hancement observed in $ScPc_2$ and to a lesser extent in $LuPc_2$ and YbPc₂. Multilevel optical pumping cannot be ruled out in any case. However, it would require more information on the nature and dynamics of the low lying states to evaluate this possibility as the source of the observed nonlinearity.

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Kinetics and Mechanism of the Chlorite-Thiourea Reaction in Acidic Medium¹

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The kinetics of the reaction between chlorite and thiourea in acidic medium have been studied. The stoichiometry of the reaction for pH > 3 is $2ClO_2^- + SC(NH_2)_2 + H_2O \rightarrow 2Cl^- + OC(NH_2)_2 + SO_4^{2-} + 2H^+$; for pH < 3 OC(NH_2)_2 is hydrolyzed to NH_4^+ and CO_2 . The reaction is characterized by an induction period after which chlorine dioxide is produced. For $[ClO_2^{-}]/[SC(NH_2)_2] < 2$ the formation of chlorine dioxide is only transient. Thiourea is progressively oxidized to sulfonic acid before cleavage of the sulfur-carbon bond and formation of sulfate. A 13-step mechanism is proposed with rate-determining step $Clo_2^- + SC(NH_2)_2 + H^+ \rightarrow HOCl + HOSC(NH)NH_2$. Computer simulation using this mechanism gives good agreement with experiment.

Introduction

The chlorite ion is perhaps the most readily available source of nonlinear behavior in chemistry.^{2,3} In nearly all of its reactions, whether it is acting as an oxidizing or a reducing agent, it presents some degree of unconventional kinetics. Reactions of chlorite ion with the halides bromide⁴ and iodide⁵ produce clock reaction characteristics in closed (batch) and oscillatory behavior in open (flow) reactors. With a simple one-electron reductant like hexacyanoferrate(II) ion, one finds autoinhibition and evidence for an interfacial redox reaction at the interface between solution and container.6

Arguably, the most fascinating dynamical behavior of chlorite ion occurs in its reactions with the sulfur compounds that have so far been studied. These reactions display exotic reaction dynamics such as periodic oscillation,^{4,7} stochastic behavior,⁸ chemical chaos,9 traveling waves,10 stirring rate effects,8 and gravity-induced anisotropy in traveling waves.¹¹ Although the reduction of chlorite to chloride is far from simple, the main reaction driving so many examples of nonlinear behavior is oxidation of sulfur to sulfate with variable stoichiometries that depend on the pH of the solution

and the relative concentrations of chlorite and reductant.

The exact cause of nonlinearities in chlorite-sulfur compound reactions is not entirely certain. Before any generalized theory on the source of these nonlinearities can be advanced, many reactions need to be studied in detail, with mechanisms for single-step reactions being understood. One major contribution to nonlinear behavior in chlorite reactions is the instability of Cl(III) species with respect to Cl(IV) and Cl(V) in the presence of Cl(I)in acidic medium. Since the reduction of Cl(III) via a nonradical mechanism goes through Cl(I), hypochlorite can compete with the reductant for chlorite, giving transient or permanent formation of chlorine dioxide. Another strong source of nonlinear behavior arises from the sulfur compound. In the oxidation of sulfur from a - 2 to a + 6 oxidation state, several intermediate oxidation states assert themselves.¹² The tendency to form sulfur-sulfur bonds is very strong, and polymeric sulfur species enhance the possibility of nonlinear kinetics.¹³ These polymeric sulfur species, S_n where n < 8, can be further oxidized in the presence of a stoichiometric excess of oxidant.¹⁴ In the absence of further oxidant, S_8 is formed and is precipitated.

We have for some time been interested in the reaction of chlorite with thiourea. This reaction produces fascinating dynamics in both batch and flow conditions.¹⁵ In batch environments it is a clock reaction characterized by a long quiescent initial period followed by rapid formation of chlorine dioxide. The reaction also displays (in unstirred conditions) spatial inhomogeneity in the formation of chlorine dioxide. The onset of chlorine dioxide formation is irregular and is dependent on the type of container used. In flow conditions. It has not been possible to explain the origin of such complex behavior, because the mechanism of this reaction is unknown.

