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Kinetics of Metal-Catalyzed Reactions of Alkanes and the Compensation Effect

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For a bimolecular reaction $A + B \rightarrow C$ obeying simple Langmuir–Hinshelwood kinetics, the apparent activation energy $E_{\mathbf{app}}$ is a function of the gas-phase concentrations of each reactant; where A is the more strongly chemisorbed, the limiting values of $E_{\mathbf{app}}$ at low and high pressures of A are given respectively by ($E_{\mathrm{t}} + n_A \Delta H_A^{\ominus} + n_B \Delta H_B^{\ominus}$) and ($E_{\mathrm{t}} - n_A \Delta H_A^{\ominus} + n_B \Delta H_B^{\ominus}$), where $E_{\mathbf{t}}$ is the true activation energy, $n_{\mathbf{A}}$ and $n_{\mathbf{B}}$ are the magnitudes of the orders of reaction (each having a value of one for these limiting cases), and $\Delta H_A^{\ominus}$ and $\Delta H_B^{\ominus}$ are the enthalpies of adsorption of the two reactants. $E_{\mathbf{t}}$ is usually greater than $E_{\mathbf{app}}$, and values of $E_{\mathbf{app}}$ and the corresponding values of ln $\mathrm{A}_{\mathbf{app}}$ show a compensation effect. With alkane hydrogenolysis, the opening step is the endothermic dehydrogenative chemisorption of the alkane; this accounts for the very high values of $E_{\mathbf{app}}$ that are often observed. In the case of $\mathrm{Ru/Al_2O_3}$ catalysts, analysis of the rate dependence on $\mathrm{H_2}$ pressure by an expression based on the subsequent rate-limiting C−C bond breaking affords values of $E_{\mathbf{t}}$ that are generally $\approx$60 kJ $\mathrm{mol^{-1}}$ and values of $\Delta H_C^{\ominus}$ (C = alkane) in the range 60–80 kJ $\mathrm{mol^{-1}}$. At $\mathrm{H_2}$ pressures greater than that at which the rate is maximal, $E_{\mathbf{app}}$ exceeds $E_{\mathbf{t}}$; below the maximum, the reverse is the case. Compensation between $E_{\mathbf{app}}$ and ln $\mathrm{A}_{\mathbf{app}}$ is again found; other literature reports confirm the general validity of the model. Our analysis supports a recent speculation which reported that compensation effects originate in differences in adsorption enthalpy terms, but the sign of the term for the alkane will be positive where its dehydrogenation initiates the reaction. Such compensation effects are not however *true* kinetic phenomena and are better described by the term *apparent*.

1. INTRODUCTION

The compensation effect describes a sympathetic variation of activation energy E with the logarithm of the pre-exponential factor $\mathbf{A}$: it takes the form (1)

$$\ln \mathbf{A} = mE + c, \qquad [1]$$

where m and c are constants. This relation is predicated on the intersection of all the Arrhenius plots of the selected group of reactions at a single temperature called the *isokinetic temperature*. In the area of heterogeneous catalysis the effect is often observed either when a given reaction is followed on a series of different catalysts or when the same catalyst is used for a number of different reactions (1), but its appearance is not confined to this field: it is observed in homogeneous catalysis and indeed in such a variety of other activated processes (2) that a common mechanistic explanation would seem improbable. The numerous attempts to explain it have been described in comprehensive reviews (3, 4), but in spite of its long history (5, 6) its origin has remained obscure. Recently, however, the rationale of its occurrence in heterogeneously catalysed reactions has started to become clearer.

It was recognized by the earliest students of the kinetics of catalyzed reactions that as the temperature is raised in order to measure the activation energy the concentrations of adsorbed intermediates will usually decrease because of the exothermic nature of their chemisorption. Thus the rate of reaction increases less rapidly than would be the case if the surface concentrations were to remain constant, and the measured or *apparent* activation energy E_{app}, which is of necessity derived from the measured rates is less than the *true* value E_{t}, which would be obtained by using the *rate constant*, by some function of the enthalpies of adsorption of the reactants (7). Only when a reactant is so strongly chemisorbed that its surface concentration is effectively temperature-independent in the range of measurement does its adsorption enthalpy not moderate E_{app}; the same of course applies if a molecule reacts at the surface without chemisorption. Only rarely, however, are the reaction kinetics determined and analyzed to reveal values of true rate constants from which E_{t} might be estimated.

It has been suggested on several occasions that the compensation effect might be a direct consequence of the use of apparent Arrhenius parameters (2, 3, 8, 9) and that the variable factors which result in the appearance of compensation are in fact the enthalpies of adsorption. In most cases it is difficult to decide whether experimental activation energies are apparent or true, but they must be presumed apparent until they are proved to be true. These suggestions (2, 3, 8, 9) have been qualitative in nature, and it is only in the recent paper by Patterson and Rooney (10) that the concept has been given quantitative expression. While eschewing the use of the term “apparent activation energy,” these authors propose, in the formalism of transition state theory, that

$$k_{\text{exp}} = (k\text{T}/h)K_A K^{\ddagger} \qquad [2]$$

where k_{exp} is the experimentally determined rate constant, and K_A is the equilibrium constant for the reactants' adsorption and $K^{\ddagger}$ that for the formation of the transition state; they draw attention to the flexibility provided by the wide potential range of variability of K_A for explaining the great range of E_{app} values sometimes recorded. While this analysis is almost certainly valid in principle, it suffers from the limitation, so common with theoretical exercises of this kind, of lacking conviction because its truth cannot be demonstrated by reference to a set of detailed experimental measurements.

