

# RATE LAWS AND MECHANISMS OF OXYANION REACTIONS WITH BASES<sup>1</sup>

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## I. INTRODUCTION

In recent years the trend in the interpretation of rate laws with orders greater than 2 has been to formulate the mechanisms of these reactions as a series of uni-, bi-, and ter-molecular steps. This idea merits serious consideration, for it enables simple explanations to be applied to complex reactions, especially those of inorganic anions. As a result of this trend in differentiation between order and molecularity (55, 124), many new chemical intermediates have been postulated for the rapid equilibria before the rate steps. Review papers of interest have been written by Abel (3), Bray (43), Day and Ingold (57), Forbes (80), Gillespie and Millen (92), Hinshelwood (110), de la Mare (140), Price (155), Westheimer (187), and Williams (191).

In the reactions of inorganic oxyanions catalyzed by hydrogen ions, the intermediate most often proposed has been an electron acceptor (an acid of the

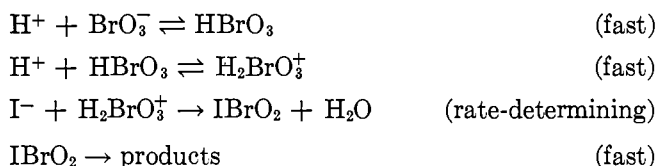
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Lewis kind) formed by reaction of an oxyanion with protons. This article is made up of a tabulation of the rate laws of inorganic oxyanions with donor particles (bases in the Lewis sense) and a discussion of many of the recently investigated reactions in terms of bimolecular equilibria, acceptor intermediates, and complex particles formed by the acceptor intermediate and a donor. In Section II four basic types of reaction kinetics and the reactions fitting each type are presented. Section III deals with certain lines of evidence for the existence of the postulated intermediates, while Section IV covers recent developments in the kinetics of inorganic anion reactions.

The reactions of the oxyanions with electron donors when catalyzed by hydrogen ions follow patterns which are suggestive of an oxide ion being taken off the oxyanion by the protons. Since oxyanions have a large amount of resonance stabilization (153), it is necessary to overcome this stability in order that a chemical reaction take place. On the addition of hydrogen ions, the oxyanions are converted to less stable forms (152), which can then react with other chemical entities.

In the following example, the oxidation of iodide by bromate, the rate law is of the first order in each of the reactant concentrations and of the second order in hydrogen-ion concentration. The mechanism proposed in this article is



in which the rate-determining step is the collision of an iodide ion and the "super-acid" ion  $\text{H}_2\text{BrO}_3^+$  or the anhydrous acceptor form  $\text{BrO}_2^+$ . In this article the hydrated form will be employed in nearly all of the equations, although there are cases which are better fitted by the anhydrous form and the anhydrous form is known to exist for many of the oxyanions.

Primary consideration is being given to the oxyanions and their respective acids; the halogen reactions will be included in some instances, for they form the hypohalous acids and halogen cations by rapid equilibria. Some reactions of oxyanions with organic donors will be included in order to supplement the main idea. The Lewis base (electron donor) will be designated as the "donor" and will be represented by the symbol  $\text{B}^z$ . The oxyanion will be designated as such and will be symbolized by  $\text{AO}_m^-$ . The Lewis acid formed from the oxyanion will be called the "acceptor."

The term "stability" in reference to equilibrium intermediates is used to denote a short, but finite, time of existence for the particle, which is assumed to have the properties of a chemical species. The word "complex" will not denote the transition state (the activated complex), but will be used for the stable intermediate formed by a donor and an acceptor.

In the rate equations  $R$  stands for the absolute rate of change in reactant concentration with time and  $k$  for the rate constant. Brackets are used to denote concentrations. The form of some rate laws in the tables and discussions

is, of necessity, different from the form found in the original literature. In no case, however, have the basic kinetic patterns been altered, for the only changes made involve known, rapid equilibria such as proton transfer and halogen hydrolysis.

## II. TYPES OF RATE EQUATIONS AND THE CORRESPONDING MECHANISMS

### A. The first type of rate law

This type of rate equation is of the first order in the concentration of oxyanion, of donor, and of hydrogen ion. It is a well-known fact that two ions whose

TABLE 1  
Reactions fitting the first rate law

OXYANION	DONOR	ORDER IN [H <sup>+</sup> ]	REFERENCES	REMARKS
<i>Group I:</i>				
OBr <sup>-</sup> .....	C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	1	(139)	CO <sub>2</sub> formation
OBr <sup>-</sup> .....	Anisoate ion	1	(63)	Bromination
OCl <sup>-</sup> .....	Br <sup>-</sup>	1	(77)	HOBr formation
OCl <sup>-</sup> .....	NH <sub>3</sub> , CH <sub>3</sub> NH <sub>2</sub>	1	(186)	Chloramine formation
OCl <sup>-</sup> .....	Cl <sup>-</sup>	1	(150)	Cl <sub>2</sub> formation
OI <sup>-</sup> .....	Phenoxide ion	1	(125)	Iodination of certain phenols
BrO <sub>3</sub> <sup>-</sup> .....	S <sub>2</sub> O <sub>3</sub> <sup>-</sup>	1	(73)	Oxidation of S <sub>2</sub> O <sub>3</sub> <sup>-</sup>
<i>Group II:</i>				
HCrO <sub>4</sub> <sup>-</sup> .....	N <sub>2</sub> H <sub>5</sub> <sup>+</sup>	1	(164)	Oxidation of hydrazine
HCrO <sub>4</sub> <sup>-</sup> .....	2-Propanol	1	(112)	Oxidation to acetone
HCrO <sub>4</sub> <sup>-</sup> .....	S <sub>2</sub> O <sub>3</sub> <sup>-</sup>	1	(73)	Oxidation of S <sub>2</sub> O <sub>3</sub> <sup>-</sup>
HCrO <sub>4</sub> <sup>-</sup> .....	I <sup>-</sup>	1	(21, 58)	Oxidation of I <sup>-</sup>
HSO <sub>3</sub> <sup>-</sup> .....	IO <sub>3</sub> <sup>-</sup>	1	(151)	Oxidation of SO <sub>2</sub>
HSO <sub>3</sub> <sup>-</sup> .....	IO <sub>3</sub> <sup>-</sup>	1	(176)	Oxidation of SO <sub>2</sub>
HCO <sub>3</sub> <sup>-</sup> .....	H <sub>2</sub> O	1	(147)	Oxygen isotope exchange
HSO <sub>4</sub> <sup>-</sup> .....	Aromatics	1	(53)	Sulfonation by SO <sub>3</sub>

charges have the same sign can join in the rate-determining step of a reaction; an example of this is the displacement of bromide from bromoacetate by thio-sulfate. Many other reactions between ions of like charge are catalyzed by ions of opposite charge, and proton catalysis of anionic reactions might be tentatively ascribed to this phenomenon. For an oxyanion whose charge is  $-n$ , the catalysis by hydrogen ion should be of the  $n^{\text{th}}$  order, and the observed rate law would be

$$R = k_1[\text{AO}_m^{-n}][\text{B}^z][\text{H}^+]^n$$

(if B<sup>z</sup> were an ion of negative charge). In table 1, in which there are two groups of reactions, some rate laws which might fit the equation are presented. It is seen, however, that  $x$  may be +1, 0, -1, or -2, whereas only those cases where  $x$  was negative would be expected to show proton catalysis if electrostatic repulsion were the major factor. Therefore, there is little basis for accepting this explanation for proton catalysis.

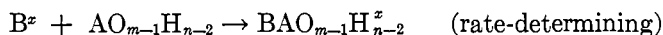
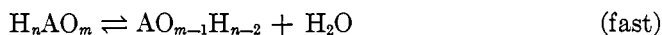
The Group I reactions, all but one of which involve hypohalite ions, contain

anions which are univalent when all replaceable protons are off, whereas the Group II reactions involve polybasic anions. In the former group, the mechanism postulated is



and the rate step is believed to be the nucleophilic displacement of a hydroxyl ion by the donor from the oxy acid, with a water molecule acting as a general acid to catalyze the displacement of the hydroxyl ion.

