have resonances broadened to invisibility, is not excluded. As in conventional copper(II) alkoxides, the oligomers of **2** are likely held together by internuclear alkoxide–oxygen bridges, but solubility is likely imparted by the presence of *some* chelating ether oxygens that reduce the extent of alkoxide bridging. The high solubility of previously reported[2] $[Cu(OCH_2CH_2OCH_2CH_2CH_2CH_3)_2]$ (one ether oxygen per ligand), and the insolubility of **3** (no ether oxygens) is consistent with this view.

Our studies of mixed-alkoxide solutions employed **2**, Ba(O-*i*-Pr)$_2$,[12] and $Y_5(O)$(O-*i*-Pr)$_{13}$.[13] Benzene or THF solutions of **2** and Ba(O-*i*-Pr)$_2$ (Ba:Cu = 2:3), or **2** and $Y_5(O)$(O-*i*-Pr)$_{13}$ (Y:Cu = 1:3) were homogeneous and blue. Addition of the third component (giving Y:Ba:Cu = 1:2:3) resulted in dark-green homogeneous solutions. NMR spectra of the mixed-alkoxide solutions (C_6D_6) were complex, and resonances for the free precursors were not present.

Hydrolysis of freshly prepared THF solutions having a total alkoxide concentration of 0.1 M (Y:Ba:Cu = 1:2:3) gave a gelatinous blue precipitate, which aged to a blue powder. Chemical analysis fit an empirical formula $YBa_2Cu_3(OH)_{13}(H_2O)_n$ (n = 0–2); carbon as residual organics was present in 1.5%.[14] The product was amorphous to X-ray powder diffraction (XRD), and crystalline grains were not detected by electron diffraction in the transmission electron microscope (TEM).[15] For comparison, the independent hydrolyses of **2**,[16] Ba(O-*i*-Pr)$_2$,[17] **2**/Ba(O-*i*-Pr)$_2$ mixtures,[18] and a **2**/$Y_5(O)$(O-*i*-Pr)$_{13}$ mixture (Y:Cu = 1:3)[19] all gave crystalline products.

Two compositionally distinct microstructures were found in TEM images: (1) lacy grains composed entirely of loosely aggregated 10–30 nm diameter particles and (2) grains similar to the first type but containing regions ca. 200 nm across with a much smoother appearance. By energy-dispersive X-ray spectroscopy (EDS),[15] the lacy grains were uniformly Cu rich (Y:Ba:Cu = 1.0:2.0:3.9), whereas the grains with smooth regions had nonuniform compositions. More of the regions analyzed in the latter were Ba rich than were Y rich; all were Cu poor. *No* regions were completely deficient in any of the three metals. Type 1 grains were more abundant than type 2 grains in the TEM specimens. Thus, the $YBa_2Cu_3(OH)_{13}(H_2O)_n$ stoichiometry above apparently represents an intimate mixture of noncrystalline phases, which does not contain expected binary or ternary hydrolysis products.

When $YBa_2Cu_3(OH)_{13}(H_2O)_n$ was fired under O_2 or air at 700–750 °C (10–15 h), XRD showed the formation of $BaCO_3$,[20] CuO,[16] $BaCuO_2$,[21] and $Y_2Cu_2O_5$[21] mixtures, which did not completely convert to $YBa_2Cu_3O_{7-x}$[22] below 900 °C. However, as in the previous study,[2] significantly lower conversion temperatures were observed by using inert atmospheres. When $YBa_2Cu_3(OH)_{13}(H_2O)_n$ was heated under a vigorous Ar or N_2 stream, some $BaCO_3$ formed below 300 °C (presumably from the residual organics) but decomposed readily at 650–700 °C with the formation of $YBa_2Cu_3O_{7-x}$. Samples heated for 10–15 h under inert atmosphere at 700 °C contained just-detectable quantities of $BaCO_3$, $BaCuO_2$, and $Y_2Cu_2O_5$, but $YBa_2Cu_3O_{7-x}$ was obtained with *no* detectable impurity phases at 750 °C (9 h). Quenching to room temperature gave tetragonal $YBa_2Cu_3O_{7-x}$, whereas samples cooled more slowly (750–400 °C in ca. 2 h) *under inert atmosphere* gave orthorhombic $YBa_2Cu_3O_{7-x}$. In cases where air was less efficiently excluded during the firing of $YBa_2Cu_3(OH)_{13}(H_2O)_n$ at 750 °C, large amounts of $BaCuO_2$ and $Y_2Cu_2O_5$ were found.