At this point in the argument we encounter a problem of considerable size. Formal text-book derivations of the basic kinetic equations relating to heterogeneous catalysis are usually confined to the simplest unimolecular and bimolecular reactions proceeding by a Langmuir–Hinshelwood mechanism, and the Patterson–Rooney treatment (10) is similarly restricted. Unfortunately, many reactions having both practical and theoretical interest do not behave in such a straightforward way, and it is sometimes quite difficult to deduce the appropriate rate equation from the experimental data: indeed, if we follow Popper, it is impossible to prove there is none better. However, the identification of an *acceptable* rate equation is essential if we are to proceed further either with the understanding of complex reaction mechanisms or with modeling such reactions in an industrial plant. The use of an incorrect rate equation can lead for example to numerical values of its constants that are intuitively unreasonable (11) or, as we shall show below, to a purely incidental relation between E_{app} and ln $\mathbf{A}_{\text{app}}$ (12).

However, the *principal purpose* of this paper is to show that even within a given catalytic system (i.e., with the same catalyst and the same reactants) E_{app} in the general case is not a fixed quantity but is inevitably a function of the pressure of the reactants, and that therefore the relationship between E_{t} and E_{app} is more complex and subtle than text-book treatments suggest. We shall first illustrate the principles by reference to an artificial example of Langmuir–Hinshelwood kinetics, and then survey examples either from the literature or from our own work which extend the theoretical basis by showing the effect of pre-equilibria on measured Arrhenius parameters. Apparent compensation effects arise naturally in consequence of this kinetic analysis.

2. DEPENDENCE OF APPARENT ACTIVATION ENERGY ON REACTANT PRESSURES: MODEL CALCULATIONS

We first demonstrate how, for a hypothetical model system obeying simple bimolecular Langmuir–Hinshelwood kinetics, the apparent activation energy varies with the pressure of the reactants. The relevant rate equation is

$$\text{rate} = k_1 K_A P_A K_B P_B/(1 + K_A P_A + K_B P_B)^2, \qquad [3]$$

where the subscripts A and B represent the two reactants, the K's their adsorption coefficients, the P's their pressures in the gas phase, and k_1 represents the rate constant. We select values of the corresponding standard enthalpies and entropies of adsorption such that K_A/K_B is 21.4 at 393 K and 18.4 at 413 K: thus (in kJ mol^{-1} and e.u.) $-\Delta H_A^{\ominus} = 22$, and $-\Delta H_B^{\ominus} = 12$; $\Delta S_A^{\ominus} = \Delta S_B^{\ominus} = -40$. E_{t} is assigned a value of 65 kJ mol^{-1} and ln($\mathbf{A}_{\text{t}}$/mmol g^{-1} h^{-1}) = 23. These latter values are essentially those found to describe the hydrogenolysis of alkanes on Ru/Al$_2$O$_3$ catalysts (13) (see below). Rates as a function of P_{A} at 373, 393, 413, and 433 K are shown in Fig. 1: the rate maxima become less pronounced and move to higher values of P_{A} as the temperature is increased. The rates at each of the pressures used in constructing Fig. 1 give very good Arrhenius plots (see Fig. 2 for examples) with apparent activation energies that increase with P_A (Fig. 3) by some 70% over the calculated range, and although there is no unique intersection point (Fig. 2) a convincing apparent compensation effect is shown (Fig. 4). The value of the isokinetic temperature T_{i} derived from the slope by the relation [1],

$$T_i = (mR)^{-1}, \qquad [4]$$

R being the gas constant, is 422 K. While accepting that strict adherence to the compensation equation [1] requires all lines to pass through a single point (4), we use the term "compensation" where changes in E are partially mitigated by changes in ln $\mathbf{A}$, even if there is no single value of T_{i}. We

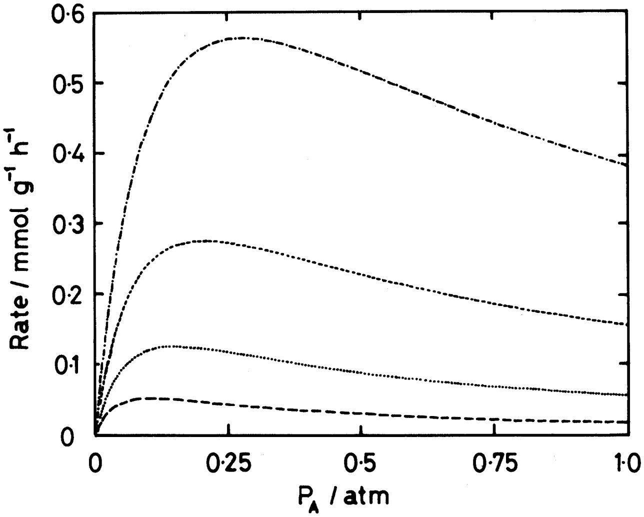

FIG. 1. Rates as a function of the gas-phase concentration of reactant A at 373, 393, 413, and 433 K, calculated by the Langmuir–Hinshelwood bimolecular rate expression (see text for activation, enthalpic, and entropic parameters used: $P_{\text{B}} = 0.0714$ atm).

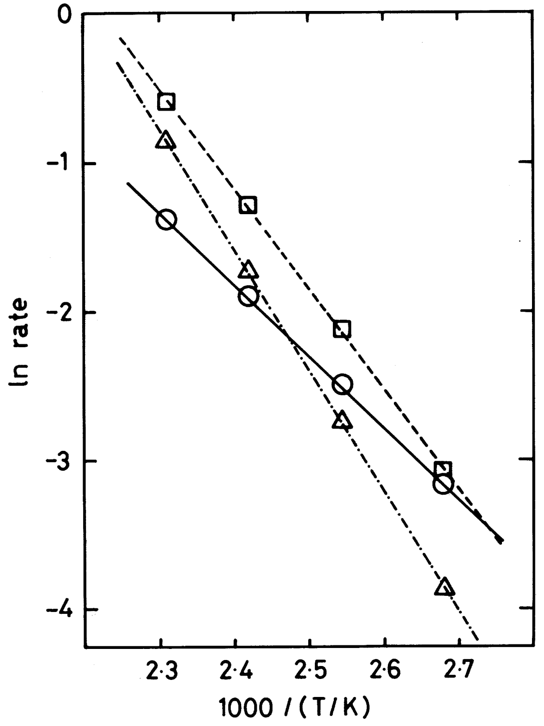

FIG. 2. Selected Arrhenius plots based on the rates shown in Fig. 1: 0.040 atm (○), 0.227 atm (□), and 0.817 atm (△).

