

Alkane Transformations on Supported Platinum Catalysts

4. Kinetics of Hydrogenolysis of Ethane, Propane, and *n*-Butane on Pt/Al₂O₃ (EUROPT-3) and PtRe/Al₂O₃ (EUROPT-4)

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The dependence of the rate of hydrogenolysis of C₂H₆, C₃H₈, and *n*-C₄H₁₀ on 0.3% Pt/Al₂O₃ (AKZO CK303, EUROPT-3) has been determined at several temperatures, using short reaction pulses to minimise deactivation by carbon deposition. Rate maxima, which with C₂H₆ occur at very low H₂ pressures, become broader and move to higher H₂ pressures as the chain-length or temperature increases. Criteria for selecting an appropriate rate expression with which to model the results is discussed in detail: one is selected that is based on the competitive chemisorption of the reactants, that of the alkane requiring the loss of more than one H atom to activate it. For each data set, optimum values of the constants of the rate equation are obtained by computation. Changes in the form of the kinetic curves are described by (i) values of the rate constant k_1 and the equilibrium constant for alkane chemisorption K_A that increase with alkane chain length and with temperature, (ii) values of K_H , the adsorption coefficient for H₂, that decrease with alkane chain-length but are not very temperature-dependent, and (iii) a decreasing degree of the needful alkane dehydrogenation as the chain-length increases. For C₃H₈ and *n*-C₄H₁₀, true activation energies are respectively 82 and 76 kJ mol⁻¹, and enthalpy changes for alkane chemisorption are 88 and 79 kJ mol⁻¹. Apparent activation energies increase with H₂ pressure in consequence of the Temkin equation and show compensation effects. Rate dependences on H₂ pressure were measured at a single temperature using 0.3% Re-0.3% Pt/Al₂O₃ (AKZO CK433, EUROPT-4): rates were faster than for Pt/Al₂O₃, and values of k_1 , K_A , and K_H were larger. Measurements were also made with catalysts partially deactivated by carbon deposition; slower rates were associated with lower values of k_1 and K_A . Changes in product selectivities with operating variables are recorded, but are only significant for PtRe/Al₂O₃, and for *n*-C₄H₁₀ on Pt/Al₂O₃, where at 547 K the extent of internal C–C bond fission decreases as H₂ pressure increases. The difficulty of devising a simple rate expression to embrace all the experimental observations is discussed. © 1997 Academic Press

INTRODUCTION

This paper addresses the problem of elucidating mechanisms of catalysed reactions through measurement of the dependence of rate and product selectivities on reactant

concentrations under a variety of conditions. This approach, which was for many years the *only* means of understanding mechanisms (1–6), fell into desuetude as it came to be appreciated that more than one mechanism can be devised to fit the observed kinetics and as subtler methods for probing the mechanism became available. This neglect is unfortunate, since we believe that *while measurement of kinetics can rarely if ever lead by itself to an unambiguous statement of mechanism, no such statement is acceptable until it is shown to be consistent with the observed kinetics.*

The kinetics of reactions of alkanes with H₂ have been studied over a period of some 60 years (6, 7), and, because of their relevance to petroleum reforming, catalysts containing Pt have been the chief focus of attention. Although hydrogenolysis is a parasitic reaction in the industrial context, its reputation as a structure-sensitive process has been responsible for continuing intensive study of the reactions of simple alkanes with many different metal catalysts (8, 9). The study of alkane transformations tends to fall into one of two categories: (i) reactions of C₅ and higher alkanes, with emphasis on product analysis (10, 11) but with little attention to quantitative kinetics (except by some of our chemical engineering colleagues (12)), and (ii) hydrogenolysis of C₂H₆ which, because of its simplicity, lends itself to rigorous mechanistic analysis. Many papers have been devoted to this seemingly straightforward reaction (6–9, 13, 14).

At present, however, the situation is unsatisfactory in a number of respects. (A) With C₂H₆ hydrogenolysis, kinetic arguments have often been conducted on the basis of the power rate law formalism (6, 13), in which more fundamental rate expressions, for example, those of the Langmuir–Hinshelwood type, are *approximated* to simple “orders of reaction.” Attention is thereby focused on the frequently observed “negative order in H₂” rather than on events occurring at or below the rate maximum which must exist in such cases, as the rate must inevitably fall to zero when no H₂ is present. (B) C₂H₆ is incapable of revealing structure-sensitivity through product selectivity, and although C₃H₈ can do so in theory, it does not always do so in

practice, especially with Pt catalysts. The additional possibilities afforded by a four-carbon chain mean that the reaction of $n\text{-C}_4\text{H}_{10}$ is much more responsive to surface structure, and its study reveals aspects of catalytic behaviour which the lower alkanes fail to do (15, 16). There is however a price to pay, for the tendency for Pt catalysts to deactivate due to the formation of "carbonaceous residues" increases with the number of carbon atoms in the alkane (17, 18). C_2H_6 rarely causes much difficulty, but $n\text{-C}_4\text{H}_{10}$ invariably does: the behaviour of C_3H_8 is intermediate. For this reason it is often impossible to judge the degree of surface contamination present on catalysts described in the published work. (C) This last consideration is of importance in the study of particle size effects, as there is good evidence to show that the tendency to form "carbonaceous residues" is itself particle-size dependent. In this way, spurious effects may easily arise and are likely to be at least partially responsible for the very variable results which a recent review (19) of the literature has revealed. (D) Structure sensitivity and other variables of catalyst composition are often studied under a single arbitrarily chosen set of conditions; it is usually not known whether some alternative choice would lead to the same ranking.

In our present work we have tried to remedy some of these shortcomings by determining the "order in H_2 " for hydrogenolysis of C_2H_6 , C_3H_8 , and $n\text{-C}_4\text{H}_{10}$ at several different temperatures using a Pt/ Al_2O_3 catalyst (EUROPT-3) kept in a substantially clean state by a so-called short reaction pulse technique (18); less extensive measurements have also been made with a clean PtRe/ Al_2O_3 catalyst (EUROPT-4), and with both catalysts in partially deactivated states produced by first performing the reaction with the reactant alkane at high temperature. "Orders" with respect to alkanes have also been determined in a number of cases. We also report on the mathematical modelling of our results using rate equations found in the literature (14, 20) and others which we have devised (21). A preliminary account of this work has already appeared (22).

EXPERIMENTAL

Materials and Procedures

The catalysts used in this work were 0.3 wt% Pt/ Al_2O_3 (CK303 \equiv EUROPT-3) (23) and 0.3 wt% Pt-0.3 wt% Re/ Al_2O_3 (CK433 \equiv EUROPT-4 (23)), both kindly supplied by the AKZO Company. The mean particle sizes of the metallic components of both are about 1 nm (18).

Procedures for the measurement of catalytic behaviour have been described before (15–18, 20) and are briefly as follows. Experiments were performed in a flow system at atmospheric pressure: all results reported here were obtained by the "short reaction pulse" technique (18) in which reactants and N_2 were passed over the catalyst (~ 0.2 g) at known flow rates for only 1 min, after which a sample

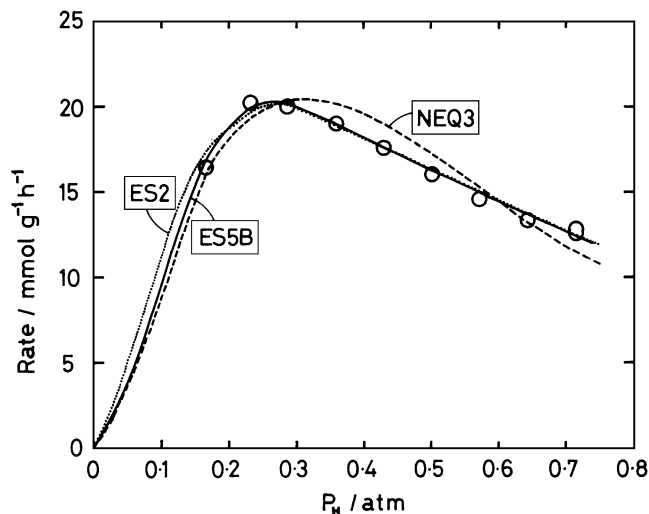


FIG. 1. Dependence of rate of C_3H_8 hydrogenolysis on H_2 pressure at 609 K using clean CK433. Experimental points modeled by rate expressions ES5B (—), ES2 (···), and NEQ3 (---).

was extracted for analysis, and the $\text{H}_2\text{-N}_2$ mixture was then passed for 19 min while the sample was analysed. Flow rates were then adjusted to those desired for the next reaction pulse. This procedure minimised but did not always totally eliminate deactivation due to carbon deposition, which was sometimes noted, especially with $n\text{-C}_4\text{H}_{10}$, after the use of low H_2 :alkane ratios. Experimental scatter was generally low (see Figs. 1, 3, and 4 for "good" sets of results, Fig. 2 for one of the worst): no correction for deactivation within any one series of experiments has been made. Rate dependences on H_2 pressure were determined within

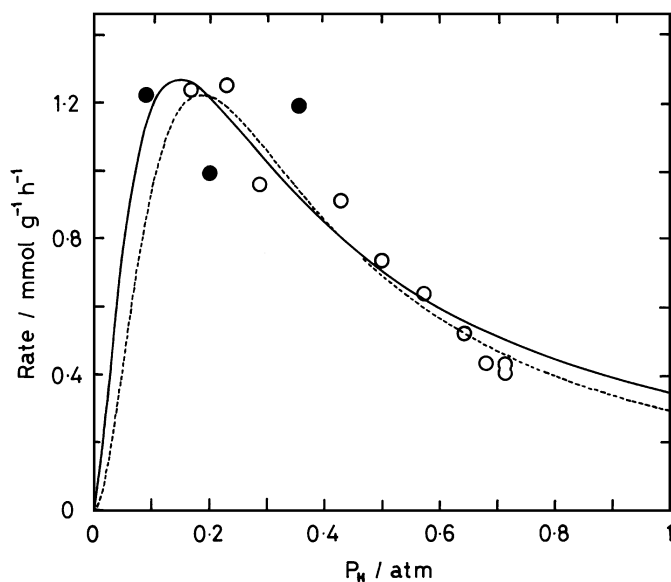


FIG. 2. Dependence of rate of C_3H_8 hydrogenolysis on H_2 pressure at 609 K using clean CK303. Experimental points modeled by equation ES5B: all points included (—), three filled points omitted (---).

