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The Action of Polar Organic Inhibitors in the Acid Dissolution of Metals

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by

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The Action of Polar Organic Inhibitors in the Acid Dissolution of Metals

by

Norman Hackerman and A. C. Makrides

Abstract

The theory of cathodic inhibition by polar organic compounds principally developed by Mann and his co-workers is critically examined and found inadequate to account for experimental results reported in the literature. Modifications of this theory are also not in agreement with experiment, particularly with the shift in the cathodic direction of the open circuit potential generally observed upon addition of inhibitors. General adsorption theories, on the other hand, are not in conflict with reported results but a specific mechanism for inhibition is lacking.

A mechanism for inhibition by polar organic compounds based on recent advances in the field of chemisorption on metals is presented. Inhibition is considered to be the result of both physical adsorption and chemisorption. Electrostatic bonding at cathodic areas contributes to over-all inhibition. However, polarization of anodic dissolution because of chemisorption of inhibitor is more pronounced than cathodic polarization. Inhibitor chemisorption occurs through coordinate covalent bond formation with surface atoms of the metal. The inhibitor acts as donor and the metal as acceptor.

Dependence of inhibitive power on electronic structure of the functional group, on solubility, and on substituents on the inhibitor is satisfactorily explained by this mechanism. The theory allows for different metals and permits both positive and negative temperature coefficients. Stereochemical effects occur but are of less importance than previously thought. Results reported in the literature for nitrogen- and sulfur-containing compounds, aldehydes, and ketones are shown to be in agreement with this mechanism. The effect of an ethylenic linkage in the inhibitor and the "ortho effect" are also consistent with this mechanism.

The three prerequisites of an electrochemical mechanism of corrosion are (i) a potential difference, (ii) a conduction path, and (iii) availability of electrode reactions for transferring charges across the metal-solution interface (14, 22). Thus, an inhibitor may function: (a) by increasing the true ohmic resistance and (b) by interfering with either the anodic, the cathodic, or both the electrochemical processes. Examples of case

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(a) are inhibition by the formation of an oxide film or by precipitation of a non-conducting reaction product onto the metal. Inhibition caused by an increase in the activation hydrogen overpotential, or by a decrease of potential differences on the metal surface, or by activation polarization of anodic dissolution are examples of case (b).

Theories of Cathodic Inhibition

A theory for the action of organic inhibitors was suggested by Chappell, Roetheli, and McCarthy (5) who studied the effect of quinoline ethiodide on cathodic and anodic polarization of iron and steel in $N H_2SO_4$ and concluded that inhibition was cathodic. The same conclusion was reached by Mann who proposed a comprehensive theory of inhibition by organic compounds (33). Essential features of this theory (6, 31, 32, 33) are that organic inhibitors are capable of forming onium ions and accordingly exist in acid solution as cations. These are cathodically adsorbed by virtue of electrostatic attraction and thus blanket cathodic areas. The resultant film increases the interfacial resistance to passage of current by preventing hydrogen ions from reaching the surface, the nature of the cathode not being actually changed. Depending on extent of adsorption, the closeness of packing in the adsorbed film, and cross sectional area of the molecule, various degrees of inhibition obtain. Thus, according to Mann, organic inhibitors operate by mechanism (a).

Evidence for this theory comes from cathodic polarization studies and from changes of the inhibitive power caused by substitution on the inhibitor. Results of measurements of film resistance (2, 30, 40) are conflicting and difficult to interpret theoretically. Machu (30) found a direct relationship between film resistance and inhibition. Bockris and Conway (2), however, found a negligible film resistance and concluded that Machu's explanation of inhibition as a resistance effect was highly improbable.

A number of polarization studies have been reported (2, 5, 13, 28, 34, 38, 43). In general, the major effect of inhibitors at the current densities employed was on cathodic polarization. At high current densities and very negative potentials, as used in such studies, the effect of inhibitors on the cathodic reaction undoubtedly becomes greater. However, these conditions are quite removed from those existing during corrosion (open circuit) and any conclusion drawn from such studies are liable to be erroneous (25).