note that, as expected, most values of E_{app} are less than E_{t}. P_B being set at a low value, as P_A tends to zero the values of both θ_A and θ_B will become small, and the corresponding orders of reaction n_A and n_B will both be unity. E_{app} then tends to a limiting value determined by the equation due originally to Temkin (7),

$$E_{\text{app}} = E_{\text{t}} + \Delta H_A^{\ominus} + \Delta H_B^{\ominus}, \tag{5}$$

of 31 kJ mol^{-1}. However, at very high values of P_A, such that θ_A greatly exceeds θ_B, the former naturally decreases with increasing temperature but the latter actually increases significantly (Fig. 5), and this accounts for the appearance of E_{app} values greater than E_{t}. Qualitatively the additional space made available by the desorption of A becomes available to allow more adsorption of B; the limiting value of E_{app} as P_A is increased is then

$$E_{\text{app}} = E_{\text{t}} - \Delta H_A^{\ominus} + \Delta H_B^{\ominus} = 75 \text{ kJ mol}^{-1}. \tag{6}$$

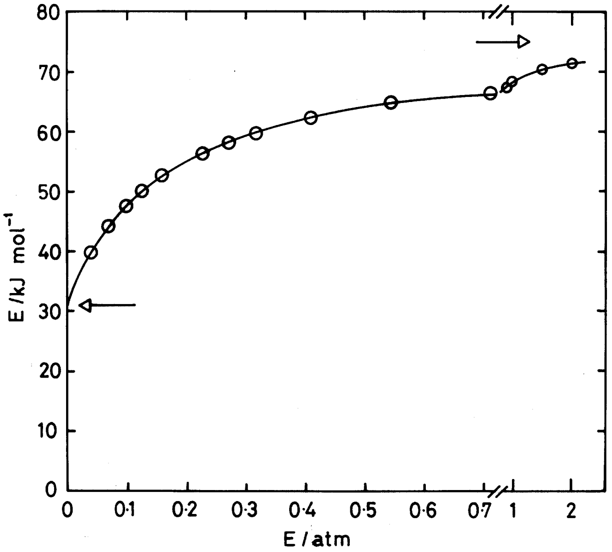

FIG. 3. Dependence of E_{app} (vertical axis) derived from the rates shown in Fig. 1 on the pressure of A (horizontal axis): arrows point to theoretical upper and lower limits.

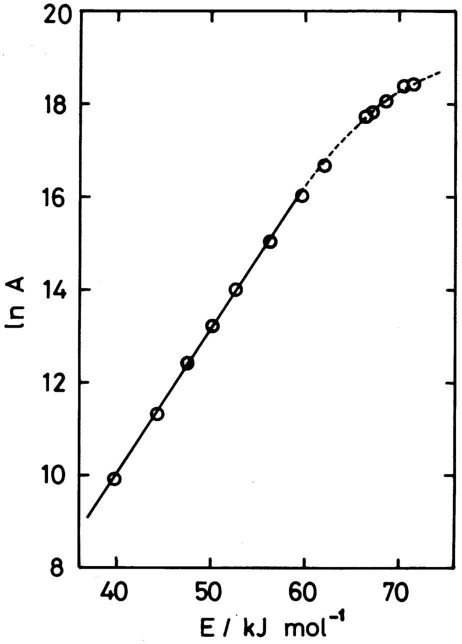

FIG. 4. Compensation effect shown by the values of E_{app} in Fig. 3 and the corresponding values of ln $\mathbf{A}_{\text{app}}$.

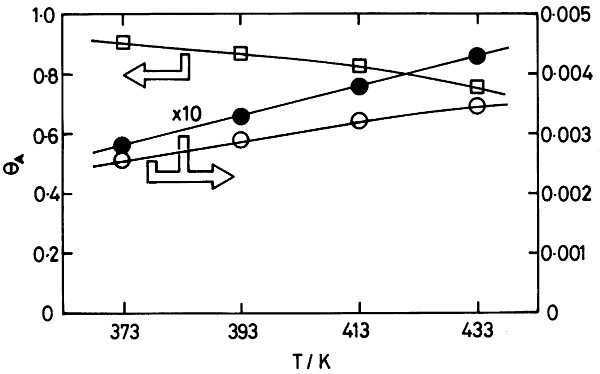

FIG. 5. Calculated surface coverages θ_A and θ_B as a function of temperature, using the same constants as before. Open points, $P_A = 1$ atm; filled points, $P_A = 10$ atm, $P_B = 0.0714$ atm.

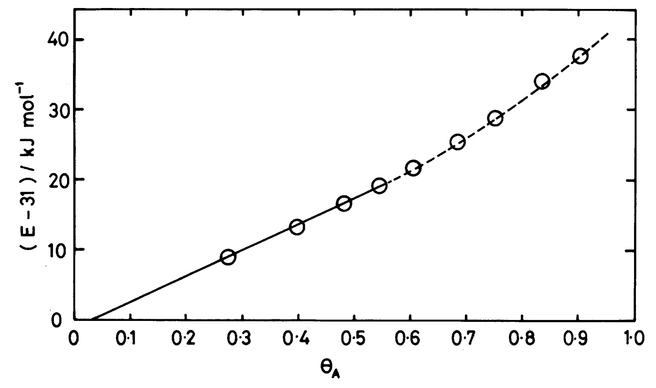

FIG. 6. Increase in E_{app} with θ_A (strictly, with the area available for A to adsorb on).

The calculated value when $P_A/P_B = 140$ is 74.8 kJ mol^{-1}. The condition for E_{app} to equal E_t is that θ_B shall be independent of temperature, and this occurs when P_A is about 0.6 atm. The activation energy calculated from values of r_{max} is very close to that found for $P_A = 0.227$ atm (Fig. 2; ~56 kJ mol^{-1}) and is thus somewhat lower than E_t. The functional relation between E_{app} and P_A (Fig. 3) is then determined by the changing value of θ_A, and the increase in E_{app} above the value of 31 kJ mol^{-1} is proportional to θ_A less the allowance for θ_B (Fig. 6); i.e., it is proportional to the surface available for the adsorption of A.

