Oxidation of Thioethers by Iodine to Sulfoxides. Catalytic Role of Certain Inorganic Nucleophiles[1]

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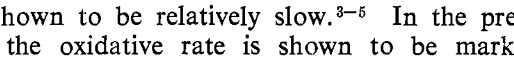
Contribution from the School of Pharmacy, University of Wisconsin, Madison, Wisconsin. *Received June 30, 1966*

Abstract: The rate of oxidation of several thioethers by iodine in aqueous solution has been found to be a complex function of the concentrations of sulfide, iodine, nucleophilic species, and iodide. In the absence of buffer species the rate law agrees with the formulation $-d[RSR']/dt = k[RSR'][(I_2)_{total}]/[H^+][I^-]^2$. In the presence of species such as HPO_4^{2-} the rate has been found, however, to be substantially increased (10^4 times in 0.1 *M* HPO_4^{2-}) and follows the relationship $-d[RSR']/dt = k[RSR'][(I_2)_{total}][HPO_4^{2-}]/[H^+][I^-]^2$ over a limited range. A mechanism is proposed on the basis that the catalyzed reaction probably involves in this instance an oxidative phosphorylative step.

The rate of formation of sulfoxides from the corresponding thioethers by oxidation with free iodine in aqueous solution as represented in eq 1 has



$$R\text{–}S\text{–}R' + I_2 + H_2O \longrightarrow \underset{\overset{\downarrow}{O}}{R\text{–}S\text{–}R'} + 2H^+ + 2I^- \qquad (1)$$

been shown to be relatively slow.[3-5] In the present paper the oxidative rate is shown to be markedly accelerated by certain nucleophiles. The doubly charged anion, HPO_4^{2-}, for example, exhibits a catalytic activity such that the effect of concentrations as low as 1 × 10^{-5} *M* is readily detectable. The behavior of these systems suggests that the observed effect such as in the case of phosphate may occur through an oxidative acylative mechanism.

Results and Discussion

Oxidation in the Absence of Catalytic Buffer Species. Although the rate of oxidation of thioethers by iodine in the absence of catalytic species is relatively slow, these reactions can be conveniently followed for nearly all aliphatic and alicyclic sulfides by determining the amount of acid produced in accordance with eq 1. In the presence of a constant concentration of iodide and hydrogen ions and with a large excess of thioether, the loss of iodine, as reflected in the amount of base required to maintain constant pH, occurred in a simple pseudo-first-order fashion. Since these observed pseudo-first-order rate constants were found to be, as may be expected, directly proportional in all cases to the concentration of the thioethers, it was possible to calculate observed second-order rate constants from these data. Over-all second-order rate constants obtained in this manner for the oxidation of tetramethylene sulfide are shown in Figure 1 at several pH values.[6] The observed second-order rate constant at 25° as defined by the equation

$$k_{\text{obsd}} = \frac{\text{d(mmoles of base consumed per ml)}}{2[R_2S][(I_2)_{\text{total}}]dt}$$

was found to be, for example, 6.2 × 10^{-3} M^{-1} sec^{-1} at pH 5 and 8.0 M^{-1} sec^{-1} at pH 8.3, both in the presence of 0.008 *M* potassium iodide. The total iodine was so designated since it included all related species, *i.e.*, I_2, I_3^-, etc. As is evident from Figure 1, the order with respect to hydroxide ion was very close to one. Although there were 2 equiv of acid produced for each mole of thioether oxidized, the rate dependence suggests that the rate-determining step involved only a single hydroxide ion.

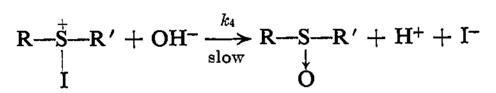
The dependence of the observed rate of the uncatalyzed oxidation of tetramethylene sulfide on iodide concentration can be seen at pH 8.0 in Figure 2. The essentially linear plot passing through the origin obtained when the observed second-order constant (determined with a pH-Stat) was plotted against $1/[I^-]_2$ suggests that the over-all rate is essentially inversely proportional to the second power of the halide ion, at least at higher concentrations of iodide.

A part of the observed iodide dependency can be attributed to the influence of the ion on the activity of free iodine in the system. Since the stability constant for formation of the triodide species from iodine and iodide ion

$$I_2 + I^- \underset{\text{fast}}{\overset{K_1}{\rightleftharpoons}} I_3^- \qquad (2)$$

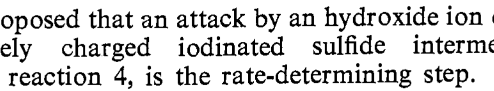
has been shown to be 7.23 × 10^2 M^{-1} at 25°,[7] it is apparent that the concentration of the free halogen in these systems is small and approximately inversely proportional to the iodide concentration even at the lowest level of the halide concentration investigated.

