the ortho ester 7, *under neutral conditions*,[17] and (ii) the mildness of the activation procedure.

Developmental studies are continuing and will be reported in due course.[20]

Supplementary Material Available: Experimental details of the preparation of compounds **1–4**, **5c,d**, **8–10**, **11**α/β, and **11**α (12 pages). Ordering information is given on any current masthead page.

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(20) An invention disclosure has been filed to cover the use of *n*-pentenyl glycosides as glycosyl donors.

A Slow Proton Transfer from Trifluoroacetic Acid to Tribenzylamine in DMSO Solution

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We have discovered a remarkably small rate constant of $2.8 \times 10^2\ M^{-1}\ s^{-1}$ for the proton transfer from trifluoroacetic acid ($pK_a = 3.50$) to tribenzylamine ($pK_a = 3.64$ for the conjugate acid) in DMSO-d_6 (dimethyl sulfoxide-d_6) solution at 20 °C.

Since the work by Eigen and his co-workers[1] in the early 1960s, it has been believed that proton transfer reactions between nitrogen and oxygen acids and bases in solution occur at, or near, the diffusion-controlled limit. There have been occasional reports of such reactions occurring well below the diffusion limits, but these have all been thought to be highly unusual in some respect. For example, Bernasconi[2] and Ritchie[3] have reported rate constants of less than $10^6\ M^{-1}\ s^{-1}$ for thermodynamically favorable proton transfers from several large, presumably sterically hindered, tertiary amines to amine and oxygen bases in DMSO solution. Kreevoy and Wang[4] studied the rates of protonation of ring-substituted tribenzylamines by the solvated proton in DMSO-d_6 and found rate constants ranging from $2.2 \times 10^3\ M^{-1}\ s^{-1}$ for tris(3-chlorobenzyl)amine to $1.8 \times 10^4\ M^{-1}\ s^{-1}$ for tribenzylamine. They also found that the *N,N*-dimethylbenzylamine protonation rate constant of $4.2 \times 10^6\ M^{-1}\ s^{-1}$ fit on the Brønsted correlation line for protonations of the tribenzylamines, indicating that the tribenzylamine protonations were not appreciably slowed by a steric effect. The slow protonations were rationalized as being due to the solvation of the proton in DMSO. Delpuech[5] has reported rate constants near diffusion limited for protonations of ammonia and of trimethylamine, but much lower than diffusion limited ($6.7 \times 10^5\ M^{-1}\ s^{-1}$) for protonation of *cis*-2,6-dimethyl-*N*-methylpiperidine, all in DMSO solution.

We have determined the proton transfer rates to tribenzylamine by ^1H NMR line-shape fitting using the Kaplan–Fraenkel density matrix method.[6] The pertinent parts of the NMR spectra in DMSO-d_6 solution are a doublet, $J = 5.2$ Hz, for the six equivalent benzyl protons of the tribenzylammonium ion centered at δ 4.32 ppm (1728 Hz) and a singlet for the six equivalent protons of tribenzylamine at δ 3.50 ppm (1401 Hz) in the 400-MHz spectrum. The T_2 relaxation time for the benzyl protons of tribenzylamine in DMSO-d_6 was found to be 0.93 s; the T_2 for the benzyl protons of the tribenzylammonium-d_1 ion in DMSO-d_6 was determined to be 1.06 s under conditions of very slow exchange in the presence of 1.6 M CF_3COOD. The J value for the protons was determined for the tribenzylammonium ion in the presence of 0.04 M CF_3SO_3H and found to be the same as that observed in $CDCl_3$ solution containing 0.06 M tribenzylamine plus 0.2 M CF_3SO_3H. Spectra of dilute solutions, typically 5×10^{-4} to 2×10^{-3} M of the amine, were obtained by using supression of the residual solvent protons in the purified "99.9%" DMSO-d_6 (Cambridge Isotope Laboratories). The solvent was purified as described by Bordwell[7] for the nondeuterated material; water content of the purified solvent was determined, typically, to be slightly less than 10^{-3} M by NMR analysis. All solutions were prepared and kept under argon atmospheres; normally capped NMR tubes of the purified solvent showed no increase in water content over periods of several days. The pK_a's were determined by Bordwell's indicator techniques;[8] the value of 3.5 for CF_3COOH is in good agreement with that of 3.45 reported by Bordwell,[9] and that of 3.6 for the tribenzylammonium ion is in good agreement with that of 3.65 reported by Kreevoy.[4]

