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The Relationship of Reaction Rate to Amounts Adsorbed for the Low-Temperature ortho–para Hydrogen Shift

DAVID KAUFFMAN,[1] LEE F. BROWN,[2] AND WILLIAM H. MANOGUE[3]

Department of Chemical Engineering, University of Colorado, Boulder, Colorado 80309

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The relationships between the amounts of adsorbed reactant and product and the forward and reverse reaction rates were measured for the ortho–para hydrogen system on a chromia–alumina catalyst at 75.7 K. Total adsorption was measured rapidly; individual species isotherms as functions of pressure and composition were extracted from the total adsorption data. Reaction rates were determined as functions of pressure and composition using an integral, packed-bed reactor. The resulting relationships between individual surface reaction rates and the amounts of adsorbed reactants are nonlinear. The observed results can be explained by a reaction mechanism involving mobile adsorbed products and reactants. The reactants in this system primarily are physically adsorbed, so these results may be generalized to other systems only with caution.

INTRODUCTION

The amounts of various substances actually present on a catalyst surface during reaction are of great interest in catalysis. Information concerning these amounts can give insight into the behavior of the adsorbed and solid phases and other facets of catalytic mechanisms. Simple theories have the catalytic reaction rate proportional to the concentration of adsorbed reactant, and measurements of the amount of reactant adsorbed during reaction have confirmed this on occasion (*1–6*).

Other studies giving more complicated relationships have yielded valuable insight into the mechanism of the reaction involved (*7, 8*).

Among the methods used, unsteady-state techniques have been popular for determining the amounts of various adsorbed species on the catalyst surface. Transient-response experiments have been used by some investigators (*9–12*) for the measurement of the amounts of adsorbed species present during reaction. In another approach, Syverson and co-workers (*13, 14*) used adsorption data from high-speed pressure and temperature measurements to predict total conversion with time.

Much has been gained from these studies which relate the amounts of substances on the catalyst surfaces to the behavior of catalytic reaction rates. This paper presents a study of the relationship between surface reaction rate and amounts of reactant and product adsorbed for a very simple system—the low-temperature (75.7 K) ortho–para hydrogen shift over a chromia–alumina catalyst.

This system offers several advantages for such a study. The heat of reaction is quite small—at 75.7 K it is 1385 J/mol (*15*), so heat effects are small. No possible side reactions exist; the only two stable species are orthohydrogen and parahydrogen. The reaction involves no net change in the number of moles present. The overall reaction rate on all except highly active catalysts can be described adequately by a first-order rate expression (*16*). Interpretation of the data is, therefore, less subject to question-

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[1] Present address: The University of New Mexico, Albuquerque, New Mexico.

[2] To whom inquiries concerning this paper should be addressed. Present address: Los Alamos National Laboratory, Los Alamos, New Mexico.

[3] Present address: E. I. duPont de Nemours and Company, Wilmington, Delaware.

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able assumptions than it would be for more complex systems.

Many studies have agreed that the reaction at low temperatures (90 K and below) over oxide catalysts is unimolecular. Some investigators have found essentially no hydrogen–deuterium exchange at low temperatures, while observing significant ortho–para hydrogen shift (*17, 18*). Others have observed H–D exchange on oxide catalysts at low temperatures (*19–22*), but when the rate of ortho–para conversion has been compared with the rate of H–D exchange, the former has been substantially greater and so the primary mechanism even in these situations is indicated as being unimolecular (*20, 21*). The magnetic field effect on this reaction at low to moderate temperatures (*23, 24*) also indicates a unimolecular mechanism.

The results of these studies also imply that the surface-reaction step is the rate-limiting one. The adsorption and desorption steps are apparently very fast and so these steps are in essential equilibrium. Theoretical calculations of adsorption rates under appropriate reaction conditions confirm this conclusion (*25*).

A possible disadvantage of studying this reaction at low temperature lies in the adsorption being generally of a physical nature (*21*); in most catalytic systems of commercial interest the adsorption has more chemical characteristics. As a consequence, the results of this investigation may be generalized to other systems only with caution.

METHODS

To achieve the goals of this study, it was necessary to measure the amounts of both adsorbed reactant and product under nonequilibrium conditions. A high-speed unsteady-state technique was used to provide data in the form of total hydrogen adsorbed over wide ranges of pressure and gas composition. Given a total amount adsorbed as a function of the component partial pressures in a gaseous mixture, the individual isotherms of the components may be extracted from the total isotherm data (*26*). Thus, adsorption expressions for both ortho- and parahydrogen were determined as coupled functions of the two partial pressures. In the experiments reported here, the temperature was 75.7 K, the total pressure ranged from 87 to 1700 kPa, and the parahydrogen mole fraction varied from 0.250 to 0.514.

