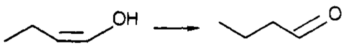
proton NMR signals which differ from those of corresponding vinyl ethers in the way shown by Figure 2.[4] Ketonization of the enol would then constitute the second phase of the observed process.

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_2O and 0.001–0.01 M in D_2O, ionic strength = 0.10 M), lead to the following hydronium ion catalytic coefficients: $k_{\mathrm{H}^+} = 14.6 \pm 1.3$ $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ and $k_{\mathrm{D}^+} = 28.6 \pm 1.9$ $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ for the initial phase and $k_{\mathrm{H}^+} = 6.80 \pm 0.46$ $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ and $k_{\mathrm{D}^+} = 0.960 \pm 0.019$ $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ for the second phase. These catalytic coefficients give an inverse isotope effect, $k_{\mathrm{H}^+}/k_{\mathrm{D}^+} = 0.51 \pm 0.06$, for the first phase, which is consistent with expectation for a preequilibrium proton-transfer reaction such as acetal hydrolysis, and a normal isotope effect, $k_{\mathrm{H}^+}/k_{\mathrm{D}^+} = 7.1 \pm 0.5$, 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, $k_{\mathrm{H}^+} = 6.1 \pm 0.1$ $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$, and isotope effect, $k_{\mathrm{H}^+}/k_{\mathrm{D}^+} = 5.8 \pm 0.4$, obtained for ketonization of the model enol *cis*-1-butenol, eq 4.[5] The mineral acid results also agree well with



(4)

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,[6] 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 $k_{\mathrm{H}^+} = 15.8 \pm 0.4$ $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$, nicely consistent with $k_{\mathrm{H}^+} = 14.6 \pm 1.3$ $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ 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,[2] 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[7] 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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(4) Capon, B.; Rycroft, D. S.; Watson, T. W.; Zucco, C. *J. Am. Chem. Soc.* **1981**, *103*, 1761–1765. Capon, B.; Siddhanta, A. K. *J. Org. Chem.* **1984**, *49*, 255–257.

(5) Chiang, Y.; Yin, Y., unpublished work.

(6) Chiang, Y.; Kresge, A. J.; Walsh, P. A. *J. Am. Chem. Soc.* **1982**, *104*, 6122–6123. Chiang, Y.; Kresge, A. J.; Tang, Y. S.; Wirz, J. *J. Am. Chem. Soc.* **1984**, *106*, 460–462. Chiang, Y.; Kresge, A. J.; Wirz, J. *J. Am. Chem. Soc.* **1984**, *106*, 6392–6395. Pruszynski, P.; Chiang, Y.; Kresge, A. J.; Schepp, N. P.; Walsh, P. A. *J. Phys. Chem.* **1986**, *90*, 3760–3766. Kresge, A. J. *Chem. Tech.* **1986**, 250–254. Chiang, Y.; Kresge, A. J.; Walsh, P. *J. Am. Chem. Soc.* **1986**, *108*, 6314–6320. Chiang, Y.; Kresge, A. J.; Capponi, M.; Wirz, J. *Helv. Chim. Acta* **1986**, *69*, 1331–1332. Chiang, Y.; Hojatti, M.; Keeffe, J. R.; Kresge, A. J.; Schepp, N. P.; Wirz, J. *J. Am. Chem. Soc.*, in press. Capon, B.; Zucco, C. *J. Am. Chem. Soc.* **1982**, *104*, 7567–7572. Capon, B.; Siddhanta, A. K.; Zucco, C. *J. Org. Chem.* **1985**, *50*, 3580–3584.

(7) Capon, B.; Guo, B.-Z.; Kwok, F.-C.; Wu, Z.-P. *Pure Appl. Chem.*, in press.

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

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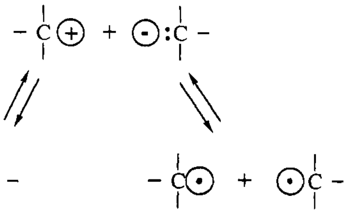
There is considerable current interest[1] in single-electron-transfer (SET) processes as an alternative to or as an important component in bond-forming reactions previously believed to occur by the classical S_N2 pathway. Although redox equilibria via electron transfer between ions are familiar for inorganic systems, we know of no comparable examples in organic chemistry[2] 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.[3] The reverse process, reaction of organic radicals to produce cations and anions, has also been reported.[4]



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.[5-9] 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[5] 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[2] absorbance of the carbanion was correlated with development of an increasing ESR absorption[10,11] of the corresponding radical as authenticated by

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(1) See numerous references in the following recent key articles. (a) Pross, A. *Acc. Chem. Res.* **1985**, *18*, 212. (b) Ashby, E. C.; Argyropoulos, J. N. *J. Org. Chem.* **1986**, *51*, 472. (c) Kornblum, N.; Kelley, W. J.; Kestner, M. M. *J. Org. Chem.* **1985**, *50*, 4720. (d) Eberson, L.; Radner, F. *Acc. Chem. Res.* **1987**, *20*, 53. (e) Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79.