For the second group of reactions (involving polybasic anions), the postulated rate-determining step is the nucleophilic displacement of a water molecule by the donor. An alternative possibility has the following mechanism:



These two mechanisms differ only slightly, and are, in fact, merely variations of one basic type. The reactions of acid chromate ion are good evidence for this type of mechanism, for the rate laws are similar with iodide ion, thiosulfate ion, hydrazone ion, and 2-propanol as donors. This lack of dependence on the donor seems to be quite general in the rate laws of inorganic oxyanions.

#### *B. The second type of rate law*

The example presented in the introduction belongs to this type. It will be noted that there is one more hydrogen ion in the rate law than is needed for overcoming repulsion between two univalent negative ions. As in the previous type, the fundamental nature of hydrogen-ion catalysis is believed to lie in the alteration of the basic properties of an oxide ion in the oxyanion as successive protons are added (152). The oxide ions in oxyanions are held to the central atom by their strong basicity and by the double-bond resonance stabilization (153). Addition of one proton to form a hydroxide ion somewhat lowers the basic nature of the oxygen and decreases the resonance stabilization markedly (152). It is postulated that a second proton changes the hydroxide ion to the weak base water, thereby forming a place for easy substitution by another donor.

As before, the reactions are subdivided into two groups; the first is made up of those with monobasic anions and the second is concerned with polybasic anions. The postulated mechanism for the first group is

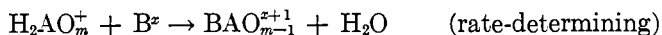


TABLE 2  
Reactions fitting the second rate law

OXYANION	DONOR	ORDER IN [H <sup>+</sup> ]	REFERENCES	REMARKS
<i>Group I:</i>				
HOCl	Cl <sup>-</sup>	1†	(167, 177)	Formation of Cl <sub>2</sub>
HOCl	Aromatics	1	(63, 64)	Chlorination; also bromination
HOCl	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	1*	(102)	CO <sub>2</sub> formation
HOBr	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	1*	(104, 139)	CO <sub>2</sub> formation
HOI	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	1*	(103)	CO <sub>2</sub> formation
HOI	H <sub>2</sub> AsO <sub>3</sub> <sup>-</sup>	1*	(39, 127, 150, 193)	Reverse of arsenate-iodide reaction
HOI	Formate ions	1	(65)	Oxidation to CO <sub>2</sub>
HOI	Aniline	1	(30)	Iodination
HOI	Phenoxide ions	1	(125)	Iodination
HClO <sub>2</sub>	ClO <sub>2</sub> <sup>-</sup>	1*	(19, 183)	Disproportionation
HBrO <sub>2</sub>	Br <sup>-</sup>	1	(198)	Halide oxidation
ClO <sub>3</sub> <sup>-</sup>	Br <sup>-</sup>	2	(111)	Halide oxidation
ClO <sub>3</sub> <sup>-</sup>	I <sup>-</sup>	2	(37, 40, 41)	Halide oxidation
BrO <sub>3</sub> <sup>-</sup>	Br <sup>-</sup>	2	(49, 118, 175)	Halide oxidation
BrO <sub>3</sub> <sup>-</sup>	I <sup>-</sup>	2	(49)	Halide oxidation
IO <sub>3</sub> <sup>-</sup>	H <sub>2</sub> O <sub>2</sub>	2	(154)	Reduction of iodate
NO <sub>2</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	2*	(114)	Formation of N <sub>2</sub> O <sub>5</sub> in nitrosation
NO <sub>2</sub> <sup>-</sup>	I <sup>-</sup>	2	(110)	Formation of I <sub>2</sub>
NO <sub>2</sub> <sup>-</sup>	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	2	(72)	Oxidation of S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>
HNO <sub>2</sub>	NH <sub>3</sub> , CH <sub>3</sub> NH <sub>2</sub>	1	(70)	N <sub>2</sub> formation
HNO <sub>2</sub>	NO <sub>2</sub> <sup>-</sup>	1	(6, 7, 8, 9)	N <sub>2</sub> O <sub>4</sub> formation
HNO <sub>2</sub>	BrO <sub>3</sub> <sup>-</sup>	1	(135)	Oxidation of NO <sub>2</sub> <sup>-</sup>
HNO <sub>2</sub>	ClO <sub>3</sub> <sup>-</sup>	1	(135)	Oxidation of NO <sub>2</sub> <sup>-</sup>
Organic acid	HOH	1	(157)	Isotope exchange
HNO <sub>3</sub>	Aromatics	1	See later section	Nitration by NO <sub>2</sub> <sup>+</sup>
<i>Group II:</i>				
HCrO <sub>4</sub> <sup>-</sup>	H <sub>2</sub> AsO <sub>3</sub>	2	(58, 59, 187)	Oxidation to arsenate
HCrO <sub>4</sub> <sup>-</sup>	2-Propanol	2	(112, 187)	Oxidation to acetone
H <sub>2</sub> SeO <sub>3</sub>	Acetone	1	(68)	Specific oxidation of carbon
H <sub>2</sub> OsO <sub>5</sub>	Br <sup>-</sup>	1	(119)	Oxidation to Br <sub>2</sub>
H <sub>3</sub> AsO <sub>4</sub>	I <sup>-</sup>	1	(39, 127, 161, 184)	Oxidation to I <sub>2</sub>
O <sub>3</sub>	Cl <sup>-</sup>	1‡	(196)	
H <sub>2</sub> O <sub>2</sub>	I <sup>-</sup>	1‡	(132)	
H <sub>2</sub> O <sub>2</sub>	Br <sup>-</sup>	1‡	(148)	
H <sub>2</sub> O <sub>2</sub>	Cl <sup>-</sup>	1‡	(148)	
H <sub>2</sub> O <sub>2</sub>	OI <sup>-</sup>	1*‡	(129, 130)	
H <sub>2</sub> O <sub>2</sub>	OCl <sup>-</sup>	1*‡	(51, 134, 138)	Not conclusive
H <sub>2</sub> O <sub>2</sub>	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	1‡	(1)	
H <sub>2</sub> O <sub>2</sub>	IO <sub>3</sub> <sup>-</sup>	1‡	(45, 128)	
H <sub>2</sub> O <sub>2</sub>	BrO <sub>3</sub> <sup>-</sup>	1	(44, 198, 199)	
H <sub>2</sub> O <sub>2</sub>	OBr <sup>-</sup>	1*	(18, 46, 133, 198)	
H <sub>2</sub> SO <sub>4</sub>	Aromatics	1	(35, 36, 155)	Sulfonation by HSO <sub>3</sub> <sup>+</sup>

\* The rate laws reported in the literature have the form

$$R = k[\text{H}_n\text{AO}_m][\text{HB}^{z+1}]$$

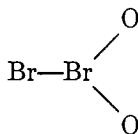
as the donor is strong enough in these examples to have a known undissociated acid.

‡ Morris (144) assumes this reaction to have the rate law:

$$\frac{d[\text{Cl}_2]}{dt} = k_1[\text{HOCl}][\text{Cl}^-] - k_2[\text{Cl}_2][\text{OH}^-]$$

‡ These eight reactions show a second rate term which is of zero order in [H<sup>+</sup>]. A similar rate law independent of acidity is found for the reactions of peroxide with hydrazine (94) and ozone (174), and of ozone with bromide ion (173).

This mechanism is analogous to that given for the second group of the type 1 reactions, as the rate step is the displacement of a water molecule from the acceptor intermediate or the addition of the donor to the anhydrous form of the intermediate ( $\text{AO}_{m-1}^+$ ). The complex ( $\text{B}\cdot\text{AO}_{m-1}^{z+1}$ ) may exist as an equilibrium intermediate, for in some cases it is approached from both sides. The bromate-bromide reaction (and the reverse reaction) is a fine example, and the postulated donor-acceptor intermediate is



In the balance of the cases, the complex presumably decomposes rapidly after formation.

The reactions of this second type are presented in table 2. In comparison with the number of reactions in table 1, the number here is surprising, particularly since the  $n + 1$  hydrogen ion plays no part in overcoming electrostatic repulsion. The concept of the acid-base complex as an intermediate is strengthened by the large number of applicable cases.

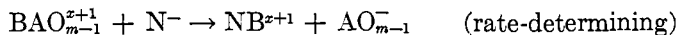
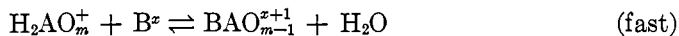
The second group of reactions for this type of rate law presents a complicated picture. Explanation for some of these reactions will be given in the final sections.

