inductive measurements on a single-crystal specimen. However, superconductivity was detected by rf penetration depth measurements at 500 kHz in a 1.5-mg sample consisting of many crystal specimens. This sample gave an onset temperature for superconductivity (T_c) of 8.5–9.0 K, a broad transition, and a low signal response (increase in resonant frequency). These properties indicate that only a small fraction of the sample had bulk superconductivity and that the crystals possessed a range of T_c values. Resistivity measurements would likely give a much higher (average) T_c, as evidenced by a comparison between published resistivity and magnetic studies of the polycrystalline samples. We plan to investigate the doping levels, oxygen deficiencies, and conductivity in our crystals as larger amounts of material become available.

Acknowledgment. Work at Argonne National Laboratory is sponsored by the Office of Basic Energy Sciences, Division of Materials Science, U.S. Department of Energy (DOE), under Contract W-31-109-Eng-38. We especially thank Joseph S. Gregar for assistance with the special glassware used in the synthesis, E. A. Huff for chemical analysis, and D. G. Hinks, J. D. Jorgensen, D. W. Capone, M. B. Brodsky, D. Lam, and J. Z. Liu for helpful discussions. M.R.M., T.J.A., R.B.P., and D.L.S. are student undergraduate research participants, sponsored by the Argonne Division of Educational Programs, from St. Michael's College, Winooski, VT; College of the Holy Cross, Worcester, MA; Luther College, Decorah, IA; and Illinois Benedictine College, Lisle, IL, respectively.

Note Added in Proof. It has been reported[12] that the Sr content and T_c in $La_{2-x}Sr_xCuO_4$ are reflected in the c/a ratio of the lattice constants. In our study we find $c/a = 3.47$, thus giving the formula $La_{1.92}Sr_{0.08}CuO_4$ and $T_c \approx 8$ K, which is consistent with our single-crystal results. Since Pb-doped La_2CuO_4 is not superconducting,[13] we believe that very little, if any, lead has been incorporated into our crystals.

Supplementary Material Available: Tables of crystal structure data collection and refinement parameters (Table X1) and anisotropic thermal parameters (Table X2) (2 pages). Ordering information is given on any current masthead page.

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Occurrence of Superoxide Radical Ion in Crystalline $12CaO\cdot 7Al_2O_3$ Prepared via Solid-State Reactions

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Superoxide radical ion O_2^- is an active species of oxygen and is known to play important roles in many chemical reactions involving O_2. The formation of O_2^- on or in solid oxides is usually achieved with the aid of energetic photons such as UV, X-ray, or γ-ray radiation. It has been found that O_2^- occurs in the $12CaO\cdot 7Al_2O_3$ crystal prepared by the solid-state reaction between $CaCO_3$ and Al_2O_3 or $Al(OH)_3$ powder without any accompanying irradiation; the concentration of O_2^- goes up to ca. 4×10^{18} units/g. From the change in the line shape with temperature, the O_2^- is concluded to be included in the structural cavity inherent in the crystal lattice. A drastic reduction in the concentration of O_2^- on anion substitution and on heating under an oxygen-free atmosphere strongly suggests that the occurrence of O_2^- is closely related with "free oxygen", which is a unique characteristic of the $12CaO\cdot 7Al_2O_3$ crystal. Such characteristics found for $12CaO\cdot 7Al_2O_3$ are analogous to those for ultramarine, $Na_8[Si_6Al_6O_{24}]S_2$.

Introduction

The superoxide radical ion O_2^- is of importance as an active species of oxygen in the oxidation reactions of inorganic molecules as well as hydrocarbons.[1] Curiosity about the role of oxygen at surfaces led to extensive studies on O_2^- adsorbed on oxide surfaces being carried out as summarized in two thorough reviews.[1,2] In these studies, O_2^- formation is induced by irradiation of solid oxides in an atmosphere containing oxygen with energetic photons such as X- or γ-rays except for a few cases.[3,4]

In this paper the authors report that high concentration (4×10^{18} units/g) of O_2^- occurs as a guest of inherent structural cavity in crystalline $12CaO\cdot 7Al_2O_3$ prepared without the aid of irradiation by such energetic photons. A compound $12CaO\cdot 7Al_2O_3$, one of the crystalline phases in the system of CaO and Al_2O_3, is a major constituent in aluminous cements. It has attracted much attention from cement chemists and crystallographers because of its atmosphere-sensitive properties and structural characteristics.[5-9]

