Kinetics of the Oxidation of Ethylene by Aqueous Palladium(II) Chloride

BY PATRICK M. HENRY

The oxidation, $C_2H_4 + PdCl_2 + H_2O \rightarrow CH_3CHO + Pd^0 + 2HCl$, studied in an aqueous $HClO_4$–$NaClO_4$ system, was found to consist of an initial rapid ethylene uptake followed by a slow reaction which is first order in palladous ion and strongly inhibited by chloride ion. The volume of gas initially taken up decreased as the chloride ion increased, this chloride dependence being consistent with the formation of a π-complex, $PdCl_4^{-2} + C_2H_4 \rightleftarrows [PdCl_3C_2H_4]^- + Cl^-$. The rate expression of the slow reaction was $-d[C_2H_4]/dt = k[PdCl_3C_2H_4^-]/[Cl^-][H^+]$ for the ranges $[Cl^-] = 0.1$ to 1.0 M, $[H^+] = 0.04$ to 1.0 M, and $[Pd^{+2}] = 0.005$ to 0.04 M. Only a secondary isotope effect was observed for C_2D_4. Increasing ionic strength increased the rate until $\mu = 0.4$. Further increase in μ decreased the rate. From the variation of k with temperature, values of $\Delta H^* = 19.8$ kcal. and $\Delta S^* = -8.7$ e.u. were calculated. A mechanism involving the rearrangement of a hydroxo π-complex $[PdCl_2(OH)C_2H_4]^-$ to a σ-complex consistent with the salt and isotope effects is proposed.

Introduction

Metal ions of the platinum and palladium groups oxidize olefins only to carbonyl compounds[1,2] whereas mercury(II),[3] thallium(III),[4] and lead(IV)[5] produce both carbonyl compounds and glycol derivatives.[6] This difference in products may result from the ability of the platinum metals to react *via* a π-complex without proceeding through the σ-bonded intermediate suggested for the other oxidations.[7] On the other hand, different modes of decomposition of a common σ-bonded intermediate may be involved. Both π-bonded[1,8] and σ-bonded[9] intermediates have been postulated for the oxidation of ethylene to acetaldehyde by palladous chloride in aqueous solutions. This study was undertaken to clarify the mechanism of this reaction, especially in regard to differences between it and other metal ion oxidations.

Recently, several studies of the kinetics of the palladous ion oxidation of olefins have been reported. The ethylene oxidation was found to be first order in ethylene and palladous ion[10,11] and inhibited by protons[10] and chloride ions.[10,12] The proton inhibition was first order, while the rate depended on the inverse square of the chloride ions. Propylene obeyed the same rate expression[13] while the oxidation of cyclohexene to cyclohexanone displayed a second-order chloride inhibition but no acid inhibition.[14] The ethylene oxidation displayed an isotope effect, k_H/k_D, of 4.05 when the reaction was run in D_2O.[15] In one study[16] π-complex formation between olefin and pal-

ladous chloride was detected under conditions of high acid and chloride concentration. However, no formation constants could be measured under the usual reaction conditions.

Results

At low chloride ion concentration (<0.2 M) the rate of ethylene uptake was mass-transfer controlled when creased flasks with magnetic stirring bars were used. However, when a high speed reactor especially designed for gas-to-liquid transfer was employed, the reaction was found to consist of a very rapid initial ethylene uptake followed by a slower ethylene absorption. The volume of ethylene initially taken up exceeded that required to saturate the solution with ethylene. This volume of ethylene taken up in excess of solubility requirements was found to be unaffected by acid concentration but decreased as the chloride ion concentration increased.

Since the net initial uptake decreased with increasing chloride ion, it seemed reasonable to assume that the initial reaction can be represented by the equilibrium[17]

$$PdCl_4^{-2} + C_2H_4 \underset{}{\overset{K}{\rightleftarrows}} \underset{I}{(PdCl_3C_2H_4)^-} + Cl^- \quad (1)$$
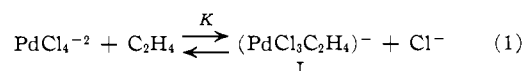
The values of K calculated on the basis of this equilibrium are listed in Table I at a constant ionic strength of 2. The value of K varies less than 5% even though the acid concentration is varied by a factor of 5.