Mann's theory enjoyed a wide following mainly because it conformed to the inherent notion that positively charged particles should be adsorbed only on negatively charged areas. There are, nonetheless, numerous

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difficulties barring its acceptance. One major difficulty is presented by the change of the open circuit potential in the cathodic direction generally observed on addition of inhibitors. This shift can be explained easily if one assumes that the main effect of the inhibitor is on the anodic reaction (26). To account for this potential change on the basis of Mann's theory, or any modification of it, the assumption must be made that the organic compound is either reducible or can depolarize the cathode (13). It is difficult, however, to see how a compound at some fixed concentration can be both a depolarizer and an inhibitor of the same process simultaneously. Further, many inhibitors which give such shifts, e.g., the amines (21, 26), are incapable of undergoing cathodic reduction under conditions existing in corrosion.

A second major difficulty is that both anodic and cathodic effects occur in polarization studies at small current densities. Cavallaro and Bolognesi (3) found by polarization methods that a number of inhibitors were of a mixed type and in many cases prevalently anodic. Hackerman and Sudbury (21) report both anodic and cathodic effects in polarization studies with *n*-octyl amine. Kuznetsov and Iofa (29) also report that in many cases the increase in overpotential caused by inhibitors is greater on anodic polarization (29).

A third difficulty arises from specific effects observed with inhibitors. Sulfur-containing compounds are better inhibitors than corresponding nitrogen compounds. The theory of cathodic inhibition makes no provision for such effects since electrostatic forces are not specific. If there is any difference in the extent to which an amine or a thiol exist as cations in acid solution, the amine ought to exist to a greater extent as the cation since it is the more basic. Hackerman and Cook (20) found that irreversible adsorption of acids, alcohols, and esters occurred on the same portion of a steel surface while amines adsorbed irreversibly on a different portion. This is another instance of specific adsorption which indicates that other forces besides electrostatic ones are operative.

A similar difficulty is encountered when it is necessary to account for the effect of the nature of the metal. Thiourea is a good inhibitor for aluminum, whereas it has no effect on zinc and accelerates the dissolution of cadmium (27). Potassium cyanide is an inhibitor for aluminum and zinc but has no effect on cadmium; KCNS stimulates corrosion of cadmium and zinc by HCl but retards that of aluminum and iron (3). Also, organic inhibitors are in general poorer for zinc than for iron.

The theory of cathodic inhibition requires that the temperature coefficient for inhibition be negative, whereas experimentally (21, 28) both positive and negative temperature coefficients are reported.

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As the number of substituents on the functional group of an inhibitor increases, the inhibitive power in general also increases. Mann attributes this to a more complete coverage of cathodes because of increased cross sectional area and increased adsorption (6, 33). Swearingen and Schram(42), however, report that a series of amines of approximately equal cross sectional area exhibit quite different inhibitive properties. From this they conclude that specific adsorption is important in inhibition. Cardwell and Eilers (4) also found a specific effect upon introduction of a methyl group in the ortho position of various heterocyclic nitrogen compounds used as inhibitors. Cavallaro and Bolognesi (3) have shown that high molecular weight is not necessary for good inhibition if a strongly sorbing group is present in the molecule. The degree of inhibition exhibited by small molecules is also unexpected on the basis of this theory. For example, KCNS shows 65 per cent inhibition (3) as compared to 55 per cent by *n*-butyl amine and 65 per cent by *n*-amyl amine (33).

The suggestion that all substances employed as inhibitors exist in acid solution as charged ions has been questioned (26, 30). Hoar (26) points out that *o*-tolyl thiourea probably, and sulfonated castor oil certainly, are neutral molecules in 10 per cent H_2SO_4 but nevertheless, are excellent inhibitors. To these can be added methyl sulfide, butyl disulfide, and other sulfur compounds. Hoar further considers that electrolytic migration of a large positive ion in a solution containing a great excess of H_3O^+ would be negligible. He also points out that cathodes on the surface are polarized by the corrosion current to a potential "which is probably well within a millivolt" of that of anodes and therefore "the absolute potential difference between the bulk of the metal and the bulk of the solution is substantially uniform over the entire surface so that no specific (cathodic) adsorption can be expected". Finally, Hackerman and Schmidt (19) point out that compounds giving negatively charged ions in solution function as inhibitors.