The remaining dependence on the iodide ion can be rationalized on the basis of the following mechanism



$$R\text{–}S\text{–}R' + I_2 \;\underset{\rightleftharpoons\ R\text{–}S(I_2)\text{–}R'\ \rightleftharpoons}{\overset{K_R}{\rightleftharpoons}}\; \underset{\underset{I}{|}}{R\text{–}\overset{+}{S}\text{–}R'} + I^- \qquad (3)$$

fast fast



$$\underset{\underset{I}{|}}{R\text{—}\overset{+}{S}\text{—}R'} + OH^- \xrightarrow[\text{slow}]{k_4} \underset{\overset{\downarrow}{O}}{R\text{—}S\text{—}R'} + H^+ + I^- \qquad (4)$$

It is proposed that an attack by an hydroxide ion on the positively charged iodinated sulfide intermediate, R_2SI^+, reaction 4, is the rate-determining step. Since the concentration of the reactive species R_2SI^+ at constant free iodine activity is inversely proportional

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[1] This research was supported in part by grants from the National Institutes of Health under AM-03437 and GM-05830.

[2] NATO Scholar during the year 1961.

[3] E. Fromm, *Ann.*, **396**, 75 (1913).

[4] W. Steinkopf and S. Müller, *Ber.*, **56**, 1926 (1923).

[5] K. H. Gensch, Dissertation, Freie Universitat Berlin, Germany, 1960.

[6] The formation of tetramethylene sulfoxide in this particular system was verified by extracting the sulfoxide with chloroform from reacted solutions and identifying it by paper chromatographic comparison with tetramethylene sulfoxide.

[7] G. Daniele, *Gazz. Chim. Ital.*, **90**, 1068 (1960).

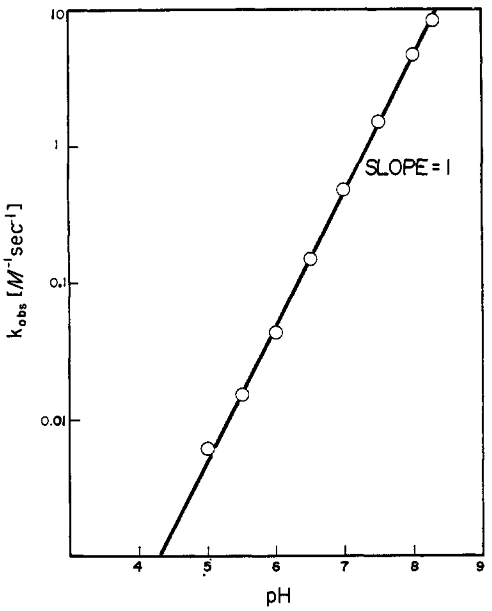

Figure 1. pH profile of the observed second-order rate constants (measured titrimetrically) *vs.* pH for the oxidation of tetramethylene sulfide with iodine in the absence of any buffer. Initial C_4H_8S = 6 to 85 × 10^{-4} *M*; initial total I_2 = 10^{-4} *M*; KI = 8 × 10^{-3} *M*; temp, 25.0°.

to iodide, this phase of the reaction will also be inversely dependent on the halide. It is then apparent that

$$\frac{-d[(I_2)_{\text{total}}]}{dt} = k_{\text{obsd}}[R_2S][(I_2)_{\text{total}}] = k_4[R_2SI^+][OH^-] \quad (5)$$

If we assume $[I^-]$ and $[R_2S]$ to be essentially constant and $[R_2SI^+] \ll [I_2]_{\text{total}}$ (this was justified since the addition of thioethers did not practically decrease the initial absorbance of I_3^- species at 353 mμ) from reactions 2 and 3, an expression for $[R_2SI^+]$ can be obtained

$$[R_2SI^+] = \frac{K_R[R_2S][(I_2)_{\text{total}}]}{K_I[I^-]^2 + [I^-]} \quad (6)$$

Combining eqs 5 and 6, we find

$$k_{\text{obsd}} = \frac{k_4K_R[OH^-]}{K_I[I^-]^2 + [I^-]} \quad (7)$$

Since K_I is relatively large, the square term in the denominator is dominant except at very low iodide concentrations.

At present the formation of an iodosulfonium cation is, admittedly, only supported indirectly by evidence derived from conductivity studies of dimethyl sulfide dibromide in liquid sulfur dioxide which suggest that the halide sulfide complex dissociates to a bromosulfonium cation and a bromide anion.[8]

Oxidation in the Presence of Phosphate. The pronounced influence of phosphate ion on the rate of the reaction is evident in Figure 3 where the apparent over-all second-order rate constants obtained titrimetrically (pH-Stat) are shown for several low concentrations of phosphate ions at pH 6.9 and 0.008 *M* iodide. The extrapolated rate at zero buffer concentration is consistent with the results shown in Figure 1. From the data it appears that the presence of 1 × 10^{-5} *M* phosphate produces approximately a 2-fold increase in oxidation rate.

