Catalysis Letters 9 (1991) 159–172

CATALYTIC HYDROGENOLYSIS ON METALS

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Two issues of broad interest in catalysis are reaction mechanisms and comparisons of catalytic activities of different substances. Metal-catalyzed hydrogenolysis reactions of simple molecules provide examples in which both issues have been investigated in some detail. While hydrogenolysis of carbon-carbon bonds in alkanes has received most of the attention to date, some work has also been reported on the hydrogenolysis of carbon-nitrogen bonds in amines and of carbon-halogen bonds in alkyl halides. General mechanistic features of hydrogenolysis reactions on metals and comparisons of catalytic activities of metals for such reactions are considered in this brief review.

Keywords: Hydrogenolysis: (i) of C–C bonds, (ii) of C–N bonds, (iii) of C–Cl bonds, (iv) mechanism of, (v) kinetics of, (vi) activities of metals

1. Introduction

Two broad kinds of issues which are generally of interest to workers in catalysis are (a) the mechanisms of catalytic reactions and (b) the activities of different types of catalysts. Both types of issues are important, and they are not totally divorced from each other. Obviously, the factors determining catalytic activity must also be responsible for the mechanism for achieving it. The two issues are separated here simply for the purpose of organizing our discussion of hydrogenolysis reactions on metal catalysts.

The mechanism of a catalytic reaction is concerned with the question of how it occurs, i.e., what are the intermediate chemical species involved and what is the sequence of elementary steps into which the overall reaction may be dissected? Information on mechanism can be obtained in a variety of ways, e.g., from kinetic studies designed to determine the form of the rate law for the reaction, from studies employing isotopic tracers to establish possible reaction intermediates and the degree of reversibility of certain reaction steps, from detailed investigations of product distributions in complex reactions, from chemisorption studies (possibly involving various types of spectroscopies), and from studies involving the systematic variation of the structure of a reactant molecule or a catalytic surface [1]. All of these approaches have been employed in obtaining information on the mechanisms of various types of hydrogenolysis reactions. Results of several of them will be considered briefly in our discussion of hydrogenolysis reactions in this article.

The issue of catalytic activity is of interest to all workers in catalysis, whether it is approached from the practical goal of obtaining the best catalyst for a reaction or from the viewpoint of obtaining an understanding of the factors underlying such activity. It has long been known that the chemical nature of a surface is important in determining the rate of a reaction catalyzed by the surface. Although the factors determining this specificity of catalytic action are not understood in a detailed microscopic sense, much has been learned from a more macroscopic point of view from systematic studies of reactions over different types of catalysts. Studies of this type have been very useful in establishing patterns of variation in catalytic activity from one substance to another for various types of reactions [2–6]. These patterns introduce a measure of order into heterogeneous catalysis and are important for the development of a more fundamental understanding of the subject.

In considering patterns of activity variation among catalysts, one can generally rationalize the results in terms of a rather broad principle relating catalytic activity to the adsorption properties of the reactants. According to this principle, the formulation of which owes much to ideas advanced by Sabatier many years ago [7], catalytic activity does not continue to increase indefinitely with increasing strength of chemisorption of a reactant molecule to the surface. While some affinity of the reactant for the surface is obviously required for chemisorption to proceed, it is possible for the chemisorption bond to be too strong for catalysis to occur at a reasonable rate. The catalyst either becomes covered by a reactant species which is too stable to undergo reaction or by a product species which cannot be desorbed readily from the surface. Thus, the adsorption affinity can either be too low or too high for effective catalysis. Optimum catalytic activity is attained for an adsorption affinity which is intermediate between these extremes. This corresponds to an intermediate degree of coverage of the surface by the adsorption complex undergoing reaction [8,9].

