

Lawrence Berkeley National Laboratory

Recent Work

Title

Rates of Reaction of Ozone with Sulfite, Iodide, and Nitrite Ions in Aqueous Solution

Permalink

<https://escholarship.org/uc/item/5pd17163>

Author

Littlejohn, D.

Publication Date

1990-03-01



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

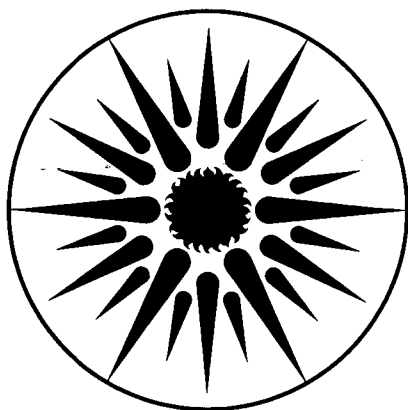
ENERGY & ENVIRONMENT DIVISION

To be submitted for publication

Rates of Reaction of Ozone with Sulfite, Iodide, and Nitrite Ions in Aqueous Solution

D. Littlejohn

June 1994



ENERGY & ENVIRONMENT
DIVISION

LOAN COPY
Circulates
for 4 weeks
Bldg. 50 Library.
Copy 2

LBL-29791

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Rates of Reaction of Ozone with Sulfite, Iodide,
and Nitrite Ions in Aqueous Solution

David Littlejohn

Lawrence Berkeley Laboratory
Energy and Environment Division
Berkeley, California 94720

June, 1994

This work was supported by the Assistant Secretary for Fossil Energy, Office of Coal Utilization Systems, U.S. Department of Energy under Contract No. DE-AC03-76SF00098 through the Pittsburgh Energy Technology Center, Pittsburgh, PA

Abstract

The reaction of dissolved ozone with iodide, nitrite, and sulfite ions was studied using stopped-flow and pulsed-accelerated-flow techniques. The rate expressions and rate constants at 25°C are:

$$-d[\text{O}_3]/dt = k_7 [\text{O}_3] [\text{I}^-] \quad 4 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1} < k_7 < 7 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1} \quad \text{pH 4.5 - 5} \quad \mu = 1 \times 10^{-3} \text{ M}$$

$$-d[\text{O}_3]/dt = k_{11} [\text{O}_3] [\text{NO}_2^-] \quad k_{11} = 3.0 \pm 0.2 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1} \quad \text{pH 6.0 - 9.9} \quad 7 \times 10^{-3} < \mu < 2.9 \times 10^{-2} \text{ M}$$

$$-d[\text{O}_3]/dt = k_{17} [\text{O}_3] [\text{SO}_3^{2-}] \quad k_{17} = 7.5 \pm 1.8 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1} \quad \text{pH 4.1 to 9.3} \quad 2 \times 10^{-3} < \mu < 4.5 \times 10^{-1} \text{ M}$$

The ozone-sulfite reaction appears to proceed primarily by a direct reaction to form sulfate. This may not be the case under very acidic and very basic conditions where free radical intermediates could influence the reaction. The ozone-iodide reaction occurs very quickly and forms I_2 as a product, presumably via an IO^- intermediate. No enhancement of the ozone-nitrite reaction, due to radical production by the hydroxide-ozone reaction, was observed at high pH (9.9) conditions. Ozone reactions, with rate constants (k) varying over eleven orders of magnitude, show a linear dependence on the nucleophilicity (n) of the reacting anions. The slope of $\log k$ versus n was found to be approximately 6.2.

Introduction

The reaction of aqueous ozone with a number of inorganic anions is quite rapid. The ozone-iodide reaction has not been measured because it is too fast for conventional kinetic techniques. The only estimate of the ozone-iodide reaction was obtained from observations of ozone loss from the gas phase when exposed to seawater and iodide solutions.¹ A determination of the rate constant for the ozone-iodide reaction in a more direct manner is desirable. Also, the ozone-nitrite reaction has only been studied at $\text{pH} \leq 5$.¹ It was decided to extend the range of study to alkaline conditions to ensure that free radical processes at high pH conditions did not influence the rate. A number of kinetic studies have been done on the ozone-S(IV) (where S(IV) represents $\text{SO}_2(\text{aq})$, HSO_3^- , and SO_3^{2-} collectively) system. Results from low pH studies (pH 2-4) had been extrapolated to higher pH conditions in order to obtain an estimate of the rate constant at conditions where SO_3^{2-} predominates, since the rate has been found to be too rapid to measure directly until recently. Since the studies to date have been done only under acidic conditions, the reaction behavior under alkaline conditions has not been definitely established.

Penkett and co-workers¹⁻³ have reported the kinetics of the ozone-hydrogen sulfite reaction in several studies, along with reactions of ozone with other anions. A stopped-flow system was used to study the reactions. The rate of the ozone-S(IV) reaction was found to increase with pH and fractional hydrogen ion dependence was observed. The possibility that

ozone reacted with sulfite and hydrogen sulfite ions with differing rates was not discussed. In addition to the ozone-S(IV) reaction, reactions of nitrite, ammonia, and bromide with ozone were studied with a stopped flow system. The rate constants are listed in Table I. The ozone-iodide reaction was too fast to be measured by the stopped-flow method.

Another ozone-S(IV) reaction study was done by Larson et al⁴ by bubbling an ozone-oxygen mixture through a S(IV) solution and measuring the concentration of S(IV) with time. Solution pH values of 4.0 to 6.2 were used. They concluded that the values of the ozone-S(IV) rate that they observed were in reasonable agreement with the results obtained by Penkett.¹ However, they did not observe a significant pH dependence on the rate. Their value for the ozone-S(IV) rate constant is also listed in Table I.

Erickson and co-workers⁵ studied the reaction of ozone-aqueous SO₂ over a pH range of <1 to 4. They reasoned that the O₃-SO₃²⁻ reaction was much faster than the O₃-HSO₃⁻ reaction and used this assumption in their data analysis. They made measurements at 16° and 25°C and obtained an estimate of the activation energies. The rate constants that they obtained are listed in Table I.