Some of the above objections can be met by a modification of Mann's theory which retains the basic concept of the theory, viz. cathodic adsorption, but ascribes inhibition to an increase of the hydrogen activation overpotential. This theory, favored by Bockris and Conway (2), and Elze and Fischer (13) among others, can account for the specific effects by inhibitors but not for the shift in the cathodic direction of the open circuit potential unless the previous unsatisfactory assumptions are made.

Inhibition and General Adsorption

The difficulties encountered by Mann's theory have led to consideration of inhibition as the result of general rather than cathodic adsorption. Machu (30) attributed inhibition to increased ohmic resistance resulting from physical adsorption over the entire surface. Fink (16, 17) also proposed that general adsorption of the inhibitor occurred. According to him, however, this adsorption is "chemical" in nature and leads to polarization of both anodes and cathodes, with consequent surface "equipotentialization" and diminished corrosion. This thesis is substantially the same as that of Hackerman and Sudbury (21) and Hackerman and Schmidt (19). The theory of general adsorption is also favored by Hoar (26). A mechanism, however, that would count for the observed facts is still lacking and the nature of the adsorption forces is not clear.

Considerable progress has been made in recent years in elucidating various types of bonds formed in adsorption, particularly in connection with studies in heterogeneous catalysis (8, 9, 12). Of special interest here is the work of Maxted (35, 36) who observed that compounds containing elements of groups Vb and Vlb of the periodic table were particularly effective as poisons of platinum and nickel catalysts. A common characteristic of these elements is the presence of a pair of electrons that can be donated in coordinate covalent bond formation. That the toxic character was a function of this pair of electrons was shown by the absence of toxicity in compounds where these electrons were shielded. Corroborating evidence was provided by the observation that substances which contain unsaturated bonds, such as ethylene, carbon monoxide, and cyanogen compounds, are also strong poisons.

Catalytic poisoning results from strong adsorption of a substance (the poison) which ties up active sites of the catalyst that could otherwise be utilized in the catalytic process. Thus, a poison operates by being strongly chemisorbed on the metal catalyst. Maxted, therefore, concluded that chemisorption of these compounds on metallic hydrogenation catalysts of group VIII was accomplished through a dative link, the metal functioning as acceptor and the sorbate as donor. In addition, he postulated that the electron pair was donated to the d-shell of the metal. This last assumption received experimental support from magnetic susceptibility measurements (7).

Polar organic compounds containing elements of groups Vb or Vlb are effective as inhibitors in the acid dissolution of metals. Some particularly effective functional groups are -CN, -CNS, -CNO, >CO , and -CHO. These compounds are "electron rich" and can act as electron donors. It will be shown that a satisfactory explanation of inhibitive action of

these compounds can be found along lines suggested by Maxted in his work on catalytic poisoning. The two systems are similar in that adsorption is the primary step in both cases.

Adsorption of Polar Organic Inhibitors

It is postulated that adsorption is general and not decisively controlled by the existence of local cells. The improbability of any considerable electrolytic migration of inhibitors during corrosion was shown above.

This adsorption is both physical and chemical in nature. Physical adsorption results from weak van der Waals, or dispersion, forces which are operative over the entire surface. In addition adsorption because of electrostatic interaction occurs at cathodes. The amount adsorbed because of dispersion forces, though not negligible, is of little importance in inhibition by compounds discussed here. This, of course, does not apply to substances like gelatin which are barrier-type or diffusion inhibitors. Electrostatic bonding at cathodic areas contributes, however, to over-all inhibition*.

It is postulated that considerable chemisorption occurs under the conditions existing in acid dissolution. The studies of Hackerman and Cook (20) on adsorption of inhibitors from benzene solution on steel powder constitute the experimental basis for this postulate. Additional experimental support is provided by the persistence of inhibition when pre-treated iron coupons are transferred from protected solutions to unprotected ones (3, 31).