For metal surfaces there is extensive information available on the heats of adsorption of a number of simple gases [10,11]. These data have been very valuable in leading to certain general conclusions about the interaction of molecules with metal surfaces. They show clearly that the transition metals stand out in their ability to chemisorb a variety of molecules [11,12]. Although present understanding of the details of chemisorption by metals is far from complete, a simple generalization can be made regarding the abilities of metals to chemisorb gases. If we begin with the metals of Group VA of the periodic table and proceed in the direction of increasing atomic number through the metals of Group VIII to Group IB, we find that the strength of chemisorption declines in a continuous manner. Kinetic limitations in chemisorption become increasingly important for

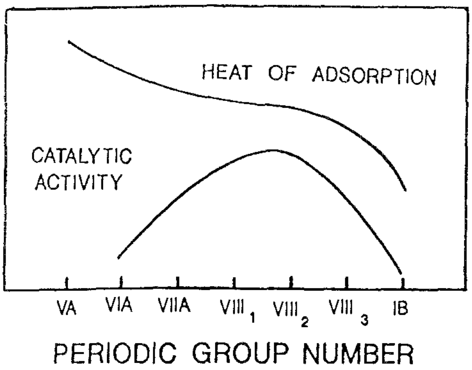

Fig. 1. Schematic diagram illustrating the pattern of variation of heats of adsorption of simple molecules on metal surfaces across a series of metals in the periodic table, and the corresponding pattern of variation of catalytic activity.

some molecules (e.g., hydrogen and alkanes) as one moves from Group VIII to Group IB.

For many reactions catalyzed by metals, the chemisorption affinity corresponding to maximum catalytic activity is found among the metals of Group VIII, and consequently these metals are especially important in catalysis. A schematic illustration of the manner in which heats of adsorption and catalytic activities vary with the position of a metal in the periodic table is given in fig. 1. While maximum catalytic activity within a given period is frequently observed for a metal within Group VIII, the exact position of the maximum among the various sub-groups within Group VIII will in general depend on the particular type of reaction. For example, the position of maximum activity may be different for the hydrogenolysis of a carbon-carbon single bond in an alkane and the hydrogenation of the carbon-carbon double bond in an alkene.

Metal catalyzed hydrogenolysis reactions of simple molecules provide good illustrations of the general remarks made in the previous paragraphs. The term hydrogenolysis refers to a type of reaction in which the rupture of a given bond A–B is accompanied by addition of hydrogen to both A and B. An example is the rupture of the C–C bond in ethane with addition of hydrogen to each of the methyl fragments to form methane. Such reactions are generally not desirable ones in industrial catalysis, but often occur in competition with reactions which yield more valuable products. Fundamental studies of hydrogenolysis reactions can be justified on the basis that the knowledge gained may provide ideas for the selective inhibition of hydrogenolysis, and hence lead to improvements in the selectivities of metal catalysts for the desired reactions. Indeed, the discovery of certain types of bimetallic catalysts for accomplishing this objective was influenced strongly by the results of systematic studies of the activities of metals for hydrogenolysis of C–C bonds [13].

In this article we consider hydrogenolysis of C–C, C–N, and C–Cl bonds in the molecules ethane, methylamine, and methyl chloride, respectively, in the following reactions:

$$H_3C\text{-}CH_3 + H_2 \rightarrow 2CH_4$$

$$H_3C\text{-}NH_2 + H_2 \rightarrow CH_4 + NH_3$$

$$H_3C\text{-}Cl + H_2 \rightarrow CH_4 + HCl.$$

The reactions are all exothermic and thermodynamically highly favorable over a wide range of conditions. The dissociation energies of the C–C, C–N, and C–Cl bonds in the molecules involved in these reactions are virtually identical, with values very close to 80 kcal/mole [14].

We begin with a brief review of some general mechanistic features of hydrogenolysis reactions of ethane, methylamine, methyl chloride, and related molecules. The ease of rupture of the C–C, C–N, and C–Cl bonds relative to the ease of exchange of deuterium with hydrogen atoms in these molecules is considered in each case, since such information provides valuable insight regarding the primary mode of activation of the reactant molecule in the initial chemisorption step. Some consideration is also given to results of simple chemisorption studies and to results of kinetic studies of hydrogenolysis reactions. After completing the discussion of mechanistic features, we compare the catalytic activities of a series of metals for each of the hydrogenolysis reactions. Emphasis is placed on the pattern of variation of catalytic activity from one metal to another in the series. We call attention to the way in which the pattern changes as the bond undergoing hydrogenolysis changes from C–C to C–N to C–Cl, and how the change in the bond affects the spread in hydrogenolysis activities.