The physical properties such as density, refractive index, or unit cell volume vary with atmosphere in the preparation or in heat treatment. Because of reversible absorption of water over a wide temperature range without a major change of structure, $12CaO\cdot 7Al_2O_3$ is termed a zeolitic phase. The crystallographical

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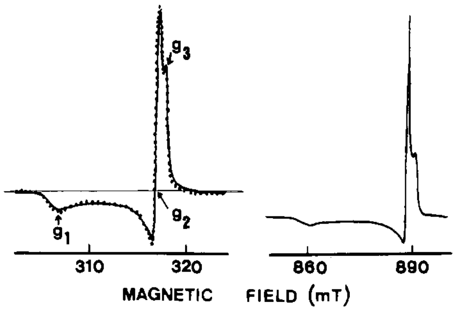

Figure 1. ESR spectra of crystalline $12CaO{\cdot}7Al_2O_3$ prepared by solid-state methods measured at 77 K: right, K-band (≅25 GHz); left, X-band (≅10 GHz). The dotted trace is a powder pattern generated by using the set of g values given in Table I.

data are[9] space group $I\bar{4}3d$, $a = 11.989$ Å, and two formula units in the unit cell. The most characteristic feature in the crystal structure is the presence of two oxygens in the unit cell, which statistically occupy $^2/_{24}$ths of the O_3 sites. These are often called "free oxygens" or "excess oxygens".

Experimental Section

Polycrystalline $12CaO{\cdot}7Al_2O_3$ was prepared by two methods, a solid-state reaction between $CaCO_3$ and $Al(OH)_3$ or Al_2O_3 and a slow-cooling method using a melt with the composition $CaO/Al_2O_3 = 12/7$. No significant difference was observed between the specimens prepared by these two methods. Highly pure chemicals (paramagnetic impurities less than 3 ppm) were used as starting materials in order to reduce the interference from contaminant paramagnetic transition-metal cations in the ESR spectra measured. In the preparation by the former method, mixtures of the two chemicals in a given ratio were heated up to 1200 °C in Pt crucibles by using an electric furnace and held for 48 h with a crush of the resulting agglomerate intervening after 24 h, and the crucible was rapidly removed from the furnace to prevent hydration of the product.[7] In the latter method, polycrystalline $12CaO{\cdot}7Al_2O_3$ was obtained by a slow cooling (ca. 100 K/h) of the melt with composition $CaO/Al_2O_3 = 12/7$. All the procedures stated above were, unless otherwise noted, made in the ambient atmosphere. The products were confirmed to be entirely composed of $12CaO{\cdot}7Al_2O_3$ by a powder X-ray diffraction (Cu Kα) method. Glasses with the composition $12CaO{\cdot}7Al_2O_3$ were prepared by a melt-quenching method; polycrystalline $12CaO{\cdot}7Al_2O_3$ was melted in a high-purity alumina crucible at 1450 °C for 5 min to 5 h. The melt was quenched into the glass by two techniques. One is a conventional quenching; i.e., the melt was poured onto a stainless-steel plate and pressed with a carbon block. Another is a rapid-quenching technique using a twin-roller quenching device.[10] The quenching rates in the former and the latter are estimated to be on the order of 10^2 and 10^5 K/s, respectively.

ESR spectra were measured for solid-state-prepared polycrystalline or vitreous $12CaO{\cdot}7Al_2O_3$ at X- and K-band frequencies by applying 100-kHz field modulation. The magnetic field was calibrated with a proton resonance marker. The measurement temperature was varied in the range 77–500 K by employing a Dewar vessel and a variable-temperature attachment. The spin concentration was evaluated by a comparison method[11] using $CuSO_4{\cdot}5H_2O$ as a standard.

Table I. **g** Tensor Data for the ESR Signal Observed in Crystalline $12CaO{\cdot}7Al_2O_3$ and for Oxygen-Associated Radical Species Adsorbed on Oxide Surfaces in the Literature[1,2,16]

species[a]	oxides	g: g_1	g: g_2	g: g_3
	crystalline	2.071^b	2.008^b	2.002^b
	$12CaO{\cdot}7Al_2O_3$	2.071^c	2.008^c	2.002^c
O^-	ZnO	2.002	2.021	2.021
	MgO	2.001	2.042	2.042
O_2^-	ZnO	2.052	2.009	2.002
	MgO	2.077	2.007	2.001
	CaO	2.093	2.006	2.000
O_3^-	MgO	2.017	2.010	2.001

[a] Signal observed at 77 K. [b] X-Band. [c] K-Band.

