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Compensation Effect of Benzene Hydrogenation on Pt(111) and Pt(100) Analyzed by the Selective Energy Transfer Model

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Abstract Kinetic measurements at low temperatures (310–360 K) using gas chromatography (GC) for benzene hydrogenation on Pt(100) and Pt(111) single crystal surfaces have been carried out at Torr pressures. These kinetic measurements demonstrated a linear compensation effect for the production of cyclohexane. A detailed application of the model of selective energy transfer to the experimentally obtained results yields the vibrational frequency of the adsorbate leading to reaction. This frequency is attributed to ring distortion modes. The vibrational frequency of the heat bath, or catalyst, is ascribed to a Pt-H mode. An approximate heat of adsorption of the reacting molecule is also calculated from the model.

Keywords Catalytic reaction · C_6 hydrocarbons · Pt(111) · Pt(100) · Hydrogenation · Compensation effect · Isokinetic temperature · Benzene · Selective energy transfer model

1 Introduction

Benzene hydrogenation is an industrially relevant reaction for several essential steps in petroleum refining and downstream chemical processing [1]. Understanding how energy is transferred from the heat bath, or catalyst, to the reactant to facilitate reactions by identifying the reactive surface intermediates are central issues in understanding the mechanism of benzene hydrogenation and heterogeneous catalysis. The rate law for benzene hydrogenation (and nearly all simple, thermally activated processes) can be described by a standard empirical power law

$$r = kP_{\mathrm{BZ}}^{a}P_{\mathrm{H_2}}^{b} \tag{1}$$

where r is the rate of reaction, P_{BZ} and $P_{\mathrm{H_2}}$ are the pressures of the reactant gases (benzene and H_2, respectively, in this case), a and b are the reaction order with respect to the reactant species, and k is the rate constant. The rate constant can be expressed as

$$k = Ae^{-E_{\mathrm{a}}/RT} \tag{2}$$

where A is the pre-exponential factor, E_{a} is the activation energy, R is the gas constant, and T is the temperature. For some classes of systems with varying activation energies, a compensation effect exists such that as the apparent activation energy changes, so does the pre-exponential factor as demonstrated in the following equation:

$$\ln A = bE_{\mathrm{a}} + c \tag{3}$$

where

$$b = \frac{1}{RT_{\mathrm{iso}}} \tag{3a}$$

and

$$c = \ln k_{\mathrm{iso}} \tag{3b}$$

where T_{iso} and k_{iso} are the isokinetic termperature and isokinetic rate, respectively.

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The compensation effect in heterogeneous catalysis was first observed by Constable [2] in heterogeneous catalysis and has been found to hold true for a whole host of chemical reactions [3–6]. An isokinetic temperature (T_{iso}) is defined by the slope of the relation (3), at which all the considered reactions have the same rate constant. Possible explanations for the compensation effect have been explored extensively and are reviewed by Bond et al. [7]. One of the interpretations of the compensation effect cited by Bond et al. [7] is a model proposed by Larsson [8] which assumes there is a transfer of energy into the vibrational mode of the reactant that "most effectively distorts the molecule towards the structure it has in the 'activated complex' of the reaction." In another interpretation, Norskov and co-workers [9] suggest the compensation effect arises from "a switching of kinetic regimes," meaning that there is a monotonic relationship between "the activation energy of the rate-limiting step and the stability of the reaction intermediates on the surface."

Here, we consider the compensation effect of benzene hydrogenation to cyclohexane on Pt(111) and Pt(100) using the selective energy transfer (SET) model proposed by Larsson [10, 11]. Kinetic measurements of benzene hydrogenation to cyclohexane on Pt(111) and Pt(100) at low temperatures (310–360 K) and Torr pressures show a linear compensation effect between activation energy and the pre-exponential factor. Employing the SET model to the experimentally obtained Arrhenius parameters generates vibrational frequency of the adsorbate leading to reaction along with the vibrational frequency of the heat bath, or catalyst. The heat of adsorption of the reacting adsorbate is also determined from the SET model.

