the relaxation of Q_4 silicon atoms has to occur via adjacent proton-containing T, Q_2, or Q_3 moieties, which leads to rather long $^{29}Si-^1H$ distances. Hence, the Q_4 sites detected in **1** should be assigned to those which are directly bound to a T site or a Si-OH-containing moiety. Increasing amounts of $Si(OEt)_4$ used for the cocondensation with $(MeO)_3SiR$, combined with an incomplete hydrolysis of Si-OR residues, result in the occurrence of non-detectable Q_4 silicons. However, their numbers can be estimated from the difference of the Q:T ratio determined by CP-MAS and the Q:T ratio expected from the stoichiometry of the reaction. This reveals that in the case of **1** ca. 43% of all Q groups are Q_4 sites that are too far away from protons to be detected by CP-MAS and should therefore be predominantly bound to other Q_4 groups. Compound **1** contains considerable proportions of Q_2 and Q_3 groups (see Table II), and this indicates that the polycondensation reaction has not proceeded to full completion. The structural consequence of this is the occurrence of layers of partially opened siloxane rings, which in turn are interconnected to give a relatively open three-dimensional network. This is supported by the ability of the material to form swollen gels in alcohols. Figure 2 shows the proposed structure of the polysiloxane **1**. The relative numbers of the T and Q species present in this model reflect their ratios as determined above.

Registry No. **1**, 135339-91-2; **2**, 135339-89-8; $Si(OEt)_4$, 78-10-4; $(n-Bu)_2Sn(OAc)_2$, 1067-33-0; $RuCl_3$, 10049-08-8; $RuCl_2(CO)_2$ (homopolymer), 28986-72-3; 2-methoxyethanol, 109-86-4.

Contribution from the Department of Chemistry,
Miami University, Oxford, Ohio 45056

Complex Formation Reactions of the Chlorite Ion

István Fábián[†] and Gilbert Gordon*

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Unique kinetic phenomena[1-4] and important practical applications[5,6] have generated great interest in the chemistry of chlorite ion. Previous studies in this field have extensively covered stoichiometric, kinetic, and mechanistic aspects of the oxidation-reduction reactions of ClO_2^-. In contrast, little is known about the coordination chemistry of chlorite ion.

The formation of only a few complexes with ClO_2^- has been confirmed. The preparation and the properties of the inert Co-$(NH_3)_5ClO_2^{2+}$ complex was discussed by Thompson.[7] This species was shown to be stable in solid phase and undergo slow decomposition in acidic solution. Two labile complexes were reported with chlorine dioxide[8] and the uranyl ion.[9] The formation of these species was undoubtedly confirmed, but only rough estimates could be given for their stability constants. Other chlorito complexes were also postulated in redox reactions of chlorite ion but were not detected directly.

The lack of stability data for the chlorito complexes is mainly due to the inherent difficulties with finding suitable experimental conditions for the equilibrium studies. In order to avoid complications caused by the hydrolysis of the metal ions, precipitation of hydroxo species, formation of polynuclear complexes, etc., the experiments should be performed in acidic solutions. In the case of the most common di- and trivalent transition-metal ions, the pH should not exceed ~2.5. However, in the acidic pH range

the chlorite ion is quite susceptible to decomposition reactions.[10]

The number of the appropriate methods for monitoring these reactions also appears to be somewhat limited. This is because the formation of relatively weak complexes is anticipated. Consequently, the pH effect of the complex formation cannot be measured with acceptable precision. The same problem is expected with other electrochemical methods, including potentiometry by using metal ion selective electrodes.

Spectrophotometry is one of the most frequently applied methods for studying the formation of weak complexes. However, in the case of chlorite ion, certain experimental difficulties must be anticipated. First of all, in the decomposition reactions of chlorite ion, chlorine dioxide is one of the products.[10] ClO_2 is characterized with a strong absorbance band in the near-UV-visible spectral region[11] ($\lambda_{max} = 358.5$ nm, $\epsilon_{max} = 1250$ M^{-1} cm^{-1}), which overlaps the spectrum of the chlorite ion. It also may overlap the spectra of the ClO_2^- complexes. Accordingly, the decomposition reactions do not only compete with the complex formation but also may interfere with the spectrophotometric detection of the corresponding complex.

