A Spectroscopic Study of the Homogeneous Catalytic Conversion of Ethylene to Vinyl Acetate by Palladium Acetate

David D. Kragten* and Rutger A. van Santen

Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Michael K. Crawford, William D. Provine, and Jan J. Lerou
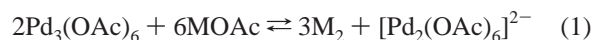
DuPont, Wilmington, Delaware 19880-0356

We have studied the various aspects of the homogeneous acetoxylation of ethylene to vinyl acetate by palladium acetate using ultraviolet−visible (UV/vis), Raman, and infrared spectroscopic methods. Vibrational assignments for the Raman and the infrared spectra of crystalline palladium acetate have been made. Density functional theoretical calculations were used to help with our assignments. Raman spectroscopy demonstrated that Pd acetate solvated in glacial acetic acid maintains a trimeric structure, similar to that of the crystal. Upon addition of potassium acetate in concentrations between 0.10 and 0.20 M, the palladium acetate trimers decompose to dimers. It remains, however, an open question whether monomers, or perhaps dimers that are fully coordinated by acetate ligands, form with increasing potassium acetate concentration. In the presence of ethylene, dimeric species appear to form by decomposition of the trimers, and it is the dimers which are the catalytically active and selective species in the formation of vinyl acetate. During reaction with ethylene, palladium(II) in palladium acetate is reduced to palladium black, and the hydrocarbon products vinyl acetate and acetaldehyde are formed. Monomeric palladium acetate species are apparently not formed by this reaction.

I. Introduction

Vinyl acetate (VAc) is an important monomer in the polymer industry. A great deal of research has been concentrated on the development of a process to produce vinyl acetate via the selective acetoxylation of ethylene.[1] Due to the success of the homogeneous Wacker process for the synthesis of acetaldehyde, research first concentrated on the development of an analogous process to produce vinyl acetate. Vinyl acetate is formed by reaction of ethylene with Pd acetate in acetic acid solution, accompanied by the reduction of Pd to Pd black, as reported first by the groups of Moiseev and Smidt.[2] A gas-phase heterogeneous process developed by Hoechst[3] and Bayer[4] proved more favorable. Presently, vinyl acetate is produced on a large scale by a related heterogeneous process.[1] The catalyst used most is a silica-supported Pd−Au alloy with potassium acetate added in large excess.[1,5] However, questions exist concerning the active phase of the catalyst. Since Pd solvates as Pd acetate in glacial acetic acid under oxidizing conditions,[6] a homogeneous route to vinyl acetate is still possible, at least as a side reaction to the heterogeneous process. We therefore decided to study the homogeneous chemistry of the formation of vinyl acetate in the presence of Pd acetate using UV/Vis, Raman and infrared spectroscopic methods.

Solvated Pd acetate can exist in at least three different forms, related to each other by equilibria that can be controlled through the addition of alkali metal acetates.[7,8] The equilibria are described by reactions 1 and 2.

$$2Pd_3(OAc)_6 + 6MOAc \rightleftarrows 3M_2 + [Pd_2(OAc)_6]^{2-} \quad (1)$$

$$M_2 + [Pd_2(OAc)_6]^{2-} + 2MOAc \rightleftarrows 2M_2 + [Pd(OAc)_4]^{2-} \quad (2)$$

In reactions 1 and 2, M represents an alkali metal. The Pd trimers are completely converted to dimers when the solution contains 0.5 M lithium or 0.2 M sodium acetate. At higher concentrations of alkali acetates, some of the dimers are converted to monomers, but the equilibrium is strongly in favor of the dimers. Decomposition of Pd acetate trimers involves an S_N2 attack by acetate ions or acetic acid molecules on an acetate bridge.[7] Due to the nature of the equilibria, the concentration of dimers depends on the Pd and the acetate concentrations. An important point is that there are generally two types of acetate groups,

(1) (a) Miller, S. A. *Ethylene and Its Industrial Derivatives*; Ernest Benn Limited: London, 1969; p 946 and references therein. (b) Davidson, J. M.; Mitchell, P. C.; Raghavan, N. S. *Front. Chem. React. Eng. (Proc.−Int. Chem. React. Eng. Conf.)* **1984**, *1*, 300 and references therein. (c) *Ullman's Encyclopedia of Industrial Chemistry*, 5th edition; Elvers, B., Hawkins, S., Ed.; VCH Verlagsgesellschaft mbH: Weinheim, 1996; Vol. A27, p 419. (d) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis. The Application and Chemistry of Catalysis by Soluble Transition Metal Complexes*, 2nd edition; John Wiley & Sons: New York, 1997; p 137.

(2) Moiseev, I. I.; Vargaftic, M. N.; Syrkin, Ya. K. *Dokl. Akad. Nauk SSSR* **1960**, *133*, 377. (b) *Angew. Chem.* **1959**, *71*(5), 176. (c) Smidt, J.; Hafner, W.; Jira, R.; Sedlmeier, J.; Sieber, R.; Rüttinger, R.; Kojer, H. *Angew. Chem.* **1962**, *74*(3), 93.

(3) *World Pet. Congr. Proc.* **1968**, *5*, 41.

(4) (a) *Eur. Chem. News* **1967**, *11*(272), 40. (b) *Chem. Ind.* **1968**, 1559.

(5) Bissot, T. C. U.S. Patent 4,048,096, 1977.

(6) (a) Brown, R. G.; Davidson, J. M.; Triggs, C. *Am. Chem. Soc., Div. Petrol. Chem. Prepr.* **1969**, *14*, B23. (b) Hausman, E. A.; Grass, J. R.; Pond, G. R. Fr. Patent 1,403,398, 1965.

(7) Henry, P. M.; Pandey, R. N. *Homogeneous Catalysis, II;* Advances in Chemistry Series 132; American Chemical Society: Washington, DC, 1973; p 33 and references therein.

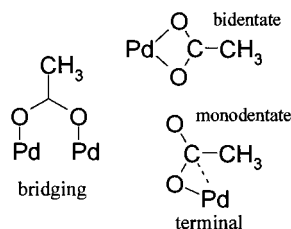(8) Pandey, R. N.; Henry, P. M. *Can. J. Chem.* **1974**, *52*, 1241.

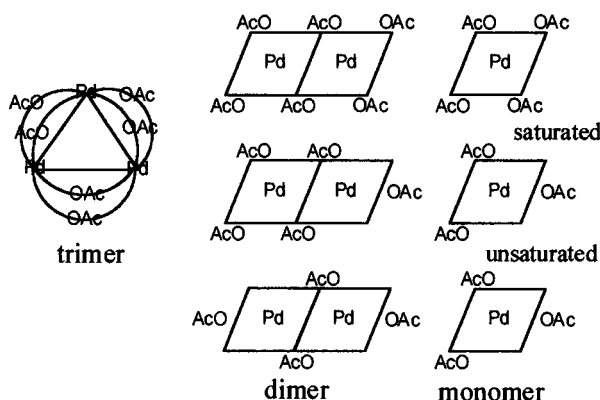**Figure 1.** Coordination modes of acetate.