2 Experimental

All experiments were carried out in a high-pressure/ultra-high-vacuum (HP/UHV) system on prepared Pt(111) and Pt(100) single-crystal surfaces. The HP/UHV system consists of a UHV chamber operating at a base pressure of 2×10^{-9} Torr and a high-pressure (HP) cell isolated from the UHV chamber by a gate valve. The UHV chamber is equipped with an Auger electron spectrometer (AES), quadrupole mass spectrometer (QMS) and Ar^+ ion sputter gun. The HP cell is equipped with a re-circulation loop that includes a diaphragm pump and a septum for gas chromatographic (GC) analysis. The reactant and product gases are constantly mixed via a recirculation pump while kinetic data is acquired by periodically sampling the reaction mixture and measuring the relative gas phase composition (FID detection and 0.1% AT-1000 on Graphpac GC 80/100 packed column (Alltech)).

The Pt(111) and Pt(100) crystals were cleaned by sputtering with Ar^+ ions (1 keV) for 20 min, heating to 1,123 K in the presence of 5×10^{-7} Torr O_2 for 2 min, and then annealing at 1,123 K for 2 min. AES and low-energy electron diffraction (LEED) were used to verify the cleanliness of the Pt(111) and Pt(100) surfaces after several cleaning cycles. The Pt(111) or Pt(100) crystal was then transferred into the HP cell for reaction studies. Benzene (≥99.0 wt.%, EM Science) was purified by several freeze-pump-thaw cycles before introduction into the HP cell. Prior to the experiment, benzene was checked for impurities by means of GC. Such impurities were below 0.5% and consisted of mostly light alkanes below C_6.

3 Results and Discussion

3.1 Apparent Activation Energies and Compensation Effect to Form Cyclohexane Under Varied Pressures of Benzene and Hydrogen on Pt(111) and Pt(100)

Figure 1 shows the Arrhenius plot for 11 Torr benzene and 11, 52, and 158 Torr hydrogen, respectively, and 105 Torr hydrogen and 8, 11, 13, and 17 Torr benzene pressures, respectively, over a temperature range from 310 to 360 K on Pt(111) and Pt(100). The rate constants (k) [molecules site^{-1} s^{-1} P(benzene)$^{-a}$ P(H_2)$^{-b}$] are calculated from the turnover rates using the empirical equation 1, with the reaction orders listed in Table 1, assuming that every platinum surface atom is an active site. Apparent activation energies and pre-exponentials for cyclohexane formation are listed in Table 2.

The apparent activation energies depend upon the pressure of each reactant. In many hydrogenation reactions (e.g. ethylene, propylene, *n*-hexene, cyclohexene etc.), H_2 is more strongly adsorbed than the hydrocarbon reactant and has a dominant effect on the apparent activation energies [7]. Benzene, in contrast, binds very strongly to the Pt(111) surface and large changes in the apparent activation energies are expected upon varying its partial pressure. The exponents a and b in Eq. 1 are determined over a range of reaction temperatures (310–360 K) using

$$a = \left[\frac{\partial \ln r}{\partial \ln p_{C_6H_6}}\right]_{p_{H_2}}, \quad b = \left[\frac{\partial \ln r}{\partial \ln p_{H_2}}\right]_{p_{C_6H_6}}. \tag{4}$$

3.2 Selective Energy Transfer Model

One notes that the Arrhenius lines in Fig. 1 intersect in a temperature region of about $1{,}000/T = 2.6$–2.8 K^{-1}. This

