and

$$Z^{\gamma} = \sum_{u=0}^{\gamma}\sum_{v=0}^{u} \frac{\gamma!}{(\gamma-u)!v!(u-v)!}[-2\xi\eta\cos\alpha]^{\gamma-u} \times [-2\xi\eta\sin\alpha]^{u-v}[\xi^2-\eta^2]^{v}X_0^{\gamma-u}Y_0^{u-v}Z_0^{v}$$

It is perhaps worth mentioning that a FORTRAN program to evaluate one- and two-center moment integrals of the type

$$\langle\psi_{\text{I}}|X^{\alpha}Y^{\beta}Z^{\gamma}|\psi_{\text{II}}\rangle$$

has been coded by the author and can be obtained from the Quantum Chemistry Program Exchange of Indiana University.

CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY, PROVIDENCE, RHODE ISLAND 02912

The Nucleophilic Reactivity of Chlorite Ion as Indicated by Its Reaction Rate with Peroxymonosulfuric Acid[1]

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In a survey of nucleophilic substitution reactions, Edwards and Pearson[2] have shown that the reactivities of nucleophiles can be related to three properties: basicity, polarizability, and an effect not completely understood called the "α effect." Basicity of the nucleophile is the important property when the substrate atom is like a proton, *i.e.*, when it has a localized positive charge and few valence electrons. Polarizability predominates when the substrate atom is electronegative and has a number of outer-orbital electrons. Some nucleophiles are more reactive than expected from their polarizability and basicity. These electron donors, which are said to exhibit the "α effect," are characterized by the presence of one or more unshared pairs of electrons on an electronegative atom adjacent to the nucleophile atom.

The chlorite ion, ClO_2^-, with unshared electrons on the chlorine and oxygen atoms, might be expected to exhibit the "α effect" when acting as a nucleophile and in fact there has been some evidence of high reactivity. It is an intermediate in the two-step disproportionation of hypochlorite

$$ClO^- + ClO^- \longrightarrow ClO_2^- + Cl^-$$
$$ClO^- + ClO_2^- \longrightarrow ClO_3^- + Cl^-$$

The reaction between ClO_2^- and ClO^- is 100 times faster than the first step in the disproportionation.[3] Owing to a common dependence on donation of electrons, nucleophilicity and ability to form complexes often follow parallel orders.[4,5] Gordon and Kern observed that ClO_2^- forms a complex with uranyl ion.[6] The present study was begun to obtain quantitative data on the nucleophilic reactivity of ClO_2^-.

Experimental Section

Reagents.—Laboratory distilled water and reagent grade chemicals were used in all cases. Peroxymonosulfuric acid (Caro's acid) was prepared using Becco 98% H_2O_2 and practical grade HSO_3Cl. The procedure was that of Fortnum.[7] Peroxyacetic acid solutions were prepared by diluting Becco 40% peroxyacetic acid with appropriate buffers.

Analytical Methods.—The peroxy acids were analyzed in the presence of hydrogen peroxide by the method of Greenspan and MacKellar.[8] A 10.0-ml sample of the peroxy acid solution was placed in 150 ml of 5% H_2SO_4 cooled to 0°. Ceric sulfate with ferroin indicator was used to analyze for H_2O_2. Then 5 ml of 20% KI was added and the liberated iodine was titrated with thiosulfate and starch indicator to determine the peroxy acid concentration.

Stoichiometry.—A paper chromatography method[9] was used to analyze for the various species of chlorine. Strips (3 × 20 cm) of Whatman No. 1 filter paper were used. Development time was approximately 10 hr in a 15:2:2:2 mixture of 2-propanol, water, pyridine, and concentrated ammonium hydroxide. Chloride was revealed as a purple spot at R_f 0.25 by spraying with 0.2 N aqueous $AgNO_3$, drying, and exposing to ultraviolet light for 2 min. When the strip was sprayed with equal parts of a 1:1 mixture of 3 M hydrochloric acid–acetone and 5% ethanolic diphenylamine, ClO_2^- was immediately revealed as a blue-green spot at R_f 0.36. After drying, chlorate appeared as a yellow spot at R_f 0.54. (Hypochlorite ion could not be detected in the presence of peroxy acids because both ClO^- and the peroxy acids oxidize I^- with similar rates.) To facilitate comparison of relative concentration of the oxy anion species, solutions of known initial concentrations were applied to the paper using calibrated capillary tubes.

