Radical Anions Related to Naphtho[1',8']bicyclo[3.2.0]hepta-2,6-diene

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The title radical anion is unstable, and its esr spectrum is replaced by that of the ring-opened dihydro compound (2-pleiadene radical anion) at -80° . Possible reasons for this result are discussed. The esr splitting constant for the methylene hydrogens of 2-pleiadene and related compounds are surprisingly high, and this is attributed to π spin density in the vinyl group arising from weak overlap of the vinyl group with the naphthalene π system.

Electrocyclic bond cleavage reactions of the type $\sigma + n\pi \rightarrow (n + 1)\pi$ were the first to which orbital symmetry concepts were applied, and have received a great deal of study.¹ There has been a limited amount of work on such cleavage reactions in radical anionic systems. The stereochemistry of ring opening in radical anionic systems has received some attention. If the symmetry of the highest occupied MO is the determining factor, one would expect the opposite preferred stereochemistry as for the reaction of the neutral molecule. Winstein and coworkers² showed that cis-bicyclo [6.1.0] nonatriene (1) reduced to give the opened radical anion $(2 \cdot -)$, the same species as is formed by reduction of cyclononatetraene (2),³ whereas only the closed anion $(3 \cdot -)$ was observed upon reduction of trans-bicyclo [6.1.0] nonatriene (3).4



This result is consistent with the reversal of the Woodward-Hoffmann-predicted stereochemistry for neutral species being operative for radical anions. With the reversal, $1 \cdot -$ should open in an allowed reaction to *all-cis*-cyclononatetraene, as observed, but $3 \cdot -$ would be required to open to *trans,cis,cis,cis*-cyclononatetraene, which is very strained and has poor overlap.⁴ The generality of such concepts seems rather limited, however. Russell and coworkers⁵ showed that, although the radical anion produced from **4** has the opened structure $5 \cdot -$, the closed radical anion is observed upon reduction of **6**.

The cyclobutene-butadiene interconversion, the parent case of electrocyclic reactions, was studied in radical anions using substituted compounds such as benzo- and naphthocyclobutene. It has been established that the radical anions observed from these substrates at low temperatures have the closed structures,⁶ although the ring-opening reaction is "allowed"



using the reversed prediction for the radical anion, and substantial ring strain would be relieved.

We report here our esr studies of the reduction of 2-naphtho[1',8']bicyclo[3,2.0]hepta-2,6-diene (8) and related compounds. Ring opening of 8 is, of course, a forbidden reaction, since it is required to be disrotatory. Heating 8 for 30 sec at 250° results in only partial ring opening to pleiadiene (9).⁷ We expected



that the radical anion of **8** would open to that of **9** much more rapidly than the neutral species, and that $9 \cdot -$ would be stable under the reaction conditions.

Results

The splitting constants for pleiadiene radical anion have been reported separately.^{8a} We found that the esr spectrum of $9 \cdot -$, generated from 9 and sodiumpotassium alloy in THF, persists for hours at room temperature, and that several minutes of heating on a steam bath are required to destroy the spectrum. It could also be generated electrolytically in DMSO, although under these conditions further reduction took place at high applied potentials.

In contrast, $\mathbf{8}$ - proved to be an extremely labile species. We had to work at low temperatures to even observe it, but were ultimately successful using a 1:2 mixture of dimethoxyethane and 2-methyltetrahydrofuran with sodium-potassium alloy as the reductant,

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and developing the radical anion in an ethanol slush $(ca. -110^{\circ})$. The procession of radical anions observed upon careful warming of such a tube is outlined below. When the temperature of the tube was raised from -90° to -80° , the esr spectrum of $8 \cdot -$ faded rapidly, and was replaced by that of the symmetrical dihydro radical anion, $10 \cdot -$, as was verified by carrying out the reduction starting with 10. Upon further warming, the spectrum of $10 \cdot -$ faded and was replaced by that of the unsymmetrical dihydropleiadiene, $11 \cdot -$, also verified by starting with the authentic



neutral compound. Finally, near 0° , the esr spectrum of the tetrahydro compound appeared and eventually was the only radical anion observable. Exactly analogous behavior was shown by 3',6'-di-*tert*-butyl-**8** (8a) and led to observation of $8a \cdot -$, $10a \cdot -$, $11a \cdot -$, and $12a \cdot -$.

