

RELATIONS BETWEEN FRACTURE  
AND COORDINATION CHEMISTRY

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INTRODUCTION

This paper summarizes certain mechanistic techniques used in inorganic chemistry to study processes occurring at metal centers, and suggests applications of these techniques to the study of the atomistic mechanism(s) of fracture of metals. Coordination chemistry, organometallic chemistry, and catalysis also offer a number of kinds of structural and mechanistic information pertinent to the study of fracture.

In considering the process of fracture of materials, as in considering other processes, the questions of interest are questions of rates: Under a given set of conditions, how rapidly will a material fracture? Under what conditions will this material fracture rapidly? To begin to answer these questions in atomic or molecular terms, it is necessary to be able to identify the slowest step in the fracture process: that is, the elementary step whose rate determines the overall rate of fracture. This elementary step might be any of a large number of possibilities: breaking individual metal-metal bonds as the fracture advances; rearranging bonds within the bulk metal close to the fracture zone as part of plastic deformation of the metal; breaking metal-oxygen or metal-sulfur bonds in a passivating surface layer; removal of products from the cathodic or anodic regions of a local electrochemical cell; rearrangement of groups of bonds (slipping), either individually or in a concerted manner; formation or migration of surface metal hydrides; many others. When the slow step has been identified, one can profitably consider in detail the interactions of the participating atoms in the step, and perhaps develop rational strategies for slowing (or accelerating) it.

In many (perhaps at present most) cases it is difficult or impossible to rigorously identify the slow step in a fracture process. In the absence of firm information, one is restricted to discussion of probable, plausible, or possible cases, and of phenomena which seem generally likely to be important or relevant to fracture a priori. Here we consider one such general topic which is relevant to fracture: viz., the qualitative coordination chemistry of the fracture surface, and methods for exploring this type of coordination chemistry. This topic is a very broad one, and this manuscript concentrates on approaches drawn from organometallic, mechanistic, and catalytic chemistry. Other approaches based on surface physics are not discussed.<sup>1-3</sup>

Fracture of a metal creates new surface. The free-energy change accompanying this process has contributions from many sources, of which several are the structure and composition of the bulk material which is cleaved, the energy of breaking metal-metal (or metal-hydrogen or metal-oxygen) bonds, the energy of forming bonds between the new surface atoms and any adsorbed species, and the energy of reconstructing the surface (that is, the energy of modifying the bonding of the newly-formed surface atoms with their immediate neighbors and of these immediate neighbors with more distant centers. Consideration of factors influencing the rate of formation of new surface is clearly relevant to the fracture process, but formation of new surface is not necessarily the slow step in fracture. Nonetheless, the formation of new surface, and its concurrent or subsequent modification by adsorption of species the environment is undoubtedly an important process in many fractures.

Adsorption on a metal surface is, of course, also critical to other areas of science -- heterogeneous catalysis, corrosion, adhesion, friction, wear -- and one might hope to find useful parallels between these areas. In catalysis, in particular, reactants adsorb on the surface of a metal or metal salt. After adsorption they undergo combinations of migrations, reactions with the surface, and reactions with one another which lead ultimately to products. The products must then desorb to create room on the surface for fresh reactants. Again, the adsorption processes are often not overall rate limiting, but they are important in determining the energetics of the overall transformation of reactants to products.

It is, of course, difficult to answer questions of detailed mechanism concerning any surface reaction, in part because it is so difficult to obtain detailed information concerning the structure of surfaces. Fortunately, many of the same questions concerning adsorption at metal centers, and about the making and breaking of bonds among metals and between metals and adsorbates arises in another, related field: homogeneous catalysis.<sup>4</sup> Here the metallic species which are involved are (at least initially) in structurally well-defined environments (howbeit in environments in which the

nearest-neighbor groups are usually organic phosphines, carbon monoxides, and olefins instead of other metal atoms). The structures of these catalytic groups provide models for surface species which are at least stimulating and provocative (and which may even be relevant to fracture), and it is often possible to follow the course of catalytic reactions in very great detail at the molecular level.

#### RATES OF REACTIONS: TRANSITION STATE THEORY

To provide some background for discussion of these soluble organometallic analogs of surface structures and surface processes, it is useful to mention several details of the formalism which is almost universally used in chemistry in discussing rates. This theory is the so-called "transition state theory". This theory is, of course, well-known in materials science, but the aspects of the theory which are emphasized in materials science and chemistry are surprisingly different. The utility of transition state theory in chemistry is that it limits problems in rates to the consideration of only two structures: that of the starting material(s) in their ground state, and that of the species having the highest free energy between starting material and product. The rate of the process is then given by an equation of the familiar form 1 which relates this rate to the differences in energy,  $\Delta G^\ddagger$ , between these two states (figure 1). The vertical axis in this figure is the Gibbs free

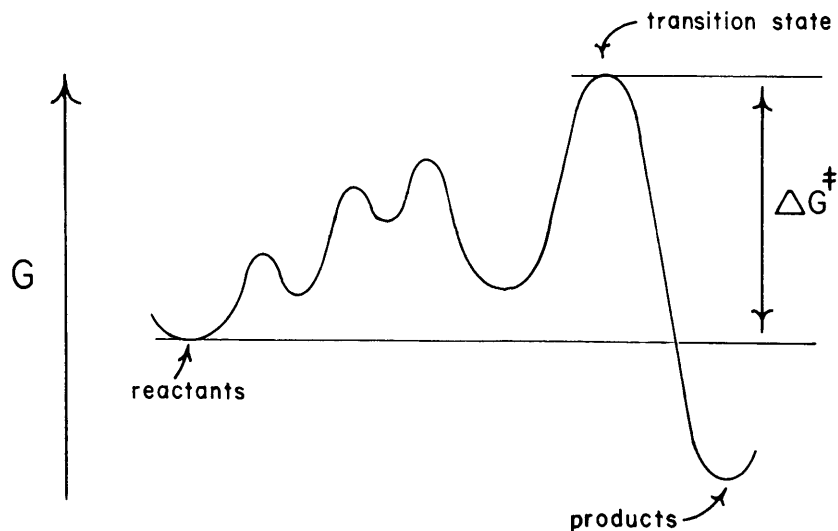


Fig.1. Schematic reaction coordinate (lowest-energy section through a potential surface) connecting reactants and products.

energy (which includes contributions from entropy: equation 1).