In the case of low oxidation state metal ions, possible redox reactions between the metal ion and ClO_2^- are an additional source of interference. Relatively fast redox reactions were reported between chlorite ion and several transition-metal ions and their complexes.[12-16] The rate of the electron-transfer process can be comparable, or even higher, than that of the complex formation reaction. Moreover, the redox reactions may generate strongly absorbing transient species, which obviously may complicate the evaluation of the data.

In order to avoid, or at least minimize, the effects of side reactions, the complex formation reactions should be monitored as soon as possible after mixing the reactants. Recent technical developments in fast kinetic methods make it possible to record the spectrum of the reacting systems a few milliseconds after triggering the reactions.[17] These techniques can effectively be applied for investigating both kinetic and equilibrium aspects of fast chemical processes. In this report, we present our stopped-flow–rapid-scan spectrophotometric (SF–RS) studies on the protolytic equilibria of the chlorite ion and the formation of the $CuClO_2^+$ complex.

Experimental Section

Chemicals. Reagent grade chemicals and deionized triply distilled water were used in all experiments. $NaClO_2$ was prepared from commercially available sodium chlorite (Olin, approximately 80% purity) according to the method described by Peintler et al.[18] In the final stage

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[†]On leave from the Institute of Inorganic and Analytical Chemistry, Kossuth L. University, Debrecen, Hungary.

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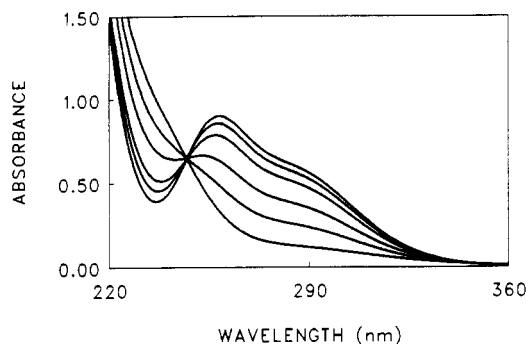
Figure 1. Spectrophotometric determination of the pK_a of chlorous acid. Each spectrum is the average of the first three to five SF–RS scans. Scan rate: 190 nm/40 ms. Interval between consecutive scans: 40 ms. $C_{ClO_2^-}$ = 6.22 × 10^{-3} M; the concentration of added perchloric acid is 0, 3.46 × 10^{-3}, 6.92 × 10^{-3}, 1.98 × 10^{-2}, 4.94 × 10^{-2}, and 0.494 M in the order of decreasing absorbance at 290 nm.

of this process, NaClO$_2$ was recrystallized three times from 75% acetone–water mixture instead of the originally proposed 80% ethanol–water mixture. NaClO$_2$ was stored over anhydrous P$_2$O$_5$ in the dark and in vacuo. Standard iodometric analysis showed better than 99.7% purity. The pH of an 0.05 M aqueous solution of NaClO$_2$ was ~7.3. No chloride ion could be detected in the purified NaClO$_2$.

The Cu(ClO$_4$)$_2$ stock solution was prepared by dissolving cupric oxide in perchloric acid (both Fisher Scientific). The excess copper oxide was filtered off. In order to prevent hydrolysis of cupric ion, the solution was acidified by adding known amounts of HClO$_4$. The Cu^{2+} concentration was determined by using a standard iodometric method.[19]

NaClO$_4$ was prepared from Na$_2$CO$_3$ and HClO$_4$ as it is detailed elsewhere.[20] The NaClO$_4$ concentration was determined by weight, by drying known aliquots of the final solution at 150 °C. In all experiments, the ionic strength was adjusted to 1.0 M by adding appropriate amounts of NaClO$_4$. The temperature was set at 25.0 ± 0.05 °C.