We present in this paper a study of the kinetics and mechanism of the chlorite-thiourea reaction in a closed system. The mechanism and rate constants from this study together with equilibrium data should aid in explaining more complex phenomena such as traveling waves and the complex dynamics observed in flow systems.

Experimental Section

Materials. The following analytical grade chemicals were used without further purification: thiourea (Aldrich) and perchloric acid, 70-72% (Fisher). Commercially available sodium chlorite (Aldrich) varied in purity from 78% to 88% and was recrystallized twice from water only. The temperature of the water was not allowed to exceed 50 °C. This treatment brought the chlorite assay to between 94% and 97%. Analysis of chlorite was done iodometrically by adding acidified iodide and titrating the liberated iodine against standard sodium thiosulfate with starch as indicator.¹⁶ Stock solutions of sodium chlorite were prepared just before use and sometimes stabilized with 1×10^{-3} M sodium hydroxide if reactions were going to be run in high acid environments over extended periods of time. All chlorite solutions were stored in dark Winchester bottles to reduce exposure to light. Thiourea was assumed to be a good enough standard and was not analyzed before use

Methods. Reactions were carried out in a Plexiglas reactor with a Teflon cap and stirred vigorously from below. The water jacket around the reactor was thermostated at 25 ± 0.1 °C. The reaction was followed by pH, redox potential, and absorbance measurements. The water used to make up all the solutions was deaerated with either argon or nitrogen before use. Ionic strength was maintained at 0.5 M with NaClO₄.

To ensure that production or consumption of H^+ ions by the main reaction could be detected by changes in the potential of a pH electrode, reactions were not buffered. A Teflon-capped reactor prevented the escape of volatile chlorine dioxide under vigorous stirring. Redox potential measurements were performed by using a platinum electrode with a mercuric sulfate reference. Absorbance measurements were made at 360 nm, where chlorine dioxide has an absorptivity coefficient of 1265 M^{-1} cm^{-1,17}

Both slow and fast reactions were run in a Hi-Tech SF-3L stopped-flow spectrophotometer for consistency. This precaution was taken because the photocell material (Plexiglas, plastic, or quart2) greatly influenced the rate of reaction, especially in slow reactions. The Hi-Tech stopped-flow spectrophotometer has a quart2 observation cuvette which is fed by Tygon tubes. Greatest reproducibility occurred at relatively shorter reaction times, which were not subject to the stochastic behavior often encountered in chlorite-based reactions. After initial rapid mixing of reactants in the stopped-flow ensemble, there is essentially no further stirring until the end of the reaction. The photomultiplier output from the stopped-flow was amplified and digitized via a Metrabyte 12-bit A/D converter and interfaced to a Tandy HD-1200 microcomputer for storage. The data were analyzed for induction periods, initial rates, and maximum absorbance.

Stoichiometric Determinations. Reaction solutions used for stoichiometric determinations were stored for at least 48 h before any analyses were performed. These solutions were stored in tightly capped 100-mL volumetric flasks wrapped in aluminum foil and placed in the dark. The solutions were later analyzed quantitatively for chloride, sulfate, acid, and chlorite and qual-



Figure 1. Absorbance at 360 nm (solid line) and pH (dashed line) traces. Production of chlorine dioxide coincides with a rapid decrease in pH. $[NaClO_2]_0 = 3.52 \times 10^{-3} \text{ M}; [SC(NH_2)_2]_0 = 1 \times 10^{-3} \text{ M}; \text{optical path} \text{ length} = 1.00 \text{ cm}.$ Two drops of 0.1 M HClO₄ is added to decrease induction period.

itatively for ammonium ion and urea. Excess chlorite was determined iodometrically. Sulfate was determined gravimetrically with BaSO₄ in excess thiourea conditions only, because chlorite forms a precipitate with BaCl₂. Silver nitrate gave precipitates of both AgCl and (Ag)₂SO₄. By running two determinations of AgCl + Ag₂SO₄ and solving two simultaneous equations, we obtained the unambiguous contributions from sulfate and chloride. Acid was determined qualitatively by using the pH electrode and quantitatively by titrating the final reagent solution against 0.001 M NaOH with methyl orange as indicator. The Davies equation¹⁸ proved inaccurate in deducing hydrogen ion concentration from hydrogen ion activity; therefore, we made no activity coefficient corrections of the pH measurements.