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (1)$$

The horizontal axis is a not-very-well-defined quantity which represents progress along the potential surface connecting reactants and products. The rate of the process being considered is given by the familiar equation 2

$$\text{rate} = \kappa \frac{kT}{h} e^{-\Delta G^\ddagger / RT} \quad (2)$$

(In equation 2, the constants  $k$  (Boltzman),  $h$  (Planck) and  $R$  (Gas) have their usual meaning, and  $\kappa \approx 0.5$  is an adjustment factor included for not very satisfying reasons and often ignored.) The general form of this treatment is familiar to almost everyone with technical interests, but two of its implications deserve emphasis in the particular context of fracture.

- Only two structures are of interest in considering the rate of a process: the ground state and the transition state. Other intermediate states which may seem scientifically interesting or which may appear to be high energy are of no importance to calculation of rates, if their energy ( $G$ ) is not the in fact highest along the reaction coordinate.

The great virtue of transition state theory is just its simplicity: one need only know  $\Delta G^\ddagger$  to calculate an approximate rate. If one knows the elemental composition and structure of the transition state, one may be able to calculate its energy and estimate the rate of the process. If one does not know what the transition state is, discussion of rates in atomic and molecular detail is meaningless.

- The Gibbs free energy,  $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$ , includes contributions from both enthalpy and entropy. This simple fact is widely ignored by theoreticians interested in estimating rates. Such individuals calculate energy (that is, a quantity which can be roughly equated with enthalpy); they almost never consider entropies. There is, as a result, a critical weakness in their methods and conclusions. Until it can be demonstrated that entropy terms are not important, or until some method is available for calculating them, calculations of  $\Delta H^\ddagger$  should be considered at best a poor approximation to  $\Delta G^\ddagger$ . This caution holds particularly true for any process involving water or other solvents (for example water solvating a newly created fracture surface), adsorption of components on the new surface, or release of atoms from the surface into solution: in all of these cases entropy terms may be large.<sup>5</sup>

Consider the application of transition state theory to consideration of the rate of propagation of a fracture along a crystal plane, with the fracture tip in contact with a medium which contains a species L which adsorbs on the metal surface (Figure 2). To repeat a point for emphasis: the utility of the transition state theory is in focusing attention on the highest energy state (i.e. the transition state). What is the elemental composition of this state? What is the character of the bonds connecting the atoms in the transition state? What is its energy, relative to reactants? In the case at hand, one can imagine two limiting cases. In one case, the metal-metal bonds break completely before the species L adsorbs at the resulting, newly formed surface metal atoms (Figure 2A); in the second, L adsorbs as the metal-metal bonds are breaking, and lowers

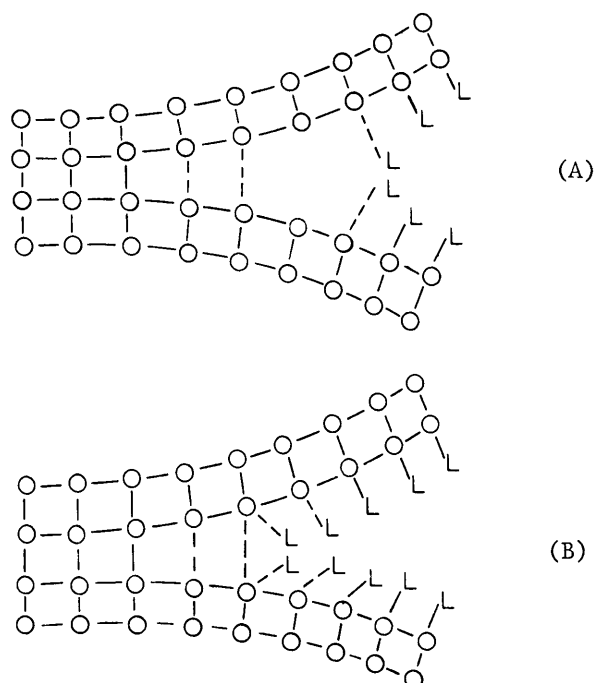


Fig.2. Schematic representation of a fracture tip propagating by a process in which a component L from the medium does not (A) and does (B) participate actively in breaking metal-metal bonds.

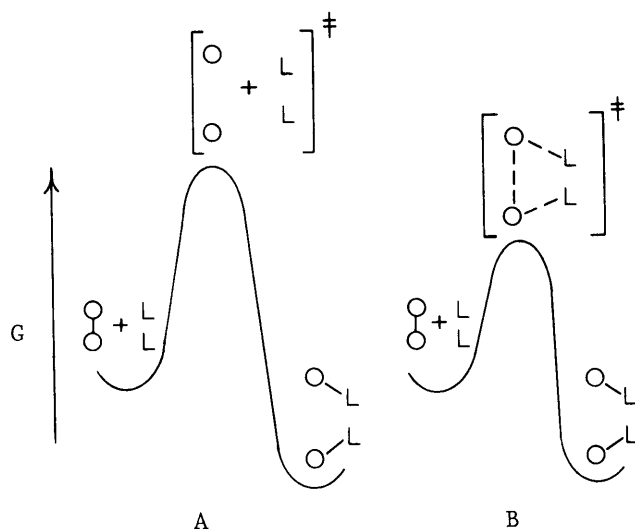


Fig.3. Simplified reaction coordinates for the cleavage of metal-metal single bonds in the fracture processes indicated in Figure 2.

the energy of this bond breaking process (Figure 2B). These two alternatives would be represented in free energy diagrams as shown in Figure 3. In this figure we consider only one pair of metal atoms for simplicity. In the first process, a full metal-metal bond is broken without any compensation other than that reflecting some small structural reorganization of the surrounding metal atoms. In the second, as the metal-metal bond breaks, metal-L bonds form. The sequence of events in path B seems preferable from the vantage of the energetics of the four-center  $M_2L_2$  system, but is probably entropically less favorable than path A, and may also have a significantly unfavorable energetic contribution due to non-bonding interactions between the L group. One does not know at present which is actually important in a real instance of fracture, but the inference that surface-active species (in this context, hydrogen, liquid metals, perhaps species such as chloride ion) accelerate some fracture processes suggests that path B may be important in at least some instances.