Overall net reaction rates were measured in a standard fashion using a packed-bed reactor. The reactor was maintained at a constant temperature of 75.7 K with the pressure ranging from 240 to 2400 kPa. The inlet mole fraction was 0.250, and various outlet compositions between this and equilibrium (0.514 mole fraction parahydrogen) were obtained by varying the reactor space velocity. Conversion data were analyzed to obtain a rate expression in terms of gas-phase composition and pressure. With expressions for both the amounts adsorbed and the reaction rate in terms of pressure and composition, the reaction rate can then be calculated in terms of the amounts adsorbed.

We used a 19% chromia-on-alumina catalyst supplied by Harshaw Chemical Company (type CR 1403-T-1/8, received in the form of $\frac{1}{8}$-in. pellets). It was crushed, and size 14-30 mesh (0.6 to 1.4 mm in approximate diameter) was used in the experiments. The surface area of this catalyst is approximately 180 m^2/g.

Adsorption Measurements

A modification of a technique described by Winfield (*27*) and used by Macarus (*28*) and Haering and Syverson (*13*) was used for the adsorption measurements. The basic principle is to expose a catalyst suddenly to a reactive gas mixture, and to take adsorption measurements in a time sufficiently long for adsorption equilibrium to be established but sufficiently short so that only a negligible amount of reaction can take place. A two-chamber adsorption apparatus was built. The first chamber, or hold tank, had a bonded strain gauge pressure transducer mounted on it. The second chamber, which held the catalyst, was connected to the first by a fast-acting pneumatically controlled control valve. The entire assembly was immersed in a liquid nitrogen constant-temperature bath. Hydrogen gas of known composition was fed into the hold tank until the desired starting pressure was reached. The feed line was sealed off and the valve between the two chambers opened. By measuring the pressure in the hold tank, using the P–V–T properties of the gas, and knowing the volumes of the two chambers, it was possible to determine the total amount of gas adsorbed on the catalyst. A schematic diagram of the adsorption subsystem is presented in Fig. 1.

A full description of the adsorption apparatus, including dimensions, physical layout, detailed operating procedures, possible safety hazards and precautions, and operating problems and solutions, is presented in the thesis upon which this paper is based (*25*). In addition, a detailed estimation of expected experimental precision is given. Using the approach illustrated by Benson (*29*), the estimated uncertainty in a_T, the total amount adsorbed, ranged from 0.009 mg-mol/g-catalyst at 87 kPa to 0.020 mg-mol/g-catalyst at 1700 kPa. The values of a_T on the catalyst ranged from 0.147 to 0.710 mg-mol/g-catalyst. The uncertainty thus ranged from 6.1% at 87 kPa to 2.8% at 1700 kPa.

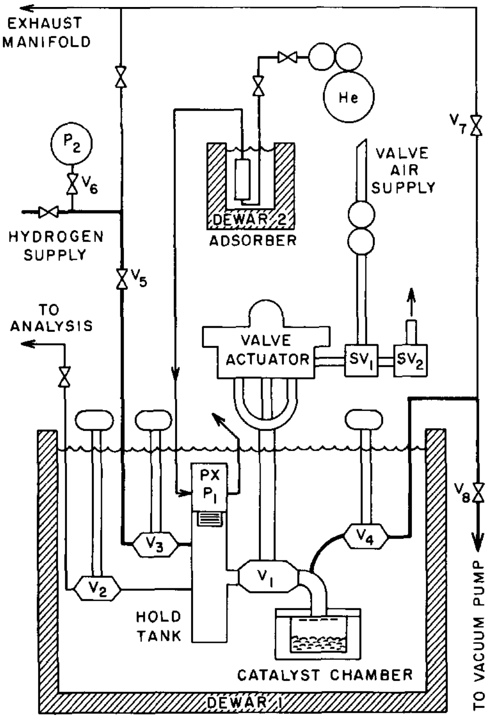

FIG. 1. Adsorption measurement apparatus.

Reaction Rate Measurements

Various systems for measuring rates of the catalytically promoted ortho–para hydrogen shift have been described before (*15–18, 20, 21*), and the apparatus used in this study was not significantly different from these. A full description of the reaction rate measurement apparatus is presented in the thesis (*25*), along with a detailed estimation of expected precision. The uncertainty in the measured value of x was about ±0.001. Again using the approach illustrated by Benson (*29*), the uncertainty in r as a function of x and P was estimated to be about 1.2%. This figure is used in later correlations of r and adsorption measurements. Note that any rate expression which correlates the experimental data to within experimental precision (i.e., predicts the dependent variable x to within ±0.001, root-mean-square (RMS) error) still has an inherent uncertainty of 1.2% in the actual value of the reaction rate.

RESULTS

Reaction Rate Measurements

A mole balance for a plug-flow packed-bed catalytic reactor yields the differential equation

$$r = F(dx/dm_c). \qquad (1)$$

One frequently used technique for identifying the proper reaction rate expression is to substitute various expressions for the rate into the left-hand side (LHS) of the above equation, solve it, and see if the behavior predicted by the solution matches the observed experimental behavior. This is the method used in the present study.