Compensation effects therefore arise not only by variation of the enthalpy terms but also by alteration of reactant pressures; as long as the K_iP_i term is affected in some way, apparent compensation will occur.

3. DEPENDENCE OF ACTIVATION ENERGY ON REACTANT CONCENTRATIONS: SOME REAL EXAMPLES

In their recent paper (10), Patterson and Rooney remark on the surprisingly wide ranges of values of E_{app} that are sometimes reported, and indeed, in the example they quote (14), E_{app} attains the remarkably high value of 370 kJ mol^{-1}. This leads them to attribute these results to the intrusion of the enthalpy of adsorption of the reactants into the enthalpy of activation, thus

$$E_{\text{app}} \simeq \Delta H^{\ominus}_{\text{ads}} + \Delta H^{\ddagger}, \qquad [7]$$

and in what is the kernel of their argument, they go on to state:

(i) ... the main variable is by far $\Delta H^{\ominus}_{\text{ads}}$ and not $\Delta H^{\ddagger}$.

(ii) “As the adsorption strength increases, and therefore E (i.e., E_{app}) decreases, there is a corresponding decrease in $\Delta S^{\ominus}_{\text{ads}}$ and hence in the value of **A**.”

(iii) “That (the above) equation can hold over such a wide range of E (i.e., E_{app}) values is now understood.”

The first of these three statements appears to be based purely on intuition and is not supported by any experimental evidence. If the reactants are adsorbed exothermically (as is assumed in the model discussed above) E_{app} is generally less than E_t, except in a limited range of conditions not often encountered. Thus in the example quoted (14) E_t should be *greater* than 370 kJ mol^{-1}, which seems implausible. The second statement rests on the arguments used previously by Conner (15); the third is a matter of opinion.

Despite its obvious limitations, the Power Rate Law is still employed as the basis for efforts to obtain a more profound understanding of the mechanisms of catalyzed reactions. The catalysis literature does not disclose many examples where the kinetics of a straightforward catalyzed reaction have been measured and analyzed in sufficient detail by means of a rate expression of the Langmuir–Hinshelwood type to afford values of E_t and E_{app}, and of adsorption enthalpies derived from the temperature dependence of the constants of the equation. We therefore lack any substantial body of information to help us to decide what are reasonable values for E_t in such cases. A study in the older literature (12) seemed to provide such an example: the rate of *n*-butane hydrogenolysis was followed on a Ru/Al_2O_3 catalyst at various total pressures up to 6.44 atm over temperature ranges of 10–30 K. Analysis of the results using a simple Power Rate Law expression gave values of E_{app} that showed a good compensation effect (Fig. 7), not in fact remarked on by the authors, but further analysis using a Langmuir–Hinshelwood rate equation led to a value of E_t *smaller* than all the E_{app} values. Unfortunately, the rate equation chosen failed to account for the occurrence of a maximum in the rate as the H_2 pressure was

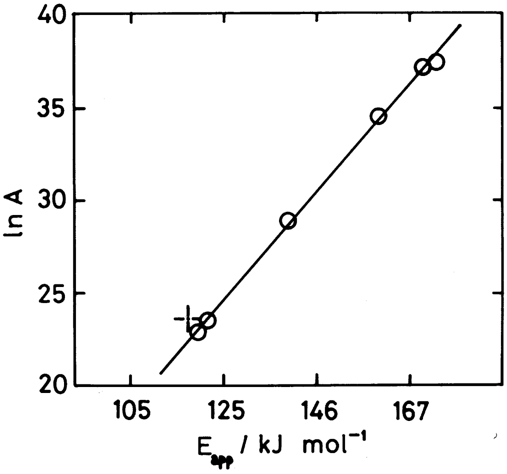

FIG. 7. Hydrogenolysis of *n*-butane on Ru/Al_2O_3 (12): compensation effect shown by Arrhenius parameters derived at various total pressures (or pressure ranges) as indicated by the Power Rate Law: +, “true” Arrhenius parameters given by a Langmuir–Hinshelwood rate expression.

$$\begin{array}{llll}
\text{H}_2\text{ chemisorption}\ldots\ldots\ldots\ldots\ldots & K_\mathrm{H} & H_2 + 2^* \rightleftharpoons 2H^* & (1)\\
\text{Alkane dehydrogenation}\ldots\ldots & K_C & C_mH_n + (n+1-x)^* \rightleftharpoons C_mH_x^* + (n-x)H^* & (2)\\
\text{Rate determining step}\ldots\ldots\ldots & k_1 & C_mH_x^* + H^* \rightarrow C_pH_y^* + C_{m-p}H_{x-y+1}^* & (3)\\
\text{Final fast step}\ldots\ldots\ldots\ldots\ldots\ldots & k_\mathrm{j} & C_pH_y^* + (2p+2-y)H^* \rightarrow C_pH_{2p+2} + (2p+3-y)^* & (4)
\end{array}$$

$$r = \left[k_1K_CP_C(K_\mathrm{H}P_\mathrm{H})^{(n+1-x)/2}\right]\Big/\left[K_CP_C + (K_\mathrm{H}P_\mathrm{H})^{(n-x)/2} + (K_\mathrm{H}P_\mathrm{H})^{(n+1-x)/2}\right]^2$$

SCHEME I

varied, and so this analysis cannot be regarded as completely satisfactory. Nevertheless, it suggested that the classical text-book treatment was inappropriate for complex reactions.

More recently, Shang and Kenney (11) have examined the effect on the rate of hydrogenolysis of ethane over a Ru/Al_2O_3 catalyst produced by altering H_2 and ethane concentrations and temperature; both steady state and transient conditions were used. The results were tested against a number of rate equations found in the literature (not all accurately reproduced), and of these one denoted as ES4 gave the best fits. The dependence of E_app on reactant concentrations was not however revealed, and the lack of numerical (as opposed to purely graphical) data makes reprocessing difficult. The use of the ES4 equation leads to somewhat improbable conclusions, e.g., $K_\mathrm{H} \simeq 10^6 K_\mathrm{E}$ (where K_E is the equilibrium constant for ethane adsorption) and an activation energy for dissociative H_2 chemisorption of 33 kJ mol^{-1}.

