Frequency Response Study of the Dynamics of the Platinum Catalyzed Interconversion of Methylcyclohexane, Toluene, and Hydrogen near Equilibrium[†]

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The dynamics of the platinum catalyzed interconversion of methylcyclohexane, toluene, and hydrogen near equilibrium were investigated in a closed reactor system by a frequency response method at temperatures in the range of 433 to 473 K and at total pressures in the vicinity of 80 to 110 Torr. The gas phase in contact with the platinum catalyst was always hydrogen-rich, with hydrogen to hydrocarbon mole ratios maintained in the range of 3.2 to 4.6. The frequency response method utilized small perturbations (lower than 1%) of the volume of the system, with measurements of the total pressure being used to determine the response of the system. The range of perturbation frequencies investigated was approximately 0.002 to 3 Hz (0.013 to 19 rad s^{-1}). The experiments revealed two characteristic relaxation frequencies that are associated with the dynamics of the interconversion. The dynamics of the system are interpreted in terms of a simple two-step interconversion sequence with the aid of a phenomenological frequency response theory formulated in terms of relaxation frequencies of the steps and equilibrium properties of the system. It is concluded that one of the steps, a toluene adsorption−desorption step, is much slower than the other, a step involving the interconversion of the gas-phase methylcyclohexane and chemisorbed toluene that releases or consumes hydrogen in the process.

Introduction

In this paper we report results of an investigation of the dynamics of the platinum catalyzed interconversion of methylcyclohexane, toluene, and hydrogen near equilibrium:

$$+ 3H_2 \tag{1}$$
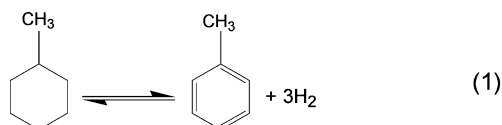
A frequency response approach, which is one version of a more general category of methods used to study relaxation phenomena,[1−7] was employed in the investigation.

In such methods, a system in a steady state or in a state of thermodynamic equilibrium is perturbed by a change in an external parameter (e.g., temperature, pressure, volume, and electric or magnetic field intensity) affecting the state. The rate of relaxation back to such a state is then followed in some manner, thereby producing data for the characterization of one or more relaxation times or relaxation frequencies for the system. In the frequency response approach, the external parameter is oscillated at a frequency which can be varied over a range suitable for the system under investigation. If the frequency of oscillation is large compared to the relaxation frequency of the system, the response of the system is nil; that is, a property of the system such as a concentration of a component of a reaction mixture will not exhibit corresponding oscillations about the steady state or equilibrium values. At the other extreme, the relaxation frequency may be so high that the concentrations

oscillate in phase with the externally imposed oscillations. When the relaxation frequency is comparable to the frequency of oscillation of the external parameter involved in the perturbation of the system, the concentrations oscillate at the imposed frequency but out of phase with it. Measurements of the amplitude and phase lag of these resulting oscillations as a function of the frequency of the imposed oscillations provides the information for the determination of relaxation frequency or its reciprocal, the relaxation time.

The frequency response approach has attracted the attention of scientists and engineers for a variety of problems, including the automatic control of processes,[8,9] the study of diffusion and adsorption in porous solids[10−25] and investigations of reaction engineering.[26−28] For fundamental studies of the kinetics of chemical reactions, it has received particular attention for very fast reactions in solution.[5,6,29,30] However, it has received very little attention for fundamental investigations of the dynamics of reactions catalyzed by surfaces. In 1989 Yasuda[31] reported results of a study of the kinetics of the hydrogenation of propylene on a platinum catalyst by a frequency response method. Shortly after the Yasuda work appeared, Schrieffer and Sinfelt[32] presented a theoretical frequency response analysis of simple surface reactions in flow systems, since heterogeneous catalysis is most commonly carried out by passage of a fluid stream through a bed of catalyst particles under steady-state conditions. The paper placed emphasis on how frequency response studies of the perturbation of the steady state could yield kinetic information not obtainable in a conventional steady-state mode of operation. Since the paper was strictly theoretical in nature, however, it still remained to be seen how well experiments could be conducted to obtain the data required for the quantitative determination of kinetic parameters. Since the magnitude of the perturbation imposed on the system must be very small (of the order of 1%) to enable one to work with

linear equations in the mathematical treatment of the data, the experimental challenge is a highly demanding one.

In our application of frequency response measurements in the work described in the present paper, we utilized a closed reaction vessel rather than a flow reactor system since we had not yet developed an apparatus of the latter type for frequency response studies. As described in the Experimental Section, the closed system was very similar to that developed by Reyes et al.[23,24] for studies of adsorption, desorption, and diffusion processes in porous solids. Since the system was found to be admirably suited for the study of such processes, all of which are of fundamental importance in heterogeneous catalysis, it seemed reasonable to attempt to utilize the same kind of system for an investigation directed toward the acquisition of information of use in understanding at least certain aspects of a surface catalyzed reaction.

The reaction system we chose for our investigation is an example of a kind of reaction that has long been of interest in heterogeneous catalysis. The dehydrogenation of cyclohexane and its homologues to aromatic hydrocarbons has been widely exploited in the petroleum industry in catalytic reforming processes for the production of gasoline components with high "anti-knock" quality.[33-37] Because of the high heats of reaction, the equilibria are in all cases strongly dependent on temperature. The equilibria are also strongly influenced by pressure, in view of the substantial change in the number of moles of components present as reaction proceeds. The equilibrium conversion to aromatic hydrocarbons increases with increasing temperature and decreasing pressure.

In a study of methylcyclohexane dehydrogenation to toluene on a platinum catalyst reported by Sinfelt et al. in 1960,[36] the kinetics were investigated in a steady-state flow reactor at conversion levels far removed from equilibrium. The reaction temperatures and pressures ranged from 588 to 645 K and 1.5 to 6.3 atm, respectively, which are somewhat lower than those commonly employed in catalytic reforming. The reaction was extremely selective to toluene and hydrogen; no other products were observed. The failure to detect any methylcyclohexene or methylcyclohexadiene is consistent with available thermodynamic information demonstrating the extremely low stabilities of these hydrocarbons relative to those of either methylcyclohexane or toluene.[38,39]

The fact that the conversion of methylcyclohexane to toluene and hydrogen was extremely clean in the steady-state flow reactor was an important factor in the choice of this reaction system for the present frequency response study with the closed reactor. Since the interconversion of the components was being followed purely by total pressure measurements, any substantial formation of side products would have interfered seriously with our ability to analyze the data in a straightforward manner. Although the high selectivity was very encouraging in this respect, we still were not able to conduct the present study with the closed reactor at temperatures as high as those employed in the earlier study with the flow reactor. The slow formation of the side products cyclohexane, benzene, and methane, which did not occur to a detectable extent in the short time of contact of catalyst with reactants characteristic of the flow reactor, did, however, occur to a much larger extent in the closed reactor. This was attributed to the relatively long contact times encountered in the preparation of the starting equilibrium mixture for a frequency response experiment. Conducting the present study at lower temperatures provided a solution to the problem. The highest temperature studied was 473 K. The presence of suitable amounts of toluene in the starting equilibrium mixtures at the
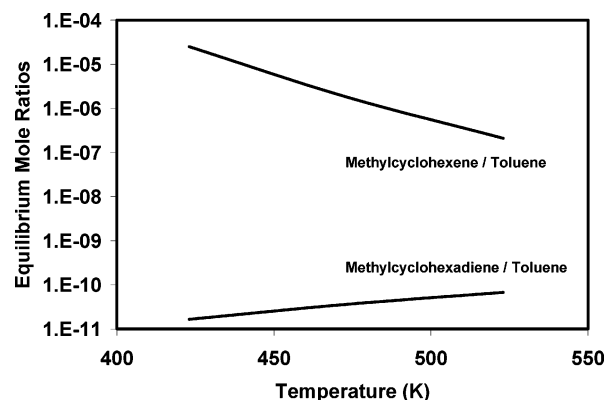
Figure 1. Equilibrium mole ratios of methylcyclohexene to toluene and of methylcyclohexadiene to toluene at a hydrogen partial pressure of 0.1 atm. The mole ratios were calculated from thermodynamic data in refs 38 and 39.

lower temperatures required the use of pressures well below 1 atm, typically in the range of 0.10−0.15 atm. Hydrogen was always present in substantial excess in the mixtures as a deterrent to the formation of carbonaceous residues on the platinum surface.