The great lability of $8 \cdot -$ is in substantial contrast to that of the hydrogenated derivative $13 \cdot -$, which gave an esr spectrum which was stable at -40° for hours. We did not observe radical anions other than $13 \cdot -$ from these sample tubes.



In contrast to the instability of $8 \cdot -$, the esr spectrum of the benzo derivative 14.-, generated in THF using sodium-potassium alloy, did not disappear rapidly even at room temperature. Brief warming of the sample tube resulted in a poorly resolved spectrum consisting of nine overlapping multiplets. The total width of this spectrum was only 17.5 G, which is by far the narrowest spectrum observed in any of this work.^{8a,b} Since Hückel calculations⁹ indicate that the spectrum of $15 \cdot -$ should be 20 G wide (Q = 24), we assign the spectrum to 15 -. Unfortunately, 15 is not stable enough to handle at ordinary temperatures¹⁰ and we did not verify our assignment by independent reduction of 15. Room-temperature electrolytic reduction of 14 in DMSO gave 16.-,11 the benzo analog of 10.

We also investigated the reduction of the housane derivative 17, in which the double bond of 8 is replaced by a cyclopropane ring. The radial anion of 17 was easily observed, but proved to be somewhat labile, and upon standing at room temperature the esr spectrum of $17 \cdot -$ was replaced by that of an unknown radical anion. The structure of this radical anion has eluded all of our efforts at guessing, although the spectrum was relatively easily analyzed, and the splitting constants 5.92 (2 H), 4.20 (2 H), 2.54 (2 H), 0.66 (1 H), 0.49 (2 H), 0.20 (2 H), and 0.09 (2 H) simulate the observed spectrum well. The only thing we can say about the structure is that it may have the naphthalene ring partially reduced, since splittings assignable to meta hydrogens are absent.

Upon standing at room temperature for 1 day, the spectrum of the "unknown" species faded, and was replaced with that of $18 \cdot -$ (verified by reduction of the authentic neutral compound^{8b}), as the ultimate reduction product. We did not observe the esr spectra of either $19 \cdot -$ or $20 \cdot -$ ^{8b} during the reduction of 1. There is no evidence from these results that the radical anion of 17 opens to 21 (which we know reduces to $20 \cdot -$



under the reduction conditions used), which is the thermal product from 17.^{8b}

The splittings of the radical anions observed in this work are summarized in Table I. We were unable to completely analyze the spectrum of the unsymmetrical reduction product, $11 \cdot -$, because of the large number of splittings. A partial analysis (using the outer lines, which are far more resolved than the center portion of the spectra) gave splittings of 0.27 (1 H), 0.79 (1 H), 1.08 (1 H), 3.07 (1 H), 2.37 (2 H), and 4.97 (2 H), leaving splittings caused by four hydrogens, summing to 15.92 G, unaccounted for.

Discussion

Splitting Constants.—The only unexpected splittings reported in Table I are the large β splittings observed for the unsaturated compounds $\mathbf{8} \cdot \mathbf{a}$ and $\mathbf{10} \cdot \mathbf{a}$. Introduction of the double bond in going from $\mathbf{13} \cdot \mathbf{a}$ to $\mathbf{8} \cdot \mathbf{a}$ results in a 53% increase of a_{β} , which certainly cannot be accounted for by a change in θ in the β coupling equation,¹² $a_{\beta} = (B_0 + B_2 \cos^2\theta)\rho_{\alpha}^{\pi}$, since the geometry for $\mathbf{13} \cdot \mathbf{a}$ and $\mathbf{8} \cdot \mathbf{a}$ must be very similar. A substantial increase in ρ_{α}^{π} for $\mathbf{8} \cdot \mathbf{a}$ is ruled out by the other ring splittings, which actually sum to indicate slightly more spin density in $\mathbf{8} \cdot \mathbf{a}$ than in $\mathbf{13} \cdot \mathbf{a}$. Increases of similar