The type of analytical exercise represented by this example is not idle: it indicates the minimum information required to rationalize the rate of a process. One must know the elementary composition of the transition state, and some elements of the structure of this state. Without this information, theoretical calculations of energetics are argueably irrelevant. The burden of taking the first steps in understanding the mechanism of fracture thus presently rest with the experimentalist, since, at present, only experimental work can provide reliable information on composition and structure.

It is easy to emphasize the importance of this type of detailed information in rationalizing rates, but much more difficult to obtain it in practice. In no instance involving fracture is the information available. In a few cases in heterogeneous catalysis it is now being developed, and a significant body of information is available for homogeneous reactions involving metals. In the following sections, I touch on examples of homogeneous and heterogeneous reactions involving metals, and sketch some of the chemical concepts and techniques which have proved useful in studying these reactions. The major focus of this discussion will be that of coordination of ligands to metals. This subject is relevant to the influence of species coordinating to a newly created fracture surface on the energy of the steps creating that surface.

#### MECHANISMS OF METAL-CATALYZED REACTIONS: THE IMPORTANCE OF VACANT COORDINATION SITES

Consider, by way of background, two important metal-catalyzed reactions: hydrogenation of ethylene using platinum metal as catalyst (Figure 4), and hydrogenation of ethylene using a soluble rhodium(I) complex as catalyst (Figure 5). Very little is known with great certainty concerning the heterogeneous catalytic reaction. The current interpretation of the available experimental data is that the catalyst adsorbs ethylene strongly at vacant coordination sites (to yield one or several surface complex(es) whose structure(s), especially under the conditions encountered during catalysis, is (are) not well known).<sup>6</sup> Dihydrogen subsequently adsorbs on remaining vacant coordination sites with dissociation into surface metal hydrides. The adsorbed ethylene and this surface hydride react and form surface ethyl groups. These surface ethyls react subsequently with more surface hydride and generate ethane. When the ethane desorbs from the surface, vacant coordination sites are regenerated which reenter the catalytic cycle.

The mechanism for hydrogenation of ethylene by the soluble rhodium complex is conceptually similar.<sup>7</sup> Ethylene coordinates at a vacant coordination site on the metal, dihydrogen adsorbs dissociatively, the coordinated ethylene and a metal hydride react and form an intermediate ethylrhodium intermediate, and ethane is produced by reaction of this species with a second equivalent of metal hydride.

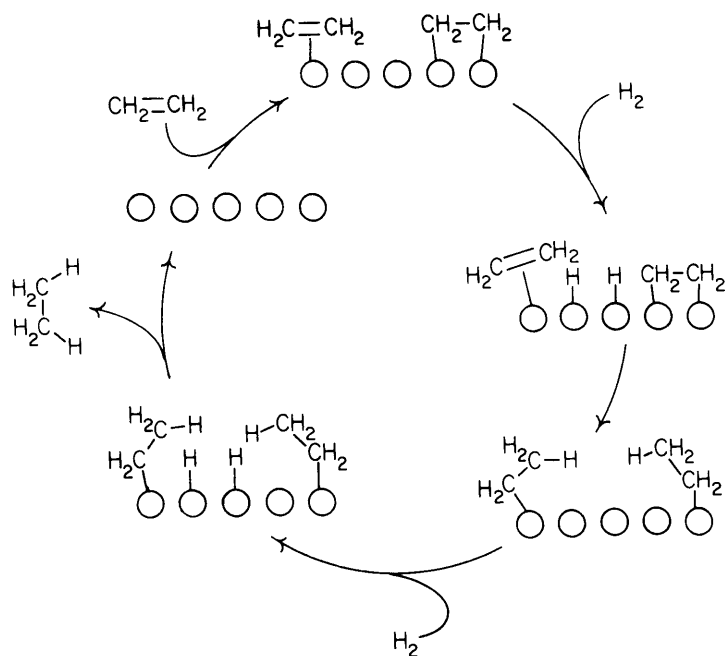


Fig.4. Schematic mechanisms for hydrogenation of ethylene over platinum.

In both of these mechanisms there remain substantial ambiguities: Does dihydrogen or ethylene adsorb first? Which adsorbs more strongly? What are the detailed structures of the reaction intermediates? What is the overall rate-limiting step? Some of these questions can be answered tentatively (for example, formation of ethane by reaction of ethylmetal and metal hydride is probably rate-limiting in both reactions under at least some circumstances); others cannot. Nonetheless, from the vantage of a discussion of fracture, these details are irrelevant. The important aspects of these reactions is their dependence on the availability of a vacant coordination site on the metal: if no vacant coordination site is available, no reaction occurs. Thus, adsorption of the reactants at vacant metal coordination sites is a critical element of coordination catalysts, and an understanding of the factors influencing this



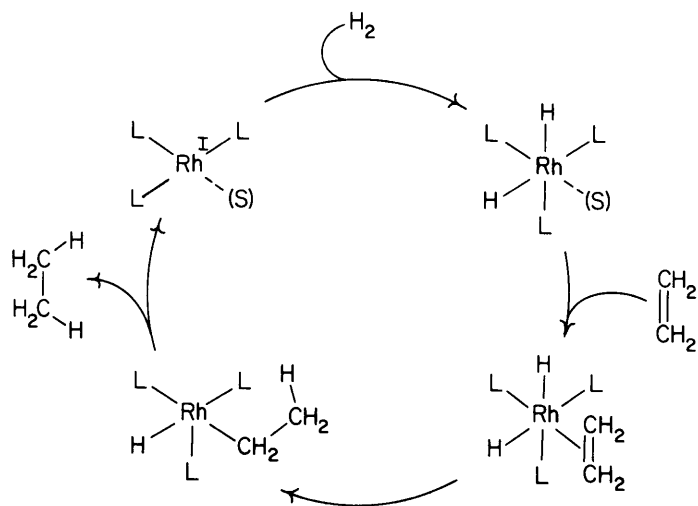


Fig.5. Schematic mechanism for hydrogenation of ethylene by dihydrogen catalyzed by a soluble rhodium(I) complex:  
 $\text{L} = (\text{C}_6\text{H}_5)_3\text{P}$ ,  $\text{S} = \text{solvent typically } \text{CH}_2\text{Cl}_2 \text{ or } \text{CH}_3\text{COCH}_3$ .

adsorption is essential to understanding catalysis. Similar adsorption phenomena are certainly involved in adhesion, lubrication, and corrosion, and in adsorption at freshly created fracture surfaces.