The dynamics of a surface reaction can often be treated satisfactorily in terms of a two-step sequence involving a single surface species. For the methylcyclohexane−toluene−hydrogen interconversion occurring on a platinum surface, we consider the following two-step sequence

$$M+S \underset{}{\overset{I}{\rightleftharpoons}} TS \underset{}{\overset{II}{\rightleftharpoons}} T+S \qquad (2)$$
$$+$$
$$3H_2$$
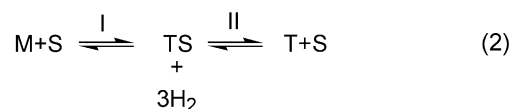
in which M and T represent, respectively, methylcyclohexane and toluene in the gas phase, S represents a surface site, and TS represents toluene chemisorbed on such a site. The sequence consists of two adsorption−desorption steps. In the forward part of the first step, methylcyclohexane interacts with a site S to yield chemisorbed toluene TS, with concomitant release of hydrogen into the gas phase. Although this step in all likelihood involves intermediate hydrocarbon species with different degrees of unsaturation, e.g., chemisorbed methylcyclohexene and methylcyclohexadiene, we assume that such species are present in concentrations much lower than that of chemisorbed toluene on the basis of what is known about the relative stabilities of the corresponding gas phase species (see Figure 1). In the forward part of the second step of the sequence, toluene simply desorbs into the gas phase and the site S is regenerated.

The results of the steady-state flow reactor studies conducted far from equilibrium, as reported in the 1960 paper, indicated that the back reactions in both steps of the sequence could be ignored. However, in a relaxation study of the dynamics of the system near equilibrium, as reported in the present paper, the back reactions are inherent in the nature of the investigation.

Frequency Response Analysis

A typical frequency response experiment with our reaction system begins with a gaseous mixture of methylcyclohexane, hydrogen, and toluene in a state of equilibrium over the catalyst at a particular temperature and pressure. The reaction chamber is designed so that its volume $\bar{V}$ can be continuously subjected to a small periodically varying perturbation $\hat{v}$, such that the instantaneous volume V at a time t is given by the expression

$$V = \bar{V}(1 + \hat{v}) = \bar{V}(1 + v e^{i\omega t}) \qquad (3)$$

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in which ω is the angular frequency of the perturbation, equal to $2\pi f$ where f is the frequency in Hz. The quantity v is the amplitude of $\hat{v}$, both of which are dimensionless. As a consequence of the volume perturbation, the pressure of the system undergoes a periodic variation, as does the gas-phase concentration C_j (in molecules mL^{-1}) of a component j (where j is M for methylcyclohexane, T for toluene, and H for hydrogen). The time dependence of C_j is given by the expression

$$C_j = \bar{C}_j(1 + \hat{c}_j) = \bar{C}_j(1 + c_j e^{i\omega t}) \qquad (4)$$

where $\bar{C}_j$ is the unperturbed initial equilibrium value of C_j corresponding to the equilibrium volume $\bar{V}$. The quantity $\hat{c}_j$ is the fractional change in $\bar{C}_j$ at time t occurring as a consequence of the volume perturbation $\hat{v}$, and c_j is the amplitude of $\hat{c}_j$. Both C_j and $\hat{c}_j$ oscillate with a frequency identical to that of the oscillation of V and $\hat{v}$.

Division of $\hat{c}_j$ by $\hat{v}$ yields a quantity H_j characteristic of the response of C_j to the perturbation of the system at a given frequency f

$$H_j = \frac{\hat{c}_j}{\hat{v}} \qquad (5)$$

If ω, i.e., $2\pi f$, is large compared to the relaxation frequency of a surface process involving component j, $\hat{c}_j$ and $\hat{v}$ will simply be equal in magnitude but opposite in sign, as is characteristic of the simple compression or expansion of the gas in the absence of any response of a surface process to the volume perturbation. The quantity H_j is then simply equal to -1. Stated in another way, $\hat{c}_j$ and $\hat{v}$ are then $180°$ out of phase with one another, or a minimum in one is precisely in phase with a maximum in the other. However, if ω is comparable to the relaxation frequency, the value of H_j will differ from -1 because of a response of the surface process to the perturbation, and $\hat{c}_j$ and $\hat{v}$ will be out of phase by an angle different from $180°$.

For the treatment of experimental data, it is useful to introduce a quantity H to characterize the combined response of the concentrations of all the gas-phase components to the volume perturbation $\hat{v}$. We define H by the relation

$$H = -\frac{\hat{c}}{\hat{v}} = -\sum_j \bar{x}_j H_j \qquad (6)$$

where the minus sign is introduced so that H will be a positive quantity. We note that $\hat{c}$ is the fractional change in $\bar{C}$, the unperturbed initial equilibrium value of the total concentration C of all of the molecules in the gas phase. The quantity $\bar{x}_j$ is the mole fraction of component j in the initial equilibrium mixture. As $\hat{v}$ is varied with time over a range of frequencies in an experiment, measurements of the pressure of the gas phase, and hence of the concentration C via the perfect gas law, provide data on the frequency dependencies of $\hat{c}$ and H and of a corresponding phase angle θ. As a consequence of the introduction of the minus sign in eq 6, the phase angle is $0°$ rather than $180°$ when there is either no response of the surface processes to the volume perturbation of the system at one extreme or complete response (continuous reequilibration of all gas phase and surface entities) at the other extreme.

In the literature of frequency response, the term transfer function is commonly used in referring to H.[20,23] As applied in the present investigation, it varies from a value at very low frequencies that corresponds simply to the perturbation of the thermodynamic equilibrium properties of the system to a value of 1 at very high frequencies where none of the surface processes

are fast enough to exhibit a response. At both extremes of frequencies, the phase angle goes to zero.

Since the transfer function H is in general a complex number with real and imaginary parts, it has the form

$$H = |H|e^{i\theta} = |H|\cos\theta + i|H|\sin\theta = H_{\text{Re}} + iH_{\text{Im}} \qquad (7)$$

where $|H|$ is the magnitude of H, θ is the phase angle, H_{Re} is the real part of H, and H_{Im} is the imaginary part of H. The magnitude $|H|$ and phase angle θ are given by the expressions

$$|H| = \sqrt{H_{\text{Re}}^2 + H_{\text{Im}}^2} \qquad (8)$$

$$\theta = \arctan[H_{\text{Im}}/H_{\text{Re}}] \qquad (9)$$

Both $|H|$ and θ are frequency dependent, and the experimental investigation consists of the determination of these quantities as a function of frequency.