TABLE I

CALCULATION OF EQUILIBRIUM CONSTANTS FROM INITIAL ETHYLENE UPTAKE[a]

Run	$[HClO_4]$	$[Cl^-]$	$[(PdCl_3-C_2H_4)^-]$	$[PdCl_4^{-2}]$	$[C_2H_4]^a$	K
1	0.2	0.085	0.0033	0.0057	2.78	17.6
2	.2	.182	.0020	.0077	2.67	17.6
3	.2	.184	.00175	.00725	2.67	16.8
4	.2	.383	.000905	.00805	2.61	17.2
16	1.0	.187	.0016	.0056	2.96	17.9

Average 17.4 ± 0.4

[a] All concentrations are in moles/l., except for $[C_2H_4]$ which is moles × 10^3/l.

A plot of log $(V_\infty - V)$ *vs.* time for the residual reaction is linear until chloride ion inhibition becomes significant, indicating a first-order reaction. Since

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

(2) J. Smidt, *et al.*, *Angew. Chem. Intern. Ed. Engl.*, **1**, 80 (1962).

(3) G. F. Wright, *Ann. N. Y. Acad. Sci.*, **65**, 436 (1957).

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

(5) R. Criegee, *Angew. Chem.*, **70**, 173 (1958).

(6) In addition, these metal ions also give allylic oxidation with some olefins. See, for instance, C. B. Anderson and S. Winstein, *J. Org. Chem.*, **28**, 605 (1963).

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

(8) I. I. Moiseev, M. N. Vargaftik, and Ya. K. Sirkin, *Dokl. Akad. Nauk SSSR*, **130**, 821 (1960).

(9) J. Halpern, Abstracts, 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962, p. 10Q.

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

(11) K. Teramoto, T. Oga, S. Kikuchi, and M. Ito, *Yuki Gosei Kagaku Kyokai Shi*, **21**, 298 (1963).

(12) M. N. Vargaftik, I. I. Moiseev, and Ya. K. Sirkin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1147 (1963).

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

(14) M. N. Vargaftik, I. I. Moiseev, and Ya. K. Sirkin, *Dokl. Akad. Nauk SSSR*, **139**, 1396 (1961).

(15) I. I. Moiseev, M. N. Vargaftik, and Ya. K. Sirkin, *Izv. Akad. Nauk, Otd. Khim. Nauk SSSR*, 1144 (1963).

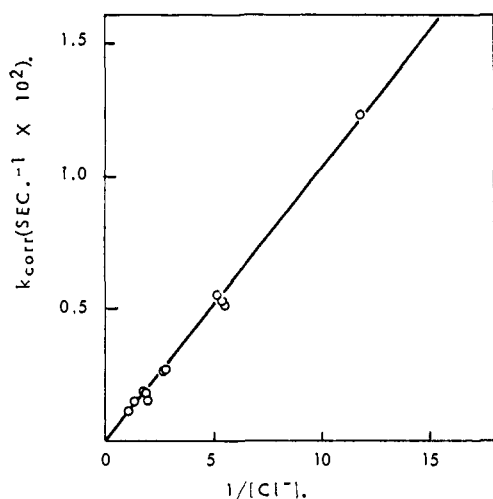(16) I. I. Moiseev, M. N. Vargaftik, and Ya. K. Sirkin, *Dokl. Akad. Nauk SSSR*, **152**, 147 (1963).

(17) The assumption that the palladous ion is present almost entirely as $PdCl_4^{-2}$ at the chloride ion concentration used in this work is justified by the formation constants of H. A. Droll, B. P. Block, and W. C. Fernelius, *J. Phys. Chem.*, **61**, 1000 (1957).

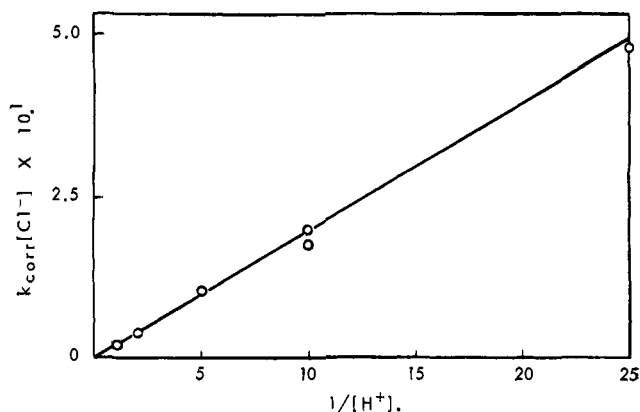Fig. 1.—Variation of k_{cor} with $1/[Cl^-]$ at constant acid concentration (0.2 M).