### C. The third type of rate law

With this type, serious complexities appear in the rate laws; however, the equations can be correlated and simplified to some degree. These reactions are most interesting subjects for speculation when they are considered as an extension of the second type. The generalized rate law is

$$R = k_3[\text{AO}_m^-][\text{B}^z][\text{H}^+]^{n+1}[\text{N}^-]$$

where  $\text{N}^-$  is a nucleophilic ion or particle. In some of the cases given in table 3 the following mechanism can be postulated:



Certain of these reactions will be covered in more detail later.

As will be seen in Section III, this type of rate law is excellent evidence for the presence of donor-acceptor complexes in these rate laws. In order to give a reasonable explanation to these fifth-order rate equations, it is quite necessary to bring in some form of intermediate before the rate-determining step. The different particles which act as  $\text{N}^-$  are given in the third column of table 3.

## D. The fourth type of rate law

This type is believed to be an extension of the previous type, for the rate law is of the sixth order. There are only two examples, both of which are oxidations by iodate ion. The iodide oxidation was studied indirectly through the iodine

TABLE 3  
Reactions fitting the third rate law

OXYANION	DONOR	N <sup>-</sup>	ORDER IN [H <sup>+</sup> ]	REFERENCES	REMARKS
IO <sub>3</sub> <sup>-</sup> .....	I <sup>-</sup>	I <sup>-</sup> , I <sub>3</sub> <sup>-</sup>	2	(5, 11, 71, 144, 176)	Halide oxidation
BrO <sub>3</sub> <sup>-</sup> .....	Br <sup>-</sup>	Br <sup>-</sup>	2	(173)	Halide oxidation
BrO <sub>3</sub> <sup>-</sup> .....	Cl <sup>-</sup>	Cl <sup>-</sup>	2	(111)	Halide oxidation
ClO <sub>3</sub> <sup>-</sup> .....	Cl <sup>-</sup>	Cl <sup>-</sup> , Cl <sub>2</sub> O <sub>2</sub>	2	(38, 111, 137, 160)	Also N <sup>-</sup> = I <sup>-</sup> , Br <sup>-</sup>
NO <sub>2</sub> <sup>-</sup> .....	NO <sub>2</sub> <sup>-</sup>	H <sub>3</sub> AsO <sub>3</sub>	2*	(10)	
OI <sup>-</sup> .....	I <sup>-</sup>	OI <sup>-</sup>	2	(42, 123, 131, 174)	Formation of IO <sub>3</sub> <sup>-</sup>
HOBBr.....	OBr <sup>-</sup>	OBr <sup>-</sup>	1*	(123, 131, 174)	Formation of BrO <sub>3</sub> <sup>-</sup>
HOCl.....	OCl <sup>-</sup>	OCl <sup>-</sup>	1*	(79, 172, 174)	Formation of ClO <sub>3</sub> <sup>-</sup>
HOI.....	OI <sup>-</sup>	OI <sup>-</sup>	1*	(81, 169)	Formation of IO <sub>3</sub> <sup>-</sup>
IO <sub>3</sub> <sup>-</sup> .....	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	2	(156)	Oxidation of S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>
IO <sub>3</sub> <sup>-</sup> .....	SO <sub>3</sub> <sup>2-</sup>	SO <sub>3</sub> <sup>2-</sup>	2	(176)	Oxidation of SO <sub>3</sub> <sup>2-</sup>
HCrO <sub>4</sub> <sup>-</sup> .....	I <sup>-</sup>	I <sup>-</sup>	2	(21, 58)	Oxidation of I <sup>-</sup>
HSeO <sub>3</sub> <sup>-</sup> .....	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	2	(73)	Oxidation of S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>

\* The rate laws reported in the literature have the form

$$R = k[\text{H}_n\text{AO}_m][\text{HB}^{x+1}]$$

as the donor is strong enough in these examples to have a known undissociated acid.

isotope exchange of IO<sub>3</sub><sup>-</sup> and I<sub>2</sub> by Meyers and Kennedy (144) and by Connick and Hugus (52). The rate law reported was

$$R = k_4[\text{IO}_3^-][\text{I}^-][\text{H}^+]^3[\text{N}^-]$$

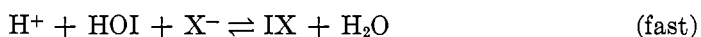
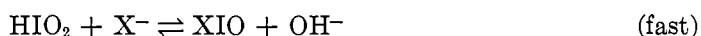
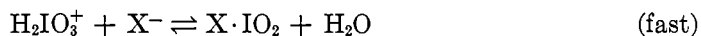
where N<sup>-</sup> is iodate or perchlorate ion (or possibly iodide, nitrate, or sulfate). The reduction of iodate by bromide proceeds through an identical type of rate law where N<sup>-</sup> is Br<sup>-</sup> (111).

The reaction between chloride and iodate is of the ninth order (approximately) and Hirade (111) presented the rate law

$$R = k[\text{IO}_3^-][\text{Cl}^-]^4[\text{H}^+]^4$$

to explain his kinetic results. It is likely that the mechanism of this reaction is related to the other iodate-halide reactions in certain parts.

Carrying through the previous concepts, the postulated mechanism is



where  $\text{X}^-$  is any halide ion.

The step marked "rate-determining I" is the rate-determining step in the oxidations of iodide and bromide. The step marked "rate-determining II" fits the observed rate law for the chloride oxidation, but this result probably has no great significance.

### III. EVIDENCE FOR THE EXISTENCE OF INTERMEDIATES

#### A. *Types of intermediates postulated*

The intermediates which are formed by reaction of oxyanions with protons and subsequent dehydration are acceptors or, as otherwise called, electrophilic particles. They have also been called cationic particles. Anhydrides such as  $\text{SO}_3$ ,  $\text{SO}_2$ ,  $\text{SeO}_2$ , and  $\text{CrO}_3$ , which are formed from dibasic acids, are good examples of acceptor intermediates. The isolated salts of  $\text{NO}_2^+$ ,  $\text{NO}^+$ ,  $\text{I}^+$ , and  $\text{Br}^+$  show that  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{OI}^-$ , and  $\text{OBr}^-$ , respectively, can be changed to acceptor, anhydride-like intermediates. It is assumed in this article that  $\text{IO}_2^+$ ,  $\text{BrO}_2^+$ ,  $\text{Cl}^+$ , and others are also intermediates.

The intermediates which are a type of donor-acceptor complex are not as well established, although some of the anhydrides of the monobasic acids may be considered as complexes. The compound  $\text{N}_2\text{O}_5$  is a molecular species in nonpolar solvents and in the gaseous state, yet it was found to be ionic, as  $\text{NO}_2^+$  and  $\text{NO}_3^-$ , when in a crystal lattice (76) and in certain solvents.  $\text{SO}_3\text{F}^-$ ,  $\text{SeO}_3\text{Cl}^-$ ,  $\text{CrO}_3\text{Cl}^-$ ,  $\text{CrO}_2\text{Cl}_2$ , and other similar particles may be considered as compounds formed from the acceptors  $\text{SO}_3$ ,  $\text{SeO}_3$ ,  $\text{CrO}_3$ ,  $\text{CrO}_2\text{Cl}^+$ , and donors. Unfortunately, few kinetic intermediates of this complex variety have been isolated, probably as a result of their reactivity. It should be stressed that the bond in most of these complex intermediates is not ionic, but rather more covalent in nature, as in nitrosyl chloride (22).

#### B. *Types of evidence for intermediates*

The existence of these two classes of reactive species has been demonstrated by several lines of investigation. The most unequivocal is chemical evidence,



such as the isolation of the intermediates in their salt forms or the molecular form. Spectroscopic studies are excellent in principle and have given valuable evidence in certain lines. Physicochemical methods such as conductivity, electrolysis experiments, and cryoscopic measurements give a large amount of information on the constitution of species in solution. In recent years, the application of tracer isotopes has cast some light on the problem. Finally, the study of the rate laws provides much useful information on the intermediates in the mechanism steps. Quite generally, it can be said that mechanisms are satisfactorily elucidated only by the conjunction of several experimental methods. The review article by Westheimer (187) is an excellent summary of methods of clarification of mechanism as applied to one oxidizing agent, hexavalent chromium.