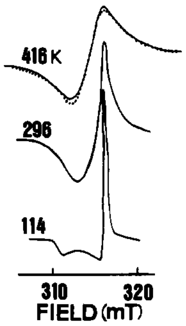

Figure 2. Variation in ESR line shape (X-band) of O_2^- in crystalline $12CaO{\cdot}7Al_2O_3$. The shape change is completely reversible within the range examined (77–500 K). For each recording the spectrometer gain was appropriately adjusted. A simple derivative Lorenzian function is indicated by the dotted line.

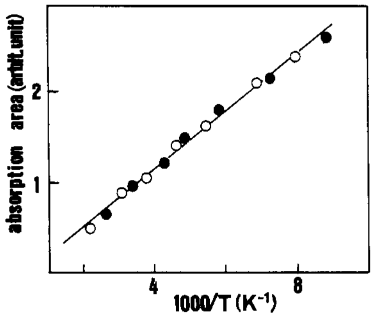

Figure 3. Relationship between ESR absorption area and the reciprocal of absolute temperature: (○) measured by raising the temperature; (●) measured by lowering the temperature. The area was evaluated by integrating the first-derivative spectrum two times.

Results and Discussion

An intense ESR signal with asymmetric shape is observed in polycrystalline $12CaO{\cdot}7Al_2O_3$ prepared by solid-state methods. Figure 1 is the ESR line shape observed at 77 K. No significant change in the intensity and shape were seen upon when a specimen prepared by solid-state methods was allowed to stand at ambient temperature in air. The spin concentration was evaluated to be ca. 4×10^{18} units/g and its scatter was rather small (<10%) for each run under the conditions described. The line shape is completely controlled by the g tensor (**g**) because an excellent agreement of the g values at three singular fields in Table I is seen between the X- and K-band spectra. The shape can be simulated by a simple powder pattern[12] employing the principal values of orthorhombic **g** listed in Table I. Here, the chemical species responsible for the ESR signal will be considered on the basis of the g values. The paramagnetic species may be limited to oxygen-associated ones judging from the absence of hyperfine structures[13,14] due to an ^{27}Al nucleus (natural abundance 100%; $I = {}^5/_2$) and extremely high thermal stability as will be described in the following. Three possible candidates, O^- (oxide radical ion), O_2^- (superoxide radical ion), O_3^- (ozonide radical ion), are anticipated and the typical g values[1,2] of each radical adsorbed on the surfaces of oxides are listed in Table I. From the close agreement of the set of g values obtained here with those in the literature, especially from a characteristic g_1 that is far from 2.00, the signal observed is attributed to superoxide radical ion O_2^-.

When the measurement temperature is raised, the ESR line shape of O_2^- drastically changes as shown in Figure 2. The anisotropy monotonically decreases, and the shapes beyond 140 °C can be almost reproduced by a simple Lorenzian function as in a less viscous liquid. In temperature range examined (77–500 K), the shape change is completely reversible and the concentration of O_2^- remains constant because the plots (Figure 3) of the ab-

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Table II. Concentration of O_2^- in Anion-Substituted Derivatives of Crystalline $12CaO{\cdot}7Al_2O_3$

specimen	modifcn of lattice const, Å	O_2^- concn, units/g
$12CaO{\cdot}7Al_2O_3$ ($C_{12}A_7$)	(±0)	4×10^{18}
F-subst $C_{12}A_7$	−0.017	5×10^{16}
Cl-subst $C_{12}A_7$	+0.026	3×10^{16}
OH-subst $C_{12}A_7$[a]	−0.008	3×10^{17}

[a] The concentration recovers up to the level in $C_{12}A_7$ prepared by solid-state methods when the derivative is heated at temperatures higher than 1200 °C for 1 h in air.