A further possible example of how an apparent compensation effect could be generated by an incorrect method of data analysis is provided by the study (16) of the kinetics of thermal desorption from a Ni (111) surface.

We have ourselves conducted detailed examinations of the kinetics of hydrogenolysis of the lower alkanes on Pt/Al_2O_3, $Pt\text{-}Re/Al_2O_3$ (17, 18), and Ru/Al_2O_3 (13, 19–21): full details of the work on the Pt catalysts have not yet been published, so in what follows emphasis is placed on the work with the Ru catalysts.

We have shown (13, 20, 21) that rates as a function of H_2 pressure are well described by a rate expression derived from the familiar and generally accepted mechanism (Scheme I) which supposes that before the alkane can reach it must lose several H atoms, with the consequent formation of multiple carbon–metal bonds. The rate equation to which this mechanism gives rise, denoted ES5B ((11); see also Scheme I) gives a reasonably good (and in some cases excellent) fit with the experimental results, and the use of a standard optimization procedure (13) enables values of the four constants (k_1, K_C, K_H, and x or a) to be evaluated. Of the four, the first is simply a scaling factor, and the last does not sensitively affect the calculated rate. The effect of varying H_2 pressure on rates and on product selectivities has been determined for Ru/Al_2O_3 catalysts having different particle sizes and reduced in various ways, using ethane (13, 21), propane (13, 20), and *n*-butane (13, 19) as reactants; Ru powder has also been examined (21). Changes in reduction procedure produce a wide range of activities (22). In some cases, especially with *n*-butane, results have been obtained at different temperatures, and values of E_t and of the enthalpy changes associated with steps 1 and 2 in the reaction scheme (i.e., $\Delta H_\mathrm{H}^\ominus$ and $\Delta H_C^\ominus$) have been obtained.

A full discussion of the results has already been presented (13, 21) and need not be repeated: for the present purposes, only the salient features need be recapitulated. They are as follows:

(1) Changes in rate produced by alteration in particle size, reduction temperature, and type of alkane are due as much (and sometimes more) to changes in K_C and K_H as to changes in k_1.

(2) Values of E_t are most often in the range 50–65 kJ mol^{-1}, lower values being occasionally met; there is no systematic increase with chain length as is usually found (22) with E_app.

(3) Values of $\Delta H_C^\ominus$ for propane and butane are mainly between 60 and 85 kJ mol^{-1}, but are higher for ethane ($\sim$125 kJ mol^{-1}).

(4) K_H has only a low temperature coefficient; it sometimes passes through a gentle maximum as temperature is increased, but accurate values for $\Delta H_\mathrm{H}^\ominus$ cannot be obtained.

(5) There is no exact correlation between values of k_1 and turnover frequency (TOF) determined under specified conditions, e.g., with a tenfold excess of H_2 over alkane (13, 18–21): this reflects the dominant role that the equilibrium constants play in the rate expression.

It is necessary to emphasize that the values of the constants and of their temperature coefficients depend critically on the form of the rate equation used to analyze the experimental results. Use of the ES4 equation, which does not greatly differ from ES5B (11), gives constants describing ethane hydrogenolysis that are vastly different from those we have found (13). However, we must admit that ES5B is not necessarily the perfect rate expression to model the results, and indeed in some instances it is quite obviously imperfect. Further work is clearly required in this area.

The review of these results leads to the following principal conclusions.

- The magnitudes of E_t and $\Delta H_C^{\ominus}$ are similar; while it may be true, as Patterson and Rooney have suggested (10), that there is greater scope for variation in $\Delta H_{ads}^{\ominus}$ than in $\Delta H^{\ddagger}$, comparatively small changes in the former can produce marked alterations in kinetic behavior.
- Most significantly, K_C increases with temperature and it therefore pertains to an *endothermic* process, i.e., $\Delta H_C^{\ominus}$ is positive.

Quite evidently, the concentration of the activated (i.e., dehydrogenated) alkane increases with temperature as the position of equilibrium moves to the right, in conformity with thermochemical expectation. This system of reactions, unlike the text-book case treated above, is therefore predicated on the establishment of a pre-equilibrium, and in consequence E_t is sometimes *lower* than E_{app}. This simple fact explains why E_{app} for hydrogenolysis reactions on Ru (19) and Pt (17, 22, 23) catalysts assumes such high values, and why it decreases with increasing chain length (19, 22–24); this is because the thermochemistry for dehydrogenation becomes more favorable. With the Pd-catalyzed reactions of neopentane (14), the high values of E_{app} are probably also a consequence of the endothermic formation of a reaction intermediate.

We can show that this state of affairs also leads to values of E_{app} that change with H_2 pressure and to a consequential compensation effect. We first confirm that the experimentally measured rates behave in this way, so the phenomenon is not the consequence of the use of any particular reaction model.

Figure 8 shows values of E_{app} as a function of H_2 pressure for *n*-butane hydrogenolysis on RuEC1 (1% Ru/Al_2O_3) pretreated by oxidation and low-temperature reduction (O/LTR: dataset BH36–38 (13)); the same figure shows the corresponding results for RuEC3 (4% Ru/Al_2O_3, dataset BH21–24), together with the values calculated using the best-fit constants for equation ES5B (13). The agreement is very good except at the highest H_2 pressures, and this confirms the general utility of this equation. Calculation of E_{app} from rates derived directly from E_t and $\Delta H_C^{\ominus}$ ($\Delta H_H^{\ominus}$ being approximated as zero) gives values that increase smoothly with H_2 pressure and which in most cases agree with those deduced from the best-fit constants at each temperature (to <1 kJ mol^{-1}). Values of E_t calculated from k_1 are close to 65 kJ mol^{-1} in each case, i.e., in the middle of the range of E_{app} values and approximating those that would be given by the maximum rates at each temperature (13). Once again, as with the model system, we find E_{app} values that are both greater and less than E_t. It might have been expected from the argument above that the existence of the preequilibrium would imply E_{app} always being greater than E_t, but this is the case only when the size of θ_C determines the rate, viz at H_2 pressures above the maximum. Below the maximum the rate is governed by θ_H, which decreases as the temperature rises, so the usual inequality then prevails. The manner in which E_{app} varies with H_2 pressure is thus determined by the contributions that the θ terms make to the rate, and these are related to reactant pressures via the ES5B equation.