### *C. Electrophilic or acceptor intermediates*

Some of the best work on the acceptor intermediates in reaction rates and mechanisms has been carried out by the chemists at University College, London, in connection with the study of the nitration of aromatic compounds. Their publications include reports on cryoscopic measurements in sulfuric acid (85, 87, 88, 89) and in nitric acid (90), on the kinetics and mechanisms of aromatic nitration (25, 47, 91, 93, 95, 96, 105, 113, 115), on the chemistry of nitronium salts (94), and on the vibrational spectra of ionic forms of oxides and oxy acids of nitrogen (98, 116, 117, 145). Aside from conclusive evidence that  $\text{NO}_2^+$  is the active nitration agent, they have shown that  $\text{H}_2\text{NO}_3^+$ ,  $\text{NO}_2^+$ ,  $\text{NO}^+$ , and other species exist as stable particles in concentrated acid. Investigations of the nitration mechanism have been carried out in other laboratories in recent years (26, 27, 28, 33, 34, 136, 143, 188, 192) and these ably substantiate the results of the London group.

The nitrosonium (nitrosyl) salts of strong acids have been known for a long time, and the ion  $\text{NO}^+$  is stable in acidic solution (13, 14, 54). Some of the analogous nitronium (nitryl) compounds have more recently come to light in the course of work on the structure of nitrogen pentoxide and on nitration mechanisms. The chemistry of nitrosonium salts is presently under investigation in Germany (161, 162, 163). Yost and Russell (197) have discussed these classes of compounds. The preparation, properties, and reactions of nitrosyl chloride,  $\text{NOCl}$ , are the subjects of a recent review article (22).

The intermediates in the sulfonation reaction are not well clarified, although the evidence seems to favor sulfur trioxide as the electrophilic agent (53). It had been felt in some quarters that the reactive species is  $\text{HSO}_3^+$  (35, 36, 155). A similar problem arises in the mechanism of alcohol sulfation (60).

Evidence for ions such as  $\text{CH}_3\text{CO}^+$  has been presented by Gillespie (86) as a result of his work with anhydrides in concentrated sulfuric acid.

The literature on the halogenation of organic olefins and aromatic compounds is vast and the reactions have unusual rate laws. Despite this complexity, there seems to be good reason to believe that the principal agent is a positive halogen ion or a coordination compound of a positive halogen ion and a weak base,

although other paths, such as free-radical mechanisms, are known. The subject has been treated in three review articles (140, 155, 191). The role of the positive halogen ion and the kinetic means for discerning these intermediates in solution reactions have been discussed in three papers, one each on bromination (166), chlorination (141), and iodination (30). The cationic forms have been discussed in several other papers (61, 63, 64). Kleinberg (121) has reviewed the work on salts of  $I^+$  and  $Br^+$  in a chapter of his book on unusual valence states. Salts with  $I^{+3}$  and  $IO^+$  are also mentioned. It is the feeling of Bartlett and Tarbell (20) that the role of  $Br^+$  in halogenation has been overemphasized, and they prefer to write it as a complex with another molecule. They present evidence to show that some halogenations by  $Br^+$  call for specific reaction rates greater than that predicted by the collision frequency of the reactant species. Some recent electrolysis experiments in concentrated acid gave no evidence for the existence of a bromine cation (122).

Although there is no direct evidence for electrophilic intermediates from other monobasic oxyanions, the second-order dependence on hydrogen-ion concentration is support for their existence as kinetic intermediates.

#### *D. The donor-acceptor complex*

More than twenty years ago, Bray (42) and Skrabal (170) presented kinetic evidence for the compounds  $I_2O_2$ ,  $H_2I_2O_3$ , and  $HI_3O$  in their analyses of the reaction of iodine compounds; they evaluated the observed rate laws in terms of these postulated equilibrium intermediates.

In the reactions of the third and fourth type, a striking kinetic pattern is observed which is indicative of a complex in solution. These reactions are of the fifth or sixth order, and most have several rate laws with different particles in the  $N^-$  capacity. It appears that the complex is decomposed by collision with the  $N^-$  nucleophilic particle. In the chlorate-chloride reaction, the nucleus of all the rate laws is the complex  $Cl_2O_2$ , whose concentration is given by the expression

$$[Cl_2O_2] = K[ClO_3^-][Cl^-][H^+]^2$$

and the complete rate law designates the bimolecular reaction between the complex and the nucleophilic particle. Sand (160) and Hirade (111) observed the rate law

$$R = k[ClO_3^-][Cl^-]^2[H^+]^2$$

while Luther and MacDougall (137) found

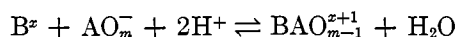
$$R = k[ClO_3^-]^2[Cl^-]^2[H^+]^4$$

In the presence of iodide ion and bromide ion, respectively, Bray (38) and Hirade (111) observed the equation:

$$R = k[ClO_3^-][Cl^-][H^+]^2$$

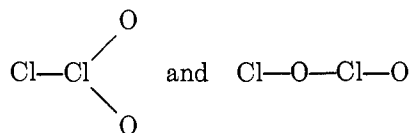
It appears that the complex can be decomposed by collision with another complex or with a chloride ion. When bromide or iodide is present, the complex is probably reduced as fast as it is formed.

The large magnitude of the experimental rate constant in many of the type 3 and type 4 reactions is a strong point in the evidence for an intermediate complex. The observed rate constant for the reaction between iodate and thio-sulfate is  $5 \times 10^8$  liter<sup>4</sup> mole<sup>-4</sup> sec.<sup>-1</sup> (156), and those of the other fifth-order reactions between iodate and sulfite (176), iodate and iodide (144), and hydrogen selenite and thiosulfate (73) are even larger. If the collision (bimolecular) rate is  $5 \times 10^{13}$  sec.<sup>-1</sup>, a lower limit can be set on the value of the equilibrium constant for the reaction:



It is difficult to reconcile these large observed rate constants with the frequency of molecular collisions, unless one assumes that a complex with a formation constant of almost 1 or more than 1 exists.

The presence of an unsymmetrical intermediate in the interaction of ions of chlorine in various oxidation states was demonstrated by Dodgen and Taube (67, 183) with radioactive isotopes. Two possible structures



were suggested; the one with the chlorine-chlorine bond fits the donor-acceptor complex postulated in this article exactly. It is found in the oxidation of chlorite ion by chlorine and in the reduction of chlorate ion by chloride ion.

In a recent communication (112), the role of the monoisopropyl ester of chromic acid in the oxidation of the alcohol to acetone was discussed. It is entirely consistent to consider this ester as a complex of the acceptor  $\text{CrO}_3$  and the donor 2-propanol, for the rate law suggests that chromic acid anhydride is the electrophilic intermediate in the ester formation. A more complete discussion of this and other similar reactions will be given in a later section.

The effect of heavy water on the rate of reactions catalyzed by acids has been presented as a tool for differentiating between general acid catalysis and specific catalysis involving an equilibrium intermediate (195). The results are encouraging, but are still not conclusive, as Bell (23) points out in his book. The theoretically predicted result for specific catalysis is found in the change of rate of the halate-halide systems in aqueous solution, for the rates are faster in deuterium oxide than in water (4). This is taken to be an indication of equilibrium involving the protons before the rate-determining step. The reaction of peroxide with iodide ion was found to proceed only 60 per cent as fast in deuterium oxide as in water (48). This is in agreement with other data, for the reactions of peroxide with donor particles have rate laws which support a picture of general acid catalysis (74).

In the section on thiosulfate reactions, many complex ions are presented; most of these are kinetic intermediates in the oxidation of thiosulfate to tetrathionate.

#### IV. DISCUSSION OF CERTAIN REACTIONS

##### A. Oxygen exchange in oxyanions

Although a considerable amount of qualitative work has been done in the studies on the exchange of oxygen isotopes of oxyanions with the solvent water, few quantitative data on rate equations are found in the literature. This is unfortunate, for these reactions are of fundamental significance in the field of oxyanion reactions. For the present work, oxy acids are divided into three classes: (1) organic carboxylic acids, (2) inorganic oxy acids with one replaceable proton, and (3) inorganic oxy acids which are polybasic.

The exchange of the oxygen atoms of a carboxylic acid with water has been investigated by many (29, 50, 108, 109, 142, 157, 158). The rate law is

$$R = k_2[\text{ArCOOH}][\text{H}^+][\text{H}_2\text{O}]$$

where ArCOOH is the organic acid. This equation is identical to those found for esterification and hydrolysis and the rate constants are of similar magnitude. Day and Ingold (57) have adequately discussed the mechanisms of these reactions in their review on esterification. A recent article by Bender (24) throws additional light on the intermediate formed in this type of reaction.