Results

Stoichiometry. Two stoichiometries were obtained. At high pH (>3), the stoichiometry was found to be

$$2ClO_2^- + SC(NH_2)_2 + H_2O \rightarrow OC(NH_2)_2 + 2Cl^- + SO_4^{2-} + 2H^+ (M1)$$

At low pH (<3), the stoichiometry was

$$2ClO_{2}^{-} + SC(NH_{2})_{2} + 2H_{2}O \rightarrow 2NH_{4}^{+} + SO_{4}^{2-} + CO_{2} + 2Cl^{-} (M2)$$

The qualitative test for urea¹⁹ was strongly positive at low acid concentrations and faintly positive in high acid. At low [H⁺] the pH decreased significantly during the course of the reaction. These stoichiometries were found at stoichiometric (2:1 ratio) or excess chlorite conditions. In excess thiourea milky turbid deposits of sulfur could be observed in the reaction medium, hampering both absorbance and redox potential measurements. Generally, combinations of stoichiometries M1 and M2 exist except in the limits of pH less than 1 and greater than 4 (but not greater than 5, because at pH > 5 the reaction either does not proceed or is very slow). All kinetics experiments were performed with $R = [ClO_2^{-}]_0/[SC(NH_2)_2]_0 > 2$.

Reaction Kinetics. The reaction displayed the same induction period that had previously been reported.¹⁰ Absorbance-time curves were sigmoidal in shape and characteristic of autocatalytic production of chlorine dioxide at the end of the induction period (Figure 1). The pH traces are strongly correlated with the absorbance traces. At the point of rapid production of chlorine dioxide there is a concomitant rapid decrease in pH. Redox potential traces also parallel the above traces, though the redox potential change was relatively small.

Acid catalyzes the reaction. Above pH 2.5 there exists an inverse relationship between the induction period and the initial acid concentration (Figure 2). As the acid concentration is increased further, however, the inverse relationship is lost. Below pH 2 the reaction becomes fairly insensitive to acid concentration. The acid does not retard the reaction, but it ceases to accelerate



Figure 2. Inverse acid dependence of induction period between 1×10^{-3} and 7×10^{-3} M for $[NaClO_2]_0 = 3.76 \times 10^{-3}$ M and $[SC(NH_2)_2]_0 =$ 9.8×10^{-4} M.



Figure 3. Induction period vs $R = [NaClO_2]_0/[SC(NH_2)_2]_0$: $[SC(NH_2)_2]_0$: $H_2)_2]_0 = 9.85 \times 10^{-4} \text{ M}.$ (\odot) $[H^+]_0 = 0.005 \text{ M};$ (\Box) $[H^+]_0 = 0.01 \text{ M}.$

it as the initial acid concentration is progressively increased. For example, the induction period observed at $[H^+]_0 = 0.1$ M is nearly the same as at $[H^+]_0 = 0.01$ M. The inverse relationship is also lost above pH 4.5, where the reaction becomes very slow. At this point induction times (especially those from stopped-flow data) became stochastic.

The induction period decreases with the ratio R = $([ClO_2^-]_0/[SC(NH_2)_2]_0)$. Figure 3 shows two ratio-induction period graphs at different initial acid concentrations. (The data were less noisy and more reproducible at high R values and low acid.) The rate of formation of chlorine dioxide was also much faster at high R values.

The final amount of chlorine dioxide produced depends on the quantity of chlorite in excess of the 2:1 stoichiometric ratio. The rate of formation of this chlorine dioxide depends on the acid concentration. For those reactions run with stoichiometric ratios less than two but greater than one, chlorine dioxide formation was only transient. Since chloride is one of the major impurities in commercially available chlorite, a number of experiments were performed with controlled amounts of chloride added initially. No appreciable difference in induction period was observed between experiments with chloride and those without, although chloride did accelerate the rate of formation of chlorine dioxide after the induction period.