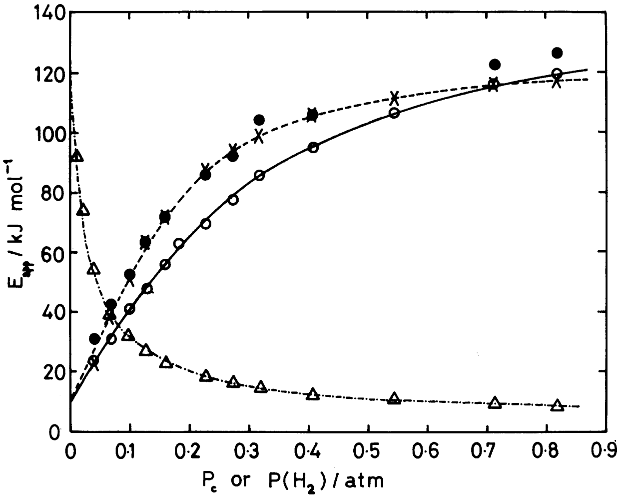

FIG. 8. Hydrogenolysis of *n*-butane on Ru/Al_2O_3 (O/LTR pretreatment) (18): E_{app} as a function of H_2 pressure (*n*-butane pressure, 0.0714 atm). (○) RuEC1, E_{app} derived from measured rates up to 0.5 atm; above this, values are derived from best-fit constants for equation ES5B. (●) RuEC3, E_{app} derived from measured rates. (×) RuEC3, E_{app} derived from best-fit constants for equation ES5B. (△) E_{app} as a function of *n*-butane pressure (P_C): values calculated using best-fit constants for rate data for RuEC3 (H_2 pressure, 0.0714 atm).

We now consider the limiting values of E_{app} at high and low H_2 pressures. Following the earlier arguments we might expect at high H_2 pressure

$$E_{app} = E_t + \Delta H_C^{\ominus} - n_H \Delta H_H^{\ominus}, \qquad [8]$$

and as the H_2 pressure tends to zero

$$E_{app} = E_t + n_H \Delta H_H^{\ominus} - \Delta H_C^{\ominus} \qquad [9]$$

where the order of reaction in H_2 ($\mp n_H$) is, in terms of the ES5B mechanism shown in Scheme 1, given by $n_H = (n + 1 - x)/2$ and the order of reaction in the alkane is ± 1. We may now use these relations to estimate the value of $\Delta H_H^{\ominus}$ for this system. Consider first the high H_2 pressure limit (Eq. [8]): the experimental limiting value of E_{app} will exceed that at an H_2 pressure of 1 atm ($\simeq$125 kJ mol^{-1}, Fig. 8) by a small but unknown amount, yet the sum of E_t and $\Delta H_C^{\ominus}$ alone equals about 132 kJ mol^{-1}. This implies that $\Delta H_H^{\ominus}$ is very small.

From Eq. [9], setting n_{H} equal to $(n + 1 - x)/2$ which has a value of about 1.7 (13) and taking the limiting E_{app} as 10 kJ mol^{-1} (Fig. 8), we obtain $\Delta H_{\mathrm{H}}^{\ominus}$ at about 6 kJ mol^{-1}. Its value as derived using the ES5B equation passes through a broad maximum (13) and cannot be far from zero at the temperature used for obtaining the results in Fig. 8. Bearing in mind the uncertainty of the extrapolation, the agreement is reasonable.

The apparent Arrhenius parameters provide very good compensation plots (Fig. 9), although with RuEC3, where experimental results in the high H_2 pressure range (0.5–0.8 atm) are available, there is a decrease in the slope of the line when E_{app} exceeds E_{t}. The same may be true for RuEC1, but this conclusion relies on parameters calculated with the ES5B equation.

Although we have not carried out extensive measurements on the dependence of rate upon alkane pressure, for the reason explained elsewhere (13), the expected effect is readily calculated from the best-fit constants: this is also shown in Fig. 8, using the best-fit constants for the BH36–BH38 data set. Values of E_{app} decrease with increasing *n*-butane pressure, and where overlap occurs it appears that E_{app} is simply a function of the P_{H}/P_C ratio. Thus as P_C is increased, E_{app} falls to the same limiting value as that when P_C tends to zero, and it rises to ~125 kJ mol^{-1} as P_C tends toward zero.

The dependence of E_{app} on reactant concentrations was first noted in the case of Pt catalysts in 1972 (25), the reaction being ethane hydrogenolysis. Recently the reactions of ethane, propane, and *n*-butane with H_2 on Pt/Al_2O_3 (EUROPT-3) and $Pt\text{-}Re/Al_2O_3$ (EUROPT-4) catalysts have been studied in depth (16, 17), and again it is found that E_{app} generally increases with H_2 pressure: for *n*-butane (Fig. 10) it rises from about 20 to 135 kJ mol^{-1}, the E_{t} (derived from equation ES5B) being 75 kJ mol^{-1}. A very good compensation effect is again observed (see also Fig. 10). Because of the lower activity of Pt compared to that of Ru, these results were obtained in a higher range of temperature (550–625 K), but the limiting values of E_{app} and those of E_{t} are remarkably similar to those reported above for Ru/Al_2O_3 catalysts. $\Delta H_C^{\ominus}$ is evaluated at 78 kJ mol^{-1}, so that the sum of $E_{\mathrm{t}} + \Delta H_C^{\ominus}$ slightly exceeds the high temperature limit for E_{app}.