Sixteen runs were made in order to establish a rate expression for the o-H_2 $\leftrightarrows$ p-H_2 shift reaction on chromia–alumina. A simple first-order rate expression,

$$r = k_1(x_e - x) \qquad (2)$$

was found to be adequate for correlating the data within the expected experimental error. The integrated form of Eq. (1), using Eq. (2) for the rate expression, is

$$\ln[(x_1 - x_e)/(x_2 - x_e)] = k_1 m_c/F. \qquad (3)$$

The data from one typical run are presented in Fig. 2. In this figure the LHS of Eq. (3) is plotted as a function of m_c/F. If the reaction is indeed first order, then the data should exhibit straight-line behavior with a zero intercept. This behavior requirement is fulfilled well.

To check further whether the first-order rate expression was adequate to describe the behavior of this reaction, a nonlinear least-squares fit of the data was made to determine the root-mean-square error and whether there was any observable trend of the data with the independent variable (m_c/F). If the RMS error is within the same range as the estimated error in measurement, and if there is no observable trend in the data with a change in independent variables, then the rate expression can be considered a satisfactory description of the reaction rate within experimental error over the range of variables investigated. For this nonlinear regression, the data were weighted proportional to $(x_2 - x_e)(x_1 - x_2)$ in order to weight most heavily those data points which could give the most information about the rate. Any reasonable rate expression correlates data well both near and far from equilibrium; it is in the area between the two extremes that the differences in rate expressions may be found, and the weighting method used accentuated the data points in this area.

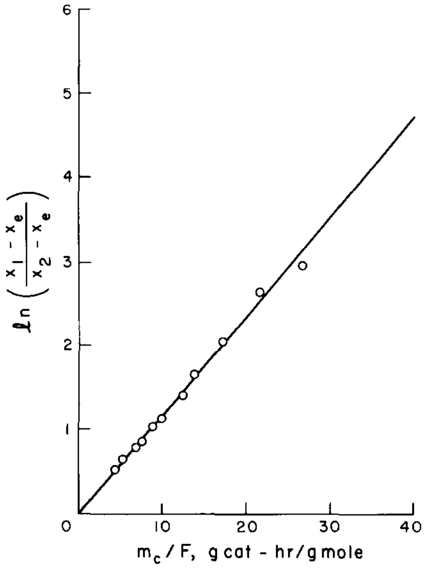

FIG. 2. First-order plot.

The weighted RMS error in x_2 for these runs varied from 0.0009 to 0.0020. This was quite reasonable when compared with the estimated uncertainty in measuring x_2 of 0.001 (*25*). In addition, no observable trend of the data with changing m_c/F could be detected. It was concluded that the first-order rate expression satisfactorily described the relationship between reaction rate and gas-phase composition of reactant and product.

Following these 16 runs, a series of 5 runs was made to develop a relationship between k_1 and P. The data in these runs were all taken in a range where x_2 was approximately midway between x_1 and x_e. In the nonlinear least-squares analysis, therefore, the data were equally weighted. A single empirical expression was found which correlates k_1 with the total pressure of hydrogen:

$$k_1 = 0.01058 \ln P - 0.07030 \left(\frac{\text{g-mol}}{\text{hr g-catalyst}}\right) \quad \text{(With } P \text{ in Pa).} \qquad (4)$$

Using this expression, the RMS error in x_2 for all 49 data points in the five runs is

0.0014. Again, this is quite reasonable when compared with the estimated uncertainty of 0.001 in measuring x_2. No theoretical significance is claimed for this expression for k_1; it is simply an empirical expression which expresses the reaction rate constant at 75.7 K in terms of P over the range of pressures used in the adsorption experiments.

The absence of axial and radial diffusion effects (including the effects of deviation from flat velocity profile) and the absence of any significant radial temperature gradients are inherent in the use of Eq. (1) to describe the operation of a tubular reactor. Further, when this expression is used to determine catalytic surface reaction rates, intraparticle transport resistances must be negligible. The measurements of reaction rates are much more direct when the reactor is isothermal. These requirements were studied in detail in the thesis on which this paper is based (*25*), and all were well fulfilled. Both axial and intraparticle diffusion were negligible, and the calculated maximum temperature difference between the liquid nitrogen bath and any point in the reactor usually did not exceed 0.1 K. The worst possible situation (maximum conversion at maximum pressure) showed a calculated maximum temperature difference of 0.57 K, but it was only a small fraction of this value under most operating conditions. Within the limits of experimental accuracy in this study, therefore, these nonideal effects were concluded to be negligible.