Mechanism

We propose a mechanism of 13 steps, reactions R1-R13 (Table I). Any reaction that involves the oxidation of sulfur coupled

TABLE I: Proposed Mechanism

- **R**1 $H^+ + ClO_2^- \Rightarrow HClO_2$ $H^+ + SC(NH_2)_2 \rightleftharpoons [H-SC(NH_2)_2]^4$ **R**2
- $ClO_2^- + SC(\tilde{NH}_2)_2 + H^+ \rightarrow HOSC(NH)NH_2 + HOCl$ **R**3
- $ClO_2^- + [H-SC(NH_2)_2]^+ \rightarrow HOSC(NH)NH_2 + HOCl$ R4
- $Cl_2 + H_2O \Rightarrow HOCl + Cl^- + H^+$ **R**5
- R6
- $\begin{array}{l} \text{Cl}_2 + 2\text{ClO}_2^- \rightarrow 2\text{ClO}_2 + 2\text{Cl}^- \\ \text{HOCl} + 2\text{ClO}_2^- \rightarrow 2\text{ClO}_2 + 2\text{Cl}^- \\ \text{HOCl} + 2\text{ClO}_2^- + \text{H}^+ \rightarrow 2\text{ClO}_2 + \text{Cl}^- + \text{H}_2\text{O} \end{array}$ **R**7
- **R**8 $2CIO_2 + HOSC(NH)NH_2 + H_2O \rightarrow HO_3SC(NH)NH_2 +$ $HOCI + CI^{-} + H^{+}$
- $ClO_2^- + HOSC(NH)NH_2 \rightarrow HO_3SC(NH)NH_2 + Cl^-$ **R**9
- $ClO_2^- + HO_3SC(NH)NH_2 + H_2O \rightarrow SO_4^{2-} + CO(NH_2)_2 + H_2O \rightarrow SO_4^{2-} + H_2O \rightarrow SO$ R10 $HOC1 + H^+$
- R11 HOCl + HO₃SC(NH)NH₂ + H₂O \rightarrow SO₄²⁻ + CO(NH₂)₂ + Cl⁻ + 3H⁺
- R12 HOSC(NH)NH₂ + SC(NH₂)₂ \rightarrow >CS-SC< + H₂O
- >CS-SC< + ClO_2^- + H_2O + $H^+ \rightarrow 2HOSC(NH)NH_2$ + **R**13 HOCI

TABLE II: Rate Laws and Rate Constants Used in Computer Simulation⁴

	forward reaction	reverse reaction
R 1	$1.0 \times 10^{10} [H^+] [ClO_2^-]$	$3.16 \times 10^{7} [HClO_{2}]$
R2	$2 \times 10^{4} [H^{+}] [SC(NH_{2})_{2}]$	1×10^{4} [HSC(NH ₂) ₂ ⁺]
R3	$10.5[ClO_2^{-}][SC(NH_2)_2][H^+]$	
R4	15.0[ClO ₂ -][HSC(NH ₂) ₂ +]	
R5	11.0[Cl ₂ (aq)]	1.8×10^{4} [HOC1][Cl ⁻][H ⁺]
R6	2.2×10^{1} [Cl ₂ (aq)][ClO ₂ ⁻]	
R 7	1.06×10^{6} [HOC1][C10 ₂ ⁻][H ⁺]	
R 8	5×10^{3} [ClO ₂ (aq)][HO-SC<]	
R9	$7.5 \times 10^{2} [ClO_{5}^{-}] [HO-SC<]$	
R 10	1.2×10^{3} [ClO ₂ ⁻][HO ₃ SC<]	
R 11	8.5×10^{3} [HOC]][HO ₃ SC<]	
R12	$3 \times 10^{3} [SC(NH_{2})_{2}] [HO-SC<]$	
R 13	1×10^{3} [>CSSC<][ClO ₂ -]	

^a Concentration units M; time units s.

with the reduction of a chlorine species is considered essentially irreversible. Therefore, the proposed mechanism has only three reversible reactions. Rate laws and rate constants for R1-R13 are summarized in Table II. For simplicity, we write NH₂ and NH groups attached to a carbon as C<. Thus, >CSSC< represents NH₂(NH)CSSC(NH)NH₂.

