

ethoxide but inhibited by 2,6-lutidine, while addition of NaOH precipitated the catalyst. Gagné and Marks have reported<sup>7</sup> oxidative dehydrogenation of alcohols catalyzed by ruthenium complexes of 1,3-bis(2-pyridylimino)isindolines. The necessary addition of strong base in their oxidations was attributed to base-promoted disproportionation<sup>8</sup> of Ru(III):  $2\text{Ru(III)} \rightleftharpoons \text{Ru(II)} + \text{Ru(IV)}$ . Catalysis with the triruthenium carboxylates may involve intramolecular disproportionation, precluding the need for base promotion. Unique to this system, however, is the redox role of the ancillary metal centers<sup>9</sup> and the possible participation of the central  $\mu_3$ -oxygen atom. More detailed mechanistic and kinetic studies are under way.

**Acknowledgment.** This research was supported by the Army CRDEC through the University of Florida Technology Center and the National Science Foundation through Grant 86 18766.

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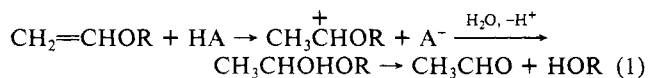
## Reexamination of the Alleged Vinyl Ether Hydrolysis Reaction of 9-Methoxy-1-oxacyclonon-2-ene: Disproof of Reversible Carbon Protonation

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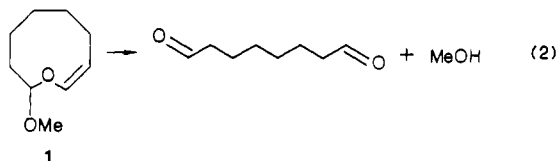
Received February 2, 1987

The conventional reaction mechanism for acid-catalyzed hydrolysis of vinyl ethers consists of rate-determining proton transfer from catalyst to substrate followed by rapid hydration of the cation so formed and further fast decomposition of the ensuing hemiacetal, eq 1. This reaction scheme is based upon a sizeable body



of evidence obtained by examining a number of different substances,<sup>1</sup> and the reaction has acquired the status of a prototype process; it has been used to provide detailed information not only about the proton-transfer process but also on the hydration of carbon-carbon double bonds.

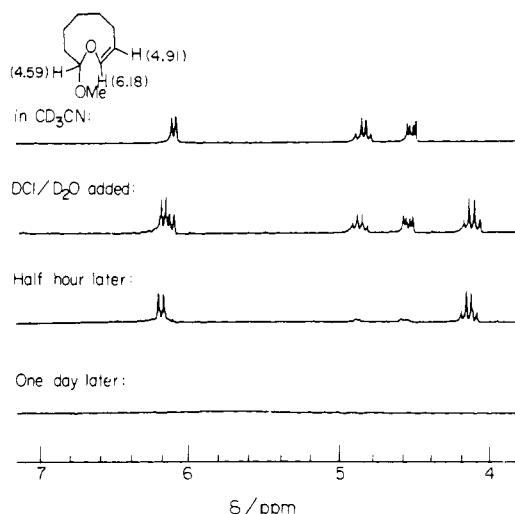
Some time ago an exception to this general mechanism was claimed for the case of 9-methoxy-1-oxacyclonon-2-ene (**1**).<sup>2</sup> The hydrolysis of this substance to suberaldehyde, eq 2, appeared to



occur by reaction of its vinyl ether functional group through the

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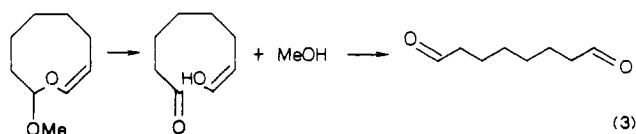
**Figure 1.** Proton NMR spectral changes occurring during the hydrolysis of 9-methoxy-1-oxacyclonon-2-ene; spectra measured at 200 MHz in  $\text{CD}_3\text{CN}$  and in 10:1  $\text{CD}_3\text{CN}/0.1 \text{ M DCl-D}_2\text{O}$  solutions.

mechanism of eq 1 when the reaction was carried out in dilute hydrochloric acid solutions. In acetic acid buffers, however, buffer catalysis became saturated as buffer concentration increased, and the hydronium ion isotope effect, which was normal ( $k_{\text{H}^+}/k_{\text{D}^+} > 1$ ) in hydrochloric acid solutions, became inverse ( $k_{\text{H}^+}/k_{\text{D}^+} < 1$ ). This behavior was taken to indicate that carbon protonation had become reversible in the presence of a sufficient concentration of buffer base and that some subsequent step was then rate determining.