2. General mechanistic features of hydrogenolysis reactions

The hydrogenolysis of ethane to methane will be considered first, since it has been investigated much more extensively than the other reactions. There is broad agreement that the scission of the C–C bond in ethane is preceded by the scission of C–H bonds [15–17], with formation of a hydrogen-deficient surface species C_2H_x

$$C_2H_6 \rightleftharpoons C_2H_x(\text{ads}) + aH_2$$

where the symbol (ads) signifies an adsorbed species and the quantity a is equal to $(6-x)/2$. The species C_2H_x then undergoes C–C scission to yield chemisorbed C_1 fragments (e.g., chemisorbed CH or CH_2) which are subsequently hydrogenated to methane. The conclusion that C–H bonds are activated more readily than C–C bonds is supported by several kinds of evidence: At temperatures much lower than are required for hydrogenolysis, the chemisorption of ethane is accompanied by evolution of hydrogen [18]. Furthermore, the exchange reaction of ethane with deuterium to yield deuteroethanes occurs at similar temperatures [19].

There have been many studies of the kinetics of ethane hydrogenolysis [15–17,20–32]. The first experimental investigations were those of Taylor and associates on nickel [20], cobalt [21], and iron [16] catalysts. Somewhat later, the first experimental studies of the kinetics on the remaining Group VIII metals [22–25] and on rhenium [26] were conducted in our laboratories. The most interesting result of the kinetic studies is the strong inverse effect of hydrogen pressure on the reaction rate over most of the metals investigated. For example, the reaction rate is approximately inversely proportional to the 2.5 power of the hydrogen pressure on nickel [20,23], platinum [23], and palladium [24].

An explanation which has been proposed to account for this strong inverse hydrogen pressure dependence is a low value of x in the formula C_2H_x for the surface species undergoing C–C scission, said species being in equilibrium with ethane and hydrogen in the gas phase [16,17]. According to this view, the scission of the C–C bond in C_2H_x is the rate limiting step, and coverage of the surface by hydrogen during reaction can be neglected. When kinetic data are analyzed on this basis for a number of metal catalysts, it is found that the value of x varies from four to zero, depending on the metal. A value of x as low as zero in the species C_2H_x (indicative of a dicarbon residue C_2 totally devoid of hydrogen) seems extreme and could be a consequence of an oversimplified analysis. Although the absolute values of x obtained from the analysis may be suspect, the way in which x varies with the metal is physically very reasonable. The value of x tends to decrease as the ratio $A(\text{C–H})/A(\text{C–C})$ for the metal increases, where $A(\text{C–H})$ and $A(\text{C–C})$ are the activities for the dissociation of C–H and C–C bonds, respectively [17]. As the value of x decreases, the extent of bonding between C_2H_x and metal surface atoms increases, if one assumes that the C–C bond remains as a single bond until it is broken in the reaction. In this regard, it has commonly been hypothesized that a site consisting of an array of metal atoms is required for the surface intermediate undergoing C–C scission in hydrogenolysis reactions of alkanes [33–35].

If the assumption of low surface coverage by hydrogen is in error in the analysis, at least part of the inverse dependence of rate on hydrogen pressure would be attributable to blocking of hydrogenolysis sites by chemisorbed hydrogen, and the value of x would necessarily increase. Values of x equal to zero would therefore not be encountered. However, if competition between hydrogen and the species C_2H_x for surface sites is to be included in the analysis, some assumption must be made about the number of metal atoms which constitute a suitable site for the latter. This assumption itself introduces uncertainty in the analysis, and it is doubtful that trends in variation of values of x determined in this way are any more meaningful than those determined by the simpler analysis ignoring hydrogen chemisorption.

The extent of dehydrogenation of ethane which occurs prior to the scission of the C–C bond has been the subject of much discussion in the literature [16,17,28,31,32]. On a given surface, which may well be non-uniform, it is possible that C_2H_x species with different values of x may undergo C–C scission and thereby make separate contributions to the overall hydrogenolysis reaction. It is also possible that the contribution due to a particular species may vary with reaction conditions such as temperature and hydrogen partial pressure, as indicated in a recent comprehensive kinetic simulation of ethane hydrogenolysis on a series of metals by Dumesic's group at the University of Wisconsin [32]. For example, as temperature increases or hydrogen pressure decreases, there is a greater contribution by more highly dehydrogenated species.