The rate law for oxygen exchange in oxy acids containing one replaceable proton is probably similar to the above exchange. The reactions of nitrate, nitrite, chlorate, bromate, iodate, and perchlorate ions with water take place in all likelihood through the equilibrium



or through the displacement of one water molecule from  $\text{H}_2\text{AO}_m^+$  by another water molecule. The exchange of oxide ions in inorganic oxyanions of both classes has been widely investigated (31, 56, 106, 120, 146, 147, 184, 185, 194). The exchange is, as a rule, catalyzed by acids and repressed by bases.

The acceptor forms for the polybasic acids are usually their anhydrides, as, for example,  $\text{SO}_3$ ,  $\text{SO}_2$ ,  $\text{SeO}_2$ ,  $\text{CrO}_3$ , and  $\text{CO}_2$  from  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{SO}_3$ ,  $\text{H}_2\text{SeO}_3$ ,  $\text{H}_2\text{CrO}_4$ , and  $\text{H}_2\text{CO}_3$ , respectively. Indeed, the exchange of oxygen atoms in carbonate ion has been shown to pass through the anhydride mechanism (147). The postulated mechanism for this type of reaction is



although the exchange of oxygen atoms in the strong acids is complicated by the change in the medium, from  $\text{H}_2\text{O}$  to  $\text{H}_3\text{O}^+$ .

Further investigation of the exchange of oxygen atoms in oxyanions with the solvent is of prime importance, for the mechanism is linked to the reactions involving the displacement of a water molecule from a coordination sphere by a different donor particle. Undoubtedly the esterification of inorganic acids can

be treated in terms of the above exchange mechanism in the same manner as is the case for the carboxylic acid esterification.

*B. Decomposition of the hypohalites and the reverse reaction*

Since the formation of the halates from the hypohalites takes place by several distinct rate laws, a single reaction scheme could not hold. In heavily alkaline solutions these reactions proceed with mechanisms which are not related to the present concept (78, 126, 131) and, further, the reverse reactions (oxidation of the halides by the halates) proceed only in acidic solutions. For these reasons, only the types of rate law which are prevalent in weakly alkaline solution will be considered.

Liebhafsky and Makower (131) have shown that many previous types of rate law reduce to one,

$$R = k \frac{[\text{X}_2]^3}{[\text{H}^+]^4 [\text{X}^-]^3}$$

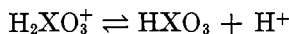
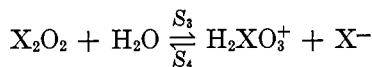
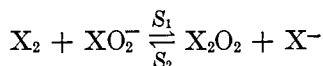
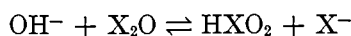
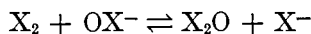
which they felt was best explained by the third-order step:

$$R = k[\text{HOX}]^2[\text{OX}^-]$$

The other observed rate law is

$$R = k \frac{[\text{X}_2]^3}{[\text{H}^+]^4 [\text{X}^-]^4}$$

In terms of the present article, the mechanism could be



in which  $S_1$  and  $S_3$  are the two alternative rate-determining steps in the hypohalite decompositions. Upon substitution of molecular species from the rapid equilibrium



and from proton transfers, it may be seen that  $S_1$  corresponds to the former observed rate law and  $S_3$  to the latter.

The complete change from hypohalite to halate and halide is accomplished with a minimum of bimolecular steps, each of which is only a single-atom trans-

fer or a displacement reaction. The rate law which was experimentally observed for the reverse reaction follows that correctly predicted by the forward reaction  $S_1$  in the chlorate-chloride case (38, 111, 137, 160). In the hypobromite decomposition, some evidence has been found that the  $S_1$ - $S_2$  equilibrium is rate determining, while other investigators (175) found that the decomposition was best characterized by the  $S_3$  step in agreement with the often observed fourth-order rate law  $S_4$  in the oxidation of bromide by bromate.

In terms of this scheme, there is no explanation for the iodate-iodide rate equation found by Meyers and Kennedy (144). The fifth-order rate law

$$R = k_3[\text{IO}_3^-][\text{I}^-]^2[\text{H}^+]^2$$

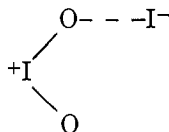
which is consistent with an  $S_2$  rate step, has been reported by several independent investigators (11, 71, 176), while Abel and Hilferding (5) observed a fourth-order law which is probably related to the others with  $\text{H}_2\text{O}$  as the nucleophilic particle. The hypoiodite decomposition follows the  $S_1$  rate step (81, 169).

Connick and Hugus (52) at the University of California repeated the work of Abel and Hilferding (5), using a somewhat altered procedure. Their results, in perchlorate medium of constant ionic strength, gave most closely

$$R = k[\text{IO}_3^-][\text{I}^-][\text{H}^+]^3$$

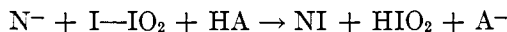
in which the hydrogen-ion dependence agrees with that found in the exchange studies (52, 144).

The latest article on the iodate-iodide reaction is the proposal of a new mechanism involving the intermediate  $\text{IO}_2^+$  and a complex (149). The postulated complex for the fourth-order rate law was



and that for the fifth-order law (with a second-order dependence on iodide concentration) was similar, with one iodide ion on each oxygen of  $\text{IO}_2^+$ . The first one of these two is like the unsymmetrical configuration,  $\text{Cl}-\text{O}-\text{Cl}-\text{O}$ , which was reported as a possible intermediate by Dodgen and Taube (67, 183).

An intermediate involving an iodine-iodine bond is favored in this article and a possible explanation for the many reported rate equations lies in the mechanism



where  $\text{N}^-$  is a nucleophilic particle (iodide, iodate, perchlorate, water, etc.) and  $\text{HA}$  is a general acid such as water or hydronium ion. A similar mechanism seems to be operative in the acid chromate-iodide reaction, as will be seen later. Unfortunately, the data available on the oxidation by iodate are not sufficient to give a conclusive answer.

Bray (42) and Skrabal (169, 170, 171) discussed the halate-halide reactions

and the hypohalite decompositions in some detail. Hirade (111) has reinvestigated the rate equations for five of the reactions of this series and has given some general points of interest, including correlations of relative rates. Skrabal and Schreiner (173) also showed that the reduction rate of chlorate and bromate followed the order  $I^- > Br^- > Cl^-$ .

The catalysis of the chlorate-bromide reaction by arsenic acid was studied by Grieger (99). The results are quite complicated, for there are at least four competing mechanisms.

### C. Halate oxidation of sulfite ion

Using the stable heavy isotope of oxygen, Halperin and Taube (107) demonstrated that almost complete transfer of the chlorate oxygen atoms to the sulfite took place under certain conditions. Assuming that the reaction proceeds through  $ClO_2^+$  formation, a maximum of two-thirds of the chlorate oxygens would end up in sulfate ions. On the other hand, if sulfur dioxide were the acceptor intermediate, theoretically all of the oxygen could be transferred, as was found. The investigators explained the lack of complete transfer as a result of the chlorine hydrolysis equilibrium occurring when the chlorate has been reduced to the hypochlorite state.

The rate law for the oxidation of sulfurous acid by chlorate is in agreement with this mechanism, for it shows that sulfur dioxide may be the acceptor (75, 151). A similar rate law was found for the iodate-sulfite reaction in dilute acid (176) and the pH-time curve for the bromate-sulfite reaction is well explained by the same mechanism (178).

It has been recently observed that both oxygens of hydrogen peroxide are transferred to a sulfite molecule during the oxidation to sulfate (180). This is further evidence that sulfur dioxide is an acceptor intermediate.

