borderline by Pearson. What about the effect of oxidation number? Pearson[5] argues that Tl^{3+} is softer than Tl^+, yet the opposite conclusion will be drawn from the polarizabilities. The same is true[5] for Pb^{4+} and Pb^{2+}. In fact, using the polarizability criterion we would conclude that Pb^{2+} is nearly the softest of the cation acids. This is not true. If CN^- is added to a solution of Pb^{2+} one can identify $Pb(OH)_3^-$ in the solution, but there is little evidence[8] for coordination of CN^-, although the latter is one of the "softest" of bases. Pearson also assumes that the presence of unshared pairs of electrons (p or d electrons) in the valence shell leads to high polarizability.[5] This is untrue as shown in Table I, where for example, the polarizability of K^+ is greater than that of either Cu^+ or Zn^{2+}, the latter two having ten d electrons. Yet Pearson classifies Cu^+ as soft and Zn^{2+} as borderline.

One other bit of information can be obtained from Table I. In general the polarizabilities of the cations are so small as compared to the anions that the polarizability of the former can be neglected. An example might be the species ZnI_4^{2-}. This is especially true when we consider that Zn^{2+} has a much greater polarizing effect on I^- than I^- has on Zn^{2+}.

There is a case in which more detailed numerical testing is possible. Pearson[4] proposes an equation of the form

$$\log K = S_A S_B + \sigma_A \sigma_B \qquad (1)$$

to represent acid-base combination. The product $S_A S_B$ is equated with the strength of ionic bonding, the product $\sigma_A \sigma_B$ with covalent bonding. For the combination of "soft" acids with "soft" bases the product $\sigma_A \sigma_B$ is high, the contribution of covalent bonding is high, and the polarizabilities are high. He compares this general equation with the Edwards equation

$$\log (K/K_0) = \alpha E_n + \beta H \qquad (2)$$

and concludes[4] that the product αE_n is to be identified with $\sigma_A \sigma_B$. Edwards gives the values of α for several cations. If polarizability is indeed related to σ_A (or α) then a graph of α *vs.* molar polarizability should show it. Such a graph shows scattered points, with no correlation between α and polarizability.

Ahrland[9] has come to a similar conclusion. He states that ". . .high polarizability alone, without the presence of a well-filled d-shell, does not confer (b)-properties on a metal ion."

Polarizability will, however, enter into bond strength. There is an inherent electrical attraction between a metal ion and the ligand. This attraction will be enhanced by the polarizing effect of the cation on the ligand, such polarization increasing the electrical charge near the metal ion and increasing the force of attraction. But this is an increase in ionic bonding rather than covalent bonding.

Underlying much of the difficulty is an error in a basic assumption: the strength of covalent bonding increases as the polarizability of the atoms increases. As polarizability increases we find that size increases (in general). And as size increases the bond strength decreases (both ionic and covalent). If the polarizability criterion were correct then CsBr would be a very covalent compound (*cf.* data in Table I). The truth is that covalent character increases as electronegativities of the two atoms approach each other.

In summary the following can be said. Pearson has introduced the terms "soft" and "hard" for class b and class a behavior of acids and bases, respectively. He has suggested that "soft" implies high polarizability and "hard" implies low polarizability. The data in this paper show that there is essentially no relation between class a and class b behavior and polarizability, at least for metal ion acceptors. These constitute the major part of the so-called "hard" acids. Consequently the terms "hard" and "soft" should be dropped from our vocabulary, and we should seek an explanation of class a and class b behavior using other concepts. Pearson himself has described some of these briefly in one of his papers.[5]

Drago and Kabler[10] have also suggested, on other grounds, that the designations "hard" and "soft" be given up.

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Kinetics of the Reactions of Sodium Dithionite with Dioxygen and Hydrogen Peroxide

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Sir:

The reaction of dioxygen with sodium dithionite was reported by Rinker, *et al.*, to obey the rate law

$$-d[S_2O_4^{2-}]/dt = k_1[O_2][S_2O_4^{2-}]^{1/2} \qquad (1)$$

with $k_1 = 0.15\ M^{-1/2}\ sec^{-1}$ at 30° in $0.10\ M$ sodium hydroxide.[1] They invoked the following scheme, with eq 3 being rate determining, to rationalize this rate law

$$S_2O_4^{2-} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} 2SO_2^- \qquad (2)$$

$$SO_2^- + O_2 \xrightarrow{k_3} \text{products} \qquad (3)$$

This scheme, together with $K_2 = 1.4 \times 10^{-9}\ M$,[2] leads to $k_3 = 4.0 \times 10^3\ M^{-1}\ sec^{-1}$ at 30°.