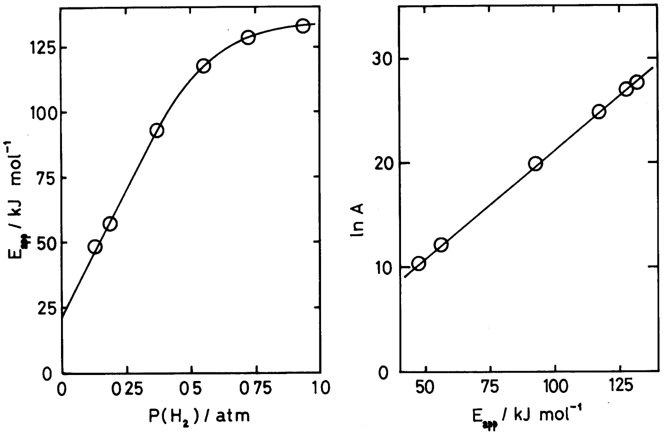

FIG. 10. Hydrogenolysis of *n*-butane on Pt/Al_2O_3 (EUROPT-3): E_{app} as a function of H_2 pressure and the corresponding compensation effect.

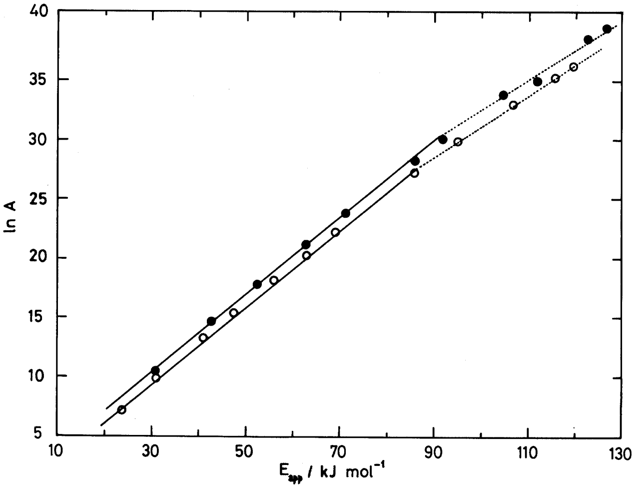

FIG. 9. Values of E_{app} for H_2 pressure variation shown in Fig. 8 as a compensation effect.

We remarked above that the idea of a preequilibrium offered an explanation of the somewhat high values of E_{app} that are observed and of their dependence on alkane chain length: this concept can be given a more quantitative expression. First, we note that the enthalpy change for the gas phase dehydrogenation $\Delta H_{\mathrm{h}}^{\ominus}$ of linear alkanes decreases with increasing chain length. Equating this with the enthalpy change for hydrogenation of the corresponding alkene (1) and reversing the sign, we find for $C_2H_6 \rightarrow C_2H_4$ the value of 137 kJ mol^{-1}; for $C_3H_8 \rightarrow C_3H_6$, 126 kJ mol^{-1}; and for $C_4H_{10} \rightarrow C_4H_8$, cis-2-butene, 120, and trans-2-butene, 115 kJ mol^{-1}. Now if these values reflect the enthalpy change for the dehydrogenation of each alkane to the form that is reactive in hydrogenolysis, we should expect some correlation between $\Delta H_{\mathrm{h}}^{\ominus}$ and $\Delta H_C^{\ominus}$ as determined from the reaction kinetics: exact numerical equality is not of course expected, because amongst other things the reactive form of the alkane may have lost more than two H atoms. Results obtained with Ru/Al_2O_3 catalysts (13) give semi-quantitative confirmation of the expectation ($\Delta H_C^{\ominus}$ (C_2H_6) = 120–130; $\Delta H_C^{\ominus}$ (C_3H_8) $\simeq$ 80; $\Delta H_C^{\ominus}$ ($n\text{-}C_4H_{10}$) = 52–80 kJ mol^{-1}). All values of $\Delta H_C^{\ominus}$ are to some extent uncertain. Second, there is no further significant change in $\Delta H_{\mathrm{h}}^{\ominus}$ as the chain length is increased above four C atoms: values of E_{app} observed (22) in alkane hydrogenolysis on Pt/SiO_2 (EUROPT-1) also attain a limiting minimum value of ~120 kJ mol^{-1}.

It is now possible to understand how the thermochemistry of the interaction of an alkane with a metal catalyst determines the observable parameters of the subsequent hydrogenolysis reaction.

(i) The value of K_C at any temperature controls the concentration of reactive species and is a dominant factor in determining the rate; it increases with temperature because formation of the reactive intermediate is endothermic.

(ii) The ease of dehydrogenation of the reactant alkane $\Delta H_{\mathrm{h}}^{\ominus}$ controls $\Delta H_C^{\ominus}$ and hence E_{app}, but not apparently E_{t} (at least in the case of Ru); the difficulty of surmounting the potential barrier in these reactions does not change systematically with chain length and is probably fixed by the sector of the molecule undergoing change.

(iii) Thus the low reactivity of ethane and its high E_{app} are manifestations respectively of the unfavorable thermochemistry of its dehydrogenation and the rapid increase in the concentration of dehydrogenated reactive species as temperature is increased.

(iv) The kinetic parameters of hydrogenolysis are a consequence of the thermochemical stability of the reactant alkane.

We believe that this is the first time explicit recognition has been given to these correlations. The somewhat small differences between the values of E_{t} and especially of $-\Delta H_C^{\ominus}$ for *n*-butane hydrogenolysis on Ru and Pt catalysts (13, 17) is quite surprising, bearing in mind the great difference between their activities and hence the temperature ranges in which measurements have to be made. We can conclude that to bring the reaction into the region of measurability, it is necessary to employ a temperature such that the constants of the rate expression fall within the appropriate range. This implies that temperature needs to be raised to the point where the entropic terms $-T\Delta S^{\ddagger}$ (corresponding to E_{t}) and $-T\Delta S_C^{\ominus}$ (corresponding to $\Delta H_C^{\ominus}$) achieve sufficiently low values of $\Delta G^{\ddagger}$ and of $\Delta G_C^{\ominus}$ as to permit the reactions to proceed at the required speed. If our method of analyzing the observations is correct, these entropy changes assume an important role in determining the relative activities of different metals.