Experimental Section

The interconversion of methylcyclohexane, toluene, and hydrogen near equilibrium was studied in a closed reaction vessel having a volume of 173.7 cm^3. The vessel was loaded with 5 g of 0.3 wt % Pt on alumina catalyst (80–100 mesh). The surface area of the alumina support was 205 m^2/g and the pore volume was 0.55 cm^3/g. The dispersion of the platinum on the support was very close to 1. Prior to the frequency response experiments, the reaction vessel containing the catalyst was first heated to 623 K under dynamic vacuum and kept under those conditions overnight. After this drying procedure, and with the system at a temperature of 623 K, the catalyst was reduced under a static hydrogen pressure of 100 Torr for a period of 3 h. The system was then evacuated, and the 3-h hydrogen reduction procedure was repeated once more. The system was then dynamically evacuated and cooled to 423 K where it was kept overnight prior to the admission of the reactants.

While the system was at 423 K, hydrogen was admitted into the vessel containing the catalyst until the pressure reached 60 Torr (pressure transducer MKS, model 128A, 0–1000 Torr). This was followed by the addition of methylcyclohexane until the total pressure within the vessel reached 80 Torr. After the pressure of 80 Torr was reached and the system was closed off, the total pressure did not show a discernible change over time. This observation was consistent with thermodynamic equilibrium calculations indicating a conversion of methylcyclohexane of less than 1% at 423 K, 20 Torr methylcyclohexane, and 60 Torr hydrogen. The temperature of the system was then increased to 433 K. As the temperature was increasing from 423 to 433 K, the pressure was also increasing. The pressure increase exceeded that expected from ideal gas law behavior for the effect of temperature, consistent with an evolution of hydrogen due to reaction. The pressure later stabilized to a steady value that signaled the attainment of thermodynamic equilibrium. This took place in a period of less than about 1 h, but the system was left undisturbed for an additional hour. No further changes in pressure were observed during this additional waiting period. This was considered to be the initial thermodynamic equilibrium state for the reaction mixture at 433 K, which would subsequently be subjected to the frequency response experiments.

The volume of the system was then sinusoidally modulated with a moving diaphragm (metal bellows, Senior Flexonics, Inc.). The diaphragm was modulated with a linear actuator (BEI, model LA30-27-004Z) that was controlled by a computer. The

amplitude of the volume perturbation was about 0.5% and the range of frequencies from 0.002 to 3 Hz. At each frequency, with the use of a differential pressure transducer (Tavis, model P4, 0−5 Torr), the pressure response of the system to the applied perturbation (165 points/cycle) was monitored. After the data from the first three cycles were discarded, the data from the next 12 consecutive cycles were used to obtain the magnitude and phase angle of the pressure response to the applied perturbation. However, to eliminate any frequency response effects associated with the physical system, which were unrelated to the dynamics of the chemical transformation, blank runs containing alumina particles of the same mesh size as the catalyst and at the same conditions of composition and temperature of the equilibrium reaction mixture were also run. Thus, the magnitude of the transfer function and the phase angle were obtained as the ratio of the pressure amplitudes and the difference in phase angles for the catalyst and the blank, respectively. These are the data displayed in Figures 2 and 3.

At a given temperature, the frequency response experiment lasted for several hours. Upon completion of the frequency response experiment at 433 K, the temperature was increased in 10 K increments up to a maximum temperature of 473 K. The same thermodynamic equilibration and dynamic procedures as described for a temperature of 433 K were used at all temperatures investigated.

Results

Figures 2 and 3 show data on the magnitude of the transfer function H and phase angle θ as a function of the angular frequency ω over a range of temperatures from 433 to 473 K. Data on the equilibrium composition of the unperturbed gas phase in contact with the catalyst at the various temperatures are given in Table 1.

If we consider the data in Figure 2, we note that the attenuation of the magnitude of H to a value significantly lower than 1 over the whole range of frequencies investigated is indicative of an appreciable response of processes involving the catalyst to the perturbation of the system. In large part, we attribute the observed attenuation to the dynamics of interconversion of methylcyclohexane, toluene, and hydrogen on the surface of the platinum in the catalyst, especially the large attenuation observed at the lowest frequencies. Support for this will appear in our analysis of the data with the aid of a phenomenological theory to be developed in subsequent sections of the paper. In the plots of the magnitude of H vs the angular frequency ω in Figure 2, there appear to be two perceptible points of inflection in the data, one at an angular frequency between 0.01 and 0.10 rad s^{-1} and the other at an angular frequency about 2 orders of magnitude higher.

The magnitude of the transfer function does not quite reach a value of 1 at the highest frequencies investigated, presumably because there are processes of relatively minor significance associated with the catalyst that are rapid enough to exhibit a response to the volume perturbation of the system at frequencies beyond those employed in the present investigation. Very likely, processes involving the alumina support contribute to this.

Turning to the data in Figure 3, we observe that the plots of the phase angle θ vs the angular frequency ω exhibit two maxima at values of ω corresponding roughly to the values of ω at which the points of inflection in the data in Figure 2 are observed. The maximum in the phase angle plot at the low angular frequency is much more pronounced than the maximum at the high frequency.

The angular frequencies corresponding to the points of inflection in the magnitude of the transfer function in Figure 2
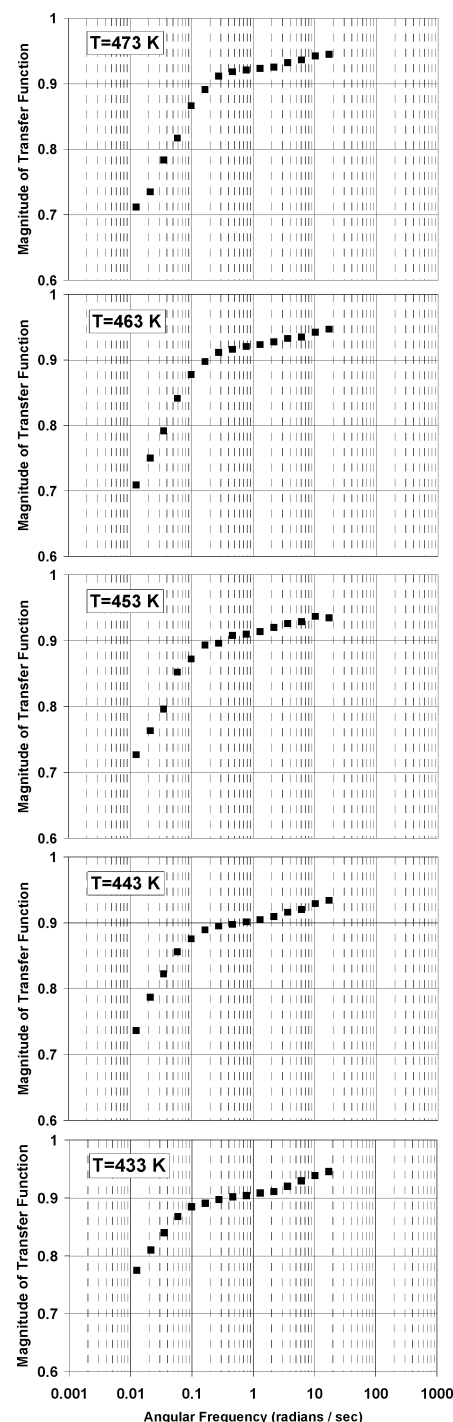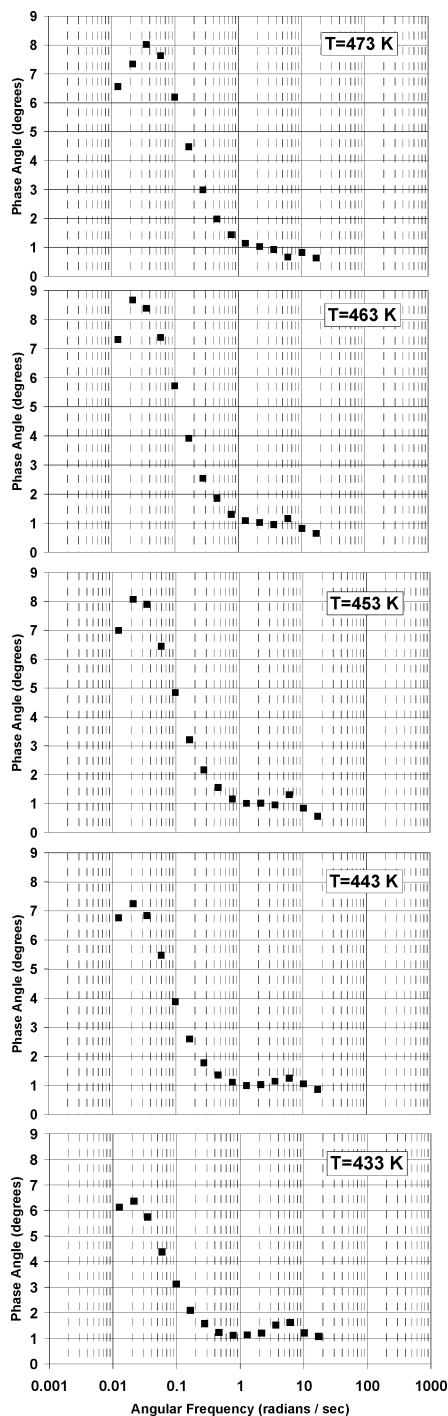

