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Catalysis in a Kinetic Perspective

First Berzelius Lecture in Catalysis

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Catalysis is a rate phenomenon, its very essence is an increase in rate, caused by the presence of the catalyst. In most definitions of catalysis this central fact is recognised.

One would then expect that a study of the rates of catalytic reactions – catalytic kinetics – should be an awarding exercise. Until the 1950's this idea was amply reflected in the catalytic literature. The mechanisms of such industrially important catalytic reactions as ammonia synthesis, sulphur dioxide oxidation and production of phtalic anhydride were elucidated mainly on the basis of kinetic evidence. The names of Horiuti, Polanyi, Emmett, Temkin, de Boer, Langmuir, Hinshelwood, Rideal and of many other famous scientists are associated with observation and interpretation in mechanistic terms of the rate behaviour of catalytic reactions.

By their very nature catalytic reactions must be necessarily complex, their mechanism involves a number of steps as the natural result of the participation of the catalyst in the reaction mechanism. Obviously then, also catalytic rate behaviour should be and is complex. In the general case the rate equation also must be a complex function, involving a sometimes large number of rate constants. Catalytic kinetics is essentially a multiparameter problem. Curiously the recent literature reflects an alarming tendency to ignore this intrinsic complexity by oversimplification.

Any complex rate equation will reduce to a much simpler equation, applicable within a narrow range of conditions. The fewer the rate data available, the wider is the scope for simplification. Few investigators seem to realise that the simple equation – easy though it may be to handle and to fit to data – contains little information of fundamental significance for the reaction mechanism. Deeper mechanistic insight is badly served by forcing a complex case into the narrow straightjacket of first order rate behaviour. In catalytic kinetics one should beware of straight lines; curves are generally much more informative: the really interesting information lies just around the corner.

The trend towards over-simplification in recent studies of catalytic kinetics is the more surprising since the multiparameter problem inherent in catalytic kinetics nowadays provides less of a problem than ever before. Intelligently programmed computers are a tremendous help in fitting large numbers of data to complex equations.

One intrinsic advantage of the use of kinetics in mechanistic studies is the fact that it provides information on those intermediates, which do participate in the catalytic act. In a catalytic reaction the catalyst surface may be covered by hundreds of different species of which a majority is not really involved in the critical pathway of the catalytic act but are located in dead-end side lines, whilst only a few are the really vital intermediates, and those are the ones which show in the kinetic behaviour.

The choice of my subject for this lecture has been strongly inspired by the fact that this Berzelius Memorial symposium is taking place in Scandinavia, which has been particularly fertile ground especially with respect to my subject matter of to-day. First of all of course we pay homage to Jöns Jacob Berzelius, who was born two hundred years ago in Sweden and who contributed so much to the recognition of catalysis as a distinct scientific phenomenon. At the same time I recall the vital contributions of some other great Scandinavians: Guldberg and Waage, brothers in law, formulated the mass action law, which laid the first basis for quantitative description and understanding of chemical reaction rates. It is to be regretted that this law so often seems to be abused. It only applies to elementary reactions and the elementary steps of complex reactions. It generally does not describe the overall rate behaviour of a complex reaction, so that it gives no basis for the assumption that catalytic reactions should have invariant and integral reaction orders.

Another great Scandinavian is Svante Arrhenius, who gave his name to a law describing the temperature dependence of chemical reaction rates. He made a further step to fundamental understanding by the conception of activation energy and by forging a bridge towards the theory of chemical equilibrium. Again it is often ignored that also the Arrhenius law fundamentally applies only to elementary steps and that a straight Arrhenius plot for an obviously complex catalytic reaction is exception rather than rule.

It is wellknown that two points define location and direction of a straight line. It is too often ignored that the same two points may also be part of an infinite number of curves so that acquisition of a few additional data points may be more than desirable. If this lesson is taken, one often finds that the apparent activation energy varies significantly with temperature and even with reactant partial pressures at any one temperature. Such disorderly findings should not be ignored but rather recognised as a valuable source of information. Obviously this information can only be tapped when a sufficient number of data points have been measured with sufficient accuracy, over a sufficiently wide range of conditions.

My paper of today will not deal with any novel theory. The greater part of the theoretical basis I will use dates back a hundred years or more. I would point out that the invention of abstract disciplines in mathematics does not make simple arithmetic obsolete.

Let me first introduce yet another great Scandinavian. One nasty aspect of complex reactions is that the description of their rates is equally complex and the derivation of exact rate equations is next to impossible. A valuable contribution to the solution of this problem is the introduction of the Stationary State Approximation, often ascribed to Bodenstein, but in reality dating back to Christiansen, yet another Scandinavian physical chemist.

I have now introduced my tools, which look a bit rusty, but will still prove to be as useful as the hammer and the wagon wheel. To introduce a modern element I will also use transition state theory first formulated by Eyring and Polanyi 50 years ago.

Before really embarking on my subject I would consider a bit further the present state of catalytic kinetics, which I consider to be one of dire neglect. Why is this so?

The past two decades especially have seen the advent of a large number of instrumental techniques. These, applied on many systems in many laboratories, have yielded a vast wealth of information on the detailed character of catalytic surfaces and the intermediates present on these surfaces. One product of these endeavours is the realisation that heterogeneous catalysis is even more complex than originally thought. This knowledge most certainly has a discouraging effect on in-depth analysis of catalytic kinetics. The full complexities of heterogeneous surfaces, further aggravated by their generally heavily contaminated state, in conjunction with the vast possibilities of many different possible intermediates will generally defy an unique, exact and realistic quantitative description of rate behaviour in mechanistic terms.

Still I would maintain that this is no justification for a return to stone age kinetics. It is my thesis of today that we cannot say that we really understand a catalytic reaction until we can rationalise its rate behaviour in mechanistic terms. Obviously – especially in heterogeneous catalysis – this description will have to rely on judiciously chosen simplifying approximations to reduce the number of parameters and keep the equations manageable. Obviously any relevant information provided by modern instrumental techniques should be taken into account. It is my firm conviction that responsible application of kinetic methods has its own contribution to make towards mechanistic understanding. But this it can only do by not ignoring the complexity of the system – it is always a multi-parameter problem and to resolve it with a fair degree of realism many rate data are required.

I would venture to draw a parallel with x-ray single crystal structure determination. In this field great advances have been made which receive universal recognition, including several Nobel Prizes. Modern electronic advances have given new scope and impetus to the field. Also here we are faced with a multi-parameter problem: the coordinates of the many atoms in a complex structure imply a large number of parameters to be determined. The crystallographer does not shrink from the measurement of the required large number of data: automatic diffractometers churn out 5000 intensities in a week. In international cooperation the analysis approach has been developed to cope with complex structures. An IBM 370 in about 10 hours computing time produces routinely the required structure for "normal" molecules. For really complex structures maybe a hundred thousand intensities are measured and used. Obviously computing time goes up a few orders. In such more complex cases human ingenuity is still required. In any case any available chemical physical and spectroscopic information is utilised.

With the advent of microprocessors and modern control systems the measurement of a vast number of rates could equally well be organised. The development of adequate basic theory and the associated software should not meet with really major obstacles. Obviously also here the incorporation of other sources of information is a must.