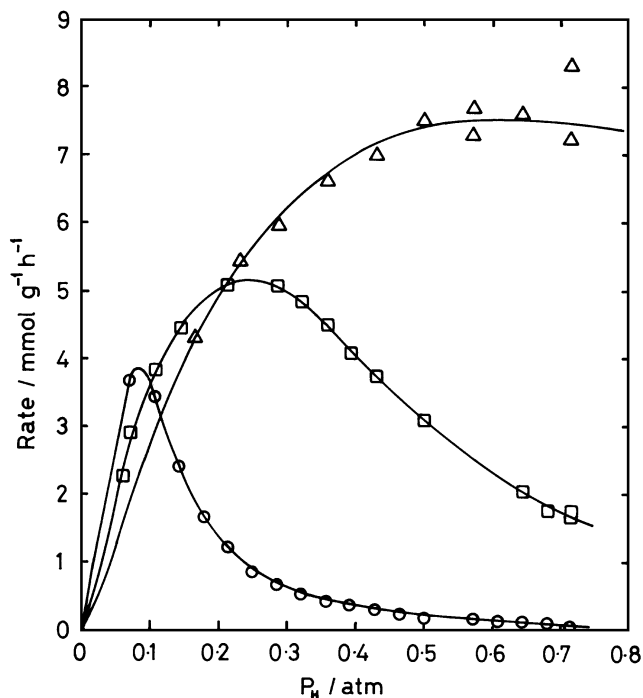


FIG. 3. Dependence of rate of hydrogenolysis on H_2 pressure at 608 ± 1 K using clean CK303: \circ , C_2H_6 ; \square , C_3H_8 ; \triangle , $n-C_4H_{10}$. Curves calculated by equation ES5B.

the range from 0.06 to 0.93 atm with constant alkane pressure of 0.0714 atm, the N_2 concentration being altered in sympathy; for rate dependence on $n-C_4H_{10}$ pressure, this was varied between 0.03 and 0.10 atm with a constant H_2 pressure of 0.714 atm. Simultaneous random change in the pressures of both reactants was attempted, but the results were not satisfactory (see below) and are not reported here. Catalyst samples were pretreated by the "Froment method"

(18) which involves calcination at 673 K before reduction at 763 K. Deliberately deactivated ("coked") samples were treated in H_2 /alkane flows (in $cm^3 \text{ min}^{-1}$, $H_2 : C_2H_6 = 30 : 30$; $H_2 : C_3H_8 = 40 : 10$; $H_2 : n-C_4H_{10} = 100 : 10$) for 2 h at 713 K, flow rates being selected to allow for the different propensities of the alkanes to cause deactivation. Even so, samples, treated with $n-C_4H_{10}$ were substantially more deactivated than those treated with C_3H_8 (see Table 2).

Expression of Rates and Selectivities

Rates of reactant removal are given as $\text{mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$. For the reactions of C_3H_8 and for $n-C_4H_{10}$, product selectivities S_j are defined by the equations

$$S_j = 3c_j / \sum j c_j \quad (j = 1, 2)$$

and

$$S_j = 4c_j / \sum j c_j \quad (j = 1-3),$$

respectively, where j is the number of carbon atoms in the product and c_j is its mol fraction. Thus for C_3H_8

$$S_1 + 2S_2 = 3$$

and for $n-C_4H_{10}$

$$S_1 + 2S_2 + 3S_3 = 4$$

so it is unnecessary to tabulate or plot values of S_1 .

In the Kempling-Anderson treatment (24), the hydrogenolysis of $n-C_4H_{10}$ takes place through a sequence of adsorbed intermediates C_j^* ($j=1-4$), together with a short-circuit from C_4^* to C_2^* to allow for central C-C bond breaking, which occurs with a fractional probability F . The fractions of C_3 or C_2 intermediates that desorb as the

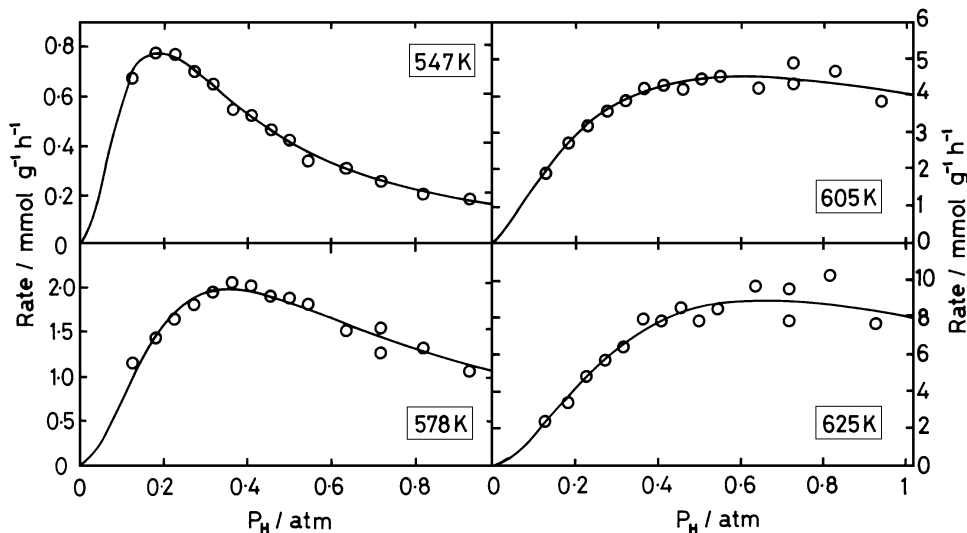


FIG. 4. Dependence of rate $n-C_4H_{10}$ hydrogenolysis on H_2 pressure at various temperatures using clean CK303.

corresponding alkane are given by

$$T_j = k'_j / (k'_j + k_j^*) \quad (j = 2, 3),$$

where k' and k^* are the rate constants for desorption and for further bond-breaking respectively. Steady-state analysis (24) leads to equations which at low conversion simplify to

$$(S_2/T_2) + S_3 = 1 + F$$

$$S_3/(1 - F) = T_3.$$

A similar but simpler scheme describes the reaction of C_3H_8 , where $S_2 \equiv T_2$. The above equations are not soluble unless one either (i) substitutes for T_2 the value of S_2 obtained from the reaction of C_3H_8 under the same conditions, this procedure giving what we have called "true" values of F and T_3 , or (ii) assumes T_2 equals unity. The former procedure does not work well with the PtRe catalyst (18), presumably because the C_2^* intermediates in the two reactions are not equivalent; we therefore use the latter assumption for both catalysts, as it is certainly acceptable for the Pt catalyst, where S_2 from C_3H_8 is *always* close to unity. The resulting values of F and T_3 are distinguished from "true" values by the use of primes.

Data Processing and Mathematical Modelling (20)

Considerations relating to the selection of an appropriate rate equation are discussed below.

Optimum values of the four constants in the chosen equation were obtained by using the Levenburg–Marquardt al-

gorithm (25). The values of one of the constants was altered until the standard deviation was minimised, and the values of all four were then noted. Optimisation was greatly helped by having a distinct maximum in the rate vs H_2 pressure curve, the proper location of which is a critical factor in establishing the values of the constants: when, as with the reaction of C_2H_6 , this occurred at an inaccessibly low pressure, the optimum constants appeared to be somewhat unsatisfactory (see below), so that greater prominence is given to results obtained with C_3H_8 and $n-C_4H_{10}$.

Except where stated to the contrary, curves shown in figures relating rate to reactant pressure are calculated by using equation ES5B (see below) together with the relevant constants taken from Table 2.