For some years sodium dithionite has been used to destroy O_2 in studies of oxyhemoglobin dissociation kinetics. In these studies the dithionite-dioxygen reaction is assumed to be very rapid. Concerned by the incompatibility of the results of Rinker, *et al.*, with this assumption, Morello, *et al.*, reinvestigated the reaction of dithionite with dioxygen at 37° in the above medium and found the rate of disappearance of dioxygen to be zero order in dioxygen and first order with respect to dithionite, with the "initial" rate constant 42.5 sec^{-1}.[3] This result is inconsistent with eq 1. It is, however, consistent with the above kinetic scheme (eq 2 and 3) if the rate of production of SO_2^- radicals, $2k_2[S_2O_4^{2-}]$, is rate determining. Most recently Lambeth and Palmer[2] studied the reaction at excess dioxygen in $0.1\ M$ sodium hydroxide. They found $k_2 = 1.7\ sec^{-1}$ at 25° and 8.6 sec^{-1} at 37°. From analysis of the lag period in the dithio-

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[3] J. A. Morello, M. R. Craw, H. P. Constantine, and R. E. Forster, *J. Appl. Physiol.*, 19, 522 (1964).

nite-ferricytochrome c reaction (which appears when dioxygen is present), they calculated that $k_3 = 1.3 \times 10^6$ M^{-1} sec^{-1} at 25° and pH 8 (which corresponds to k_1 = 47 $M^{-1/2}$ sec^{-1}). Below we report the results of our studies of the dioxygen-dithionite reaction which differ in significant respects from those summarized above. In connection with this work we have also investigated the kinetics of the hydrogen peroxide-dithionite reaction.

Kinetics of the Dithionite-Dioxygen Reaction. The reaction was studied with either excess dioxygen or excess dithionite on a Durrum D-110 stopped flow spectrophotometer. In all experiments the disappearance of dithionite was followed using wavelengths between 250 and 372 nm ($\lambda_{\max}$ 315 nm). With either reagent in excess, the observed kinetics were consistent with a rate-determining dissociation of $S_2O_4^{2-}$ into SO_2^- (eq 2). With O_2 in excess, the disappearance of $S_2O_4^{2-}$ was exponential, giving excellent first-order fits for at least 3 half-lives. The following results were obtained for solutions at pH 6.5 (3 mM phosphate), $\mu = 0.15\,M$ (sodium chloride) at 25°: $[O_2] = 0.65$ mM,[4] $[S_2O_4^{2-}] \sim 10$ μM, $k_{\text{obsd}} = 2.5$ sec^{-1};[5] $[O_2] = 0.33$ mM, $[S_2O_4^{2-}] \sim 50$ μM, $k_{\text{obsd}} = 2.4$ sec^{-1}; $[O_2] = 0.14$ mM, $[S_2O_4^{2-}] \sim 10$ μM, $k_{\text{obsd}} = 2.3$ sec^{-1}, and k_2, the dithionite dissociation rate constant, is 2.5 sec^{-1}. Thus dissociation of dithionite is essentially rate determining under these conditions. Similar experiments carried out in 0.1 M sodium hydroxide at 25° ($[O_2] = 0.65$ mM, $[S_2O_4^{2-}] \sim 10$ μM, $k_{\text{obsd}} = 1.80$ sec^{-1}; $[O_2] = 0.14$ mM, $[S_2O_4^{2-}] \sim 10$ μM, $k_{\text{obsd}} = 1.81$ sec^{-1}) give $k_2 = 1.8$ sec^{-1} for these conditions, in excellent agreement with the value 1.7 sec^{-1} measured by Lambeth and Palmer.[2]

With dithionite as excess reagent, the reaction was studied at 25° at both pH 6.5 ($\mu = 0.15\,M$) and pH 13 (0.10 M sodium hydroxide) using dithionite levels ranging between 0.11 and 7.8 mM, with the initial dioxygen concentration in a given run being 10-20% that of dithionite. In *all* such experiments, zero-order decays were observed, with the time (Δt) required for complete reaction being consistent with the fraction of the total dithionite consumed and the k_2 value appropriate for the conditions used, *i.e.*

$$\Delta[S_2O_4^{2-}]/[S_2O_4^{2-}]\Delta t = k_2 \tag{4}$$

Calculations of $\Delta[S_2O_4^{2-}]$ were based on absorbance changes measured on the Durrum D-110.[6] From the above kinetic scheme (eq 2 and 3) it is evident that when $S_2O_4^{2-}$ is in large excess over O_2 an exponential decay will be observed if eq 3 is rate determining and that the zero-order decay pattern is found when eq 2 is rate determining, *i.e.*, when