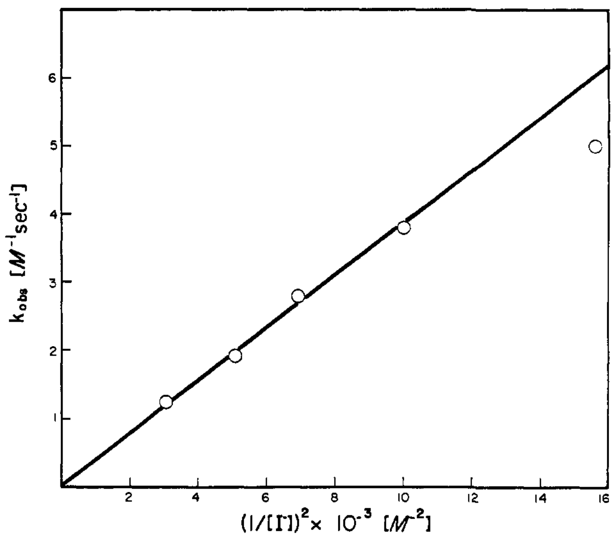

Figure 2. Observed second-order rate constants (measured titrimetrically) *vs.* $(1/[I^-])^2$ for the oxidation of tetramethylene sulfide with iodine in the absence of buffer. Initial C_4H_8S = 5 × 10^{-4} *M*; initial total I_2 = 10^{-4} *M*; pH 8.00; temp, 25.0°.

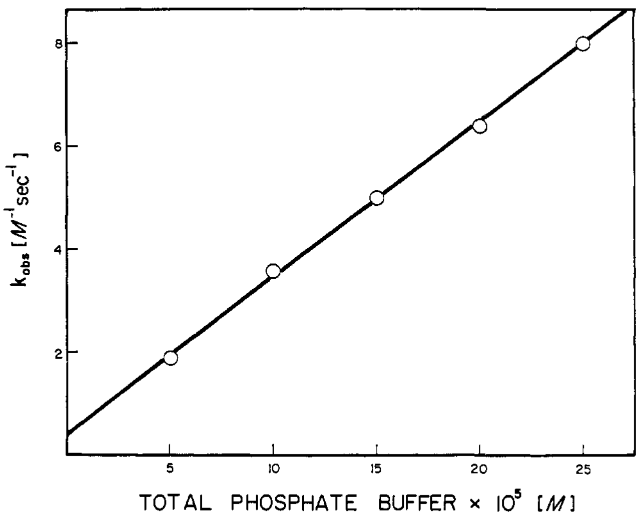

Figure 3. Observed second-order rate constants (measured titrimetrically) *vs.* total phosphate buffer concentration for the oxidation of tetramethylene sulfide with iodine. Initial C_4H_8S = 7 to 38 × 10^{-4} *M*; initial total I_2 = 10^{-4} *M*; KI = 10^{-2} *M*; pH 6.90; temp, 25.0°.

In Figure 4 the rate constants obtained spectrophotometrically by following the disappearance of I_3^- at 353 mμ are shown for higher concentrations of the buffer species. Under these conditions the spontaneous rate becomes insignificant. Two points obtained separately by the pH-Stat method in the presence of low phosphate concentration are shown to fall on the same plot indicating that the same mechanism can be assumed for a wide range of phosphate concentration.

The dependence of the catalytic effect on the nature of the phosphate species is evident in Figure 5, where the observed second-order constant has been plotted against pH for a reaction in the presence of 0.02 *M* phosphate buffer and 0.08 *M* potassium iodide. In the plot the dotted line represents values calculated from above the limiting rate at pH 9.0 and the measured pK_{a_2} of phosphoric acid (6.77) on the basis that only HPO_4^{2-} was the effective catalytic species (in presence

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[8] H. Böhme and E. Boll, *Z. Anorg. Allgem. Chem.*, **17**, 290 (1957).

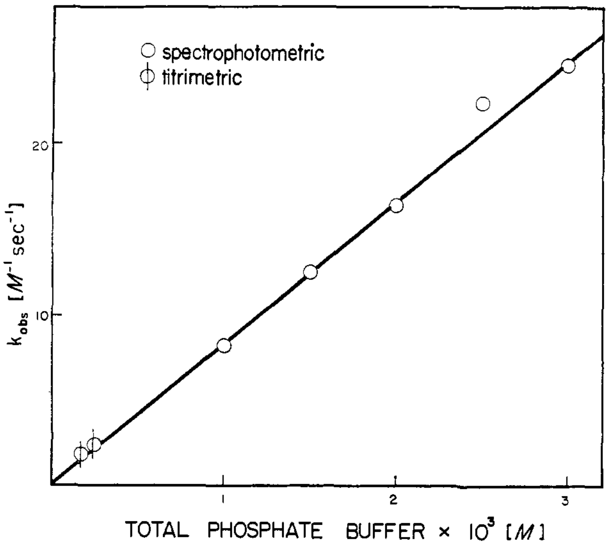


Figure 4. Observed second-order rate constants (measured titrimetrically and spectrophotometrically) *vs.* total phosphate buffer concentration for the oxidation of tetramethylene sulfide with iodine. Initial C_4H_8S = 5 × 10^{-4} *M;* initial total I_2 = 10^{-4} *M;* KI = 0.02 *M;* pH 7.00; temp, 25.0°.