Forward and Reverse Reaction Rates

The rates measured and correlated above represent the net reaction rate of o-H_2 to p-H_2. But the net reaction rate is composed of both a forward and a reverse rate,

$$r = r_{o-p} - r_{p-o} \tag{5}$$

and it is the dependence of these individual forward and reverse rates upon the amount of individual species adsorbed that is of interest. It is thus necessary to separate the measured reaction rate into forward and reverse reaction rates. Since the net reaction rate can be represented by a first-order expression, it is reasonable to assume that the individual rates can also be represented, at least in part, by similar first-order expressions.

$$r_{o-p} = k_{o-p}(1 - x) + f_{o-p}(x,P), \tag{6}$$

$$r_{p-o} = k_{p-o}x + f_{p-o}(x,P). \tag{7}$$

These expressions are of course quite general, since the functions f_{o-p} and f_{p-o} could completely dominate the first terms on the right-hand side (RHS) of Eqs. (6) and (7). A discussion of the nature and magnitude of the functions f_{o-p} and f_{p-o} necessitated by the first-order behavior of the net reaction rate is presented in the Appendix. The conclusion is drawn that the value of both of these functions is almost certainly zero everywhere. Under these conditions, the first terms on the RHS of these two equations can be easily manipulated to show

$$k_{o-p} = x_e k_1, \tag{8}$$

$$k_{p-o} = (1 - x_e)k_1, \tag{9}$$

where k_1 is the observed net first-order rate constant. The individual rate expressions are therefore expressed as simple first-order expressions:

$$r_{o-p} = k_1(1 - x)x_e, \tag{10}$$

$$r_{p-o} = k_1 x(1 - x_e). \tag{11}$$

These expressions are used to relate the individual forward and reverse rates to the amount of reactant and product adsorbed.

Adsorption of Orthohydrogen and Parahydrogen

The independent variables in the adsorption data measurement were total pressure and parahydrogen mole fraction, and the adsorption data were in the form of total moles adsorbed at various values of these variables. The method used to break these data down into adsorbed o-H_2 and p-H_2 involved assuming appropriate adsorption relationships containing undetermined parameters. Since the two reacting species were so much alike, similar functional forms were specified for both species in all numerical runs for obtaining the unknown parameters in the adsorption expressions. The two relationships were then summed to obtain the relationship between total amount adsorbed and the independent variables. The optimum values of the parameters in the total adsorption relationship were found by using nonlinear least-squares regression. The criteria as to whether the total adsorption relationship was satisfactory were that the mean square error was approximately the same as that predicted by the error analysis of the experimental procedures and data, and that there were no systematic errors or trends in the differences between the calculated and experimental adsorption values. In addition, the total adsorption relationship had to contain the significant variables involved (pressure and composition) and had to be able to give the shape of the experimentally determined adsorption curves.

As stated in the beginning of the Methods section, once the optimum total adsorption relationship was found, the individual relationships of adsorbed o-H_2 and adsorbed p-H_2 as functions of the independent variables followed directly. They were the component functional relationships, containing the appropriate optimum parameter values, whose sum formed the relationship for the total amount adsorbed. If the optimum parameter values obtained were unique, the isotherms for the individual components of our system could be determined once the total adsorption isotherms were obtained for a range of compositions and pressures.

Table 1 lists the adsorption isotherms considered and the RMS error found for each set of isotherms using the optimum set of variable parameters. Isotherms A through N showed systematic errors in the calculated value of a_T, the total adsorption, compared with the experimental values. For example, high-pressure data might have tended to produce negative errors while low-pressure data produced positive errors, even with the optimum set of parameters. Isotherms O, P, and Q produced fairly random distributions of errors and also approached the level of error predicted by the analysis of probable errors in the system. Isotherm Q was selected for the correlation studies. This choice was made because its residual errors were no greater than those for any other isotherm investigated and because it had one less arbitrary constant than the other two comparable isotherms. Since the addition of extra terms containing the significant variables did not improve the agreement between the calculated relationship and the data, it was concluded that the results obtained from Model Q were correct within the experimental accuracy of the data.

The relationship studied certainly did not include all possible adsorption relationships. There are undoubtedly many other relationships which might fit the data as well as did isotherm Q. This relationship, however, fitted the data as well as could be expected from experimental considerations with no obvious trends in the errors and could therefore be considered correct within the experimental accuracy of the data. Any other relationships which might be used would give values of a_o and a_p in very close agreement with the values obtained in the present analysis, once the optimum parameters were determined, provided that the RMS errors were as low as those found for isotherm Q.