(2) See, however: (a) Taft, R. A.; Jenson, E. D. *J. Am. Chem. Soc.* **1966**, *86*, 116. (b) Taft, R. A.; McKeever, L. D. *Ibid.* **1966**, *88*, 4544. (c) Breslow, R.; Chu, W. *Ibid.* **1973**, *95*, 411.

(3) (a) Murray, R. W.; Kaplan, M. L. *J. Org. Chem.* **1966**, *31*, 962. (b) Arnett, E. M.; Troughton, E. B. *Tetrahedron Lett.* **1983**, *24*, 3299.

(4) (a) Pokhodenko, V. D.; Khizhnyi, V. A.; Samarskii, V. A. *Teor. Eksp. Khim.* **1975**, *11*, 674. (b) Pokhodenko, V. D.; Khizhnyi, V. A.; Koshechko, V. G.; Samarskii, V. A. *Teor. Eksp. Khim.* **1975**, *11*, 579.

(5) Troughton, E. B.; Molter, K. E.; Arnett, E. M. *J. Am. Chem. Soc.* **1984**, *106*, 6726. As of this writing we have not measured their redox potentials in THF or sulfolane. These would be necessary for a quantitative treatment of the system described here according to Eberson.[1e]

(6) Arnett, E. M.; Molter, K. E. *Acc. Chem. Res.* **1985**, *18*, 339.

(7) Arnett, E. M.; Chawla, B.; Molter, K. E.; Amarnath, K.; Healy, M. *J. Am. Chem. Soc.* **1985**, *107*, 5288.

(8) Arnett, E. M.; Molter, K. E. *J. Phys. Chem.* **1986**, *90*, 383.

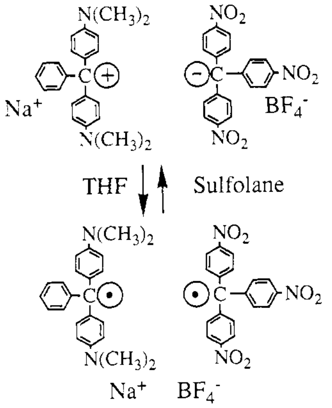
(9) Arnett, E. M.; Chawla, B.; Amarnath, K.; Whitesell, L. G., Jr. *Energy Fuels*, in press.

(10) Kulkarni, S. V.; Trapp, C. *Magn. Reson. Chem.* **1986**, *24*, 5.

0002-7863/87/1509-3788$01.50/0

a sample produced by the reaction of the 4,4′,4″-trinitrotrityl bromide with mercury.[12] When this experiment was repeated with sulfolane (tetramethylenesulfone) as solvent only a trace of radical could be detected at the highest sensitivity. This highly polar solvent is an excellent medium for conducting carbocation–carbanion coordination reactions[9] since it is not attacked readily by either type of species and its high dielectric constant ($\epsilon = 43.3$) stabilizes ions relative to other species—in this case radicals.

The above experiments demonstrate that single electron transfer from the carbanion to the carbocation occurs readily in THF ($\epsilon = 7.5$) to produce a higher concentration of radicals than in sulfolane where the ions are stabilized by electrostatic solvation. *Evidence that electron transfer is reversible* in this system was obtained by diluting a THF solution of radicals, formed as described above, with an equal volume of sulfolane. Within the time needed to transfer the sample and obtain the ESR spectrum, the signal had decreased sharply and the carbanion absorbance had increased. A corresponding dilution experiment adding an equal volume of THF to a sulfolane solution of the cation (6.5 mM) and anion (6.3 mM) salts produced rapid development of an ESR signal.



In order to test the effect of solvent polarity on the ESR signal intensity of this system, two aliquots of 4,4′,4″-trinitrotrityl radical (produced by the reaction of trinitrotrityl bromide with mercury)[11,12] from a stock solution were diluted separately with equal volumes of THF and sulfolane, and spectra from these two solutions were compared under identical saturation conditions. Within experimental error, the ESR signal intensity for a given concentration of 4,4′,4″-trinitrotrityl radical was found to be the same in THF and sulfolane. These control experiments indicate that the solvent effects on 4,4′,4″-trinitrotrityl radical, used to monitor the equilibrium between ions and radicals, is due to changes in concentration of the radical rather than medium effects on its excitation energy.

We have not as yet been able to follow the corresponding spectral change for the radical derived from malachite green. If the system described above is truely at equilibrium, its concentration must vary in response to solvent variation exactly as the radical derived from the carbanion does.

Difficulties in making quantitative comparison of ESR spectra have so far prevented the exact analysis of these preliminary results in terms of equilibrium constants. Nonetheless, they provide very strong evidence that organic radicals and ions can engage in reversible equilibrium which can be shifted in favor of either species by manipulation of the solvent polarity.