In summary, it is shown here and elsewhere[2] that syntheses based on the hydrolysis of homogeneous mixed-alkoxide solutions afford reductions of 200–250 °C in the temperature of $YBa_2Cu_3O_{7-x}$ formation. Although $BaCO_3$ decomposition may be the temperature-limiting event here, such decomposition occurs much more readily than is typical.[23] Our results suggest that O_2 may inhibit the decomposition of $BaCO_3$, and enhance the formation of $BaCuO_2$ and $Y_2Cu_2O_5$, all of which inhibit production of $YBa_2Cu_3O_{7-x}$. Work is in progress to define conditions for obtaining gels from alkoxide-precursor solutions and for subsequent conversion to fabricated superconductors.[24]

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(14) Data for $YBa_2Cu_3(OH)_{13}(H_2O)_n$. Anal. Calcd for $YBa_2Cu_3(OH)_{13}(H_2O)_1$: Ba, 34.62; Cu, 24.03; H, 1.89; C, 0.00. Found: Ba, 34.48; Cu, 24.07; H, 1.29; C, 1.49. IR (cm^{-1}, KBr): ν_{O-H} 3660–3200 s; ν_{H-O-H} 1590 m br, 1380 s br; ν_{M-O} 440 m br.

(15) JEOL 2000FX with Tracor Northern EDS instrument. Powder samples were dispersed on holey C films supported by Al grids. The EDS instrument was calibrated by measurements of single-phase orthorhombic samples with [110] twins visible in image and diffraction modes.

(16) CuO, Tenorite: JCPDS File 5-0661.

(17) γ-$Ba(OH)_2(H_2O)$: JCPDS File 24-104.

(18) 1:1 and 3:2 ratios gave products fitting empirical formulas $BaCu(OH)_4(H_2O)$ and $Ba_2Cu_3(OH)_{10}(H_2O)_2$, respectively. XRD ($d$(Å), relative intensity for the four most intense reflections). For $BaCu(OH)_4(H_2O)$: 4.38, 52%; 3.07, 95%; 3.00, 82%; 2.98, 100%. For $Ba_2Cu_3(OH)_{10}(H_2O)_2$: 5.21, 96%; 3.36, 100%; 3.28, 51%; 2.75, 36%.

(19) (a) $Ba(OH)_2(H_2O)$: JCPDS File 26-154. (b) Independent hydrolysis of $Y_5(O)$(O-*i*-Pr)$_{13}$ gave an amorphous solid.

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(24) Application of the dark green, mixed-alkoxide solution to a glass slide followed by exposure to atmospheric moisture at room temperature results in a transparent blue gel within a few minutes. The gel dries under ambient conditions to a transparent, blue, glassy film.

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Observations on the Dynamics of Hydrazine Oxidation by Permanganate in Aqueous Acidic Solutions

The study of bistable and oscillatory chemical reactions, known as chemical instabilities, has been advancing rapidly in recent years.[1,2] Although early examples of such reactions were discovered accidentally, a wide variety of other chemical systems displaying nonlinear dynamic phenomena, under closed as well as open conditions, have been systematically designed within the last decade.[2,3] These recent discoveries are based on the cross-shaped phase diagram technique,[4] for which a bistable chemical system is a prerequisite. A vital but common characteristic of all known bistable and/or oscillatory systems is autocatalysis. Hence, it should be possible to design new chemical oscillators by suitable modification of a known autocatalytic reaction.[5] (It is possible that the desired modification of the chosen autocatalytic reaction may not be physically feasible). This later approach is

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strongly dependent on detailed kinetics and mechanistic information. If a satisfactory mechanism is available or can be elucidated for the autocatalytic reaction of interest, its stability properties can be assessed by using standard mathematical procedures.[6,7] Results from the stability analysis can then be utilized to choosing appropriate experimental conditions, in order that the computational predictions could be verified experimentally. Observations of oscillations and other nonlinear dynamic phenomena have been successfully utilized to draw important conclusions regarding mechanisms of a few complex reactions,[8,9] which is almost impossible if methods of chemical kinetics alone are employed.

The oxidation of a number of reductants by permanganate ion are known to be autocatalytic.[10,11] Therefore MnO_4^- oxidations can serve as precursors in the design of new chemical systems that exhibit one or more nonlinear dynamic phenomena. In fact, under open conditions, the MnO_4^-–$C_2O_4^{2-}$ reaction has been found to be bistable,[12] and the MnO_4^-–H_2O_2 reaction[13] and the MnO_4^-–NO_2^-–HCOOH–CH_3OH system[14] have been found to be oscillatory; however, mechanistic interpretations of the observed intriguing behaviors of these systems are yet to be worked out. From this point of view, detailed investigations of the kinetics of the former two systems have been undertaken within the last 3 years,[15,16] and a few interesting features have been observed. We expected that the MnO_4^-–N_2H_4 reaction would be similar to the MnO_4^-–H_2O_2 reaction in some respects and are interested in the possibility that the title reaction may have the potential to display one or more nonlinear phenomena. Furthermore, mechanisms of MnO_4^- oxidations in general are poorly understood in acidic solutions. Hence, we have begun to investigate the dynamics of the title reaction, with the aim of formulating a satisfactory mechanism that could be used to predict its nonlinear dynamic properties.