Maahs⁶ made stopped-flow measurements of the ozone-S(IV) reaction over a range of pH 3.1 to 6.2. Maahs indicated that his results were consistent with those obtained by Erickson et al.⁵ Rather than attributing the increase in rate with pH to the O₃-SO₃²⁻ reaction, he indicated that the observed pH dependence could be due to hydroxide ion-initiated decomposition of ozone to form the hydroxyl radical. Formation of such an intermediate could cause more than one oxygen atom to be transferred from ozone to sulfate, as observed by Espenson and Taube.⁷ He stated that kinetic data alone would be insufficient to discriminate between the two potential processes. Analysis of the data presented in Maahs' Figure 1 indicates that Maahs obtained rates that were about 50% of those from Erickson's study at pH ≥ 4.

Hoigne et al⁸ used the indigo method⁹ to determine the reaction rates for ozone with a number of compounds, including S(IV) and nitrite. The ozone-S(IV) reaction was studied over a pH range of 1 to 5.3. The data were analyzed assuming that ozone reacts increasingly rapidly as the S(IV) is deprotonated. The rate constants they obtained for the S(IV) species and some of the other compounds studied are listed in Table I. The value of the rate constant they obtain for the reaction of ozone-sulfite is intermediate between the values obtained by Erickson⁵ and Garland.¹ The ozone-nitrite reaction was studied over a pH range of 2 - 5. The rate constant derived was greater than that obtained by Penkett,² but agreed well with the study by Garland et al.³ Their results indicate that nitrous acid reacts much more slowly with ozone than does nitrite.

There is some uncertainty in the ozone-sulfite reaction rate because of the extrapolation from pH 3-5 to higher pH conditions. The reaction rate would be expected to level off at about

pH 8 if the process is a direct reaction between ozone and sulfite. If the reaction involved the ozone-hydroxide reaction, it would be expected to increase steadily as $[\text{OH}^-]$ increases. It is desirable to measure the ozone-S(IV) reaction at higher pH conditions where SO_3^- predominates. It would also be useful to know what process is responsible for the increase in rate with pH. These three reaction systems have been studied by stopped-flow and pulsed-accelerated-flow (PAF) techniques.¹⁰⁻¹² Use of the PAF system to study the ozone-S(IV) reaction provided a more direct measurement than the indigo method.

Experimental

Reagents. Buffer solutions of citrate, phosphate, and boric acid, for pH ranges of about 4, 7, and 9, respectively, were prepared by dissolving the analytical reagents in distilled deionized water. The nitrite and iodide solutions were prepared from NaNO_2 and NaI , respectively. The S(IV) solutions were prepared by degassing the buffer solution with Ar prior to addition of either $\text{Na}_2\text{S}_2\text{O}_5$ or Na_2SO_3 . The S(IV) solution was kept under Ar until it was transferred to the instrument syringe for use in rate measurement. The S(IV) concentration in solution was determined by iodimetry. Adjustment of the pH of the solution was done with HClO_4 or NaOH solutions. The pH measurements were made with an Orion 610A digital pH meter and a Corning combination electrode that had been previously calibrated with solutions of ionic strength similar to the solutions under study.

Raman spectra of the reaction mixtures were collected using a Coherent 90-5 argon-ion laser and a Spex 1403 spectrometer controlled by a Spex Datamate data acquisition system. UV-visible spectra of the solutions were taken with Varian Cary 219 and Perkin-Elmer Lambda 9 spectrophotometers.

Ozone was prepared by passing research grade oxygen through a coaxial ozonator tube powered by a luminous sign transformer (9kV, 30mA).¹³ Aqueous ozone solutions were prepared by passing the gas stream containing ozone through a glass frit immersed in the solution. The gas phase ozone concentration was adjusted by varying the oxygen flow rate through the ozonator. The aqueous ozone concentration was estimated from literature ozone solubility measurements¹⁴ and determined more accurately by UV absorption. An extinction coefficient of $3000 \text{ M}^{-1}\text{cm}^{-1}$ at 260 nm was used in the determination. Measurements of the extinction coefficient for aqueous ozone have been reviewed by Maahs.⁶ Since ozone decay rates in alkaline buffers were unacceptably high, ozone solutions for alkaline runs were prepared in unbuffered solutions with ionic strengths matching those in the S(IV) reactant solutions. In these cases, the ionic strength was adjusted using sodium chloride. Once the instruments were conditioned, ozone decay rates of less than 2% per minute were consistently obtained in the

reactant solution during the experiments. Sodium chloride was used to adjust the ionic strength of the S(IV) reactant when desired.

Citrate buffers were used with some of the S(IV) solutions used in stopped flow measurements of the ozone-S(IV) reaction. Citrate absorbs weakly at 260 nm ($\epsilon \sim 0.4$) and did not interfere with the absorption measurements. Hoigne and Bader^{14a} note that many organic carboxylic acids react with ozone. We found that citrate ion reacts slowly with ozone ($k \sim 5 \text{ M}^{-1} \text{ sec}^{-1}$) at pH > 7. As noted by Hoigne and Bader^{14a}, the dissociated carboxylic acids are more reactive than the acid form, so the effective rate constant at the conditions of our experiments (pH 4 - 5) would be less than the value listed here. The loss due to the ozone - citrate reaction was not significant at any of the conditions used.

Stopped-Flow Measurements. A Durrum D-110 stopped-flow spectrometer (1.88 cm cell path length) interfaced to a Zenith 151 PC with a MetraByte DASH-16 A/D was used for the ozone-nitrite measurements and the low pH (< 5.5) ozone-S(IV) measurements. Data from runs with large values of k_{obsd} (>60 sec^{-1}) were corrected for mixing using the equation¹⁵

$$1 / k_{\text{obsd}} = 1 / k_{\text{reaction}} + 1 / k_{\text{mix}} \quad (1)$$

where $k_{\text{mix}} = 1700 \text{ sec}^{-1}$ for the system used. The $\text{NO}_2\text{-O}_3$ reaction was studied under pseudo-first order conditions only.