Kinetic studies were carried out in solutions buffered by trifluoroacetic acid–trifluoroacetate ion prepared by partial neutralization of trifluoroacetic acid solutions with dimsylpotassium solution. Concentrations of trifluoroacetate ion were varied from 9.8×10^{-3} M to 1.0×10^{-1} M, and concentrations of tribenzylamine varied from 3.4×10^{-4} to 9.8×10^{-4} M. At low concentrations of trifluoroacetate, the benzyl proton doublet of the tribenzylammonium ion collapses to a singlet, and at higher concentrations, both this peak and the one due to the benzyl protons of tribenzylamine are considerably broadened, but not coalesced. Simulations of the spectra require two adjustable parameters: the $1/\tau_{BH^+}$ value and the amine/ammonium ion concentration ratio. It was observed that the concentration ratio required for fitting was not equal to that calculated from the buffer ratio and the pK values. This was found to be an ionic strength effect on the equilibrium constant, as is expected for this type of reaction involving neutral acid plus neutral base producing ionic conjugate base and ionic conjugate acid. The apparent pK_a of tribenzylammonium ion measured with 2,4-dinitro-4-chlorophenol varies with ionic strength, adjusted with sodium perchlorate, in quantitative accord with the NMR observations of the amine concentration ratios in the trifluoroacetate buffers at the same ionic strengths. A plot of Log K_{app} for the amine–phenol reaction vs the square root of the ionic strength of solutions is nicely linear with a slope of 1.44 (note that limiting Debye–Hückel theory gives a slope of 2.40).

The plot of $1/\tau_{BH^+}$ vs concentration of trifluoroacetate ion is linear with a slope of $2.0 \times 10^2\ M^{-1}\ s^{-1}$ and an intercept of 2.4 s^{-1}. The intercept corresponds to the rate of deprotonation of tribenzylammonium ion by solvent and is in reasonable agreement with the value of $4.0 \pm 1.5\ s^{-1}$ obtained by Kreevoy[4] as the intercept of plots of rates of deprotonation of tribenzylammonium ion by solvent vs water concentration. The value $1/\tau_{BH^+} = 4.3\ s^{-1}$ obtained at a trifluoroacetate ion concentration of 9.8×10^{-3} M is the same for tribenzylamine concentrations of 3.9×10^{-4} and 9.8×10^{-4} M; we conclude that the direct proton transfer from tribenzylammonium ion to tribenzylamine must have a second-order rate constant of much less than $10^3\ M^{-1}\ s^{-1}$.

These extremely slow proton transfers are similar to those found for strongly intramolecularly hydrogen bonded acids in aqueous solution[10] and could be due to hydrogen bonding of acids to solvent in DMSO solution. It seems less likely, but still conceivable, that steric effects are large enough, even for the small carboxylate ion or solvent, to severely decrease rates of reactions of tribenzylammonium ions. We are currently studying rates of other nitrogen and oxygen acid–base reactions in DMSO in hopes of defining the factors responsible for the slowness of the reactions.

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(1) Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1.

(2) Bernasconi, C. F.; Carrě, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 2698. Bernasconi, C. F.; Fox, J. P.; Fornarini, S. *J. Am. Chem. Soc.* **1980**, *102*, 2810.

(3) Ritchie, C. D. *J. Am. Chem. Soc.* **1983**, *105*, 3573.

(4) Kreevoy, M. M.; Wang, Y. *J. Phys. Chem.* **1977**, *81*, 1924.

(5) Delpuech, J. J.; Bianchin, B. *J. Am. Chem. Soc.* **1979**, *101*, 383.