Figure 2. Various palladium acetate species at increased unsaturation.

bridging and terminal (see Figure 1). In the Pd trimer or monomer, either bridging or terminal acetates are present, respectively. In the Pd dimer, both bridging and terminal acetates are present (see Figure 2).

Different Pd acetate species have different catalytic activities for the acetoxylation of ethylene to vinyl acetate. The activity increases in proportion to the Pd acetate and alkali metal acetate concentrations, up to concentrations of the latter for which all the trimers are converted to dimers.[7,9] At higher concentrations, the reaction rate is inversely proportional to the alkali metal acetate concentration.[7] Thus, adding alkali metal acetate first creates catalytically active species, but at high concentrations, the acetate ions function as inhibitors. These results can be interpreted as follows.

At low alkali metal acetate concentrations, the relatively inactive Pd trimers are partially converted to active dimers. At high concentrations, however, less active species also form. The less active species could be either Pd monomers or dimers that are fully coordinated by acetate ligands. Since ethylene molecules are expected to coordinate to terminal positions on the dimer,[10] coordination of ethylene to Pd followed by reaction to form vinyl acetate requires the presence of vacant terminal sites on the dimers. The maximum activity would then be expected to occur when the concentration of coordinatively unsaturated Pd acetate dimers is highest. It is also possible that coordination of ethylene could convert Pd acetate dimers to monomers, but this reaction is expected to be significantly slower than the competing acetoxylation.

II. Materials and Methods

A. Sample Preparation. Pd(II) acetate of 99.99% purity was purchased from Aldrich Chemical Co. The solvents used were glacial acetic acid (99.8% purity) and deuterated glacial acetic acid-d_4 (99.9 at. % D). Potassium acetate was 98% pure. Ethylene was >99.7% pure.

The solutions were prepared by equilibrating an excess of Pd acetate for 12 h in glacial acetic acid at room temperature. The Pd acetate concentration was determined by ICP to be 0.12 wt % Pd in glacial acetic acid, which corresponds to a saturation concentration of 3.9 mM of the trimeric species. The solution color was orange-brown, similar to that of the crystal. This solution was used to prepare all other solutions. After the addition of potassium acetate, the solutions were allowed to equilibrate for an additional 12 h, since long equilibration times are reported to be essential at room temperature.[8] All samples were prepared at room temperature, except where noted otherwise.

B. Spectroscopic Measurements. UV/vis absorption measurements were performed with a Perkin-Elmer Lambda 9 spectrometer. A quartz cell of 0.1 cm path length was used. These measurements provide a basis for comparison with the literature.

The Spex Raman spectrometer was equipped with a triple monochromator and a liquid nitrogen cooled CCD detector. Excitation was provided by an Ar-ion laser (wavelength 514.5 nm), using a maximum power of 10−20 mW at the sample. Where indicated, excitation was provided by an Ar-ion laser-pumped Ti:sapphire laser (wavelength ranged from 457.9 to 488.0 nm). The spectra were recorded in a 180° backscattering geometry at room temperature. Laser-induced decomposition of Pd acetate did not take place under these conditions. The samples were placed in quartz cells with 1 cm path length. The polycrystalline Pd acetate was measured in a quartz capillary using a Raman microscope.

For the flow experiments, the reactor was a quartz tube with a diameter of 1 cm, equipped with capillary tubes to allow gas to bubble through the solution. The gas flow was regulated so that the solution was saturated with ethylene during the flow period. The saturation concentration of ethylene in glacial acetic acid is 0.082 M.[10] After ethylene flowed through the solution for some period of time, Pd metal would precipitate since there was no oxidation step included in our reaction setup. Therefore, the Raman measurements were made after enough of the Pd had precipitated to permit a reasonable penetration length for the laser excitation. In several cases, the solution was analyzed with GC/MS after the reaction was run.

Infrared spectroscopy measurements were performed with a Bruker FT-IR spectrometer equipped with a MCT detector, operated at liquid nitrogen temperature. Measurements were performed at room temperature. Polycrystalline Pd acetate was pressed into a pellet with dry FT-IR grade potassium bromide, which does not affect the spectrum. Measurements were performed in transmission mode. The spectrum of Pd acetate in Nujol can be found in the literature.[11] We prefer, however, to refer to our own measurement, as Nujol gives rise to very strong bands in the regions of interest.

C. Theoretical Calculations. Density functional theoretical (DFT) calculations for model systems have been performed to support interpretation of the Raman spectra. The calculations have been performed with the DGauss program[12] (version 4.0). All molecular structures have been completely geometry optimized at the GGA level. Optimizations have been performed spin-unrestricted. We have used the local density approximation (LDA) in the form given by Vosko−Wilk−Nusair[13] with self-consistently incorporated gradient corrections due to Becke[14] and Perdew.[15] The program represents the molecular orbitals

(9) Helden, R. van; Kohl, C. F.; Medema, D.; Verberg, G.; Jonkhoff, T. *Recueil* **1968**, *87*, 961.
(10) Pandey, R. N.; Henry, P. M. *Can. J. Chem.* **1975**, *53*, 1833.

(11) *Sadtler Standard Spectra*; Sadtler Research Laboratories, Inc.: Philadelphia, PA, 1973.
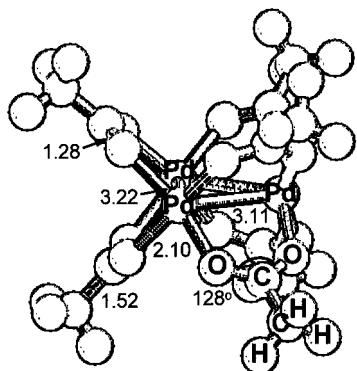(12) Andzelm, J.; Wimmer, E. *J. Chem. Phys.* **1992**, *96*, 1280.

Figure 3. Palladium acetate trimer structure as used for the evaluation of vibrational wavenumbers. Calculated bond lengths (Å) and angles are given.

Table 1. Results of Group Theoretical Analysis for the Normal Mode Vibrations of Pd Acetate, Assuming D_{3h} Point Group Symmetry

irreducible representations	$13A_1' + 9A_1'' + 9A_2' +$ $12A_2'' + 22E' + 21E''$
Raman active vibrations	$13A_1' + 22E' + 21E''$
infrared active vibrations	$12A_2'' + 22E'$

as linear combinations of atomic Gaussian-type orbitals. The basis sets were of double-ζ quality and included polarization functions for all non-hydrogen atoms (DZPV).[16] A second set of basis functions, the auxiliary basis set,[17] was used to expand the electron density in a set of single-particle Gaussian-type functions. Second derivatives have been evaluated analytically.

