11. R. C. Brown and J. M. Davidson, Homogeneous Catalysis II, Washington (1974), p. 49.
12. A. K. Yatsimirskii, A. D. Ryabov, and I. V. Berezin, Izv. Akad. Nauk SSSR, Ser. Khim., 1764 (1977).
13. A. K. Yatsimirskii, A. D. Ryabov, and I. V. Berezin, Izv. Akad. Nauk SSSR, Ser. Khim., 1493 (1976).

A KINETIC STUDY OF THE OXIDATIONAL DIMERIZATION OF OLEFINS IN THE PRESENCE OF PALLADIUM(II)

2. REACTION OF PALLADIUM ACETATE WITH 1,1-DIPHENYLETHYLENE AND STYRENE

A. K. Yatsimirskii, A. D. Ryabov,
and I. V. Berezin

UDC 541.127:542.97:547.538.141

The oxidational addition of olefins in the presence of palladium acetate

$$2R^1R^2C{=}CH_2 + Pd(OAc)_2 \rightarrow R^1R^2C{=}CHCH{=}CR^1R^2 + Pd(0) + 2HOAc \tag{1}$$

is accompanied by the formation of allyl-type π complexes [1], thus giving rise to complications such as those met in the α-methylstyrene reaction ($R^1 = CH_3$, $R^2 = C_6H_5$). It therefore seemed desirable to study olefin reactions which do not give rise to such complexes. The present paper will report kinetic data on the reactions of $Pd(OAc)_2$ with 1,1-diphenylethylene (DPhE, $R^1 = R^2 = C_6H_5$) and styrene (ST, $R^1 = C_6H_5$, $R^2 = H$).

EXPERIMENTAL

1,1-Diphenylethylene was synthesized by the method of [2]. The styrene used here was redistilled before use. The characteristics of the remaining materials used in the work and the technique of the kinetic experiments have been described in [1]. Identification of the reaction products was made spectrophotometrically, using the following values of the extinction coefficients: for 1,1,4,4-tetraphenylbutadiene, $2.3 \cdot 10^4$ liters/mole·×cm at 345 nm (TPhB, $3.3 \cdot 10^4$ at 345 nm [3]); for 1,4-diphenylbutadiene, $4.8 \cdot 10^4$ liters/mole · cm at 330 nm (DPhB, $5.5 \cdot 10^4$ at 328 nm [4]).

DISCUSSION OF RESULTS

Both reactions proceeded almost stoichiometrically to form the addition products, the respective yields being 92% for TPhB and 83% for DPhB, as calculated from $Pd(OAc)_2$. Measurement of initial rates and application of integral methods showed that the ST oxidation followed a second-order rate equation

$$\frac{d\,[\mathrm{DPhB}]}{dt} = k_2\,[C_6H_5CHCH_2]\,[Pd\,(OAc)_2] \tag{2}$$

over the concentration intervals: 0.25-3.5 moles/liter for ST and 0.005-0.05 mole/liter for $Pd(OAc)_2$, where $[C_6H_5CHCH_2] \gg [Pd(OAc)_2]$.

The kinetic curve for TPhB formation was somewhat more complex, showing a brief induction period at the beginning of the reaction (Fig. 1). Attempts to linearize this curve by plotting the data in semilogarithmic coordinates showed the reaction to be first-order overall of its course beyond a certain initial low-time region. Calculated values of k_{obs}, the pseudo-first-order reaction rate constant, agreed with values calculated from stationary rates through the equation

$$k_{obs} = v_{stat}/[Pd(OAc)_2] \tag{3}$$

v_{stat} being the reaction rate on the stationary section of the curve (Fig. 2). The value of k_{obs} was independent of the $Pd(OAc)_2$ concentration over the interval from 0.02 to 0.06 mole/liter, the reaction being obviously first-

---

M. V. Lomonosov Moscow State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1764-1768, August, 1977. Original article submitted May 31, 1976.

This material is protected by copyright registered in the name of Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for $7.50.