(6) Kaplan, J. I.; Fraenkel, G. *NMR of Chemically Exchanging Systems*; Academic Press: New York, 1980.

(7) Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006.

(8) Bordwell, F. G.; McCallum, R. J.; Olmstead, W. N. *J. Org. Chem.* **1984**, *49*, 1424.

(9) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.

(10) Hibbert, F. In *Advances in Physical Organic Chemistry*; Academic Press: New York, 1986; Vol. 22, p 113.

0002-7863/89/1511-8542$01.50/0

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Minimal Permanganate Oscillator: The Guyard Reaction in a CSTR[1]

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The concept[2] of a minimal oscillator within a family of oscillating chemical reactions has been extremely useful in guiding the design of new chemical oscillators. Both the minimal bromate[3] and the minimal chlorite–iodide systems[4] have led to the discovery and categorization of families of related oscillating reactions.[5,6]

Recently, the first transition metal based oscillator, the $KMnO_4$–H_2O_2–H_3PO_4 reaction, was found,[7] and this has been followed by reports of two other permanganate oscillators.[8,9] We have discovered oscillatory behavior in a large number of other permanganate oxidation reactions in a flow reactor (CSTR). From these systems, we have been able to construct the simplest version of a permanganate oscillator, in which only manganese species play principal roles. This reaction, the venerable Guyard reaction[10] between permanganate and manganese(II) ions in a CSTR, may be regarded as a core system from which many other oscillators may be built, since other oscillatory permanganate reactions generate Mn(II).

We report here the most important results on the minimal permanganate oscillator. Further details as well as a characterization of several new oscillators derived from this system will appear elsewhere.

The experiments were carried out at 25.0 °C in a 20.5-cm^3 glass CSTR equipped with a magnetic stirrer and Pt and glass electrodes. The four feed streams from the peristaltic pump contained $KMnO_4$, $MnSO_4$, KH_2PO_4, and NaOH. In Figure 1, we show typical oscillations observed in the Pt electrode potential. The pH remains constant during the oscillations at a value between 6 and 7, depending on the input concentrations. The solution is yellow-brown during the oscillations, which are accompanied by periodic precipitation of MnO_2.

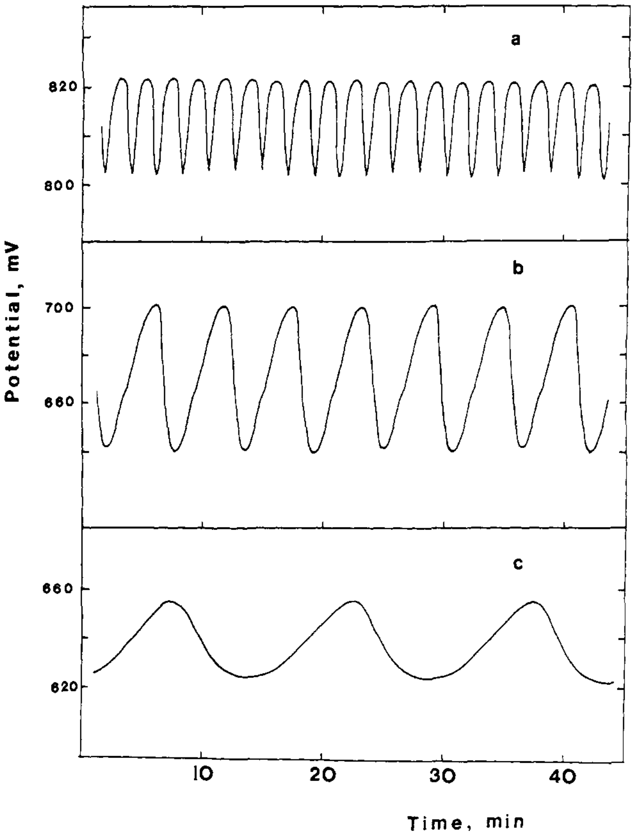

Figure 1. Oscillations in the potential of a Pt electrode with $[KMnO_4]_0 = 9 \times 10^{-5}$, $[MnSO_4]_0 = 2.5 \times 10^{-4}$, $[KH_2PO_4]_0 = 1.5 \times 10^{-3}$, and $[NaOH]_0 = 1.0 \times 10^{-3}$ M. Flow rates: (a) 0.048, (b) 0.019, and (c) 0.0085 s^{-1}.