Present trends in catalytic kinetics are in the reverse direction. The measurement of a large number of rate data and their use in mechanistic interpretation is considered as somewhat indecent and a waste of time. Often the remark is heard: one can fit any curve with an eight parameter equation. In saying this the fact is ignored that the parameters, like the spatial coordinates in structure determination, must have physical meaning and consistency.

Actual practice is far too often to measure two rates, rather than three, because straight lines and simple descriptions are considered to have a beauty all their own. The parallel in structure determination with measurement of only a few intensities would produce the conclusion that all crystals are cubic and that the unit cell contains a single somewhat blurred atom.

In the following I will discuss two simple examples, which I hope will illustrate that catalytic kinetics is still a worthwhile exercise. The two examples are closely related in that they both deal with the interconversion of isomeric olefins.

The first example is the isomerization of cis- to trans-stilbene. Because of steric hindrance in the cis-isomer the trans-isomer is much more stable so that the reverse reaction can be largely ignored. This example I have chosen to demonstrate that Berzelius' "catalytic force", very much a secret in his days, can now be understood quantitatively. By applying transition state theory to both the uncatalysed reaction and to the reaction catalysed by iodine, we will find that the accelerating effect of the catalyst can be understood with surprising accuracy. As the experimental basis I will use published data. For the thermal reaction the data of Kistiakowsky and Smith (1) will be used. For the iodine-catalysed reaction we draw upon the data of Muizebelt (2). The treatment owes very much to methods polished to a fine art by Sydney Benson (3). Because of lack of time and space this example will only be treated very briefly. A more complete description will be published elsewhere.

The second example moves to heterogeneous catalysis. In a recent thesis Hartmann (4) published very extensive rate data for the interconversion of the three isomeric linear butenes, catalysed by silicas in which impurities induce acidity in the surface. We will show that by pushing the interpretation somewhat further these data provide valuable information on the mechanism of these much studied reactions, which is difficult to obtain by other means.

THE ISOMERIZATION OF CIS-STILBENE TO THE TRANS ISOMER

In this example we compare the rate of the uncatalysed thermal reaction with that of the same reaction catalysed by iodine and we will see in how far the catalytic acceleration can be rationalized on the basis of present knowledge and theory.

The kinetics of uncatalysed reaction were measured in the gas phase by Smith and Kistiakowsky (1). They found the reaction to be of first order and we may assume that it is a real unimolecular reaction. The transition state then is the cis-stilbene molecule in which the central double bond has been twisted over 90° either way, obviously with attendant decoupling of the π-bond. The rate equation as expected is found to have the form

$$r_u = k_u \cdot C_{cis} \tag{1}$$

The suffix u refers to the uncatalysed reaction. In terms of transition state theory the rate constant k_u can be expressed as

$$k_u = \frac{ekT}{h} \exp\left(\Delta S_u^{\ddagger}/R - E_u/RT\right) \tag{2}$$

in which $\Delta S_u^{\ddagger}$ is the activation entropy and E_u the Arrhenius activation energy.

Following methods as described by Benson (3) the values of both the activation entropy and the activation energy can be estimated by consideration of the differences between the activated complex and the starting molecule. In this context we will not go into the detailed reasoning, which will be published elsewhere, we will only give the result as indicated in table 1 under "predicted", together with the experimental data.

The catalysed reaction was measured in CCl_4-solution by Muizebelt. The empirical rate equation has the form

$$r_c = k_c \cdot C_{cis} \cdot C_{I_2}^{1/2} \tag{3}$$

The suffix c refers to the catalysed reaction.

Expression (3) can be rationalised by the following mechanism:

$$I_2 \xrightleftharpoons{1} 2\,I$$

$$I + C \xrightleftharpoons{2} C\,I$$

$$C\,I \xrightleftharpoons{3} T\,I$$

$$T\,I \xrightleftharpoons{4} T + I$$

which involves the successive steps:

formation of iodine atoms, which form the real catalyst, addition of atomic iodine to the substrate, rotation around the now single central bond in the radical iodine substrate intermediate and finally dissociation of iodine with formation of the trans product.

On the basis of judicious assumptions it then is easy to demonstrate that the rate equals

$$r_c = K_1^{1/2}\cdot K_2\cdot k_3\cdot C_{cis}\cdot C_{I_2}^{1/2} \qquad K_1^{1/2}\cdot K_2\cdot k_3 = k_c \tag{4}$$

in agreement with experimental observation.

For k_c we can also write:

$$k_c = \frac{ekT}{h}\exp\left(\Delta S_c^{\ddagger}/R - E_c/RT\right) \tag{5}$$

in which for the overall activation entropy can be written:

$$\Delta S_c^{\ddagger} = \tfrac{1}{2}\Delta S_1^0 + \Delta S_2^0 + \Delta S_3^{\ddagger} = S_3^{\ddagger} - S_{cis}^0 - \tfrac{1}{2}S_{I_2}^0 \tag{6}$$

and an expression of similar form can be given for E_c.

These expressions can then be used along similar lines as for the uncatalysed reaction to estimate – predict – the expected values of activation entropy and activation energy.

Table 1. The rate isomerization of cis-stilbene, recalculated to 370 K

		$\Delta S^{\ddagger}$ cal/K·mol	E kcal/mol	Rate mol/l·sec.	
Uncatalysed	Obs.	-3.3	42.8	$3.1\times10^{-13}\cdot C_{cis}$	correct within
	Pred.	-3.5 ± 1	44 ± 2	$5.6\times10^{-14}\cdot C_{cis}$	factor 5.6
Catalysed	Obs.	-17.1	21.7	$1.88\times10^{-5}\cdot C_{cis}$	correct within
1 mmol I_2/l	Pred.	-18 ± 1	23 ± 3	$2.0\times10^{-6}\cdot C_{cis}$	factor 9.4
Catalytic acceleration:	Observed:			6×10^{7}	correct within
	Predicted:			3.6×10^{7}	factor 1.67

The result is again given in table 1.

First of all we note that the methods applied allow prediction of the rates of both the uncatalysed and the catalysed reaction well within an order of magnitude. More significantly in the present context is the fact that the *catalytic acceleration* for a chosen iodine catalyst concentration is almost exactly predicted.

We may thus conclude that the mysterious "catalytic force" of Berzelius does not hold a mystery any longer. Obviously the example we have chosen is an extremely simple one. In more complex cases we could not possibly make a similar prediction, simply because too many parameters would be unknown and virtually impossible to estimate with any degree of confidence. This, however, does not detract from the main conclusion and we may be confident that the same principles will apply also in more complex cases.

We now move to a consideration of a heterogeneously catalysed reaction, where we may expect uncertainties to be more pronounced. For today's demonstration I have selected from the literature a kinetic study of a heterogeneously catalysed reaction, for which we may expect that uncertainties and complications are not excessive. For this example we give the complete analysis and we will find that the results obtained give additional insight in the mechanism of a much studied reaction, for which the mechanism is subject to controversion.

THE CATALYTIC INTERCONVERSION OF LINEAR BUTENES ON ACIDIC SURFACES

Experimental

The experimental basis for this example is formed by the very extensive kinetic data recently measured by Hartmann, as published in her PhD-Thesis (4). We will not give much experimental detail here, since this will be published shortly by the originators of the work.

In the following analysis we will use the data obtained on two catalysts, both technical silica samples. Spherosil X0A 400 ex Rhône Progil, further referred to as Spherosil, and a silica ex Ketjen (AKZO Amsterdam), further referred to as Ketjensil.