Figure 2. Experimental data on the frequency dependence of the magnitude of the transfer function over a range of temperatures. The experimental conditions at the various temperatures are given in Table 1.

and to the maxima in the phase angle in Figure 3 are approximate indicators of relaxation frequencies associated with processes involving the catalyst. It appears reasonable to infer that they are related in some manner with relaxation frequencies characteristic of the two steps in the sequence depicted earlier for the catalyzed interconversion of methylcyclohexane, toluene, and hydrogen, as will be discussed subsequently.

We now turn our attention to the development of a phenomenological theory of the transfer function that will account for the frequency response data shown in Figures 2 and 3. The theory includes a consideration of the perturbation of both the

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Figure 3. Experimental data on the frequency dependence of the phase angle over a range of temperatures. The experimental conditions at the various temperatures are given in Table 1.

TABLE 1: Equilibrium Compositions of Unperturbed Gas Phase at Various Temperatures

temperature (K)	pressure (Torr)	mole fractions[a]		
		$\bar{x}_T$	$\bar{x}_M$	$\bar{x}_H$
433	86.8	0.03	0.20	0.77
443	91.3	0.04	0.18	0.78
453	96.3	0.06	0.15	0.79
463	102.5	0.07	0.12	0.81
473	112.5	0.10	0.08	0.82

[a] Toluene $\bar{x}_T$, methylcyclohexane $\bar{x}_M$, hydrogen $\bar{x}_H$.

equilibria and the dynamics associated with the interconversion of the components of the system.

Phenomenological Theory

The number of molecules of species j present in the gas phase at a time t is VC_j. Its time dependence during the volume perturbation of the system is given by the equation

$$\frac{d}{dt}(VC_j) = i\omega \bar{V} \bar{C}_j(\hat{c}_j + \hat{v}) \tag{10}$$

A term involving the product of $\hat{c}_j$ and $\hat{v}$ has been deleted, since it is negligible for very small perturbations. Also, because we make the simplifying assumption that toluene is the only significant surface species and that changes in the amount of hydrogen in the gas phase are simply consistent with the stoichiometry of eq 1, we have the relation

$$\frac{d}{dt}(VC_H) = -3\frac{d}{dt}(VC_M) \tag{11}$$

where the subscripts H and M, respectively, refer to the gas-phase hydrogen and methylcyclohexane molecules. If we define α as the ratio $\bar{C}_M/\bar{C}_H$, we obtain from eqs 10 and 11 the following relation between the fractional changes $\hat{c}_H$ and $\hat{c}_M$ of the initial equilibrium concentrations $\bar{C}_H$ and $\bar{C}_M$ of hydrogen and methylcyclohexane due to the volume perturbation of the system

$$\hat{c}_H = -3\alpha \hat{c}_M - (3\alpha + 1)\bar{v} \tag{12}$$

It therefore follows from eq 5 that

$$H_H = -3\alpha H_M - (3\alpha + 1) \tag{13}$$

On substituting eq 13 into eq 6 and representing the ratio $\bar{x}_T/\bar{x}_M$ by γ, we obtain for the transfer function H the expression

$$H = 1 + \frac{\bar{x}_T}{\gamma}[2(H_M + 1) - \gamma(H_T + 1)] \tag{14}$$

Equations for H_M and H_T in terms of relaxation frequencies for the individual steps of the two-step sequence describing the system, to be developed in a subsequent section of the paper, allow us to extract values of these dynamic parameters from experimental data on the dependence of H and the phase angle θ on frequency.

Thus far, we have considered relationships involving only the gas-phase species in the system. We now turn our attention to surface entities, which include unoccupied platinum surface sites S and chemisorbed toluene molecules TS occupying the remainder of the sites. The number of platinum surface atoms constituting a suitable site for a toluene molecule, which could conceivably be much higher than the number of platinum atoms forming bonds with the molecule, is unknown. Thus, we do not know the total number of sites present in the platinum surface and, hence, do not know the total number of toluene molecules chemisorbed at saturation coverage. Nevertheless, if we let L represent the total number of surface platinum sites per surface platinum atom and let C_{TS} and C_S be the concentrations of chemisorbed toluene molecules and unoccupied sites, respectively, again expressed as numbers of these entities per surface platinum atom, we have the conservation relation

$$L = C_{TS} + C_S = \bar{C}_{TS} + \bar{C}_S \tag{15}$$

By analogy with eq 4 for the gas-phase species, we note that

$$C_{TS} = \bar{C}_{TS}(1 + \hat{c}_{TS}) = \bar{C}_{TS}(1 + c_{TS}e^{i\omega t}) \tag{16}$$

$$C_S = \bar{C}_S(1 + \hat{c}_S) = \bar{C}_S(1 + c_S e^{i\omega t}) \tag{17}$$

where $\bar{C}_{TS}$ and $\bar{C}_S$ are the unperturbed initial equilibrium values of C_{TS} and C_S, respectively, corresponding to the unperturbed equilibrium volume $\bar{V}$. The quantities $\hat{c}_{TS}$ and $\hat{c}_S$ are the fractional changes in $\bar{C}_{TS}$ and $\bar{C}_S$ at time t due to the volume perturbation $\hat{v}$, with corresponding amplitudes c_{TS} and c_S. From eqs 15−17, we obtain the relation

$$\hat{c}_S = -(\bar{C}_{TS}/\bar{C}_S)\hat{c}_{TS} \tag{18}$$

We assume that the platinum surface sites are all equivalent in our analysis, thereby ignoring any surface nonuniformity, and we observe that the ratio $\bar{C}_{TS}/\bar{C}_S$ is equal to $K_{II}\bar{C}_T$, where K_{II} is the adsorption equilibrium constant of step II of the postulated two-step sequence and $\bar{C}_T$ is the initial equilibrium concentration of gas-phase toluene molecules. From eq 18, we then have the relation

$$\hat{c}_{TS} - \hat{c}_S = [1 + (\bar{C}_{TS}/\bar{C}_S)]\,\hat{c}_{TS} = [1 + K_{II}\bar{C}_T]\,\hat{c}_{TS} \tag{19}$$

which will be of use shortly.