III. Results and Discussion

A. Raman and Infrared Spectra of Crystalline Pd Acetate. The structure of Pd(II) acetate in the crystalline state has been determined by X-ray diffraction.[18] The Pd ions occupy the corners of a (nearly) equilateral triangle. Each pair of Pd (II) ions is bridged by two acetate groups in which the two equivalent oxygen atoms are directed toward each Pd ion (Figure 3). Thus, it is reasonable to assume as a first approximation that the Pd acetate "molecule" has D_{3h} point group symmetry. In Table 1, we list the irreducible representations for the vibrational modes expected for Pd acetate based upon this symmetry.

The Pd acetate molecule has the chemical composition $Pd_3(CH_3COO)_6$, implying 129 vibrations corresponding to the $3N-6$ internal degrees of freedom. Several comments are worthwhile regarding Table 1. First, the X-ray data for the crystalline form of palladium acetate indicates some deviation from perfect D_{3h} symmetry. This reduces the degree of degeneracy of some of the vibrations listed in Table 1, which causes corresponding effects on the vibrational spectrum. Second, it is possible that factor group band splittings arise in the crystal. This may be due to the presence of crystal fields that have the lower symmetry of the molecular site. Another
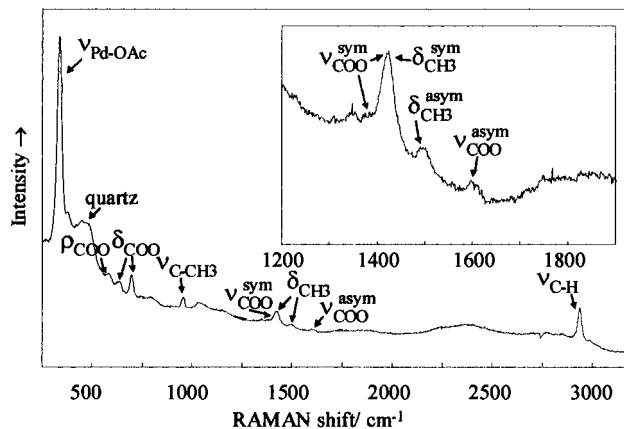
(13) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.
(14) Becke, A. D. *Phys. Rev. A* **1988**, *33*, 3098.
(15) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *32*, 13244.
(16) Godbout, N.; Andzelm, J.; Wimmer, E.; Salahub, D. R. *Can. J. Chem.* **1992**, *70*, 560.
(17) Andzelm, J.; Russo, N.; Salahub, D. R. *Chem. Phys. Lett.* **1987**, *142*, 169.
(18) (a) Skapski, A. C.; Smart, M. L. *Chem. Commun.* **1970**, *531*, 658. (b) Cotton, F. A.; Han, S. *Rev. Chim. Miner.* **1983**, *20*(4−5), 496. (c) Bancroft, D. P.; Cotton, F. A.; Falvello, L. R.; Schwotzer, W. *Polyhedron* **1988**, *7*(8), 615. (d) Lyalina, N. N.; Dargina, S. V.; Sobolev, A. N.; Buslaeva, I. P. *Koord. Khim.* **1993**, *19*, 57.

Figure 4. Raman spectrum of the palladium acetate trimer crystal.

possible cause may be the variation in phase of vibration of the different molecules in the unit cell. Because of these effects, some or all of the vibrational degeneracies of the free molecule may be lifted in the solid state.[19] Of course, the magnitudes of the frequency splittings will depend on the strength both of the crystal fields and of the interactions between molecules, and thus may not lead to resolvable bands in the infrared or Raman spectra. Finally, we list the infrared and Raman selection rules in Table 1.[20] Since the solid state spectrum presented in Figure 4 was measured on a powder sample rather than a single crystal, it is not possible to perform polarization analysis. On the other hand, in the solution data described below, it is possible to distinguish between totally symmetric and nontotally symmetric vibrations using polarization analysis: the A_1' modes should be polarized ($0 \leq \rho < {}^3/_4$; ρ is the depolarization ratio), whereas the modes with lower symmetries will be depolarized ($\rho = {}^3/_4$).

In Table 2, the Raman and the infrared vibrational wavenumbers for solid Pd acetate are listed along with vibrational mode assignments based upon the results of our calculations. Raman and infrared spectra are presented in Figures 4 and 5, respectively. The vibrational bands are assigned to particular group vibrations based upon correspondence of the observed and the predicted wavenumbers. It is worth noting that the Pd acetate molecule does not possess inversion symmetry (due to the presence of the 3-fold (C_3) axis), so there is no mutual exclusion of Raman and infrared active vibrations. Only the doubly degenerate E' modes are active in both types of spectroscopy (see Table 1), however, so the observation that the 1605 cm⁻¹ Raman vibration is also present in infrared data (1604 cm⁻¹) suggests that the symmetry of that vibration is E'. In addition, the variation of intensities in the infrared (high) and Raman spectra (low) are in agreement with an asymmetric O−C−O mode. The situation regarding symmetry is less clear for the symmetric O−C−O mode near 1400 cm⁻¹, which appears near the strong CH_3 vibration at 1421 cm⁻¹, thus making it more difficult to assign an accurate Raman wavenumber to this mode. Furthermore, the Fermi resonance between the modes, caused by the coupling, obscures the assignment of the mode based on infrared and Raman intensities. On the other hand, the 582 cm⁻¹ vibration appears in both the Raman and the infrared spectra and is thus likely to have E' symmetry.

The most striking aspect of the spectrum in Figure 4 is the strong vibration at 338 cm⁻¹. Based upon our calculations, we

(19) Sherwood, P. M. A. *Vibrational Spectroscopy of Solids*; Cambridge University Press: Cambridge, 1972.
(20) Herzberg, G. *Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra of Polyatomic Molecules*; Van Nostrand Reinhold Co.: New York, 1945.

Table 2. Comparison of Measured and Calculated Vibrational Wavenumber (cm^{-1}) of Bridging Palladium Acetate, and Bi- and Monodentate Terminal Acetates. Wavenumbers Have Been Calculated for a Trimer Model Structure (See Figure 3) and Two Types of Terminal Acetates (See Figure 1)

	bridging acetate			terminal acetate		
mode/system	ν(calculated)	$\Delta\nu$(Raman)	ν(infrared)	ν bidentate (calcd)	ν monodentate (calcd)	$\Delta\nu$(Raman)^a
ν(Pd−OAc) out of phase	288			293	299	300
ν(Pd−OAc) in phase	335	338				
ρ(COO)	535	582	582	418	425	
δ(COO) wag	630	640	622	521	637	533
δ(COO) sciss	695	697	692	642	650	677
ν(C−CH$_3$)	964, 1092	954	1020, 1046	900	850	
ν(C−O)^c					1287	
ν(COO) sym^{b,c}	1267, 1332, 1380, 1429, 1517	shoulder of δ(CH$_3$)	1332, 1372, 1392, 1430	1397		1345(?)
δ(CH$_3$) sym^b	1267, 1332, 1380, 1429	1421	1332, 1372, 1392, 1430	1327	1333	
δ(CH$_3$) asym	1517	1497		1437	1411	
ν(COO) asym^c	1590	1605	1604	1497		
ν(C=O)^c					1629	1730
ν(C−H) sym	2812	2935	2933	2995	2860	
ν(C−H) asym	3042		3000	3073, 3111	3036, 3092	