RESULTS AND DISCUSSION

Reproducibility and Accuracy of Rate Measurements

Preliminary results on the extent of deactivation for each alkane as a function of temperature, H_2 /alkane ratio, and modus operandi were presented in Part 3 (18). There it was concluded that deactivation increased with alkane chain-length, with temperature, and with decreasing H_2 /alkane ratio. With the short reaction pulse (SRP) method, deactivation was reduced to an acceptable level except when low $H_2/n-C_4H_{10}$ ratios were used at high temperature. Our experience with this technique is summarised in Table 1, which shows the first and the final rates measured at the standard H_2 /alkane ratio for each alkane on clean Pt/ Al_2O_3 and PtRe/ Al_2O_3 catalysts, for each alkane on "coked" Pt/ Al_2O_3 ,

TABLE 1
Changes in Rate and in Selectivity Parameters for *n*-Butane Hydrogenolysis at $P_H = 0.714$ atm during Measurement of Rate Dependence on P_H

Catalyst	State	Alkane	T (K)	${}_1R$	No. of pulses	${}_2R$	% change	${}_1F$	${}_2F$	${}_1T_3$	${}_2T_3$
CK303	Clean	C_2H_6	578	0.0025	18	0.0030	+20	—	—	—	—
			607	0.0844	20	0.104	+23	—	—	—	—
			632	0.551	15	0.542	-1.6	—	—	—	—
			652	0.673	15	0.673	0	—	—	—	—
		C_3H_8	573	0.121	15	0.116	-4.1	—	—	—	—
			587	0.321	15	0.339	+5.6	—	—	—	—
			608	1.68	15	1.76	+4.8	—	—	—	—
			632	5.49	15	5.62	+2.4	—	—	—	—
		$n-C_4H_{10}$	547	0.262	15	0.251	-4.2	0.151	0.146	0.983	0.991
			578	1.54	15	1.26	-18	0.271	0.244	0.988	0.989
			605	4.86	15	4.30	-12	0.280	0.251	0.979	0.979
			625	9.58	15	7.85	-18	0.292	0.209	0.970	0.976
CK303	Coked	C_3H_8	609	0.152	10	0.128	-16	—	—	—	—
CK433	Clean	C_2H_6	630	2.81	20	3.05	+8.5	—	—	—	—
		C_3H_8	609	12.9	10	12.6	-2.3	—	—	—	—
		$n-C_4H_{10}$	609	11.0	12	11.7	+6.4	0.340	0.333	0.806	0.863
CK433	Coked	C_3H_8	609	7.35	10	7.47	+1.2	—	—	—	—

Notes: Pre-subscript 1 signifies the first measurement, and 2 the last; rates (R) in $mmol\ g_{cat}^{-1}\ h^{-1}$.

and for C_3H_8 on "coked" $PtRe/Al_2O_3$. Between these measurements, the H_2 /alkane ratio was varied widely in order to determine the H_2 kinetics, as will be described below: the number of reaction pulses ranged between 10 and 30. With readily measurable rates, i.e., between 0.01 and 10 $mmol\ g_{cat}^{-1}\ h^{-1}$, the percentage change is less than 10% except for $n-C_4H_{10}$ at 625 K on Pt/Al_2O_3 , and for C_3H_8 and $n-C_4H_{10}$ on coked Pt/Al_2O_3 . The extent of random variation will be seen by the scatter of the experimental points around the calculated curves in the figures shown below. In computing best-fit constants for theoretical rate expressions, some discretion was used in neglecting occasional rogue experimental points which differed from their calculated values by much more than the standard deviation; optimisation was then repeated without them. Such points usually occurred following the use of a very low H_2 /alkane ratio, which for this reason was used only towards the end of the series. The extent of the changes in the selectivity parameters F' and T'_3 is also shown in Table 1; except for $n-C_4H_{10}$ on Pt/Al_2O_3 at 625 K, they are small.

The Selection of a Rate Expression and Estimation of Best-Fit Constants

The literature contains quite a number of rate equations that have been devised to describe the hydrogenolysis of alkanes (14, 21), and the first task in analysing the experimental results is to select the one that is considered most satisfactory, on the following grounds. (i) The rate equation should afford a curve that agrees reasonably well with the optimum curve that can be drawn through the experimental points as pressures of H_2 or alkane are varied, over a range of temperatures and catalyst surfaces, for each alkane. (ii) It should be derivable from a logical reaction mechanism that contains within it all probably-occurring unit steps. (iii) It should afford values of the constants estimated by the optimisation that are of reasonable magnitude, and in particular that vary with temperature in the appropriate way. (iv) It should employ the smallest possible number of adjustable parameters: excluding the rate constant k_1 which is simply a scaling factor, we have not used rate expressions containing more than three other adjustable constants, since the more that are used the better the fit obtained will inevitably be. This of course means that some aspects of the mechanism that one might wish to see represented cannot be accommodated.

The mechanism of alkane hydrogenolysis has been discussed on many occasions (6, 9, 14–18, 20). According to one school of thought, the rate-determining step is the reaction of a gaseous alkane molecule with an adsorbed H atom plus some vacant surface (26), but although this qualitatively describes the observed kinetics the full implications have not been explored in a quantitative manner, and so we prefer to stay with the more generally accepted postulate that

Generalized Kinetic Scheme for Alkane Hydrogenolysis

H_2 chemisorption	$H_2 + 2^* \rightleftharpoons 2H^*$	K_H
Alkane dehydrogenation	$C_pH_n + (n + 1 - x)^* \rightleftharpoons C_pH_x^* + (n - x)H^*$	K_C
Rate-determining step	$C_pH_x^* + H^* \rightarrow C_qH_y^* + C_rH_{x-y+1}^*$	k_1
Final fast steps	$C_qH_y^* + (2q - 2 + y)H^* \rightarrow C_qH_{2q+2} + (2q + 3 - y)^*$	

SCHEME 1

the alkane chemisorbs dissociatively in competition with H_2 and later loses a number of H atoms to bring it to the activated state. Thus the positive order in H_2 observed at pressures below the rate maximum reflects the need for H atoms to react with the dehydrogenated species and to split a C–C bond (see Scheme 1), while the negative order above the maximum is due to the need for vacant sites to accommodate the H atoms which the alkane must lose in order to be activated. Loss of more than the minimum number of H atoms needed for this purpose results in strongly bonded and unreactive species having too many C–Pt bonds (17). Thus the various rate equations to be found in the literature (14, 20) follow from this basic scheme, being modified by assumptions concerning the reversibility of the alkane chemisorption, whether H_2 and alkane compete for the same sites, the source of the H atoms used in splitting C–C bonds, and the number of "sites" required to bond the various intermediates.

In what follows, the following symbolism is used.

k_1	rate constant for the rate-determining step
P	pressure of reactant
subscript A	alkane
subscript H	H_2
K_H	equilibrium constant (adsorption coefficient) for H_2
K_A	equilibrium constant for alkane chemisorption, including its partial dehydrogenation if postulated
k_2, κ	other constants
a	number of H_2 molecules released by the alkane
x	the number of H atoms remaining on the alkane: thus $a = (n - x)/2$ where n is the number of H atoms originally present
ΔH_H	enthalpy change for H_2 chemisorption
ΔH_A	enthalpy change for dehydrogenative chemisorption of alkane
E_{app}	apparent activation energy
E_t	true activation energy
θ	surface coverage.

All the experimental data sets have been tested according to 10 rate expressions, beginning with a simple power rate law (21); of these, 8 have been described previously (6, 9, 14) and 2 are new. The latter are coded 2A and NEQ3; both are derived from those formulated by Gudkov, Gucci, and Tétényi (27) whose Route 1 and Route 2 expressions for C_2H_6 hydrogenolysis are as follows:

$$r = k_1 P_A P_H^{0.5} / (P_A + k_2 P_H)^2 \quad [\text{GGT1}]$$

$$r = k_1 P_A P_H^2 / (P_A + k_2 P_H^{2.5})^2 \quad [\text{GGT2}]$$

These assume the reactive intermediates to be respectively C_2H_5 and C_2H_2 , but since there is no good reason for neglecting other species the more general expressions

$$r = k_1 P_A P_H / (P_A + k_2 P_H^\kappa)^2 \quad [2A]$$

and

$$r = k_1 P_A P_H^\kappa / (P_A + k_2 P_H^{\kappa+0.5})^2 \quad [\text{NEQ3}]$$

were considered. Thus the exponent κ in NEQ3 (which is half the number of H atoms assumed to be lost by C_2H_6 in forming the reactive species) should be directly obtained by fitting the experimental results to this expression.

It would be tedious and pointless to rehearse the values of the best-fit constants and standard deviations obtained with all the data sets for each of the 10 rate expressions (21); however, a few general remarks are in order. First, it is surprising how linear the plots of the \ln rate vs $\ln P_H$ are, especially for the reaction of C_2H_6 and for the other alkanes under conditions where there is an extended region of negative reaction order. Examples of such plots obtained for alkane hydrogenolysis on Ru/Al_2O_3 catalysts have recently been shown (20), and since we do not propose to utilise the exponents there is little point in adding further instances. It is also surprising how good the fits obtained with the equation [ES2] originally proposed by Cimino *et al.* (28) are:

$$r = k_1 K_A P_A P_H / (K_A P_A + P_H). \quad [\text{ES2}]$$

However, this derives from a very simple statement of the mechanism in which there is no provision for the dissociative chemisorption of H_2 or for the formation of CH_4 from adsorbed C_2 species other than by molecular H_2 . With some regret, this expression is therefore rejected as being based on a physically unrealistic mechanism.