#### COORDINATION TO METALS: USEFUL QUALITATIVE CONCEPTS

Coordination chemistry is an area of great sophistication, but much of the information in it which is immediately useful to considerations of the (atomistically) less sophisticated area of fracture can be summarized in a limited number of simple empirical models for the interaction of metals and metal ions with ligands, and for the interaction of ligands with one another. I outline two of these here: the theory of "Soft and Hard Acids and Bases", developed by Pearson (and related to an earlier classification by Chatt and Ahlrand) and Tolman's classification of the sizes of ligands by "cone angles". In addition, I mention the Hammett equation as an example of a Linear Free Energy Relation (LFER), an intellectual construct which has proved invaluable in mechanistic chemistry. Finally, I touch

briefly on the subject of entropies. Other useful models used to rationalize the reactivities of metal ions in solution -- especially classical ligand field theory and its mathematical developments -- are not discussed, since these have not proved particularly useful in discussing organometallic chemistry or catalysis, and do seem likely to be useful in fracture at this stage in its development.

Hard and Soft Acids and Bases (HSAB).<sup>8</sup> The most commonly used model used in classifying the relative strengths of coordination of metal ions and ligands is based on the idea that there are two major types of bonding: ionic and covalent. Ionic bonding (for example, in  $\text{Na}^+\text{F}^-$ ) is familiar. Covalent bonding is most commonly discussed using a model developed by Dewar and Chatt (illustrated for a complex of silver(II) and ethylene in Figure 6).<sup>9</sup> In this model the covalent bond between silver and ethylene is considered to be composed of two components: one component (the  $\sigma$ -bond component) reflecting overlap between the filled  $\pi$  orbital of ethylene and a vacant  $s$  orbital on silver, and another component (the  $\pi$ -bond component) reflecting overlap between a filled silver  $d$  orbital and the vacant  $\pi^*$  orbital on ethylene. The  $\sigma$ -component is believed to be the more important in determining the energy of most metal-ligand bonds, and the  $\pi$ -component serves the primary function of preventing a large separation of charge by transfer from olefin to metal by allowing back-donation of charge from metal to olefin.

The SHAB classification is based on the idea that ions which are small, highly charged, and non-polarizable ("hard" ions) can interact with one another strongly ionically, but will not interact strongly with large, polarizable species with low charges ("soft" ions or molecules). The latter, in turn can interact with one

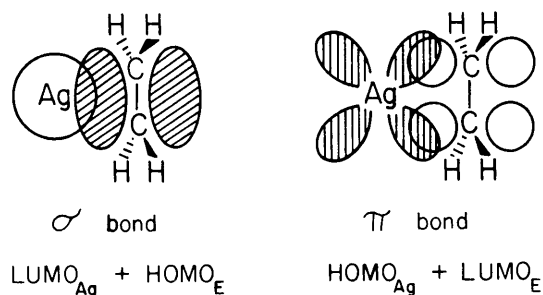


Fig. 6. Dewar-Chatto model for the bonding of silver ion to ethylene. LUMO = lowest unoccupied molecular orbital; HOMO = highest occupied molecular orbital.

Table I. Examples of Hard and Soft Species

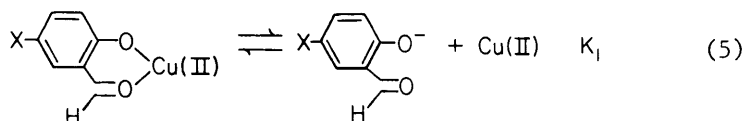
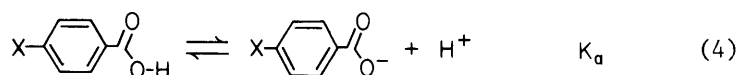
Hard	Soft
$H_2O$	$H_2S, H_2Se$
$H_3N$	$H_3P, H_3As$
$Li^+, Na^+, K^+$	$M^O$ , bulk metals
$Mg^{+2}, Ca^{+2}$	$M^O L$
$Al^{+3}$	
$Cu^{+2}$	$Cu^{+1}$
	$CO, CH_3N \equiv C$
	$CH_2=CH_2$
	$HC \equiv CH$
$F^-, OH^-$	$Br^-, I^-$
$SO_4^{2-}, ClO_4^-$	$CH_3CS_2^-, CN^-$
$H^+$	$H^-$

another covalently. Table I gives examples of species classified as "hard" and "soft". Empirically, hard ions coordinate one another more strongly than soft ions, and vice versa: like prefers like.

The usefulness of this classification for discussions of fracture, freshly created fracture surfaces of metals) are "soft", zero-valent metals (that is, in the context of a discussion of fracture freshly created fracture surfaces of metals) are "soft", and would thus be expected to coordinate especially strongly with soft species (liquid sodium and mercury metals, sulfur- and phosphorous-containing species, hydrogen, olefins, carbon monoxide). After these metal surfaces have reacted oxidatively (with  $O_2$  or  $H_2O$ ), they are usually covered with "hard" species (high-valent ions, metal oxides and hydroxides), and would be expected to coordinate more strongly with hard ligands.

It is difficult to argue the empirical usefulness of the SHAB classification, and it in no way detracts from its usefulness to point out that this classification may be incorrect in its fundamental assumptions. It is a theory which entirely ignores the interaction of the coordinating species with solvent, and there is a growing suspicion that solvation may play a dominant role in





$$\Delta(\Delta G^\circ)_x^{\text{reaction 1}} \propto \Delta(\Delta G^\circ)_x^{\text{reaction 2}} \quad (6)$$

$$\log \frac{(K_i)_x}{(K_i)_{x=\text{H}}} = \rho \log \frac{(K_a)_x}{(K_a)_{x=\text{H}}} \quad (7)$$

$$= \rho \sigma_x \quad (8)$$

salisaldehydes; equation 5). One postulates a LFER (equation 6): the change in the free energy of this reaction which accompanies a particular change in substituent in one reaction is assumed to be linearly proportional to that accompanying the same change in a second reaction. Equation 7, which relates the observed equilibrium constants for the two types of reaction to one another, follows from this assumption. In equation 7, or its alternative form equation 8, there are two types of parameters. The so-called  $\sigma$  parameters characterize the substituents X; the  $\rho$  parameters are characteristic of the reactions. Table 2 gives a short list of  $\sigma$  constants; much more complete lists can be found elsewhere, together with lists of  $\rho$  values.