^{a} Most bands are masked by the solvent bands and the bands listed are visible only at high acetate concentration. ^{b} Strongly coupled modes. ^{c} $\Delta = \nu$(COO)asym $- \nu$(COO)sym values are calculated to be 161 cm^{-1} and measured as 184 cm^{-1} for the bridging acetates, and calculated to be 100 cm^{-1} for the bidentate acetates; $\Delta = \nu$(C=O) $- \nu$(C−O) is calculated to be 342 cm^{-1} for the monodentate acetate.
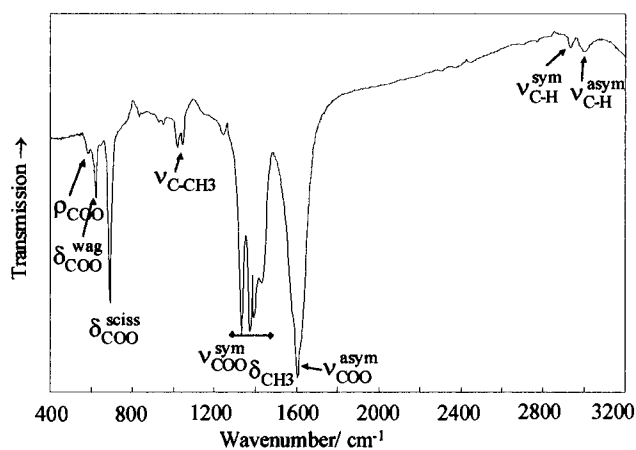
Figure 5. FT-IR spectrum of the palladium acetate trimer crystal.

assign this vibration as a Pd acetate breathing mode, whereby acetate ligands stretch against the Pd ions. It is interesting to note that in acetic acid solution this band appears at 346 cm^{-1} (see below), whereas in deuterated acetic acid-d_4 solution it occurs instead at 334 cm^{-1}. This shift of 12 cm^{-1} is slightly larger than the shift expected for a vibration in which the acetate ligands vibrate harmonically against the Pd ions (8.5 cm^{-1}, as calculated for complete deuteration of acetate) but is, in general, consistent with our assignment for this vibration, which will be discussed in more detail below.

The relatively strong intensity of the 338 cm^{-1} band deserves some discussion. Resonance Raman spectra have been reported for several compounds containing palladium.[21] The resonance enhancement was attributed to charge-transfer transitions between Pd ions, or between ligand and metal. In our study, the lowest lying electronic states are the acetate-to-Pd(II) charge-transfer bands near 30 000 cm^{-1}; therefore, we do not expect

significant resonant enhancement using 514 nm excitation. The apparent lack of resonance enhancement for laser excitation energies near these high energy bands in the earlier experiments is consistent with our own studies, which show no evidence for resonance enhancement when the wavelength of the laser excitation is varied from 457 nm (Ar-ion laser) to 780 nm (Ti: sapphire laser). We thus interpret the strength of the 338 cm^{-1} band to be a result of a large conventional Raman polarizability and not due to electronic resonance.

Returning to Table 2, the second strongest Raman band is the carbon−hydrogen stretch at 2935 cm^{-1}. This band is easily assigned due to its very high wavenumber, characteristic of carbon−hydrogen bonds. The remaining features in the spectrum of Figure 4 were assigned based upon the results of quantum chemical calculations for the trimer depicted in Figure 3. In this calculation, we used the palladium acetate structure as found by X-ray measurements. The calculations yield a Pd−Pd distance of 3.11−3.22 Å for the acetate-linked palladium ions, which is in very good agreement with the distance of 3.11− 3.20 Å determined by X-ray diffraction.[18] The calculated Pd− oxygen and oxygen−carbon bond lengths also agree within 4% with the X-ray diffraction values. This reasonably accurate modeling of the trimer structure increases our confidence in the vibrational wavenumber predictions made by the calculations. We therefore used these predictions to make the vibrational assignments given in the tables that we now discuss.

Differences in the wavenumbers of carboxyl symmetric and asymmetric stretch modes are important in the identification of the coordination mode of acetates.[22] The magnitude of the difference is sensitive to the angle between the oxygen atoms of the carboxyl group, which is a general feature of triatomic systems.[23] The symmetric carboxyl stretch and methyl bending modes are expected to be strongly coupled. We calculated an energy difference of 161 cm^{-1} between the carboxyl stretching modes, which is in good agreement with reported[24] and

(21) (a) Clark, R. J. H.; Kurmoo, M.; Mountney, D. N.; Toftlund, H. *J. Chem. Soc., Dalton Trans.* **1982**, *9*, 1851. (b) Clark, R. J. H.; Croud, V. B.; Kurmoo, M. *Inorg. Chem.* **1984**, *23*(16), 2499. (c) Clark, R. J. H.; Croud, V. B.; Kurmoo, M. *J. Chem. Soc., Dalton Trans.* **1985**, *4*, 815.

(22) (a) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Chapman and Hall: London, 1975. (b) Bellamy, L. J. *The Infrared Spectra of Complex Molecules, Vol. 2, Advances in Infrared Group Frequencies*; Chapman and Hall: London, 1980.
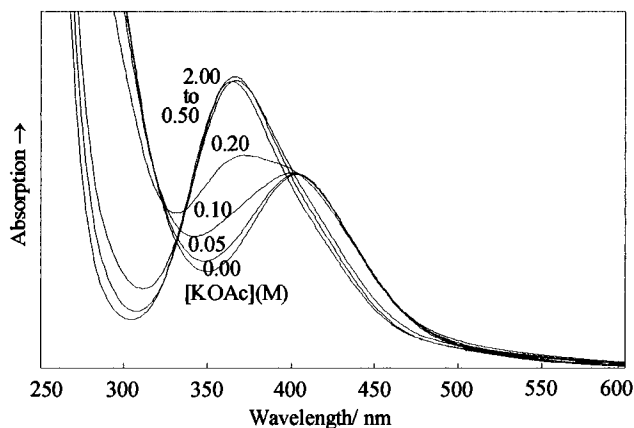
Figure 6. UV/vis spectra of palladium acetate in glacial acetic acid on increasing the potassium acetate concentration.

measured differences of 173 and 184 cm^{-1}, respectively. We used the theoretical wavenumbers that agree most closely with observed values to calculate the difference, since each vibration gives rise to two bands.

As stated above, the very strong band at 338 cm^{-1} is assigned to an acetate−Pd stretch mode. These acetate vibrations can be either in or out of phase with each other. When the individual vibrations are in phase, the resulting vibrational mode is fully symmetric (A_1' symmetry). This mode is of particular interest since it will be sensitive to structural changes in the Pd acetate species. Furthermore, its intensity is high enough to be seen in the dilute solutions we are studying, and this vibration is not overlapped by the much stronger solvent bands in the glacial acetic acid solution (see e.g. Figure 7a).