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Radical anion of	Temp, °C	Line width, ^b mG	ap	$a_{ m in}$	a_{0}	a_{β}	Other
19	-45	110	4.18	2.48	1.11	6.60	0.28(4 H)
13	-40	115	4.24	2.42	1, 17	5.80	0.57, 0.14
17	-90	70	4.22	2.37	1.20	6.23	$\begin{array}{c} 0.25 (2 \text{ H}), \\ 0.24 (1 \text{ H}), \\ 0.17 (1 \text{ H}) \end{array}$
8	-100	95	4.39	1.94	1.48	8.87	0.12
8a	-100	220	4.04		1.52	9.05	Unobsd
8b	-70	90	4.25	2.10	1.71	7.97	0.32(6 H)
10	-80	110	4.70	1.89	1.66	10.84, 0.50	0.24
10a	-75	150	4.47		1,91	11.28, 0.53	Unobsd
10b	10	110	4.61	2.02	1.50	9.57, 0.28	$0.28~(6~{\rm H})$
14	-100	160	4.33	2.14	1.42	7.70	Unobsd

TABLE I ESB SPLITTING CONSTANTS (G)

^a In THF or THF-MeTHF mixtures, generated with Na-K alloy. ^b Peak-to-peak line width used in simulation of the spectra.



magnitude in a_{β} were also observed for sym-pleiadenes compared to pleiadanes; the largest β splitting of $10 \cdot$ is 50% larger than that of $12 \cdot -.^{8b}$ Although $10 \cdot -.^{8b}$ and $12 \cdot -$ probably have somewhat different θ values, application of the β coupling equation leads to unreasonably large ρ_{α}^{π} values for 10 \cdot . We also determined the spectra of $8b \cdot -$ and $10b \cdot -$, which have the vinyl hydrogens of 8 and 10 replaced by methyl groups. As Kosman and Stock have discussed,¹³ such a replacement will result in a methyl splitting which is slightly larger than the hydrogen splitting of the unsubstituted compound if the hydrogen splitting had been caused by π spin density in the vinyl group, whereas a much smaller methyl splitting would result if a long-range spin polarization mechanism had been responsible for the hydrogen splitting. Since we observed methyl splittings for $8b \cdot -$ and $10 \cdot -$ this is evidence for a modest π spin density in the vinyl groups of these compounds. Even a modest π spin density at a second center next to a CH group can cause large changes in the observed splittings, however, as was first pointed out by Whiffen.¹⁴ When a C-H bond can hyperconjugate with two π centers (designated here as α and α'), the splitting depends upon the amount of spin at each π center, as given by the relation in eq 1. The coefficients c_{α}^{π} must be summed before squaring $[\rho_{\alpha}^{\pi} = (c_{\alpha}^{\pi})^2]$. To see the enhanced a_{β} values we do,

$$a(\mathbf{H}) = Q(C_{\alpha}^{\pi} + c_{\alpha}^{\pi'})^2 \tag{1}$$

the signs of the coefficients must be the same at both carbons attached to c_{β} , as is shown diagramatically in 22, which represents positive coefficients with dark circles and negative ones with open circles. It should be noted that the pattern of coefficients which would result from spin introduction into the vinyl group by homohyperconjugation (as indicated in 23a and 23b) is that shown in 24, and would result in low a_{β} values. The pattern of coefficient signs shown in 22 does result when a vinyl group is allowed to overlap with the 1,8 positions of a naphthalene ring, and, if the overlap is



0.1 β , McLachlan calculations give a vinyl spin density of 0.011, quite close to the ρ of 0.010 estimated from the observed splitting of 0.24 G for 10. - using $Q_{\alpha} = 24$. Assuming that ρ_{α}^{π} for 10. - has the same value as it does for the saturated compound 12. -, about 0.13,^{8b} the apparent spin density necessary for calculation of a_{β} of 10. - would be $[(0.13^{1/2} + (0.010)^{1/2}]^2 = 0.22$, considerably larger than ρ_{α}^{π} . The low spin density shown to be present at the vinyl group does adequately account for the large increase in a_{β} observed.