Although the NEQ3 rate expression gave fits to the experimental points that were in many cases acceptable, there were instances where the best fit was obviously unsatisfactory, and in general smaller standard deviations are obtained using the equation [ES5B] in the terminology of Shang and Kenney (14). This equation, first formulated by Kristyan and Szamosi (29), is shown in Scheme 1, together

with the mechanism from which it stems. We judge it to be acceptable for all four criteria listed above, although we do not claim that it is ideal or perfect or incapable of further refinement. One point of weakness may be the assumption that the reactive intermediate is attached to only one "site," but the concept of "site" is still imprecise. It is for example improbable that the "sites" on which H atoms reside are the same as those to which the dehydrogenated species are bound, although they are usually treated as kinetically equivalent (see, however, Ref. (6)). We therefore consider any further effort to improve on the ES5B rate expression to be premature, but do not deny that (following Popper's dictum) there may be a better one to come. By way of illustration, Fig. 1 shows how one set of results is fitted by the equations [ES2], [NEQ3], and [ES5B]; all are visually acceptable and give almost equally good fits. The form of the results does not at once discriminate between candidate equations, and the selection of the most suitable therefore calls for an element of personal judgment. Standard deviation is not a suitable criterion to use, as it only averages discrepancies over the whole data set and ignores any systematic variation of divergence with the level of the controlled variable.

Although as will be seen the scatter of experimental points about the theoretical curves is in general satisfactory, as noted above it was sometimes thought necessary to eliminate points that were patently incorrect. The effect of removing points that were possibly in error was investigated using a data set for which the scatter of points was somewhat worse than normal (C_3H_8 , clean CK303, 609 K; Fig. 2); these results were obtained before the technique was perfected, and the catalyst may have been slightly poisoned. With Eq. [ES5B], taking out the three indicated points scarcely alters the position of the calculated best-fit curve and only changes k_1 from 13.3 to 12.6, K_A from 6.1 to 5.3, K_H from 3.1 to 2.4, and x from 5.74 to 5.14. The standard deviation improves (from 0.031 to 0.017) although the number of points is decreased. These observations are reassuring in the sense that a modicum of experimental scatter is unlikely to affect the conclusions critically. The amount of scatter tends to increase with temperature and with alkane chain-length.

A number of determinations of orders of reaction in the alkane have been made. The term "order" is used for the manner of rate dependence on reactant pressure, regardless of whether it can be represented by a unique exponent of pressure. In principle it is possible to estimate best-fit constants for any rate expression as easily by changing alkane pressure as by changing H_2 pressure, but because orders are usually positive and close to unity the sensitivity of the calculated curve to the values of the constants is low, and hence reliable values cannot be obtained. We shall however show examples of how well curves based on values of constants obtained by altering H_2 pressure describe the effects of alkane pressure variation.

For this reason also, attempts to economise on the number of measurements made by random simultaneous change in both alkane and H₂ pressures proved unrewarding, since in effect it was only those points obtained by altering the H₂ pressure that contributed significantly to raising the reliability of the computed constants. After several attempts, this procedure was therefore abandoned in favor of the traditional method of keeping one pressure constant while changing the other.

Kinetics of Hydrogenolysis on Clean CK303

(i) *Comparison of the three alkanes at constant temperature.* Figure 3, showing the dependence of rate on H₂ pressure at 608 ± 1 K for each of the alkanes, demonstrates clearly how greatly chain-length affects reaction kinetics. Although it is commonly thought (23, 30) that for Pt the order of reactivity is C₂H₆ < C₃H₈ < *n*-C₄H₁₀, this is so only for H₂ pressures greater than about 0.2 atm; indeed, below 0.05 atm the sequence is reversed. The difference in the behaviours of the three alkanes may be explained in terms of the best-fit constants given by Eq. [ES5B] (Table 2): *k*₁

TABLE 2

Values of the Constants of Equation ES5B

Catalyst	State	Alkane	<i>T</i> (K)	<i>k</i> ₁	<i>K</i> _A	<i>K</i> _H	<i>x</i>	<i>a</i>	Note				
CK303	Clean	C ₂ H ₆	607	33.4	9.7	8.7	1.50	2.25	α				
			632	52.5	16.7	6.6	1.58	2.21					
			652	60.4	18.5	5.7	1.24	2.38					
		C ₃ H ₈	573	17.3	5.5	4.7	3.78	2.22	α				
			590	28.4	9.6	4.3	3.96	2.02					
			608	45.0	17.7	4.5	4.95	1.52					
		<i>n</i> -C ₄ H ₁₀	612	46.8	16.5	4.0	4.35	1.82	β				
			632	89.0	32.3	4.5	4.85	1.57					
			547	8.4	3.4	2.0	6.77	1.61					
	CK433	Clean	C ₂ H ₆	630	171	16.7	28.1	4.50	0.75	γ			
				609	141	53.4	6.5	5.50	1.25				
			<i>n</i> -C ₄ H ₁₀	609	87.7	34.7	2.7	7.50	1.25				
CK303				Coked	C ₃ H ₈	609	4.6	2.2	1.6		5.45	1.27	δ: 38%
					<i>n</i> -C ₄ H ₁₀	650	19.3	7.9	1.9		6.95	1.62	δ: 8%
CK433	Coked	C ₃ H ₈	609	81.7	29.8	3.9	4.87	1.56	δ: 57%				
		<i>n</i> -C ₄ H ₁₀	609	1.3	1.5	0.23	8.59	0.70	δ: 2%				

Notes. (α) These three series were performed at an early stage, to compare the behaviour of the three alkanes at about the same temperature; the results are shown in Fig. 3.

The other series carried out later with clean CK303 were performed in succession, for the sake of best consistency, although temperature was altered randomly. The constants obtained in the α series are interpolated to show the measure of reproducibility attainable.

(β) These series are depicted in Fig. 4.

(γ) See Fig. 1.

(δ) Rate after coking as a percentage of estimated rate before coking (*P*_H = 0.714 atm).

increases less than threefold with increasing chain-length, but *K*_A increases about threefold and *K*_H decreases about fourfold; the value of *a* decreases markedly. The picture that emerges is that the larger the molecule, the greater the ease of its dehydrogenation; i.e., the larger the concentration of reactive species, the fewer are the number of H atoms that must be lost to activate the molecule, and the less able H₂ is to compete for the available surface (i.e., *K*_H and *K*_A show an inverse correlation). The values of *K*_A run parallel to the enthalpy changes for dehydrogenation to alkane, as measured by enthalpy changes for hydrogenation (7, 20).

(ii) *Temperature-dependence of the constants of Eq. [ES5B].* The rate-dependence on H₂ pressure has been determined on clean CK303 for each alkane at four temperatures; the results for *n*-C₄H₁₀ are shown in Fig. 4, from which is clear that the rate-maximum becomes more clearly defined and moves to lower H₂ pressures as the temperature is decreased. Similar behaviour was shown with C₃H₈. Best-fit constants obtained for Eq. [ES5B] are listed in Table 2. With C₃H₈ and *n*-C₄H₁₀, *k*₁ increases with temperature as expected, and so does *K*_A, but *K*_H remains almost constant at respectively ~4.5 and ~1.8, and values of *x* or *a* tend to decrease. The constants for C₂H₆ are however of doubtful reliability because even at the highest temperature the rate maximum occurs at an inconveniently low H₂ pressure and is not clearly delineated (see Fig. 3 for results at 607 K), notwithstanding the good description that the theoretical curve provides over much of the measured range (see also Fig. 3). It has to be appreciated that the optimisation routine can yield constants of great apparent precision, but their worth is conditional upon the accuracy of the experimental rate measurements and on the range of pressure covered. The results for one series with C₂H₆ at 578 K are not included, because rates were very low and derived constants were not as expected. Qualitatively, however, between 607 and 652 K the constants change with temperature much the same as for C₃H₈ and *n*-C₄H₁₀: *K*_H tends to decrease with rising temperature.

Application of the Arrhenius equation to *k*₁ and of the van't Hoff isochore to *K*_A and *K*_H should afford respectively the true activation energy and the enthalpy changes for the chemisorptions. The relevant plots for C₃H₈ and *n*-C₄H₁₀ are shown in Fig. 5 and the values of the energy terms are shown in Table 3. The linearity of plots for C₂H₆ are not as satisfactory, this being an additional reason for doubting the accuracy of the constants: the values of *E*_{*t*} (~56 kJ mol⁻¹) and of Δ*H*_A (~48 kJ mol⁻¹) may therefore be only very approximate.

The observation that values of *K*_A increase with temperature (Table 2), and the positive values of Δ*H*_A derived therefrom (Table 3), signify that the process of alkane activation is not a simple reversible chemisorption, which, being usually exothermic, would be expected to show a decrease in *K*_A with rising temperature and a negative value

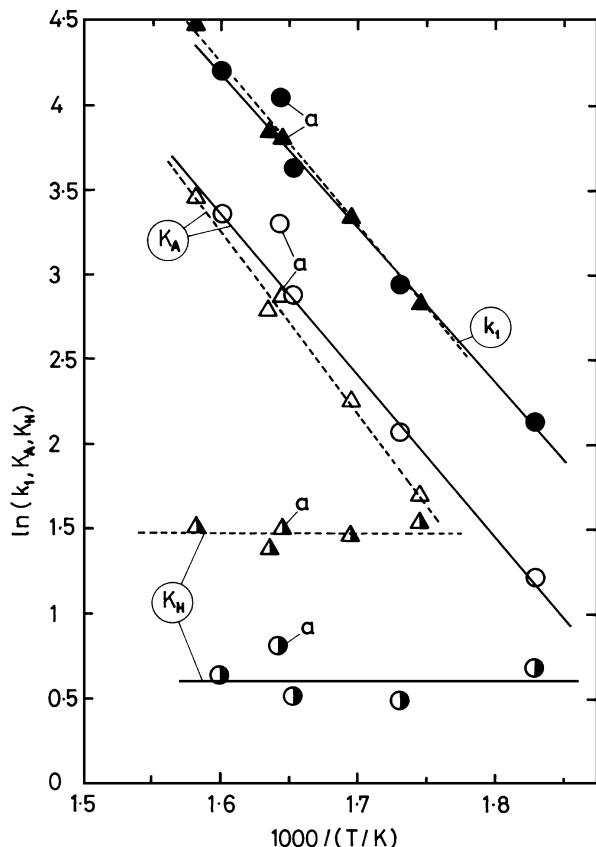


FIG. 5. van't Hoff isochore plots for K_A (Δ , \circ) and K_H (Δ , \bullet), and Arrhenius plot for k_1 (Δ , \bullet), obtained by applying equation ES5B results for hydrogenolysis of C_3H_8 (triangles) and $n-C_4H_{10}$ (circles) on clean CK303. Points labeled α are those so designated in Table 2.

of ΔH_A . We take this as strong supporting evidence for the idea that activation of the alkane requires preliminary dehydrogenation, which because of its endothermic nature will increase in extent as temperature is raised. Values of ΔH_A for both alkanes can only be given as about zero (Fig. 5); the most likely explanation for this is that over most of the range covered θ_H will be close to unity, and the adsorption enthalpy will have fallen to a low value.