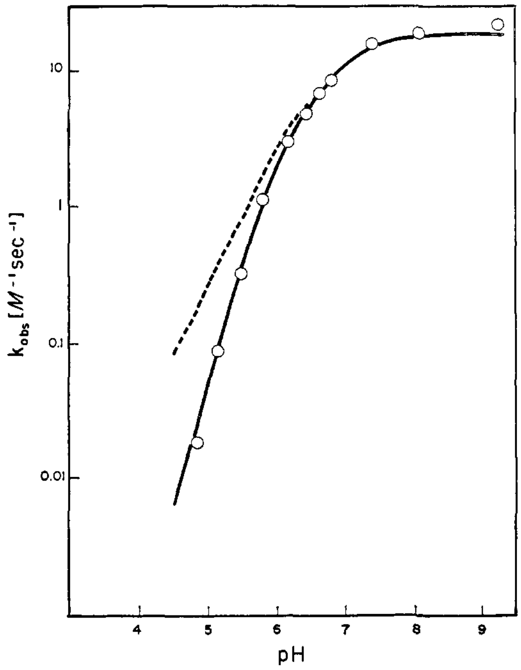


Figure 5. Observed second-order rate constants (determined spectrophotometrically) for oxidation of tetramethylene sulfide with iodine at constant iodide (0.08 *M*), ionic strength of 0.14 *M* and total phosphate of 0.02 *M*. The dotted line corresponds to the pH profile of HPO_4^{2-} species normalized to fit the rate constant at pH 8.0. The solid line represents the pH profile predicted on the basis of reactions 8–12 fitted to best fit C_1 and C_2 values following eq 17. Initial C_4H_8S = 5 to 80 × 10^{-4} *M;* initial total I_2 = 0.2 to 1 × 10^{-4} *M;* KI = 0.08 *M;* ionic strength = 0.14; pK'_a of H_3PO_4 = 6.77; temp, 25°.

of 0.08 *M* KI the reaction with hydroxide ions can be neglected).

It is evident that the data obtained above pH 6.5 are quite consistent with the proposal that the doubly charged anion is the catalytic species. In the lower pH range the departure from the calculated values was, however, much greater than can be expected. This behavior was accompanied by a change in the observed iodide dependence of the reaction as is shown in Table I, which summarizes the results of five series of rate studies carried out at several constant pH values.

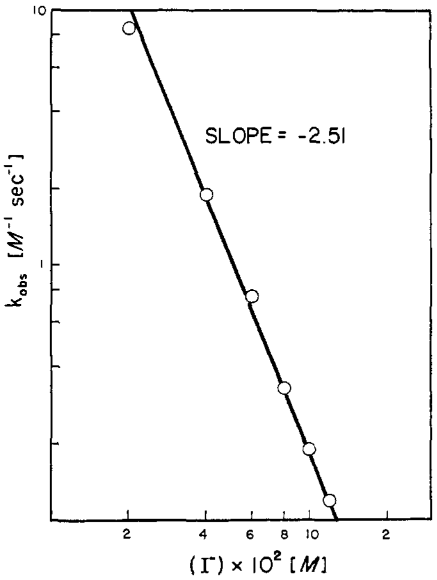


Figure 6. Log-log plot of observed second-order rate constants *vs.* iodide concentration for the oxidation of tetramethylene sulfide with iodine in the presence of phosphate buffer at pH 5.46. Experimental conditions: see Figure 8.

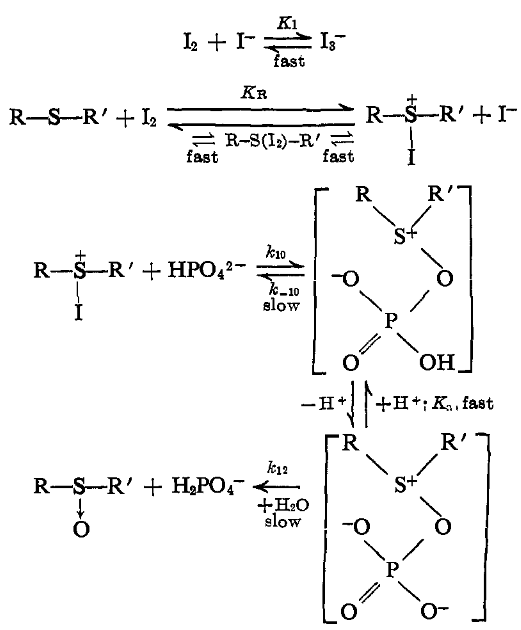
Table I. Rate Dependence on Iodide Concentration for the Oxidation of Tetramethylene Sulfide in the Presence of Phosphate Buffer at Several pH Values[a]

pH	Slope of log k_{obsd} *vs.* log [I^-]
7.80	−2.0
6.74	−1.9
5.93	−2.3
5.46	−2.5
5.28	−2.6