Kinetics.—The peroxy acid was diluted with cold water and KH_2PO_4 buffer was added. Owing to the acid impurity, 1.0 M NaOH was added to bring the pH within the 4.5–7.0 range. The chlorite solution was prepared by dissolving the appropriate weight of $NaClO_2$ in water. The reaction was followed using a Beckman DK-1 spectrophotometer at 260 mμ, the absorption peak of chlorite (ϵ_{260} 176).

Results

Stoichiometry.—The observed stoichiometry was found to be

$$HSO_5^- + ClO_2^- \longrightarrow ClO_3^- + SO_4^{2-} + H^+$$

The pH was kept above 4.6 to minimize decomposition of ClO_2^- and below 7.0 to minimize decomposition of HSO_5^-. Within this pH range and when peroxide was in excess, the absorbance at "infinite time" was that expected for loss of nearly all ClO_2^- and a small fraction of HSO_5^-. The chromatography results showed that the ClO_2^- concentration decreased as the ClO_3^- concentration increased. Also the Cl^- spot was absent or barely detectable. No evidence for ClO^- was found in the ultraviolet spectra.

In the chosen pH range, Caro's acid is present as the mononegative anion[10] and ClO_2^- is the predominant form of the reductant.

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[1] Taken from the Sc.B. Thesis of R. W. J. at Brown University, 1966.

[2] J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).

[3] M. W. Lister, *Can. J. Chem.*, **34**, 465 (1956).

[4] J. O. Edwards, *J. Am. Chem. Soc.*, **76**, 1540 (1954).

[5] R. G. Pearson, *ibid.*, **85**, 3533 (1963).

[6] G. Gordon and D. M. H. Kern, *Inorg. Chem.*, **3**, 1055 (1964).

[7] D. Fortnum, Ph.D. Thesis, Brown University, 1958, p 47.

[8] F. P. Greenspan and D. G. MacKellar, *Anal. Chem.*, **20**, 1061 (1948).

[9] B. L. Harrison and D. H. Rosenblatt, *J. Chromatog.*, **13**, 271 (1964).

[10] D. L. Ball and J. O. Edwards, *J. Am. Chem. Soc.*, **78**, 1125 (1956).

Kinetics.—Initial experiments indicated that the reaction is first order each in the reactant concentrations. Before confirming this (*vide infra*), the dependence of rate on pH was checked; some results are presented in part A of Table I. Over a 300-fold range of hydrogen ion concentration (from pH 4.58 to 7.02), the second-order rate constant defined by the law

$$-\frac{d[ClO_2^-]}{dt} = k_2[HSO_5^-][ClO_2^-]$$

is independent of pH. In those runs wherein HSO_5^- was in large excess, good first-order plots (to 80% reaction) for ClO_2^- were obtained. In part B of Table I, data on experiments with variable reactant concentrations are presented. These data, plus those from part A, indicate that over a range of concentrations the second-order constant as defined above is appropriate.

TABLE I

DEPENDENCE OF RATE CONSTANT ON CONCENTRATIONS[a]

pH	$[HSO_5^-]_0$, $M \times 10^3$	$[ClO_2^-]_0$, $M \times 10^3$	10^2k_2[b]
A. Influence of pH			
4.58	9.10	3.33	1.78
4.84	9.10	3.33	1.78
5.34	9.10	3.33	2.83
5.35	9.10	3.33	2.09
6.43	9.10	3.33	2.40
6.90	9.10	3.33	1.95
7.02	9.10	3.33	1.97
B. Influence of Reactant Concentrations			
4.67	3.10	1.67	2.35
5.15	1.83	1.17	2.24
5.15	1.92	1.93	2.55
4.15	3.77	2.42	2.00
4.59	3.51	1.00	2.71

[a] At 30.0° and $\mu = 0.8$. [b] Units are M^{-1} sec^{-1}.