For each alkane there is a quite remarkable linear correlation between k_1 and K_A , with points for the experiments on temperature variation already mentioned, for other isolated kinetic series with clean CK303, for coked CK303, and for CK433 all lying around the same line (Fig. 6). The

TABLE 3

True Activation Energies and Enthalpy Changes for Chemisorption of Alkanes

Alkane	E_i (kJ mol ⁻¹)	ΔH_A (kJ mol ⁻¹)
C_3H_8	81.7	88.1
$n-C_4H_{10}$	76.3	78.6

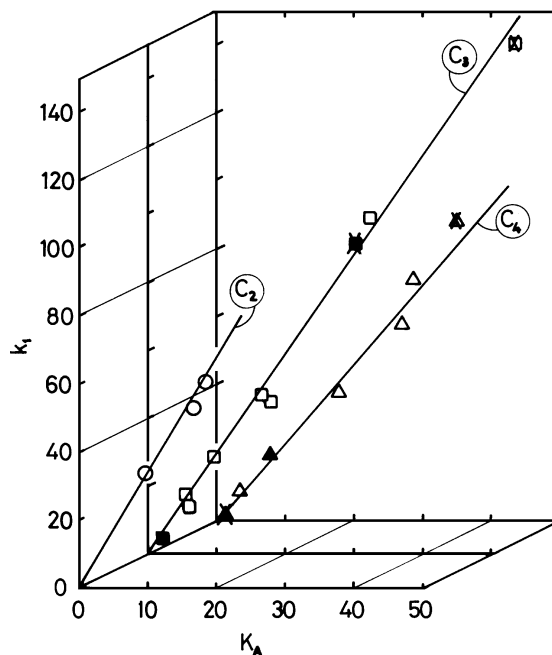


FIG. 6. Correlations between k_1 and K_A for hydrogenolysis of C_2H_6 (circles), C_3H_8 (squares), and $n-C_4H_{10}$ (triangles): open points, CK303; crossed points, CK433; filled points, coked samples.

linearity of the plots is such that the number of variables in the rate expression might be reduced by introducing the subsidiary relation

$$K_A = f k_1,$$

where f is 3.2 for C_2H_6 , 2.9 for C_3H_8 , and 2.3 for $n-C_4H_{10}$. The significance of this relation is unclear: it may bespeak some flaw in the methodology used to derive the rate expression, but the immediate deduction is that the reactivity of each reacting centre (i.e., k_1) is proportional to the number of other such centres that are occupied by adsorbed hydrocarbon species awaiting reaction, this being determined by the value of K_A . The Pt and PtRe particles are probably very small (18), so the number of reacting centres that each can accommodate at any one time will be limited and may not reach double figures. The fact that orders in alkane are usually positive and close to unity (see below) suggests that at low alkane pressures there may be some (or perhaps many) particles with no reacting centres. If the bonding of the dehydrogenated reactive species alters the electronic structure of the particle, then species formed as a result of a change in operating conditions that increases their concentration may experience a more reactive surface. Specifically, the formation of C-M multiple bonds may withdraw electrons from the metal, making it electron-deficient and giving it something of the character of Ir. A similar relation between k_1 and K_A has been reported for Ru/Al₂O₃ catalysts (20).

(iii) *Dependence of apparent activation energy of H₂ pressure.* We have previously noted (31) that for hydrogenolysis of alkanes the apparent activation energy E_{app} will vary the H₂ pressure used because of the change in the form of rate dependence on H₂ pressure with temperature, as shown most directly by the movement of the rate maximum (see Fig. 4). Examples of Arrhenius plots obtained at different H₂ pressures are shown in Fig. 7. This variation is not of course dependent on any particular mechanism or rate equation; values of E_{app} derived from measured rates increase with H₂ pressure as shown for C₃H₈ and *n*-C₄H₁₀ in Fig. 8. However, the use of Eq. [ES5B] with the constants given in Table 2 also permits us to model these results and it is found (Fig. 8) that the calculated curve neatly fits the experimental points: this is further confirmation that this rate expression is broadly satisfactory.

We have previously suggested (31) that the dependence of E_{app} on H₂ pressure can be explained by the Temkin equation (32) which describes the relationship between E_{app} and E_t . Consider first the bimolecular reaction between M and N , where both are reversibly adsorbed without dissociation. Then according to Temkin

$$E_{app} = E_t + n_M \Delta H_M + n_N \Delta H_N,$$

where the n 's are the experimental orders of reaction. The logic underlying this expression may be shown by examining two limiting conditions: (i) Where θ_M and θ_N are both very small, either because their adsorption enthalpies are low or their pressures are very low, $n_M = n_N = 1$. On raising the temperature both θ_M and θ_N will decrease at a rate de-

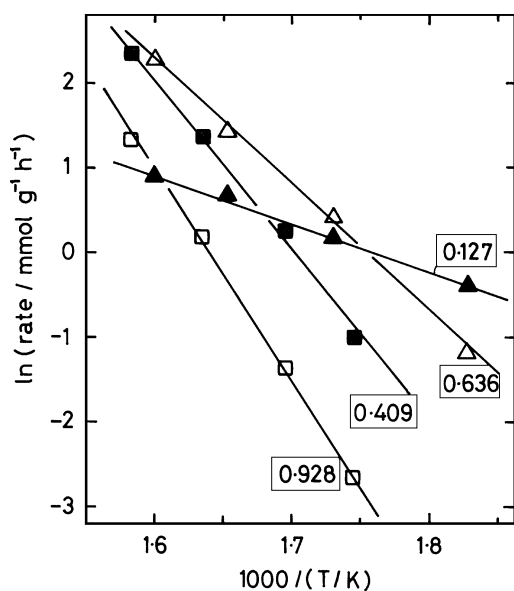


FIG. 7. Arrhenius plots of rates of hydrogenolysis of C₃H₈ (squares) and *n*-C₄H₁₀ (triangles) on clean CK303 measured at various (indicated) H₂ pressures.

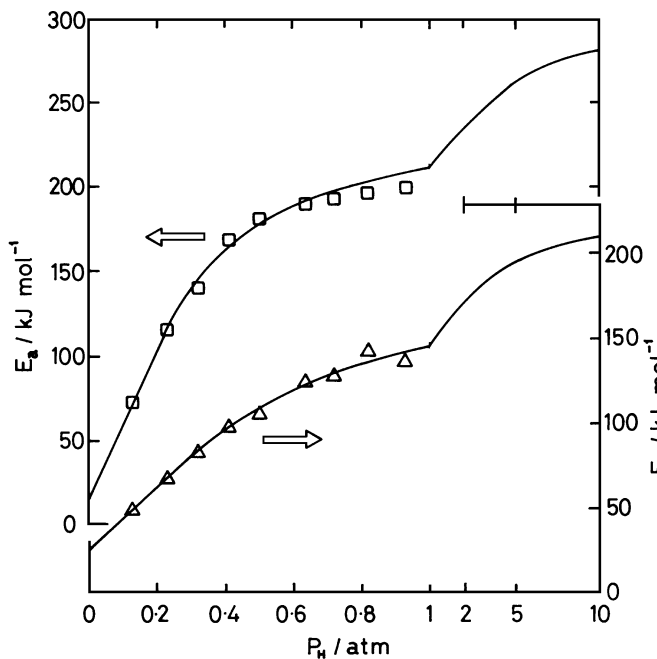


FIG. 8. Plots of E_{app} vs H₂ pressure for hydrogenolysis of C₃H₈ (squares) and of *n*-C₄H₁₀ (triangles): curves are obtained by the use of equation ES5B and the constants shown in Table 2.

termined by their adsorption enthalpies, so that the values of *both* will be added to the experimental activation energy E_{app} in order to give E_t . (ii) If $\theta_M \approx 1$ and θ_N is small, for whatever reason, n_M will be about zero and n_N will be about unity. As temperature is raised, θ_N will decrease but θ_M will be lowered only slowly, so that only ΔH_N needs to be added to E_{app} to give E_t . Equations describing these and other situations, can be found in standard kinetics texts (33, 34). It therefore follows that E_{app} will be a function both of P_M and P_N , as they affect respectively θ_M and θ_N , and that their adsorption enthalpies under reaction conditions should be derivable from the appropriate experiments. The Temkin equation thus provides a basis for understanding the results seen in Fig. 8. Adapting it to our present system, the limiting value of E_{app} as H₂ pressure is increased, where we have high θ_H and low θ_A , will be given by

$$E_{app} = E_t + n_A \Delta H_A,$$

n_A being the order in alkene because θ_H is not then expected to change rapidly with temperature, while the limiting value as H₂ pressure tends to zero, where θ_H becomes very small and $\theta_A > \theta_H$, is given by

$$E_{app} = E_t + n_H \Delta H_H,$$

n_H being the low-pressure order in H₂, which equates to $(a + 1/2)$. In this latter equation there is no term in ΔH_A because, since θ_A exceeds θ_H , the order in alkane (n_A) will approach zero under these conditions. Its value in a defined

pressure range clearly depends on the constant values of P_H employed (see Fig. 11). The precise interpretation of the Temkin equation when applied to a complex reaction such as alkane hydrogenolysis is not a straightforward matter, but further aspects of the problem are discussed in another paper (31). It is of interest to note that, because of the endothermic nature of the alkane dehydrogenation step, θ_A increases with temperature, and therefore over much of the H_2 pressure range E_{app} is greater than E_b , which cannot be the case with simple reversible chemisorption.