Pulsed-Accelerated-Flow Measurements. To permit measurements of rates faster than those in the range of the stopped-flow technique, the pulsed-accelerated-flow (PAF) method was used.¹⁰⁻¹² PAF model IV was used in the UV mode for studies of ozone-iodide reaction and ozone-S(IV) reaction at pHs of 6.5 - 9.3. Both pseudo-first order conditions, with $[\text{X}^-] \gg [\text{O}_3]$, and second order conditions were used in the study of the S(IV)- O_3 reaction and the I- O_3 reaction. The technique is described in more detail elsewhere.¹⁰⁻¹² Briefly, absorbance measurements of the mixed reactants in the cell are taken while the flow velocity ramps from 12 to 3 m sec^{-1} . At these flow velocities, the mixed solutions have a transit time of 0.8 to 3.3 milliseconds through the PAF cell. The reaction progress variable $M(v)$ is derived from

$$M(v) = (A_v - A_\infty) / (A_0 - A_\infty) = (1 - e^{-y}) / y \quad (2)$$

where A_v is the absorbance at flow velocity v , A_∞ is the final absorbance of the reaction mixture, and A_0 is the initial absorbance of the reactants. Here y is defined as

$$y = (k_{\text{app}} b) / v \quad (3)$$

where b is the optical path length in m, v is the flow velocity in m sec^{-1} , and k_{app} is the apparent rate constant

$$1 / k_{\text{app}} = 1 / (k_{\text{mix}} v) + 1 / k_{\text{obsd}}, \quad (4)$$

which is dependent of the mixing rate constant (k_{mix}) and the reaction rate constant (k_{obsd}).

When $k_{\text{app}} > 5000 \text{ sec}^{-1}$, there is a linear dependence of $M(v)$ on v

$$M(v) = 1 / (b k_{\text{mix}}) + v / (b k_{\text{obsd}}) \quad (5)$$

Plotting $M(v)$ against v gives a slope of $1/(b k_{\text{obsd}})$, providing a value of k_{obsd} and its uncertainty for each run.

Absorbance changes at 260 nm due to the reaction of ozone were in the range of 0.06 - 0.16. All measurements were made at 25°C.

Results and Discussion

Ozone - Iodide Reaction

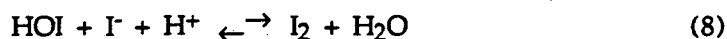
The reaction of ozone with iodide was using the PAF system to monitor the change in absorption at 260 nm. The reaction products shift the pH of the solution and the initial pH values of 4.8 and 4.5 were calculated from the measured final pH values of 6.4 and 8.0, respectively. The initial ozone concentration was 1.5×10^{-5} M in the pH 6.4 experiment and 3.4×10^{-5} M in the pH 8.0 experiment and the initial iodide concentration was 5×10^{-5} M in both experiments. The reaction mixtures were unbuffered and the measurements were made at 25°C. The reaction was too fast to measure at both conditions. We estimate that the second order rate constant is greater than $4 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$. Diffusion limits the rate constant to $7 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$. The estimate of the rate constant given by Garland et al,¹ 2×10^9 , is significantly less than the estimate that we have obtained. As mentioned by Hoigne et al,⁸ the most plausible reaction products are OI^- and O_2 .



The pK_a for hypoiodous acid is 10.7¹⁷ and the conversion of OI^- to HOI is rapid.¹⁸



HOI rapidly equilibrates with the remaining I^- to form I_2 ,¹⁹ and I_2 and I^- exists in equilibrium with I_3^- .²⁰



Using the literature values of the equilibrium constants for reactions (7)-(9), the final concentrations were calculated for the two experimental conditions, shown in Table II. The final absorbances due to the iodine-containing species were calculated using the extinction coefficients^{21,22} listed in Table II. For the pH 6.4 and 8.0 experiments, the final absorbances were found to be 9% and 22% of the initial absorbances, respectively.

Exhaustive ozonation of iodide solutions yielded IO_3^- , which was observed by Raman spectroscopy. The IO_3^- could be formed by the reaction of ozone with HOI , or by the slow disproportionation of OI^- .



From the study of the reactions of ozone with Br^- and HOBr by Haag and Hoigne,¹⁶ we expect that the reaction of ozone with HOI is slower than the reaction of ozone with I^- . Ozonation of

iodine solutions also showed the appearance of IO_3^- . The rate constant that we have obtained indicates the ozone-iodide reaction in seawater is an important loss process for tropospheric ozone.

Ozone - Nitrite Reaction

The reaction was studied over a pH range of 6.1 to 9.9 at 25°C by stopped-flow only.



In this pH range, no corrections were required for the presence of HNO_2 ($\text{pK}_a = 3.0$).²³ The initial ozone concentrations ranged from 7×10^{-6} to 4×10^{-5} M and the initial nitrite concentrations ranged from $1.0 - 2.5 \times 10^{-4}$ M. The values of the rate constant are shown in Figure 1. Over the limited range studied, the rate showed first order dependence on nitrite concentration, in agreement with earlier studies.^{2,8} The average second-order rate constant that we obtain for the reaction is $3.0 \pm 0.2 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$ at ionic strengths of $\mu = .007$ to $.029$, which agrees well with the values obtained by Hoigne et al⁸ and Garland et al¹ at lower pH conditions. No dependence on ionic strength was observed in the range studied. The second order rate constants are independent of pH, so we conclude that radicals generated by the ozone-hydroxide ion reaction do not substantially influence the ozone-nitrite reaction in the range of conditions studied. Nitrate ion was the only product observed in Raman spectra taken of reacted nitrite solutions.

Ozone - S(IV) Reaction

For this reaction, the dependence of the rate on the reactants has been well established by other studies. The rate can be expressed as

$$-d[\text{O}_3]/dt = k [\text{O}_3] [\text{S(IV)}] \quad (12)$$

The ozone-S(IV) reaction was observed over a pH range of 4.0 to 5.2 with the stopped-flow system and pH 6.5 to 9.3 with the PAF system. Since there is good agreement among earlier studies, no effort was made to determine the value for the reaction of ozone with hydrogen sulfite. The ozone concentrations used were 6×10^{-6} to 5×10^{-5} M and the S(IV) concentrations used were 1×10^{-5} to 4×10^{-4} M. The pH values, ionic strengths, concentrations, and averaged values of the observed rate constant obtained in the experimental runs are tabulated in Table III. The data were obtained from both the stopped-flow system and the PAF system. The values of k_{reaction} were corrected for contribution from the ozone-hydrogen sulfite reaction, using a rate constant of $3.2 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$. The corrections were insignificant above pH 7. The values of $k_{\text{corrected}}$ were then used to calculate the rate constant, k . In calculating the fraction of S(IV) as SO_3^{2-} , the equilibrium constant for