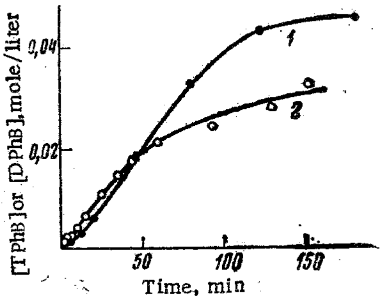


Fig. 1

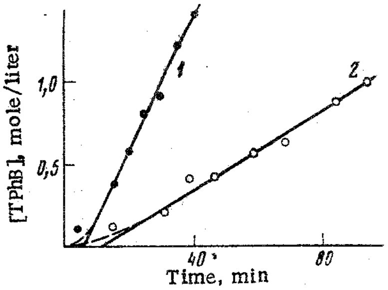


Fig. 2

Fig. 1. Kinetic curves for the formation of TPhB (1) and DPhB (2) n reaction (1). Concentrations (mole/liter): $Pd(OAc)_2$, 0.05; styrene, 0.58; 1, 1-diphenylethylene, 0.38; in glacial HOAc at 70°C.

Fig. 2. Initial segments of kinetic curves for TPhB formation. The slopes of the full-line portions of the curves give values of the v_{stat} of Eq. (3). Concentrations (mole/liter): $Pd(OAc)_2$, 0.012; 1,1-diphenylethylene, 0.13 (1) and 0.03 (2); in glacial HOAc at 70°C.

order with respect to Pd(II). The fact that the k_{obs} vs DPhE concentration plot was not linear (Fig. 3) could not have been due to the change in medium (1 mole/liter DPhE is roughly 20 vol. %) since the introduction of 20–50 vol.% toluene or heptane had almost no effect on the reaction rate. Approach to a limiting value here could not be taken as an indication of an intramolecular $Pd(OAc)_2$ reaction (a slow depolymerization of the $Pd_3(OAc)_6$ trimer [5], for example, which would limit the reaction rate at high olefin concentration), the reactions with ST and α-methylstyrene being strictly first-order in the olefin at these rates [1]. Thus, the formation of an intermediate π-type complex between the Pd(II) and the olefin, possibly through the reaction

$$Pd(OAc)_2 + \text{Olefin} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{Complex} \xrightarrow{k_2'} \text{Products} \tag{4}$$

remains as the most likely cause of the nonlinearity of the plot of Fig. 3a. By applying the steady-state approximation to (4) one obtains the equation

$$k_{obs} = k_2' [\text{olefin}]/(K_M + [\text{olefin}]) \tag{5}$$

with $K_M = (k_2' + k_{-1})/k_1$. The data of Fig. 3a were linearized satisfactorily by plotting in the reciprocal coordinates of Eq. (5) (Fig. 3b): $K_M = 1.0 \pm 0.1$ mole/liter, $k_2' = 0.034 \pm 0.003$ min^{-1}. The rate of reaction (1) with DPhE and ST diminished markedly on adding Cl^- ions to the system, and increased somewhat on adding AcO^- ions.

The data of Table 1 make it clear that the rate of reaction (1) was not affected by the nature of the hydrocarbon substituent at the double bond adjacent to the phenyl ring. The values of the rate constants for epoxidation of the various olefins by peracetic acid, a typical electrophilic process, indicated a considerable variation of the C = C bond nucleophilicity in these compounds. Double bond attack by Pd(II) ions is also an electrophilic process and one in which the rate of formation of the palladium π complexes correlates with the rate of peracid epoxidation in the substituted cyclopropene [7]. Lack of a similar correlation in the present case was taken as indication of diphilicity in the transition state of reaction (1). There is also a certain symbatic relationship between the activation energies for oxidational dimerization and epoxidation (cf. Table 1). Although this parameter cannot be given a clear-cut interpretation here, its value does suggest that electrophilic double-bond attack from the Pd(II) does come into play in this system. The rate of aromatic compound oxidational dimerization, a closely allied reaction,

$$2RC_6H_5 + Pd(II) \rightarrow RC_6H_4{-}C_6H_4R + Pd(0) + 2H^+ \tag{6}$$

is also only weakly dependent on the nature of the R substituent [8].