Both silica samples contain some foreign elements, notably Al, which induce surface acidity. The purity analysis given is not highly accurate. For Ketjensil the impurity level is of the order of 1 %, for Spherosil it is roughly a factor of 10 lower.

Very careful and extensive rate measurements were performed in a stainless steel thermostated differential flow reactor. Conversions were always limited to well below 10 %. All rates were extrapolated back to zero conversion and these will be referred to as initial rates.

Measurements covered an extremely wide temperature range, roughly from 350 to 750 K. Reactant pressures were varied from 0.12 to 0.24 MPa, but most data were obtained at 0.12 MPa. Rates were measured in two series on either catalyst.

In the first series 1-butene was used as the feed with Z- and E-2-butene as the products. Rates were expressed as disappearance rate of 1-butene and will be referred to as $_{-1}r_0$

In this series also the product ratio Z/E was obtained from GLC analysis and will be denoted by m.

In the second series Z-2-butene was used as the feed. In this case data on initial rate of formation for both products were obtained and will be referred to as $_1r_o$ and $_Er_o$ respectively. The product ratio (1)/(E) was also obtained and will be called n.

It is a wellknown fact, often discussed in the literature of butenes isomerization on acidic surfaces, that the product ratios n and m deviate significantly from thermodynamic equilibrium, so that they are kinetically controlled. The ratio m on both catalysts showed hardly any temperature dependence and stayed close to unity.

The most significant and novel observation in Hartmann's data is that the selectivity ratio n passes through a maximum value of about 2 near 600 K, sloping off to a value near unity at about 400 and 750 K. This observation will prove of crucial importance for the analysis on which we will now embark.

Mechanistic basis for analysis

Before we can proceed to analyse the data we must choose a reaction mechanism. Most extensively used in the literature is a mechanism involving a single surface intermediate, generally visualised as a secondary carbonium ion bonded to the surface, formed by addition of an acid surface proton to either of the two β-carbon atoms of any of the three isomeric butenes. For the isomerization of Z-2-butene the mechanism will then be as shown in fig. 1, where we omitted the reverse reactions (−2) and (−3) because we will only consider initial rates. In the mechanism of fig. 1 the symbols Z, E and 1 denote the three butene isomers, the suffix g refers to the gaseous state and C represents the carbonium surface intermediate.

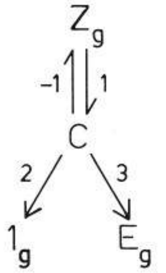

Fig. 1 Mechanism with a single surface intermediate C

For the mechanism the following equations apply:

$$\left(\frac{d1}{dt}\right)_0 = k_2\theta_C \; ; \; \left(\frac{dE}{dt}\right)_0 = k_3\theta_C \; : \; n = \left(\frac{d1}{dE}\right)_0 = k_2/k_3$$

Assuming the mechanism to be realistic, that is composed of elementary reaction steps, then $n = f(T)$ cannot have a maximum:

$$E_n = RT^2\left(\frac{d \ln n}{dT}\right) = E_2 - E_3$$

which is either positive or negative at all reaction temperatures. If E_n is positive n will increase with T, if negative then n will decrease with T. It is clear then that this simple mechanism cannot explain the most vital observation in Hartmann's data, viz. the maximum in the selectivity ratio $n = f(T)$.

We are thus forced to introduce additional complication in the assumed mechanism. For the moment we will postpone any physical visualisation of assumed surface intermediates, to be considered in the final discussion. In view of the symmetry of the reaction mixture, involving three isomeric reactants/products, it will be logical to consider a triangular network, as shown in fig. 2, where the same symbols as in fig. 1 apply, whilst * indicates a surface site, to which

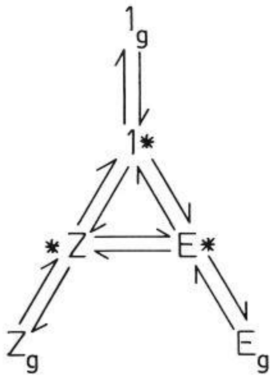

Fig. 2 Mechanism with three surface intermediates

an intermediate is bound. Although it is possible to derive for this mechanism the relevant equations for the rates and the selectivity ratio n, the resultant equations are very unwieldy and it is practically impossible to fit the data to them. The equation for the initial rate involves no less than 10 rate constants.
Hartmann intuitively proposed a simpler mechanism halfway between fig. 1 and 2 by merging the two surface intermediates Z∗ and E∗ into a single one 2∗. This mechanism is shown in fig. 3. It has proved to be the simplest one which can

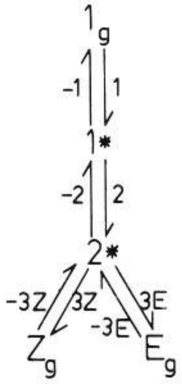

Fig. 3 Mechanism with two surface intermediates

explain a maximum in the n = f(T)-selectivity ratio and it will prove a fruitful basis for the analysis of the kinetic data. As before we leave consideration of the physical significance of the intermediates until later. For the analysis of the data we must make a few further necessary assumptions:

i. At all reaction conditions the same sites in equal number are operative.
ii. The usual Langmuir-Hinshelwood assumptions apply: homogeneous surface, no interaction between adsorbed molecules.

Before proceeding to analyse the data, it appears useful to consider first the expected shape for the enthalpy profile, associated with the mechanism of fig. 3. This profile is qualitatively shown in fig. 4. We note that for interconversion of 1-butene and either E- or Z-butene three maxima must be overcome. Their relative heights are yet to be determined and that will be one of the results of the exercise on which we now embark.

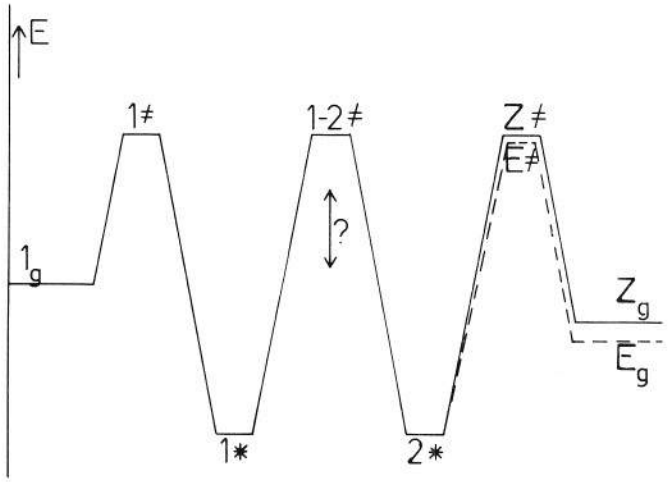

Fig. 4 General expected shape of the enthalpy curve for the mechanism with two surface intermediates. Relative height of the barriers is as yet undefined.

We remarked already that the most salient observation in Hartmann's data is the maximum in the n = f(T)-curve. It will prove very fruitful to use this data as the starting point for the analysis, for two reasons:

i. The selectivity ratio n is a ratio of rates and as such will be somewhat less sensitive to deviations in process conditions than the rates.
ii. We will find that whereas the individual rates are governed by six temperature dependent rate constants and therefore by twelve parameters, the selectivity ratio obeys a much simpler expression containing only two temperature dependent parameters, so that the 12-parameter problem is reduced to a four parameter problem.