[a] For experimental conditions, see Figure 6.

In each set of experiments reported in Table I the iodide concentration was changed and the logarithms of the observed second-order rate constants were plotted *vs.* the logarithms of the iodide concentration. A typical plot is shown in Figure 6. The slope of each line thus obtained is given in the second column of the table and represents approximately the effective iodide dependence of the oxidative rate at these particular pH values. The data suggest that the iodide dependence changes with decreasing pH from $1/[I^-]^2$ toward $1/[I^-]^3$.

The rates of iodine oxidation of diethyl sulfide and 4-methylthiobutyric acid showed similar dependence on phosphate, iodide, and hydrogen ion concentrations. On the basis of these observations the tentative overall mechanism, eq 8–12, is proposed for the oxidation of sulfides with iodine in the presence of phosphate. In the proposed mechanism reactions 8 and 9 are identical with reactions 2 and 3 and provide an explanation for the observed rate being inversely proportional at least to the square of the iodide concentration. The observed change of the iodide dependence from inverse



$$I_2 + I^- \underset{\text{fast}}{\overset{K_I}{\rightleftharpoons}} I_3^- \quad (8)$$

(9)

(10)

(11)

(12)

square toward inverse cube with decreased pH can be rationalized on the basis of eq 10 and 11. Reaction 10 can be considered as proceeding largely in the forward direction only at lower iodide levels and higher pH values. With decreasing pH a greater proportion of the phosphorylated sulfonium compound stays in the acid form, which can react reversibly with iodide according to reaction 10. The postulated reverse reaction is offered as the reason for the observed change in the dependence of the over-all rate on the iodide concentration from $1/[I^-]^2$ toward $1/[I^-]^3$; reaction 12 under these circumstances will then become rate determining.

On the basis of the proposed mechanism the following expression for the observed second-order rate constant can be formulated. The over-all rate is given by

$$\frac{-d[(I_2)_{total}]}{dt} = \frac{d[R_2SO]}{dt} = k_{obsd}[R_2S][(I_2)_{total}] = k_{12}[R_2S\cdot PO_4^-][H_2O] \quad (13)$$

Applying the steady-state treatment to reactions 10 and 11, we obtain

$$\frac{d\{[R_2S\cdot PO_4H] + [R_2S\cdot PO_4^-]\}}{dt} = k_{10}[R_2SI^+][HPO_4^{2-}] - k_{-10}[R_2S\cdot PO_4H][I^-] - k_{12}[R_2S\cdot PO_4^-][H_2O] = 0 \quad (14)$$

Solving for $[R_2S\cdot PO_4^-]$ we find

$$[R_2S\cdot PO_4^-] = \frac{k_{10}[R_2SI^+][HPO_4^{2-}]}{\dfrac{k_{-10}[I^-][H^+]}{K_a} + k_{12}[H_2O]} \quad (15)$$

where K_a is the dissociation constant of the phosphorylated sulfonium compound. From eq 6 the term $[R_2SI^+]$ can be substituted into eq 15. The resulting expression for $[R_2S\cdot PO_4^-]$ is substituted into eq 13 to give

$$k_{obsd} = \frac{[HPO_4^{2-}]}{\left(\dfrac{k_{-10}K_I[H^+][I^-]^3}{k_{10}k_{12}K_aK_R[H_2O]} + \dfrac{K_I[I^-]^2}{k_{10}K_R}\right)\left(1 + \dfrac{1}{K_I[I^-]}\right)} \quad (16)$$

Combining the constants in the denominator, we set $C_1 = (k_{-10}K_I)/k_{10}k_{12}K_aK_R[H_2O]$ and $C_2 = K_I/k_{10}K_R$, and obtain the following relationship