Experimental Section. Fisher Certified $N_2H_4{\cdot}H_2SO_4$, Na_2SO_4, and $NaHSO_4$ and Aldrich $LiClO_4$ were used as received. Aqueous solutions of $KMnO_4$ (from Fisher) were prepared and standardized according to the procedure reported elsewhere.[17] Baker analyzed $Na_2C_2O_4$ was dried at 105 °C and used for the standardization. $[MnO_4^-]$ in these solutions was checked periodically by absorbance measurements at 526 nm, where the molar absorptivity is 2.46 ($\pm$0.02) $\times 10^3$ M^{-1} cm^{-1}. Doubly distilled water was used to prepare all solutions. $LiClO_4$ solution was filtered through Pyrex glass wool and was used to maintain constant ionic strength. Solutions for the stopped-flow experiments were purged with Ar for 15 min prior to the experiments, which were carried out by rapidly mixing two solutions—one containing $KMnO_4$ in water and the other containing all other constituents.

Stopped-flow experiments were carried out in a Dionex D-100 rapid kinetics spectrophotometer, equipped with a 2-cm observation cell and constant-temperature assembly, and interfaced to a Zenith Z100 computer. The absorbance at 526 nm was monitored as a function of time typically during a period of 5 s, corresponding to between 2 and 3 half-lives. Temperature was maintained at 25.0 ($\pm$0.3) °C. pH measurements were made using a Fisher 805MP pH meter and a Fisher Accu-pHast combination glass electrode, which were calibrated by using Fisher buffer solutions of pH 4.00 and 7.00.

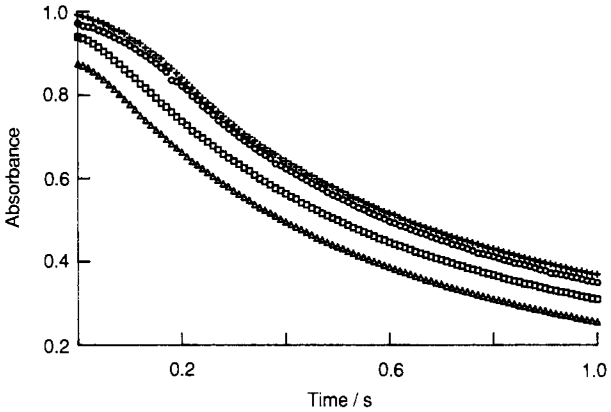

Figure 1. Experimental stopped-flow absorbance at 526 nm vs time. Path length = 2.00 cm. Initial concentrations: $N_2H_4{\cdot}H_2SO_4$, 5.0×10^{-3} M; Na_2SO_4, 1.00×10^{-2} M; MnO_4^-, 2.00×10^{-4} M. Reaction pH: 2.40 before the addition of MnO_4^-; 2.61 after the addition of MnO_4^-. For the pH measurements, 5.00 mL of 4.00×10^{-4} M $KMnO_4$ was added to a solution that was 2.00×10^{-2} M in Na_2SO_4 and 1.00×10^{-2} M in $N_2H_4{\cdot}H_2SO_4$. Key: (+) Neither Mn(II) nor Mg(II) was present initially; (○) $[Mg(II)] = 1.5 \times 10^{-4}$ M; (□) $[Mn(II)]_0 = 5.0 \times 10^{-5}$ M; (△) $[Mn(II)]_0 = 1.5 \times 10^{-4}$ M. Curves marked with ○, □, and △ have been shifted down vertically by 0.025, 0.050, and 0.10 absorbance units, respectively, for clarity. The absorbance decreases to zero if the reaction was run for longer times. For the curves shown here, kinetics data were collected during the first one second so that the inflection is easy to see.