sorption area vs. the reciprocal of measurement temperature in kelvin fall on a straight line as expected from the Boltzmann law.[15] The partial or complete averaging of the anisotropic component (g_{an}) of **g**, which results in the decrease of g_{an}, is generally observed in liquid media.[11,15] Although the host of O_2^- in this study is solid, the line shapes observed at temperatures higher near 77 K are liquidlike. Here, the structural origin responsible for such unusual behaviors will be considered on the basis of this pronounced line shape change and the crystal structure of $12CaO{\cdot}7Al_2O_3$. The crystal has two structural characteristics.[9] One is the presence of large structural cavities like sodalite in the three-dimensional-connected network, which is entirely composed of tetrahedral AlO_4. Another characteristic is the presence of the peculiar oxygens that are called "excess oxygens" or "free oxygens" by cement chemists.[5-8] These oxygens (two per unit cell) are not bound to Al, but are coordinated by Ca, and are disordered over 24 equivalent positions in the unit cell. Little information has been obtained so far about either the physical or the chemical state. The liquidlike line shape generally originates from the fairly rapid tumbling motion of a paramagnetic center; i.e., the correlation time of the motion is comparable to or shorter than the ESR time scale.[11,15] It may be concluded from such a less restricted motional state of O_2^- that O_2^- found here is included in the structural cavity inherent to the crystal structure. The presence of O_2^- is limited to $12CaO{\cdot}7Al_2O_3$ in the crystalline phases of the $CaO{-}Al_2O_3$ system. No ESR signal is detected for CaO, $3CaO{\cdot}Al_2O_3$, $CaO{\cdot}Al_2O_3$, $CaO{\cdot}2Al_2O_3$, and Al_2O_3. For instance, no signal is observable for the product prepared in an oxygen-free atmosphere, such as under a dry oxygen-free N_2 flow, because the resultant is a mixture of $3CaO{\cdot}Al_2O_3$ and $CaO{\cdot}Al_2O_3$ instead of $12CaO{\cdot}7Al_2O_3$.[6] A close relation is, therefore, suggested between the occurrence of O_2^- and the occurrence of "excess oxygens" in $12CaO{\cdot}7Al_2O_3$ crystal. This can be experimentally verified by examining the anion-substituted derivatives of $12CaO{\cdot}7Al_2O_3$; i.e., the "excess oxygens" can be replaced by an appropriate anion (X) such as F^-, Cl^-, or OH^- ($[Ca_{24}Al_{28}O_{64}]O_2 \rightarrow [Ca_{24}Al_{28}O_{64}]X_4$). The preparation procedures were carried out by following those described in ref 7. The formation of each derivative was confirmed by referring the modification of the lattice constant from the mother crystal to that in ref 7. Table II summarizes the concentration of O_2^- in the derivatives together with the modification of the lattice constant. A sharp drop of the concentration on anion substitution is obvious for all derivatives. The remainder of O_2^- in each specimen may be attributed to the incompleteness of the substitution. The result suggests that a part of the "excess oxygens" is present as O_2^-. The number of oxygen atoms for observed O_2^- corresponds to 2% of the "excess oxygens" in $12CaO{\cdot}7Al_2O_3$.

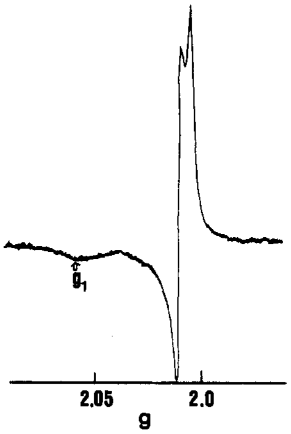

Figure 4. X-Band ESR spectrum for quenched glass with the composition of $12CaO{\cdot}7Al_2O_3$. The arrow denotes the characteristic shoulder of O_2^- in solids. A pronounced broadening appearing in the shoulder originates from the distribution of the g_1 value, which, in turn, reflects the "site-to-site fluctuation" in amorphous solids.[17]

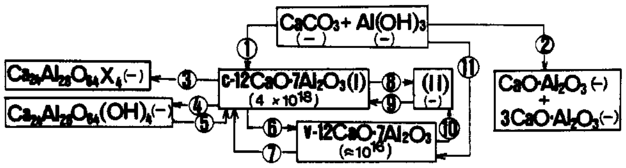

Figure 5. Preparations and reactions of $12CaO{\cdot}7Al_2O_3$ and the concentration of O_2^- in some of these reactions. Numbers parentheses are the concentration of O_2^- in each host (− means that no ESR signal was detected in the specimen). Procedures are described as follows: (1) heating at >1000 °C in air; (2) heating at >1000 °C in a dry and oxygen-free atmosphere; (3) substitution of "excess oxygen" by halogen ion (F^- or Cl^-); (4) hydration (heating at 900 °C under ambient atmosphere); (5) dehydration (heating at >1100 °C in air); (6) melting in air and quenching; (7) crystallization in air; (8) heating at >1100 °C in vacuo; (9) heating at >1100 °C in air; (10) crystallization in vacuo; (11) melting in air and quenching.