B. Decomposition of Pd Acetate by Potassium Acetate in Acetic Acid Solution. Pd acetate dissolved in acetic acid decomposes upon addition of alkali metal acetates, and UV/vis spectroscopy has been used to study these decomposition reactions for the addition of sodium and lithium acetate.[7,8] Here we describe a similar study of the decomposition induced by potassium acetate (KOAc). New structural information on the Pd species present was obtained using Raman spectroscopy and ab initio calculations. The decomposition of Pd acetate was studied for KOAc concentrations ranging from 0.00 to 2.00 M.

a. Electronic Spectroscopy. Pd acetate solvated in glacial acetic acid gives rise to a broad absorption band in the UV/vis spectrum, with a band maximum near 400 nm. The high intensity and energy of this band suggest that it involves ligand-to-metal charge transfer, as is expected to take place from the acetate ligands to the Pd ions. For comparison, KOAc does not give rise to absorption bands in this spectral range.

On addition of potassium acetate to a solution of palladium acetate in acetic acid, a number of changes in the spectra are observed (see Figure 6). For concentrations up to about 0.10 M, a band maximum at 404 nm is found. Furthermore, isosbestic points at 320 and 425 nm appear; this suggests an equilibrium between two species.[25] At 0.50 M KOAc, the band maximum shifts to 362 nm. Intermediate concentrations (such as 0.20 M) show an absorption band that can be represented by a superposition of the two peaks seen individually at low and high KOAc concentrations. Bands at concentrations of 0.20 M or lower show an isosbestic point at about 450 nm. Bands at higher concentrations also show isosbestic points, though less clearly. We assign
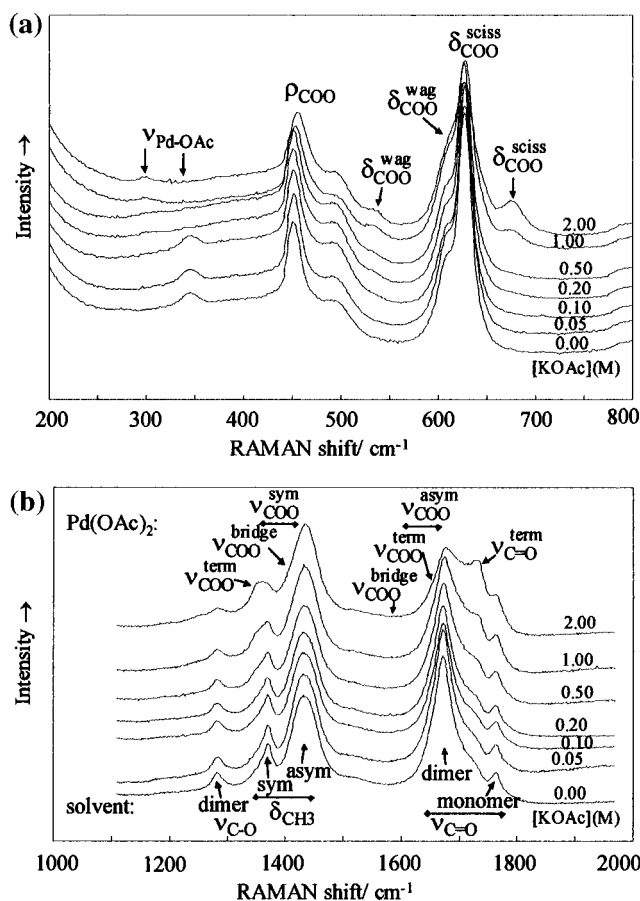

Figure 7. Raman spectra of palladium acetate in glacial acetic acid on increasing the potassium acetate concentration. Changes in the acetate−palladium and carboxyl stretch bands are shown in the 200−800 (a) and 1000−2000 cm^{-1} (b) ranges, respectively.

these bands to charge transfers of bridging (404 nm) and terminal acetates (about 362 nm).

In agreement with earlier literature,[7,8] we assign the shifts in the UV/vis spectra to decomposition of palladium acetate trimers to coordinatively unsaturated dimers, and successively to dimers that are coordinatively saturated by acetate ligands or to monomers, depending on the concentration of alkali metal acetate. Conversion of trimers to dimers takes place in the concentration range where isosbestic points are observed (up to about 0.20 M). At higher concentrations, above 0.50 M KOAc, changes in the absorption bands are minor and indicate an equilibrium that does not go to completion. From the UV/vis spectra alone it is not clear whether the dimers become coordinatively saturated with acetate ligands, or whether monomers are formed at high KOAc concentration.

Fitting the bands observed in our UV/vis spectra gives some additional information, confirming that the bands are indeed composed of just two peaks. This agrees well with the expectation that all possible Pd acetate species are composed of two kinds of acetate groups, bridging and terminal. The sum of the integrated areas of the bands remains approximately constant with KOAc concentration; that is, the decrease of the integrated intensity of the peak at 404 nm is compensated by an increase of the intensity of the peak at 362 nm. At higher KOAc concentrations, the peak at 404 nm still has an integrated intensity greater than half its value with no KOAc added. We

(23) *Infrared and Raman Spectroscopy*; Schrader, B., Ed.; VCH Verlagsgesellschaft mbH: Weinheim, 1995.

(24) Stephenson, T. A.; Morehouse, S. M.; Powell, A. R.; Heffer, J. P.; Wilkinson, G. *J. Chem. Soc.* **1965**, 3632.

(25) (a) Rao, C. N. R. *Ultra-Violet and Visible Spectroscopy. Chemical Applications*, 3rd ed.; Butterworth & Co.: London, 1975. (b) Nowicka-Jankowska, T. *J. Inorg. Nucl. Chem.* **1971**, *33*, 2043.

thus conclude that at high KOAc concentrations, palladium acetate species with bridging acetate groups, such as dimers, are present. The structure of the dimers is unknown. It is also not certain that monomers are actually formed, since the absorption data can be well described by two bands only. However, it is clear that on addition of KOAc, more species with terminal acetate groups are formed, and that the most significant increase takes place between 0.20 and 0.50 M KOAc. Since our observations are in general agreement with the literature for other alkali metal acetates,[10] we refer to the Pd acetate species formed in our experiments using the nomenclature proposed in the literature, which allows ready comparison with the earlier studies.