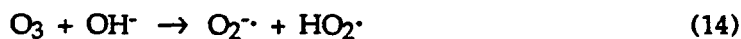


was adjusted for ionic strength.²⁴ The stopped-flow runs were done with ionic strengths of $\mu = .002 - .013$ and the PAF runs were done with $\mu = .022 - .45$. There was no noticeable ionic strength

dependence observed in either the stopped-flow runs or the PAF runs. A plot of $\log(k_{app})$ versus $\log([SO_3^{2-}])$ is shown in Figure 2. The data show a first order dependence on sulfite concentration. There was a fair amount of scatter in the high pH PAF data due to the rapid reaction and the small signal. However, there is no systematic deviation in the value of the rate constant as the fraction of S(IV) as SO_3^{2-} approaches unity. Such a deviation could occur if the ozone-hydroxide ion reaction contributed substantially to the ozone-S(IV) reaction process.²⁵ The values of $k_{corrected}$ below pH 4.5 are not considered as reliable as the values obtained at higher pH conditions, in part because the correction applied for HSO_3^- was significantly larger than for the higher pH conditions. A least squares fit to the data from conditions with pH 4.5 and above yields a value of $k_{corrected} = 7.5 \pm 1.8 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ at $[SO_3^{2-}] = 1 \text{ M}$, where $k_{corrected} = k$ for the ozone + sulfite reaction. An average of the individually calculated values of k gives a similar value of $7.3 \pm 4.1 \times 10^8$.

Espenson and Taube⁷ studied the reaction of ozone with $SO_2(aq)$ and SO_3^{2-} that were isotopically enriched with O^{18} . These studies were done only at very acidic (pH<1) and very alkaline (pH>12) conditions. Their results indicated that more than one oxygen atom was transferred from ozone to the sulfate product. They observed that ozone induced sulfate to slowly undergo oxygen atom transfer with water in the absence of sulfite. They also studied oxygen atom transfer in the ozone-nitrite reaction. In this reaction, they observed the transfer of one oxygen atom to the nitrate product, in agreement with expectations. It is noted that the experimental conditions used by Espenson and Taube which generated higher aqueous ozone concentrations during reaction created larger values of oxygen atom transfer to S(IV). They offer a possible mechanism for the transfer of two oxygen atoms to S(IV) under very acidic conditions, but they do not speculate about a possible process involved with the transfer of two oxygen atoms at high pH conditions.

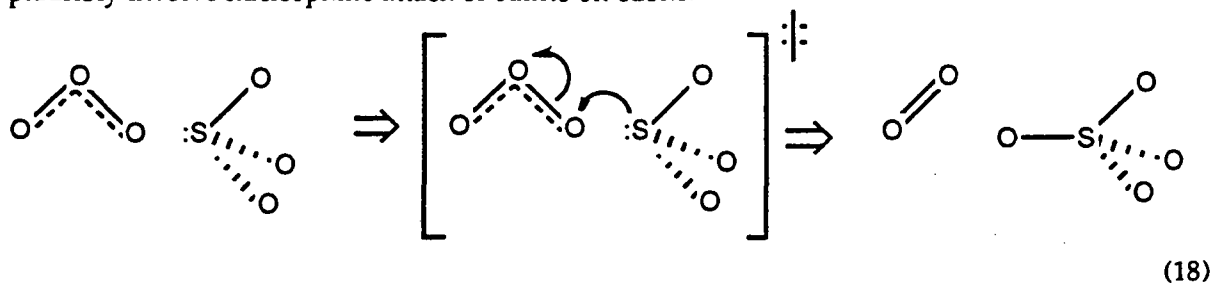
Under such alkaline conditions, it is possible that hydroxyl radicals could be formed by a process such as



The reaction of OH^{\cdot} with S(IV) could generate additional radicals which could effect greater than unitary oxygen atom transfer from ozone to S(IV). The $O_2^{\cdot-}$ formed by reaction 16 could react with S(IV) to produce the same result. However, at moderate OH^- concentrations, the free radical contribution would be expected to be much smaller.

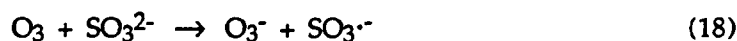
With solution conditions at moderate pH (4.1 - 9.3), where $[S(IV)] > [OH^-]$, it is expected that the direct reaction would predominate, since the rate of the ozone-hydroxide reaction is significantly less than the ozone-S(IV) reaction.²⁶ Kinetic studies of the ozone-

S(IV) reaction have been, by and large, reasonably consistent and no fractional order dependence on [S(IV)] has been reported.^{2-6,8} The reaction of ozone with sulfite would most plausibly involve nucleophilic attack of sulfite on ozone.



The ozone bonds have multiple bond character. The transfer of an oxygen atom from ozone to sulfite gives O_2 and SO_4^{2-} . In this study, the rate plateaued in the pH 8-9 region, which would not be expected in a system where the ozone-hydroxide reaction made a significant contribution to the reaction process. It does not seem necessary to invoke a free radical process to explain the reaction process when a direct reaction, shown above, is straightforward.

It is unlikely that the reaction would proceed by electron transfer to a significant degree.²⁷



If this pathway was important, a significant amount of dithionate would be present in the reaction products from the reaction^{28,29}



The branching for reaction 19 was studied by Waygood and McElroy.²⁸ The product distribution was checked by Raman spectroscopy. Ozone was trapped on silica gel at dry ice temperature and the oxygen was removed by purging with nitrogen. The silica gel was warmed to about $-50^\circ C$, and the flow of N_2 and O_3 was directed through a solution of 0.5 M SO_3^{2-} . There was no detectable $S_2O_6^{2-}$ in the Raman spectra of the oxidized solution, which indicated that less than 1% of the SO_3^{2-} was converted into $S_2O_6^{2-}$. We conclude that ozone-S(IV) reacts primarily by O atom transfer under the conditions studied.

The ozone-cyanide reaction is one in which free radicals have been implicated in the reaction process. The reaction of ozone with cyanide has been studied by Gurol and Bremen³⁰ and the reaction displays behavior typical of free radical involvement. At high pH (>9), the rate shows fractional order dependence on $[CN^-]$. The addition of *tert*-butyl alcohol or other free radical scavengers brought the $[CN^-]$ order dependence close to unity. The reaction displays first order dependence on $[CN^-]$ at neutral pH conditions where the ozone-hydroxide ion reaction would be less important. Gurol and Bremen proposed a mechanism involving both a

direct reaction of ozone with cyanide and a reaction of hydroxyl radical with cyanide. They propose that OH^\cdot , the hydroxyl radical, is formed indirectly from the reaction of ozone with hydroxide, OH^- , as indicated in reactions (14) - (16), above. Our studies generally were at pH 9 or lower and the reactions did not appear to involve a radical pathway.