The binding responsible for chemisorption is the formation of a dative link between the metal and the organic molecule. The bond is formed through sharing a pair of electrons from the inhibitor with the metal. Since such a transfer leaves the organic molecule with a formal positive charge, it is unlikely that more than one electron pair per molecule will be donated even though the acceptor might have available orbitals for more

It should be noted that chemisorptive bonds can also be formed where the metal acts as donor and the adsorbate as acceptor. Such a mechanism is probably responsible for inhibition by various metal ions. It is,

*Since most of these inhibitors exist as positively charged ions in solution, the adsorption resulting from electrostatic forces is cathodic. In the case of inhibitors yielding anions in solution, such adsorption will occur at anodes.

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however, doubtful that any organic inhibitors are chemisorbed in this fashion

Chemisorption might cause inhibition either by decreasing the dissolution tendency of the metal at anodes, or by increasing the activation overpotential for hydrogen discharge, i.e., by poisoning the cathodes. It should be emphasized that either of these requires that the inhibitor be chemisorbed: physical adsorption involves energies which are not of the right order of magnitude for such effects.

No a priori reason can be given as to why the effect of chemisorbed inhibitor should be greater on anodes rather than on cathodes. The requirements for anodic and cathodic inhibition are the same, viz. chemisorption of the inhibitor, though the result of such chemisorption is different in the two cases. At anodes the inherent reactivity of the metal is decreased whereas at cathodic points the hydrogen reaction is poisoned. It is impossible to decide between the two on theoretical grounds since neither of these phenomena is well understood. Experiment, however, indicates that the inhibitive action is prevalently anodic. Largely, the experimental evidence comes from the cathodic shift of the open circuit potential on addition of inhibitors. This requires that polarization of the anodic reaction be more pronounced than polarization of cathodic hydrogen deposition.

Anodic polarization may be looked upon as the result of chemisorption with consequent stabilization of the metal ion in the surface lattice. Alternatively, it may be described as complex formation in situ, many inhibitors are capable of forming complexes with ferrous ion, and on the basis of this property only they should be accelerators rather than inhibitors. A similar situation exists with amines and copper. In these cases complex ion formation in situ offsets the accelerating effect of complexing the metal ion in solution so that over-all inhibition rather than acceleration results.

A third way of looking at anodic polarization is to follow Evans and Hoar(15) and consider it as the arrest of emergent cations, a description which permits a smooth transition from oxidation studies at high temperature to wet corrosion. All of these descriptions are equivalent. The first viewpoint is used here because it proves to be not only the most convenient but also the most fruitful.

Inhibition, then results from both increased resistance to current flow caused by electrostatic adsorption at cathodic areas and from anodic polarization caused by chemisorption. The relative contribution of the two depends on the inhibitor. Three classes of inhibitors may thus be distinguished. Anodic inhibitors function by polarizing anodic dissolution

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An example is the sulfide series. A second class consists of mixed inhibitors. Examples are amines and thiols. Finally, there are cases where cathodic polarization is the most important effect. Quaternary amine salts belong to this class. Here, although physical adsorption probably occurs over the entire surface, chemisorption does not take place since there is no possibility of electron transfer. The strongest possible bonding with R_4N^+ is electrostatic attraction and this obtains at cathodes.

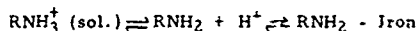
Factors that critically influence the extent of chemisorption are the nature of the metal and the electronic structure of the adsorbed group. The strength of bonding is a function of the metal since it is related to residual valence orbitals existing at the metal surface. Without going into various treatments of chemisorption it may be noted that residual metal valencies at the surface are not alone sufficient for strong chemisorption, in addition, unfilled atomic orbitals are required. Pauling's treatment of the metallic state would apply here. These are principally of d character. Inhibitors of this type should, therefore, be more effective, for example, with iron than with zinc.

An elementary approach to the influence of the electronic structure of the adsorbed group is possible in terms of the availability of electrons for bond formation. This can be considered to be a function of electron density and polarizability of the functional group or, for simple molecules, of the Vb or Vlb element that the compound contains. This is admittedly an approximation, but the complexity of the system here considered does not permit a more rigorous treatment.