Instrumentation. Potentiometric titrations were made with a Radiometer ABU93 Triburette autoburet station controlled by a Radiometer VIT90 Video Titrator unit. A P101 platinum–K401 SCE electrode pair (Radiometer) was used for the iodometric titrations. Regular spectra were recorded on a Hewlett Packard 8450 UV–visible diode-array spectrophotometer.

Fast photometric measurements were made with an Atago Bussan/Photal Otsuka Electronics RA-401 stopped-flow spectrophotometer equipped with an RA-451 data processor. With a 10-mm cell, the dead time is estimated to be about 2 ms. In SF–RS mode, a 190-nm-wide spectral range can quasi-simultaneously be detected with an optional RA-415 rapid-scan attachment (Atago Bussan/Photal). The available maximum scan rate with this instrument is 190 nm/2 ms. The photodiode-array detector provides a 512 points/190 nm spectral resolution. The applied transient memory has the capacity of storing 16 consecutive spectra. On the basis of a standard calibration procedure, the reproducibility of the SF–RS measurements is ±2%.

Results and Discussion

Protonation of the Chlorite Ion. Previously published pK_a values for chlorous acid[21] are in the range 1.3–2.3. The scatter of these data is considerably greater than acceptable for a simple acid–base equilibrium, even taking into account the variation in the applied experimental conditions.

In our SF–RS experiments, NaClO$_2$ was mixed with calculated amounts of perchloric acid and the UV spectra were recorded with a 190 nm/40 ms scan rate. The first few consecutive spectra of each series (recorded in 40-ms intervals) appeared to be identical. Also, no significant absorbance change was observed at 360 nm. These results confirm that the decomposition of chlorite ion is negligible in the 300–500-ms time interval of these experiments.
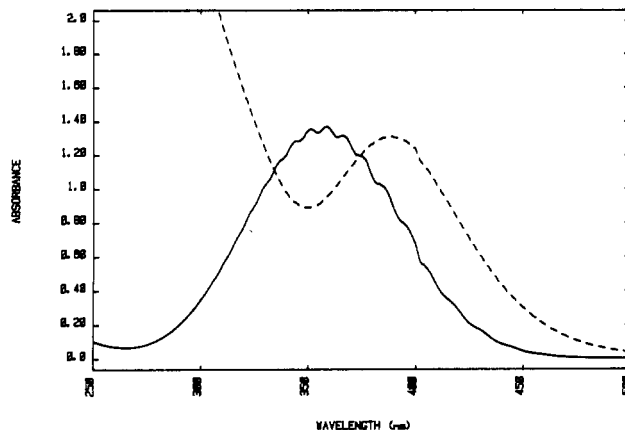
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Figure 2. Spectra of the ClO$_2^-$–Cu^{2+} system and chlorine dioxide. Dashed line: $C_{ClO_2^-}$ = 2.03 × 10^{-2} M and $C_{Cu^{2+}}$ = 3.01 × 10^{-2} M in 1.75 × 10^{-3} M perchloric acid. Solid line: 1.13 × 10^{-3} M ClO$_2$.
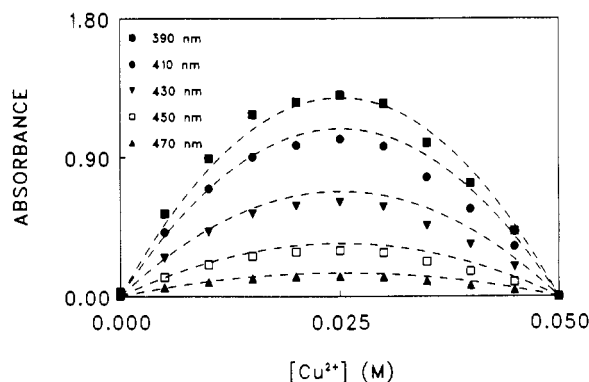

Figure 3. Job curves for the ClO$_2^-$–Cu^{2+} system. $C_{ClO_2^-}$ + $C_{Cu^{2+}}$ = 0.05 M. The marks correspond to conventional spectrophotometric measurements. Dashed lines were calculated on the basis of SF–RS measurements.