### D. Acid chromate reactions and general acid catalysis

Westheimer (187) has ably shown in his review article that the reduction of acid chromate ion passes through stages involving penta- and tetravalent chromium. On the other hand, the actual mechanisms of the rate steps in these reactions were not completely elucidated. Some calculations by A. D. Awtrey and this author have indicated that the intermediate complex in three acid chromate reactions is decomposed by general acid catalysis. The data from the latest of the studies of the oxidation of 2-propanol (112) have been used to evaluate the parameter  $\alpha$  in the Brønsted relation

$$k_{HA} = AK_{HA}^{\alpha}$$

where  $k_{HA}$  is the rate contribution from a particular acid,  $K_{HA}$  is the dissociation constant for the acid, and  $A$  is another constant. The value, which was determined for the three acids  $H_3O^+$ ,  $HPV^+$ , and  $H_2O$ , is given in table 4, along with several other comparative values. The proposed rate-determining step is

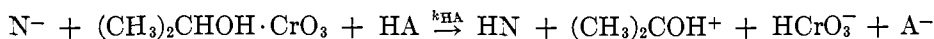


TABLE 4  
Brønsted exponents of acid-catalyzed reactions

REACTION	$\alpha^*$	REFERENCES
Acid chromate oxidations		
Oxidation of 2-propanol . . . . .	0.18	(112, 187)
Oxidation of iodide . . . . .	0.21	(21, 58)
Oxidation of arsenite . . . . .	0.23	(58, 59, 187)
Hypohalite reactions		
Iodination of aniline . . . . .	0.54†	(30)
Iodination of phenols . . . . .	0.45	(125)
Bromination of anisoate ion . . . . .	0.51‡	(63)
Oxidation of oxalate ion . . . . .	0.48	(104, 139)
Peroxide reactions		
Hydrogen peroxide and iodide . . . . .	0.17	(132)
Hydrogen peroxide and bromide . . . . .	0.26	(148)
Hydrogen peroxide and chloride . . . . .	0.25	(148)
Hydrogen peroxide and iodate . . . . .	0.22	(45, 128)
Hydrogen peroxide and thiosulfate . . . . .	0.20	(1)
Hydrogen peroxide and hypochlorite . . . . .	0.26	(51, 134, 318)
Hydrogen peroxide and iodine . . . . .	0.26	(129, 130)
Hydrogen peroxide and nitrite . . . . .	0.35§	(165, 168)
Ozone and chloride ion . . . . .	0.16	(196)

\* Data concerning this parameter and general acid catalysis may be found in reference 23. The values are calculated from the rates with  $\text{H}_3\text{O}^+$  and  $\text{H}_2\text{O}$  as the acids, unless otherwise indicated.

† Calculated from rates with the acids  $\text{H}_3\text{O}^+$  and  $\text{H}_2\text{PO}_4^-$ .

‡ Calculated from rates with the acids  $\text{H}_2\text{PO}_4^-$  and  $\text{H}_2\text{O}$ .

§ Calculated from rates with the acids  $\text{H}_3\text{O}^+$  and  $\text{HNO}_2$ .

which is almost analogous to the push-pull mechanism proposed by Swain (179) for certain organic reactions.

The acid chromate oxidation of iodide was studied by Beard and Taylor (21), who used the two-term rate law

$$R = k'_3[\text{Cr}^{\text{VI}}][\text{I}^-][\text{H}^+] + k'_5[\text{Cr}^{\text{VI}}][\text{I}^-]^2[\text{H}^+]^2$$

to get an approximate solution to the observed rate. Using the four-term rate law

$$R = k_a[\text{ICrO}_3^-] + k_b[\text{ICrO}_3^-][\text{I}^-] + k_c[\text{ICrO}_3^-][\text{H}^+] + k_d[\text{ICrO}_3^-][\text{I}^-][\text{H}^+]$$

where  $\text{ICrO}_3^-$  is an acid-base complex intermediate whose concentration is given by the relation

$$[\text{ICrO}_3^-] = K[\text{HCrO}_4^-][\text{I}^-][\text{H}^+]$$

the data have been recalculated. It is possible to show that there are more than two rate terms. The data of Beard and Taylor (21) in 1.5 M salt are sufficient



TABLE 5

*Donor-acceptor complexes in thiosulfate reactions*

COMPLEXES	EVIDENCE*	REFERENCES	REMARKS
$S_2O_3 \cdot S_2O_3^{--}$	C <sub>a</sub>	(82)	Tetrathionate ion
$S_2O_3 \cdot SO_3^{--}$	C <sub>a</sub>	(82)	Trithionate ion
$S_2O_3 \cdot SC(S)OR^-$	C <sub>b</sub>	(82)	Tetrathionate and ethyl xanthate reaction
$S_2O_3 \cdot SO_2R^-$	C <sub>b</sub>	(82)	Tetrathionate and alkylsulfinate reaction
$S_2O_3 \cdot SeR^-$	C <sub>a</sub>	(83)	Reduction of aryl seleninate by thiosulfate
$S_2O_3 \cdot I^-$	C <sub>b</sub>	(17, 66, 100)	Iodine reaction with thiosulfate and tetrathionate
$S_2O_3 \cdot SCN^-$	K	(82)	Reaction of pentathionate and cyanide ions
$S_2O_3 \cdot CN^-$	K	(82)	Reaction of tetrathionate and cyanide ions, and of trithionate and cyanide ions
$S_2O_3 \cdot NO_2^-$	K	(100)	Nitrite catalysis in iodine oxidation of thiosulfate
$S_2O_3 \cdot N_3^-$	K	(66, 101)	Tetrathionate catalysis of oxidation of azide ion by iodine
$S_2O_3 \cdot Br^-$	K	(101)	Bromine oxidation of thiosulfate and azide ions
$S_2O_3 \cdot Cl^-$	K	(17)	Intermediate in iodine-thiosulfate reactions
$S_2O_3 \cdot OH^-$	K	(1, 82)	Oxidation of thiosulfate by hydrogen peroxide
$S_2O_3 \cdot NC_5H_{10}^-$	K	(82)	Reaction of piperidine with tetrathionate
$S_2O_3 \cdot IO_2^-$	K	(156)	Oxidation of thiosulfate by iodate
$S_2O_3 \cdot BrO_2^-$	K	(73)	Oxidation of thiosulfate by bromate
$S_2O_3 \cdot CrO_3^{--}$	K	(73)	Oxidation of thiosulfate by acid chromate
$S_2O_3 \cdot SeO_2^{--}$	K	(73)	Oxidation of thiosulfate by selenious acid
$S_2O_3 \cdot NO^-$	K	(72, 73)	Oxidation of thiosulfate by nitrous acid
$S_2O_3 \cdot SO_4^{--}$	K	(73)	Oxidation of thiosulfate by peroxydisulfate

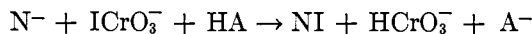
\* The symbol C<sub>a</sub> denotes an isolated compound, C<sub>b</sub> denotes a compound which is established but not isolated, and K denotes an intermediate postulated in kinetic studies.

only to solve for three of the constants in terms of the fourth. However, by using the relation

$$k_a \cdot k_c = k_b \cdot k_d$$

which should be reasonably correct (Swain (179) has found that relative reactivities in push-pull mechanisms are surprisingly constant), the author has

calculated the values of the constants. The value of  $\alpha$  as found for this reaction is presented in table 4. The postulated rate step is



The oxidation of arsenious acid by acid chromate is also catalyzed by proton acids. Westheimer (187) has recalculated de Lury's data (58, 59) and the results, employing the rate law

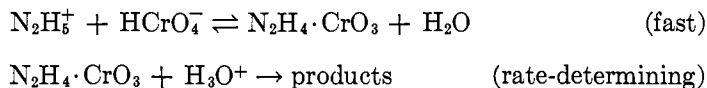
$$R = k[\text{HCrO}_4^-][\text{H}_3\text{AsO}_3][\text{H}^+]^2$$

show a wide deviation. Employing the data at low acid chromate concentration (experiments 7 to 15 in table 5 of Westheimer (187)), the plot of  $k_1/[\text{HCrO}_4^-][\text{H}^+]^2$  against  $1/[\text{H}^+]$  is linear but not horizontal. The results may be interpreted in terms of the rate law

$$R = k_a[\text{HCrO}_4^-][\text{H}_3\text{AsO}_3][\text{H}^+] + k_b[\text{HCrO}_4^-][\text{H}_3\text{AsO}_3][\text{H}^+]^2$$

and the calculated values for  $k_a$  and  $k_b$  are reasonable for the proposed mechanism. The calculated value for  $\alpha$  for this reaction is presented in table 4; the rate-determining step presumably has the same mechanism as that for the other acid chromate reactions. The increase in rate in solutions containing large amounts of acid chromate is further evidence for general acid catalysis.