Applications of the Mechanism

Taking iron as the metal to be protected, consider the action of polar organic inhibitors in the light of the above postulates. The data of Mann (31, 32, 33) and other results obtained at the University of Minnesota by Mann and his co-workers and tabulated by Eldredge and Warner (11) are used.

Amines: Inhibition by aliphatic amines considered to involve the following equilibria:

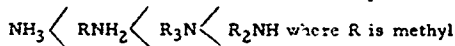


where RNH_2 - Iron denotes chemisorbed amine. The extent of chemisorption depends on the strength of the amine-metal bond and also on the solubility of the particular amine. This last factor should be particularly

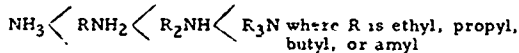
noted in view of some definitions of chemisorption as "irreversible adsorption". Chemisorption, like any other chemical reaction, is more or less easily reversible depending on the specific system under consideration. Mexted (37) has shown that catalytic poisons, which are undoubtedly chemisorbed, can be removed from a platinum catalyst simply by washing with fresh solvent. The extent of chemisorption is thus a function of the solubility of the chemisorbed compound and consequently, inhibition is also a function of solubility.

The strength of the iron-amine bond is a function of both electron density on the nitrogen atom and the availability of these electrons for coordinate bond formation. The basic strength of the amine is taken to be an indication of the electron density on the nitrogen atom, and the assumption is made that the strength of the chemisorption bond increases with increasing basic strength. This criterion alone is of limited usefulness since the availability of electrons for coordination is also a function of the polarizability of the atom or group considered. However, in the absence of any other information, this criterion must be used.

The relative order of inhibitive effectiveness of aliphatic amines is



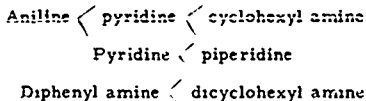
and



In the first series basic strength decreases in the order $\text{R}_2\text{NH} > \text{RNH}_2 > \text{R}_3\text{N} > \text{NH}_3$ (24). The solubility of the methylamine salts is about the same. Thus dimethyl amine is a stronger base and approximately as soluble as trimethyl amine. Dimethyl amine should thus be a better inhibitor than trimethyl amine. For the second series, however, the decrease in basicity of diethyl amine upon introduction of a third ethyl radical is significantly less (about one-fourth as much) (24), and triethyl amine is less soluble than diethyl amine (41). Consequently, triethyl amine should be more effective than diethyl amine. This is true also where R is propyl, butyl, or amyl.

The introduction of a fourth alkyl group causes a sharp drop in inhibitive power. Thus, both trimethyl and dimethyl amines are better inhibitors than tetramethyl ammonium ion. Such decrease in inhibition is understandable on the basis of this theory since chemisorption of the quaternary salt cannot occur. Inhibition by this ion is, therefore, for the main part cathodic.

Aliphatic amines are better inhibitors than aromatic amines. Heterocyclic amines, such as pyridine, while better than aromatic amines are less effective than the corresponding saturated compounds. These relations are shown schematically below:



The basic strength of these compounds is in the same order (24). A phenyl group is electron attracting and it consequently decreases the electron density on the nitrogen atom, the decrease being reflected in lower basic strength of aniline when compared to cyclohexyl amine. Piperidine is also a stronger base than pyridine. Saturation of the aromatic or heterocyclic ring increases electron density on the nitrogen atom and therefore increases inhibitive power (6).

Data for benzyl amine are not available. The theory requires that its inhibitive power lie between that of aniline and cyclohexyl amine.

The introduction of alkyl groups on the benzene ring of aniline leads to better inhibition because of both decreased solubility and increased electron density on the nitrogen atom. The same is true when hydrogen atoms on nitrogen are replaced by alkyl groups. Relations that result are similar to those for aliphatic amines.