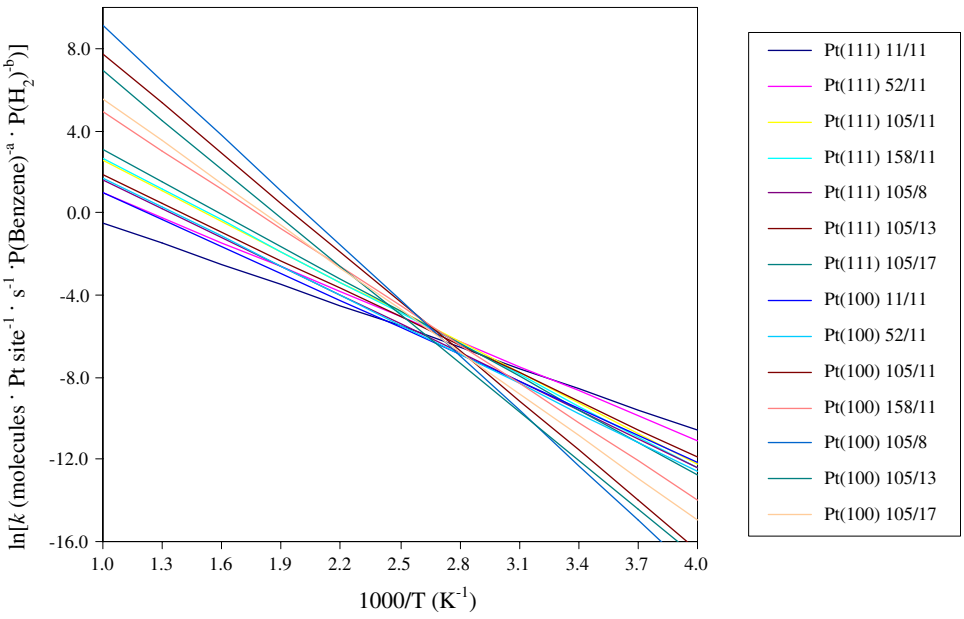

Fig. 1 Arrhenius plots of rate constants (k) (in molecules Pt site^{-1} s^{-1} P(benzene)$^{-a}$ $P(H_2)^{-b}$) on Pt(111) and Pt(100) for benzene (7.5, 10, 12.5, and 15 Torr) hydrogenation to cyclohexane in the presence of H_2 (10, 50, 100, and 150 Torr). Apparent activation energies and pre-exponentials are listed in Table 2. The legend indicates the platinum single-crystal used and the pressure combination used in pressure of benzene over pressure of H_2

Table 1 Orders for both H_2 and benzene on Pt(111) and Pt(100)

	Order Pt(111)	Order Pt(100)
Benzene	−1.1 ± 0.1	−1.1 ± 0.3
H_2	0.6 ± 0.01	0.6 ± 0.02

means that the isokinetic temperature is $T_{iso} = 1{,}000/(2.7 \pm 0.1) = 370 \pm 14$ K. This relatively good agreement between the experimental data for Pt(111) and Pt(100) makes it reasonable to use all the data in one and the same "compensation plot"; i.e. ln(A) versus E_a. Since

Table 2 Pre-exponentials (in molecules site^{-1} s^{-1} P(benzene)$^{-a}$ $P(H_2)^{-b}$); $\Delta E_a = E_{a_i} - E_{a_{i+1}}$; n' is the number of a least common factor in the absolute values of the preceding column; apparent activation energies (in kcal mol^{-1}); activation energies corrected for temperature, $E_a - RT$; and $E_a - RT$ divided by the self-consistent least common factor giving the corresponding vibrational quantum numbers, n