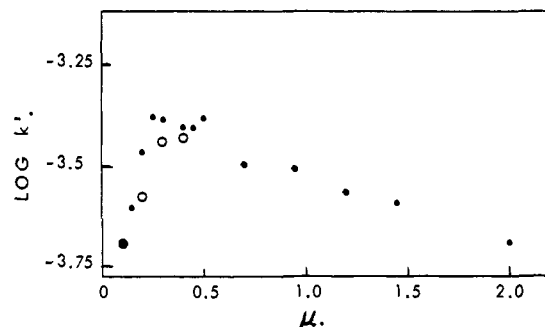Fig. 2.—Variation of $k_{cor}[Cl^-]$ with $1/[H^+]$ at various chloride ion concentrations.

Fig. 3.—Variation of k' with ionic strength: ●, μ varied by addition of NaCl or NaClO₄; O, μ varied by addition of HClO₄.

a total of 1 mole of ethylene was always consumed per mole of Pd(II) initially present, these plots represent the decrease in Pd(II) concentration with time. Thus the slower reaction is first order in palladous ion.

The first-order rate constants, k_{exp}, for this reaction were found to decrease with increasing chloride ion concentration. Such a decrease is to be expected if I is the reactive species

$$-d[C_2H_4]/dt = k_{cor}[I] =$$
$$k_{cor}K[PdCl_4^{-2}][C_2H_4]/[Cl^-] \quad (2)$$

Correcting the values of k_{exp} to k_{cor} by eq. 2 will cancel out any chloride ion inhibition by eq. 1 and k_{cor} should be constant with changing chloride ion if this is the only chloride inhibition. However, as Fig. 1 illustrates, k_{cor} varies linearly with $1/[Cl^-]$ at constant acid concentration, indicating another first-order chloride inhibition.

The hydrogen ion dependence on rate was found by plotting the product $k_{cor}[Cl^-]$ at various chloride ion concentrations vs. $1/[H^+]$. If there is no acid dependence, the product should be constant but, as Fig. 2 shows, there is a linear dependence indicating first-order inhibition by acid. Thus, the complete rate expression is

$$-\frac{d[C_2H_4]}{dt} = \frac{k'[I]}{[Cl^-][H^+]} =$$
$$\frac{k'K[PdCl_4^{-2}][C_2H_4]}{[Cl^-]^2[H^+]} \quad (3)$$

where the average value of k' is 2.03 ± 0.2 × 10⁻⁴ M^2 sec.⁻¹.

The first-order dependence on ethylene concentration was confirmed by running the reaction in a constant volume reactor. At constant chloride and acid concentrations under conditions where the concentration of I is small, the reaction was shown to be first order in palladous ion and first order in ethylene, as predicted by eq. 3. The average value of k' calculated from these data (2.04 × 10⁻⁴ M^2 sec.⁻¹) agreed well with those obtained in atmospheric pressure runs.

Results of a series of runs at various ionic strengths are plotted in Fig. 3. Lower ionic strengths were inaccessible because the reaction was too rapid to measure at chloride ion concentrations below 0.1 M. These results are in agreement with those of Vargaftik, et al.,[10] who found a decrease in rate with increasing ionic strength at ionic strengths over 0.7. The values of K for these runs increased as the solubility decreased, but the value of K' defined as

$$K' = [PdCl_3C_2H_4^-][Cl^-]/[PdCl_4^{-2}]P_{C_2H_4} \quad (4)$$

where the $P_{C_2H_4}$ is expressed in atmospheres (unity for all the runs in Fig. 3), remained essentially constant at 0.047 ± 0.006 mole/l. atm.

Average values of K and k' at 15, 25, and 35° are listed in Table II. A plot of log k' vs. $1/T$ gave a straight line. From the slope of the line values of ΔH^* = 19.8 kcal. and ΔS^* = −8.7 e.u. were calculated. A plot of log $k'K$ vs. $1/T$ did not give a straight line.