$$k_3[O_2][SO_2^-] > k_{-2}[SO_2^-][SO_2^-] \tag{5}$$

From the above k_2 measurements and the value of $K_2 = 1.4 \times 10^{-9}\,M$,[2] k_{-2} is calculated to be 1.8×10^9 M^{-1} sec^{-1} at pH 6.5. The steady state SO_2^- level under these conditions is[7]

$$[SO_2^-]_{ss} = \frac{k_2[S_2O_4^{2-}]}{k_{-2}[SO_2^-] + k_3[O_2]} \tag{6}$$

which reduces to

$$[SO_2^-]_{ss} = k_2[S_2O_4^{2-}]/k_3[O_2] \tag{7}$$

and therefore

$$k_3[O_2] > k_{-2}\ \frac{k_2[S_2O_4^{2-}]}{k_3[O_2]} \tag{8}$$

From the above considerations and the fact that zero-order decays are observed over at least 80% reaction in the following pair of experiments, the limit $k_3 \geqslant 1 \times 10^8$ M^{-1} sec^{-1} is found: $[S_2O_4^{2-}] = 0.51$ mM, $[O_2] = 50$ μM; $[S_2O_4^{2-}] = 0.11$ mM, $[O_2] = 10$ μM. This lower limit for k_3 indicates that the k_3 estimate made by Lambeth and Palmer (on the basis of the lag period kinetics in the dithionite-cytochrome c reaction) is *at least* a factor of 100 too small and confirms that the reaction of SO_2^- with O_2 is very rapid indeed (k_3 more than 2×10^4 times larger than the value reported by Rinker, *et al.*).

In an effort to understand the reasons for the disparity between the present work and the earlier studies, we carried out experiments like those of Rinker, *et al.* Air or O_2 was bubbled through 7 to 20 mM dithionite solutions prepared in 0.1 M sodium hydroxide at flow rates (1900-8040 ml min^{-1}) which include the highest used by Rinker, *et al.* (2800 ml min^{-1}). Dithionite concentration as a function of time was monitored at 372 nm on the Cary 14. We verified that the dithionite decay is indeed half-order with respect to dithionite under such conditions and that the rate increases by about a factor of 5 when pure O_2 replaces air at the same flow rate. We noted, however, two significant differences. *No* saturation flow rate was observed (in the range studied k_{obsd}[8] was proportional to (flow rate)$^{1/2}$); further, our k_{obsd} values were 40-100 times larger than those of Rinker, *et al.* We attribute these differences to the greater bubbling efficiency of our reactor, a gas scrubbing tower equipped at the base with a 7-cm diameter glass frit and charged with 300 ml of solution. We suspect that the flow-rate saturation observed by Rinker, *et al.*, may have resulted from insufficient stirring. If, under such conditions, the steady state O_2 level is far below that of saturation, eq 3 becomes rate determining. Comparison of the apparent half-order rate constant of Rinker, *et al.*, with even the lower estimate 47 $M^{-1/2}$ sec^{-1} obtained by Lambeth and Palmer[2] indicates the steady state O_2 level to have been several orders of magnitude below saturation in the former study. We wish further to point out that, for the conditions of Rinker, *et al.*, it is physically impossible to achieve O_2 levels sufficiently high for dithionite dissociation to be rate determining. Considering an experiment typical of theirs, for 500 ml of 5 mM $S_2O_4^{2-}$, 0.54 mol of SO_2^- is produced per minute. At the air flow rate 2800 ml min^{-1} (used for all their kinetic studies), only 0.03 mol of O_2 per minute enters the solution *if all the gas dissolves.* Obviously in this kind of experiment, even under optimal conditions, dithionite dissociation cannot become rate determining.

Stoichiometry of the Dioxygen-Dithionite Reaction. Rinker, *et al.*, found that 3 mol of sulfite and 1 mol of sulfate are formed from 1 mol of dithionite in the reaction with O_2 but did not measure the $S_2O_4^{2-}:O_2$ ratio or look for other oxygen products (*e.g.*, H_2O_2).[1] At excess dioxygen, Morello, *et al.*, found the reaction stoichiometry to be 1:1.[3] At excess dithionite (pH 6.5, $\mu = 0.15\,M$) we have consistently observed 1:1 stoichiometry for the rapid zero-order decay. However, in some of the excess dithionite runs we observed a slower dithionite loss indicating a second stage in the

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(4) The solubility of O_2 in 0.15 M NaCl at 25° (1 atm) is taken to be 1.3×10^{-3} M.[2]

(5) Average over six to eight individual runs, agreeing within 5%.