System $P(C_6H_6)/P(H_2)$	ln(A) (molecules site^{-1} s^{-1} P(Benzene)$^{-a}P(H_2)^{-b}$)	E_a (kcal/mol)	ΔE_a (kcal/mol)	n'	E_a−RT (kcal/mol)	n
Pt(111)						
11/11	2.9 ± 0.3	6.7 ± 0.2			6.0 ± 0.2	5
11/52	5.0 ± 0.5	8.0 ± 0.3	1.3 ± 0.4	1	7.3 ± 0.3	6
11/105	7.5 ± 0.2	9.8 ± 0.1	1.8 ± 0.3	2	9.1 ± 0.1	8
11/158	7.7 ± 0.8	10.0 ± 0.5	0.2 ± 0.5	0	9.3 ± 0.4	8
8/105	6.3 ± 0.3	9.3 ± 0.2	−0.7 ± 0.5	1	8.6 ± 0.3	8
13/105	6.4 ± 0.1	9.1 ± 0.1	−0.2 ± 0.2	0	8.4 ± 0.1	7
17/105	8.4 ± 0.3	10.5 ± 0.2	1.4 ± 0.2	1	9.8 ± 0.2	9
Pt(100)						
11/11	5.4 ± 0.7	8.7 ± 0.5	−1.8 ± 0.5	2	8.0 ± 0.5	7
11/52	6.5 ± 0.3	9.5 ± 0.2	0.8 ± 0.5	1	8.7 ± 0.2	8
11/105	15.8 ± 1.1	16.0 ± 0.7	6.5 ± 0.7	6	15.0 ± 0.2	14
11/158	11.2 ± 0.2	12.5 ± 0.1	−3.5 ± 0.7	3	11.8 ± 0.1	10
8/105	18.0 ± 1.1	17.7 ± 0.8	5.2 ± 0.8	5	18.2 ± 0.1	15
13/105	14.8 ± 0.2	15.7 ± 0.8	−2.0 ± 0.8	2	16.1 ± 0.8	13
17/105	12.4 ± 0.2	13.6 ± 0.1	−2.1 ± 0.2	2	12.9 ± 0.8	11
			−6.9 ± 0.2	7		
Sum			34.4	33		
34.4/33 = 1.04 kcal/mol						

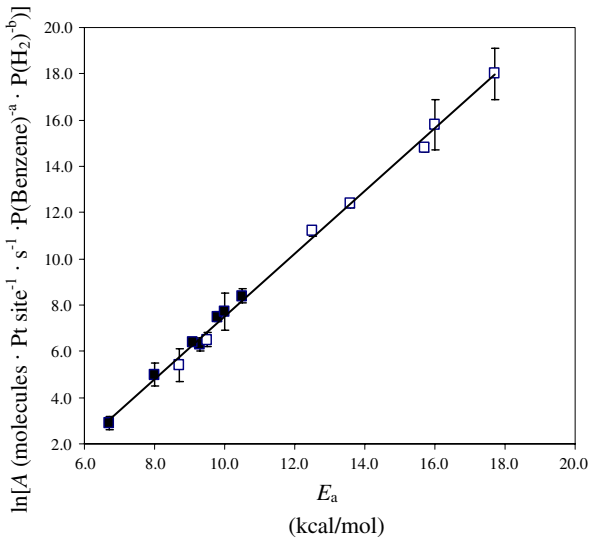

Fig. 2 Constable plot for the hydrogenation of benzene to cyclohexane on Pt(111) and Pt(100). Open symbols correspond to Pt(100) and closed represent Pt(111)

benzene hydrogenation to cyclohexane has been found to be structure insensitive [12], experimental data obtained from Pt(111) and Pt(100) are plotted on the same graph.

Plotting the Arrhenius parameter pairs listed in Table 2 forms a straight line, presented in Fig. 2. Based on Eq. 3, the slope of the line in Fig. 2 is related to the isokinetic temperature (T_{iso}). For cyclohexane formation on both Pt(100) and Pt(111), T_{iso} is 370 ± 6 K, which corresponds well with the temperature at which the Arrhenius plots intersect, 370 ± 14 K.

The general idea of the SET model is that a molecule reacting in the condensed phase must have a continuous supply of energy. This supply of energy is thought to proceed via vibrational resonance [11] in the sense that a vibrator of the catalyst, ω, transfers its energy to a vibrator in the reacting molecule, ν, that has a frequency close to ω. Based on this model, the relation between the isokinetic temperature, the vibration frequency of the heat bath (the catalyst, in this instance), and that of the reacting molecule is described by Eq. 5, as derived by Larsson [8],

$$T_{iso} = NhcR^{-1}\left(\nu^2 - \omega^2\right)\omega^{-1} \times \left\{\pm\frac{1}{2}\pi - \arctan\left[0.5\nu\omega(\nu^2 - \omega^2)^{-1}\right]\right\}^{-1} \quad (5)$$

where N is Avogadro's number, h is Planck's constant, and c is the speed of light.