Correlation of Rate Data and Adsorption Data

From the earlier analyses, r_{o-p} and r_{p-o} were found as functions of P and x. This was equivalent to knowing them as functions of P_o and P_p, since

$$P_o = P(1 - x) \tag{12}$$

and

$$P_p = Px. \tag{13}$$

TABLE 1

Adsorption Models—Hydrogen on Chromia-Alumina

Model	a_o	a_p	RMS error in a_T (mg mol/g)
A	B_1	$B_1 - a_o$	0.160
B	$B_2 + B_3P_o$	a_oP_p/B_1P_o	0.058
C	$B_1 + B_2P_o$	$B_3 + B_4P_p$	0.061
D	$B_2 + B_3P_o + B_4P_o^2$	a_oP_p/B_1P_o	0.062
E	$B_1 + B_2P_o + B_3P_o^2$	$B_4 + B_5P_p + B_6P_p^2$	0.025
F	$\frac{B_2P_o}{1 + B_3P_o}$	a_oP_p/B_1P_o	0.026
G	$\frac{B_1P_o}{1 + B_2P_o}$	$\frac{B_3P_p}{1 + B_4P_p}$	0.022
H	$\frac{B_2P_o}{1 + B_3P_o + B_4P_p}$	a_oP_p/B_1P_o	0.022
I	$\frac{B_1P_o}{1 + B_3P_o + B_4P_p}$	$\frac{B_2P_o}{1 + B_3P_o + B_4P_p}$	0.023
J	$B_2P_o^{B_3}$	a_oP_p/B_1P_o	0.023
K	$B_1P_o^{B_2}$	$B_3P_p^{B_4}$	0.023
L	$B_2 \ln(B_3P_o)$	a_oP_p/B_1P_o	0.028
M	$B_1 \ln(B_2P_o)$	$B_3 \ln(B_4P_o)$	0.024
N	$\frac{B_2P_o(1 + B_4P_p)}{1 + B_3P_o}$	a_oP_p/B_1P_o	0.018
O	$\frac{B_1P_o(1 + B_3P_o)}{1 + B_2P_o}$	$\frac{B_4P_p(1 + B_6P_p)}{1 + B_5P_p}$	0.017
P	$\frac{B_1P_o(1 + B_2P_o)}{1 + B_5P_o + B_6P_p}$	$\frac{B_3P_p(1 + B_4P_p)}{1 + B_5P_o + B_6P_p}$	0.014
Q	$\frac{B_1P_o(1 + B_2P_o)}{1 + B_5(P_o + P_p)}$	$\frac{B_3P_p(1 + B_4P_p)}{1 + B_5(P_o + P_p)}$	0.014

The adsorption data and relationships give a_o and a_p as functions of P_o and P_p. It is therefore possible to correlate the reaction rates with the adsorption parameters directly.

Figure 3 presents the forward reaction rate, r_{o-p}, as a function of adsorbed o-H_2, a_o. Solid lines are plotted for various values of a_p. In a similar manner, the reverse reaction rate, r_{p-o}, is plotted as a function of adsorbed p-H_2, using broken lines for various values of a_o. The lines are plotted only within the region of the graph where both reaction rate and adsorption data were obtained. It should be noted that conventional theories relating reaction rate to the amount of adsorbed reactant assume that single lines through the origin will correlate each of these two sets of data. The simpler theories assume that the lines are straight, but virtually all theories proposed to date assume that only one line exists for each reaction.

Figure 4 illustrates the inhibiting effect of

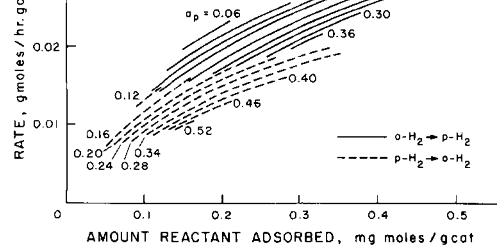

FIG. 3. Reaction rate *vs* adsorbed reactant with constant amounts of adsorbed product.

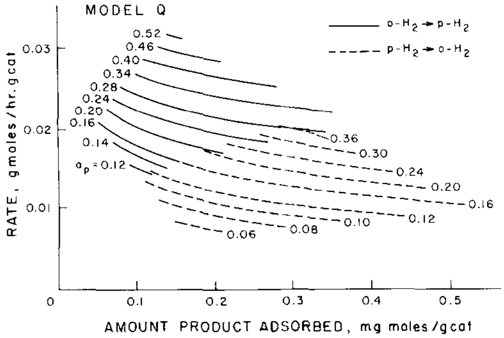

FIG. 4. Reaction rate *vs* adsorbed product with constant amounts of adsorbed reactant.

adsorbed p-H_2 on the forward reaction rate, r_{o-p}, and the same effect for adsorbed o-H_2 on the reverse reaction rate, r_{p-o}.

Figure 3 indicates that single, simple linear relationships between reaction rates and adsorbed reactants do not exist. Qualitatively, the forward rate increases with increasing reactant adsorption, but the rate of increase falls off with increasing coverage when the amount of adsorbed product is held constant. The effects are similar for both the forward and reverse rates. Figure 4 indicates that there in an inhibiting effect on both the forward and reverse reactions due to adsorbed product. With the amount of the reactant adsorbed on the surface held constant, the inhibition effect is nonlinear. If the forward reaction, for example, depended only on the amount of adsorbed o-H_2, the lines in Fig. 4 would reduce to a family of horizontal lines.