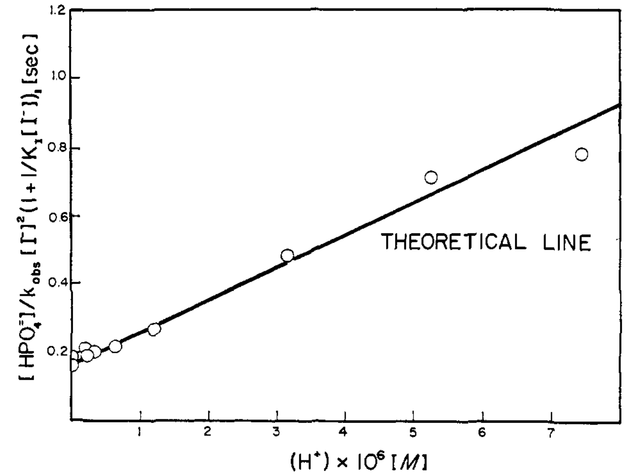


Figure 7. A plot based on eq 18. $[HPO_4^{2-}]/[k_{obsd}[I^-]^2(1 + 1/K_I[I^-])]$ has been plotted *vs.* $[H^+]$ using data of Figures 5 and 8. The theoretical curve was calculated from eq 18 and the constants given in Figure 5.

$$k_{obsd} = \frac{[HPO_4^{2-}]}{(C_1[H^+][I^-]^3 + C_2[I^-]^2)\left(1 + \dfrac{1}{K_I[I^-]}\right)} \quad (17)$$

which can usefully be rearranged to

$$\frac{[HPO_4^{2-}]}{k_{obsd}[I^-]^2\left(1 + \dfrac{1}{K_I[I^-]}\right)} = C_1[I^-][H^+] + C_2 \quad (18)$$

A fair agreement of these rate expressions with the observed second-order rate constants can be seen in Figures 5, 7, and 8. In these graphs the points represent experimentally determined values while the solid lines were calculated from eq 17 and 18, respectively, by substituting the known concentrations of secondary phosphate, hydrogen ion, and iodide into these equations. The constants $C_1 = 1.2 \times 10^6\ M^{-2}$ sec and $C_2 = 0.17$ sec were selected by trial and error to provide the best fit with the data from the plots. Figure 5 represents a check of eq 17. A more sensitive test of the relationship between the apparent second-order rate constant and the hydrogen ion concentration is shown in Figure 7, where the reciprocal of the observed rate constant multipled by the ratio $[HPO_4^{2-}]/([I^-]^2(1 + 1/K_I[I^-]))$ has been plotted *vs.* the hydrogen ion concentration according to eq 18. In spite of the 100-fold change of the hydrogen ion concentration and the experimental error inherent in estimating the ratio $[HPO_4^{2-}]/([I^-]^2(1 + 1/K_I[I^-]))$ the determined values lie essentially on the predicted straight line. The observed dependence of the rate constants on the change of the iodide concentration measured at five different pH values is compared in Figure 8 with the expected dependence according to eq 18. These experiments were carried out as already described in discussing Table I and tend to confirm the proposed mechanism.

Oxidation in the Presence of Other Inorganic Nucleophiles. The catalytic effects of several other inorganic bases are compared with that of phosphate in Figure 9. Rate profiles at 25° obtained with tetramethylene sulfide and 0.01 *M* sodium carbonate, sodium pyro-

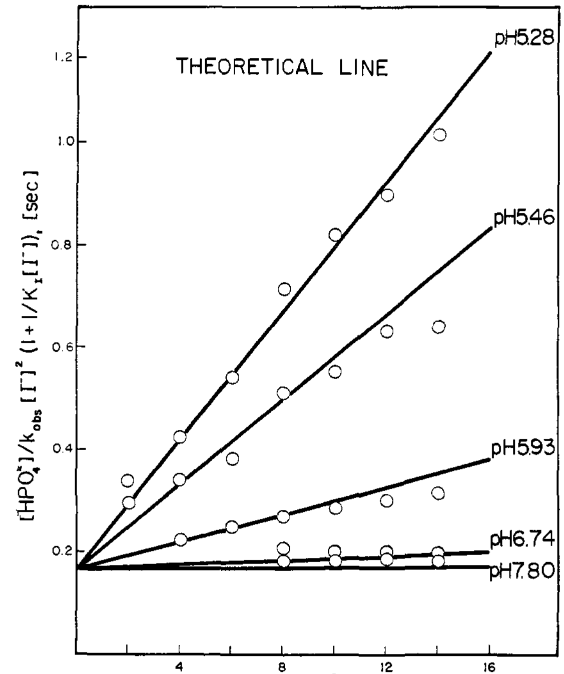


Figure 8. A plot based on eq 18. $[HPO_4^{2-}]/[k_{obsd}[I^-]^2(1 + 1/K_I[I^-])]$ has been plotted *vs.* $[I^-]$; experimental conditions: see Figure 5, except ionic strengths = 0.2 and pK'_{a_2} of H_3PO_4 = 6.70. The theoretical curve was calculated from eq 18 and the constants given in Figure 5.