A few representative spectra, each corresponding to the average of the first three to five traces, are shown in Figure 1.

It should be added that in 0.5 M HClO$_4$ the absorbance increased slightly in the near–UV–visible range at longer times. This absorbance change was attributed to the formation of ClO$_2$. In additional experiments, we have confirmed that 10–20 s after mixing the spectral effects of the chlorine dioxide formation are more pronounced and cannot be neglected.

The data were evaluated by fitting the absorbance values at six different wavelengths in the 230–290-nm range with a nonlinear least-squares fitting program. The equilibrium constant for reaction 1 and the molar absorptivities for HClO$_2$ and ClO$_2^-$ were calculated simultaneously.

$$HClO_2 = ClO_2^- + H^+ \qquad (1)$$
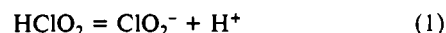
At the 248-nm isosbestic point, the molar absorbtivity is 107 ± 5 M^{-1} cm^{-1}. The pK_a value for chlorous acid was calculated to be 1.72 ± 0.02. The molar absorptivities for ClO$_2^-$ are in excellent agreement with the data obtained from our standard spectrophotometric measurements. For example, at the maximum wavelength, 260 nm, the molar absorptivities are 148.9 (SF–RS) and 149.3 M^{-1} cm^{-1}. In general, the average difference in the corresponding values is less than 4%.

Formation of the CuClO$_2^-$ Complex. Immediately after the mixing of the solutions of chlorite and Cu^{2+} ions, an intense yellow color was observed. This color strongly resembles the color of a chlorine dioxide solution. However, on the basis of regular spectrophotometric measurements using the Hewlett Packard 8450 spectrophotometer, the corresponding spectra show significant differences (Figure 2). Most importantly, the absorbance maxima appear about 27 nm apart, at 360 and 387 nm, respectively. Moreover, the characteristic fine structure of the ClO$_2$ absorbance band is not observed in the ClO$_2^-$–Cu^{2+} system. These preliminary
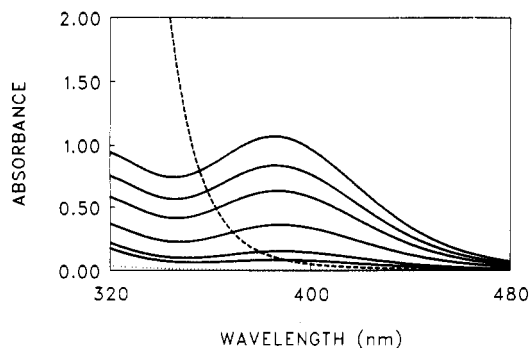
Figure 4. SF-RS spectra for the ClO_2^--Cu^{2+} system. Each spectrum is the average of the first three to five consecutive scans. Scan rate: 190 nm/100 ms. Dashed line: 0.500 M $NaClO_2$. Dotted line: 0.157 M $Cu(ClO_4)_2$. Solid lines: $C_{ClO_2^-} = 5.01 \times 10^{-3}$ M and $C_{Cu^{2+}} = 6.97 \times 10^{-3}$, 1.39×10^{-2}, 3.49×10^{-2}, 6.97×10^{-2}, 0.105, and 0.157 M in the order of increasing absorbance. $C_{H^+} = 7.0 \times 10^{-4}$-$1.1 \times 10^{-3}$ M.

experiments clearly prove the formation of a new species.