It should be pointed out that reactions (1) and (6) have a number of features in common. In the first place, both reactions are overall second-order with respect to Pd(II) and either the olefin (present work) or the aromatic substrate [9]. Both reactions occur only in systems containing AcO^- ions and in both cases the oxidation is inhibited by Cl^- ions, coming almost to a standstill when these ions are present in the system at high concentration [1, 9]. Finally, neither reaction rate is affected by the ionic strength of the solution [1, 9].

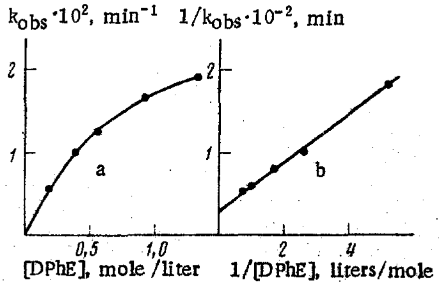


Fig. 3. Variation of the observed rate constant for the pseudo-first-order 1,2-diphenylethylene oxidation [Eq. (3)] with the olefin concentration (a). 0.033 mole/liter $Pd(OAc)_2$ in glacial HOAc at 70°C. Linearization of the data of Fig. 3a in the reciprocal coordinates of Eq. (5) (b).

TABLE 1. Second-Order Rate Constants and Activation Energies for Oxidational Dimerization and Epoxidation of Arylolefin by Peracetic Acid

Kinetic parameter	Styrene	α-Methylstyrene	1,1-Diphenylacetylene**
k_2, liter/mole·min*	0,040	0,030	0,034
E_a, kcal/mole	13,9±2,1	15,2±1,9	19,8±1,3
k_{ep}, liter/mole ·min†	0,011	‡	0,048
E_a, kcal/mole	13,9	–	16,2

---

*At 70°C.

†At 26°C [6].

‡Although data for α-methylstyrene are not available, the effect of the methyl group can be estimated by comparing rate constants for the epoxidation of propylene ($4.2\cdot 10^{-3}$ liter/mole · min) and isobutylene ($9.2\cdot 10^{-2}$ liter/mole · min) [6].

**The value listed for DPhE is that of $k_2 = k_2'/K_M$.

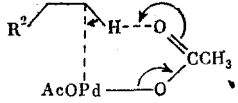
Taken together, these facts suggested that reactions (1) and (6) proceed through the same mechanism. Reasoning in analogy with the mechanism developed earlier for reaction (6) [9], it can be supposed that (1) proceeds through slow formation of a Pd(II) σ complex with the olefin, possibly through the intermediary of a π complex,

$$Pd(OAc)_2 + R^1R^2C{=}CH_2 \rightarrow R^1R^2C{=}CHPdOAc + HOAc \qquad (7)$$

this σ complex then undergoing rapid disproportionation to form the diene:

$$2R^1R^2C{=}CHPdOAc \rightarrow R^1R^2C{=}CHCH{=}CR^1R^2 + Pd(0) + Pd(OAc)_2 \qquad (8)$$

The role played by the AcO^- ions in this reaction, and the fact that the reaction rate is not affected by the nature of the substituent, can be explained, just as for reaction (6) [9], by assuming that reaction (7) proceeds through a multifunctional cyclic transition state of the type



It should be noted that the mechanisms of [10, 11] resemble that proposed here insofar as the first step is assumed to be σ complex formation through either reaction (7) or a more involved process of intermediate acetoxylation (9) with subsequent oxidational addition (10) [11]

$$Pd(OAc)_2 + R^1R^2C{=}CH_2 \rightarrow R^1R^2C{=}CHOAc + Pd(0) + HOAc \tag{9}$$

$$R^1R^2C{=}CHOAc + Pd(0) \rightarrow R^1R^2C{=}CHPdOAc \tag{10}$$

This mechanism has not been experimentally confirmed; its support in [11] is based on the appearance of acetoxylation side products in oxidational dimerization, and this despite the fact the such products are not observed in reactions of the 1,1-disubstituted ethylenes [3, 12].