The usefulness of LFER's is in the study of complex reactions and processes: it provides a way of establishing empirical analogues between reactions. For example, Figure 7 gives a plot of values of  $\log k$  for the coordination reaction shown in equation 5 versus values of the ionization constants of the corresponding salicyaldehydes (equation 9)<sup>12</sup>

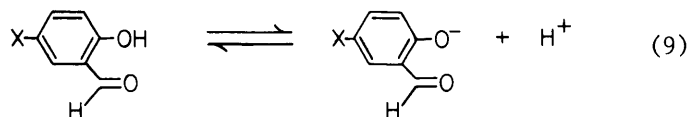


Table 2. Substituent Constants  $\sigma$ .<sup>a</sup>

X	$\sigma$	X	$\sigma$
CH <sub>3</sub>	-0.17	OH	-0.37
CH <sub>2</sub> CH <sub>3</sub>	-0.15	OCH <sub>3</sub>	-0.27
C <sub>6</sub> H <sub>5</sub>	-0.01	F	0.06
CHO	0.44	Cl	0.23
CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	0.45	Br	0.23
CN	0.66	I	0.28
CF <sub>3</sub>	0.54	SH	0.15
NH <sub>2</sub>	-0.66	SO <sub>2</sub> NH <sub>2</sub>	0.57
N(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup>	0.82	SO <sub>3</sub> <sup>-</sup>	0.09
N <sub>2</sub> <sup>+</sup>	1.91	PO <sub>3</sub> H <sup>-</sup>	0.26
NO <sub>2</sub>	0.78	Si(CH <sub>3</sub> ) <sub>3</sub>	-0.07

<sup>a</sup>From ref. 11, p 66.

The fact that this plot is (roughly) a straight line -- that is, that a LFER relates the two reactions -- makes it possible to estimate the details of bonding in the copper chelate with some precision. Although this approach has not been applied to the study of mechanisms in fracture, it holds great promise. For example, if one were to study the rate of fracture of copper metal in contact with an aqueous solution of the substituted salicylaldehydes used in Figure 7, and were to find that the rate of fracture correlated with association constants with copper(III) (equation 5), one would immediately be in a position to postulate that the salicylaldehyde molecules were involved in the rate-limiting step for fracture. If the  $\rho$  values for the fracture and for association with copper(II) were similar, one might also be able to postulate that copper(II) was involved in the fracture process.

In brief, LFER relations have proved to be an invaluable technique in very complex problems in mechanistic chemistry, and should also be applicable to problems in fracture. They provide a highly-developed method for establishing analogies between reactions and/or processes.

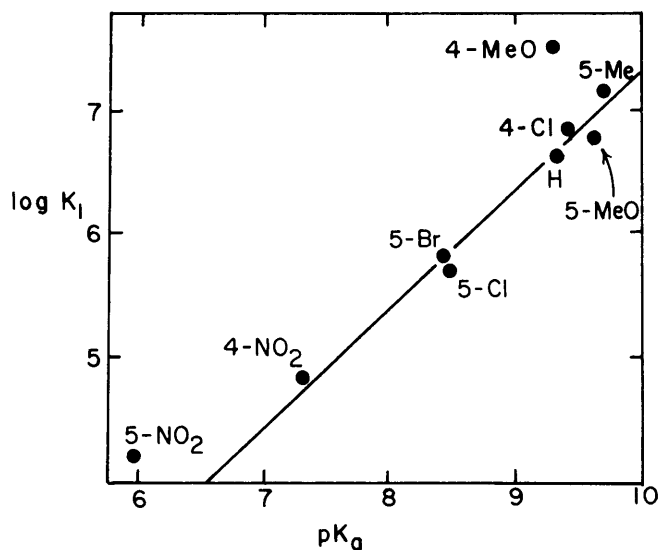
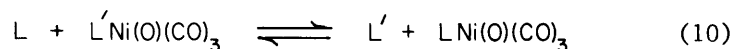


Fig.7. Plot of the logarithms of the equilibrium constants for coordination of substituted salicylaldehyde anion with copper(II) versus those for ionization of these salicylaldehydes.<sup>12</sup>

Cone Angles. The HSAB classification and LFER are useful primarily for exploring electronic effects on bonding. For many reactions of metals with ligands, purely steric effects (that is, effects due to size and non-bonded interactions) dominate. A simple approach which has proved very useful is that of Tolman.<sup>13</sup> In this approach, the "size" of ligands is estimated using molecular models, by measuring the angle subtended by the groups attached to the coordinating atom (Figure 8). This figure also gives data for a typical coordination reaction: competition among different phosphines and phosphines (L,L') for a coordination site at nickel(0) (equation 10).



This approach shares with many other techniques in mechanistic chemistry the fact that it is very empirical. It is, nonetheless, a useful way of thinking about the coordination of ligands at metals in solution, and probably also on metal surfaces.

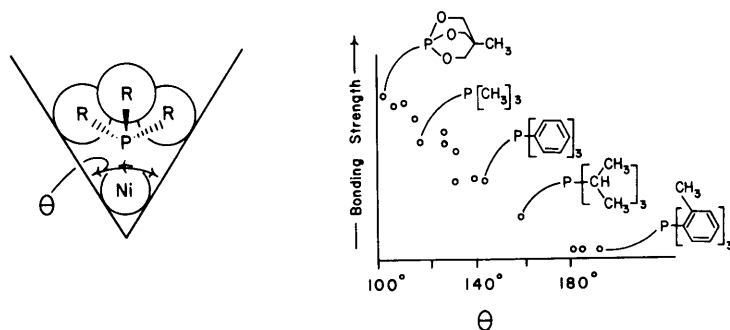


Fig.8. Cone angles and relative affinities for  $\text{Ni}(\text{CO})_3$  for several phosphines.