Application of these equations to the results shown in Fig. 8 presents two problems:

(i) While for $n\text{-C}_4\text{H}_{10}$ the upper limiting value of E_{app} (146 kJ mol^{-1} at $P_H = 1 \text{ atm}$) agrees well with the sum of $(E_t + \Delta H_A)$ (155 kJ mol^{-1} from Table 3), taking n_A to be unity, for C_3H_8 E_{app} at 1 atm ($200\text{--}210 \text{ kJ mol}^{-1}$) considerably exceeds ($E_t + \Delta H_A = 170 \text{ kJ mol}^{-1}$). It is possible but unlikely that ΔH_A for C_3H_8 is underestimated; the van't Hoff isochore plot (Fig. 5) is good. It is more probably a consequence of the difference in the orders with respect of H_2 for the two reactions in the high pressure region; reference to Fig. 3 shows that the order is much more negative for C_3H_8 than for $n\text{-C}_4\text{H}_{10}$, because of the higher K_H (Table 2), values at 609 K being respectively -1.5 and ~ 0 . Raising the temperature will therefore result in a more rapid decrease in inhibition of the rate by P_H in the case of C_3H_8 and E_{app} will therefore be greater than $(E_t + \Delta H_A)$.

(ii) The second problem concerns the evaluation of $-\Delta H_A$ from the expression for the limiting values of E_{app} at low P_H . From Fig. 8, these are about 15 and 25 kJ mol^{-1} for C_3H_8 and $n\text{-C}_4\text{H}_{10}$, respectively; taking the values of a from Table 2 as 1.8 and 1.4 respectively, this gives a consistent value of $-\Delta H_H \approx 37 \text{ kJ mol}^{-1}$. It has been argued previously (20) when a similar situation arose with reactions on $\text{Ru}/\text{Al}_2\text{O}_3$ that this value pertains to zero coverage by H atoms, for which it is of the correct order of magnitude, whereas the values of about zero derived from the temperature dependence of K_H refer to the higher ranges of coverage from which it is derived.

We may note incidentally that the values for E_{app} at $P_H = 0.714 \text{ atm}$, i.e., for H_2 /alkane ratios of 10:1, agree very closely with those obtained from the thermal cycling experiments described in Part 3 (18).

Alteration in the value of E_{app} by changing H_2 pressure produces corresponding changes in the apparent pre-exponential factor $\ln A_{app}$, and for both reactions these show very precise compensation effects (Fig. 9). The slopes have similar values, corresponding to isokinetic temperatures of 617 K for C_3H_8 and 587 K for $n\text{-C}_4\text{H}_{10}$. We may speculate that differences in surface concentrations of reactants, whether produced by gas-phase pressure or by adsorption coefficient, may be a frequent explanation of compensation (31).

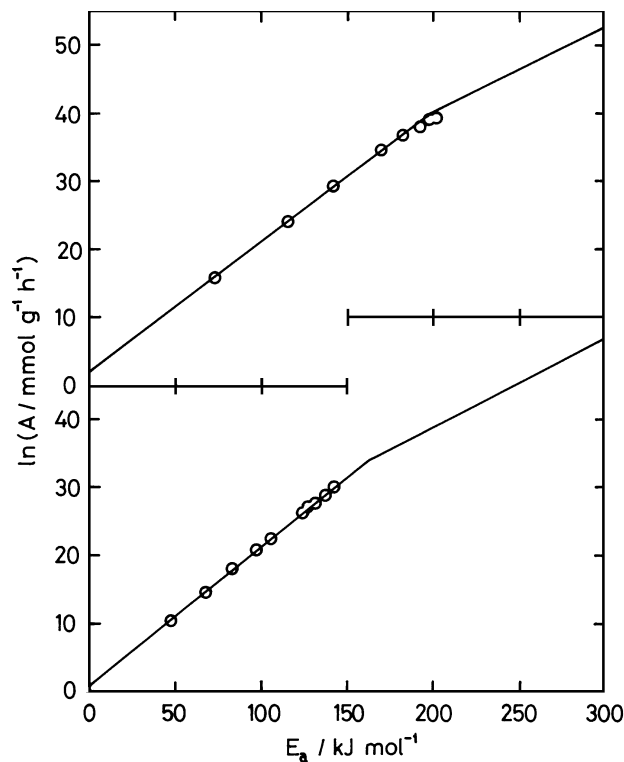


FIG. 9. Compensation plots obtained from the values of E_{app} shown in Fig. 8 and the corresponding values of $\ln A_{app}$ (upper part, C_3H_8 ; lower part, $n\text{-C}_4\text{H}_{10}$).

(iv) *Effect of H_2 pressure on product selectivities.* All the foregoing considerations are based on rates of reactant removal; we now consider what further information can be obtained from the way in which product selectivities are affected by changing H_2 pressure.

The situation with the reaction of C_3H_8 is very simple and easily summarised. S_2 is independent of H_2 pressure over the entire measured range and is essentially independent of temperature; all values lie between 0.977 and 0.990, and it would be foolish to seek any systematic variation within this narrow range. Clearly it is much easier to convert the C_2 intermediate into gaseous C_2H_6 than into two C_1 species.

There are however detectable effects in the reaction of $n\text{-C}_4\text{H}_{10}$. Figure 10 shows how the Kempling-Anderson parameters F' and T'_3 and the isomerisation selectivity S_i vary with H_2 pressure on clean CK303 at 547 and 625 K. At the higher temperature F' and T'_3 both increase slightly and S_i decreases; at the lower temperature F' decreases significantly ($P_H^{-0.77}$ between 0.2 and 0.93 atm), as does S_i , but T'_3 , which is 0.98–0.99, rises only a little. At intervening temperatures (578 and 605 K) the results have an intermediate character, such that at 605 K selectivities are not affected by changing H_2 pressure. The behaviour at low temperature contrasts with that shown by $\text{Ru}/\text{Al}_2\text{O}_3$ in a lower temperature range (20), where F is almost constant and T_3 is either

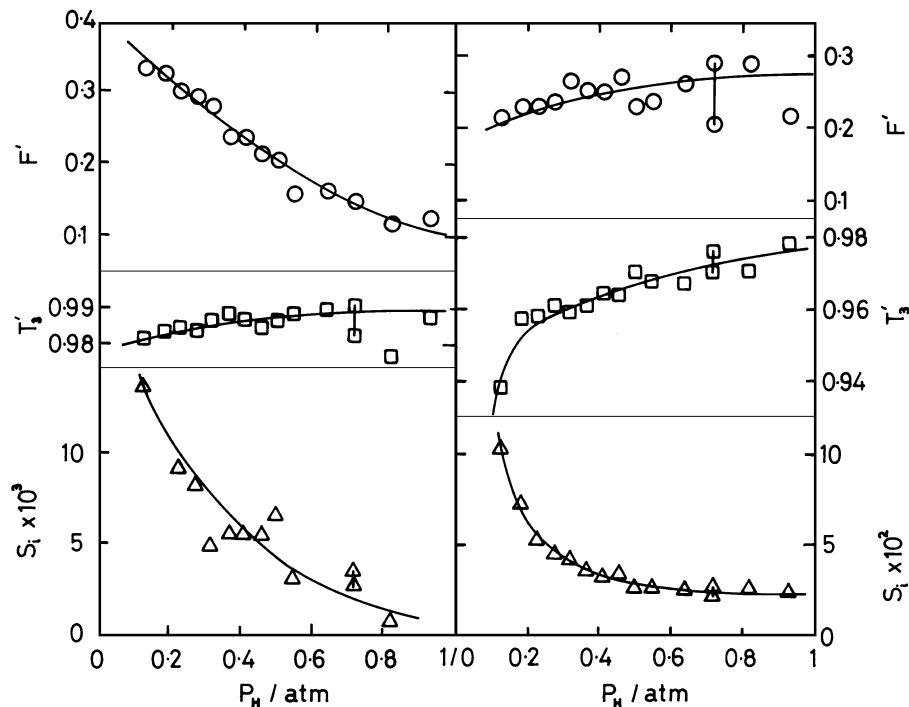


FIG. 10. Dependence of selectivity parameters F' , T_3' , and S_1 for n - C_4H_{10} hydrogenolysis on clean CK303: left side, 547 K; right side, 625 K.

also constant (when θ_H appears to be high and constant) or increases with increasing H_2 pressure (where θ_H is a positive function of the H_2 pressure). Possible explanations for this behaviour will be considered below.