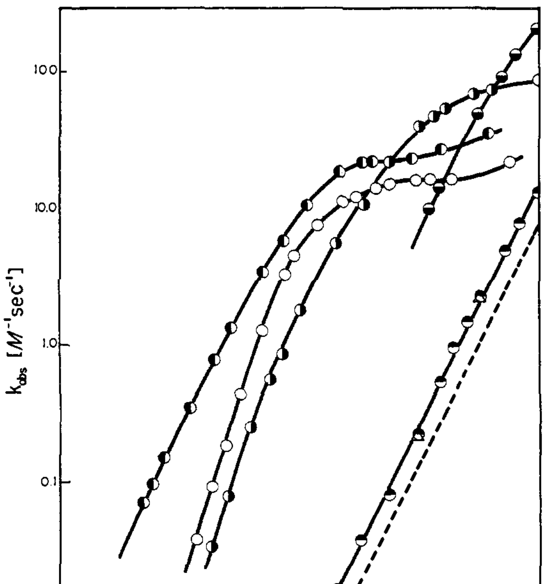


Figure 9. Observed second-order rate constants (measured spectrophotometrically) *vs.* pH for the oxidation of tetramethylene sulfide with iodine in the presence of 0.01 *M* inorganic buffers: ◐, arsenate; ◓, borate; ◒, carbonate; O, phosphate; ◑, pyrophosphate; △, extrapolated from Figure 10; ------- calculated from Figure 1. Initial C_4H_8S = 5 to 80 × 10^{-4} *M;* initial total I_2 = 0.25 to 1 × 10^{-4} *M;* KI = 0.06 *M;* temp, 25.0°

phosphate, sodium arsenate, sodium phosphate, and sodium borate buffers in the presence of 0.06 *M* potassium iodide are shown in the figure.

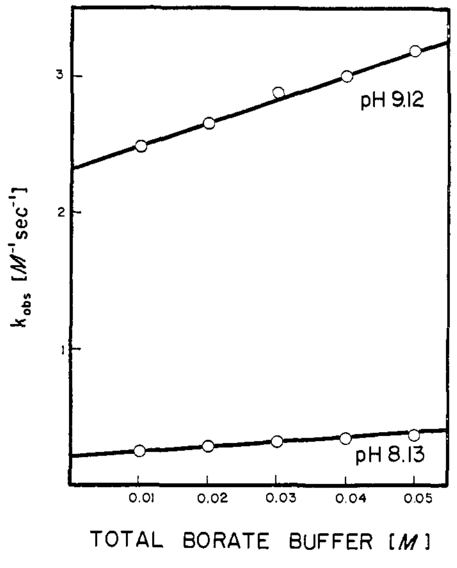


Figure 10. Observed second-order rate constants (measured spectrophotometrically) *vs.* total borate buffer concentration for the oxidation of tetramethylene sulfide with iodine at several pH values. Initial C_4H_8S = 1 to 2.5 × 10^{-3} *M;* initial total I_2 = 2.5 × 10^{-5} *M;* temp, 25.0°.

The shapes of the arsenate and pyrophosphate profiles closely resemble that of the phosphate, the catalytic activity again being closely associated with a particular form of each buffer. The doubly ionized arsenate species and the tetraionized pyrophosphate species appear to largely account for observed effects, the catalytic activities essentially reaching a plateau at pH values above pH 6.60 (pK_{a_2} for arsenic acid) and pH 8.41 (pK_{a_4} for pyrophosphoric acid) for the two buffers, respectively.

The pH profile in the presence of carbonate buffer was determined only up to pH 10 because in more alkaline solutions formation of hypoiodite would be expected to interfere with the determination. Since the pK_{a_2} of carbonate in this system is approximately 10, the high catalytic activity can only be associated with the doubly charged species CO_3^{2-}.

The low catalytic activity of borate is evident not only in Figure 9 but also in Figure 10 where the observed second-order rate constants determined in 0.06 *M* potassium iodide and at pH 8.13 and 9.12 have been plotted against several borate buffer concentrations. From the slope and the intercept the second-order rate constants attributable to both the $B(OH)_4^-$ species and hydroxide ion can be calculated. The latter values presented in Figure 9 as Δ are about twice as high as the corresponding values of the dotted line which was calculated from the pH profile in the absence of any buffer (Figure 1) considering the rate to be inversely proportional to the square of the iodide concentration. This difference may be caused by the difference in procedures, a 7.5-fold change in iodide concentration, or possibly some impurities of carbonate in the more concentrated solutions.