Reaction R1. This is a fast protolytic reaction whose equilibrium lies to the right if pH < $pK_a(HClO_2) \sim 2.5$.

Reaction R2. Formation of a stable protonated thiourea species has been established.²⁰ The proton oscillates between nitrogen and sulfur atoms. Protonated thiourea is strongly activated for nucleophilic attack, making this step essential for the success of the mechanism.

Reaction R3. This should be the first and rate-determining step in the oxidation of thiourea; further oxidation of the sulfenyl acid all the way to sulfate should be relatively easy. Experimental measurement of this rate constant is difficult. The value given here represents the best fit between simulation and experiment. There are two possible reaction sequences that are kinetically indistinguishable: (1) protonation of thiourea followed by nucleophilic attack by chlorite on the protonated thiourea species; (2) initial attack by chlorite on thiourea followed by Cl-O bond cleavage that is initiated by proton attack on oxygen.

Reaction R4. This reaction, though mechanistically indistinguishable from (R3), is nevertheless faster than (R3)

Reaction R5. The hydrolysis of aqueous chlorine has been studied experimentally; the kinetic parameters are well-known.²¹

Reaction R6. This reaction was recently studied by Peintler et al.;²² the kinetic parameters and rate law are taken from that study.

Reaction R7. One of the most important reactions in this mechanism, process R7 has also been implicated in the mechanism of the decomposition of chlorite in neutral to acidic media.²³ It is fast and essentially irreversible.²²

Reaction R8. This reaction is a composite of two steps that are essentially oxygen transfers from chlorine dioxide to the sulfur compound. The first transfer should yield a sulfinic acid,



Figure 4. Comparison between experimental data and computer simulation (\triangle). 0.025 was added to each computed data point to align the data with the experimentally observed absorbance readings. [NaClO₂]₀ = 2.85 × 10⁻³ M, [SC(NH₂)₂]₀ = 9.85 × 10⁻⁴ M, [H⁺]₀ = 0.02 M; optical path length = 1.00 cm.

HO₂SC<, which accepts another oxygen to yield the sulfonic acid, HO₃SC<. This reaction is necessary to prevent the concentration of chlorine dioxide from increasing before all the reductant has been oxidized. It is reaction R8 that is responsible for the consumption of chlorine dioxide in reactions with R < 2.

Reaction R9. This reaction is also a composite of two oxygen transfers. Inclusion of the step involving the sulfonic acid does not improve the mechanism, since both steps would be faster than (R3).

Reaction R10. This is the final step in the oxidation of thiourea, and this step involves the cleavage of the sulfur-carbon bond. The reaction is also irreversible.

Reaction R11. We expect the oxidation of the sulfonic acid by HOCl to be much faster than that by ClO_2^- .

Reaction R12. Previous studies of thiourea oxidation have shown that dimer formation is prolific in reactions with mild oxidants. Dimer formation is quantitative when iodine is the oxidant.²⁴

Reaction R13. Dimer oxidation should be facile in the presence of further oxidant. In this reaction, the dimer yields two molecules of the sulfenyl acid.

From the series of reactions R1-R4, there are two possible combinations not shown in our mechanism: (a) $HClO_2 + SC-(NH_2)_2$ and (b) $HClO_2 + [H-SC(NH_2)_2]^+$. Reaction a is assumed to be slow because $SC(NH_2)_2$ is relatively unreactive, and reaction b is retarded because H^+ would be a poor leaving group with only H_2O available as a proton acceptor. These steps can therefore be considered slow enough to be ignored.

Computer Simulations

The chlorite-thiourea reaction was simulated using the 13-step mechanism of Table I and the kinetic parameters and rate laws in Table II. Two different methods were used to simulate the reaction: the Livermore Solver of Ordinary Differential Equations (LSODE) integrator and the semiimplicit Runge-Kutta method of Kaps and Rentrop.²⁵ The two methods gave nearly identical kinetics traces. Agreement between experiments and simulations was satisfactory. Figure 4 shows a typical experimental trace with calculated data points superimposed for comparison.