(v) *Orders of reaction in alkane.* Orders of reaction by the usual method of keeping the H_2 pressure fixed were obtained only for n - C_4H_{10} (609 K, $P_H = 0.714$ atm). There was some scatter in the rate measurements, but the rate increased with alkane pressure approximately as expected from the form of the ES5B equation with the appropriate constants taken from Table 2. F' and T_3' parameters were independent of alkane pressure at ~ 0.25 and ~ 0.97 , respectively, in agreement with the results shown in Fig. 10B.

(vi) *Three-dimensional plots.* Figure 11 shows three-dimensional plots (i.e., rates as a function of H_2 and of alkane pressure) for the three alkanes at ~ 609 K on clean CK303, corresponding to the plots of rate vs H_2 pressure shown in Fig. 3. They are obtained by solving the ES5B equation at 0.05 atm intervals, using the sets of constants shown in Table 2. They demonstrate vividly (i) how the H_2 pressure for the rate maximum shifts to higher values as the alkane pressure is increased; (ii) how location of the maximum moves with alkane chain-length; and (iii) how the order in alkane is expected to change with H_2 pressure. Such plots are of value in suggesting critical areas for experimental verification, although substantial areas of the reaction would require the use of superatmospheric pressure for their exploration.

Kinetics of Hydrogenolysis on Clean CK433

More limited measurements were made than with CK303 and in particular no systematic study of the effect of temperature on H_2 kinetics was carried out. However, rate dependences on H_2 pressure were determined at a single temperature (609 K for C_3H_8 and n - C_4H_{10} ; 630 K for C_3H_6): rates were generally faster than for CK303, by factors of about 1.5 to 4, but H_2 pressures at which rates were maximal were about the same. Table 2 gives the optimum values of the constants obtained by fitting the experimental points to equation ES5B. The inclusion of Re in the Pt catalyst produces regular changes to the values of the constants: for each alkane k_1 is increased two- to threefold, as expected, and for C_3H_8 and n - C_4H_8 (but not C_2H_6) K_A is increased by similar factors. For these alkanes, therefore, the proportionality between k_1 and K_A is maintained (Fig. 5). K_H is increased, mostly notably with C_2H_6 , and reactive intermediates are noticeably less dehydrogenated. The usual caveat has to be entered concerning the reliability of the constants for C_2H_6 .

The variation of product selectivities with H_2 pressure is also quite different with CK433. For the C_3H_8 reaction at 609 K, S_2 is much lower than for CK303 (0.73 at $P_H = 0.714$ atm) and decreases with increasing H_2 pressure. The value of S_2 of 0.73 is lower than those quoted previously (18), but probably continues the trend noted there of an inverse correlation between rate and S_2 . For the reaction of n - C_4H_{10} at 609 K, F' is constant at 0.33 but

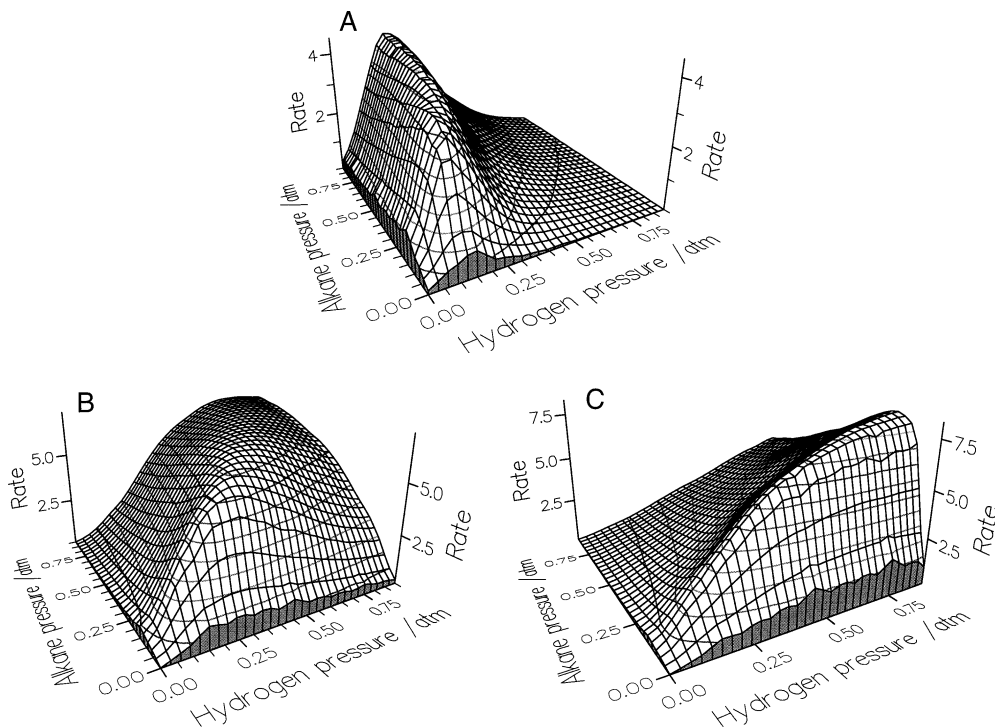


FIG. 11. Three-dimensional plots for the hydrogenolysis of (A) C₂H₆, (B) C₃H₈, and (C) n-C₄H₁₀ on clean CK303 at 608 ± 1 K, calculated using the constants of equation ES5B shown in Table 2.

T'_3 decreases with increasing H₂ pressure, as does also S_i (Fig. 12).

Rate dependence on n-C₄H₁₀ pressure was studied at 609 K with constant H₂ pressure (0.714 atm): the rates, which are closely reproducible (Fig. 13), are well modelled

by Eq. [ES5B] with the constants shown for these conditions in Table 2, save that the value for k_1 is larger by 1.15 to allow for a change in activity. Increasing alkane pressure has the same effect on F' and T'_3 as decreasing H₂ pressure does.

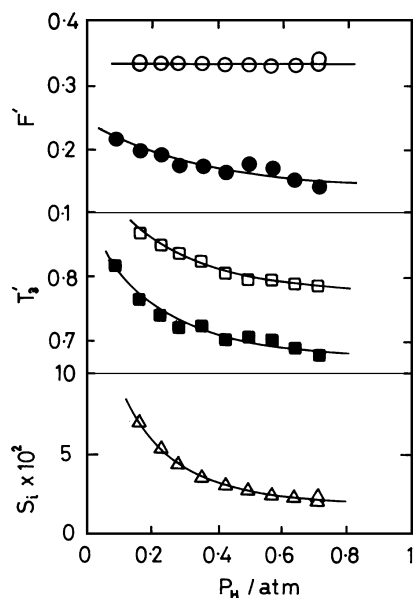


FIG. 12. Dependence of selectivity parameters F' , T'_3 , and S_i for n-C₄H₁₀ hydrogenolysis of CK433 (open points, clean; filled points, coked) at 609 K.

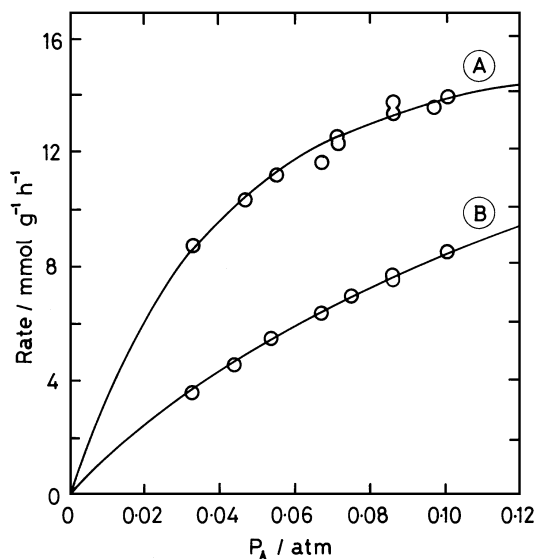


FIG. 13. Dependence of rate of n-C₄H₁₀ hydrogenolysis of n-C₄H₁₀ pressure: A, clean CK433 at 609 K; B, coked CK303 at 650 K. Curves calculated by equation ES5B with the constants given in Table 2, but with k_1 multiplied respectively by 1.15 and 0.67.

Effect of Carbon Deposition on CK303 and CK433

Samples of three catalysts were partially deactivated by carbon deposition as described in the Experimental Section, and rate dependences on H_2 pressure were determined for the hydrogenolysis of C_3H_8 at 609 K and of $n-C_4H_{10}$ at 609 or 650 K. Results for the $n-C_4H_{10}$ reactions could not be obtained at the same temperature because of the low activity of the coked CK303 sample (92% deactivated). In the case of C_3H_8 the general shapes of the curves describing the dependence were not much changed, although the position of the rate maximum was lowered by coking CK303 (62% deactivated) from 0.25–0.3 atm to about 0.15 atm. With $n-C_4H_{10}$ the coked CK303 sample showed a clearer rate maximum (at $P_H \approx 0.3$ atm) than the clean sample, and the coked CK433 showed a more positive order in H_2 in the low pressure region that did the clean catalyst. These changes are broadly consistent with the optimum values of the constants obtained by fitting equation ES5B to the experimental points given in Table 2. The principal effects are to lower k_1 and K_A proportionately (see Fig. 6), and usually also to reduce K_H , more noticeably in the case of the $n-C_4H_{10}$ reaction on CK433, where the sample was 98% deactivated. The value of x is increased following carbon deposition in two of the four cases.