A mechanism which does not include reaction (7) has been proposed in [3], where it is assumed that two olefin molecules are coordinated by the $Pd_2(OAc)_4$ dimer, one of the olefins undergoing intramolecular conversion to a carbanion which, in turn, attacks the second olefin, forming the diene and splitting off a palladium hydride ion. It is difficult to reconcile this mechanism with the fact that reaction (1) is first-order with respect to the olefin; moreover, chemical considerations make it quite unlikely that carbanions would result from the interaction of olefins with Pd(II), a fact already noted in [10]. It is clear that best consistency with the available data is attained by supposing (7) to be the limiting step in reaction (1).

The mechanism of the subsequent reactions of the σ complex is also a matter of some interest. It has been postulated in [10, 11] that diene formation proceeds through an insertion mechanism

$$\begin{gathered} R^1R^2C{=}CH_2 + R^1R^2C{=}CHPdOAc \rightarrow R^1R^2C{=}CHCH_2CR^1R^2PdOAc \rightarrow \\ \rightarrow R^1R^2C{=}CHCH{=}CR^1R^2 + Pd(0) + HOAc \end{gathered} \tag{11}$$

It is, however, not clear why reaction invariably leads to 1,4-substituted 1,3-butadienes rather than a mixture of the 1,4- and 1,3-substituted compounds. The fact that one has here to do with "head-to-head" dimerization exclusively can be most readily explained in terms of the disproportionation reaction (8). The proposed mechanism would be consistent with DPhB formation in the interaction of styrylmercury chloride with $PdCl_2$ such as described in [13].

Study of the data of the literature shows that the two most important factors for the realization of reaction (1) are the nature of the olefin and the composition of the Pd(II) coordination sphere (obligatory presence of AcO^- ions). Oxidational dimerization is never observed in unsubstituted ethylene. The alkyl-substituted olefins dimerize only when there is branching at one of the double-bond C atoms [3]. However, the effect of branching is decisive only in this one case, the aryl olefins dimerizing, as shown above, when there is a single substituent at the double bond. Vinyl acetate and monosubstituted ethylenes behave in the same way [3, 14], but β-chloro-α-olefins do not [3].

Reaction (1) is in competition with olefin acetoxylation and oxidation, reactions leading to the formation of carbonyl compounds through acetoxy palladination at the double bond [15]. It is clear that the factors which inhibit double-bond opening in these reactions are also those which favor dimerization. Branching would be one such factor in the case of the alkylolefins, since this sets up steric hindrances at one of the double bond C atoms. The result is that σ-complex formation on the opposite, unhindered double-bond C atom becomes the preferred process here. Another factor to be taken into account in the aryl olefins is the possibility of conjugation of the double bond with the aromatic ring. Such conjugation would be lost in acetoxy palladination but maintained in σ-complex formation, there being no need for a loss-compensating term in the expression for the activation energy in the latter case. Although a similar conjugation is established between the double bond and the acetoxyl group of vinyl acetate, such effects are not observed in the alkyl- and chloroolefins. This explains the above-mentioned tendency to dimerization which distinguishes vinyl acetate from the simple alkyl- and chloroolefins. The energy of resonance stabilization is especially high in the aromatic compounds where it is reaction (6), the analog of (1), which predominates. The aromatic compounds will undergo acetoxylation in the presence of $Pd(OAc)_2$, but only with difficulty, and certainly not by the mechanism of intermediation acetoxy palladination proposed in [11], since this would involve an appreciable loss of resonance energy.

CONCLUSIONS

1. Study has been made of the kinetics of oxidational dimerization of styrene and 1,1-diphenylethylene under the action of $Pd(OAc)_2$ in acetic acid. The mechanism is of overall second-order in the case of styrene and of the so-called Michaelis type in the case of the 1,1-diphenylethylene.