Of the 13 reactions considered, rate constants for reactions R5-R7 were available from the literature. The simulations were insensitive to the rates of reactions R1, R2, R8, R9, and R12, as long as they were fast enough so as not to be rate-determining. For the remaining five reactions, we assumed that on chemical grounds $k_4 > k_3$, $k_{11} > k_{10}$, and $k_{13} > k_3$. Thus, the number of free parameters was reduced considerably. The simulations were most sensitive to the value of the rate constant k_3 for the rate-determining step (R3).

The simulations correctly predict the absorbance-time traces at 360 nm as well as the dependence of the induction period on R and on acid concentration, including the insensitivity to changes in $[H^+]_0$ at pH < 2.

Discussion

The proposed mechanism offers a consistent explanation for the kinetics data and the observed nonlinear reaction dynamics.

Induction Period. The initial velocities of all reactions are limited by the starting concentrations of their reactant species, some of which may attain appreciable values at later stages of the reaction. Shortly after mixing, the reactions that form chlorine dioxide, (R6) and (R7), are not significant because concentrations of Cl_2 and HOCl are low. Even as HOCl accumulates (from reaction R3), it will be depleted by reactions such as (R11). Therefore, it is difficult for chlorine dioxide to accumulate, resulting in an induction period.

The end of the induction period does not require full consumption of reductant. Chlorine dioxide can accumulate as long as the combined rates of (R6) and (R7) are greater than the rate of (R8). When $[H^+]_0$ is high, reaction R7 can produce ClO₂ faster than reaction R8 can remove it. If $R \ll 2$, at some point all the chlorite will be consumed, and any ClO₂ present will soon be consumed by (R8); chlorine dioxide formation is therefore transient under these conditions.

Acid Dependence. The observed acid catalysis arises from reactions R2 and R3. Our mechanism adequately explains the discontinuity observed in the inverse acid dependence below pH 2.5. Above pH 2.5 the majority of the Cl(III) species exist as ClO_2^- . Below pH 2, the ClO_2^- is replaced by $HClO_2$. At very low pH, thiourea is extensively protonated (R2) and is activated for nucleophilic attack. At these very low pH conditions, however, no nucleophile exists; there is only $HClO_2$, which is not expected to react rapidly with protonated thiourea. Thus at very low pH values, we expect insensitivity to acid concentrations. As the pH is increased past the pK_a of $HClO_2$, $[ClO_2^-]$ increases while at the same time $[HSC(NH_2)_2^+]$ starts to decrease so that reaction R3 predominates. We thus expect a narrow region of inverse acid dependence.

Variations in Product Acid and Sulfate Concentrations. Previous experiments with barium chloride as indicator have shown that both sulfate and acid are produced vigorously and suddenly at the end of the induction period. This observation indicates that the oxidation proceeds all the way to the sulfonic acid before the S-C bond is broken. Any cleavage of the S-C bond at the sulfenyl or sulfonic acid level should result in continuous deposition of BaSO₄ as the reaction proceeds. Reaction R11 accounts for the rapid decrease in pH which occurs simultaneously with the formation of chlorine dioxide.

Autocatalysis. The clock nature of the reaction coupled with a sigmoidal $[ClO_2]$ -time curve suggests autocatalysis. It seems unlikely that autocatalysis is due to reactants or products involved in the overall stoichiometry M1 or M2, however. One type of evidence underlying this assumption can be seen by considering, for example, traveling waves exhibited by this system.¹⁰ Unlike a Cl(III) system that yields traveling waves because the reactivity of HClO₂ exceeds that of ClO₂⁻ and a proton is generated in the overall reaction,²⁶ in this system HClO₂ is a sluggish reactant, and front propagation is due to an autocatalytic intermediate. We suggest that such an intermediate is the sulfur-bonded "dimeric" species formed in reaction R13. The sequence R13 + 2(R12) with reaction R13 rate determining yields autocatalytic production of the dimer >CS-SC< and a concomitant rapid increase in HOCI which is then sustained via reaction sequence R7 + R8.