We have searched, in vain, for other examples of reversible carbon protonation in the hydrolysis of vinyl ethers.<sup>3</sup> We now report that this phenomenon is absent in the hydrolysis of 9-methoxy-1-oxacyclonon-2-ene as well.

The hydrolysis of vinyl ethers may be monitored by following the change in strong UV absorbance at 200-220 nm which is characteristic of carbon-carbon double bonds bearing oxygen substituents. We have found that in the case of 9-methoxy-1-oxacyclonon-2-ene this change is biphasic: there is an initial increase followed by a somewhat slower decrease. This process is accompanied by a corresponding biphasic change in the NMR spectra of reaction mixtures (Figure 1): upon addition of a small amount of aqueous acid to an acetonitrile solution of 9-methoxy-1-oxacyclonon-2-ene, the original vinyl proton signals at 6.18 and 4.91 ppm are replaced by a new set at 6.22 and 4.16 ppm, and these new signals then disappear leaving this region of the spectrum bare. Similar changes occur with wholly aqueous solutions, and these are accompanied by the appearance of signals attributable to aldehyde protons at 9.66 ppm and aldehyde hydrate methine protons at 5.02 ppm.

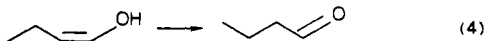
This emergence of a new set of vinyl proton NMR signals means that the hydrolysis of 9-methoxy-1-oxacyclonon-2-ene cannot be occurring through initial hydrolysis of its vinyl ether group, for that would lead to a simple monophasic loss of the original vinyl group signals without production of a new set. Initial hydrolysis of the acetal function, on the other hand, would give an enol with a new vinyl group (eq 3); enols, moreover, are known to have vinyl



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proton NMR signals which differ from those of corresponding vinyl ethers in the way shown by Figure 2.<sup>4</sup> Ketonization of the enol would then constitute the second phase of the observed process.

Further support for this explanation comes from quantitative analysis of the biphasic UV spectral changes accompanying this reaction. Fitting these changes to a double-exponential rate expression produces pairs of first-order rate constants which, when determined over a range of mineral acid concentrations (0.001–0.005 M in H<sub>2</sub>O and 0.001–0.01 M in D<sub>2</sub>O, ionic strength = 0.10 M), lead to the following hydronium ion catalytic coefficients:  $k_{H^+} = 14.6 \pm 1.3 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{D^+} = 28.6 \pm 1.9 \text{ M}^{-1} \text{ s}^{-1}$  for the initial phase and  $k_{H^+} = 6.80 \pm 0.46 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{D^+} = 0.960 \pm 0.019 \text{ M}^{-1} \text{ s}^{-1}$  for the second phase. These catalytic coefficients give an inverse isotope effect,  $k_{H^+}/k_{D^+} = 0.51 \pm 0.06$ , for the first phase, which is consistent with expectation for a preequilibrium proton-transfer reaction such as acetal hydrolysis, and a normal isotope effect,  $k_{H^+}/k_{D^+} = 7.1 \pm 0.5$ , for the second phase, consistent with expectation for a rate-determining proton-transfer process such as enol ketonization. These results for the second, ketonization, phase agree well, moreover, with the catalytic coefficient,  $k_{H^+} = 6.1 \pm 0.1 \text{ M}^{-1} \text{ s}^{-1}$ , and isotope effect,  $k_{H^+}/k_{D^+} = 5.8 \pm 0.4$ , obtained for ketonization of the model enol *cis*-1-butenol, eq 4.<sup>5</sup> The mineral acid results also agree well with