Ring Opening of $8 \cdot -$ and $14 \cdot -$. —The prediction that cyclobutene cleavage of $8 \cdot -$ should be more facile than that of 8 seems to be borne out experimentally. Since $t_{1/2}$ for opening of **8** is greater than 30 sec at $250^{\circ7}$ and $t_{1/2}$ for decomposition of $\mathbf{8} \cdot \mathbf{\bar{s}}$ is less than 2 min at -80° , the difference in activation energies is at least 9 kcal/mol (assuming the same ΔS^{\pm}). In calculating the above difference, we have assumed that the reaction leading to the destruction of the esr signal for $8 \cdot -$ is ring opening, which would give $9 \cdot -$. We believe that this contention is made reasonable by the fact that many peri-disubstituted naphthalene anions are stable for hours even at considerably higher temperatures, 8b including $13\cdot$ –. The instability of $8 \cdot \overline{}$ is unusual, and seems uniquely associated with the presence of the cyclobutene ring. We do not, however, observe $9 \cdot \overline{}$, in spite of the fact that it is quite stable, even at room temperature in DMSO. A cause for this striking anomaly is suggested by the cyclic voltammetry spectrum of 9. In addition to the reversible oneelectron $\mathbf{9} \rightleftharpoons \mathbf{9} \cdot \overline{}$ couple at $E_{1/2} = -1.85$ V (in DMSO, vs. sce),^{8a} there is a totally irreversible wave at $E_{p} =$ -2.64 (V 200 mV/sec scan rate, no corresponding reoxidation wave observed up to 300 V/sec scan rate). This second wave must correspond to reduction of $9 \cdot -$ to the dianion, which is far more basic, and immediately protonates and is further reduced, removing the electroactive species. Since reduction of 8 requires a potential somewhat more negative than the -2.6 \overline{V} of naphthalene, $9 \cdot \overline{}$ is only formed from $8 \cdot \overline{}$ under

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conditions where a reducing agent capable of forming the very basic dianion 9^{2-} is present. We suggest that this dianion protonates, giving $10 \cdot -$ rapidly, and never allowing 9⁻ to build up. We only observed $11 \cdot -$ after the solutions containing $10 \cdot -$ had stood at -40° for many minutes. This rearrangement is most reasonably formulated as a base-catalyzed tautomerization of neutral 10 to 11, followed by electron transfer. Since 11 has a lower reduction potential than 10 ($E_{1/2}$ for 11 is -2.25 V vs. see in DMSO), if substantial amounts of 11 were formed initially, the esr spectrum of $11 \cdot -$ should have been observed. The protonation reaction leading ultimately to $10 \cdot$ at -80° in THF appears to be considerably more selective than that observed at room temperature in acetate-buffered methanol, where we observed a 77:20:2.8:<0.5 mixture of 10:11:9:12 upon 8% sodium amalgam reduction of 9, although we have no proof that the latter product ratios are kinetic ones.