The maximum in the n = f(T)-relation

For the mechanism of fig. 3 the derivation of an expression is very simple: Application of the stationary state assumption on θ_1 yields:

$$\left(\frac{d\theta_1}{dt}\right)_{ss} = 0 = k_{-2}\theta_2 - k_2\theta_1 - k_{-1}\theta_1$$

$$\frac{\theta_1}{\theta_2} = \frac{k_{-2}}{k_2 + k_{-1}} \tag{7}$$

$$\left(\frac{dE}{dt}\right)_0 = k_{3E}\theta_2 \text{ and } \left(\frac{dl}{dt}\right)_0 = k_{-1}\theta_1$$

$$n = \left(\frac{dl}{dE}\right)_0 = \frac{k_{-1}\theta_1}{k_{3E}\theta_2} = \frac{k_{-1}k_{-2}}{k_{3E}(k_2 + k_{-1})} \tag{8}$$

It will prove convenient for the further analysis to define some ratios of rate constants.

$$\beta' = k_{-2}/k_{3E} \quad \text{and} \quad \alpha = k_2/k_{-1} \tag{9}$$

Then the equation for n converts to:

$$n = \beta'/(1 + \alpha) \tag{10}$$

Introducing further the Arrhenius expression for the rate constants:

$$k_i = A_i \quad \exp(-E_i/RT)$$

we find $\alpha = k_2/k_{-1} = (A_2/A_{-1})\cdot\exp(-(E_2 - E_{-1})/RT)$

$$\alpha = A\cdot\exp(-B/RT) \quad \text{defining A and B} \tag{11}$$

and likewise

$$\beta' = k_{-2}/k_{3E} = (A_{-2}/A_{3E})\cdot\exp(-(E_{-2} - E_{3E})/RT)$$

$$\beta' = D\cdot\exp(-C/RT) \quad \text{defining C and D} \tag{12}$$

Then the expression for n(T) becomes:

$$n = \frac{D\cdot\exp - C/RT}{1 + A\cdot\exp - B/RT} \tag{13}$$

Thus n(T) is governed by four parameters A, B, C and D, which are independent of temperature, and this equation we will fit to the experimental n(T)-data. To do so we need starting values for the parameters.

To find starting values we apply a further parameter reduction:

$$E_n = RT^2\ \frac{d\ln n}{dT} = C - \frac{B}{1 + A^{-1}\exp - B/RT} \tag{14}$$

From the experimental n(T)-curve approximate values for E_n at three temperatures: on the ascending branch, in the maximum and on the descending branch can easily be obtained. Substituting these in equation (14) easily yields starting values for A, B and C. With the use of equation (13) a starting value for D is then obtained.

With these starting values a computer fit of the n = f(T) data for the two catalysts to equation (14) is performed. The results is shown in figs. 5 and 6. The quality of the fit is clearly satisfactory in both cases which gives confidence that further analysis of the rate data is justified.

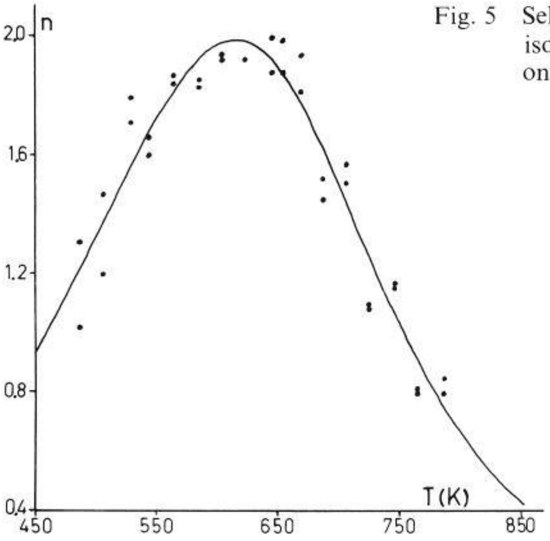

Fig. 5 Selectivity ratio n = f(T) for isomerization of Z-2-butene on Sferosil

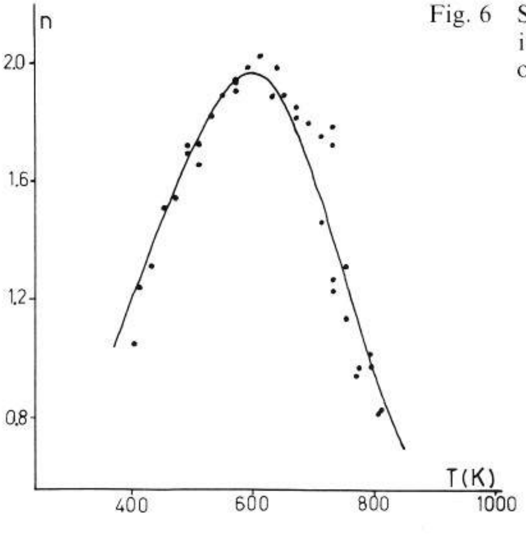

Fig. 6 Selectivity ratio n = f(T) for isomerization of Z-2-butene on Ketjensil

Before proceeding further we will now consider, whether the parameters we have found have reasonable values and see what we can learn from them regarding the reacting system. For the two catalysts the parameters and some derived quantities are shown in table 2.

Table 2. The parameters derived from the n = f(T) fit and their significance

Parameter Equal to	A $\exp(\Delta S_2^{\ddagger} - \Delta S_{-1}^{\ddagger})/R$	D $\exp(\Delta S_{-2}^{\ddagger} - \Delta S_{3E}^{\ddagger})/R$	$-$ B $E_{-1} - E_2$	$-$ C $E_{3E} - E_{-2}$
Sferosil	4.224×10^{-6}	1.468×10^{-4}	16.9 kcal/mol	13.6 kcal/mol
Entropy difference	$-$ 24.6 cal/K·mol	$-$ 17.5 cal/K·mol		
Ketjensil	1.181×10^{-5}	8.342×10^{-5}	16.8 kcal/mol	15.3 kcal/mol
Entropy difference	$-$ 22.5 cal/K·mol	$-$ 18.7 cal/K·mol		

We recall from the mechanism of fig. 3 that the reactions (-1) and (3E) are both desorption steps. It appears highly probable that the activated complex for desorption has more freedom and therefore higher entropy than the respective adsorbed state. In other words we expect positive activation entropy for these reactions. The reactions (2) and (-2) on the other hand are interconversion reactions between the adsorbed species. It is likely that the activated complex through which these two reactions pass has a closely defined configuration, so that the activation entropy is almost certainly negative. Therefore the activation entropy differences $\Delta S_{-1}^{\ddagger} - \Delta S_2^{\ddagger}$ and $\Delta S_{3E}^{\ddagger} - \Delta S_{-2}^{\ddagger}$ are expected to have rather large positive values and this we find to be the case.

A similar reasoning can be applied to the activation energies. For the desorption reactions (-1) and (3E) the activation energies must be at least equal to the heat of desorption for 1-butene and E-2-butene respectively. For the interconversion reactions (2) and (-2) between adsorbed species the activation energies should be significantly smaller than the respective heats of desorption, because otherwise desorption would be strongly favoured over surface reaction and the mechanism would not operate, this the more so since also the pre-exponential factors will favour desorption as will be clear from the entropy discussion in the last paragraph. Thus we must expect both $E_{-1} - E_2$ and $E_{3E} - E_{-2}$ to have large positive values and that is what we find.