Nucleophilicity

The Swain-Scott relationship,³¹⁻³³ which correlates rate constants with the nucleophilicity (n) of anions and the sensitivity (s) of the reaction site, was derived for nucleophilic attack at carbon.

$$\log(k/k_0) = sn \quad (21),$$

There are several nucleophilic scales in use in the literature.³¹⁻³³ The one used here is based on the scale presented by Swain and Scott.³¹ In such situations, s is typically 1 ± 0.5 . More recently, the relationship has been applied to Cl^+ transfer reactions of HOCl .^{12,34} In the case of nucleophilic attack at chlorine in HOCl , $s = 4.7 \pm 1$, indicating that these reactions are much more sensitive to the nucleophilic strength of the anions than are the reactions of carbon. Using the results of this study and other studies of ozone reactions, we have applied the Swain-Scott relationship to O atom transfer reactions of ozone. The nucleophilic anions and their second-order rate constants for reaction with ozone are listed in Table IV along with their nucleophilicity. Sulfite, hydroxyl and the halide ions are generally believed to react with ozone by O atom transfer.^{8,26} The reaction mechanisms for the other compounds in Table IV, HS^- , NH_3 , and NH_2OH , have not been established. However, it is plausible that they could also proceed by O atom transfer. If the HS^- - ozone reaction is analogous to the HO^- - ozone reaction,²⁶ HSO^- would be the initial product. The ultimate oxidation product of HS^- is believed to be sulfate.³⁵

Ammonia and hydroxylamine are ultimately oxidized to nitrate,⁸ although the mechanism has not been established. These reactions could plausibly proceed via O atom transfer. If ammonia forms NH_3O , it could rearrange to NH_2OH , which reacts more quickly with ozone than ammonia. A plot of the values of $\log k$ versus nucleophilicity from Table IV is shown in Figure 3. The data for the reactions known to proceed by O atom transfer are shown as squares and the line is a least squares fit to these points, and has a slope of 6.2 ± 0.6 . This slope is somewhat higher than the value of $s = 4.7$ obtained by Gerritsen and Margerum³⁴ for the $\text{HOCl} + \text{X}^-$ reactions. It is noteworthy that the values for HS^- , NH_3 , and NH_2OH , shown as triangles, also lie close to the line derived from the other reactions.

We conclude that the reactions of iodide, sulfite, and nitrite with ozone proceed by O atom transfer and do not show evidence of radical-mediated reactions at the conditions studied. The ozone - S(IV) reaction results support the conclusions of Hoigne et al⁸ from their

measurements using the indigo method. The rate constants for nucleophile - ozone O atom transfer reactions show good correlation with the nucleophilicity values in the literature.

Acknowledgment. This work was supported by the Assistant Secretary for Fossil Energy, Office of Coal Utilization Systems, U.S. Department of Energy under Contract No. DE-AC03-76SF00098 through the Pittsburgh Energy Technology Center, Pittsburgh, PA. I would like to thank Dale W. Margerum (Department of Chemistry, Purdue University, West Lafayette, IN 47907) for the use of the stopped-flow and PAF instruments and many helpful discussions on kinetics of ozone reactions and pointing out the nucleophilicity-rate relationship. I would also like to acknowledge the assistance of Sam W. Evetts (Purdue University Chemistry Department) in acquiring and analyzing the data.

References

1. Garland, J. A.; Elzerman, A. W.; Penkett, S. A. *J. Geophys. Res.* 1980, 85, 7488-7492.
2. Penkett, S. A. *Nature Phys. Sci.* 1972, 240, 105-106.
3. Penkett, S. A.; Jones, B. M. R.; Brice, K. A.; Eggleton, A. E. J. *Atmos. Environ.* 1979, 13, 123-137.
4. Larson, T. V.; Horike, N. R.; Harrison, H. *Atmos. Environ.* 1978, 12, 1597-1611.
5. Erickson, R. E.; Yates, L. M.; Clark, R. L.; McEwen, D. *Atmos. Environ.* 1977, 11, 813-817.
6. Maahs, H. G. *Atmos. Environ.* 1983, 17, 341-345.
7. Espenson, J. H.; Taube, H. *Inorg. Chem.* 1965, 4, 704-709.
8. Hoigne, J.; Bader, H.; Haag, W. R.; Staehelin, J. *Water Res.* 1985, 19, 993-1004.
9. Bader, H.; Hoigne, J. *Water Res.* 1981, 15, 449-456.
10. Jacobs, S. A.; Nemeth, M. T.; Kramer, G. W.; Ridley, T. Y.; Margerum, D. W. *Anal. Chem.* 1984, 56, 1058-1065.
11. Nemeth, M. T.; Fogelman, K. D.; Ridley, T. Y.; Margerum, D. W. *Anal. Chem.* 1987, 59, 283-291.
12. Fogelman, K. D.; Walker, D. M.; Margerum, D. W. *Inorg. Chem.* 1989, 28, 986-993.
13. Willard, H. H.; Merritt, Jr., L. L. *Ind. Eng. Chem. Anal. Ed.* 1942, 14, 486-489.
14. Briner, E.; Perrottet, E. *Helv. Chim. Acta* 1939, 22, 397-404.
- 14a. Hoigne, J.; Bader, H. *Water Res.* 1983, 17, 185-194.
15. Dickson, P. N.; Margerum, D. W. *Anal. Chem.* 1986, 58, 3153-3158.
16. Haag, W. R.; Hoigne, J. *Environ. Sci. Tech.* 1983, 17, 261-267.
17. Chia, Y. T. Master's Thesis, University of California, 1958, UCRL-8311.
18. Eigen, M.; Kustin, K. *J. Am. Chem. Soc.* 1962, 84,, 1355-1361.
19. Allen, T. L.; Keefer, R. M. . *Am. Chem. Soc.* 1955, 77, 2957-2960.
20. Davies, M.; Gwynne, E. . *Am. Chem. Soc.* 1952, 74,, 2748-2752.
21. Awtrey, A. D.; Connick, R. E. . *Am. Chem. Soc.* 1951, 73, 1842-1843.