These experiments show that single electron transfers and two-electron coordination can apparently exist at equilibrium as well as under kinetic conditions of competitive product formation. It is customary to think of radicals, carbanions, carbocations, and covalent bonds as species that are separated from each other by large differences in energy and conditions. Clearly, if structures and conditions are right they may coexist at equilibrium.

Acknowledgment. This work was supported by NSF Grant CHE-8412976 for which we are most appreciative.

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(11) All ESR measurements reported in this paper were taken at room temperature with a Varian E-9, X-band EPR spectrometer fitted with the E-231 multipurpose and E-232 dual-sample cavities and with the sample contained within an E-248 aqueous solution sample cell.

(12) Lewis, G. N.; Lipkin, D.; Magel, T. T. *J. Am. Chem. Soc.* **1944**, *66*, 1579.

Novel Oxygenation of Pyridine and Quinoline Rings Using Acetyl Hypofluorite

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Reagents with active fluorine have, most naturally, been used in organic chemistry for fluorination purposes. In the early stages these reagents were based on various fluorine salts, while more recently elemental fluorine and reagents derived directly from it have also been employed for introducing fluorine.[1] It is very unusual to use this most reactive element as an instrument for obtaining fluorine free products. We wish to report such a reaction which leads to a family of difficult to prepare compounds, namely, 2-oxygenated pyridine and quinoline derivatives.

Apart from Chichibabin's aminations, nucleophilic substitutions of the pyridine ring are remarkably difficult. Reaction with KOH, for example, yields only traces of 1*H*-2-pyridone,[2] while autoclave treatment with $CuSO_4$ of some substituted derivatives such as 3-picoline at 300 °C gives the corresponding pyridones in less then 7% yield.[3] Thus, up to now, the only practical method for introducing the oxygen atom at the 2-position has been to prepare the *N*-oxide moiety which then requires to be rearranged by prolonged heating with either acetic anhydride[4] or $SbCl_5$.[5]

As a step toward our goal of introducing elemental fluorine to organic synthesis methodology, a few years ago we prepared, for the first time, acetyl hypofluorite, AcOF,[6] which soon proved itself to be a useful fluorinating agent.[7] Surprisingly, when we reacted this reagent with pyridine (**1**) for a short time even at −75 °C, no fluorinated products were detected and only 2-acetoxypyridine (**2**) was obtained in 85% yield.[8] Similar results were observed

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(1) See, for example: Rozen, S.; Gal, C.; Faust, Y. *J. Am. Chem. Soc.* **1980**, *102*, 6860. Rozen, S.; Lerman, O. *J. Org. Chem.* **1980**, *45*, 672. Rozen, S.; Brand, M. *J. Org. Chem.* **1985**, *50*, 3342. Rozen, S.; Ben-Shushan, G. *J. Org. Chem.* **1986**, *51*, 3522. Adcock, J. L.; Robin, M. L. *J. Org. Chem.* **1983**, *48*, 2437. Barnette, W. E. *J. Am. Chem. Soc.* **1984**, *106*, 452.

(2) Chichibabin, A. E. *Chem. Ber.* **1923**, *56*, 1879.

(3) Tomasik, P.; Woszczyk, A. *Tetrahedron Lett.* **1977**, *25*, 2193.

(4) Katada, M. *J. Pharm. Soc. Jpn.* **1947**, *67*, 51.

(5) Yamamoto, J.; Imagawa, M.; Yamauchi, S.; Nakazawa, O.; Umezu, M.; Matsuura, T. *Tetrahedron* **1981**, *37*, 1871.

(6) Rozen, S.; Lerman, O.; Kol, M. *J. Chem. Soc., Chem. Commun.* **1981**, 443.

(7) (a) Lerman, O.; Tor, Y.; Hebel, D.; Rozen, S. *J. Org. Chem.* **1984**, *49*, 806. (b) Rozen, S.; Brand, M. *Synthesis* **1985**, 665. (c) Rozen, S.; Lerman, O.; Kol, M.; Hebel, D. *J. Org. Chem.* **1985**, *50*, 4753. (d) Jewett, D. M.; Potocki, J. F.; Ehrenkaufer, R. E. *J. Fluorine Chem.* **1984**, *24*, 477. (e) Visser, G. W. M.; Halteren, B. W.; Herscheid, D. M.; Brinkman, G. A.; Hoekstra, A. *J. Chem. Soc., Chem. Commun.* **1984**, 655.

(8) In a typical reaction, about 20 mmols of the heterocyclic derivative was dissolved in about 20 mL of precooled (−75 °C) $CHCl_3$ and added at this temperature to 30–35 mmols of AcOF solution prepared according to ref 5 and 6. The reaction was monitored by TLC or NMR until a full conversion was achieved. In some cases it was necessary to raise the reaction temperature as indicated in the text. In still other cases, it was found that a slow addition of the AcOF solution to the substrate was preferable. The final products, both new and known, were chromatographically purified and their physical and spectroscopic data were in perfect agreement with the proposed structure as well as with either an authentic sample or with the data described in the literature.