(6) We have found that at $\lambda_{\max}$ 315 nm, $\epsilon = 6.9 \times 10^3$ M^{-1} cm^{-1} (average of five independent measurements on the Cary 14 with dithionite between 0.2 and 2 mM) at pH 6.5, $\mu = 0.15\,M$, 25°.

(7) Each O_2 consumes two SO_2^- radicals in this step, *vide infra.*

(8) $k_{\text{obsd}} = 2\Delta[S_2O_4^{2-}]^{1/2}/\Delta t$.

reaction. By monitoring absorbance changes at 315 nm on the Cary 14[9] we found that the number of moles of $S_2O_4^{2-}$ consumed per O_2 appears to be a function of the dithionite level. For initially 2 mM $S_2O_4^{2-}$ and 0.5 mM O_2 solutions, 1:1 stoichiometry was observed ($\Delta S_2O_4^{2-}/O_2 = 1.07$,[10] 1.03,[10] 1.00,[10] 0.92,[10] 0.96[11]). By contrast, with initially 0.25 mM $S_2O_4^{2-}$ and 0.1 mM O_2, the stoichiometry approached 2:1 ($\Delta S_2O_4^{2-}/O_2 = 1.82$,[10] 1.76,[10] 1.84[10]), with the roughly second 50% of the dithionite loss corresponding in magnitude and rate with those found when dioxygen-free hydrogen peroxide was mixed with the dithionite. When the stoichiometry was investigated for 0.1 M sodium hydroxide and 0.25 mM $S_2O_4^{2-}$, the second stage was present but at least ten times slower than at pH 6.5 and so was not followed to completion (after 1 hr, 1.15 $S_2O_4^{2-}/O_2$). This behavior is also consistent with the production of H_2O_2 as is shown from the kinetic studies which follow. In summary, at excess dithionite the rapid zero-order decay appears always to consume one $S_2O_4^{2-}$ per O_2. At 2 mM $S_2O_4^{2-}$, no further reaction occurs. At 0.2 mM $S_2O_4^{2-}$, approximately one hydrogen peroxide per dioxygen is produced and then consumed in a slower reaction with dithionite, leading to eventual consumption of approximately 2 mol of dithionite per mole of dioxygen introduced. Since the reaction rate at excess dithionite shows a first-order dependence on the concentration of dithionite for all dithionite levels studied (0.1 to 8 mM), the variation of stoichiometry with dithionite level in the range 0.2 to 2 mM must result from reactions succeeding the rate-determining step (eq 2). The nature of these reactions is, however, obscure at this time.

Hydrogen Peroxide-Dithionite Reaction. The kinetics of the hydrogen peroxide oxidation of sodium dithionite were studied at excess peroxide on the Durrum D-110 at 25° under two sets of conditions: at pH 6.5 (3 mM phosphate) with $\mu = 0.15\ M$ (sodium chloride); and in 0.10 M sodium hydroxide. The disappearance of dithionite (monitored at 350 nm) was half-order with respect to dithionite. The observed rate constants[8] presented in Table I were obtained from plots of $(A_t - A_\infty)^{1/2}$ *vs.* time which were linear for at least 80% of the reaction. From the hydrogen peroxide concentration dependence at pH 6.5, the rate law is then

$$-\mathrm{d}[S_2O_4^{2-}]/\mathrm{d}t = k_{H_2O_2}[H_2O_2][S_2O_4^{2-}]^{1/2} \tag{9}$$

with $k_{H_2O_2} = 0.096\ M^{-1/2}\ \mathrm{sec}^{-1}$. For the data obtained in 0.10 M sodium hydroxide, the equilibrium[12]

$$H_2O_2 \rightleftharpoons HO_2^- + H^+ \qquad K = 2.4 \times 10^{-12} \tag{10}$$

is relevant. In these runs, $[H_2O_2]$, $[HO_2^-]$, and $[OH^-]$ vary. Analysis of the observed rate constants in terms of these variables (obtained by plotting k_{obsd}/total $[H_2O_2]$ *vs.* $((K/K_w)\cdot[OH^-])/(1 + (K/K_w)[OH^-])$) showed that here dithionite is oxidized both by H_2O_2 and by HO_2^-, *i.e.*

$$-\frac{\mathrm{d}[S_2O_4^{2-}]}{\mathrm{d}t} = (k_{H_2O_2}[H_2O_2] + k_{HO_2^-}[HO_2^-])[S_2O_4^{2-}]^{-1/2} \tag{11}$$

with $k_{H_2O_2} = 0.093\ M^{-1/2}\ \mathrm{sec}^{-1}$ and $k_{HO_2^-} = 2.2 \times 10^{-3}\ M^{-1/2}\ \mathrm{sec}^{-1}$ at 25° and $\mu = 0.10\ M$.