The degree of reversibility of the dehydrogenation steps preceding C–C scission has also been an issue in discussions of the kinetics of ethane hydrogenolysis [32,36,37]. A kinetic analysis based on the irreversible chemisorption of ethane on a non-uniform surface has been given by Boudart [36]. The work of the Dumesic group, however, indicates that the chemisorption is generally reversible, but that the degree of reversibility varies with reaction conditions, e.g., with temperature [32]. This finding is consistent with earlier work from our laboratory on the hydrogenolysis of ethane on cobalt [37].

From the foregoing discussion it is clear that the hydrogenolysis of ethane on metal surfaces is complex. However, while there are uncertainties regarding details of the mechanism and kinetics, the general features are reasonably well established. Studies of the reaction have drawn attention to a number of issues of broad interest in heterogeneous catalysis, and therefore have value beyond the understanding of the reaction itself.

The hydrogenolysis of the C–N bond in methylamine has been investigated by several groups of workers [38–41]. In addition to the hydrogenolysis reaction yielding ammonia and methane as products, a reaction producing dimethylamine and ammonia occurs to a significant extent on several metals. Small amounts of other products, including trimethylamine, acetonitrile, ethylenimine, and C_2–C_4 hydrocarbons, have also been observed. The available information has been obtained in studies on the surfaces of evaporated metal films as well as on more conventional forms of metal catalysts.

The exchange reaction of deuterium with hydrogen in methylamine occurs at temperatures substantially lower than those required for the scission of the C–N bond in the hydrogenolysis reaction [42]. For palladium and platinum, the exchange occurs preferentially with the hydrogen bonded to the nitrogen. With tungsten films, on the other hand, the exchange occurs most readily with the hydrogen atoms bonded to carbon [42]. The fact that palladium and platinum have much higher catalytic activity than tungsten for the exchange of deuterium with ammonia [43], and much lower activity for the methane-deuterium exchange reaction [44], is consistent with these observations.

Thus, the primary step in the interaction of methylamine with a metal surface can occur with the bonding of either the nitrogen or the carbon atom to the surface, depending on the particular metal. While an intermediate chemisorbed to the surface through one versus the other of these atoms seems reasonable in accounting for the differences in exchange behavior of methylamine with deuterium on the different metals, one might postulate that the scission of the C–N bond would involve an intermediate in which both carbon and nitrogen atoms are bonded to the metal surface. Indeed, such a suggestion has been made, along with the additional suggestion that one or both of these atoms is multiply bonded to the surface [39]. In any case, as in ethane hydrogenolysis, the formation of a dehydrogenated surface species is assumed to be the initial step in the reaction

$$H_3C\text{–}NH_2 \rightleftharpoons H_xC\text{–}NH_y(\text{ads}) + [5 - x - y]H(\text{ads})$$

where the symbol (ads) again signifies an adsorbed species. The depth of dehydrogenation of the methylamine molecule in this step is unknown. Scission of the C–N bond in the dehydrogenated intermediate yields carbon- and nitrogen-containing fragments which are hydrogenated, respectively, to methane and ammonia. Very little information has been published on the dependence of reaction rates on methylamine and hydrogen partial pressures for any of the metals which have been investigated. Such information would be useful in making inferences about the extents of coverage of the surface by the types of chemisorbed species envisioned, and possibly in arriving at an estimate of the depth of dehydrogenation of the methylamine prior to C–N scission.

The metal-catalyzed hydrogenolysis of carbon-halogen bonds in alkyl halides differs from the hydrogenolysis of C–C bonds in alkanes and of C–N bonds in alkylamines in the primary mode of activation of the molecule in the initial chemisorption step. In the chemisorption of simple alkyl halides on metals, the scission of the carbon-halogen bond is not preceded by the scission of C–H bonds. Thus, Campbell and Kemball [45] found no evidence of an exchange reaction of deuterium with the hydrogen atoms in either ethyl chloride or ethyl bromide over a number of metals. Similar observations for methyl chloride [46] and other alkyl chlorides [47] have also been reported.