The ESR signal (Figure 4) of O_2^- was observed in the quenched glass (abbreviated as v-$12CaO{\cdot}7Al_2O_3$) with the composition $12CaO{\cdot}7Al_2O_3$. The concentration was ca. 10^{16} units/g, and almost independent of melting time in the range examined (5 min to 5 h) and quenching rate (10^2–10^5 K/s) from the melt. These results suggest that such an order of O_2^- is a thermodynamic equilibrium concentration in the melt under these conditions. So far the occurrence of O_2^- has been reported only for irradiated SiO_2 glass of all the oxide glasses studied.[2,17,18] This fact is novel because in general oxide glasses prepared that are composed of diamagnetic components give no ESR signal except that due to paramagnetic transition-metal ions of an impurity such as Fe^{3+}. The line shape of O_2^- in the glass will be compared with that in the crystal. It is obvious from the figure that the line shape is solidlike. This indicates that the motional state of O_2^- is severely restricted in the glass. One can understand this distinct difference from an unusual fact that the density (2.93 g/cm^3, measured by Archimedian method) of the glass is 8% greater than that (2.69 g/cm^3)[9] of the corresponding crystal. Most of the structural cavities in the crystal are considered to be destroyed on melting, which results in a densely packed surrounding for O_2^-. Conversely, crystalline $12CaO{\cdot}7Al_2O_3$ precipitates by the crystallization of the glass (heating at 1000 °C for 24 h). In this case, a distinct difference was observed in the concentration of O_2^- included in the crystal depending on atmosphere in crystallization; the concentration for the specimen (abbreviated as c-$12CaO{\cdot}7Al_2O_3$ (I)) crystallized in air is almost the same as that prepared by the solid state reaction in air. On the other hand, the concentration in the specimen II, which crystallized in vacuo, is drastically reduced to such an extent that the ESR signal is beyond detection. This c-$12CaO{\cdot}7Al_2O_3$ (II) is unable to be prepared directly by a solid-state reaction. The conversion between I and II was found to be reversible by heating at >1100 °C in air or in vacuo. Figure 5 summarizes the preparations and reactions of $12CaO{\cdot}7Al_2O_3$, and the concentration of O_2^- in various hosts stated in this paper.

Recently dopant-free calcium aluminate glasses have been found to show two unique properties, an excellent photosensitivity to

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ultraviolet rays[19] and a marked thermal oxygen effervescency.[20] From these unusual facts and a new finding reported here, the authors imagine that certain structural defects associated with oxygen are present in calcium aluminate glasses and these are closely related with the abnormal characteristics of crystalline $12CaO\cdot7Al_2O_3$.

Finally the authors will point out a close similarity between $12CaO\cdot7Al_2O_3$ and ultramarine, which is known as a pigment.[21] Ultramarine has an idealized formula, $Na_8[Si_6Al_6O_{24}]S_2$, and its structure is composed of sodalite unit in which various kinds of sulfur-related species such as S_2^- or S_3^- are included.[21,22] The sulfur-related species are also replaced by an appropriate anion (e.g. Cl^- or SO_4^{2-})[22]. These characteristics are entirely analogous to those of $12CaO\cdot7Al_2O_3$. A marked difference in apparent color is simply due to that in including radical species, i.e., O_2^- ($\lambda_{max} \cong 250$ nm),[23] S_2^- (≅400),[21] or S_3^- (≅620).[21] Ultramarine is also known as an effective catalyst for a variety of reactions, e.g., dehydrogenation, dehydration, and hydrodesulfurization, and its activity is assumed to be due to the presence of sulfur-related paramagnetic species.[24,25] An analogous catalytic activity may be, therefore, expected for $12CaO\cdot7Al_2O_3$ including the superoxide radical ion O_2^-.