A qualitative correlation diagram for the ring opening of $8 \cdot -$ to $9 \cdot -$ shows that, as in the simple case of cyclobutene \rightarrow butadiene (disrotatory), the symmetric doubly occupied MO of cyclobutene (or 8) correlates with the first antibonding excited level of butadiene (or 9), while the antisymmetric lowest antibonding level of cyclobutene (singly occupied in $8 \cdot -$) correlates with the highest bonding level of butadiene.¹ Starting with $\mathbf{8} \cdot \mathbf{-}$, an electronically excited state of $9 \cdot -$ would result if the correlation diagram is followed. The unusual, two-quantum excitation (which only takes place in a glass) necessary for photochemical ring opening of neutral 8 to 9, which is also suggested by the correlation diagram discussed above, has received experimental verification,^{7,10} and might bolster one's belief that there is something quite unusual about the opening of 8 to 9, and that the simple correlation diagram has practical validity. Our experiments only demonstrate that $8 \cdot -$ cleaves the 1.5 bond remarkably easily compared to neutral 8, and do not address the question of the electronic state of the product. Since forcing in antibonding electron raises the energy of the starting material, a lower activation energy for cleavage does not seem qualitatively unreasonable. It should be pointed out that we cannot rule out an irreversible cleavage of 8^{2-} , instead of $8 \cdot -$, although we do not favor this explanation, since the large separation in the two reduction waves of naphthalene requires that only tiny amounts of the dianion would be present.

The benzo analog $14 \cdot -$ was considerably more thermally stable than $8 \cdot -$, which is reasonable since part of the resonance energy of benzene is lost upon benzocyclobutene ring opening. Here we were able to observe the esr spectrum of the opened form, $15 \cdot -$, in THF. Presumably the extended conjugation makes the dianion rather less basic than that of 9. We did not observe $15 \cdot -$ in the more acidic solvent, DMSO, in which protonation of the dianion apparently does occur.

Replacing the 6,7 double bond of **8** by a cyclopropyl group (giving **17**) results in substantially less reactivity for the radical anion. Hydrogenation products are not observed until room temperature is reached, and then the ultimate naphthalene-containing reduction product was $18 \cdot -$, in which the 1,5 σ bond has been

cleaved, but not the 6,7 bond. The 6,7 cyclopropyl "bent bond" was not observed to be the equivalent of a 6,7 π bond in these reactions. The unknown radical observed between the spectra of $17 \cdot -$ and $18 \cdot -$ appeared from its splittings not to contain a naphthalene ring, and, if this was the case, further reduction and proton abstraction would lead to a polyalkylbenzene derivative, which would not be expected to give an esr spectrum under our conditions as long as any naphthalene-containing products (like 18) were present.

Other cases in which substituted cyclobutene anion \rightarrow butadiene anion conversions were observed to take place only with formation of the dihydro product include the reduction of 25^{15} and $26.^{16}$ In the latter



case the unhydrogenated product, *o*-xylylene anion, is apparently stable enough for detection by esr,^{6a} if generated from the dibromide. In both cases, it seems likely that reduction of the cyclobutene occurs at potentials beyond the second reduction wave of the butadiene; so observation of dihydro product seems entirely reasonable.

Experimental Section

Reduction of Pleiadiene (9). A. By Reduction with 8% Sodium Amalgam.¹⁷—To a solution of 520 mg (2.92 mmol) of 16 in 180 ml of 95% ethanol was added 180 ml of 10% sodium acetate. Over a period of 3 hr, chunks of 8% sodium amalgam (from 16.8 g of Na and 21 g of Hg) and 4.38 g (7.3 mmol) of acetic acid were added alternately to the bright red solution. After 4 hr, the color had faded almost completely. The solution was decanted from the mercury, and ether was added. The aqueous layer which separated was extracted (2 × 100 ml) with ether and the combined organic extracts were dried, after which filtration and rotovaporation left about 520 mg of a pale reddish residue. Analysis by vpc revealed the following product ratio, compound (%): 2-pleiadene (10) (77), 1-pleiadene (11) (20), pleiadiene (9) (2.8), pleiadane (12) (0.5). Preparative tlc (PF₂₃₄, 12.5% AgNO₃, benzene) gave 380 mg (73%) of 2-pleiadene (R_t 4–5.2): mp 99–100°; nmr (HA-100, CDCl₃) δ 8.86 (m, 1 H), 6.22 (m, 2 H), 7.06–7.80 (m, 6 H); ir (CCl₄) 3.26, 3.36, 3.46, 3.50, 6.21, 6.29, 6.35, 7.19, 7.26 μ ; uv (95% EtOH) λ_{max} (log ϵ) 225 (4.73), 269 (sh) (3.60), 277 (3.79), 287 (3.89), 298 (3.76), 306 (3.43), 316 (2.97), 321 (2.97); exact mass 180.0932 (calcd for C₁₄H₁₂, 180.0939).