Carbon deposition on CK303 has no effect on S_2 for the C_3H_8 reaction 609 K, its value remaining at 0.982 ± 0.05 . Results for the $n-C_4H_{10}$ reactions could not be obtained at the same temperature because of the low activity of the deactivated sample, but at 650 K T'_3 increased slightly with increasing H_2 pressure, F' decreased somewhat (although on clean CK303 at 625 K it increased, Fig. 10) and S_1 also decreased (Fig. 14). Carbon deposition on CK433 lowered T'_3 and F' , while no isomerisation at all was seen on the coked sample.

Orders of reaction in $n-C_4H_{10}$ were determined on coked CK303 at 650 K and on coked CK433 at 609 K: results for the former system are also shown in Fig. 12, and they are well described by the [ES5B] equation with the relevant constants in Table 2 (k_1 is reduced to 12.9 to allow for a change in activity). Values of F' and of T'_3 are independent of $n-C_4H_{10}$ pressure.

Hydrogenolysis of $n-C_4H_{10}$ on Pt Single Crystal Surfaces

A number of useful studies have appeared in recent years, the aims of which have been to correlate the geometric features shown by various low Miller index planes of single crystals with catalytic behaviour and hence to identify the sites on small metal particles responsible for observed reaction characteristics. The most recent such study (35) concerns Pt (100) and (111) surfaces and reports the effects of temperature and of H_2 pressure on rates and product selectivities shown in $n-C_4H_{10}$ hydrogenolysis. Unfortunately, the somewhat large scatter shown in the selectivity mea-

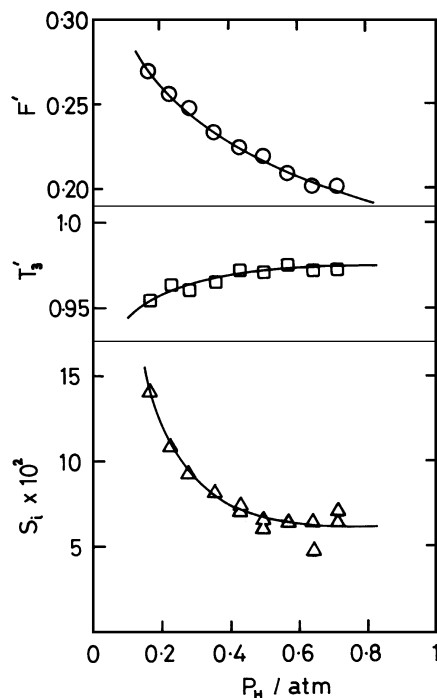


FIG. 14. Dependence of selectivity parameters F' , T'_3 , and S_1 for $n-C_4H_{10}$ hydrogenolysis on coked CK303 at 650 K.

surements precludes close comparison with our own results; however, while isomerisation selectivities were found to be low, in agreement with our findings with Pt/ Al_2O_3 catalysts (18), very high CH_4 selectivities were observed which we have not seen. Furthermore, there are serious discrepancies between this recent work and that of Davis *et al.* (36) who found dehydrogenation to be the main reaction and isomerisation rates faster than those of hydrogenolysis. Until these disagreements are resolved, it is difficult to employ the results of single crystal studies to help understand the behaviour of supported Pt catalysts.

CONCLUSIONS

We believe that a detailed kinetic study of the kind described above affords a deeper understanding of the factors determining catalytic activity and of the reactivity of hydrocarbon molecules in catalysed reactions. While the process of identifying a suitable and tractable rate equation undoubtedly involves some oversimplifications, we feel that the procedure we have adopted is broadly satisfactory and achieves results of real significance. The essential dilemma encountered in mathematical modelling lies in the perceived need to embrace all likely facets of the mechanism, without enlarging the rate expression so much as to make agreement with the observations inevitable. Thus for example we have to assume the existence of a single reactive form of the alkane, while unrestricted optimisation informs

us that the number of residue H atoms x is non-integral, clearly suggesting that two or more such intermediates, differing in the extent of dehydrogenation, participate in the reaction. Furthermore, the mechanism (see Scheme 1) supposes only one kind of site, conveniently represented by an asterisk, while it is very likely that different sites are involved in bonding H atoms and hydrocarbon species, notwithstanding the apparent competition between the two reactants. The asterisk is in fact little more than an easy way of balancing equations and disguising ignorance; indeed, it is not easy to improve on statements made (see Appendix III of Ref. 7) on the subject in 1962.

It therefore appears that further refinement of the process of mechanistic description and its subsequent analysis is an urgent requirement for any progress in understanding the catalysis of hydrocarbon transformations on metal catalysts. Such reactions are a suitable testing basis for the methodology of kinetic analysis, and they will stretch the theoretical and experimental competence of future workers in the field.

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REFERENCES

- Rideal, E. K., "Concepts in Catalysis." Academic Press, London, 1968.
- Hinshelwood, C. N., "Kinetics of Chemical Change." Clarendon, Oxford, 1940.
- Schwab, G.-M., "Catalysis from the Standpoint of Chemical Kinetics." Macmillan, London, 1937.
- Jungers, J. C., and Balacéanu, J. C., *Rev. Inst. Franç. Pétrole* **10**, 30 (1955).
- Hougen, O. A., and Watson, K. M., "Chemical Process Principles," Wiley, New York, 1948.
- Boudart, M., and Djéga-Mariadassou, G., "The Kinetics of Heterogeneous Catalytic Reactions." Princeton Univ. Press, Princeton, NJ, 1984.
- Bond, G. C., "Catalysis by Metals." Academic Press, London, 1962.
- Bond, G. C., *Chem. Soc. Rev.* **20**, 441 (1991).
- Sinfelt, J. H., *Catal. Rev.-Sci Eng* **9**, 147 (1974).
- Paál, Z., Groeneweg, H., and Paál-Lukács, J., *J. Chem. Soc. Faraday Trans. 1* **86**, 2789 (1990).
- Burch, R., and Paál, Z., *Appl. Catal. A: Gen.* **114**, 9 (1994).
- Van Trimont, P. A., Marin, G. B., and Froment, G. F., *Appl. Catal.* **24**, 53 (1986).
- Goddard, S. A., Amiridis, M. D., Rekoske, J. E., Cardona-Martinez, N., and Dumesic, J. A., *J. Catal.* **117**, 155 (1989).
- Shang, S. K., and Kenney, C. N., *J. Catal.* **134**, 134 (1992).
- Bond, G. C., and Lou, H., *J. Catal.* **137**, 462 (1992).
- Bond, G. C., and Lou, H., *J. Catal.* **142**, 512 (1993).
- Bond, G. C., and Gelsthorpe, M. R., *J. Chem. Soc., Faraday Trans. 1* **85**, 3767 (1989).
- Bond, G. C., and Cunningham, R. H., *J. Catal.* **163**, 328 (1996).
- Che, M., and Bennett, C. O., *Adv. Catal.* **36**, 55 (1989).
- Bond, G. C., and Slaa, J. C., *J. Molec. Catal.* **98**, 81 (1995).
- Cunningham, R. H., Ph.D. thesis. Brunel University, 1992.
- Bond, G. C., Cunningham, R. H., and Short, E. L., in "Proceedings 10th International Congress on Catalysis, Budapest, 1992" (L. Guzzi, F. Solymosi, and P. Tétényi, Eds.), Vol. **A**, p. 849, Akadémiai Kiadó, Budapest, 1993.
- Bond, G. C., *J. Molec. Catal.* **81**, 99 (1993).
- Kempling, J. C., and Anderson, R. B., *Ind. Eng. Chem. Process Des. Dev.* **11**, 146 (1972).
- Twizell, E. H., "Numerical Methods with Applications in the Biomedical Sciences." Ellis Horwood, Chichester, 1988.
- Frennet, A., in "Hydrogen Effects in Catalysis" (Z. Paál and P. G. Menon, Eds.), p. 399. Dekker, New York, 1989.
- Gudkov, B. S., Guzzi, L., and Tétényi, P., *J. Catal.* **74**, 207 (1982).
- Cimino, A., Boudart, M., and Taylor, H. S., *J. Phys. Chem.* **58**, 796 (1954).
- Kristyan, S., and Szamosi, J., *J. Chem. Soc. Faraday Trans. 1* **80**, 1645 (1984); **84**, 917 (1988).
- Bond, G. C., Garin, F., and Maire, G., *Appl. Catal.* **41**, 313 (1988).
- Bond, G. C., Hooper, A. D., Slaa, J. C., and Taylor, A. O., *J. Catal.* **163**, 319 (1996).
- Temkin, M., *Acta Physicochim. URSS* **3**, 312 (1935).
- Laidler, K. J., "Chemical Kinetics," 3rd ed., Chap. 7. Harper and Row, New York, 1987.
- van Santen, R. A., and Niemantsverdriet, J. W., "Chemical Kinetics and Catalysis," Chap. 6. Plenum, New York/London, 1995.
- Anderson, S. L., Szanyi, J., Paffett, M. J., and Datye, A. K., *J. Catal.* **159**, 23 (1996).
- Davis, S. M., Zaera, F., and Somorjai, G. A., *J. Am. Chem. Soc.* **104**, 7453 (1982).