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Kinetics and Mechanism of the Autocatalytic Reaction between Iodine and Chlorite Ion†

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The kinetics of oxidation of iodine by chlorite is much more complicated than previously found. The rate exhibits a minimum as a function of hydrogen ion concentration, the reaction being characteristically autocatalytic, mainly due to the fact that oxidation of iodine is even faster by hypochlorous acid and chlorine. An important feature of the reaction is the acceleration of the disproportionation of chlorite by the intermediates of the title reaction, leading to the formation of a significant amount of chlorine dioxide. The rate cannot be described by an overall equation, but all the findings can be quantitatively explained by a mechanism consisting of 13 elementary or quasi-elementary steps. The stoichiometry of the reaction is kinetically controlled. Formation and reactions of Cl_2O_2 seem to play a crucial role in the reaction and in other reactions involving chlorite.

Introduction

Recently a number of most unusual and interesting phenomena were observed in the reaction between chlorite and iodide ions. Under certain conditions the concentration of iodine exhibits two extrema, while in CSTR bistability and oscillatory behavior were found.[1] The reaction consists of three parts, which under certain conditions are distinctly separated. First, in a relatively slow autocatalytic reaction, iodide is oxidized into iodine, which is then oxidized in a fast reaction into iodine chloride. The hydrolytic disproportionation of iodine chloride leading to the partial regeneration of iodine is the third stage of the reaction.[2] The kinetics of the second reaction, by far the fastest reaction, has been studied by Grant et al.[3] However, their experiments were made in a rather narrow pH range, and the CSTR studies have been performed at much higher acidity than the experiments of the mechanistic study. Our experiments revealed that in acidic solution the oxidation of iodine by chlorite is autocatalytic, taking into consideration the acceleration of disproportionation of chlorite ion leading to the formation of chlorine dioxide, and that the stoichiometry of the reaction strongly depends on the ratio of the reactants and on the reaction conditions. Since the reduction of chlorite into chloride ion obviously takes place in several steps, to elucidate the kinetics of the title reaction it is a rerequisite to study the hypochlorous acid–iodine and the chlorine–iodine systems. The detailed kinetic studies made it possible to give a quantitative account of all the experimental findings.

Experimental Section

Commercial grade $NaClO_2$ was recrystallized from water. Freshly prepared 0.10 M sodium chlorite stock solutions contained 0.001 M sodium hydroxide to maintain an alkaline pH, which retards decomposition.

Iodine monochloride was made by treating iodine with condensed chlorine according to the method of Cornog and Karges.[4] A 0.1 M ICl stock solution was prepared in 10 M $HClO_4$.

Chlorine monoxide dissolved in carbon tetrachloride was prepared by bubbling chlorine into a slurry of dry carbon tetrachloride and mercuric oxide. Stock solutions of HOCl were prepared by shaking the cold chlorine monoxide solution with cold aqueous solutions of 0.02 M perchloric acid. Concentrations of HOCl were determined by iodometric titration.

Stoichiometric and kinetic experiments were carried out with reaction mixtures buffered at pH ranging from 1.83 to 3.7. H_3PO_4–KH_2PO_4 buffer (0.2 M) was added into iodine stock solutions. Due to mixing, the final buffer concentration was 0.1 M in the reaction mixture. Measurements of pH were made, after mixing, with a Radelkis pH meter. In the case of some kinetic experiments the hydrogen ion concentrations were adjusted with $HClO_4$.

For rapid mixing a homemade stopped-flow apparatus, the mixing time of which is about 5 ms, was used. The reservoirs, the pushing syringes, and the 0.2-cm cell were thermostated to 25.0 °C. A Hitachi 193 spectrophotometer and storage oscilloscope were used for monitoring each change in absorbance at 460 nm ($\epsilon_{I_2} = 740\ cm^{-1}\ M^{-1}$) and 360 nm ($\epsilon_{ClO_2} = 1050\ cm^{-1}\ M^{-1}$).

Results and Discussion

Stoichiometry. In an excess of chlorite, iodine is quantitatively oxidized into iodate. According to Grant et al.[3] the stoichiometry is given by eq I. However, in acidic solutions the fate of chlorite

$$5ClO_2^- + 2I_2 + 2H_2O = 5Cl^- + 4IO_3^- + 4H^+ \qquad (I)$$

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† Dedicated to Professor Viktor Gutmann on the occasion of his 65th birthday.

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