Other theories relating reaction rates to adsorbed amounts have indicated an inhibiting effect of adsorbed product, but they have always indicated that this inhibition resulted from the presence of the produce decreasing in some manner the amount of adsorbed reactant. In contrast, the present experimental results show that even at a constant amount of adsorbed reactant, the reaction rate decreases as the amount of adsorbed product increases.

Data scatter, errors due to finite extent of reaction during adsorption measurements, and errors implicit in selecting one particular adsorption relationship have no significant effect on the shape of the correlations, though they may have small effects on numerical values of variable parameters. Details of these analyses are available in the thesis (*25*). It is reasonable to conclude, therefore, that the correlations made using isotherm Q are representative of the true situation.

DISCUSSION

The relationships illustrated in Figs. 3 and 4 clearly show that the surface reaction rates are not simple functions of adsorbed reactant. The correlations are definitely nonlinear. There are also large and significant reaction rate-inhibiting effects due to adsorbed products.

The finding that the surface reaction rates are not simply proportional to the amounts of adsorbed reactants is not surprising. There have been many predictions of nonlinear behavior for this relationship with a variety of possible explanations (*30–32*). The inhibiting effect of adsorbed product for constant amounts of adsorbed reactant does not seem to have been reported before, either from an experimental standpoint or as a possible significant effect in theoretical studies of methods for correlating catalytic reaction rates. Many approaches take into account the reduction in available surface area for reactant adsorption due to product adsorption. They still, however, have always assumed that the individual forward and reverse rates were dependent only on the amounts of the particular adsorbed reactants involved and were independent of adsorbed products.

It is interesting to note that the rather complex rate/adsorption relationship found in the present study still leads to a simple, linear overall reaction rate based on gas-phase composition. Hutchinson *et al.* (*16*) considered this possibility and pointed out several conditions which could make it possible. Essentially, the surface-reaction-rate/reactant-adsorption relationships must have a qualitatively similar form to the adsorption isotherms for the individual species. Under these conditions, the surface-reaction-rate/gas-phase-composition relationships can be linear.

The most commonly suggested cause for predicting a nonlinear reaction rate–adsorption relationship for first-order surface reactions is a heterogeneous surface. If all reaction locations on the surface are equally active, or if there is no significant correlation between the activity of a reaction location and the probability that it is occupied by a reactant molecule, then the reaction rate should be directly proportional to the amount of adsorbed reactant. This direct proportionality is not observed in the present study. Rather, the slope of the rate–adsorption curve decreases for all values of the adsorbed product. To account for this kind of rate–adsorption relationship, it would have to be assumed that those sites which are most active for reaction are also the same sites which are most likely to adsorb hydrogen. As these preferred sites gradually become saturated with increasing surface coverage, the proportionality between reaction rate and amount of reactant adsorbed would decrease.

But this explanation does not account for the decrease of reaction rate with increasing amount of adsorbed product. The presence of surface heterogeneity, however, can account for the product-inhibition effect. In the system studied there is not a large difference in adsorption characteristics between reactant and product. If the most active reaction locations are most likely to adsorb reactant, then they would also be most likely to adsorb product. Thus in the presence of a larger amount of adsorbed product, a larger fraction of the most active reaction locations would be occupied by product. This explanation of the observed product-inhibition effect is also consistent with the type of curvature observed in the rate–adsorption relationship at constant amount of adsorbed product.

There is one other explanation which can also account for both the nonlinear rate–adsorption relationship and the product-inhibition effect. The mobility of adsorbed atoms and molecules in reactive systems is well known and widely observed (*33*). If the adsorbed molecules in the present system were mobile, then the residence time of a molecule at a reaction location could well be affected by both the amount of adsorbed reactant and the amount of adsorbed product. The more reactant molecules there are, the more often a molecule residing at a reaction location would be struck by other reactant molecules. If, on the average, a minimum threshold residence time at the reaction location is required for the reaction to occur, then the average reactant molecule would spend less time at a reaction location and would be less likely to react as the number of reactant molecules increased. This would account for the monotonically decreasing slope of the rate–adsorption curve at a constant amount of adsorbed product. A similar effect would occur if the amount of adsorbed product increased. The reactant molecules at the reaction locations would be struck more often by product molecules, their average residence times at the reaction locations would be decreased, and the probability of their reacting would therefore be lessened. Thus, invocation of either surface heterogeneity or mobility in the adsorbed phase can account qualitatively for both the nonlinear rate–adsorption relationship and the product-inhibition effect.