We may thus conclude that the results obtained from the data on the basis of the 2-intermediate mechanism appear very reasonable. We can now specify somewhat more closely the shape of the potential profiles with respect to the relative heights of the barriers, which we left undecided in fig. 4. The result is shown in fig. 7. We find that the barrier for the interconversion reactions on the surface is lower than the two outer barriers and further that the barrier towards 1-butene is somewhat higher than that towards the 2-butenes. The latter is to be expected, since also the enthalpy of gaseous 1-butene is higher than that of the 2-butenes.

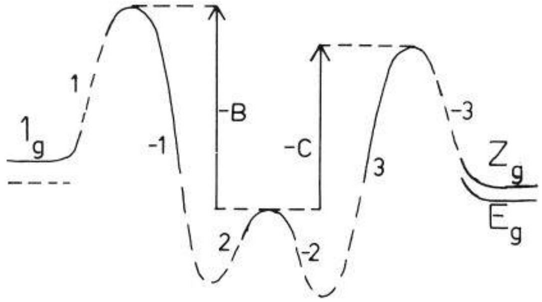

Fig. 7 Further definition of the enthalpy curve, based on the value of parameters $B = E_2 - E_{-1}$ and $C = E_{-2} - E_3$

Before proceeding to the next step in the analysis, where also the rate data will be included, we should ask ourselves how unique the solutions for the n(T)-equation which we have now found really are.

It can easily be demonstrated that equation (13) for n(T) has two mathematically real and equivalent solutions. For both solutions the approximate enthalpy profiles for catalyst Sferosil are shown in fig. 8. It is immediately obvious that for symmetry reasons the solution shown on the right cannot have physical reality: it is certainly impossible that the activation energy for desorption of 1-butene is 16 kcal/mol smaller than that for 2-butene. It is equally impossible that $\Delta S^{\ddagger}_{-3} - - \Delta S^{\ddagger}_{1}$ equals about 18 cal/mol·degree. The other solution, shown in the left-hand side of fig. 8, does not show these shortcomings and in fact shows all the characteristics which we considered to be likely in the earlier discussion.

Another type of uncertainty in the solutions found is associated with experimental error, which echos through in the value of the parameters A, B, C and D. As we may expect there is strong coupling between the pre-exponential parameters A and D and the energy parameters B and C. Complete discussion of the confidence intervals of the parameters is somewhat involved for the equation in question and would not serve a useful purpose in the present context. We will limit ourselves to some remarks on the energy parameters B and C and the shape of the enthalpy profile. With respect to the latter we drew earlier two qualitative conclusions:

i. The lefthand peak (ad/desorption of 1-butene) is higher than the righthand one (ad/desorption of 2-butenes) : $C - B > 0$. The quality of the fit proves sensitive to $C - B$. For $C - B < 0$ there is no maximum in the n(T)-curve; variation of $C - B$ by ± 15 %, with concurrent optimised shift in A and D, already reduces the quality of the fit significantly. Thus the lefthand peak must be higher than the righthand one.

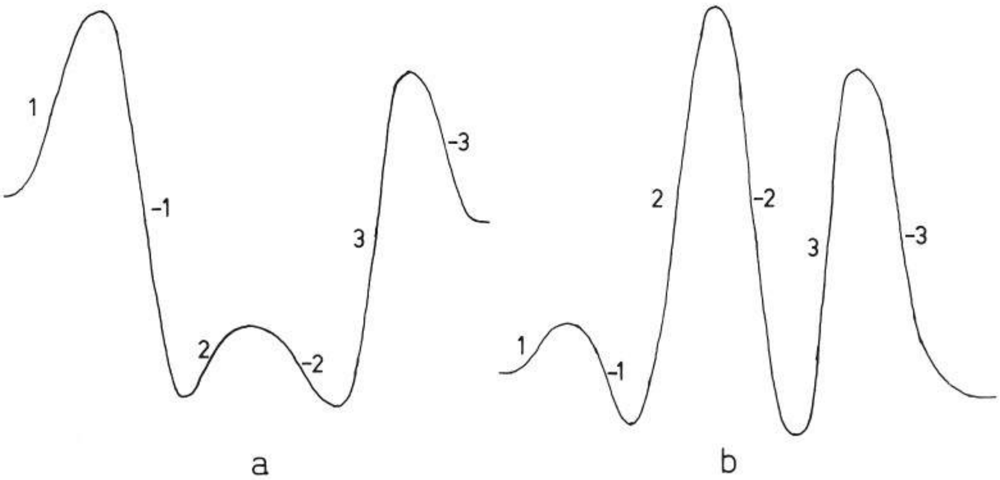

Fig. 8 Two possible shapes of the enthalpy curve, based on two mathematically equivalent solutions of the $n = f(T)$ relation. The righthand curve must be physically meaningless for symmetry reasons

ii. The middle peak is lower than the outer ones. Fit quality proves less sensitive to concurrent shift in C and B, again with attendant optimised shift in A and D : we can "push up" the middle barrier, but when it reaches 30 % of the outer barriers the fit to the data is already poor. Lowering the middle barrier to zero again eliminates the maximum in n(T). Thus also the second shape conclusion is upheld.

So the shape of the enthalpy profile as shown in fig. 7 must be roughly correct.

We can now proceed with the analysis of the rate data where the enthalpy and entropy differences already obtained will prove a great help. From the rate data we will derive the remaining enthalpy and entropy differences required to complete the profiles.

The rate equation for isomerisation of 1-butene

For the assumed mechanism the derivation of the rate equation proves relatively simple with application of the stationary state assumption to the two surface intermediates:

$$\frac{d\theta_1}{dt} = 0 = k_{-2}\theta_2 - k_2\theta_1 - k_{-1}\theta_1 + k_1 B_1 (1 - \theta_1 - \theta_2) \qquad (15)$$

$$\frac{d\theta_2}{dt} = 0 = k_2\theta_1 - k_{-2}\theta_2 - k_3\theta_2 \qquad (16)$$

in which $k_3 = k_{3E} + k_{3Z} = k_{3E}(m + 1)$ where m is the selectivity ratio $(Z/E)_0$

The initial rate of elimination of 1-butene will then be equal to the total rate of formation of 2-butenes:

$$_{-1}r_0 = -\left(\frac{dB_1}{dt}\right)_0 = \left(\frac{dB_2}{dt}\right)_0 = k_3\theta_2 \tag{17}$$

From these equations the initial rate equation is easily derived.