The range of input concentrations and flow rates in which the system oscillates is quite narrow, as seen in Figure 2. Above the oscillatory region in the figure, the solution is dark brown, while below it the solution is pinkish brown. In contrast to other minimal oscillators,[3,4] no bistability was observed under any conditions. The amplitude of the oscillations increases with the input $KMnO_4$ and Mn(II) concentrations, reaching a maximum of about 100 mV. Increasing the flow rate through its oscillatory range of $(5–20) \times 10^{-3}$ s^{-1} decreases the oscillation period from about 30 to about 2 min, while the amplitude increases to a maximum and then decreases. The inputs of KH_2PO_4 and NaOH must also be kept within relatively narrow limits, about $(1.2–3.0) \times 10^{-3}$ and 5×10^{-4} to 1×10^{-3} M, respectively.

At the pH of the minimal manganese oscillator, the stable oxidation states of manganese are +2, +4, and +7, and the overall reaction is

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2 + 4H^+ \qquad (1)$$

The rate of this reaction, important in the permanganometric determination of Mn(II), increases with pH. Reaction 1 is autocatalytic,[11,12] being accelerated by Mn(IV), which can precipitate as solid brown MnO_2 or can remain in solution in a soluble yellow form. The stability of the yellow solution to flocculation is greatly enhanced by phosphate ions, and the soluble form may be regarded as colloidal MnO_2 stabilized by phosphate[13] or as a hydroxo-bridged binuclear phosphatomanganese(IV) complex.[14–16]

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(1) Systematic Design of Chemical Oscillators. 59. Part 58: Luo, Y.; Epstein, I. R. *Adv. Chem. Phys.*, to be published.

(2) Epstein, I. R.; Orbán, M. In *Oscillations and Traveling Waves in Chemical Systems*; Field, R. J., Burger, M., Eds.; Wiley: New York, 1985; p 257.

(3) (a) Orbán, M.; De Kepper, P.; Epstein, I. R. *J. Am. Chem. Soc.* **1982**, *104*, 2657. (b) Geiseler, W.; Bar-Eli, K. *Ber. Bunsen-Ges. Phys. Chem.* **1982**, *86*, 721.

(4) Dateo, C. E.; Orbán, M.; De Kepper, P.; Epstein, I. R. *J. Am. Chem. Soc.* **1982**, *104*, 504.

(5) Alamgir, M.; Orbán, M.; Epstein, I. R. *J. Phys. Chem.* **1983**, *87*, 3725.

(6) Orbán, M.; Dateo, C.; De Kepper, P.; Epstein, I. R. *J. Am. Chem. Soc.* **1982**, *104*, 5911.

(7) Nagy, A.; Treindl, L. *Nature* **1986**, *320*, 344.

(8) Treindl, L.; Nagy, A. *Chem. Phys. Lett.* **1987**, *138*, 327.

(9) Morita, M.; Iwamoto, K.; Seno, M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3467.

(10) Guyard, G. *Bull.* Soc. *Chim. Fr.* **1864**, *1*, 89.

(11) Polissar, M. J. *J. Phys. Chem.* **1935**, *39*, 1057.

(12) Tompkins, F. C. *Trans. Faraday Soc.* **1942**, *38*, 131.

(13) Mata-Perez, F.; Perez-Benito, J. F. *Can. J. Chem.* **1985**, *63*, 988.

(14) Simándi, L.; Jáky, M.; Savage, C. R.; Schelly, Z. A. *J. Am. Chem. Soc.* **1985**, *107*, 4220.

(15) Copper, S. R.; Calvin, M. *J. Am. Chem. Soc.* **1977**, *99*, 6623.

(16) Jáky, M.; Simándi, L. I.; Shafirovich, V. Y. *Inorg. Chim. Acta* **1984**, *90*, L39.