There is a way of distinguishing between the two explanations. If mobility in the adsorbed phase is the correct explanation of both the observed rate–adsorption effect and the inhibition by adsorbed product, and if the *total* amount of adsorbed hydrogen is kept constant, the reaction rate should be directly proportional to the amount of adsorbed reactant. This should be true because, when the amount of adsorbed reactant plus adsorbed product is held constant, the probability of a molecule occupying a reaction location being displaced by another molecule will not change, irrespective of how much of the total adsorbed material is reactant. In this set of circumstances, therefore, a straight line with zero intercept should result when the reaction rate is plotted as a function of adsorbed reactant at a constant total amount of adsorbed reactant and product. This behavior would not be observed if the heterogeneous surface were the principal cause of the nonlinear rate–adsorption relationship or the product-inhibition effect.

In Fig. 5 the rate/adsorbed reactant relationships are replotted, with the parameter changed from adsorbed p-H_2 or o-H_2 to total adsorbed hydrogen. The behavior predicted by mobility in the adsorbed phase is completely matched at low surface coverages with the total amount of adsorbed hydrogen held constant, both forward and reverse rates/adsorbed-reactant relationships are straight lines with zero intercepts. At higher coverages, though the straightline behavior still exists, the lines do not appear to pass through the origin. The deviation from passing through the origin is too great to be attributed only to expected experimental errors; therefore, some curvature in the line must occur in the region not investigated at high coverages, and some surface heterogeneity does appear to be present. Nevertheless, the straight-line behavior is predicted at no point by the surface heterogeneity postulate, and so even at higher surface coverages there is strong evidence of mobility in the adsorbed phase. A wide range of surface coverage is included in the experimental data taken for this study. Assuming monolayer adsorption, the fraction of the total catalyst surface covered varies from about 0.053 and 0.414, so it is not surprising that more than one type of the rate/adsorption behavior is seen.

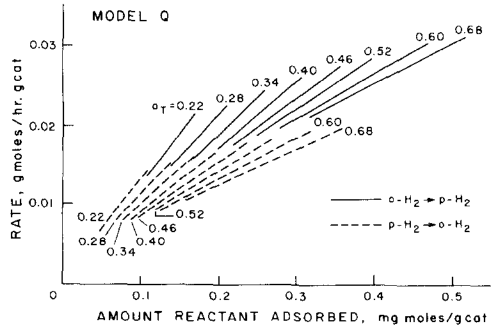

FIG. 5. Reaction rate *vs* Adsorbed reactant with constant total adsorption.

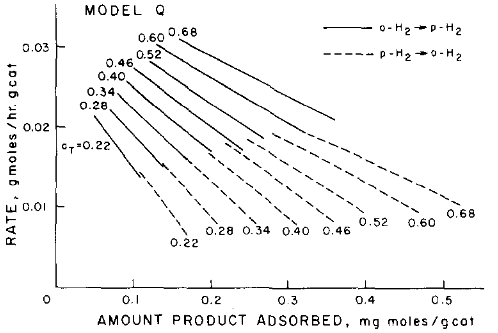

FIG. 6. Reaction rate *vs* adsorbed product with constant total adsorption.

Another prediction of mobility in the adsorbed phase is that the inhibiting effect of amount of adsorbed product should be linear at constant total hydrogen coverage. All plots of these lines should also exhibit a common intercept. These predictions are examined in Fig. 6. The straight-line behavior is exhibited at all total surface coverages, and the lower-coverage lines all have approximately the same intercept. There is some deviation from the common intercept at high coverages. This again indicates that at higher coverages, although adsorbed phase mobility can account for most of the rate–adsorption behavior, it is not the complete explanation. Some surface heterogeneity may also affect the rate–adsorption behavior at higher coverages.

In summary, therefore, we conclude that for the orthohydrogen–parahydrogen shift reaction promoted by a chromia–alumina catalyst at 75.7 K, the reaction rate depends upon the amounts of adsorbed reactants in a nonlinear fashion. The forward rate increases with increasing orthohydrogen adsorption, but the rate increase decreases with increasing coverage when the amount of adsorbed parahydrogen is held constant. There is an inhibiting effect of adsorbed parahydrogen upon the forward reaction rate. The analogous situation is true for the reverse reaction rate. At low coverages of total adsorbed hydrogen, the behavior of the rate–adsorption relationship, both the nonlinear dependence upon adsorbed reactant and the product inhibition, can be fully explained by mobility in the adsorbed phase. At high coverages of total adsorbed hydrogen, both the nonlinear dependence upon adsorbed reactant and the product-inhibition effect require the invocation of both a mobile adsorbed phase and surface heterogeneity to explain fully the behavior of the rate/adsorption relationship.

As mentioned earlier, it is a frequent assumption that the rate of a surface step in a reaction is directly proportional to the surface concentration of the step's reactant or reactants. For example, the investigators who measured the surface concentrations of adsorbed species during reaction by transient-response techniques (*9–11*) all made this assumption, and based their analyses upon it. This study shows that this assumption may not always be correct, and thus conclusions based on it may not be justified.