TABLE II

EFFECT OF TEMPERATURE ON K AND k'[a]

Temp., °C.	$[C_2H_4] \times 10^2$	K^b	k',[c] M^2 sec.⁻¹ × 10⁴
15	3.05	18.7 ± 1.4	0.53 ± 0.08
25	2.67	17.4 ± 0.4	2.0 ± .2
35	2.25	9.7 ± 1.5	5.8 ± .6

[a] μ = 2.0.   [b] Average of at least three runs.   [c] Average of at least five runs.

The isotope effect was determined by measuring the value of k'_D for C_2D_4 using the constant volume reactor and assuming K is the same as for the undeuterated material. The average value of k'_D for three
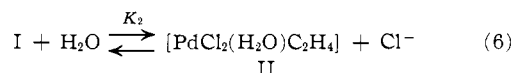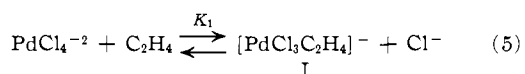
runs was $1.9 \pm 0.1 \times 10^{-4}$ M^2 sec.$^{-1}$. This corresponds to an isotope effect k'_H/k'_D of 1.07.

The agreement between the rate constants found in this work and those found by Vargaftik, *et al.*,[10,12,15] is usually within 25–75% for the chloride and acid concentrations (their k_2 is equivalent to the product $k'K$). This agreement is excellent considering the differences in ionic strength of the reaction mixtures.

Using high acid and chloride concentrations to stop the oxidation, these same workers[16] measured π-complex formation and claim to have measured equilibria corresponding to eq. 5 and 6. At 13.4° they reported values of 16.3 for K_1 and 0.4 for K_2. However, in the present work (see Table I) constant values of K_1 were obtained at 25° presuming that only the first equilibrium is taking place to any extent. Treating our data in the same fashion as these workers gives $K_2 = 0$. Even allowing for experimental error K_2 would be less than 10^{-2}. These workers maintained constant ionic strength by replacing HCl with HClO$_4$ and varied their HCl concentration from 1 to 4 M. Over this range the principle of constant ionic strength cannot be expected to hold and their apparent K_2 probably results from the change of K_1 with chloride ion concentration.
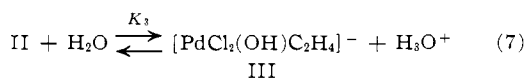
Discussion

As concluded by previous workers,[11,12] the chloride inhibition is consistent with the prior formation of an aquated palladium dichloride π-complex.

$$PdCl_4^{-2} + C_2H_4 \underset{}{\overset{K_1}{\rightleftharpoons}} [PdCl_3C_2H_4]^- + Cl^- \quad (5)$$
$$I$$

$$I + H_2O \underset{}{\overset{K_2}{\rightleftharpoons}} [PdCl_2(H_2O)C_2H_4] + Cl^- \quad (6)$$
$$II$$

The experimental technique used in this study permitted the measurement of K_1. It was found to have a value of 17.4 at 25° and $\mu = 2.0$. [PtCl$_3$H$_2$O]$^-$ and [PtCl$_3$C$_2$H$_4$]$^-$ have similar values[18,19] of the equilibrium constant for the equilibrium corresponding to eq. 6. Thus, since palladous ion has even a smaller *trans* effect than platinous ion,[20] a good estimate for K_2 would be the K of the corresponding equilibrium for [PdCl$_3$H$_2$O]$^-$. This value is *ca.* 10^{-3} M.[17]

The proton inhibition indicates that II reacts further either by attack of hydroxide ion or by dissociation of a proton from II to give a hydroxo species (III).

$$II + H_2O \underset{}{\overset{K_3}{\rightleftharpoons}} [PdCl_2(OH)C_2H_4]^- + H_3O^+ \quad (7)$$
$$III$$

The salt effects are consistent with either path since both the ionization product of water[21] and the ionization constant of neutral weak acids[22,23] show this

same type of behavior. The isotope effects in deuterated water[15] can also be rationalized by either path, since the effect observed is of the order of the decrease in ionization constants of both D$_2$O[24,25] and weak acids in D$_2$O.[26]