Entropies. All of these approaches to bonding concentrate on energies. It is essential to keep in mind the very large potential magnitudes of entropic terms. For example, for a simple dissociation of one particle into two, the change in translational entropy can be large (equation 11).<sup>14</sup>



Since this contribution to  $\Delta G^\circ$  or  $\Delta G^\ddagger$  for a reaction may be comparable to or larger than contributions from enthalpy, it must be estimated in any serious quantitative consideration of rates or equilibria.

#### THE COORDINATION OF FRACTURE SURFACES

A number of distinct types of chemistry are relevant to problems in fracture (Table 3). The chemistry of fracture and corrosion is more complex and more difficult to understand than the types of chemistry which have been studied with greatest success in mechanistic chemistry. Chemistry cannot offer easy solutions to the complex problems of fracture, but it can offer detailed information on simpler systems which seem certain to be relevant to certain elementary processes in fracture. In what follows I simply touch on several areas which illustrate representative areas in which inorganic chemistry might be able to contribute to fracture. Much of the discussion in this section will be speculation.

Corrosion Inhibition by Adsorption. A number of types of superficially different species (carbon monoxide, phosphonium salts, sulfides, acetylenes, long-chain amines) inhibit corrosion and influence the rate of crack formation and fracture initiation. Can one draw inferences about the probable modes of action of these materials from inorganic chemistry? We consider these in several groups.



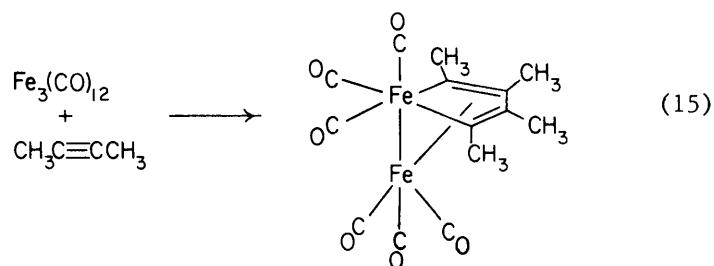
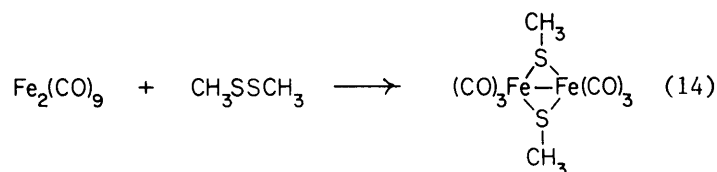
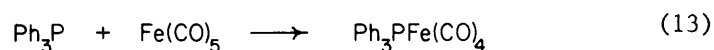
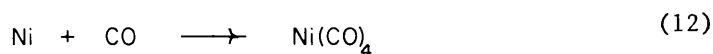
Table 3. Problems in Fracture, and Related Areas of Inorganic Chemistry.

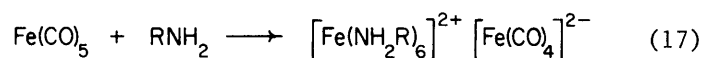
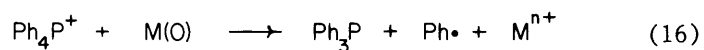
Problem	Area of Inorganic Chemistry
<u>Chemistry of Passivating Films:</u>	} Coordination Chemistry
Metal oxides and halides; formation constants and solubilities	
<u>Corrosion Inhibition:</u>	
Surface oxide films; chemistry of metal phosphates, borates, and chromium oxides	
<u>Metal Surface Chemistry</u>	} Organometallic Chemistry
Corrosion inhibition by adsorption; interaction of metals with $R_2S$ , $R_4P^+$ , $CO$ , $HC\equiv CC(CH_3)_2OH$	
Surface Electrochemistry:	
$M + H_2O \rightarrow H_2 + M_n O_m$	
$M + Ph_4P^+ \rightarrow M_n O_m + Ph_3P Ph\cdot$	
$M + RBr \rightarrow M^{n+} + R\cdot + Br^-$	} Electron Transfer Chemistry
<u>Hydrogen Embrittlement</u>	} Metal Hydride Chemistry
Metal hydride and dihydrogen formation	
Hydrogen migration (surface, bulk)	

Bulk metals (i.e. freshly-formed metal surfaces) are "soft" using the SHAB classification, and are expected and observed<sup>15</sup> to coordinate CO, phosphines, sulfides, and acetylenes strongly, but not phosphonium salts, sulfonium salts, or amines or ammonium salts. Equations 12-15 show relevant examples of stable complexes formed by interaction of metals or metal complexes with soft ligands.

Soft ligands might thus be expected to form surface organometallic compounds by adsorption. If these compounds are stable, they might provide barrier films, although the chemistry of these barrier films might be much more complex than suggested by the relatively simple structures shown in these equations. In particular, acetylenes may polymerize over clean metal surfaces, and phosphines and (bi)sulfides are reduced to metal phosphines and metal sulfides.

What is the mechanism of action of phosphonium salts and high molecular weight alkyl amines? These materials are not able to coordinate to low-valent metals. There seem several possibilities: Metals readily reduce phosphonium salts to phosphines under some conditions, so phosphonium salts may simply be precursors for phosphines (equations 16). Alternatively, the phosphonium salts,





or transformation products of the ammonium salts (of the type illustrated by equation 17) may adsorb or precipitate on an oxidized metal surface and modify its properties in a way that render it resistant to corrosion.

In any event, the initial steps in reactions of soft ligands with metal surfaces probably involve reduced metals, while those of hard ligands probably involve oxidized metals.

Corrosion By Organic Solvents. A particular but important type of corrosion is that of electropositive metals (magnesium, aluminum) in contact with halogenated organic solvents. The probable mechanism for this type of corrosion is now well established from studies of a closely related system important in organic synthesis: that is the formation of organomagnesium species (Figure 9).<sup>16</sup> The overall rate-limiting step is often breaking an oxide film on the surface. After this film is broken, the rate of reaction is limited by the rate of mass transport of RBr to the magnesium surface. The first step is a single-electron transfer from magnesium metal to alkyl halide. This step generates

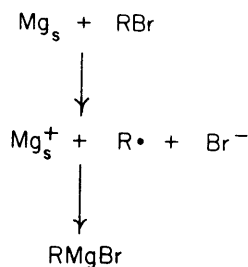


Fig.9. Mechanism of Reaction of Magnesium with an Alkyl Bromide (RBr) in Diethyl Ether Solution.  $\text{Mg}_s$  is a magnesium surface Atom.