This study represents one of a rapidly growing set of mechanistic investigations of sulfur-containing systems that exhibit interesting nonlinear dynamics. Reactions for which mechanisms have been proposed recently include methylene blue-sulfite-oxygen,²⁷ hydrogen peroxide-sulfide,²⁸ bromate-thiocyanate,²⁹ bromine-thiocyanate,³⁰ and bromate-thiourea.³¹ These studies should soon make it possible to construct a consistent picture of how sulfur compounds contribute to oscillatory and other nonlinear dynamical behavior.

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- Relaxation Kinetics and Infrared Spectra of the Complexation of Lithium Ion by Triethylene Glycol and by Tetraethylene Glycol in Acetonitrile

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Ultrasonic absorption relaxation spectra are reported covering the frequency range $\sim 1-500$ MHz for the complexation of LiClO₄ by the open-chain polyethers triethylene glycol (EG3) and tetraethylene glycol (EG4) in acetonitrile at 25 °C and at a molar ratio $R = [EG3]/[LiClO_4]$ or $R = [EG4]/[LiClO_4] = 1$. The ultrasonic spectra can be described by the sum of two Debye relaxation processes which were interpreted according to the Eigen-Winkler mechanism

$$Li^+ + EG \xleftarrow{k_0} Li^+ \dots EG \xleftarrow{k_1} Li^+ EG \xleftarrow{k_2} (Li^+ EG)$$

(where EG denotes either EG3 or EG4), giving the rate constants k_1 , k_{-1} , k_2 , and k_{-2} . The first step is taken to be a preequilibration step for which K_0 is calculated from classical statistical theory. The rate constants are compared with those of the corresponding process involving triglyme and poly(ethylene oxide) (PEO) previously reported. Infrared data for the 3800-3200-cm⁻¹ region show a shift of 70 cm⁻¹ to lower energy, indicating a strong interaction between the ethanolic oxygen of EG3 and the Li⁺ ion.

Introduction

The kinetics and mechanism of Li⁺ complexation are of interest in part because of biochemical¹ and electrochemical ramifications.² In a recent study of complexation of Li⁺ by poly(ethylene oxide) (PEO) of average molar mass $\overline{M} \sim 15000$ and by triglyme (TG3) with M = 178 amu, Eschmann et al.³ observed two concentration-dependent relaxation processes which, at the molar ratio R= $\left[-O(CH_2)_2 - \right] / \left[LiClO_4\right]$ = 4, were independent of molecular chain length. Since PEO has terminal hydroxyl groups for each chain, whereas TG3 is "capped" by methoxy (-OCH₃) terminal groups, it is interesting to see whether by shortening the chain length of PEO down to a size comparable to that of TG3, a large difference in the complexation behavior of Li⁺ with the polyether is observed.

Thus we here extend the study of Li⁺ complexation to ligands such as triethylene glycol (EG3) and tetraethylene glycol (EG4). They differ from TG3 by the replacement of the terminal methyl groups by hydrogen atoms for both ligands as well as by the addition of one -CH₂CH₂O- group in the case of EG4; see Figure 1. The interaction of the hydroxyl group with Li⁺ has been documented by infrared (IR) spectra in the 3800-3200-cm⁻¹ region as reported below. Acetonitrile was used as the solvent for all the systems investigated as in the previous work with TG3 and PEO.³

Experimental Section

Two different cylindrical resonators were used by our two research groups independently in the frequency range 1-7 MHz,⁴ yielding identical results within experimental error $(\pm 1\%)$.

For the 15-215-MHz frequency range a previously described⁵ laser Debye-Sears instrument was used. The 30-600-MHz frequency range was also studied with a pulse ultrasonic absorption apparatus.⁶ These two methods also yielded comparable results within experimental error.

A 983G computer assisted Perkin-Elmer infrared spectrometer was used to collect the digitized infrared spectra. The Perkin-Elmer sealed demountable cells equipped with NaCl windows were calibrated before each run by the fringe method. The instrument was set in the single-scan, slow-speed mode (filter no. 4), with no smoothing, to avoid distortion of the spectral envelope. The