The pH profiles shown in Figure 9 indicate relative catalytic activities of the different buffer species of 25:6:1.5:1:0.025 for carbonate, tetraionized pyrophosphate, doubly ionized secondary arsenate, doubly ionized phosphate, and singly ionized borate species. It is evident that the catalytic activity increased gener-

Table II. Dependence of Observed Second-Order Rate Constant in the Presence of Pyrophosphate Buffer on Sodium Ion Concentration. Rate of Oxidation of Tetramethylene Sulfide[a]

Na^+, M	pH	k_{obsd}, M^{-1} sec^{-1}
0.04	8.64	255
0.06	8.56	210
0.08	8.49	185
0.10	8.40	160
0.12	8.34	135

[a] Initial total tetramethylene sulfide = 5×10^{-4} M; initial total I_2 = 2.5×10^{-5} M; total pyrophosphate buffer = 0.005 M; ionic strength maintained at 0.145 with tetramethylammonium chloride; k_{obsd} measured spectrophotometrically; temp, 25.0°.

ally with increasing basicity of the nucleophiles; however, in the case of arsenate this relationship does not hold. The species $HAsO_4^{2-}$ is a weaker base than HPO_4^{2-} but shows a slightly higher catalytic activity than the phosphate species.

The triply charged species $HP_2O_7^{3-}$ appeared to be much less catalytically active than the anions HPO_7^{2-} and $P_2O_7^{4-}$. This observation may be rationalized at least in part on the basis of observed hydrogen bond[9] formation between the phosphate groups in the $HP_2O_7^{3-}$ species.

Since the species $P_2O_7^{4-}$ has been shown to form complexes[10] with Na^+ and K^+, its catalytic activity may be expected to be strongly influenced by the presence of these ions. Experimental support of such an effect can be seen in Table II which shows some observed second-order rate constants in the presence of constant pyrophosphate buffer but at several sodium chloride concentrations.

The ionic strength was maintained constant with tetramethylammonium chloride. The rate decreases considerably with an increase of the sodium concentration; the exact catalytic activity, however, was not determined because of the complexity of the system resulting from the change in pH with changing sodium concentration.

Experimental Section

Reagents. Tetramethylene sulfide (impurities 0.05 ± 0.05 mole %) were obtained as a specially purified sample from the U. S. Bureau of Mines, Laramie, Wyo.[11] Commercial tetramethylene sulfide purified by passage over neutral aluminum oxide (activity I, Woelm) followed by fractionation in a spinning-band column yielded essentially the same rate constant. All other chemicals were reagent grade. Water was purified by redistilling tap-distilled water from potassium permanganate solution acidified with sulfuric acid.

Rate Studies. In general usual spectrophotometric procedures commonly employed for rate measurements were followed. For slower runs reactants were mixed separately and then poured into the spectrophotometric cell. For faster reactions the solutions were mixed directly by injection in the cell.

All pH measurements were made to 0.01 unit. For pH-Stat rate determinations special precautions were taken to exclude atmospheric carbon dioxide and were carried out under nitrogen.

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[9] J. A. Wolhoff and J. T. G. Overbeek, *Rec. Trav. Chim.*, **78**, 759 (1959).

[10] G. Schwarzenbach and J. Zurc, *Monatsh.*, **81**, 202 (1950).

[11] The authors wish to thank the U. S. Department of Interior, Bureau of Mines, for generously providing these samples.

The Oxidation of Carbanions. I. Oxidation of Triaryl Carbanions and Other Tertiary Carbanions[1]

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Received July 27, 1966

Abstract: The rate of oxidation of triphenylmethane in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) solution is shown to be equal to the rate of ionization of the hydrocarbon to the carbanion. The oxidation reaction is rate controlled by the ionization process. Some evidence is presented to indicate that the rapid process by which the carbanion is consumed is of a free radical or electron-transfer nature. The ionization of triphenylmethane in the solvent employed is first order in hydrocarbon and in potassium *t*-butoxide. The base appears to be completely dissociated in this solvent system. The deuterium isotope effect in the ionization is 9.5 at 25°. The effects of structure and solvents on the products and rates of oxygenation of some other tertiary carbanions are considered.

The reaction of molecular oxygen with tertiary benzylic anions has not been extensively studied. It is potentially a very simple reaction of some synthetic utility because the only expected oxidation products are the hydroperoxide or the carbinol.

$$R_3C:^- + O_2 \longrightarrow R_3COO:^-$$

$$R_3COO:^- + R_3C:^- \longrightarrow 2R_3CO:^-$$

Thus, it was found possible to convert *p*-nitrocumene in dimethyl sulfoxide (DMSO) solutions containing potassium *t*-butoxide to the carbinol by reaction with oxygen at room temperature.[3] Tris(*p*-nitrophenyl)-methane has been converted to a mixture of the hydroperoxide, alcohol, and *p*-nitrophenol by reaction with oxygen in ethanolic potassium hydroxide solution,[4] by a process that shows many characteristics of a

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[1] Reactions of Resonance Stabilized Anions. XXIV. Work supported by grants from the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society.

[2] National Science Foundation Predoctoral Fellow, 1963–1966.

[3] G. A. Russell, A. J. Moye, E. G. Janzen, S. Mak, and E. R. Talaty, *J. Org. Chem.*, in press.