The other major band (R_t 0.58) contained 100 mg of 1-pleiadene contaminated with a trace of pleiadiene. Purification by preparative vpc gave pure 1-pleiadene: mp 47-47.5° (lit.¹⁸ mp 43-45°); nmr (CDCl₃) δ 3.4-3.8 (m, 2 H), 3.05-3.40 (m, 2 H), 5.95-7.85 (m, 2 H), 7.1-8.0 (m, 6 H); ir (CCl₄) 3.27, 3.30, 3.41, 3.42, 3.51, 6.30, 6.36, 6.65, 6.98, 7.21, 7.39, 7.91 μ ; uv (95% EtOH) λ_{max} (log ϵ) 231 (sh) (4.57), 235 (4.59), 246 (4.14), 255 (4.00), 297 (3.97), 309 (4.11), 324 (3.97).

B. By a Diimide Reduction.—To a suspension of dipotassium azodicarboxylate (3.93 mmol, 763 mg) in a solution of 70 mg of pleiadiene in 50 ml of pyridine was added intermittently, over a period of 3 days, 240 mg (8 mmol) of acetic acid in 10 ml of pyridine. Rotovaporation of the pyridine left a residue which was suspended in ether and extracted successively with 1 M HCl (3 \times 50 ml), saturated Na₂CO₃ (3 \times 50 ml), and finally with water.

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Chem., 269, 189 (1882). (18) P. D. Gardner and W. J. Horton, J. Amer. Chem. Soc., 74, 657 (1952). The dried extracts were rotovaporated to yield 65 mg of a residue, which was shown by vpc to be a mixture of 1-pleiadene (41%), pleiadane (21%), and pleiadiene (38%). Preparative vpc gave a sample of 1-pleiadene, mp 47-47.5°.

6.9-Di-tert-butyl-1-pleiadene (11a) was prepared as in the unsubstituted case. Treatment of 9a with diimide for 5 days gave the following mixture (vpc): 6.9-di-tert-butylpleiadane (10%), 6.9-di-tert-butyl-1-pleiadene (43%), and 6.9-di-tert-butylpleiadiene (47%). Preparative the (silica gel, PF₂₅₄ 12.5% AgNO₃, benzene, 2×, R_t 0.4) gave 28 mg of product, which was sublimed: mp 99-100.5°; nmr (CDCl₃) δ 13.8 (s, 18 H), 2.55 (m, 2 H), 3.20 (m, 2 H), 5.90-6.82 (m, 2 H), 7.2 (d, J = 2 Hz, 1 H), 7.33 (d, J = 2 Hz, 1 H), 7.58 (d, J = 2 Hz, 2 H); ir (CHCl₃) 3.48, 6.22, 6.30, 6.81, 7.39, 11.41 μ ; uv λ_{max} (log e) 238 (4.65), 256 (4.26), 299 (sh) (3.91), 3.08 (4.00), 321 (sh) (3.89); exact mass 292.2207 (calcd for C₂₂H₂₈, 292.2191).

The compounds 10a and 10b were never prepared, although esr spectra, observed upon allowing reducing mixtures of 8a and 8b to warm, were recorded. The esr spectra were recorded on a Varian E.15 spectrometer, and sample preparation was as previously described.^{8a,b}

6b,10b-Dihydrobenzo[3,4]cyclobut[1,2-a]acenaphthylene (14). —A refluxing methylene chloride solution (30 ml) of 1.25 g of acenaphthylene was treated with 1.25 g of solid benzenediazoAcknowledgment.—We thank the National Science Foundation, the Sloan Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial financial support of this work, and the National Science Foundation's major instrument program for funds used in purchase of the nmr, esr, and mass spectral equipment used.

