental procedure is not intrinsically better than the other, the procedure used in this work does give more reliable results in the high [PdCl$_4^{2-}$] region.

In conclusion, the present work does not definitely exclude the k_2 term under all reaction conditions but it does suggest this term should not be firmly accepted until more work is done.

Experimental Section

Materials. The palladium(II) chloride was purchased from Engehardt, Inc. All other chemicals were of reagent grade.

Reaction Mixtures. They were prepared by mixing the desired weights of PdCl$_2$, NaCl, and quinone and volumes of 5 M HClO$_4$ and 5 M NaClO$_4$ stock solutions, diluting almost to the final volume and heating on a steam bath until all solids were dissolved. They were then cooled to 25° and diluted to the final volume. Volume of reaction mixtures was usually 50 ml although some were 25 ml to test mass transfer effects.

Kinetic Runs. Runs were made in creased flasks. Procedure has been described previously.[8a] In the present work, the reaction mixtures were also 0.2 M in quinone. Since none of the reactant concentrations changed during the course of a run, the reactions were pseudo zero order. Thus, the olefin uptake was linear with time until all the quinone had been reduced. From the rate of linear uptake the rate constant k' of eq 8 can readily be calculated from the known concentration of reactants.