If N is the number of surface platinum atoms in the catalyst, the total numbers of chemisorbed toluene molecules and of unoccupied surface platinum sites are NC_{TS} and NC_S, respectively. Their time dependencies are given by

$$\frac{d}{dt}(NC_{TS}) = i\omega N \bar{C}_{TS}\hat{c}_{TS} = i\omega \beta \bar{V} \bar{C}_{TS}\hat{c}_{TS} \tag{20}$$

$$\frac{d}{dt}(NC_S) = i\omega N \bar{C}_S\hat{c}_S = i\omega \beta \bar{V} \bar{C}_S\hat{c}_S \tag{21}$$

where the quantity β is the ratio $N/\bar{V}$, i.e., the number of surface platinum atoms per mL of unperturbed reactor volume. Since we have assumed that hydrocarbon species other than methylcyclohexane and toluene are present in such small amounts that they can be ignored, we have another conservation equation relating the gas-phase concentrations C_M and C_T of methylcyclohexane and toluene to the surface concentration C_{TS} of toluene

$$\frac{d}{dt}(VC_M + VC_T + NC_{TS}) = 0 \tag{22}$$

which in combination with eq 10 for methylcyclohexane and toluene in the gas phase and eq 16 for chemisorbed toluene, along with the relation $\bar{C}_{TS}/\bar{C}_T = K_{II}\bar{C}_S$, gives the relation

$$\hat{c}_{TS} = -\frac{1}{\gamma \beta K_{II}\bar{C}_S}[(\hat{c}_M + \hat{v}) + \gamma(\hat{c}_T + \hat{v})] \tag{23}$$

Combining eqs 19 and 23, we obtain

$$\hat{c}_{TS} - \hat{c}_S = -\frac{1 + K_{II}\bar{C}_T}{\gamma \beta K_{II}\bar{C}_S}[(\hat{c}_M + \hat{v}) + \gamma(\hat{c}_T + \hat{v})] \tag{24}$$

Introducing the quantity K_S, defined as follows

$$K_S = \frac{\beta K_{II}\bar{C}_S}{1 + K_{II}\bar{C}_T} \tag{25}$$

eq 24 becomes

$$\hat{c}_{TS} - \hat{c}_S = -\frac{1}{\gamma K_S}[(\hat{c}_M + \hat{v}) + \gamma(\hat{c}_T + \hat{v})] \tag{26}$$

A little reflection reveals that K_S is proportional to the slope of the toluene adsorption isotherm for step II, i.e.

$$K_S = \beta\frac{d\bar{C}_{TS}}{d\bar{C}_T} \tag{27}$$

The quantity K_S is a parameter of considerable use in the analysis of frequency response data for adsorption systems.[17,23] On application of eq 5 to the surface entities TS and S, as well as the species M and T in the gas phase, we obtain from eq 26 the relation

$$H_{TS} - H_S = -\frac{1}{\gamma K_S}[(H_M + 1) + \gamma(H_T + 1)] \tag{28}$$

Perturbation of the Various Equilibria of the System. Consider step I of the two-step sequence that we have postulated for the interconversion of methylcyclohexane, toluene, and hydrogen via the platinum surface. If methylcyclohexane and hydrogen in the gas phase were to remain equilibrated with chemisorbed toluene molecules TS and unoccupied platinum surface sites S when the system is perturbed from its initial equilibrium state, the concentrations of the various entities involved in step I would obey the equilibrium equation

$$K_I = \frac{C_{TS}C_H{}^3}{C_S C_M} \tag{29}$$

where K_I is the adsorption equilibrium constant for step I. If we introduce into this equilibrium relation the expressions for the various concentrations given by eqs 4, 16, and 17, we obtain the relation

$$\hat{c}_{TS} - \hat{c}_S = \hat{c}_M - 3\hat{c}_H \tag{30}$$

In obtaining this equation, we deleted all terms involving products of $\hat{c}_j$ quantities, where the subscript j now refers to either gas phase (M or H) or surface (TS or S) entities, since, as pointed out earlier, such terms are insignificant for very small perturbations. Noting eq 12 relating $\hat{c}_H$ to $\hat{c}_M$, we see that

$$\hat{c}_{TS} - \hat{c}_S = \hat{c}_M(1 + 9\alpha) + 3(3\alpha + 1)\hat{v} \tag{31}$$

Applying eq 5 to the gas-phase species M and to the surface entities TS and S as well, we obtain from eq 31 the relation

$$H_{TS} - H_S = H_M(1 + 9\alpha) + 3(3\alpha + 1) \tag{32}$$

Since $(H_{TS} - H_S)$ must also satisfy eq 28, with H_M in the equation having its equilibrium value, we can eliminate $(H_{TS} - H_S)$ between eqs 28 and 32 to obtain a relation between the equilibrium value of H_M and the actual value of H_T for a given perturbation frequency. To emphasize the point that H_M is an equilibrium value, we add the superscript e to it, and we have the relation

$$H_M^e = \frac{-\gamma H_T - 3\gamma(3\alpha + 1)K_S - (1 + \gamma)}{1 + \gamma K_S(1 + 9\alpha)} \tag{33}$$

We note that H_M^e will, in general, be frequency dependent, except when the frequencies are low enough for both steps I and II to be equilibrated.

On the application of similar considerations to step II, we have the equation for the adsorption equilibrium constant K_{II}

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$$K_{\text{II}} = \frac{C_{\text{TS}}}{C_{\text{S}} C_{\text{T}}} \tag{34}$$

By combining eqs 4, 16, 17, and 34, we obtain the relation

$$\hat{c}_{\text{TS}} - \hat{c}_{\text{S}} = \hat{c}_{\text{T}} \tag{35}$$

and, on application of eq 5 again, the corresponding relation

$$H_{\text{TS}} - H_{\text{S}} = H_{\text{T}} \tag{36}$$

Since $(H_{\text{TS}} - H_{\text{S}})$ must again satisfy (28), we note that a relation, analogous to eq 33 obtained in our consideration of step I, now emerges in our discussion of step II. The relation in this case is one between the equilibrium value of H_{T} and the actual value of H_{M} during the perturbation of the system. If we now introduce H_{T}^{e} in place of H_{T} to call attention to its being an equilibrium value, we can write the relation

$$H_{\text{T}}^{\text{e}} = \frac{-H_{\text{M}} - (1 + \gamma)}{\gamma(1 + K_{\text{S}})} \tag{37}$$

where H_{T}^{e} will depend, in general, on the perturbation frequency, except at frequencies low enough for the overall system (both steps I and II) to be equilibrated.

In the limit of zero perturbation frequency, the quantities H_{T} in eq 33 and H_{M} in eq 37 take on their equilibrium values H_{T}^{e} and H_{M}^{e}. On solving the two resulting equations relating H_{M}^{e} and H_{T}^{e}, we obtain

$$(H_{\text{M}}^{\text{e}})_{\omega=0} = H_{\text{M}}^{0} = \frac{-(1 + 4\gamma + 9\gamma\alpha) - (3\gamma + 9\gamma\alpha)K_{\text{S}}}{(1 + \gamma + 9\gamma\alpha) + (\gamma + 9\gamma\alpha)K_{\text{S}}} \tag{38}$$

$$(H_{\text{T}}^{\text{e}})_{\omega=0} = H_{\text{T}}^{0} = \frac{2 - (\gamma + 9\gamma\alpha)}{(1 + \gamma + 9\gamma\alpha) + (\gamma + 9\gamma\alpha)K_{\text{S}}} \tag{39}$$

where the symbols H_{M}^{0} and H_{T}^{0} signify values of H_{M}^{e} and H_{T}^{e} at zero frequency. From eq 14, we then obtain for the transfer function at zero frequency (designated H^0) the expression

$$H^0 = 1 - \frac{\bar{x}_T[9 + (4 + \gamma + 9\gamma\alpha)K_{\text{S}}]}{(1 + \gamma + 9\gamma\alpha) + (\gamma + 9\gamma\alpha)K_{\text{S}}} \tag{40}$$

This equation proves to be a very useful starting place in the analysis of experimental data.