measurements of rates of hydrolysis of 9-methoxy-1-oxacyclonon-2-ene made in cacodylic acid buffers where the ketonization phase, which will be strongly catalyzed by buffer base,<sup>6</sup> should become more rapid than the first, acetal cleavage, phase: in these solutions the reaction shows only a monophasic, single-exponential absorbance decrease and gives a hydronium ion rate constant  $k_{H^+} = 15.8 \pm 0.4 \text{ M}^{-1} \text{ s}^{-1}$ , nicely consistent with  $k_{H^+} = 14.6 \pm 1.3 \text{ M}^{-1} \text{ s}^{-1}$  measured for the acetal hydrolysis portion of the biphasic change in hydrochloric acid solutions.

Our study suggests that in the original investigation of the hydrolysis of 9-methoxy-1-oxacyclonon-2-ene,<sup>2</sup> the initial fast acetal hydrolysis reaction was not observed in mineral acid solutions and only the subsequent enol ketonization process was followed; since enol ketonization and vinyl ether hydrolysis occur by similar mechanism and have similar kinetic characteristics, this process was mistaken for hydrolysis of the vinyl ether group. In acetic acid buffers, on the other hand, enol ketonization, which is buffer catalyzed, became faster than acetal cleavage, which is not buffer catalyzed; this gave the appearance of buffer catalysis saturation of the (mistaken) vinyl ether hydrolysis reaction.

**Acknowledgment.** We are grateful to Professor Brian Capon, whose hypothesis that the hydrolysis of 9-methoxy-1-oxacyclonon-2-ene occurs through initial reaction of the acetal group<sup>7</sup> inspired us to do these experiments; to Professor Dale Whalen for providing samples of 9-methoxy-1-oxacyclonon-2-ene; and to the Natural Sciences and Engineering Research Council of Canada and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

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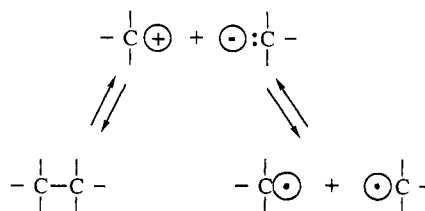
## Evidence for the Equilibration of Resonance-Stabilized Carbocations, Carbanions, and Radicals by Single Electron Transfer in Solution

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Received January 2, 1987

There is considerable current interest<sup>1</sup> in single-electron-transfer (SET) processes as an alternative to or as an important component in bond-forming reactions previously believed to occur by the classical S<sub>N</sub>2 pathway. Although redox equilibria via electron transfer between ions are familiar for inorganic systems, we know of no comparable examples in organic chemistry<sup>2</sup> presumably because of the many channels to side reactions that are available to most of the unstable species involved. However, there is clear precedent for the reaction of carbocations with carbanions to produce radicals.<sup>3</sup> The reverse process, reaction of organic radicals to produce cations and anions, has also been reported.<sup>4</sup>



The present article now describes a system in which carbocations and carbanions are apparently in equilibrium with their corresponding radicals produced by electron transfer. Recently we have reported thermodynamic and kinetic properties for covalent bond formation through direct coordination of carbocations with carbanions.<sup>5–9</sup> In several cases bond formation and heterolysis could be brought to an equilibrium which could be shifted completely to the covalent side in low-polarity solvents and completely to ions in high-polarity ones. The analogous equilibrium between ions and radicals to be described below responds to solvent polarity changes in the same manner.

Malachite green (4,4'-bis(dimethylamino)trityl) cation and 4,4',4''-trinitrotrityl anion should have redox potentials which are favorable for single electron transfer<sup>5</sup> and are sterically protected against covalent bond formation. Accordingly, a 4.8 mM solution of the tetrafluoroborate salt of the cation in THF was mixed with a 6.3 mM solution of the sodium salt of the anion containing an equivalent amount of 16.6 mM 18-crown-6 crown ether, to prevent ion pairing. Disappearance of the 790-nm<sup>2</sup> absorbance of the carbanion was correlated with development of an increasing ESR absorption<sup>10,11</sup> of the corresponding radical as authenticated by

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