However, a serious objection to the hydroxide ion attack is that the rate constant for the reaction would have to be very large. Thus, if the rate-determining step were

$$II + OH^- \xrightarrow{k_1} products \quad (8)$$
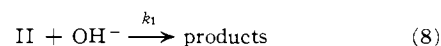
the rate expression would be

$$rate = k_1[II][OH^-] = k_1(K_2K_w/[H^+][Cl^-]) \quad (9)$$

Substituting the value of K_2 estimated above and the value of K_w and equating to the experimental rate constant we get

$$k_1 \frac{(10^{-3}\ M)(10^{-14}\ M^2)}{[H^+][Cl^-]} = \frac{2 \times 10^{-4}\ M^2\ sec.^{-1}}{[H^+][Cl^-]} \quad (10)$$

Thus, k_1 would have a value of *ca.* 10^{13} M^{-1} sec.$^{-1}$ which is about 10^4 larger than the rate for a diffusion-controlled process in solution.[27] The rate constant for the route involving the hydroxo complex would be much lower since the acidity of water is increased by a factor of 10^7 to 10^{10} by complexing.[20]

The large intrinsic activity of water in nonaqueous media[28] also favors the hydroxo species. This reactivity, which is inconsistent with comparable nucleophilicities of water and acetate ion, however, is consistent with the much greater coordinating power of water if the reaction proceeds by eq. 7.

The hydroxo complex III can decompose directly to product or proceed through another intermediate such as a σ-bonded complex. The isotope effect with deuterated ethylene favors the σ-bonded path. Since tracer experiments[2] have shown that all four hydrogens in the acetaldehyde come from the ethylene, if III decomposes directly to product, the activated complex would involve a hydride shift and a primary deuterium isotope effect would be expected. The small isotope effect actually observed argues against such a mechanism. The result would be consistent with the reactions represented by eq. 11 and 12 where the formation of the σ-complex IV is rate determining. A small

$$III \underset{slow}{\xrightarrow{k_2}} Cl-Pd-CH_2-CH_2-OH + Cl^- \quad (11)$$
$$IV$$

$$Cl-Pd-CH_2-CH_2-OH \xrightarrow{fast} HCl + Pd^0 + CH_3CHO \quad (12)$$
$$IV$$

isotope effect would be expected for k_2 since no C–H bonds are broken.

(18) D. S. Martin, Jr., and R. J. Adams in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961.

(19) I. Leden and J. Chatt, *J. Chem. Soc.*, 2936 (1935).

(20) F. Basolo and R. G. Pearson in "Progress in Inorganic Chemistry," F. A. Cotton, Ed., Vol. 4, Interscience Publishers, Inc., New York, N. Y., 1962.
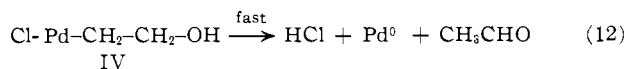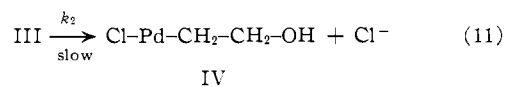
(21) H. S. Harned and W. J. Hamer, *J. Am. Chem. Soc.*, **55**, 2194 (1933).

(22) H. S. Harned and F. C. Hickey, O.P., *ibid.*, **59**, 2303 (1937).

(23) A. C. Batchelder and C. L. A. Schmidt, *J. Phys. Chem.*, **44**, 893 (1940).

(24) W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **32**, 1397 (1936).

(25) The assumption (ref. 15) that the reaction cannot go by hydroxide ion attack since the isotope effect found (4.05) does not correspond exactly with the isotope effect on the K_w of water (5.08) found by Wynne-Jones does not seem justified since the difference could easily result from secondary isotope effects.

(26) C. K. Rule and V. K. La Mer, *J. Am. Chem. Soc.*, **60**, 1974 (1938).

(27) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 11.

(28) E. W. Stern, *Proc. Chem. Soc.*, 111 (1963).

The intermediate IV is similar to those proposed for the oxidation of ethylene by thallium(III).[4] In the case of this metal ion, it is postulated that the metal leaves with its electrons to form a carbonium ion which rearranges to give acetaldehyde or reacts with the solvent to give ethylene glycol. (Treatment of β-hydroxyethylamine in aqueous solution with nitrous acid to yield this carbonium ion gives a mixture of acetaldehyde and ethylene glycol.[29]) However, decomposition of IV must not involve a carbonium ion, since no glycol is found. The activated complex V, in which palladium is assisting a hydride shift as it leaves with its electrons, would fulfill these requirements.