Relaxation Frequency Analysis. If k_{I} and k_{II} are the relaxation frequencies (in sec^{-1}) of steps I and II of the two-step sequence, the net rates r_{I} and r_{II} of these steps are

$$r_{\text{I}} = -\frac{\text{d}(VC_{\text{M}})}{\text{d}t} = k_{\text{I}}[C_{\text{M}} - C_{\text{M}}^{\text{e}}] V \tag{41}$$

$$r_{\text{II}} = -\frac{\text{d}(VC_{\text{T}})}{\text{d}t} = k_{\text{II}}[C_{\text{T}} - C_{\text{T}}^{\text{e}}] V \tag{42}$$

where C_{M}^{e} and C_{T}^{e}, respectively, are the equilibrium values of C_{M} and C_{T} at time t during the perturbation of the system. Like C_{M} and C_{T}, they are related to the initial equilibrium concentrations $\bar{C}_{\text{M}}$ and $\bar{C}_{\text{T}}$ via eq 4. On application of eqs 3, 4, and 10 to eqs 41 and 42, we obtain the equations

$$-i\omega(\hat{c}_{\text{M}} + \hat{v}) = k_{\text{I}}(\hat{c}_{\text{M}} - \hat{c}_{\text{M}}^{\text{e}}) \tag{43}$$

$$-i\omega(\hat{c}_{\text{T}} + \hat{v}) = k_{\text{II}}(\hat{c}_{\text{T}} - \hat{c}_{\text{T}}^{\text{e}}) \tag{44}$$

where $\hat{c}_{\text{M}}^{\text{e}}$ and $\hat{c}_{\text{T}}^{\text{e}}$ are the fractional changes in $\bar{C}_{\text{M}}$ and $\bar{C}_{\text{T}}$ relating these concentrations to C_{M}^{e} and C_{T}^{e}. After applying eq 5 to eqs 43 and 44, we have the following equations:

$$-i\omega(H_{\text{M}} + 1) = k_{\text{I}}(H_{\text{M}} - H_{\text{M}}^{\text{e}}) \tag{45}$$

$$-i\omega(H_{\text{T}} + 1) = k_{\text{II}}(H_{\text{T}} - H_{\text{T}}^{\text{e}}) \tag{46}$$

With eqs 33 and 37 for H_{M}^{e} and H_{T}^{e}, we can now obtain a set of two simultaneous equations relating H_{M} and H_{T}. The equations have the forms

$$H_{\text{M}} = -AH_{\text{T}} - B \tag{47}$$

$$H_{\text{T}} = -EH_{\text{M}} - G \tag{48}$$

where A, B, E, and G are defined by the expressions

$$A = \frac{k_{\text{I}}}{k_{\text{I}} + i\omega} \left\{ \frac{\gamma}{1 + (\gamma + 9\gamma\alpha)K_{\text{S}}} \right\}$$

$$B = \frac{1}{k_{\text{I}} + i\omega} \times$$
$$\left\{ \frac{i\omega[1 + (\gamma + 9\gamma\alpha)K_{\text{S}}] + k_{\text{I}}[1 + \gamma + (3\gamma + 9\gamma\alpha)K_{\text{S}}]}{1 + (\gamma + 9\gamma\alpha)K_{\text{S}}} \right\}$$

$$E = \frac{k_{\text{II}}}{k_{\text{II}} + i\omega} \left\{ \frac{1}{\gamma(1 + K_{\text{S}})} \right\}$$

$$G = \frac{1}{k_{\text{II}} + i\omega} \left\{ \frac{i\omega\gamma(1 + K_{\text{S}}) + k_{\text{II}}(1 + \gamma)}{\gamma(1 + K_{\text{S}})} \right\}$$

The solution of eqs 47 and 48 yields H_{M} and H_{T}

$$H_{\text{M}} = \frac{AG - B}{1 - AE} \tag{49}$$

$$H_{\text{T}} = \frac{BE - G}{1 - AE} \tag{50}$$

On substituting these expressions for both H_{M} and H_{T} in eq 14, we obtain the equation for the transfer function H

$$H = 1 + \frac{\bar{x}_T}{\gamma(1 - AE)}[2(1 - B + AG - AE) - \gamma(1 - G + BE - AE)] \tag{51}$$

The equations for H_{M}, H_{T}, and H are shown in terms of the quantities A, B, E, and G for simplicity of presentation. Without the use of the latter quantities, the expressions are extremely cumbersome. In any case, the cumbersome expressions can always be obtained by substitution of the defining relations for A, B, E, and G in the various equations for H_{M}, H_{T}, and H. The equations as presented here are convenient and entirely satisfactory for the fitting of experimental data with the aid of a computer.

The quantities A, B, E, G, and H are all complex quantities, with real and imaginary parts. Focusing our attention on H, we therefore note that the expression describing the dependence of H on ω, however cumbersome it may be, still has the form of eq 7 with the magnitude of H and the phase angle θ being related to the real and imaginary parts of H by eqs 8 and 9.

The theory leading to eq 51 for the transfer function was developed independent of any consideration of the relative magnitudes of the relaxation frequencies k_I and k_{II} and is therefore applicable whatever their values happen to be. However, it is of interest to consider the possibility that one relaxation frequency may be large compared to the other, since it is not at all uncommon for this situation to be encountered for processes that can be dissected into two separate steps. Suppose, for the sake of argument, that k_{II} is small compared to k_I. Then, for values of the angular frequency ω that are small compared to k_I, step I can be considered to be equilibrated. Depending on the actual value of the ratio of k_I to k_{II}, the assumption of an equilibrated first step may well apply even at values of ω that are large compared to k_{II}, so long as ω is simultaneously small compared to k_I. To proceed with an analysis in which step I is equilibrated, one can simply take the limits of the quantities A and B as the ratio $\omega/k_I \rightarrow 0$, in which case k_I disappears from the quantities H_M, H_T, and H altogether.

However, we find another approach to be more instructive, and proceed in the following way. In eq 37 for H_T^e, insert for H_M its equilibrium value H_M^e given by eq 33. Equation 46 then becomes

$$-i\omega(H_T + 1) = k_{II}[K_S/(1 + K_S)]\,\chi(H_T - H_T^0) = \\ k_R(H_T - H_T^0) \quad (52)$$

where H_T^0 is given by eq 39 and χ is given by the expression

$$\chi = \frac{(1 + \gamma + 9\gamma\alpha) + (\gamma + 9\gamma\alpha)K_S}{1 + (\gamma + 9\gamma\alpha)K_S} \quad (53)$$

Equation 52 defines a new relaxation frequency k_R

$$k_R = k_{II}[K_S/(1 + K_S)]\chi \quad (54)$$

We will refer to k_R as the relaxation frequency for reaction, a quantity that will be useful in our analysis.