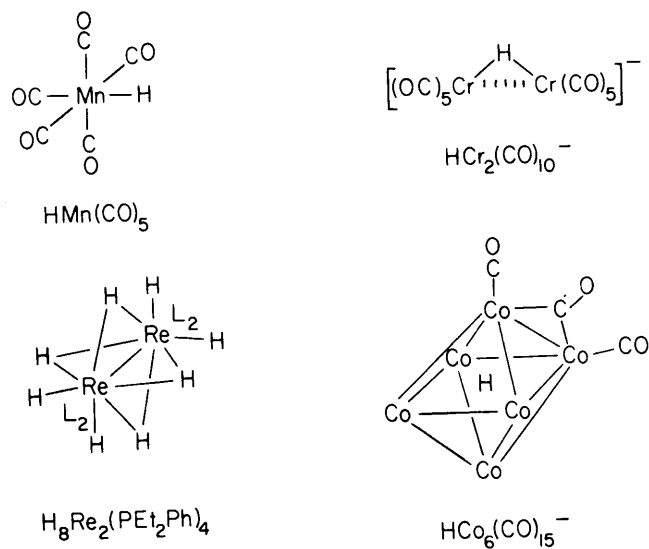
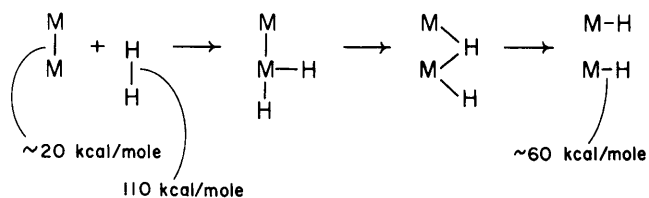


Fig.10. Examples of organometallic hydrides. The positions of most of the carbon monoxide ligands of  $\text{HCo}_6(\text{CO})_{15}^-$  are omitted to show the hydrogen and the directly-bonded cobalt atoms.

an alkyl radical ( $\text{R}\cdot$ ) as an intermediate. A subsequent step reduces this species to an alkylmagnesium species, and abstracts a magnesium atom from the surface of the metal.

**Hydrogen Embrittlement.** Hydrogen is unique as a ligand in organometallic chemistry. It is small (it has probably the smallest steric constraints of any ligand); it is mobile; it forms strong bonds to metals; it forms many different types of bonds. Figure 10 illustrates some of the bonding arrangements observed for hydrogen in organometallic complexes.<sup>17</sup>

One interesting speculation concerning the mechanism of hydrogen embrittlement of metals is that dihydrogen may cleave metal-metal bonds during fracture. A schematic mechanism would be that shown in equation 18. The bond energies necessary to estimate the thermodynamics of this process are not known, but the approximate values given in equation 18 suggest that it is not impossible. Moreover, a number of good organometallic analogs



exist for cleavage of metal-metal bonds by dihydrogen (Figure 11).<sup>18</sup> In no case is the mechanism of one of these reactions known, but a study of the reverse reaction (formation of an osmium-osmium bond with expulsion of dihydrogen) suggests that an Os-H-Os group may be an intermediate.<sup>18</sup>

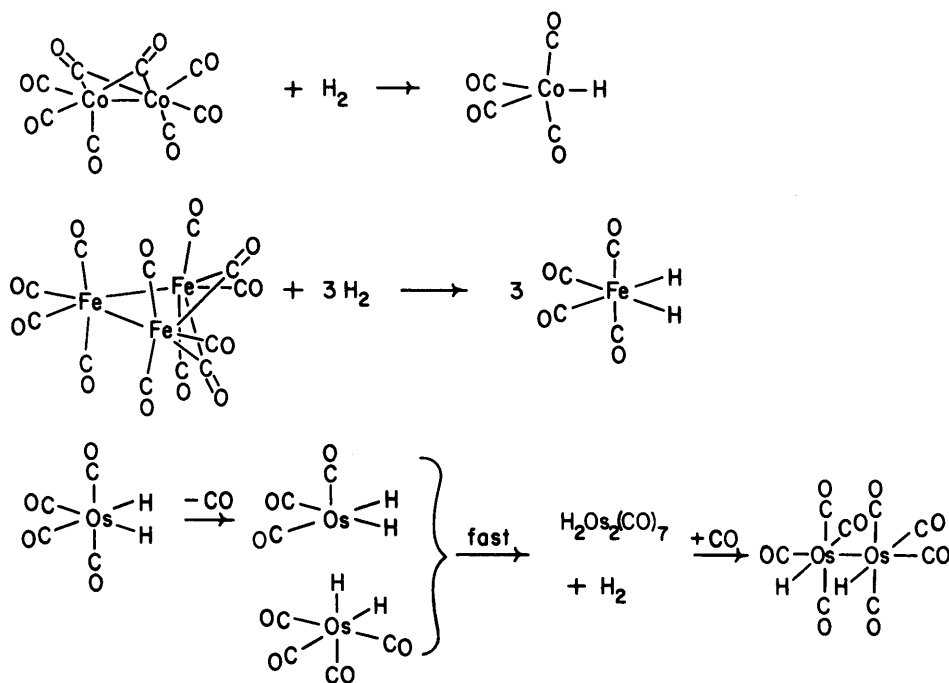


Fig.11. Cleavage of Metal-Metal Bonds by Dihydrogen.

## CONCLUSIONS

Fracture is a complex and difficult-to-study series of processes. Chemistry may have procedures and information to offer which will help in understanding these processes. The techniques developed for studying rates in chemistry are based on transition state theory. The emphasis on the concept of the transition state -- that is, the highest energy species or configuration of atoms along the reaction coordinate -- may have application in analysis of fracture mechanisms. A series of qualitative or semi-qualitative techniques and classifications (SHAB theory, linear free energy relations) have proved useful in chemistry for studying complex processes. In addition, organometallic chemistry and catalysis offer a wealth of structural and mechanistic information concerning bonding of non-metal species to metals. This information should be useful in considering in atomic detail the processes which occur in creation of fresh fracture surfaces.