The basic tenet of the SET model is that values of E_a, or rather the enthalpy of activation $\Delta H^{\ddagger}$, can be quantitized in that a specific number of vibrational quanta must be transferred from the catalyst to the adsorbed reactant in order to access the transition state [10, 13]. One must, however, consider that vibrational modes in a molecule are anharmonic, resulting in an unequal spacing of the energy levels. The vibrational energy of a molecule, measured relative to the zero energy of the vibrational mode, is described (excluding higher order terms) by Herzberg [14] as

$$G_0(n) = n\nu_0 + \nu_0 x_0 n^2 \quad (6)$$

where G_0 is the vibrational energy of the vibrator in excess of the zero energy vibrational level, n is the vibrational quantum number, x_0 is the anharmonicity constant (with negative sign) and ν_0, for small values of x_0, is twice the vibrational energy of the zero state. If the rest of the reacting molecule and all the non-reacting molecules are assumed to be in thermal equilibrium, then, following Benson [15], the activation energy can be defined as the difference between the "average energy of the reacting molecules and the average energy of the molecules in the system." This excess energy, $G_0(n)$, is then equal to the activation enthalpy of the reaction

$$G_0(n) = \Delta H^{\ddagger}. \quad (7)$$

Laidler [16] found that the following relation between activation energy and enthalpy of activation is approximately valid for reactions in the condensed phase

$$\Delta H^{\ddagger} = E_a - RT. \quad (8)$$

Any energy term representing a possible pre-equilibrium, Q, must also be taken into consideration [7]

$$\Delta H^{\ddagger} = E_a - RT + Q. \quad (9)$$

Combining Eqs. 6–9 leads to

$$E_a - RT + Q = n\nu_0 + \nu_0 x_0 n^2. \quad (10)$$

The values of $\Delta H^{\ddagger} = E_a - RT$ are reported in Table 2, using the mean of the experimental temperatures, 335 K (Fig. 3). In Table 2, we further report the consecutive differences between the E_a values. In the fifth column we estimate how many times a certain common factor (E_0) is appearing in the absolute values of those consecutive differences. By summing the absolute values of ΔE_a and dividing by the sum of n', a relatively good value of E_0 is obtained (1.04 kcal/mol). It is our proposal that E_0 is related to the vibrational energy of the adsorbate leading to reaction. To determine appropriate values of the vibrational quantum number, n is set equal to the integer value of $(E_a - RT)/E_0$ by neglecting Q and the anharmonic term in Eq. 10. If Q is relatively large, it may have to be included. With these approximate values of n, a second-order polynomial is fitted to the data to give approximate values of M_0, M_1, and M_2

$$E_a - RT = M_0 + M_1 n + M_2 n^2. \quad (11)$$

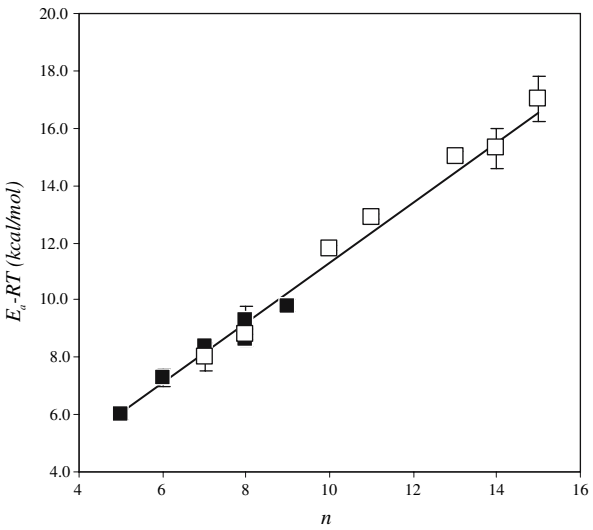

Fig. 3 Plot of experimentally determined $E_a - RT$ against the first estimated vibrational quantum number, n (cf. Table 2) for Pt(111) and Pt(100). The solid line is second order polynomial fit of the data. Open symbols correspond to Pt(100) and closed symbols represent Pt(111)