Kallo et al (5) demonstrated that for virtually any reasonable mechanisms of interconversion of linear butenes the equation for the initial rate takes the familiar form of the Langmuir-Hinshelwood rate equation for a unimolecular surface reaction, in which however the constants k and K are not simply a rate constant and an adsorption equilibrium constant, but are complex functions of a number of rate constants. This proves also the case for the mechanism we use, which in fact was also considered by Kallo et al. To indicate the complex character of k and K we will give them primes:

$$_{-1}r_0 = \frac{_{-1}k' \cdot {}_{-1}K' \cdot B_1}{1 + {}_{-1}K' \cdot B_1} \tag{18}$$

in which B_1 is the partial pressure of 1-butene and

$$_{-1}k' = \frac{k_2k_3}{k_{-2} + k_2 + k_3} \quad \text{(19a)} \quad \text{and} \quad {}_{-1}K' = \frac{k_1}{k_{-1}} \times \frac{k_3 + k_{-2} + k_2}{k_3 + \dfrac{k_2}{k_{-1}}k_3 + k_{-2}} \tag{19b}$$

Obviously under certain conditions (low reactant pressure, high reaction temperature) degeneration to first order rate behaviour may occur, if $_{-1}K' \cdot B_1 \ll 1$. In that case the first order rate constant equals

$$_{-1}k = {}_{-1}k' \cdot {}_{-1}K' \tag{19c}$$

From Hartmann's data for Sferosil $_{-1}k = f(T)$ is obtained in the range of conditions used, whilst for Ketjensil Langmuir type rate behaviour was observed and $_{-1}k'$ and $_{-1}K'$ as f(T) are obtained. Clearly the Sferosil case is less informative, which illustrates the general statement made in the introduction: straight lines contain less information than curved ones.

The total reaction network contains 8 rate constants so we need 8 independent equations to define the system completely:

The provenance of these equations is as follows:

2 are provided by the thermodynamic data of the isomeric butenes
2 were obtained from n = f(T) fit: 2 ratios of rate constants
1 is provided by the experimentally observed Z/E-ratio, which equals k_{3Z}/k_{3E}
1 will be (gu)estimated: $K_2 = k_2/k_{-2}$, as explained below
2 are provided by the values for $_{-1}k'$ and $-1K'$ for Ketjensil

However, for Sferosil we are one equation short, because of the first order rate behaviour, only yielding a value for $_{-1}k$.

For the sake of convenience – in order to bring the expressions in a more manageable form – we will introduce a series of ratios of rate constants, as shown in the following list. Some of these have already been defined:

$\alpha = k_2/k_{-1} = A\cdot\exp - B/RT$
$\beta' = k_{-2}/k_{3E} = D\cdot\exp - C/RT$
$m = k_{3Z}/k_{3E}$, experimentally observed Z/E-ratio in 1-butene conversion, which is only a weak temperature function
$\beta = k_{-2}/k_3 = \beta'/(m+1)$ $\qquad k_3 = k_{3Z} + k_{3E}$

Ratio's α, β' and β are known from the preceeding exercise, as functions of temperature. The three adsorption equilibrium constants will be among the products of the kinetic analysis:

$K_1 = k_1/k_{-1}$	the adsorption constant for 1-butene
$K_Z = k_{-3Z}/k_{3Z}$	the adsorption constant for Z-2-butene
$K_E = k_{-3E}/k_{3E}$	the adsorption constant for E-2-butene

One additional equilibrium constant, for the interconversion of the two surface intermediates, cannot be found from the analysis because it will prove that these reactions are never rate determining, so that the kinetics are blind for this constant:

$$K_2 = k_2/k_{-2}$$

We will need this constant as f(T) to complete the analysis, and we therefore made an estimation which we feel must be reasonably correct.

$$\text{Clearly } K_2 = \exp \Delta S_2^\circ/R\cdot\exp - \Delta H_2/RT$$

For the enthalpy contribution we have used the enthalpies of the gaseous species as a basis: we have assumed that the enthalpy difference of the adsorbed intermediates is half the difference of the gaseous species:

$$\Delta H_2 = H_{2^*} - H_{1^*} = \frac{1}{2}\left(\frac{1}{2}(H_{Zg} + H_{Eg}) - H_{1g}\right) = -1120 \text{ cal/mol}$$

For the entropy contribution we followed a similar reasoning, where, however, corrections must be made for rotational symmetry and for two configurations of adsorbed 2-butene:

$$\Delta S_2^\circ = S^\circ - S_1^\circ = \frac{1}{2}\left(\frac{1}{2}(S_{Zg}^\circ + S_{Eg}^\circ + R\ln 2) - S_{1g}^\circ + R\ln 2\right) = -0.5 \text{ e.u.}$$

We now return to the rate equation (18) and the constants contained therein, in which we now introduce the symbols for the ratios of rate constants defined above:

${}_1k' = bk_3$ in which $b = K_2/(1 + \beta + \beta K_2)$
${}_{-1}K' = cK_1$ in which $c = (1 + \beta + \beta K_2)/(1 + \alpha + \beta)$

For the Sferosil case with first order rate behaviour we only have k_1 as f(T), for which applies:

$$_{-1}k = ak_1 \text{ in which } a = \alpha/(1 + \alpha + \beta)$$

We recall that α, β and K_2 are known as f(T), so that also the quantities a, b and c are known as a function of temperature. For the case of Ketjensil b and c were tabulated as f(T) and thus k_3 and K_1 were obtained as f(T). For the case of Sferosil, where $_{-1}k$ was obtained from the experimental data on 1-butene conversion, a was tabulated as f(T) and thus k_1 was obtained as f(T).

The background behind this approach is that from the expressions for $_{-1}k$, $_{-1}k'$ and $_{-1}K'$ such a fundamental constant was factored out – k_1, k_3 and K_1 respectively – that the remaining expression – a, b and c respectively – were functions that are only weakly dependent on temperature and remain over the relevant temperature interval rather close to unity.

So far we have only used rate data for the conversion of 1-butene and for the case of Ketjensil these prove sufficient to obtain the required 8 equations needed to describe the reacting system completely. We have already noted that for the case of Sferosil we are one equation short. To supply the extra equation needed we had to turn to the kinetic data for the conversion of Z-2-butene to 1-butene and E-2-butene. Hartmann noted that the reaction order q in reactant pressure Z for formation of 1-butene was:

$$480-520 \text{ K} : q_{500} = 0.75 \quad \text{and} \quad 545-585 \text{ K} : q_{565} = 0.9$$

which demonstrates Langmuir type behaviour in this temperature interval, although the reaction order is still rather close to one.

We will not give the derivation for the rate equation for this case, which runs on similar lines as the one for 1-butene conversion. Also the result is similar, again a Langmuir-type rate equation:

The initial rate for formation of 1-butene from Z-2-butene equals:

$$_1r_0 = {_1k'} \cdot {_1K'} \cdot p_z/(1 + {_1K'} \cdot p_z) \qquad (20)$$

In this case

$$_1K' = f \cdot K_Z \text{ in which } f = \frac{m}{m+1} \times \frac{\alpha/K_2 + \alpha + 1}{1 + \alpha + \beta}$$

Again all quantities in f are known as f(T), so that f(T) can be calculated and also $E_f = RT^2 (d \ln f)/dT$ is known.

It can easily be demonstrated that for a Langmuir-type rate equation like (20) the reaction order q equals:

$$q = 1/(1 + {_1K'} \cdot p_Z)$$

so that at 500 K $_1K' \cdot p_Z$ equals $\frac{1}{3}$, at 565 K it equals $\frac{1}{9}$, so that $_1K'$ changes by a

factor of 3 from 500 to 565 K.
This yields ${}_1\Delta H' = RT^2 (d \ln {}_1K')/dT = 9.5$ kcal/mol

Thus $\Delta H_Z = -9.5 - E_f$, which yields ΔH_Z
K_Z at 500 K equals 1/(3f), which with use of ΔH_Z yields ΔS_Z°
We have now available for both catalysts the required number of independent equations, so that we can now proceed to draw the enthalpy and entropy diagrams. For the sake of simplicity we will only do so for the interconversion of 1-butene and Z-2-butene.