22. Deane, A. M.; Marsh, W. R. *U. K. At. Energy Res. Establ.* 1986, AERE-R 11657.
23. deMaine, M. M.; Stanbury, D. M. *Inorg. Chem.* 1991, 30, 2104-2109.
24. Wedzicha, B. L.; Goddard, S. J. *Food Chemistry* 1988, 30, 67-71.
25. Hoigne, J.; Bader, H. *Water Res.* 1976, 10, 377-386.
26. Forni, L.; Bahnemann, D.; Hart, E. J. *J. Phys. Chem.* 1982, 86, 255-259.
27. Bennett, L.E.; Warlop, P. *Inorg. Chem.* 1990, 29, 1975-1981.
28. Waygood, S. J.; McElroy, W. J. *J. Chem. Soc. Faraday Trans.* 1992, 88, 1525-1530.
29. Sarala, R.; Islam, M.A.; Rabin, S.B.; Stanbury, D.M. *Inorg. Chem.* 1990, 29, 1133-1142.
30. Gurol, M. D.; Bremen, W. M. *Environ. Sci. Tech.* 1985, 19, 804-809.
31. Swain, C. G.; Scott, C. B. *J. Am. Chem. Soc.* 1953, 75, 141-147.
32. Hine, J. S. *Physical Organic Chemistry*; McGraw-Hill: New York, 1962; p. 161.
33. Pearson, R.G.; Sobel, H.; Songstad, J. *J. Am. Chem. Soc.* 1968, 90, 319-326.
34. Gerritsen, C. M.; Margerum, D. W. *Inorg. Chem.* 1990, 29, 2757-2762.
35. Kellogg, W.W.; Cadle, R.D.; Allen, E.R.; Lazarus, A.L.; Martell, E.A. *Science* 1972, 175, 587-595.

Table I
Rate Constants for Aqueous Ozone Reactions

Source	Reactant	Temperature (°C)	Second Order Rate Constant (M ⁻¹ sec ⁻¹)	Ionic Strength (M)
Ref. 1	S(IV)	25	$\sim 3 \times 10^8$	n.a.
	NO ₂ ⁻	25	3.3×10^5	n.a.
	Br ⁻	25	3.0×10^2	n.a.
	NH ₃	25	44	n.a.
	I ⁻	25	$\sim 2 \times 10^9$	~ 0.6
Ref. 2	S(IV)	9.6	$\sim 4 \times 10^5$	$< 10^{-3}$
	NO ₂ ⁻	9.6	$1.6 \pm 0.1 \times 10^5$	$< 10^{-3}$
Ref. 4	S(IV)	25	1.6×10^5	$\sim 0.1 - 1.0$
Ref. 5	HSO ₃ ⁻	16	$1.7 \pm 0.2 \times 10^5$	n.a.
		25	$3.1 \pm 0.2 \times 10^5$	n.a.
	SO ₃ ²⁻	16	$1.3 \pm 4 \times 10^9$	n.a.
		25	$2.2 \pm 4 \times 10^9$	n.a.
Ref. 6	S(IV)	25	about 50% of ref. 6	$3 \times 10^{-4} - 1 \times 10^{-1}$
Ref. 8	SO ₂ (aq)	22	$2 \pm 2 \times 10^4$	n.a.
	HSO ₃ ⁻	22	$3.2 \pm 0.2 \times 10^5$	n.a.
	SO ₃ ²⁻	22	$1.0 \pm 0.1 \times 10^9$	n.a.
	Cl ⁻	22	$< 3 \times 10^{-3}$	$\sim 1 - 4$
	Br ⁻	22	$1.6 \pm 0.2 \times 10^2$	$\sim 5 \times 10^{-4} - 2 \times 10^{-2}$
this study	I ⁻	25	$1.7 \pm 0.1 \times 10^9$	$\sim 1 \times 10^{-3}$
	NO ₂ ⁻	25	$3.0 \pm 0.2 \times 10^5$	$7 \times 10^{-3} - 2.9 \times 10^{-2}$
	SO ₃ ²⁻	25	$7 \pm 1 \times 10^8$	$2 \times 10^{-3} - 4.5 \times 10^{-1}$

n.a. - not available

Table II

Species	Extinction Coefficient at 260 nm ($M^{-1} \text{ cm}^{-1}$)	pH 6.4 Concentration	pH 8.0 Concentration
I^-	36 [21]	$2.09 \times 10^{-5} \text{ M}$	$1.05 \times 10^{-5} \text{ M}$
I_2	109 [21]	$1.41 \times 10^{-5} \text{ M}$	$5.5 \times 10^{-6} \text{ M}$
HOI	6000 [21]	$9.1 \times 10^{-7} \text{ M}$	$2.85 \times 10^{-5} \text{ M}$
I_3^-	≤ 760 [22]	$2.3 \times 10^{-7} \text{ M}$	$4.4 \times 10^{-8} \text{ M}$

Table III

Experimental Conditions and Results for Ozone - S(IV) Measurements

pH	μ (M)	[O ₃] (M)	[S(IV)] (M)	k _{reaction} (sec ⁻¹)	k (x10 ⁸ M ⁻¹ sec ⁻¹)
Stopped-Flow					
4.0	0.007 - 0.012	2.5 - 15x10 ⁻⁶	3.0x10 ⁻⁴	480 ± 30	19.4
4.0	.003	1.2 - 1.6x10 ⁻⁵	1.5x10 ⁻⁴	270 ± 20	22.4
4.1	.006	1.0 - 3.3x10 ⁻⁵	1.4x10 ⁻⁴	260 ± 20	18.4
4.1	.003	1.6 - 1.7x10 ⁻⁵	7.0x10 ⁻⁵	113 ± 9	15.6
4.1	.002	1.6 - 3.3x10 ⁻⁵	3.5x10 ⁻⁵	51 ± 18	13.8
4.5	.010	1.45 - 4.0x10 ⁻⁵	2.5x10 ⁻⁵	32 ± 2	4.7
4.8	.010	1.6 - 1.7x10 ⁻⁵	5.0x10 ⁻⁵	230 ± 24	10.3
5.1	.013	1.2x10 ⁻⁵	2.5x10 ⁻⁵	103	4.5
5.1	.013	3.0 - 13x10 ⁻⁶	1.25x10 ⁻⁵	86 ± 17	7.9
5.2	.013	1.3 - 1.4x10 ⁻⁵	2.5x10 ⁻⁵	120 ± 20	4.3
PAF					
6.5	.022	1.4x10 ⁻⁵	9.0x10 ⁻⁵	9140 ± 770	6.3
7.0	.024	3.3x10 ⁻⁵	3.0x10 ⁻⁴	6.2 ± 0.6 x10 ⁴	5.2
7.0	.045	7.6x10 ⁻⁶	2.1x10 ⁻⁴	4.4 ± 2.3 x10 ⁴	5.3
7.0	.22	2.9x10 ⁻⁵	3.4x10 ⁻⁴	2.1x10 ⁵	12.8
7.0	.45	7.3x10 ⁻⁵	3.2x10 ⁻⁵	5.4x10 ⁴ *	3.0
7.0	.045	2.0x10 ⁻⁵	3.3x10 ⁻⁴	4.0x10 ⁴	3.0(5)
9.2	.013	4.3x10 ⁻⁵	1.6x10 ⁻⁴	8.9 ± 0.8 x10 ⁴	5.6
9.3	.013	4.7x10 ⁻⁵	3.1x10 ⁻⁴	2.0x10 ⁵	6.4(5)