In part A of Table II, rate constants as a function of ionic strength are presented. As expected for a reaction with two mononegative ions in the rate law, the constant increased with ionic strength.

In part B of Table II, three experiments at 21.0° and two at 39.0° are presented. From these data, an activation energy of 16.1 kcal mole^{-1} and an entropy of activation of -15 cal mole^{-1} deg^{-1} were obtained.

For comparative purposes several runs were made with peroxyacetic acid. An analogous stoichiometry was observed. With peroxide in excess, the plots for log $[ClO_2^-]$ against time were linear indicating first-order behavior. Part A of Table III shows that the reaction is also first order in peroxyacetic acid and part B shows the expected rate independence of pH and ionic strength. At 41.5°, the average rate constant is 3.3×10^{-3} which is one-twelfth as fast as the rate with HSO_5^-.

TABLE II

INFLUENCE OF VARIABLES ON RATE CONSTANT

A. Ionic Strength[a]

$[HSO_5^-]_0$, $M \times 10^2$	$[ClO_2^-]_0$, $M \times 10^3$	μ	10^2k_2[c]
1.80	1.67	0.23	1.16
1.80	1.00	0.40	1.67
1.80	1.00	0.56	1.80
1.80	1.00	0.90	2.77
1.80	1.00	1.23	2.73

B. Temperature[b]

$[HSO_5^-]_0$, $M \times 10^2$	$[ClO_2^-]_0$, $M \times 10^3$	T, °C	10^3k_2[c]
1.94	1.00	21.0	7.43
1.94	1.00	21.0	8.76
1.94	1.00	21.0	9.08
1.69	0.80	39.0	41.7
1.62	0.80	39.0	43.3

[a] Added salt was $NaClO_4$, pH 6.3 ± 0.3; 25.0°. [b] $\mu = 0.4$; pH 4.5–5.7. [c] Units are M^{-1} sec^{-1}.

TABLE III

KINETIC RESULTS FOR CHLORITE ION AND PEROXYACETIC ACID

$[AcOOH]_0$, $M \times 10^2$	$[ClO_2^-]_0$, $M \times 10^3$	pH	10^3k_2[a]	μ
A. Peroxyactic Acid Order Determination, $T = 50.0°$				
2.12	1.67	5.7	10.5	0.04
3.12	1.67	5.7	9.22	0.06
4.32	1.67	5.7	9.91	0.08
1.57	1.67	5.7	9.68	0.03
B. pH and Ionic Strength Dependence, $T = 41.5°$				
2.90	1.67	4.6	3.29	0.03
4.08	1.67	5.1	3.02	0.05
3.92	1.67	5.9	3.93	0.06
3.92	1.67	5.4	2.82	0.73

[a] Units are M^{-1} sec^{-1}.

Discussion

The stoichiometry, rate law, low energy and entropy of activation, and relative rates with the two peroxides are analogous to data[11,12] for systems involving nucleophilic attack on peroxide oxygen. The postulated mechanism is therefore nucleophilic attack by chlorine (in chlorite) on the outer peroxide oxygen

$$HSO_5^- + ClO_2^- \xrightarrow{k_2} SO_4^{2-} + HOClO_2 \qquad \text{slow}$$

$$HOClO_2 \longrightarrow H^+ + ClO_3^- \qquad \text{fast}$$

The rate constant for reaction of Cl^- with HSO_5^- at 25.0° is only 1.8×10^{-3} M^{-1} sec^{-1}. Therefore, ClO_2^- is a better nucleophile toward oxygen than Cl^-, even though the chlorine in chlorite is in a higher oxidation state. We conclude that ClO_2^- is another example of a nucleophile that gains reactivity due to the unshared pairs of electrons on the α atom. An interesting analogy to our system is the nitrite–ammonia system. Nitrite (oxidation state +3) is more reactive than ammonia (oxidation state −3) in nucleophilic attack on oxygen.[11,12]

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