Registry No.--8.-, 40782-39-6; 8a.-, 40782-69-2; 8b.-, 40782-70-5; 9, 208-20-8; 9a, 40949-40-4; 10, 40949-41-5; 10.-, 40949-42-6; 10a.- 40949-43-7; 10b.-, 40949-44-8; 11, 40949-45-9; 11a, 40949-46-0; 13.-, 40949-47-1; 14.-, 40949-48-2; 17.-, 40949-49-3; 18.-, 40949-50-6.

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Palladium(II) Chloride Catalyzed Decomposition of Vinyl Acetate in Dry Acetic Acid¹

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The decomposition of vinyl acetate to give acetaldehyde and acetic anhydride was found to have two regions of kinetic behavior. In one, which occurs at low chloride, high Pd(II), and high vinyl acetate concentrations, the reaction rate had little dependence on these variables and addition of acetic anhydride depressed the rate only slightly. In the second region, which occurs at high chloride, low Pd(II), and low vinyl acetate concentrations, the kinetic behavior becomes conventional and follows the rate expression $-d[C_2H_3OAc]/dt = k[Li_2Pd_2Cl_3] \cdot [C_2H_3OAc]/[LiCl]$. In this range the reaction is strongly inhibited by acetic anhydride. The mechanism which best fits all the data involves the slow formation of water and acetic anhydride in a reaction not involving Pd(II) catalysis. The water then reacts with vinyl acetate in a Pd(II)-catalyzed reaction to give acetaldehyde and acetic acid. The two regions of kinetic behavior arise from the fact that either water formation or the reaction of water with vinyl acetate can be the rate-limiting step.

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The palladium(II)-catalyzed decomposition of vinyl acetate, first reported in 1959,³ has been the subject of at least two mechanistic studies.^{4,5} Noting that both palladium(II) chloride and sodium acetate were required for the decomposition, Clement and Selwitz proposed a mechanism involving attack of acetate on a Pd(II)-olefin complex (eq 1 and 2).

$$\begin{array}{c} O \\ CH_{3}C \\ \rightarrow \\ CH_{2}C \\ \rightarrow \\ O \\ -CH_{2}CH_{2} + OAc^{-} \\ \rightarrow \\ PdCl_{2}\delta^{-} \\ PdCl_{2} \end{array} \xrightarrow{} OCH_{2}CH_{2} + Ac_{2}O \quad (1)$$

$$\begin{array}{c} -\text{OCH} \longrightarrow \text{CH}_2 + \text{HOAc} \longrightarrow \text{CH}_3 \text{CHO} + \text{PdCl}_2 + \text{OAc}^- \quad (2) \\ \downarrow \\ \text{PdCl}_2 \end{array}$$

Schultz and Rony,⁵ on the other hand, found that sodium acetate was not required for the decomposition and, in fact, was a mild inhibitor. Furthermore, they found the reaction to be zero order in vinyl

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acetate and inhibited by LiCl. They also found that addition of Ac_2O had no effect on the rate. They explained these observations by first proposing that the predominant species in solution is either Cl_2 -PdCl(CH_2 =CHOAc)⁻ or the dimeric species Cl_2 -PdCl₂PdCl(CH_2 =CHOAc)⁻, which was found to be the active species in vinyl ester exchange.⁶ Further steps in the sequence are given by eq 3-6.

$$PdCl(CH_2 = CHOAc) + HOAc = Pd(HOAc)(CH_2 = CHOAc) + Cl^{-} (3)$$

$$1$$

$$\longrightarrow > PdCH_2CH(OAc)_2 + H^+$$
(4)

$$2 \longrightarrow > PdCH_2CHO(Ac_2O)$$
(5)
3

$$3 + HOAc + CH_2 = CHOAc + H^+ \longrightarrow$$

$$1 + Ac_2O + CH_3CHO \quad (6)$$

There is one serious objection to this reaction scheme. Vinyl ester exchange, which almost certainly proceeds by way of an intermediate such as 2, exhibits quite different kinetics from decomposition. Exchange is first order in both vinyl acetate and acetate ion. This

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