* derived from second order fit

Table IV

Nucleophilicities (n) and Rate Constants (k) for Reaction with Ozone

Species	n	reference for n	k M ⁻¹ sec ⁻¹	reference for k	log k
SO ₃ ²⁻	5.1	[26]	7.3 × 10 ⁸	[a]	8.86
I ⁻	5.0	[26]	1.7 × 10 ⁹	[a]	9.23
Br ⁻	3.9	[26]	90 - 300	[8]	1.95 - 2.5
Cl ⁻	3.0	[26]	~2 × 10 ⁻⁴	[8]	-3.70
OH ⁻	4.2	[26]	40 - 80	[8]	1.60 - 1.90
HS ⁻	5.1	[26]	3.0 × 10 ⁹	[8]	9.48
NH ₃	3.85	[27,b]	20 - 44	[8]	1.30 - 1.64
NH ₂ OH	4.65	[27,b]	2.1 × 10 ⁴	[8]	4.32

[a] - this study

[b] - adjusted for different scale

Figure Captions

Figure 1. Values of the rate constant for the ozone-nitrite reaction obtained by stopped flow, shown as a function of pH. The average value for the rate constant is $3.0 \pm 0.2 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$.

Figure 2. A plot of $\log(k_{\text{app}})$ from PAF and stopped-flow measurements after correction for the $\text{HSO}_3^- - \text{O}_3$ reaction as a function of $\log([\text{SO}_3^{2-}])$. The slope is one, indicating first order dependence on $[\text{SO}_3^{2-}]$. The intercept provides the value of k for the reaction of ozone with sulfite.

Figure 3. Swain-Scott plot of $\log k$ for the reaction of ozone with Cl^- , Br^- , OH^- , SO_3^{2-} , and I^- (squares) versus the nucleophilicity of the anions. The values of $\log k$ for the reaction of ozone with HS^- , NH_3 , and NH_2OH are also shown (triangles). The slope is 6.2 ± 0.6 .