There is of course competition for surface sites between H atoms released from the alkane and those formed by chemisorption of H_2. Metals that are very active in hydrogenation and which chemisorb H atoms strongly will not tolerate high concentrations of dehydrogenated intermediates; to allow dehydrogenation to proceed as desired, it is necessary for vacant surface sites to exist. Thus the low activity of Pt for hydrogenolysis may be in part due to its ability to chemisorb H atoms strongly.

Since the variation of E_{app} with reactant concentration has been established both for a model system based on the simplest possible mechanism and for alkane hydrogenolysis on both Ru and Pt catalysts, it is worth enquiring whether it is a general phenomenon. To support this idea, we cite results from a study (26) of the hydrolysis of chloromethanes catalyzed by acidic oxides; high conversions are obtained above 673 K, and the reaction obeys the simple Langmuir–Hinshelwood bimolecular rate equation. Rates are proportional to chloromethane concentration and the reaction is inhibited by increasing the water vapor concentration. Variation of the latter between 100 and 450 Torr gives rise to values of E_{app} that increase with increasing concentration (Fig. 11) although the shapes of the curves are such as to suggest that the limiting high- and low-pressure values of E_{app} and hence the enthalpy terms differ from one system to another, except perhaps in the case of the TiO_2/SiO_2 and the amorphous $SiO_2–Al_2O_3$.

Finally, we must consider if variation of the θ terms, whether caused by changes in pressures or in adsorption coefficients, is a full, perfect, and sufficient explanation of the compensation effect in heterogeneous catalysis. Again following Popper, we might disprove the hypothesis if a single example could be found where E_{t} is shown to compensate for changes in ln $\mathbf{A}_{\mathrm{t}}$. The recently reported kinetic study (27) of acid–base catalyzed reactions proceeding on various zeolites may provide the necessary instances; however, the rate equation used contains four adjustable parameters, and no evidence is provided of the quality of fit to the experimental results that it gives. Points in some of the compensation plots are somewhat scattered, and values of E_{t} range widely (between 40 and 200 kJ mol^{-1}). The absence of rate measurements precludes further independent analysis, but the systems deserve deeper study as they may provide a possible genuine compensation effect.

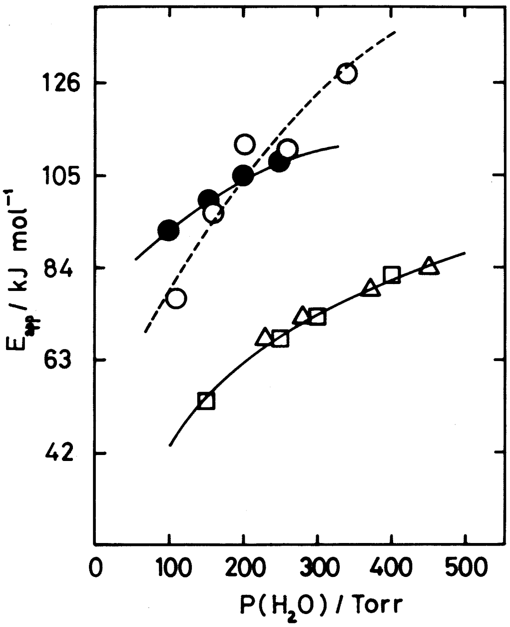

FIG. 11. Gas-phase hydrolysis of CCl_4 on various oxides: E_{app} as a function of H_2O pressure. ○, TiO_2; ●, γ-Al_2O_3; △, amorphous SiO_2–Al_2O_3; and □, TiO_2–SiO_2.

CONCLUSIONS

The purpose of the above analysis of work by ourselves and others was to separate kinetic and thermodynamic factors which together determine the rate of a catalyzed process. Because, as has been well established in basic theory, change in temperature alters the concentrations of adsorbed intermediates, and hence the rate, this effect needs to be eliminated before effects of catalyst composition and structure can be directly studied. In the course of this analysis we have shown that, for a bimolecular reaction proceeding by a Langmuir–Hinshelwood mechanism, the apparent activation energy is a function of reactant gas-phase concentrations, and that limiting values as the pressure of either reactant is raised or lowered are simply related to the true activation energy E_t and the enthalpies of adsorption of the reactants under reaction conditions. The variation in E_{app} leads to an apparent compensation effect, for which however it is not necessary for the enthalpy terms to vary.

With metal-catalyzed reactions of alkanes such as hydrogenolysis and isomerization, the mechanism is of a multistep character, usually involving an initial dehydrogenation, which being an endothermic process results in the concentration of the reactive form of the alkane *increasing* with temperature, so that under some conditions E_{app} may greatly exceed E_t. Persuasive compensation effects again arise when E_{app} is used, simply as a consequence of altering H_2 pressure. It is however unclear as yet whether changes in the enthalpy and entropy terms through alterations made to the composition or structure of the catalyst, or by changing the reactants, will prove to be a universal explication of the compensation effect in heterogeneous catalysis.

Finally, there is one consideration that has not received adequate attention. The undoubted effect that metal particle size has on the rates of alkane transformations has generally been attributed to a geometric or stearic effect, i.e., the absolute necessity for an active center comprising a certain minimum number of atoms, so that the observed rate chiefly reflects the number of such centers available to the reactants (28). Our work on alkane hydrogenolysis over Ru/Al_2O_3 catalysts of various kinds (13, 18–21) has shown that the very substantial changes in activity occurring as a result of altering particle size or surface structure by choice of reduction conditions are associated almost entirely with the equilibrium constants and adsorption enthalpies of the reactants. Similar considerations apply to the very different activities of Ru and of Pt, but here the entropic terms appear to be at least partly responsible.

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