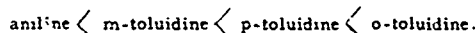
Steric effects are operative but are of less importance than previously thought(33). Further, such effects are not restricted to cathodic adsorption but influence adsorption in general as shown by studies on charcoal(44). On the basis of this theory geometrical factors should determine the closeness of packing of the adsorbed film over both anodes and cathodes and consequently affect the inhibitive power. Thus, the decrease in inhibition generally observed on substitution of a branched alkyl chain for a straight one is caused by the methyl group in iso compounds preventing close contact of neighboring adsorbed molecules. As a result, not only is adsorption decreased but also effectiveness of the film over both anodes and cathodes reduced.

The stereochemical configuration of inhibitors might also influence the extent of adsorption through its effect on the degree of association of polar organic compounds in solution. The monomeric form is known to be preferentially adsorbed and, therefore, any change in the degree of association will undoubtedly be reflected on extent of adsorption.

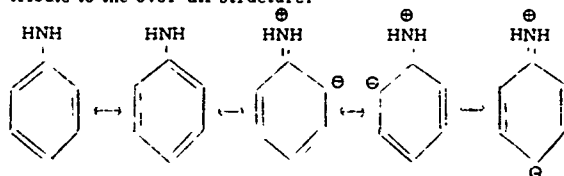
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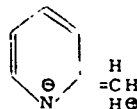
The Ortho Effect: Introduction of methyl groups on the ring of pyridine and other heterocyclic aromatic nitrogen compounds increases inhibition just as in the case of aniline and for the same reasons. Cardwell and Eilers (4) observed that a methyl group in the ortho position was particularly effective; and that it caused a constant 25 per cent increase in inhibition, independent of the original cross sectional area of the inhibitor. Rhodes and Kuhn (40) report that in the series pyridine-lutidine-picoline-collidine the introduction of a methyl group increases inhibition by about 25 per cent. Mann (11) also found that the effectiveness of toluidines is in the order



The main effect of the methyl group is on the strength of the chemisorption bond and, qualitatively, is due to its ability to supply electrons to the ring. Taking aniline as an example, the following resonance states contribute to the over-all structure:



Substitution of electron donating methyl groups decreases the contribution of the last three structures and thus leads to increased chemisorption. From these structures it seems reasonable that, other things being equal, substitution in the ortho or para positions should be more beneficial than substitution in the meta position. Similarly, in the case of pyridine an ortho group increases electron density on the nitrogen atom because of resonance, viz.



This is also true for a para methyl group but not for one in the meta position.

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The specific effect by an ortho methyl group on the adsorption bond observed by Cardwell and Eilers (4) is thus in accord with this theory

Sulfur-Containing Compounds: The protective value of sulfur-containing compounds is decidedly superior to that of nitrogen containing compounds. This is in part caused by the lower solubility of sulfur compounds. However, even making allowances for this, sulfur compounds are still found to be better inhibitors. Ethyl mercaptan, for example, is as good, if not better, an inhibitor as diamyl amine, dihexyl amine, or tripropyl amine.

Superiority of sulfur compounds results from the greater polarizability of the sulfur atom. Sulfur is less electronegative than nitrogen (2.5 compared to 3.0 on Pauling's scale). Furthermore, it has two electron pairs available for coordination whereas nitrogen has only one. Consequently, sulfur is a better electron donor than nitrogen, a property which is reflected in its greater tendency towards coordination. For this reason sulfur compounds are more extensively and more strongly chemisorbed than the "corresponding" nitrogen compounds. The inhibitive power of compounds like methyl sulfide which is entirely unexpected on the basis of cathodic inhibition becomes understandable on the basis of this theory.

Within a series of sulfur compounds the same relations obtain as within the equivalent series of nitrogen compounds. Thus the order of effectiveness of mercaptans is

methyl < ethyl < propyl < butyl < amyl

and of sulfides

methyl < ethyl < propyl < butyl

A drop in inhibitive effectiveness is again observed in going from aliphatic to aromatic compounds. Thus, thiophenol is poorer than ethyl mercaptan (data on cyclohexyl mercaptan are not available). The reason is the same as in the nitrogen compounds. As would be predicted on the basis of electron density, thiocresols are better than thiophenol.