On taking H_M to be equal to H_M^e in eq 14 for the transfer function H, and applying eq 33 for H_M^e, the frequency dependent part of the resulting expression for H resides solely in the function H_T given by eq 52 when step I is equilibrated. The final expression for the transfer function, designated H'' for values of ω small compared to k_I for this special situation when $k_{II} \ll k_I$, is conveniently written as follows

$$H'' = \{W - U\,[k_R^2/(k_R^2 + \omega^2)]\} + \\ i\{U\,[-\omega\,k_R/(k_R^2 + \omega^2)]\} \quad (55)$$

The quantities W and U are given by the expressions

$$W = \frac{[1 + K_S(\gamma + 9\gamma\alpha) - 4\bar{x}_T K_S]}{[1 + K_S(\gamma + 9\gamma\alpha)]}$$

$$U = \frac{\bar{x}_T[3 + K_S(\gamma + 9\gamma\alpha)]^2}{[1 + K_S(\gamma + 9\gamma\alpha)]\,[1 + (1 + K_S)(\gamma + 9\gamma\alpha)]}$$

The magnitude of H'' and the value of the corresponding phase angle θ'' are given by the expressions

$$|H''| = W\left\{\frac{[(W - U)/W]^2 k_R^2 + \omega^2}{k_R^2 + \omega^2}\right\}^{1/2} \quad (56)$$

$$\theta'' = \arctan \frac{U[-\omega\,k_R/(k_R^2 + \omega^2)]}{W - U[k_R^2/(k_R^2 + \omega^2)]} \quad (57)$$

If the derivative of θ'' with respect to ω is equated to zero, we obtain for the value of $\omega = \omega_m''$ corresponding to the maximum value of θ'' the following equation:

$$\omega_m'' = \left[1 - \frac{U}{W}\right]^{1/2} k_R \quad (58)$$

Thus, eq 58 gives us a relation between ω_m'' and k_R that is very useful in providing a measure of k_R directly by simple inspection of data such as those shown in Figure 3. In eq 58, the proportionality factor relating ω_m'' to k_R was never very different from unity in the present investigation.

In continuing our discussion of the possibility that k_{II} is small compared to k_I, it is also of interest to consider the transfer function at angular frequencies comparable to the magnitude of k_I, i.e., at values of ω large compared to k_{II}. At such values of ω, the quantity H_T is essentially equal to -1. On substituting -1 for H_T in eq 33 for H_M^e, and then solving eq 45 for the quantity $(H_M + 1)$, we then obtain an equation for the transfer function H, which we designate as H' to indicate that it applies only at values of ω that are large compared to k_{II}

$$H' = \frac{k_I^2(1 - 4\bar{x}_T K_S) + \omega^2}{k_I^2 + \omega^2} + i\,\frac{4\bar{x}_T K_S k_I \omega}{k_I^2 + \omega^2} \quad (59)$$

In the same manner that we obtained eq 58, we can now obtain an expression relating k_I to ω_m', the value of ω at which a high-frequency phase angle maximum is observed. The expression is

$$\omega_m' = k_I(1 - 4\bar{x}_T K_S)^{1/2} \quad (60)$$

Like eq 58, this expression is very useful in the analysis of experimental data.

Fitting Theory to Experimental Results. Figures 4 and 5 show the quality of fit of the theory to experimental results for the frequency dependence of the magnitude of the transfer function and the phase angle. In fitting the data, a small background contribution to the experimental transfer function responsible for the magnitude approaching a limiting value slightly lower than 1 at the highest frequencies (see Figure 2) was first removed from the data. As pointed out earlier, this background contribution is attributable to minor processes exhibiting a response at frequencies beyond the range accessible in the investigation. The background was removed by applying a constant offset to the real part of the transfer function for each of the original data points shown in Figure 2. As seen in Figure 4, the adjusted data points for the magnitude of the experimental transfer function then approach a limiting value of 1 at the highest frequencies. The theoretical curves fitted to the adjusted data points in Figures 4 and 5 were obtained using eq 51 in concert with eqs 7−9. The fitting was accomplished by application of a conventional least squares procedure.

The quality of the fit of the theory to the experimental results is generally very good. The main features of the data, including the two ranges of frequency in which points of inflection are observed in the magnitude of the transfer function and in which maxima are observed in the phase angle, are captured very well throughout the entire range of temperatures investigated. Moreover, the detailed fit of the theory to the data over the range of frequencies in the case of the magnitude of the transfer

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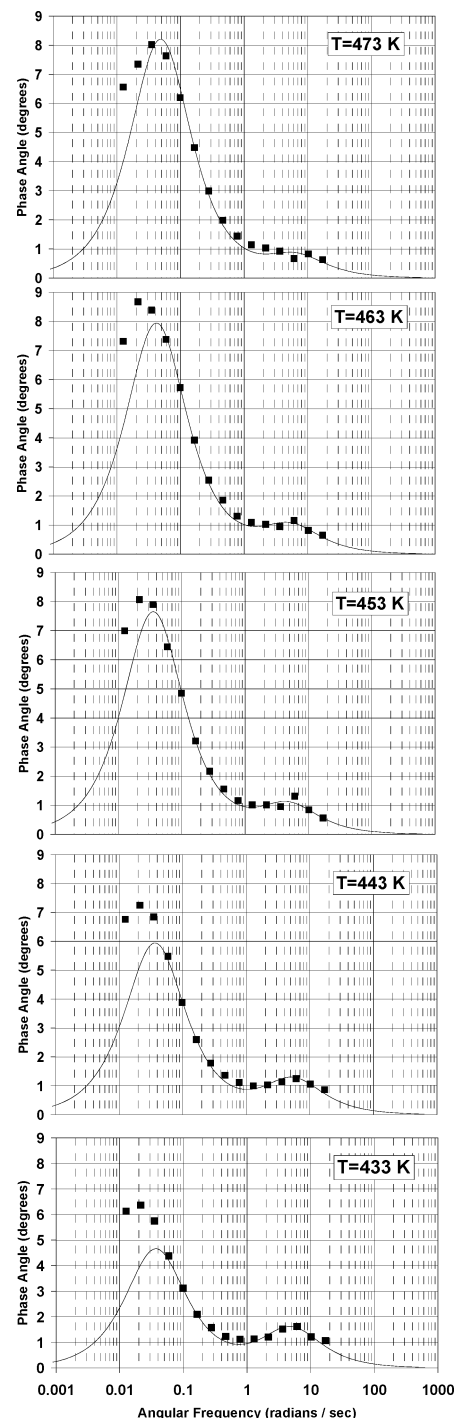*J. Phys. Chem. B, Vol. 109, No. 6, 2005* **2429**
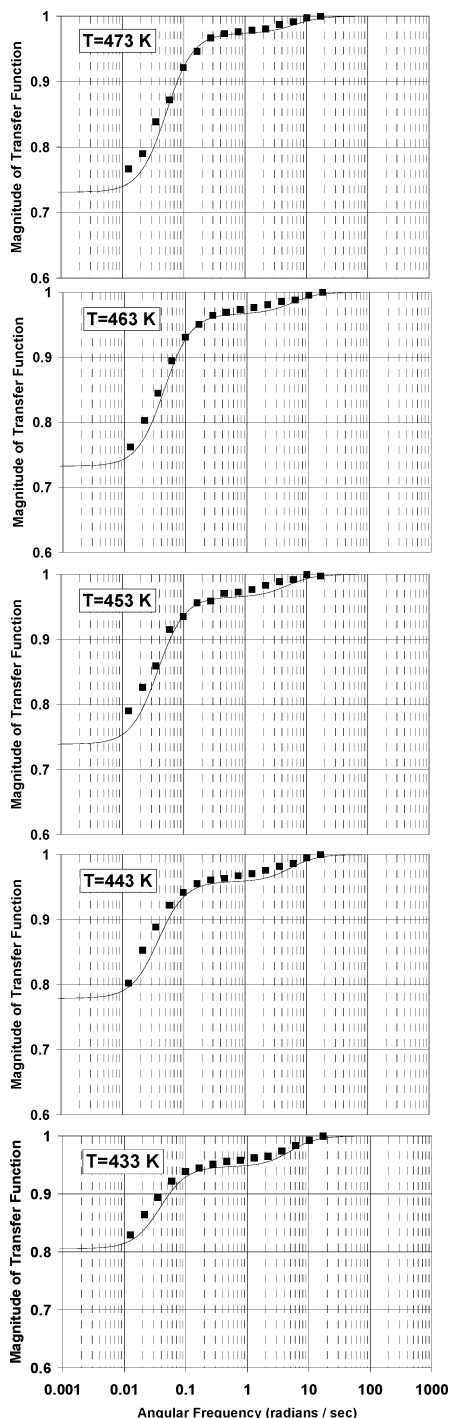
Figure 4. Results of fitting theory to experimental data for the magnitude of the transfer function, after adjustment of the experimental transfer function for a small background contribution, as discussed in the text.