$$\begin{bmatrix} \text{H} \quad \text{H} \\ \text{H} \quad | \quad | \\ \quad \text{C}\!-\!\text{C}\!=\!\text{O}\cdots\text{H} \\ \quad | \quad \diagdown \\ \text{ClPd}\cdots\text{H} \end{bmatrix} \longrightarrow CH_3CHO + HCl + Pd^0 \qquad (13)$$

V
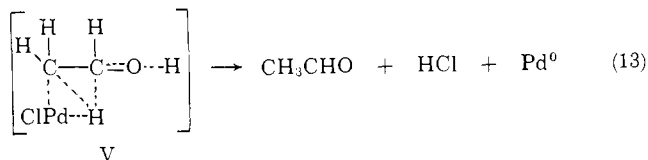
The chemical evidence appears to be compatible with the σ-bonded route. Palladous chloride seems capable of adding across olefinic double bonds to form β-oxyalkyl palladous chlorides.[30] Furthermore, the heavier group VIII metals appear capable of labilizing β-hydrogens. Platinum–ethyl compounds reversibly eliminate ethylene to give platinum hydride.[31] The instability of palladium alkyls with β-hydrogens[32] is probably due to the same type of reaction, the equilibrium being driven to the side of decomposition products by the instability of palladium hydride.[33]

One question which arises is the stereochemistry of the reactive hydroxo complex III. For rearrangement to IV, a cis arrangement of the hydroxo and ethylene would appear necessary while the trans effect of the ethylene group would lead to a trans arrangement.[20] However, even with the corresponding platinum complex of II, where the trans effect is stronger, there is evidence that as much as 10% of the complex is present as the cis isomer.[34] Thus, in the case of II or III it is quite reasonable that kinetically significant amounts of the cis isomer are present.

Assuming a reasonable value of 10^{-6} for the value of K_3 in eq. 6, we can estimate the value of k_2 in eq. 10. Thus since

$$\text{rate} = k_2 \, \text{III} = k_2 \frac{K_2 K_3}{[\text{H}^+][\text{Cl}^-]} = \frac{2 \times 10^{-4}}{[\text{H}^+][\text{Cl}^-]} \qquad (14)$$

we can calculate a value of ca. 10^5 sec.$^{-1}$ for k_2 if we use a value of 10^{-3} for K_2. This value, although large, is within a reasonable range.

The formation of vinyl esters in acetic acid[35,36] could well proceed by a similar route. Here, OH is

replaced by acetate in the activated complex V, and a rapid rearrangement to a carbonyl compound is impossible. Since 1,1-diacetates are not formed, the preferred route would have to be the elimination of proton along with the palladium. This proton could leave as palladium hydride, or the acetate on the β-carbon may assist in its removal.

The lack of an acid inhibition for the oxidation of cyclohexene to cyclohexanone is difficult to explain on the basis of this mechanism unless π-complex formation (eq. 5) is rate determining. It is also possible that the oxidation is of the allylic type, giving cyclohexenol, which rearranges to cyclohexanone in the presence of palladous chloride. Cyclohexene appears to have a tendency to undergo allylic oxidations with metal ions.[6]

Experimental

Materials.—The palladous chloride dihydrate was Fisher Scientific Co. purified grade. The ethylene was purchased from United States Industrial Chemicals. All other chemicals were reagent grade.

Kinetic Runs.—The rate was measured by ethylene uptake.

Creased Flask.—The slower reactions, in which the ethylene uptake was too slow to be mass-transfer controlled, were run in creased flasks at a constant ethylene pressure of 1 atm. The gas uptake was measured by means of gas burets thermostated at the reaction temperature. The reaction flask was a 250-ml. filter flask from which the side arm was removed and the opening sealed. The side of the flask was indented to increase stirring efficiency. A magnetic stirring bar was used for agitation.

In a typical run, the flask containing 50 ml. of the reaction mixture was placed in a constant temperature bath and connected to the gas buret by means of a large gage needle inserted through a rubber stopper in the mouth of the flask. The system was then evacuated for several minutes with the stirrer running. The stirring was then turned off and the system pressured to approximately 1 atm. with ethylene. The mercury in the gas buret and leveling bulb were then equalized, a reading taken, and the stirrer turned on to start the run. The pressure was kept constant during the run by continuously leveling the mercury in the gas buret and bulb.