Results and Discussions. Stoichiometry. We chose to investigate the title reaction in mildly acidic solutions (pH 1–3) in order to avoid complications from precipitation of MnO_2. It is interesting to note that the title reaction does not obey a well-defined stoichiometry at ambient temperatures in acidic solutions.[18,19] On the other hand, at higher temperatures (around 100 °C), the stoichiometry is given[20] by

$$4MnO_4^- + 5N_2H_4 + 12H^+ = 4Mn(II) + 5N_2 + 16H_2O$$

corresponding to a value of 4/5 for the ratio (R) of moles of MnO_4^- reduced to the moles of N_2H_4 oxidized.[21] We carried out a limited number of experiments to investigate the stoichiometry of the reaction, using a spectrophotometric procedure[22] for the determination of N_2H_4. These experiments were conducted under the condition that MnO_4^- is the limiting reagent, and values of 0.28 and 0.32 were obtained for the ratio R, basically in accordance with the observations reported in the literature.[18,19] These results indicate that N_2H_4 undergoes predominantly one-electron oxidation, mixed with multielectron processes. On the other hand, MnO_4^- undergoes reduction to the Mn(II) stage, indicated by the fact that the final solutions are colorless and that the spectra of the final solutions (after a period of about 15 min) are identical with the spectrum of the solution containing all the constituents except MnO_4^-. This is not surprising due to the facts that Mn(III) is capable of oxidizing N_2H_4 as reported by Davies and Kustin[23] and that Mn(VI) and Mn(V) are unstable in acidic solutions. A thorough investigation of the stoichiometry[24] of the title reaction under a broad range of $[MnO_4^-]$, $[N_2H_4]$, and pH is currently under way in our laboratory.

Kinetics. We have found that the title reaction exhibits several interesting kinetic features. As shown in Figure 1, the reaction

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Table I. Experimental Second-Order Rate Constant (k_{exp}),[a] at Various Initial Concentrations of (a) MnO_4^- and (b) N_2H_4

(a) Initial Concentrations: $N_2H_4 \cdot H_2SO_4$, 9.95×10^{-3} M; Mn(II), 1.01×10^{-2} M; Na_2SO_4, 2.66×10^{-2} M (Final Reaction pH = 2.10)

$10^4[MnO_4^-]_0$/M	10^3k_{exp}/M^{-1} s^{-1}	$10^4[MnO_4^-]_0$/M	10^3k_{exp}/M^{-1} s^{-1}
2.00	6.71 (±0.28)	1.25	7.78 (±0.05)
1.75	6.91 (±0.31)	1.00	7.28 (±0.09)
1.50	7.31 (±0.32)		

(b) Initial Concentrations: MnO_4^-, 1.00×10^{-4} M; $NaHSO_4$, 0.250 M (Final Reaction pH = 1.10)

$10^2[N_2H_4 \cdot H_2SO_4]_0$/M	10^3k_{exp}/M^{-1} s^{-1}	$10^2[N_2H_4 \cdot H_2SO_4]_0$/M	10^3k_{exp}/M^{-1} s^{-1}
0.480	1.94 (±0.01)	1.44	1.93 (±0.01)
0.960	1.96 (±0.01)	1.68	1.92 (±0.01)
1.20	1.96 (±0.02)	1.92	1.94 (±0.01)

[a] Values of k_{exp} were calculated from the slopes of linear plots of Abs_t versus $t(Abs_t - Abs_\infty)$ where t is time and Abs is absorbance. Abs_∞ is zero. Each value of k_{exp} given above is the mean from five experimental runs, and the reported uncertainties are one standard deviation of the five values. Correlation coefficients for the linear least-square fits were greater than 0.9990.

displays an inflection in $[MnO_4^-]$ vs time curves under certain conditions, which is similar to the behavior of the MnO_4^-–H_2O_2 reaction[15] and may arise from the autocatalytic role of Mn(II). In order to assess the validity of this view, a few experiments were carried out with initially added Mn(II). Also shown in Figure 1 is the observation that Mn(II) shifts the point of inflection to earlier times, whereas Mg(II) at comparable concentration has no noticeable effect. These observations suggest that Mn(II) probably has an autocatalytic role, as in the MnO_4^-–$C_2O_4^{2-}$ and the MnO_4^-–H_2O_2 reactions. Additional experiments are needed though, to determine the true nature of the inflection, which may also arise due to the involvement of intermediates such as hydrazyl radicals ($N_2H_3^\bullet$ or its protonated form $N_2H_4^{\bullet+}$), Mn(VI), and Mn(V). These intermediates can lead to cyclic reactions that may result in autocatalysis. From the concentration conditions given for Figure 1 and Table I, it is evident that differences in pH and the presence or absence of Mn(II) can lead to different behaviors viz. inflection or monotonic behavior.