The data, evaluated by using Job's method[22] (Figure 3), are consistent with the formation of a complex with 1:1 stoichiometry for ClO_2^- and Cu^{2+} (reaction 2). The evaluation of the data based on the Coleman–Varga method[23] led to the same conclusion.

$$Cu^{2+} + ClO_2^- = CuClO_2^+ \qquad (2)$$

At higher reactant concentrations, and at longer times, the spectra seemingly were somewhat corrupted by the formation of ClO_2. Considering the applied experimental conditions (pH = 2.5–3.5), this observation indicates that Cu^{2+} slightly catalyzes the decomposition of chlorite ion.

The SF-RS measurements were performed by varying the Cu^{2+} and ClO_2^- concentrations in the range of 1.39×10^{-3}–0.157 and 1.00×10^{-3}–0.500 M, respectively. The acid concentration of these samples was 5×10^{-4}–1.0×10^{-3} M. In general, the rate of the complex formation reactions with Cu^{2+} is close to the diffusion-controlled limit.[24] Accordingly, the formation of the $CuClO_2^+$ complex was completed in less than the dead time of the SF-RS measurements. No apparent change was observed in the consecutive rapid-scan spectra, even when the fastest available scan rate (190 nm/2 ms) was applied. A few representative spectra are shown in Figure 4. A similar concentration dependence was observed with chlorite ion.

The data for 15 wavelengths in the 360–480-nm wavelength range were evaluated with the program PSEQUAD.[25] In these calculations, the pK_a of $HClO_2$ and the spectrum of the chlorite ion were included as known parameters, and the stability constant as well as the spectrum of the $CuClO_2^+$ complex were simultaneously evaluated. The Job's curves calculated with the fitted parameters are in excellent agreement with the experimental data from standard spectrophotometric measurements (Figure 3).

The calculated stability constant for the $CuClO_2^+$ complex is 1.04 ± 0.07 M^{-1}. The molar absorptivity of this species at the maximum wavelength, 387 nm, is 1990 ± 120 M^{-1} cm^{-1}. As expected, a relatively weak complex is formed with Cu^{2+}, although its stability is considerably higher than that of the uranyl complex.[9] The complex formation is associated with the appearance of an intense, presumably charge-transfer, band in the near-UV–visible spectral region. The main implication of these results is that the complex formation can be part of any reaction system including a transition-metal ion and ClO_2^-. Most likely, these complexes

are rapidly formed at even relatively low concentration levels. However, they may be of crucial kinetic importance in the oxidation–reduction and catalytic decomposition reactions of chlorite ion. The results also indicate that proper characterization of these complexes requires the application of fast spectrophotometric methods. This subject has been addressed in our ongoing equilibrium and kinetic studies.

Contribution from the Department of Chemistry, University of Helsinki, Et. Hesperiankatu 4, 00100 Helsinki, Finland

The Large Range of Uranyl Bond Lengths: Ab Initio Calculations on Simple Uranium–Oxygen Clusters

Pekka Pyykkö* and Yongfang Zhao†

The large range of uranyl bond lengths is a classical problem.[1] We present here an ab initio study of the underlying mechanism, supposing it to be an intramolecular one, taking place inside an axial + equatorial, $[(O_{ax}UO_{ax})(O_{eq})_n]^{6-}$ ($n = 4$) distorted octahedral model cluster, including the UO_2^{m+} ($m = 0$-2), "antiuranyl" $UO_4^{2-}(D_{4h})$ and cubic UO_6^{6-} limits.

The quasirelativistic pseudopotential of Hay et al.[2] and Gaussian 90[3] were used. The oxygen basis is described in ref 4. For a possible explanation as to why structural calculations on highly charged anions work, see ref 5. The calculated bond lengths and breathing frequencies are given in Table I.

The free UO_2^{m+} bond length and its charge dependence resemble earlier studies and are for uranyl near the low end of the experimental range of about 150–208 pm.[1a] The UO_4^{2-} one is a little below and the UO_6^{6-} one a little above experiment. Taking then U–O_{eq} as the independent variable and optimizing U–O_{ax}, we find the results shown in Figure 1. They nicely parallel the

†On leave from the Institute of Atomic and Molecular Physics, Jilin University, 130023 Changchun, People's Republic of China.

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