The nature of the alkali metal counterion has a pronounced effect upon the extent of decomposition of the palladium acetate. Potassium acetate converts all trimers to dimers at concentrations between 0.10 and 0.20 M, whereas lithium or sodium acetate converts palladium acetate trimers to dimers at concentrations of 0.5 and 0.2 M, respectively.[7,8] Alkali metal acetates are thermodynamically predicted to dissociate in solution.[26] However, the concentration of alkali metal acetate needed to completely convert all palladium acetate trimers to dimers is proportional to the solvation energy of the alkali metal cation. The greater the solvation energy, the more the equilibrium is shifted in the direction of decomposed palladium acetate. Of these three alkali metal acetates, potassium acetate most efficiently decomposes palladium acetate.

b. Raman Spectroscopy. Palladium acetate in acetic acid solution gives rise to a band at 346 cm^{-1} (see Figure 7a). The band at 346 cm^{-1} is assigned to the in-phase palladium–acetate stretch mode, and is likely to be the same band observed in Figure 4 at 338 cm^{-1}. Polarization analysis shows that this band is polarized ($\rho = 0$), indicating that the palladium–acetate stretch mode has A$_1'$ symmetry and thus is totally symmetric. This is the only readily observable band of the solvated palladium acetate complex. Surprisingly, in deuterated glacial acetic acid the C–H stretch band of Pd acetate is not observed, presumably due to exchange of the acetate ligands with the solvent during the long required equilibration time. Such exchange is indicated by a shift of the 346 cm^{-1} band to 334 cm^{-1}. At elevated temperatures, the band at 346 cm^{-1} maintains the same energy and its intensity increases, reflecting preservation of the trimer structure and increased solubility. For example, at 373 K it is increased by nearly a factor of 3.

On increasing the acetate concentration, several spectroscopic changes take place. These changes are not due to the KOAc, since at high concentrations bands that would be expected for KOAc[27] are not observed. In the acetate-palladium stretch region, distinct changes occur. The band at 346 cm^{-1} disappears at KOAc concentrations above 0.20 M. At higher KOAc concentrations, between 0.50 and 1.00 M, a new weak band shows up at 300 cm^{-1}. In agreement with the UV/vis measurements discussed above, the Raman data are consistent with the trimeric species being completely converted to dimeric or monomeric PdOAc species within the small KOAc concentration range of 0.10–0.20 M. At KOAc concentrations above 0.50 M the new Raman band at 300 cm^{-1} appears. We assign this new band to an acetate–palladium stretching vibration of terminal acetate groups. This assignment is based upon our theoretical studies (see next section).

(26) *CRC Handbook of Chemistry and Physics*, 1st ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1990.
(27) Ross, S. D. *Inorganic Infrared and Raman Spectra*; McGraw-Hill Book Company (UK) Limited: London, 1972, and references therein.

Table 3. Calculated and Measured Vibrational Wavenumbers for the Acetic Acid Monomer and Dimer

mode/system	calculated wavenumber/cm^{-1}		measured wavenumber/cm^{-1} ^{a}	
	monomer	dimer	monomer	dimer
ρ(COO)	416	455		454
δ(COO) wag	550	582	536	
δ(COO) sciss	572	620	654	623
ν(C–CH$_3$)	847	887	846	896
ν(C–O)^b	1313	1299	1279	1255, 1410
δ(CH$_3$) sym	1392	1407	1340	1371
δ(CH$_3$) asym	1437	1453	1401	1431
ν(C=O)^b	1773	1691	1799	1683

^{a} Measured with infrared spectroscopy.[30,31] ^{b} Calculated values of $\Delta = \nu(C{=}O) - \nu(C{-}O)$ are 460 and 392 cm^{-1} for the monomer and dimer, respectively, whereas the measured values are 520 and 428 cm^{-1}.

Changes are also observed in regions of the spectra corresponding to carboxyl stretch and deformation modes (see Figure 7). Several new bands and shoulders appear at potassium acetate concentrations between 0.50 and 1.00 M. New bands show up at 533 and 677 cm^{-1} in this concentration range. Furthermore, a new shoulder appears on the carbon–oxygen stretching band of the acetic acid dimer at 1345 cm^{-1}. A much more pronounced band at 1730 cm^{-1} appears in the same KOAc concentration range. The new bands appear concurrently with the band at 300 cm^{-1} and therefore originate from the same palladium acetate species. Even at much lower KOAc concentrations, beginning at about 0.20 M, traces of the new bands are visible. At concentrations between about 0.50 and 1.00 M they become more pronounced. The band at 1730 cm^{-1} has been assigned to a carbonyl stretch mode of ester-like bound acetate.[28] We assign all these bands to terminal acetates, belonging either to dimeric or to monomeric palladium acetate species. These assignments are partially based on our theoretical studies (see next section).

In summary, trimeric PdOAc species decompose on addition of KOAc. Up to 0.10 M KOAc, trimeric PdOAc species are present. Between 0.10 and 0.20 M KOAc, these species convert to a different form of PdOAc. Above 0.20 M, new species that contain terminal acetate ligands are formed, as can be seen from the carboxyl deformation and stretching bands. These bands are weak between 0.20 and 1.00 M KOAc. Above 1.00 M, a third kind of palladium acetate species is present which has an acetate–palladium stretching band at 300 cm^{-1}. The carboxyl deformation and stretching bands are also more pronounced at these high KOAc concentrations. The observed spectroscopic changes suggest that the trimers first decompose to dimers, and then successively to monomers, at concentrations of 0.10–0.20 M and 0.50–1.00 M KOAc, respectively. At intermediate concentrations the dimeric species are coordinatively unsaturated by acetate ligands. Our data are also consistent with a situation in which Pd acetate dimers are the only decomposition products formed, and become coordinatively saturated only at high concentrations of KOAc.

c. Theoretical Calculation of Vibrational Wavenumbers. To form a basis of comparison for the terminal acetate ligands, the vibrational wavenumbers of acetic acid monomers and dimers have been evaluated (see Table 3). All calculated wavenumbers agree within 3.5% with experimental wavenumbers, which is accurate enough for our studies. Only the calculated scissors mode wavenumber of the acetic acid monomer differs significantly from the measured value. This

(28) Augustine, S. M.; Blitz, J. P. *J. Catal.* **1993**, *142*, 312.

mode is calculated to have far too low a wavenumber, for reasons that are presently unknown. A reason could be a large anharmonicity of the mode, which cannot be considered in our theoretical computational method.

The calculated and the measured wavenumbers of the carbon−oxygen stretching modes also do not agree. However, the trend observed experimentally, that the difference between the symmetric and asymmetric stretching modes for the monomeric acetic acid species is larger than for the dimeric species, is reproduced by the calculation. The calculated values agree well enough with experiment to assign the vibrational spectrum of the acetic acid solvent.

A number of new bands appear as palladium acetate decomposes to dimeric and monomeric species. In addition to wavenumber changes in the acetate−palladium stretching mode, the carboxyl group vibration is also affected. Most of the bands appear (see Table 2) when palladium acetate dimer and monomer species are formed. In these species, terminal acetate ligands are bound in a bidentate way to palladium. Acetate is thereby bound to palladium via two more or less equivalent palladium−oxygen bonds. These acetates are more similar to acetic acid than to the bridging acetate ligands that are present in the palladium acetate trimer.