In all runs except those showing Cl$^-$ retardation, a plot of log $(V_\infty - V)$ vs. time gave a straight line. The value of V_∞ was calculated from the solubility of ethylene in the reaction mixture plus the known concentration of the palladium chloride stock solution, which was analyzed by the dimethylglyoxime method. In the slower reactions, it was necessary to correct the value of V for a slow side reaction, independent of palladous ion, which consumed ethylene at a slow but constant rate. The rate of this reaction, which was probably hydration to ethanol, was determined by measuring the rate of ethylene uptake for several hours after the oxidation was completed. Solubilities were determined by measuring the ethylene uptake solutions of the same composition as the reaction mixtures but from which the palladous ion was omitted. Since the concentration of palladous ion was small ($\sim$0.02 M) compared to the total salt concentration (2 M), its absence would not effect the solubility.

High-Speed Reactor.—The high-speed reactor used for the faster runs consisted of a 500-ml. jacketed glass container into which were placed plastic baffles. The reaction mixture was stirred by a six-bladed turbine stirrer inserted into the reactor through a mechanical seal. The stirrer was coated with Penton[37] to prevent attack of palladous ion on the metal stirrer. Stirring speeds were about 3000 r.p.m. This reactor was designed by the Chemical Engineering Division of the Hercules Research Center.[38]

The procedure for making a run was identical with that for the creased flask runs except that 250 ml. of the reaction mixture was used. The plots of log $(V_\infty - V)$ vs. time deviated from linearity after several minutes. This resulted from the release

(29) H. C. Dehm, Hercules Powder Co., Bacchus, Utah, unpublished work.

(30) J. Chatt, L. M. Vallarino, and L. M. Venanzi, J. Chem. Soc., 3413 (1957).

(31) J. Chatt and B. L. Shaw, ibid., 5075 (1962).

(32) G. Calvin and G. E. Coates, ibid., 2008 (1960).

(33) J. Chatt, L. A. Duncanson, and B. L. Shaw, Chem. Ind. (London), 859 (1958).

(34) S. J. Lokken and D. S. Martin, Jr., Inorg. Chem., 2, 562 (1963).

(35) I. I. Moiseev, M. N. Vargaftik, and Ya. K. Sirkin, Dokl. Akad. Nauk SSSR, 133, 377 (1960).

(36) E. W. Stern and M. L. Spector, Proc. Chem. Soc., 370 (1961).

(37) Hercules Powder Co. registered trademark for chlorinated polyether.

(38) The author is indebted to Dr. V. Verplanck and J. J. Hoglen for the loan of the reactor, as well as for many suggestions regarding its use during the course of this work.

of chloride ion as the reaction proceeded, four chlorides being released per palladous ion reaction. Two runs were made in the presence of finely divided palladium metal. The rate was unaffected.

The following form was assumed in calculating the equilibrium constant K

$$K = [(\text{PdCl}_3\text{C}_2\text{H}_4)^-][\text{Cl}^-]/[\text{PdCl}_4^{-2}][\text{C}_2\text{H}_4]$$

The net ethylene uptake was converted to moles of complex and this subtracted from the total palladous ion concentration to give $[\text{PdCl}_4^{-2}]$. The value of $[\text{Cl}^-]$ was then equal to total chloride $- 3[(\text{PdCl}_3\text{C}_2\text{H}_4)^-] - 4[\text{PdCl}_4^{-2}]$.

Constant Volume Reactor.—The constant volume reactor was essentially a 250-ml. florence flask connected to a mercury capillary manometer. The flask was creased to increase the stirring efficiency of the magnetic stirring bar. An outlet equipped with stopcock was used to transfer gas into the apparatus or to pull a vacuum. The volume of the reactor was found to be 253.8 ml. by measuring the pressure before and after the injection of a weighed amount of mercury.