The hydrogenolysis of methyl chloride on metals may therefore be represented by the following sequence of steps:

$$H_3C\text{–}Cl \rightarrow CH_3(\text{ads}) + Cl(\text{ads})$$

$$CH_3(\text{ads}) + H(\text{ads}) \rightarrow CH_4$$

$$Cl(\text{ads}) + H(\text{ads}) \rightleftarrows HCl.$$

In the first step the methyl chloride is chemisorbed with dissociation of the C–Cl bond. The methyl and chlorine fragments are then hydrogenated to methane and hydrogen chloride, respectively. The reaction between adsorbed chlorine and hydrogen to form hydrogen chloride is shown as a reversible step, since Campbell and Kemball showed that the hydrogenolysis reactions of ethyl chloride and ethyl bromide on platinum and palladium were inhibited by the hydrogen halide in the product [45]. From their kinetic data, these workers estimated that the heat of adsorption of hydrogen chloride on platinum and palladium under reaction conditions was 8 kcal/mole.

3. Comparisons of catalytic activities of metals for hydrogenolysis reactions

Extensive comparisons of the catalytic activities of a series of metals for the hydrogenolysis of ethane [4], methylamine [41], and methyl chloride [48] have been reported from our laboratories. The metals were all supported on silica, a material which is catalytically inert for all of the reactions, at least for the range of temperatures required for catalysis on any of the metals investigated. Details on the method of preparation of the catalysts and on the determination of metal dispersions can be found in the original papers. The metal dispersion refers to the ratio of surface atoms to total atoms in the metal clusters or crystallites present in the catalysts. In general, metal dispersions were determined by a method involving the selective chemisorption of a gas (H_2 and/or CO) on the metal component of the catalyst, although some use was also made of X-ray diffraction and EXAFS data.

Catalytic activities were determined at a total pressure of 1 atm in a flow reactor system. Rate data were obtained over a range of temperatures at fixed reactant partial pressures. Helium was employed as a diluent for the reactants. The partial pressure of hydrogen was 0.20 atm, while that of the primary reactant (ethane, methylamine, or methyl chloride) was 0.030 atm. Reaction rates were obtained under differential reactor conditions (i.e., at low levels of conversion of reactants) to minimize variation of reactant partial pressures along the catalyst bed. From the data on the temperature dependence of hydrogenolysis rate r_0, values were determined for the apparent activation energy E and the preexponential factor r_0' in the equation

$$r_0 = r_0' \exp(-E/RT). \tag{1}$$

The units of r_0 and r_0' are molecules per second per surface metal atom.

With the use of eq. (1), rates of a given hydrogenolysis reaction may be compared for a series of metals at a common temperature. In such a comparison of rates, it is convenient to normalize all of the rates to the rate on a reference metal and thereby obtain a series of values of relative catalytic activities. If rhenium is chosen as the reference metal, we obtain the comparisons shown in fig. 2 for the series of metals rhenium through gold. In the upper field of the figure, the metals are compared for the hydrogenolysis of the C–C bond in ethane. In the middle and lower fields, respectively, the comparisons are for the hydrogenolysis of the C–N bond in methylamine and the C–Cl bond in methyl chloride.

For each of the reactions, a maximum in catalytic activity is observed for one of the Group VIII metals in the series, but the metal exhibiting maximum activity

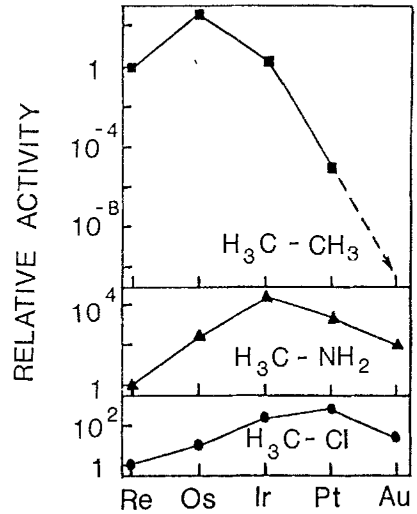

Fig. 2. Patterns of variation of catalytic activity across the series of metals Re, Os, Ir, Pt, and Au for the hydrogenolysis of the C–C bond in ethane (upper field), the C–N bond in methylamine (middle field), and the C–Cl bond in methyl chloride (lower field). The metals were all dispersed on silica [4,41,48].