## ACKNOWLEDGEMENT

The writing of this manuscript was supported by the National Science Foundation (Grants 80-12722CHE and DMR 78-24185 ). My interest in the area of fracture is due in major part to conversations with Professor Ron Latanision.

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## DISCUSSION

Comment by J.O'M. Bockris:

I share Professor Whitesides' opinion that an approach to cracking most likely to yield fruit is in terms of chemical mechanism determination. The key process in this approach is the determination of the rate-determining step. Thus, in general,  $A \rightarrow B \rightarrow C_{\text{---}} \rightarrow \text{R.D.S.} \rightarrow E$  for the process  $A \rightarrow E$ . If the R.D.S. is known, the rate of  $A \rightarrow E$  is immediately calculable by standard formalism.

Many persons unfamiliar with the ubiquitous approach of the theory of absolute reaction rates may think that the identification of the nature of the activated complex may be a difficult matter, particularly for a complex process involving many partial steps, some of which may be parallel and simultaneous. Whilst I do not wish to project the image of a utopian pathway to clarity, my experience of the method (applied to reactions in liquids) suggests that fairly complex processes have sometimes quite simple rate-determining steps. If the situation were that one had to compute the step without the aid of experiment, I think we should be no better off than the physicists. However, a cautious and well thought out campaign of experiments often gives a strong indication of what the r.d.s. may be. (At the worst, it greatly reduces the possibilities.)

It so happens that I can give a strikingly relevant example. My co-worker, P.K. Subramaniam, determined the rate of hydrogen permeation through a series of Fe-Ni alloys. He found a  $P_H$ -composition relation in which the values varied by some 5 orders of magnitude. There was much structure (following phase changes in the alloy). By happenstance, we came across the work of K. Nobe, who had determined the corrosion rate under stress of a similar alloy

series. The corrosion rate and permeation (rate) had identical structure and degree of variation. I can surely conclude that the r.d.s. in the corrosion and permeation are identical. But now I face a totally different and much easier problem: it is likely that the r.d.s. in this case is  $\text{H}_2\text{O} + e_{(m)} \rightarrow \text{MH}$ , proton discharge from solution across the double layer to the metal surface.

Two minor points:

1. The distinction between  $\text{H}_{\text{ads}} + \text{H}_{\text{ads}} \rightarrow \text{H}_2$  and  $\text{H}^+ + \text{H}_{\text{ads}} + e \rightarrow \text{H}_2$  in removal processes for H on a metal is most important when it comes to cracking. Thus, for the first, the coverage is low and for the second, high. Other matters being equal, the latter is more likely to constitute a danger--promote cracking--than the former.
2. In respect to the effect of solution-borne inhibitors and promoters of permeation, one mechanism for promotion is simply bond weakening by means of lateral electrostatic interaction between M-H bonds and the organic adsorbate.

Comment by R. Bullough:

You began your talk by drawing an analogy between fracture and polymerization. I presume this analogy only applies to the thermally activated propagation of an ideally brittle crack in a crystalline lattice. In any real fracture process there is some plastic deformation with the emission of dislocations or the stimulation of dislocation sources at the crack tip. In the work of fracture this plastic work usually dominates the energetics of the crack propagation and defines the rate of crack propagation. Can the chemical rate theory approach with molecular analogs give any insight into such dislocation dominated processes?

Reply:

Yes, in the sense that one can construct an analogy to the formalism in which only chemically activated reactions are employed in which activation energies contain a significant contribution from potential energy terms originating in strain. The essential ideas remain the same. There are also useful procedures analogous to transition state theory which are used to analyze photochemical reactions and others in which the transition state energy is attained by some process other than thermal fluctuation. In any event, the value of the transition state theory in fracture is less for its particular utility in quantitative analysis of rates and more for its qualitative emphasis on the elemental composition and structure of the transition state.



Comment by A.R.C. Westwood:

You have noted that certain organic reactions require (or involve) a reorientation of the ligands of one or other of the participating species. Is it likely that an equivalent function is played by lattice strain at the tip of a crack, i.e., is strain-assisted (dependent) chemisorption of an active species at a crack tip a likely situation in embrittlement. As an example, note that in order to constitute a liquid metal embrittlement "couple" the participating metals usually exhibit low mutual solubility, and little tendency to form intermetallic compounds. In other words, in equilibrium conditions, they tend not to associate. Hence the surmise that, perhaps, non-equilibrium configurations may be involved, e.g., a strained crack tip.

Reply:

A very similar idea has been used to rationalize rates observed in enzymatic catalysis. It is certainly possible that strain may assist certain reactions, but no exact model is known.

Comment by D.J. Duquette:

I would like to support the speaker in emphasizing the importance of rate determining steps in the fracture problem. It is a factor often ignored by structural scientists who study beginning and end states and ignore transitional states which may, in fact, control the process of interest. A minor point of contention, however, related to the role of chromate on corrosion resistance. While the model suggested by the speaker, involving transitional states of Cr, may have relevance to Cr containing alloys where anodic dissolution is still not thoroughly understood, passivity of Fe by chromate is generally considered to be a simple process involving a compound with a noble redox potential and low activation energy for reduction which accordingly stimulates anodic dissolution of the metal thus forming a protective film. Identical results can be obtained for iron using molybdates, tungstates, and other heavy metal oxide complexes as well as with nitric acid and, in some cases, simply dissolved oxygen.

Reply:

I stand corrected.

Comment by R.M. Latanision:

Almost without exception, as far as I am aware, catalysts are used in an essentially unstressed (mechanical) condition. On the other hand, if the reactivity of a metal catalyst is related to the presence of exposed metal atoms, I would expect that the action of a catalyst might be changed significantly if it were strained plas-

tically (i.e., dynamically strained rather than prestrained or statically stressed) while performing as a catalyst. Plastic deformation generates surface steps by virtue of the egress of dislocations. Are you aware of any attempt to examine the reactivity of dynamically deforming catalysts?

Reply:

No, I am not aware of any such effort. A practical problem with an attempt to carry out this sort of experiment lies in reporting it: Catalytic rate constants are usually reported as turnover numbers (moles product/mole of catalyst surface atoms/time). It is not clear how one would measure surface areas under dynamic conditions.