Table I. Observed Rate Constants for the Reaction of Sodium Dithionite with Excess Hydrogen Peroxide[a]

	$10^3 \times k_{\mathrm{obsd}}$,[b] $M^{1/2}\ \mathrm{sec}^{-1}$	
$10^2 \times$ total $[H_2O_2]$, M	pH 6.5, $\mu = 0.15\ M$	In 0.1 M NaOH[c]
0.899	0.860	
4.50	4.07	0.50
8.99	8.42	2.10
13.5	13.6	
18.0	16.7	10.0
22.5		12.7
45.0		33.8

[a] The peroxide concentration was determined by titration with acidic permanganate. Dithionite disappearance was followed at 350 nm on the Durrum D-110; $[S_2O_4^{2-}] = 0.25$–0.5 mM. [b] As the decay of dithionite is half-order with respect to dithionite, $k_{\mathrm{obsd}} = 2\Delta[S_2O_4^{2-}]^{1/2}/\Delta t$. [c] Stock peroxide diluted with water was mixed with sodium dithionite 0.20 M in sodium hydroxide.

For all three oxidants investigated in this study (O_2, H_2O_2, and HO_2^-), the common, kinetically important, reducing agent is the SO_2^- radical and not its parent ion $S_2O_4^{2-}$. By contrast, the ferricyanide reaction with dithionite exhibits *only* a path first order in dithionite and first order in iron(III),[2] while the kinetics of the reactions of spinach plastocyanin[2] and ferricytochrome c[2,13] with dithionite have been described in terms of parallel paths involving both SO_2^- and $S_2O_4^{2-}$.[14] The second-order rate constants for the reactions of H_2O_2 and HO_2^- with SO_2^- ($k' = 260$ and $5.9\ M^{-1}\ \mathrm{sec}^{-1}$, respectively[15]) are not large and in these cases reaction of SO_2^- with the oxidant is rate determining. On the other hand, the rate constant for combination of O_2 with SO_2^- is very high ($k_3 > 10^8\ M^{-1}\ \mathrm{sec}^{-1}$), and consequently the rate of O_2 reduction depends only on the rate of radical production, $2k_2[S_2O_4^{2-}]$. At pH 6.5, $\mu = 0.15\ M$ (25.0°), k_2, the first-order rate constant governing dithionite dissociation into SO_2^-, is 2.5 sec^{-1}; at pH 13, $\mu = 0.10\ M$ (25.0°), $k_2 = 1.8$ sec^{-1}. Thus, depending on the system and conditions used, either the dissociation of dithionite or the reaction of the SO_2^- radical can be rate determining. We may conclude with some confidence, however, that the former situation is the one that obtains in the reaction of dithionite with dioxygen.

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Registry No. $S_2O_4^{2-}$, 14844-07-6; O_2, 7782-44-7; H_2O_2, 7722-84-1.

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(9) In these, 5–15 ml each of stock dithionite and stock air or O_2 solutions loaded in syringes were mixed *via* a short Luer-to-Luer adapter by repeatedly discharging one syringe into the other. The resulting mixture was then loaded into a modified (to contain 20 ml) 1- or 10-mm cell. The no-gas-space mixing procedure was used to minimize introduction or loss of O_2. The large volume cells permitted effectively "leak-free" measurements for times up to ~90 min.

(10) At pH 6.5, $\mu = 0.15\ M$.

(11) In 0.1 M NaOH.

(12) L. G. Sillen, *Chem. Soc., Spec. Publ.*, No. 17, 210 (1964).

(13) C. Creutz and N. Sutin, *Proc. Nat. Acad. Sci. U. S.*, **70**, 1701 (1973).

(14) Although the interpretation of the kinetics of the latter reaction is not free of ambiguities, both studies ascribe an important role to the direct reaction of ferricytochrome c with dithionite; both also demonstrate that the SO_2^- radical is much more reactive than $S_2O_4^{2-}$ toward cytochrome c. However, our observations of the very rapid reaction of dioxygen with dithionite suggest that the Lambeth-Palmer interpretation of the induction period is over-simplified.

(15) These second-order rate constants k' are calculated from the three-halves-order rate constants k using $k' = kK_2^{-1/2}$.

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