varies with the nature of the bond undergoing hydrogenolysis. As the bond changes from C–C to C–N to C–Cl, the maximum activity shifts from Os to Ir to Pt. Moreover, the range of variation of hydrogenolysis activities for the full series of metals including Re and Au decreases from an estimated twelve orders of magnitude to three orders of magnitude when the reactant is changed from ethane to methyl chloride. For methylamine, the range is intermediate between these extremes, but much closer to the range for methyl chloride.

For the hydrogenolysis of the C–C bond in ethane, the activity of gold is so low that it can not be measured satisfactorily in the same apparatus used for the other metals, thus accounting for the absence of a data point for gold in the figure. A measurable reaction rate for ethane hydrogenolysis could not be observed on gold at temperatures well above those used for platinum, the least active of the other metals in the series. Consequently, it has been concluded that the activity of gold is lower than that of platinum by several orders of magnitude [4]. This is reflected in fig. 2 by the dashed extension of the line from the position of platinum to the position of gold in the series. The extremely low catalytic activity of gold for ethane hydrogenolysis is attributed to its inability to chemisorb ethane. This may be a consequence of very weak metal-carbon bonding or a high activation barrier for dissociative chemisorption of ethane, or both (activation barriers commonly increase with decreasing heats of adsorption). In contrast, the Group VIII metals in general are not limited by their ability to chemisorb ethane. On platinum, for example, chemisorption occurs at temperatures far lower than those required for scission of the carbon-carbon bond. This is illustrated by data showing that platinum catalyzes the exchange reaction of ethane with deuterium at temperatures as low as 400 K [19], while hydrogenolysis requires temperatures in the vicinity of 600 K [4]. For platinum, the rate determining step in ethane hydrogenolysis is the scission of the carbon-carbon bond in the intermediate C_2H_x. On moving from platinum to iridium to osmium in Group VIII, the strength of the metal-carbon bond would be expected to increase, leading to higher rates of scission of the carbon-carbon bond. At some point the rate of scission becomes high relative to the rate of the subsequent process in which methane is formed from the chemisorbed monocarbon fragments. This latter process may consist of several steps, which are commonly lumped together and considered to represent the product desorption step in the reaction. When this process constitutes the slow part of the reaction, one says that desorption of the product is rate limiting. An increase in metal-carbon bond strength then lowers the rate of desorption of methane, thus decreasing hydrogenolysis activity. A maximum activity for hydrogenolysis is therefore observed at the point where the rate limiting step changes from carbon-carbon scission to methane desorption. For the series of metals considered here, this change is observed on moving from osmium to rhenium. The purpose of this discussion on rate determining steps is to provide some rough guidance on how they might be expected to change when one considers ethane hydrogenolysis on a group of metals within a given period of the periodic table. It must be realized, however, that the rate determining step for a given metal can change if the reaction is conducted over a wide enough range of conditions. Consequently, the details of such a discussion may be affected to some extent by the choice of conditions, particularly if one considers conditions substantially different from those ordinarily employed in studies of the reaction.

Although the activity of gold for ethane hydrogenolysis is so low that it escapes detection, its activity for the hydrogenolysis of methylamine and methyl chloride can be measured without difficulty. For these reactions its activity is actually comparable to that of osmium in Group VIII and higher than that of rhenium in Group VIIA. Although gold does not chemisorb ethane, it clearly chemisorbs methylamine and methyl chloride. In the case of methyl chloride, the ability of gold to form a metal-chlorine bond, as demonstrated by the existence of a stable chloride of gold, provides a strong driving force for the chemisorption of the methyl chloride molecule and for the associated rupture of the carbon-chlorine bond. The activation of the hydrogen molecule in the hydrogenolysis of methylamine and methyl chloride on gold is intriguing, since hydrogen chemisorption supposedly does not occur on gold. Perhaps the chemisorption of hydrogen is assisted by the chemisorption of the other reactant, either because the latter modifies the chemical properties of the gold surface in a way that is favorable for hydrogen chemisorption or because the hydrogen reacts directly with the surface species formed from the other reactant on chemisorption.