In addition to the inflection, the title reaction has a few other intriguing features. Under a different set of initial conditions, the reaction exhibits monotonic behavior. When these kinetics data (absorbance at 526 nm versus time) were analyzed according to pseudo-first-order behavior, unsatisfactory fits resulted. Consequently, a pseudo-second-order treatment was attempted, which gave excellent fits as indicated in Table I. The observed second-order behavior is more prevalent under a wider range of concentration conditions than the inflection behavior. This second-order dependence on $[MnO_4^-]$ is unusual in the sense that no other known MnO_4^- oxidation shows a second-order dependence on MnO_4^-. Also shown in Table I is the zero-order dependence[26] on N_2H_4. Figure 2 illustrates that an increase in pH increases the rate of the reaction, indicating that protonation equilibria are part of the mechanism.

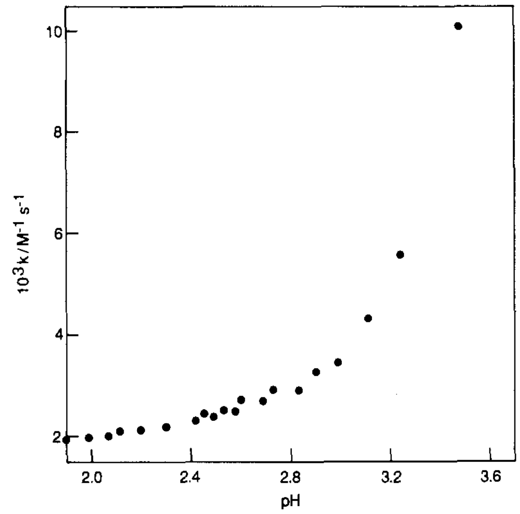

Figure 2. Experimental dependence of the pseudo-second-order rate constant k_{exp} (determined as described in Table I) on $[H^+]$. Initial concentrations: Na_2SO_4, 0.104 M; $N_2H_4 \cdot H_2SO_4$, 1.00×10^{-2} M; MnO_4^-, 1.00×10^{-4} M. Different pHs were obtained by the addition of 1.0 M $NaHSO_4$ or 0.100 M NaOH. Appropriate volumes of 1.0 M $LiClO_4$ were added to these solutions to maintain constant ionic strength. pH was measured as described in Figure 1. Addition of 5.00 mL of MnO_4^- solution or 5.00 mL of water to the solution containing the other constituents resulted in the same final pH within ±0.02 pH unit.

The acid dissociation equilibrium of $N_2H_5^+$ to N_2H_4 is unlikely to be responsible for the observed dependence of the rate of the reaction on pH, since the acid dissociation constant of $N_2H_5^+$ is on the order of 3×10^{-9} (pK_a around 8.5),[23] whereas the rate of the reaction increases abruptly around a pH of 3.5 (Figure 2). Such a pH dependence of the rate may arise due to the acid dissociation equilibrium of the intermediate $N_2H_4^{\bullet+}$ radicals and/or due to the involvement of hydrolysis equilibria involving Mn in oxidation states 3 to 6. In highly acidic solutions (0.5–3.6 M $HClO_4$), Davies and Kustin[23] observed that the oxidation of N_2H_4 by Mn(III) has a simple 1:1 stoichiometry, indicating that N_2H_4 undergoes one-electron oxidation, giving rise to $N_2H_4^{\bullet+}$. It is probable that this radical intermediate undergoes deprotonation at higher pH to give $N_2H_3^\bullet$, which may undergo further oxidation by MnO_4^- and/or intermediates like Mn(VI), Mn(V), and Mn(IV), thereby leading to varying stoichiometry.

At the present stage, our understanding of the mechanism of the title reaction is rather sketchy. In fact, rationalization of the observed second-order dependence on MnO_4^- and the varying order with respect to N_2H_4 requires a complex mechanism. Combined with results on the end products and isotopic labeling studies reported in the literature,[19,27] we believe further investigations of the stoichiometry of the reaction at different pH and at different ratios of $[MnO_4^-]_0/[N_2H_4]_0$ and additional kinetics experiments under wider concentration ranges will lead to important information on the mechanism. These studies are currently under way. In addition to the unique second-order dependence on MnO_4^-, the inflection point in the kinetics is also encouraging from the point of autocatalysis, which is essential for nonequilibrium nonlinear dynamic phenomena such as bistability and oscillations.

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Registry No. N_2H_4, 302-01-2; MnO_4^-, 14333-13-2.

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(26) Recent experiments carried out in our laboratory indicate that the pseudo-second-order rate constant k_{exp} decreases as $[N_2H_4]_0$ decreased when $[N_2H_4]_0/[MnO_4^-]_0$ is around 10. Therefore, the zero-order dependence shown in Table I does not prevail under relatively low $[N_2H_4]$. This feature is currently being investigated in greater detail.

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