2. The data on the oxidational dimerization of olefins have been reviewed and a reaction mechanism posed.

LITERATURE CITED

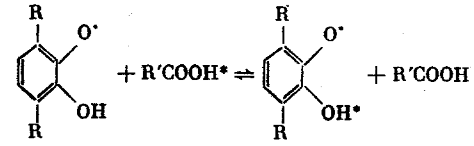
1. A. K. Yatsimirskii, A. D. Ryabov, and I. V. Berezin, Izv. Akad. Nauk SSSR, Ser. Khim., 1759 (1977).
2. Synthesis of Organic Preparations [Russian translation], Vol. 1, IL (1941), p. 206.
3. H. C. Volger, Rec. Trav. Chim., 86, 677 (1967).
4. J. H. Pinckard, B. Wille, and L. Zeichmeister, J. Am. Chem. Soc., 70, 1938 (1948).
5. R. N. Pandey and P. M. Henry, Can. J. Chem., 52, 124 (1974).
6. E. N. Prilezhaeva, The Prilezhaeva Reaction. Electrophilic Oxidation [in Russian], Nauka (1974).
7. M. A. Battiste, L. E. Friedrich, and R. A. Fiato, Tetrahedron Lett., 45 (1975).
8. R. Van Helden and G. Verberg, Rec. Trav. Chim., 84, 1263 (1965).
9. A. K. Yatsimirskii, A. D. Ryabov, and I. V. Berezin, Izv. Akad. Nauk SSSR, Ser. Khim., 1493 (1976).
10. P. M. Maitlis, The Organic Chemistry of Palladium, Academic Press, New York (1971).
11. E. V. Stern, Usp. Khim., 46, 232 (1973).
12. R. Hüttel, J. Kratzer, and M. Bechter, Chem. Ber., 94, 766 (1961).
13. R. C. Larock, J. Org. Chem., 40, 3237 (1975).
14. S. Danno, I. Moritani, and J. Fujiwara, Tetrahedron, 24, 4819 (1969).
15. I. I. Moiseev, in: Problems in Kinetics and Catalysis, XIII. Complex Formation in Catalysis [in Russian], Nauka (1968), p. 36.

EFFECT OF THE SOLVENT ON INTERMOLECULAR PROTON EXCHANGE BETWEEN 3,6-DI-tert-BUTYL-2-HYDROXYPHENOXYL AND ORGANIC ACIDS

A. S. Masalimov, A. I. Prokof'ev, N. N. Bubnov,
S. P. Solodovnikov, and M. I. Kabachnik

UDC 541.12.038.2:541.127:
547.56-128:547.292

It has been shown earlier [1] that the proton of the OH group of 3,6-di-tert-butyl-2-hydroxyphenoxyl (I) undergoes exchange with CH_3COOH and CF_3COOH.



(I)

$R = C(CH_3)_3$

This exchange leads to a uniform splitting of each of the hyperfine interaction components in the ESR spectrum of radical (I), the spectrum itself having the form of a triplet ($a_H = 3.92$ Oe) (interaction of the unpaired electron with the ring protons), each component of which is split into a doublet ($a_H^{OH} = 1.62$ Oe) (interaction with the OH group proton). Each doublet pair passes over to a single line at elevated temperatures and high acid concentrations, this line contracting as the exchange rate rises (Fig. 1).

The present work was a study of the effect of the solvent on the kinetics of proton exchange between (I) and CH_3COOH. When working under such conditions that the lines in the spectrum have widened but not yet merged, the exchange frequency (ν_{ex}) is given by the expression [2]

$$\nu_{ex} = \frac{\gamma_e a_0}{\sqrt{2}} \sqrt{1 - (a_{ef}/a_0)^2}$$

in which γ_e is the gyromagnetic ratio of the electron, and a and a_0 are the respective hyperfine coupling constants for the OH group proton, with and without exchange. Since the CH_3COOH was largely in dimer form

---

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1796-1773, August, 1977. Original article submitted April 30, 1976.

This material is protected by copyright registered in the name of Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for $7.50.