The enthalpy diagram

The reaction sequence from 1 to Z and vice versa involves six reactions and therefore six activation enthalpies. These can be calculated from the equations shown in table 3.

Table 3. Calculation of the enthalpy diagram

For calculation of the six activation enthalpies involved in conversion of butene-1 in butene-2-Z we need and have 6 equations:

1. $\Delta H_1^{\ddagger} - \Delta H^{\ddagger}_{-1} + \Delta H_2^{\ddagger} - \Delta H^{\ddagger}_{-2} + \Delta H_{3Z}^{\ddagger} - \Delta H^{\ddagger}_{-3Z} = \Delta H_{1\to Z} = -2.13$ kcal
2. $\Delta H^{\ddagger}_{-1} - \Delta H_2^{\ddagger} = -B$ From n = f(T)-fit, see table 2
3. $\Delta H_{3Z}^{\ddagger} - \Delta H^{\ddagger}_{-2} = -C$
4. $\Delta H_1^{\ddagger} - \Delta H^{\ddagger}_{-1} = \Delta H_1 = \Delta_{-1}H' - E_c$
5. $\Delta H_{3Z}^{\ddagger} = E_3 - RT_m = {}_{-1}E' - E_b - RT_m$ From kinetics of 1-butene conversion
6. $\Delta H_2^{\ddagger} - \Delta H^{\ddagger}_{-2} = \Delta H_2$, assumed -1.12 kcal/mol

Note: $E_c = RT^2 (\partial \ln c/dT)$; $E_b = RT^2 (\partial \ln b/dT)$
$b = K_2/(1 + \beta + \beta K_2) : c = (1 + \beta + \beta K_2)/(1 + \alpha + \beta)$
α and β are known as f(T) from n = f(T)-fit
K_2 as f(T) was assumed. So E_c and E_b are known.

The resulting enthalpy diagrams for both catalysts are shown in fig. 9 (p. 38) in which the successive states are indicated by 1_g, $1^{\ddagger}$, 1^*, $1-2^{\ddagger}$, 2^*, $Z^{\ddagger}$ and Z_g. From this figure we note that for both catalysts indeed the middle barrier is lower than the outer ones as anticipated early in the analysis. We further note that for Ketjensil, the catalyst with the higher impurity level, the adsorption heats are greater than for Sferosil and the adsorption activation energies are smaller. This is a wellknown effect which can be understood by looking at the potential curves, shown in fig. 10 (p. 39) which have been discussed extensively in the catalytic literature. Curve a shows van der Waals interaction between a substrate molecule and a surface site, curves b visualise the chemical interaction between a substrate molecule, first brought into an excited state in the gaseous state and the site.

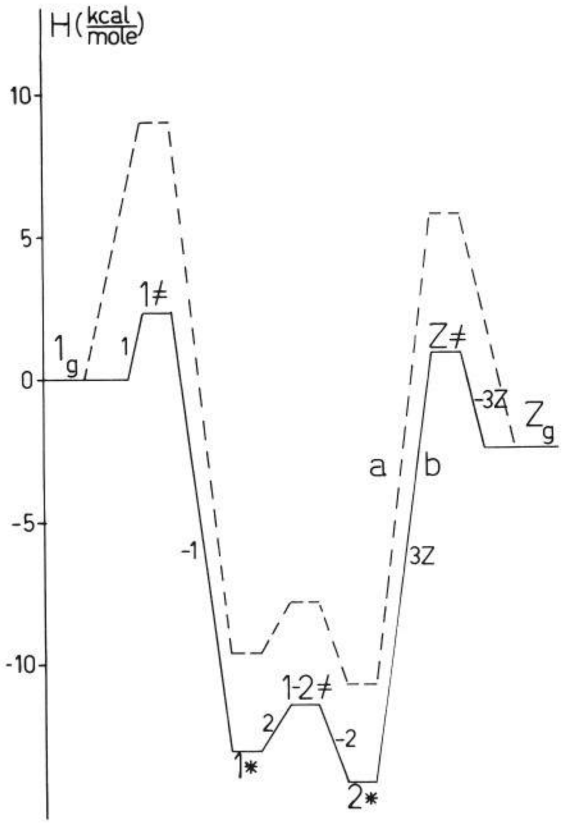

Fig. 9 The enthalpy diagram for catalyst Spherosil (a) and Ketjensil (b)

The entropy diagram

In the drawing of this diagram we face a difficulty. The relative levels of the stable states 1_g, 1^*, 2^* and Z_g can easily be defined:

From $K_1(T)$ and ΔH_1 we easily find $\Delta S^\circ_1 = S^\circ_{1^*} - S^\circ_{1g}$

Likewise $K_Z(T)$ and ΔH_Z yield $\Delta S^\circ_Z = S^\circ_{2^*} - S^\circ_{Zg}$

$\Delta S^\circ_2 = S^\circ_{2^*} - S^\circ_{1^*}$ has been assumed, as explained earlier.

These values yield one half of the entropy diagram.

The entropy levels of the three activated complexes $1^\ddagger$, $1-2^\ddagger$ and $Z^\ddagger$ are likewise interlocked by the relations:

$$R \ln A = R \ln A_2 - R \ln A_{-1} = \Delta S^\ddagger_2 - \Delta S^\ddagger_{-1} = S^\circ_{12^\ddagger} - S^\circ_{1^\ddagger}$$

$$R \ln (D/m) = R \ln A_{-2} - R \ln A_{3Z} = \Delta S^\ddagger_{-2} - \Delta S^\ddagger_{3Z} = S^0_{12^\ddagger} - S^0_{2^\ddagger}$$

The two halves of the entropy diagram are shown next to each other in fig. 11.