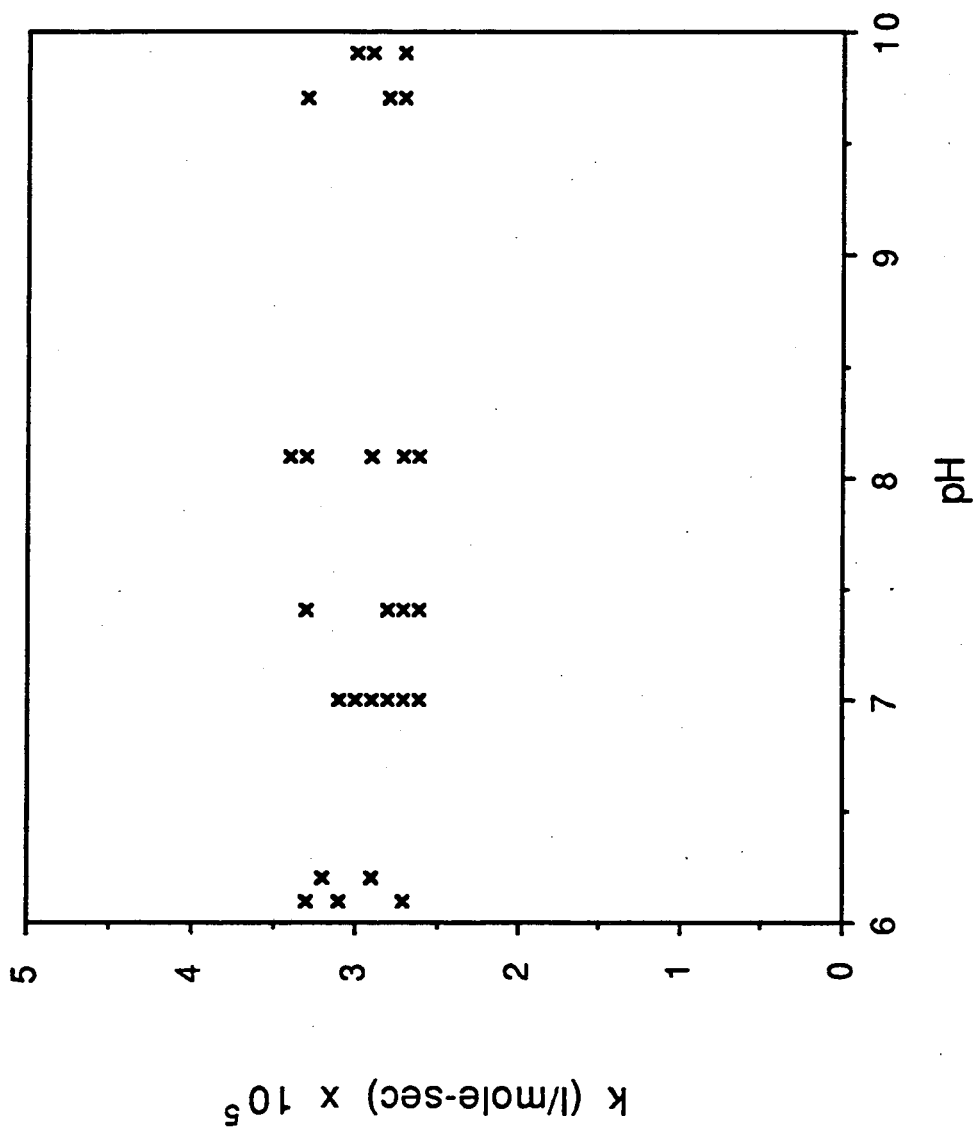


Figure 1

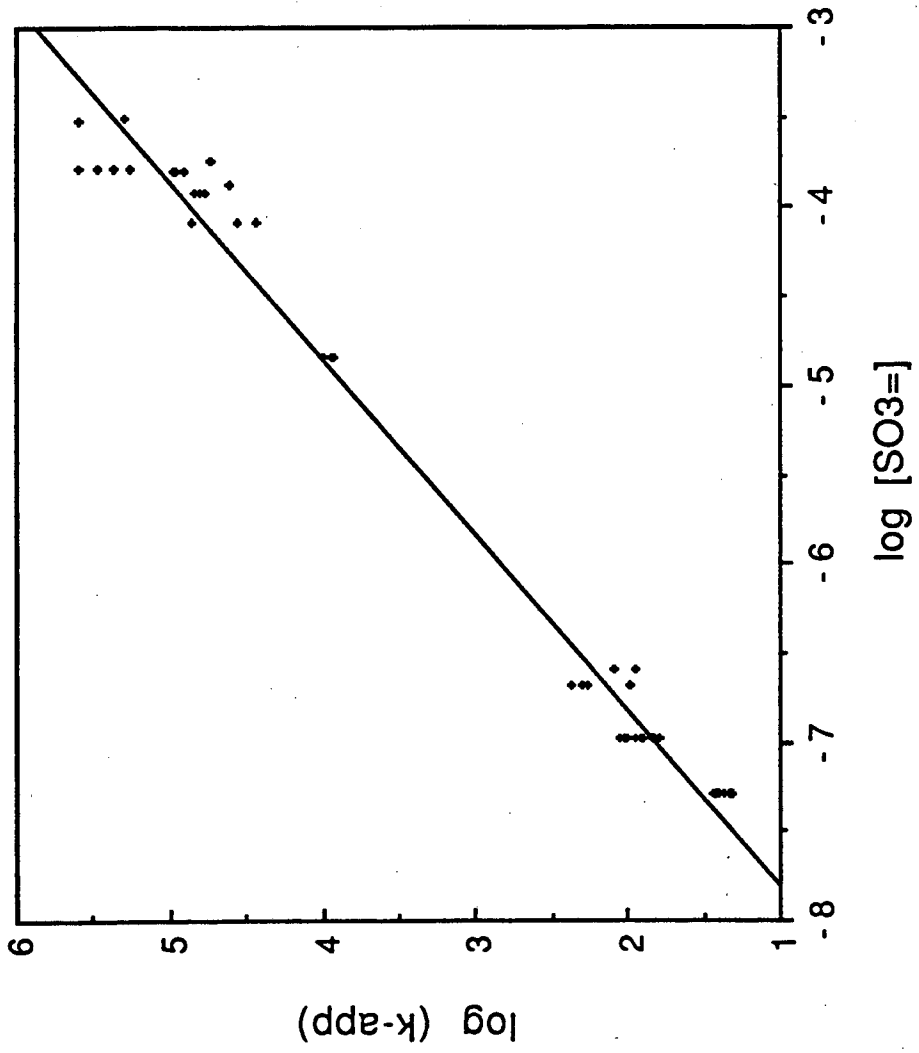


Figure 2

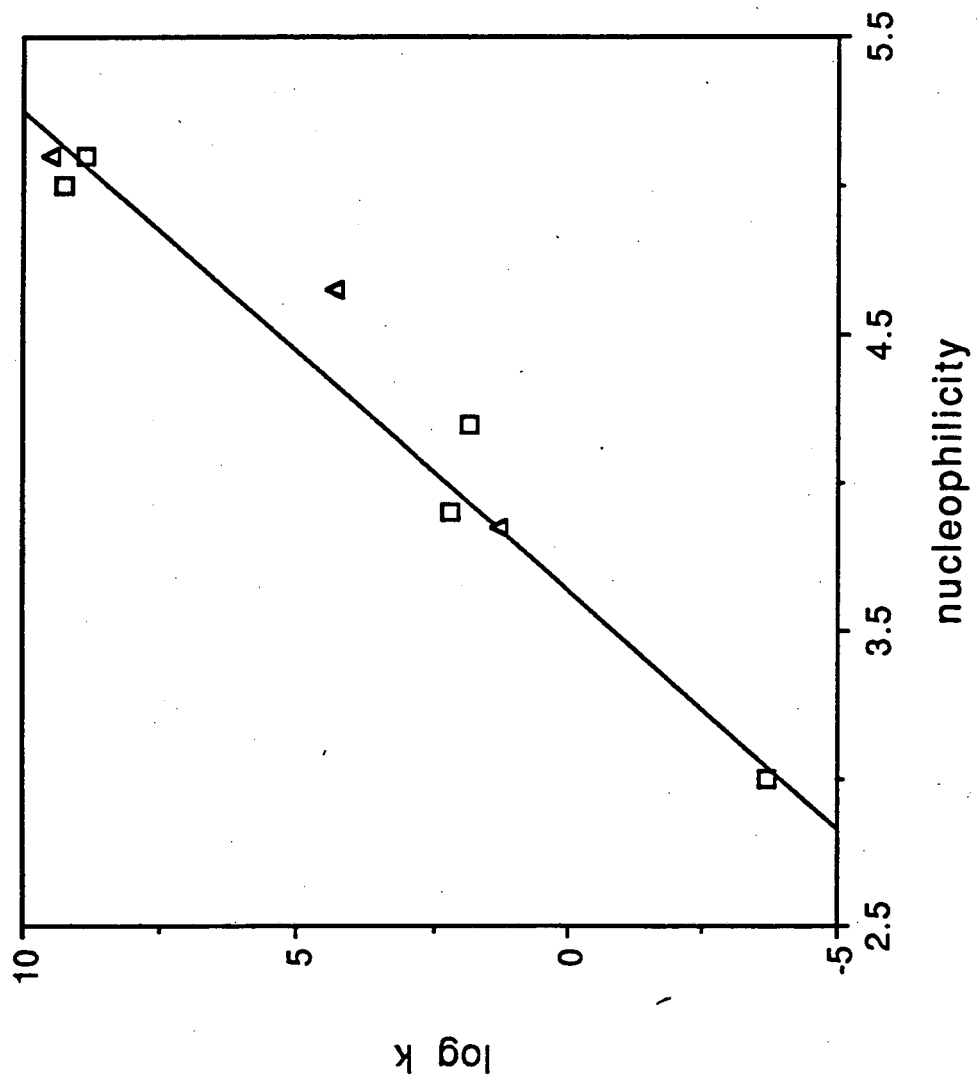


Figure 3

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720