The terminal acetate groups are modeled as an acetate group bound to a single palladium ion, with highly localized acetate vibrations. Assuming the accuracy of this terminal acetate model, all the observed spectroscopic changes can be understood. The wavenumber of the terminal acetate−palladium stretching vibration is calculated to be 293 cm^{-1}. This value is shifted by 44 cm^{-1} to lower wavenumber compared to the in-phase stretching vibration of bridging acetate groups. The Raman band at 300 cm^{-1} can therefore be assigned to a terminal acetate ligand. The terminal acetate carboxylic group vibrational modes are predicted to appear at 521 cm^{-1} (wag) and 642 cm^{-1} (scissor), the first at lower and the second at higher wavenumber compared to similar vibrations of the acetic acid dimer (582 and 620 cm^{-1}). This agrees reasonably well with the wavenumber shifts we observe. These bands are therefore assigned to terminal acetates as well. Since terminal acetate groups are present in both the palladium acetate dimer and monomer, the observation that these bands increase in intensity with increasing KOAc concentration is consistent with the formation of either of these species, but does not permit a simple differentiation between the two species based upon their wavenumbers.

The most likely palladium acetate species are shown in Figure 2. There is actually a whole range of monomeric and dimeric species conceivable. Both the dimer and the monomer could be more or less completely coordinatively saturated. In our spectroscopic studies, we observe that palladium acetate species become more saturated as the potassium acetate concentration increases. It is not clear if this is caused by the formation of palladium acetate monomeric species or if the dimeric species become more coordinatively saturated. Both schemes fit all data from our experiments and from experiments performed in the past.

d. Semi in Situ Study of the Vinyl Acetate Formation. The heterogeneous acetoxylation reaction has been studied by means of DRIFT spectroscopy by Augustine and Blitz.[28] They utilized Pd supported on α-alumina (1.2 wt % Pd) as catalyst, and a mixture of KOAc and KOH as promoter. From their experiments, they concluded that the active phase of the heterogeneous catalyst is some form of surface palladium acetate, which is formed under reaction conditions. They also concluded that vacancies in the Pd coordination sphere are important in the
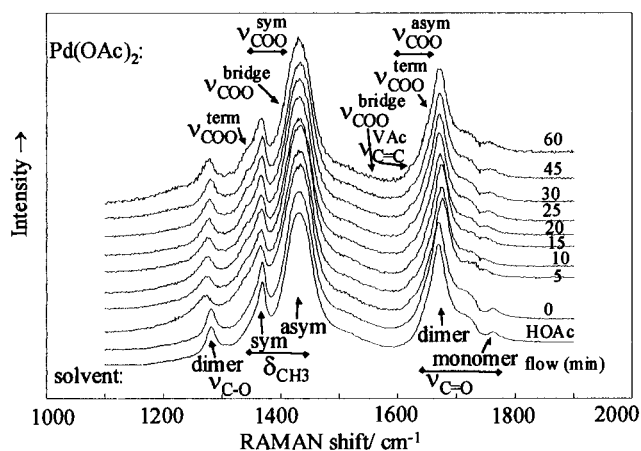

Figure 8. Raman spectra of palladium acetate in glacial acetic acid on reacting with ethylene. In this range, changes in carboxyl stretch modes are shown. The bottom part of the scheme shows assignments to the acetic acid solvent, whereas the top part shows assignments to palladium acetate species.

mechanism. It is interesting to compare the homogeneous and heterogeneous reactions in order to determine if some of the steps in the acetoxylation mechanism are the same.

In our work, the homogeneous acetoxylation of ethylene by Pd acetate was followed using Raman spectroscopy. During the course of the reaction, the trimer concentration decreased gradually (see Figure 9a). In contrast to the effect of adding KOAc to the solution, the absence of any observable changes in the acetate−palladium stretch region (near 300 cm^{-1}) suggests that decomposition to the monomer does not take place. The Pd acetate is gradually reduced to Pd black by reaction with ethylene (we did not reoxidize the Pd in our study).

Several changes are seen in the carboxyl stretch region (1200−1800 cm^{-1}), as illustrated in Figure 8. A shoulder appears on the low-energy side of the band assigned to the carbonyl stretch mode of the acetic acid dimer. The same shoulder also appears upon addition of KOAc. We suggest that this shoulder signals the decomposition of the palladium acetate trimers to dimers. Another very weak shoulder at about 1648 cm^{-1} appears soon after ethylene begins flowing through the solution. This band could originate from a vinylic carbon−carbon stretch, indicating that vinyl acetate is formed. A band characteristic of the vinyl acetate carboxyl group is not observed due to the very low concentration. We would expect such a band to occur at a wavenumber higher than that of the carbonyl stretch mode of dimeric acetic acid, rather than at the observed lower wavenumber of 1648 cm^{-1}.

Some GC/MS measurements were performed to determine the products formed. Vinyl acetate is formed, which indicates that acetoxylation indeed occurs under our reaction conditions. The selectivity for vinyl acetate is low, with acetaldehyde being the main product. Also, a number of other byproducts are formed to a lesser extent as a result of coupling reactions. The bands observed by Raman spectroscopy in the C−H stretch region could correspond to the vinyl acetate and acetaldehyde products, whereby the former is formed first according to the Raman spectra.

The formation of products has also been followed spectroscopically. Unfortunately, most of the product vibrational bands overlap the solvent bands. This problem can be somewhat alleviated by using deuterated glacial acetic acid-d_4 as a solvent. All hydrocarbons that form containing hydrogen from Pd acetate or ethylene will be observable in this solvent. Since the product concentrations are very low, however, the bands are weak.
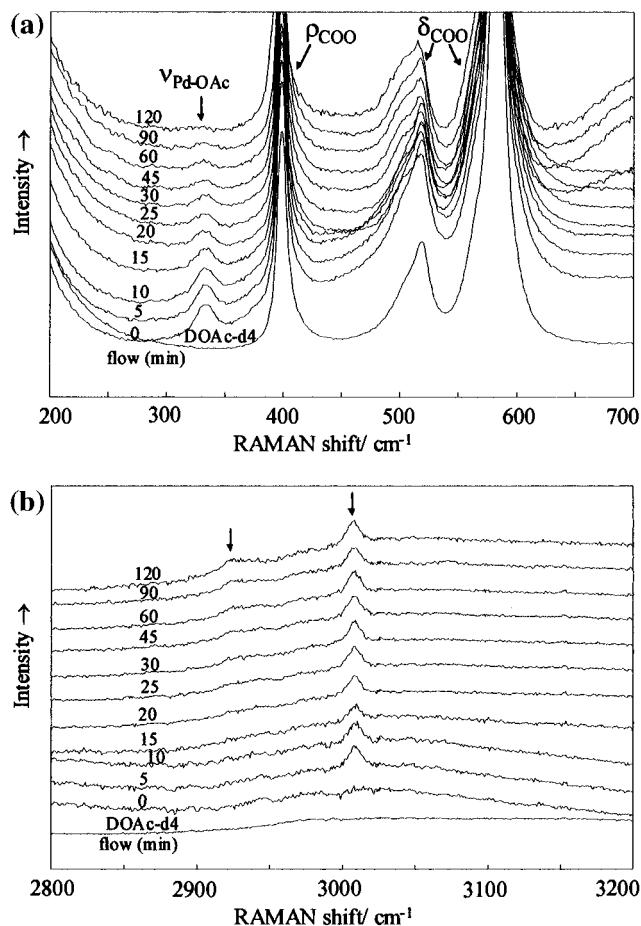
Figure 9. Raman spectra of palladium acetate in glacial acetic acid-d_4 on reacting with ethylene. The progression of the reaction is followed by the decreased intensity of the 334 cm^{-1} band (a) and appearance of small bands in the hydrogen−carbon stretch region (b).