The reactions were run at an ethylene pressure of about 70 mm. Since at this pressure the concentration of complex is small, eq. 2 can be written

$$d[\text{C}_2\text{H}_4]/dt = k_2[\text{Pd}^{+2}][\text{C}_2\text{H}_4]$$

where

$$[\text{Pd}^{+2}] = [\text{I}] + [\text{PdCl}_4^{-2}] \quad \text{and} \quad k_2 = \frac{k'K}{[\text{Cl}^-]^2[\text{H}^+]}$$

The solution of this equation for a constant volume reactor is

$$\frac{(\alpha + \beta)2.3}{\alpha(\beta P_0 - [\text{Pd}^{+2}]_0)} \times$$

$$\log \frac{(\alpha + \beta)P[\text{Pd}^{+2}]}{\beta P_0[(\text{Pd}^{+2}]_0 - \beta P_0) + (\alpha + \beta)P]} = k_2t$$

where α is the Henry's law constant, $[\text{Pd}^{+2}]_0$ is the initial palladous ion concentration, and β is an instrument constant[39] whose value is 8.5×10^{-5} for this reactor when 100 ml. of solution is used. The plots of the log term $vs.$ t for all runs were linear, indicating the reaction is first order in palladous ion and first order in ethylene.

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Crystal Structure of Diammonium Croconate and Molecular Orbital Calculations on the Croconate Ion

By N. C. Baenziger and J. J. Hegenbarth

The crystal structure of $(\text{NH}_4)_2\text{C}_5\text{O}_5$ was determined, and the molecular geometry of the croconate ion is reported. Molecular orbital calculations were carried out to check the effect of the parameters h and k on the calculated bond orders, electron densities, and delocalization energies. Values of the parameters which give the best agreement with the experimental bond orders and prescribed electron densities are reported.

Recent interest in a series of aromatic ions of general formula $\text{C}_n\text{O}_n^{-2}$ has sparked renewed interest in the structure of the croconate ion.[1,2] A normal coordinate analysis of the infrared and Raman spectral data of the croconate ion indicates an anion of D_{5h} symmetry.[3] The structure of $(\text{NH}_4)_2\text{C}_5\text{O}_5$ was undertaken to determine the molecular geometry (bond distances, bond angles) of the croconate ion. A preliminary account of the structure was reported.[4]

Bond orders, electron densities, and delocalization energies (obtained from Hückel molecular orbital (HMO) calculations) have been reported for a whole series of oxygenated anions. The parameters used in these calculations were $h = 1.0$ and $k = 0.8$.[5]

The molecular orbital calculations reported in this paper were carried out to test the dependence of the calculated bond orders, bond lengths, and delocalization energies on the parameters h and k. It was hoped that a set of h and k could be found that would give the observed bond orders, reasonable electron densities,[6] and a maximum delocalization energy. The

effect of including the overlap parameters in the calculation was also investigated.

Experimental

The Crystal Structure of Ammonium Croconate.—$(\text{NH}_4)_2\text{C}_5\text{O}_5$ crystallizes from aqueous solution as monoclinic needles or laths with unit cell dimensions $a = 7.444 \pm 0.003$ Å., $b = 13.345 \pm 0.002$ Å., $c = 3.582 \pm 0.001$ Å., $\beta = 99.4 \pm 0.3°$, $D_{\text{measd}} = 1.66$ g./cm.³ (pycnometrically), $Z = 2$, $Dx = 1.60$ g./cm.³. The cell constants were determined by a least-squares fitting of the $(h0l)$, $(hk0)$, and $(0kl)$ Weissenberg back-reflection data with extrapolation to $\theta = 90°$. The systematic absences, (hkl) when $h + k = 2n + 1$, indicate space groups C2/m, C2, or Cm. Space group C2/m, which requires the croconate ion to have a symmetry center, seemed unlikely from previous information.

The intensity data were taken using crystals (approximate cylinders) maintained at $80°K$. by use of a gas-flow dewar designed in our laboratory.[7] The data were taken using the equi-inclination Weissenberg camera, multiple film technique, and Cu $K\alpha$ radiation (λ 1.5418 Å.). Some diffraction spots at high angles were split into two spots due to thermal shock damage to the crystal. The amount of splitting varied from crystal to crystal, but the crystals used to take the intensity data showed little effect of the splitting. The splitting was observed only when the crystal was aligned along the needle (c) axis.

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(5) R. West and D. L. Powell, *ibid.*, **85**, 2577 (1963).

(6) Reasonable electron densities were determined by using the equations: $q_c = 5E_c{}^P/12(E_o{}^P + E_c{}^P)$; $q_o = 5E_o{}^P/12(E_o{}^P + E_c{}^P)$; $E_c{}^P$ and $E_o{}^P$ are Pauling's electronegativity numbers for carbon and oxygen. With the use of the above equations, q_c is calculated to be 1.0, q_o to be 1.4.

(7) G. F. Richards Thesis, Feb., 1964.