Whether this type of decomposition of the intermediate is typical for the reactions of acid chromate is not known. The oxidation of thiosulfate was studied in the pH range where catalysis by hydrogen ion would not be found (73). The reaction of acid chromate with hydrazonium ion suggests the mechanism

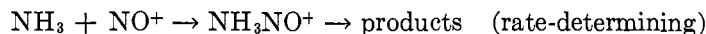
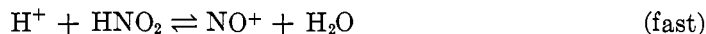


but there are not enough data to tell if the rate-determining step is of the general acid-catalyzed type (164). The oxidation of bromide by chromic acid in concentrated solutions of sulfuric acid has been studied, but the rate law has not yet been completely elucidated (32).

#### *E. Reaction of nitrous acid with nitrogen bases and other donors*

Hughes, Ingold, and Ridd (114) in their report on the kinetics of diazotization consider the types of nitrosating agents that are found in aqueous solutions of nitrites. These are  $\text{NO}^+$ ,  $\text{H}_2\text{NO}_2^+$ ,  $\text{N}_2\text{O}_3$ , and  $\text{HNO}_2$  in decreasing order of reactivity. With the reasonable assumption that proton transfer cannot be rate determining, these investigators tabulated the six possible types of nitrosation kinetics. Two types have the formation of the agent ( $\text{NO}^+$  or  $\text{N}_2\text{O}_3$ ) as the rate step, and the other four types have the attack by the agent on the base as the rate step. Experimentally, it was observed that the formation of  $\text{N}_2\text{O}_3$  was the step which governed the rate of *N*-nitrosation of aromatic amines in dilute acid.

For the formation of nitrogen from nitrous acid and ammonia (or methylamine) Dusenbury and Powell (70) proposed the mechanism



At first sight it is surprising that the rate steps for these two similar nitrosations are identical while the rate law with aromatic amines is so different, particularly since the only chemical change in the reactants is substitution of an aromatic group for a hydrogen or a methyl group on the ammonia molecule. It has been suggested by a referee that the reason for this difference lies in the weak basicity of the aromatic amines.

Abel (2, 3) has treated the reactions of nitrous acid in terms of the intermediate  $\text{NO}^+$ .

The reaction of nitrous acid with other donors probably proceeds through the acceptor form  $\text{NO}^+$ , for there is a large amount of chemical evidence for the formation of a bond between the nitrogen in  $\text{NO}^+$  and a donor. Hydrazoic acid,  $\text{HN}_3$ , is formed from hydrazine and nitrous acid, while hyponitrous acid,  $\text{H}_2\text{N}_2\text{O}_2$ , is an intermediate in the reaction between hydroxylamine and nitrous acid (15). At room temperature this reaction proceeds rapidly all the way to nitrous oxide. The rate laws for formation of the anhydrides  $\text{N}_2\text{O}_3$  (114) and  $\text{N}_2\text{O}_4$  (6, 7, 8, 9) are consistent with the concept of  $\text{NO}^+$  adding to the donors  $\text{NO}_2^-$  and  $\text{NO}_3^-$ , respectively. The reduction of chlorate and bromate by nitrite follows a similar rate pattern (135), and the oxidations of iodide (110) and thiosulfate (72) agree with the picture of  $\text{NO}^+$  joining the donor in a complex ion.

It is quite likely that some of the reactions of nitric acid with donor particles follow a similar course, with  $\text{NO}_2^+$  as the acceptor intermediate. The thermal decomposition of ammonium nitrate is catalyzed by water and the mechanism is postulated to pass through nitramide,  $\text{H}_2\text{NNO}_2$  (84). The stable isotope  $\text{N}^{15}$  has been employed to follow this reaction; the results are given by the equation



which is the isotope arrangement expected for this mechanism.

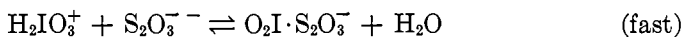
#### *F. The oxidation of thiosulfate ion*

Hydrogen peroxide reacts with thiosulfate with a rate law typical for peroxide and a donor (1, 74), while peroxydisulfate probably oxidizes it through a free-radical chain mechanism (73). Acid chromate, bromate, and nitrite ions were found to oxidize thiosulfate to tetrathionate in aqueous acid of pH 4–6 (73). The rate laws for these reactions were determined, but the results were not conclusive and further work should be carried out. The kinetic results with acid chromate follow a rather general pattern, which is the addition of a base to chromic oxide, as may be seen in table 1. The reaction with nitrite is interesting, for the order in thiosulfate ion concentration is almost zero in the pH range

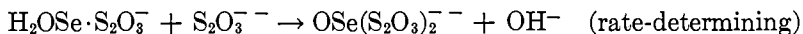
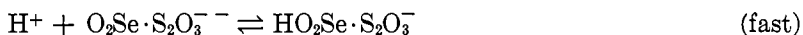
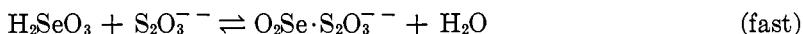
where the reaction was studied. A possible explanation for this rate equation is that the formation of  $\text{NO}^+$  is not quite rate-determining.

Data on the oxidation of thiosulfate by bromate in phthalate buffer in the pH range from 4.1 to 5.6 show that the reaction is of the first order with respect to the concentration of bromate ion, of thiosulfate ion, and of hydrogen ion. It was found that inert salts lowered the rate of the reaction, which fact is in agreement with the proposed mechanism for a type 1 reaction (73, 178). The pH-time curves for this reaction and for the iodate-thiosulfate reaction cross when started at different initial pH values. This is indicative of steps after the rate-determining step which are by no means instantaneous. For example, the reduction of iodite by thiosulfate probably is not much faster than the reduction of iodate.

The type 3 rate laws for the reaction of thiosulfate ion with iodate (156) and with hydrogen selenite ion (73) are evidence that thiosulfate ions can replace oxide ions in these oxyanions. The intermediate  $\text{IO}_2^+$  was postulated in other cases and it fits well in the mechanism



for the iodate-thiosulfate reaction. For the selenious acid-thiosulfate case, the mechanism



is postulated, since the selenopentathionate ion is one of the reaction products.

Despite the rapidity of the reaction of thiosulfate with iodine, it has recently been investigated with considerable success by Awtrey and Connick (17). They showed that the ion  $\text{I}\cdot\text{S}_2\text{O}_3^-$  is a stable intermediate whose concentration can be determined by an indirect method. This complex reacts with thiosulfate to give tetrathionate and iodide ions. Another, slower decomposition path results in the formation of sulfate ion; sulfate is also formed by the decomposition of the postulated complex  $\text{Cl}\cdot\text{S}_2\text{O}_3^-$ . The complexes  $\text{I}\cdot\text{S}_2\text{O}_3^-$  and  $\text{HOS}_2\text{O}_3^-$  were postulated in the reaction of iodine with tetrathionate (16).

In a long publication on polythionates and related compounds, Foss (82) has suggested that the uncharged species  $\text{S}_2\text{O}_3^0$ , which is an oxidation product of thiosulfate, acts like an acceptor. Several compounds which may be considered as donor-acceptor complexes were mentioned and some new ones were prepared by Foss.

The examples of compounds and intermediates of the donor-acceptor complex type are presented in table 5. Many of these are formed from  $\text{S}_2\text{O}_3^{2-}$  and

an acceptor, and others by displacement of  $S_2O_3^{2-}$  from  $S_4O_6^{2-}$  by another donor. While it is true that most of the examples are kinetic intermediates whose existence has only been postulated, the large number of examples is indicative of the fundamental soundness of the concept. These complexes are not analogous in every case to those considered in the balance of this article, but their inclusion is important, for they show how reactions can pass smoothly from reactants to products by means of intermediate complexes of the donor-acceptor type. A good example is the ion  $I \cdot S_2O_3^{2-}$ , which may undergo reactions in two ways. When iodide ion is present the complex goes to  $I_3^-$  and  $S_2O_3^{2-}$ , with the latter rapidly reacting with further  $I \cdot S_2O_3^{2-}$  to give tetrathionate and iodide. When thiosulfate is in excess, the complex reacts directly with the thiosulfate to give iodide and tetrathionate as above (17).