Corresponding oxygen compounds, e.g., alcohols and phenol, are poor inhibitors. This is because oxygen is more electronegative than sulfur, and it does not readily function as a donor in coordinate bond formation. Selenium, on the other hand, should give compounds that are better inhibitors than corresponding sulfur compounds. Data are available only for ethyl selenide. Judging from this alone, selenium is more effective than sulfur.

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Aldehydes and Ketones: In aldehydes and ketones the electronic configuration of the functional group as a whole rather than that of any particular atom is of importance, and a discussion of their inhibitive action is consequently more involved. The inhibitive action of these compounds is a function of the reactivity of the functional group. Aldehydes, which are more reactive, are better inhibitors than ketones. The inhibitive efficiency in the series $RCHO$, where R is H , CH_3 , C_2H_5 , or C_3H_7 , does not follow the pattern for amines or thiols but is in the order:

butyraldehyde < acetaldehyde < propionaldehyde < formaldehyde.

This relative order for inhibition indicates that two opposing effects are operative as molecular weight increases, viz. adsorption tends to increase but reactivity decreases.

Substitution of a methyl group on the benzene ring of benzaldehyde causes an increase in inhibitive power just as for nitrogen- and sulfur-containing compounds. Further meaningful comparisons cannot be made because experimental data on aldehydes are much less available than for either nitrogen or sulfur compounds. This is also true for ketones.

The Effect of the Double Bond: Cavallaro and Bolognesi (3) observed that an ethylenic double bond has considerable inhibitive power. For example, where propyl alcohol is of very little inhibitive value, allyl alcohol is a very good inhibitor. Similarly, they found that under conditions where thiourea is an accelerator, allyl thiourea is a good inhibitor.* Mann (11) also found that crotonaldehyde is a much better inhibitor than butyraldehyde and phorone is superior to valerone.

Chemisorption of ethylenic compounds on metal catalysts is known to occur. The superiority of unsaturated compounds is the result of enhanced chemisorption brought about by the double bond, which constitutes a second point of attachment of the inhibitor. In conjugated systems the electron density of the aldehyde, or keto, or other functional group is augmented by the resonance that results, and this also contributes to stronger chemisorption.

*The data reported in the literature concerning the inhibitive actions of thiourea and its N-substituted derivatives are conflicting. This is because these compounds function in more than one way depending on conditions. Reference (23) is an attempt to clear up the conflicting reports on the basis of a study of eight of these compounds under various conditions.

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Other Inhibitors: For inhibitors having other functional groups there is insufficient information for significant comparisons. An interesting observation is that substitution of sulfur for oxygen leads to better inhibitors as is expected. Thus, thioureas are better inhibitors than ureas and thiocyanates, better than cyanates.

Of the diverse list of inhibitors remaining to be considered, some are difficult to account for with the proposed mechanism. For example, according to this theory sulfates and sulfonate should not have inhibitive properties to any considerable extent. Experimentally it is found that sulfates are not good inhibitors (4), (11), (and data obtained in this laboratory). Results reported on sulfonates are conflicting. Eldredge (11) found two commercial wetting agents (both sulfonates) to be good inhibitors. Cardwell and Eilers (4), however, report no inhibition by a saturated hydrocarbon sulfonate. In order to account for the discrepancy it would be necessary to know about the purity of the compounds used. This suggests that further work with carefully purified materials is needed.

The problem of high molecular weight inhibitors should be mentioned here. When the carbon chain gets up to about twelve carbon atoms or more, influence of the functional group on inhibitive properties is less pronounced than with low molecular weight inhibitors. With high molecular weight inhibitors, a densely packed film, with the hydrocarbon chains oriented outward, is formed on the metal surface. Such films are known to be both hydrophobic and oleophobic (1)(39). It is probable that in this case inhibition is caused by a mechanical separation of the two phases, i.e., by the establishment of a diffusion barrier to both Fe^{++} and H^+ . The functional group here aids adsorption at the interface and contributes to formation of an oriented structure. One way in which the functional groups of high molecular weight compounds cause differences is in the persistence of inhibition. The order of effectiveness of functional groups in this respect is similar to that for low molecular weight inhibitors. Thus inhibition by amines, thiols, and acids is more persistent than by alcohols and esters (20).

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