This procedure has been successfully used for a hydrodechlorination reaction of chlorobenzene over a series of nickel catalysts [17].

In order to get a more precise, self-consistent value of M_1, however, one must use an iterative procedure, the aim of which is to obtain $E_0 = M_1$. For this purpose, it turned out best to use the differences of ΔE_a. Using Eq. 10 one can then write

$$\Delta E_a = E_{a_1} - E_{a_2} = v(n_1 - n_2) + x_0 v(n_1^2 - n_2^2) \quad (12)$$

$$n_1 = \text{round}[(E_{a_1} - RT)/E_0] \quad (13)$$

$$n_2 = \text{round}[(E_{a_1} - RT)/E_0] \quad (14)$$

For a set of activation differences, ΔE_a, given in Table 2, the fitting problem is to find the best fitting parameters v and $x_0 v$, and to make sure the parameters are self-consistent by $E_0 = v$. This means that for a specified value of E_0, Eqs. 10 and 11 will have the same coefficient for the first and second order terms in n; thus, $M_1 = v$. By a suitable iteration, one finds that $E_0 = 1.13$ kcal/mol is the value that gives a set of converged M_1 and M_2, as shown in Table 3. The self-consistent procedure is performed by first setting E_0 to an arbitrary number around 1. Equations 13 and 14 are then calculated for all the activation energies. Equation 12 is then solved for v and $x_0 v$, which correspond to M_1 and M_2. This procedure was repeated until E_0 was found to equal M_1. The heat of adsorption, Q, is calculated by averaging Eq. 10 for all activation energies.

Comparison of Eq. 11 to Eq. 10 shows that the fitting parameter M_1 should correspond to the vibrational frequency of the adsorbate leading to reaction and M_2 should correspond to the anharmonicity term. From this comparison of Eqs. 10 and 11, the self-consistent fit yields a value of 393 ± 77 cm^{-1} for the vibrational frequency of the adsorbate and an anharmonicity of -1.53 ± 3.59 cm^{-1}. This value of the anharmonicity is quite reasonable for single bonded, low frequency vibrations. The vibrational frequency at 393 cm^{-1} is most likely related to the E_{2u} mode for free benzene, 404 cm^{-1}, described by Painter and Koenig [18], implying a ring distortion and a C–H out of plane bending mode. This C–C distortion is expected to cause an anharmonicity of 1–2 cm^{-1}. It may be of interest to note that the out-of-plane C–H bending of benzene at 740 cm^{-1} has an anharmonicity of -0.7 cm^{-1} [19, 20].

In addition to yielding information regarding the vibration of the adsorbate leading to reaction, the SET model can also indicate the strength of adsorption of the reacting molecule, $M_0 = -Q$, from Eqs. 10 and 11. The corresponding M_0 value for the fit is -0.55 ± 0.39 kcal/mol, thus indicating that the heat of adsorption, Q, is 0.55 ± 0.39 kcal/mol.