Since the oxidation of thiosulfate in the pH range from 4 to 7 generally takes up hydrogen ions, a series of experiments with a pH meter was made to see if the oxyanions of strong acids would react with thiosulfate. When nitrate, sulfate, chlorate, or perchlorate was present, no pH change was observed in 10 to 15 min. (73). In spite of the sizable oxidizing power available, these oxyanions do not react, for they have large resonance energies which stabilize their configurations. In similar fashion, nitrate ion does not oxidize iodide ion directly, although nitrite ion will oxidize iodide in a solution of the same acidity.

Periodate ion is an electron-pair acceptor, as is shown by its variable hydration number, so it is not surprising to find that it reacts rapidly with iodide, thiosulfate, and sulfite ions. Arsenate oxidizes thiosulfate in acid solution, probably through the acceptor form  $HAAsO_3$ . On the other hand, permanganic acid is strong, yet permanganate ion reacts with thiosulfate rapidly. In view of the known complexity of permanganate reactions, this is not a serious discrepancy. Peroxydisulfate oxidizes thiosulfate, but only through a free-radical chain mechanism. The presence of catalytic ions such as  $Cu^+$  seems necessary, for there is no evidence for a direct reaction between thiosulfate and peroxydisulfate (73).

These observations indicate that reactions of oxyanions with thiosulfate and other donors take place readily when a donor-acceptor complex can be formed. When resonance stabilization prevents displacement of an oxide ion from the oxyanion, the reaction must proceed indirectly if it goes at all.

#### G. The type 1 rate law of the hypohalous acid reactions

The oxidation of oxalate ion by hypochlorite (102), hypobromite (104, 139), and hypoiodite (103) has been carefully investigated. The predominant rate equation for these similar oxidations is

$$R = k[HOX][C_2O_4^{2-}][H^+]$$

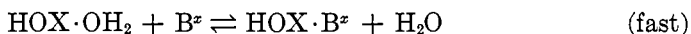
where HOX is a hypohalous acid. The original investigators felt that  $HC_2O_4^-$  was the reactive species; however, Hinshelwood (110) has noted that this rate equation can satisfy the kinetics for a reaction between an oxalate ion and a halogen acceptor. Makower and Liebafsky (139) observed that an alternative path for the oxidation of oxalate by hypobromite exists and has a type 1 rate law.

The rate of formation of hypobromite from bromide and hypochlorite is dependent on the first power of hydrogen-ion concentration in the pH range from 10 to 13. It was postulated that the rate is proportional to the concentrations of bromide ion and hypochlorous acid (77). It is possible that the formation of chlorine from hypochlorous acid and chloride ion follows a similar kinetic pattern, for Morris (150) has presented results of the reverse reaction which suggest this rate law. The rate of chlorination of ammonia and methylamines was studied by Weil and Morris (186) in both alkaline and acid solution. The observed rate law is

$$R = k[\text{OCl}^-][\text{NH}_3][\text{H}^+]$$

which they proposed was the reaction of ammonia with hypochlorous acid.

The number of reactions of type 1 involving the reactive species HOX is somewhat surprising, in view of the fact that only one other reaction of a donor with a monobasic oxy acid has been observed. A possible explanation lies in the observation that many halogen compounds (in the +1 valence state) have a coördination number of 2 (121). Thus the mechanism might be



in which the intermediate is consistent with the acid-base intermediate as found in the other reactions of oxy acids.

Another, and probably more general, explanation is that the splitting of the oxygen-halogen bond in the hypohalous acids is accomplished through general acid catalysis, in similar fashion to the cleavage of the oxygen-oxygen bond in peroxide (74). Four reactions from the literature have rate equations which give substance to this postulate. The oxidation of oxalate by hypobromous acid has been mentioned; the second reaction is the iodination of certain biologically important phenols. Li (125) observed that the rates of iodination were related to the dissociation constants of the phenols, and that certain basic ions (like phosphate) catalyzed the reaction. The iodination of aniline, which was carefully investigated by Berliner (30), has a rate law which on first sight appears to be general base catalysis, yet it is probably general acid catalysis. It is likely that the mechanisms of the iodinations of aniline and of phenoxide ion are identical. The bromination of sodium *p*-anisoate in bromide-free hypobromous acid solutions has a compound rate equation that is suggestive of general acid catalysis (63).

The objections of Bartlett and Tarbell (20) to  $\text{Br}^+$  as a brominating agent and the lack of electrolytic evidence for positive bromine (122) make the general acid catalysis picture more sound. In table 4 the calculated values of  $\alpha$  for these reactions are presented. Although they are considerably higher in magnitude than those for acid chromate and for peroxide reactions, all four values are similar in size. Caution must be exercised in the postulation of the mechanism, for certain intermediates are in such low concentration as to make the rate constant greater than the collision frequency of molecular species.

*H. Other reactions*

The reactions of hydrogen peroxide with donors conform to one general type of rate law

$$R = k_1[\text{H}_2\text{O}_2][\text{B}^x] + k_2[\text{H}_2\text{O}_2][\text{B}^x][\text{H}^+]$$

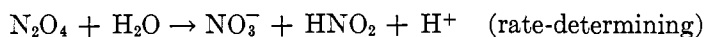
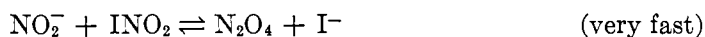
which is suggestive of general acid catalysis (74). The rate equation for the oxidation of nitrous acid to nitrate by peroxide has two terms, one of which is different from the  $k_1$  term in the above equation. The equation is, nevertheless, reasonable on the basis of a general acid-catalyzed mechanism (165, 168). Other peroxide reactions have one or the other of the two terms of the above equation. Abel and Ziffer (12) investigated the reactions in the periodate-iodate-peroxide system but had little success, for the results were quite complicated. Despite the claim of Derbyshire and Waters (62) that a cationic intermediate such as  $\text{OH}^+$  or  $\text{H}_3\text{O}_2^+$  explains the acid catalysis of certain peroxide reactions, it seems probable that peroxide reactions are not similar to those of the oxy acids. Under certain conditions,  $\text{IO}_2^+$  appears to be the important kinetic species in the iodate-peroxide system (154).

Some of the oxidations of donors by ozone have rate laws similar to those of oxidations by hydrogen peroxide (181, 196). In table 4 the values of  $\alpha$  from the Brønsted equation for ozone and peroxide reactions are presented.

Complexes of the kind found with thiosulfate are certainly to be found in other reactions. The complicated rate law for the oxidation of nitrite by iodine

$$R = k \frac{[\text{NO}_2^-][\text{I}_2]}{A[\text{I}^-]^2 + [\text{NO}_2^-]}$$

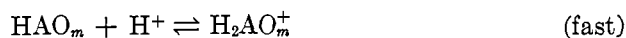
is indicative of intermediates being present (69). The possible mechanism



will satisfy the observed kinetics if the reaction of  $\text{INO}_2$  with  $\text{NO}_2^-$  is faster than with  $\text{I}^-$ . The reverse reaction, the oxidation of iodide by nitric acid, presumably passes through this mechanism. The intermediate, which is nitryl iodide, may also be present in the nitrite-ion catalysis of the reaction between thiosulfate and iodine to form sulfate (100).

The oxidation of azide ion by iodine and bromine, as catalyzed by various sulfur compounds, probably involves reactive intermediates such as  $\text{IN}_3$ ,  $\text{BrN}_3$ ,  $\text{CS}_2 \cdot \text{N}_3^-$ ,  $\text{N}_3 \cdot \text{S}_2\text{O}_3^-$ , and others (66, 101).

Although it is generally found that proton transfer is very fast, it is occasionally true that the formation of the electrophilic agent is rate-determining. This differs, of course, from proton transfer, because a bond is broken as in the following scheme:



The nitration of some reactive aromatics has been shown to follow this mechanism (91) and there is evidence that certain chlorination reactions have rates which are dependent on the formation of  $\text{Cl}^+$  (141). Further study of the reaction of nitrous acid with thiosulfate may show that the rate-determining step of this oxidation is the formation of the nitrosonium ion,  $\text{NO}^+$  (72).

Duke (68) studied the reaction of selenious acid with acetone. From the data and the rate law, he concluded that the oxidation takes place by disproportionation of a complex in which the oxygen atom of acetone is coordinated to the selenium atom in  $\text{HSeO}_2^+$ .

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