Figure 5. Results of fitting theory to data for the phase angle.

function leaves little to be desired at any of the temperatures investigated. The detailed fit in the case of the phase angle is not quite as good, particularly in regard to the maximum value of the phase angle in the low-frequency region at the lowest temperature in the investigation. The limitations of the experimental procedure used in obtaining the data seemed to become more pronounced as the temperature was decreased. Moreover, the reliability of the information on the equilibrium composition of the unperturbed vapor phase at the beginning of a frequency response run was poorer at the lowest temperatures.

A summary of the "best fit" parameters obtained in the fitting of the theory to the data, including values of K_S, k_I, and k_{II}, is

TABLE 2: Summary of Parameters Determining the Interconversion of Methylcyclohexane, Toluene, and Hydrogen on Pt near Equilibrium[a]

temperature (K)	$\bar{x}_T$	γ	α	K_S	k_I	k_{II}	k_R	H^0
433	0.03	0.15	0.26	0.67	5.0	0.08	0.04	0.80
443	0.04	0.22	0.23	0.33	5.5	0.11	0.04	0.79
453	0.06	0.40	0.19	0.20	4.8	0.14	0.04	0.74
463	0.07	0.58	0.15	0.15	5.3	0.17	0.05	0.73
473	0.10	1.25	0.10	0.09	6.2	0.25	0.06	0.73

[a] Parameters defined in the text; the relaxation frequencies k_I, k_{II}, and k_R have units of s^{-1}, whereas the other parameters are all dimensionless.

given in Table 2. Also given in the table are values of the parameters γ and α defined earlier, and of the transfer function

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at zero frequency, i.e., H^0. The latter quantity is a function only of equilibrium properties of the unperturbed vapor phase at the beginning of a run, and is directly obtainable from the theory via eq 40. Although H^0 depends on K_S, the dependence is very weak for the range of K_S values characteristic of the system, and for all practical purposes, H^0 is determined solely by the parameters γ and α. Therefore, very good estimates of H^0 can be obtained without any information on the values of K_S obtained by the fitting of the frequency response data. The fact that such estimates yield an excellent prediction of the transfer function at low frequencies provides support for the conclusion that the pronounced attenuation of the magnitude of the transfer function over the range of frequencies investigated is due to the interconversion of methylcyclohexane, toluene, and hydrogen over the catalyst, rather than to some other process. We call attention to the fact that eq 40 for H^0 is derived strictly from a consideration of the equilibria of the system.

As can be seen from the values of the parameters given in Table 2, the values of k_{II} are much smaller than those of k_I. Therefore, values of k_R are included in Table 2. This indicates that step II of the proposed two-step process for the interconversion of the reaction species is a much slower process than the process designated as step I. It is therefore reasonable to assume that step I is equilibrated for all values of the angular frequency ω smaller in magnitude than k_{II}, and for values of ω substantially larger than k_{II} as well, so long as the latter values of ω remain sufficiently small compared to k_I. Equations 52 and 58 are then applicable, and, because they simplify the analysis, are very useful in the analysis of the data over a certain range of frequencies. For values of ω comparable in magnitude to k_I, or for all larger values, eqs 59 and 60 become applicable and find use in the analysis of data at the higher frequencies.

Concluding Remarks

In heterogeneous catalysis it is frequently observed that the kinetics of a reaction can be treated satisfactorily by treating the reaction as if it occurred in two steps via a single surface intermediate, any other intermediates on the active sites being present at such low concentrations that they may be ignored. Boudart has referred to such an intermediate as the most abundant reaction intermediate, the *mari*.[40] It is important to realize that this intermediate may not be the most abundant surface species, since there may well be species that do not participate in the reaction.

Kinetic data in heterogeneous catalysis are commonly obtained in a steady state flow reactor at very low conversion levels so that reactant concentrations are essentially constant throughout the reaction zone. If the extent of conversion that is possible is limited by the reaction equilibrium to any significant degree, obtaining data at low conversions also serves to minimize any complication due to the reverse reaction, often eliminating the need to consider it at all. The rate of the reaction is commonly investigated as a function of concentrations or partial pressures of the reactants, with the objective of obtaining one or more rate constants, and possibly an adsorption equilibrium constant, in a rate equation representative of a postulated two-step sequence. From data on the temperature dependence of these parameters, information on activation energies and heats of adsorption are obtainable.

The investigation described in the present paper is very different in kind, with the objective of obtaining different kinds of information regarding the dynamics of the reaction. In place of studying the reaction far from equilibrium, we investigate the reaction very near equilibrium with attention directed to the net rate of reaction, i.e., the difference in the rates of the processes occurring in the two directions. Sufficiently close to equilibrium, the net rate is first order in the distance from equilibrium. The rate parameter characterizing this proportionality is a relaxation frequency obtainable by a frequency response method involving a very small volume perturbation of the system. Since the perturbation frequency was variable over a sufficiently wide range, it was possible to obtain relaxation frequencies for both of the steps comprising the postulated two-step process. From features observed in plots showing the frequency dependence of the magnitude of the transfer function and the phase angle obtained from the frequency response measurements, a *direct* indication of the relative rates of the two steps is obtained from simple inspection of the plots. This illustrates the power of the approach, since such direct information is not obtainable from conventional kinetic studies. In effect, the frequency response measurements provide us with a spectrum of relaxation frequencies. In the particular reaction described in this paper, two characteristic relaxation frequencies differing by almost 2 orders of magnitude were identified. Via a postulated two-step sequence for the reaction, they were identified with a very rapid hydrogenation-dehydrogenation step and a much slower toluene adsorption−desorption step.

An important feature of the present investigation is the development of a phenomenological theory describing the frequency dependence of the transfer function and phase angle obtained from the frequency response measurements. No consideration is given to details of the kinetics of the individual steps in terms of rate constants, adsorption equilibrium constants, surface coverages, etc. Herein lies a limitation, but at the same time also the strong point, of the theory. The theory is based entirely on rates expressed in terms of relaxation frequencies of the two steps and differences between concentrations and their equilibrium values as a function of time during the perturbation of the system. Thermodynamic properties including the equilibrium composition of the unperturbed vapor phase and a parameter relating to the toluene adsorption equilibrium are the other quantities entering into the theory. While further consideration could have been given to kinetic details and the relation of relaxation frequencies to rate constants of the individual steps, the determination of rate constants would have required extensive further investigation of the variation of the relaxation frequencies as the initial equilibrium composition of the unperturbed vapor phase was changed over a suitably broad range. Such studies fell outside the scope of what we intended to accomplish in the investigation, namely, the demonstration of the feasibility of a kind of "relaxation frequency spectroscopy" providing information of a kind different from that commonly obtained in studies of the kinetics of chemical transformations on surfaces.

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