NOMENCLATURE

a_o	Specific adsorption of o-H_2 (mol/g)
a_p	Specific adsorption of p-H_2 (mol/g)
a_T	Total specific adsorption (mol/g)
B_i	Parameter in adsorption models (various units)
F	Flow rate (mol/hr)
f_{o-p}	Reaction rate function (mol/hr · g)
f_{p-o}	Reaction rate function (mol/hr · g)
k_1	First-order rate constant (mol/hr · g)
k_{o-p}	Forward first-order rate constant (mol/hr · g)
k_{p-o}	Reverse first-order rate constant (mol/hr · g)
m_c	Catalyst mass (g)
P	Pressure (Pa)
P_o	Partial pressure of o-H_2 (Pa)
P_p	Partial pressure of p-H_2 (Pa)
r	Net reaction rate (mol/hr · g)
r_{o-p}	Forward reaction rate (mol/hr · g)
r_{p-o}	Reverse reaction rate (mol/hr · g)
x	Mole fraction of p-H_2
x_1	Mole fraction of p-H_2 at reactor inlet
x_2	Mole fraction of p-H_2 at reactor outlet
x_e	Equilibrium mole fraction of p-H_2 (0.514 at 75.7 K)

APPENDIX: FORWARD AND REVERSE REACTION RATE TREATMENT

The experimentally measured reaction rate was actually the difference between the forward and reverse reaction rates. It was determined experimentally to fit a first-order rate expression:

$$r = r_{o-p} - r_{p-o} = k_1(x_e - x). \quad \text{(A-1)}$$

In this study, it was necessary to use rate expressions for the individual forward and reverse reaction rates. The simplest pair of expressions that would result in a net first-order rate expression were first-order expressions for the individual rates.

$$r_{o-p} = k_1(1 - x)x_e, \quad (10)$$

$$r_{p-o} = k_1(1 - x_e)x. \quad (11)$$

Although these two represent the simplest pair of expressions that result in a first-order expression for the net reaction rate, they are not the only possible pair which do so. A very general pair can be formulated using both first-order terms and non-first-order terms.

$$r_{o-p} = k_{o-p}(1 - x) + f_{o-p}(x,P), \quad (6)$$

$$r_{p-o} = k_{p-o}x + f_{p-o}(x,P). \quad (7)$$

The net reaction rate is then given by

$$k_1(x_e - x) = k_{o-p}(1 - x) + f_{o-p}(x,P) - k_{p-o}x - f_{p-o}(x,P). \quad \text{(A-2)}$$

Since the reaction rate data can be adequately fit by

$$r = k_1(x_e - x) = k_{o-p}(1 - x) - k_{p-o}x \quad \text{(A-3)}$$

it follows that, for all x and P,

$$f_{o-p}(x,P) = f_{p-o}(x,P). \quad \text{(A-4)}$$

Obviously, r_{o-p} must be zero when $x = 1$

since there is no orthohydrogen present. Similarly, r_{p-o} must be zero when $x = 0$. It follows, therefore, that

$$f_{o-p}(1,P) = 0, \tag{A-5}$$

$$f_{p-o}(0,P) = 0. \tag{A-6}$$

Combining with (A-4) also gives

$$f_{p-o}(1,P) = 0, \tag{A-7}$$

$$f_{o-p}(0,P) = 0. \tag{A-8}$$

These five equations lead to the conclusion that one of the following three conditions must be correct: (a) The function $f_{o-p}(x,P)$ is everywhere zero. (b) If the forward rate shows increasing deviation from first-order behavior at low values of x, it must show a decreasing deviation from first-order behavior at high values of x. The reverse rate must of course show the identical behavior. (c) If the forward rate shows a decreasing deviation from first-order behavior at low values of x, it must show increasing deviation from first-order behavior at high values of x.

Neither option (b) nor (c) seems likely. While f_{o-p} might be a steadily increasing function for awhile, and then perhaps level off, complex behavior like that postulated in choices (b) and (c) does not appear to have been noticed before. In addition, the behavior of the reverse rate would have to be just as unusual. First-order behavior, of course, has been widely noted for individual catalytically promoted reactions. It is concluded that f_{o-p} (and therefore f_{p-o}) is almost certainly equal to zero everywhere and the forward and reverse reactions are first order.

Another approach to this problem can be taken. From a quantitative study of the effect of f_{o-p} and f_{p-o} upon the conclusions of this paper (*25*), it is found that f_{o-p} and f_{p-o} would have to represent as high as 42% of the measured reaction rates in order for the forward and reverse reaction rates to be strictly linear functions of reactant surface coverage. While it is conceivable that a nonlinear function could represent nearly half of the reaction rate terms, it would seem to be most unlikely. Therefore the most probable values of f_{o-p} and f_{p-o} are zero.

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