With regard to the differences in the positions of the maxima in fig. 2, one

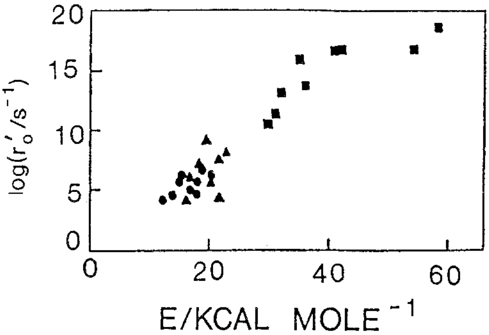

Fig. 3. Relationship between the logarithm of the preexponential factor r_0' and apparent activation energy E for hydrogenolysis reactions on metals. The squares, triangles, and circles represent values for the hydrogenolysis of ethane, methylamine, and methyl chloride, respectively.

would expect them to be related to the relative strengths of metal-carbon, metal-nitrogen, and metal-chlorine bonds. A shift of maximum catalytic activity to the right in Group VIII would seem to be reasonable if the change in reactant increases the strength of interaction with the metal. Presumably, this is what happens when the reactant undergoing hydrogenolysis is changed from ethane to methylamine to methyl chloride.

In heterogeneous catalysis there is frequently a relation between the parameters r_0' and E in eq. (1) when values for several closely related reactions on a given catalyst are compared, or when a comparison of values is made for a series of related catalysts for a single reaction. Either type of comparison yields such a relation for the different hydrogenolysis reactions and the series of metals considered here. It is common to find an approximately linear relation between log r_0' and E. As a consequence, differences in rates are smaller than would be expected on the basis of differences in the activation energy alone; i.e., an increase in the preexponential factor compensates for an increase in the apparent activation energy. Hence, the term “compensation effect” is used in referring to such a relationship [49]. In fig. 3, values of log r_0' (common logarithm) and E are shown for a number of metals for each of the three hydrogenolysis reactions which have been considered here. For the ethane hydrogenolysis reaction, the values of r_0' were converted from units of molecules per square centimeter per second in ref. [4] by using factors of approximately 10^{15} metal surface atoms per square centimeter. The figure embodies a number of compensation effects of the two types mentioned at the beginning of this paragraph. The various values of log r_0' and E for each reaction are represented by a particular symbol, so there are three different types of symbols used in the figure. No attempt is made to identify each point with a particular metal because of the large number of points. For the reader who may be interested in further details, reference is made to the publications containing the information [4,41,48]. These details are not essential for our purpose here, which is simply to point out that the apparent activation energies for the ethane hydrogenolysis reaction are much higher than for the hydrogenolysis reactions of methylamine and methyl chloride. This difference is observed despite the fact that the dissociation energies of the C–C, C–N, and C–Cl bonds are nearly equal. Perhaps this is a consequence of extensive dehydrogenation of ethane prior to C–C scission, i.e., a consequence of the formation of adsorbed C_2H_x being highly endothermic. It could also reflect a high surface coverage by hydrogen during ethane hydrogenolysis, so that desorption of hydrogen on increasing temperature would have a strong multiplying effect on the number of free sites available for chemisorption of ethane. Either or both of these factors could conceivably be involved.

5. Concluding remarks

Metal-catalyzed hydrogenolysis reactions have long been of interest with regard to their kinetic and mechanistic features. They also provide dramatic examples of the specificity of metal surfaces in catalysis. For these reasons, among others, studies of hydrogenolysis reactions have provided useful insight into factors of importance in the general area of catalysis by metals.

Acknowledgements

The writer gratefully acknowledges contributions by a number of collaborators, including D.J.C. Yates, W.F. Taylor, G. Meitzner, and S.C. Fung, to work discussed in this article.

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