After obtaining the vibrational frequency of the adsorbate leading to reaction, determining the frequency of the energy donating bath is necessary. To this end, the full resonance formula (Eq. 5) for $v = 393 \pm 77$ cm^{-1} is plotted in Fig. 4 along with the error limits. The value of T_{iso} obtained from Fig. 2 is 370 K and is drawn on the plot in Fig. 4. The point of intersection indicates an abscissa of 513 ± 33 cm^{-1}. Frequencies values of this magnitude have been reported for the Pt–H system. On Pt(111), a mode at 470 cm^{-1} has been assigned to a Pt–H bend of an atop adsorbed hydrogen [21]. Baro et al. [22] have attributed a mode at 550 cm^{-1} on Pt(111) to the A_1 mode of hydrogen adsorbed to a three-fold hollow site. However, Zemlyanov et al. [23] observed a mode at 555 cm^{-1} on Pt(100) $-$ (5 $\times$ 20) which was assigned to bridge bound hydrogen, displaying the ambiguity of the assignments. It is important to note that these measurements have a resolution of 60–90 cm^{-1}, indicating that the calculated

Table 3 Fitting parameters M_0, M_1, and M_2 for the self-consistent iterative procedure and the vibrational energy (in cm^{-1}) and anharmonicity constant (in cm^{-1}) derived from the fitting parameters

Q (kcal/mol)	M_1 (kcal/mol)	M_2 ($\times 10^{-3}$ kcal/mol)	v (cm^{-1})	$x_0 v$ (cm^{-1})
-0.55 ± 0.39	1.13 ± 0.22	-4.4 ± 10.3	393 ± 77	-1.53 ± 3.59

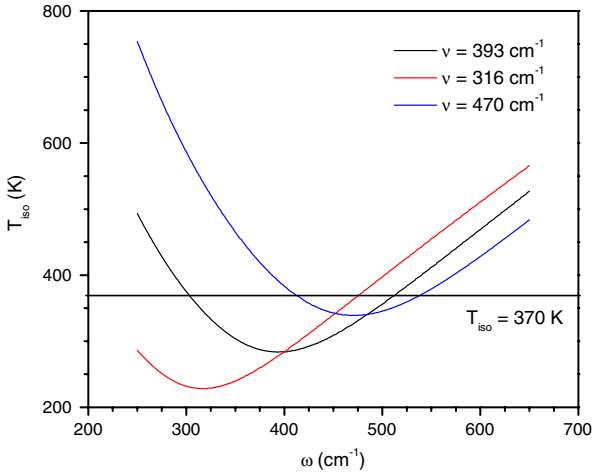

Fig. 4 Isokinetic temperature, T_{iso}, calculated for $\nu = 393 \pm 77\ cm^{-1}$ using the full resonance formula. A line at $T_{iso} = 370$ K is drawn to obtain the vibration of the heat bath, ω

frequency of the heat bath may correspond to any of these Pt–H modes.

The most striking result from employing the SET model is that the reacting molecules are not strongly adsorbed to the catalyst surface. Upon analysis of the step-wise change of the activation energies, the heat of adsorption is found to be quite low. The heat of adsorption found is not at all corresponding to what one instinctively considers the strength of adsorption of a molecule and may be severely disturbed by the adsorption and catalysis process. Nevertheless, the molecules have been assumed to be in thermal equilibrium. Based on previous vibrational spectroscopy studies [12, 24, 25] most of the molecules are assumed to be strongly adsorbed. In a mobile equilibrium there must be at any given time a certain number of molecules that are far from being strongly adsorbed to the surface [18]. It may be possible that these weakly adsorbed molecules have the possibility to present an easy route for an approaching reactant than strongly adsorbed molecules have. Additionally, many high-pressure studies have shown that the key intermediate for catalysis is commonly a weakly adsorbed species [26–28].

4 Conclusions

Benzene hydrogenation on Pt(100) and Pt(111) single crystal surfaces was carried out at low temperatures (310–360 K) and Torr pressures using gas chromatography. Indications of a compensation effect between activation energy and the pre-exponential factor for cyclohexane production led to a detailed application of the SET model. A possible vibrational frequency of the adsorbate leading to reaction was attributed to the E_{2u} mode of free benzene. Further application of the SET model assigned the vibrational frequency of the catalyst to a Pt–H mode. The heat of adsorption of the reactant molecule was approximated as very small.

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