While the concentration of Pd acetate trimers gradually decreases, products are sequentially formed (see Figure 9). Soon after ethylene begins flowing through the solution, a weak band at 3006 cm^{-1} is observed. This is a primary product, which is not converted to a secondary product. Since this band is at a different wavenumber than the C−H stretch of acetic acid, it cannot be assigned to a methyl group of an acetate. An even weaker band gradually appears at 2927 cm^{-1} after a much longer period of passing ethylene through the solution, perhaps indicating formation of a secondary product. The weak band at 3006 cm^{-1} appears during the same time period as the very weak shoulder at 1648 cm^{-1}. This band could therefore originate from vinyl acetate, with the C−H stretch assigned to the vinyl group. There are no other bands that appear at this time which could be assigned to a methyl group. The much weaker band at 2927 cm^{-1} might originate from a methyl group. Since several products are formed at low concentrations, assignment of this band is not possible. Acetaldehyde is, however, the main product in this reaction (see below) and could give rise to the band at 2927 cm^{-1}. It is interesting to note that acetaldehyde has been reported to form as a secondary product due to decomposition of vinyl acetate or acetic acid anhydride catalyzed by palladium-(II) chloride in acetic acid.[31]

Table 4. Selectivity of Various Palladium Acetate Species on Reacting with Ethylene[a]

added KOAc (M)	expected species	MS area AcH/VAc
0.0	trimer	21
0.2	dimer	12
2.0	monomer	159

[a] Given are relative proportions of formed acetaldehyde (AcH) to vinyl acetate (VAc) as a function of added potassium acetate (KOAc). Products have been determined by GC/MS.

In addition to the acetoxylation reaction catalyzed by Pd acetate trimers, the reactions with dimers and monomers were also studied. By adding 0.20 or 2.00 M KOAc to the solution, the predominant palladium acetate species are dimers or monomers, respectively. By visual observation, it is seen that Pd black forms fastest when dimers are present. The monomers and trimers are less active than the dimers. Thus, it is plausible that the trimers must decompose to dimers to become active, whereas monomers must be converted to dimers. Analyses of the solutions show that the various palladium acetate species have different selectivities (see Table 4). GC/MS product analysis shows that acetaldehyde is the main product, independent of the Pd acetate species present. Dimers appear to be the most selective species in the acetoxylation, followed by trimers and monomers. More extensive studies of the kinetics are given in the literature.[7,9]

One of the important questions that remains unanswered concerns the catalytic activity of the Pd black formed by reduction of Pd acetate by ethylene. It is not possible at this time to exclude completely a catalytic role for these particles. The formation of products is, however, observed when virtually no visible Pd black has formed. Furthermore, Pd black is not catalytically active for vinyl acetate formation; rather, surface acetates are the active species[28] and they are formed only in the presence of oxygen.[28,29] Moreover, the formation of acetaldehyde from vinyl acetate is, to our knowledge, reported to be catalyzed only by palladium(II) complexes.

IV. Summary and Conclusions

The Raman and the infrared spectra of the palladium acetate trimer have been assigned. A very strong Raman band at about 340 cm^{-1} is characteristic of the trimer structure and probably corresponds to an in-phase acetate−palladium stretch mode. In glacial acetic acid, the trimer structure is stable, with a solubility that is a function of temperature. However, the bridging acetate ligands seem to exchange readily with acetate from the solvent.

Both UV/vis and Raman spectroscopy indicate the decomposition of palladium acetate trimers to dimers, and perhaps also to monomers, upon addition of potassium acetate to the acetic acid solution. This observation agrees with literature reports of decomposition by addition of lithium or sodium acetate.[7,8] Equilibria between Pd acetate species are shifted further toward the dimers and monomers if K, rather than Li or Na, is the counterion. Dimers become the predominant Pd acetate species at KOAc concentrations between 0.10 and 0.20 M. Above about 0.50 M KOAc, a new species is formed, presumably monomeric. A strong Raman band appears at 1730 cm^{-1} as the decomposition progresses. This same band has been assigned in the literature to the active phase in the heterogeneous system.[28] We assign this band to terminal acetate ligands. In

(29) (a) Debellefontaine, H. *J. Chim. Phys.* **1978**, *75*, 801. (b) Nakamura, S.; Yasui, T. *J. Catal.* **1970**, *17*, 366.

(30) (a) Weltner, W., Jr. *J. Am. Chem. Soc.* **1955**, *77*, 3941.(b) *J. Chem. Phys.* **1964**, *41*(6), 1554. (c) Nakamoto, K.; Kishida, S. *J. Chem. Phys.* **1964**, *41*(6), 1558.

(31) (a) Maitlis, P. M. *The Organic Chemistry of Palladium*; Academic Press: New York, 1971; Vol. 2 and references therein. (b) Henry, P. M. *Palladium Catalyzed Oxidation of Hydrocarbons*; Reidel: Dordrecht, 1980; Vol. 2 and references therein.

the heterogeneous system, acetate bound in an ester-like way to palladium, rather than at bridging sites, would be analogous to the terminal acetates. The studies in the literature of the heterogeneous reaction are therefore in general agreement with our observations for the homogeneous reaction.

Acetoxylation of ethylene to vinyl acetate by Pd acetate solvated in glacial acetic acid takes place at room temperature. Palladium acetate trimeric species are probably converted only to dimers during the reaction, which are far more catalytically active than the trimers and the monomers. The formation of hydrocarbon products can be followed by Raman spectroscopy. Product analysis shows that acetaldehyde, formed either by the Wacker process or by the secondary decomposition of a primary product, is the major product. Vinyl acetate is also formed. Two small bands in the C−H and C−C stretch regions suggest that the acetoxylation takes place first. In contrast to the heterogeneous system, the strong band at 1730 cm^{-1} does not appear during the reaction. Since this band indicates the presence of monomeric palladium acetate species, it is clear that this band does not correspond to the most active and selective Pd acetate species in the homogeneous system.

In summary, the results of our study show that the Pd acetate species present in acetic acid solvent are strongly dependent on the concentration of alkali metal acetate added. We have used UV/vis and Raman spectroscopic methods to study this concentration dependency, as well as DFT theoretical modeling. Furthermore, we show that DFT theoretical methods are able to predict vibrational wavenumbers very accurately, as we have demonstrated by comparison with our Raman and FT-IR spectroscopic measurements on trimeric Pd acetate. Finally, we show that dimeric Pd acetate species are the active and selective species in the homogeneous catalyzed vinyl acetate formation, which can be followed in-situ by Raman spectroscopy.