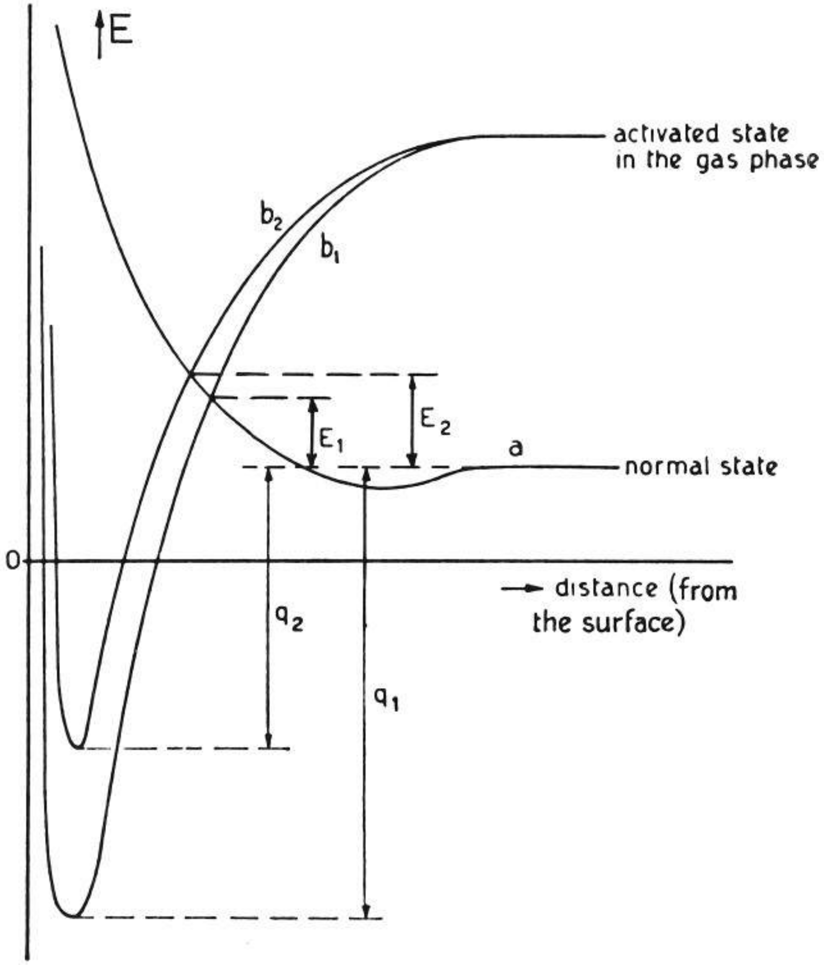

Fig. 10 Relation between activation energy for adsorption E and heat of adsorption q. Curve a is the potential curve for van der Waals interaction of an adsorbate molecule with a surface site. Curves b are potential curves for the approach of an excited gas molecule to the surface site. The cross-over point of a and b gives the activation barrier.

The link between the two halves of the diagram, the way in which they must be superimposed with respect to the vertical axis is the active site density n_S, which is as yet unknown.

Superimposing the two halves of the diagram and moving one vertically with respect to the other we soon find that, although we have no firm clue regarding their correct relative position, we have in fact less degree of freedom than might be expected. This is mainly so because again the diagram must have a certain

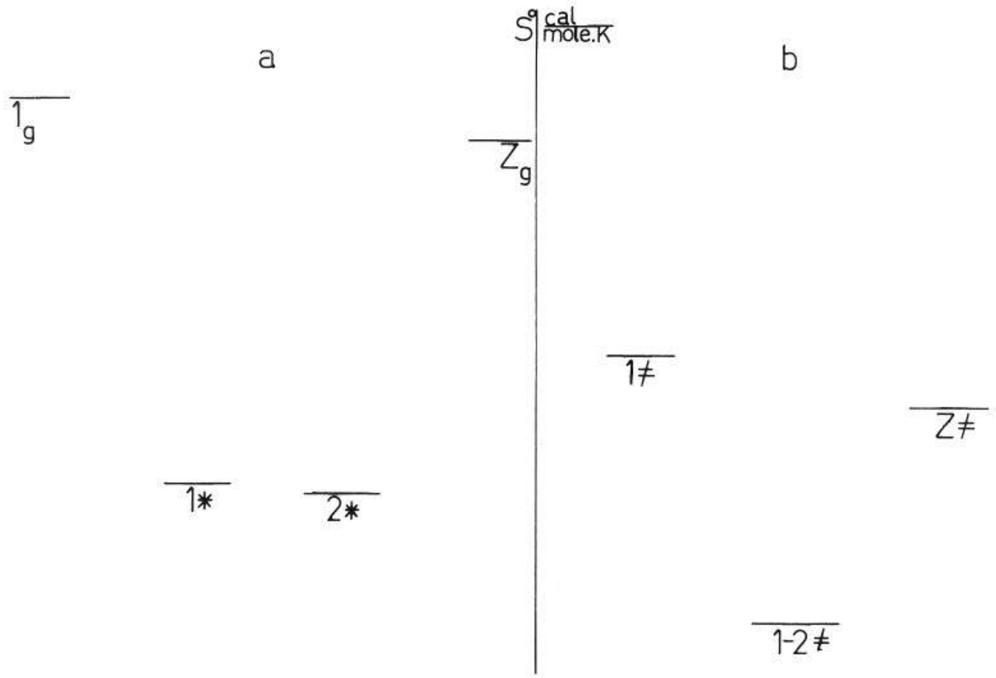

Fig. 11 Two halves of the entropy diagram: for Sferosil:
a. Entropy differences between the gaseous states and the stable adsorbed intermediates
b. Entropy differences between the transition states

symmetry because of the great similarity of reactant and product. The result, as we have chosen it, is shown in fig. 12.

The values of the entropy differences appear reasonable: in the transition state for adsorption only part of the translational entropy of the gaseous state is lost. The lowest entropy level is reached in the transition state for the interconversion of the two adsorbed states. The differences $\Delta S_2^{\ddagger}$ and $\Delta S^{\ddagger}_{-2}$ are of the correct order to imply the loss of the one degree of rotational freedom, presumably still preserved in the adsorbed state. We must expect that this activated complex has the closest conformational confinement, since it involves shift of the double bond, for which a narrowly defined configuration may well be required.

As we mentioned the link between the two parts of the entropy diagram is the active site density n. It will be clear that we cannot determine this very accurately. The uncertainty in the relative positioning in the two halves of the entropy diagram is about 5 cal/K·mol., so that the uncertainty in N_S is about an order of magnitude.

Still our conclusion is that the active site density for both catalysts is extremely low: only about one millionth of the concentration of Al ions in the catalyst surface. Very tentatively we put forward as a possible explanation that possibly an

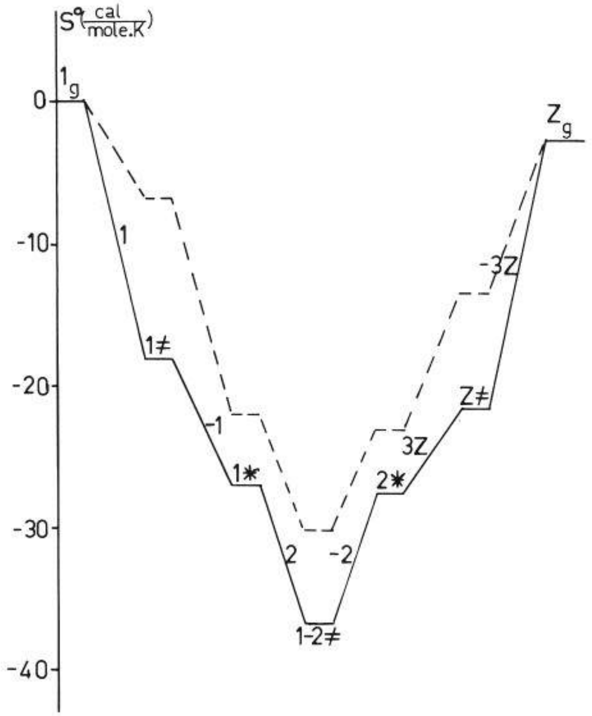

Fig. 12 The combined entropy diagram for Sferosil and Ketjensil

ensemble of e.g. three impurity ions in the surface is responsible for catalytic activity. Similar to the situation with alloy catalysts the surface concentration of such ensembles declines much more rapidly than the concentration of the active ingredient.

The Gibbs Free Energy Diagram

It will be clear that the rate behaviour of the reacting system is governed both by the enthalpy and the entropy differences, combined in the Gibbs Free Energy differences $\Delta H - T\Delta S = \Delta G$.
The ΔG-diagrams for two temperatures, 400 and 750 K, near both ends of the temperature range covered by the measurements, are shown in figs. 13 (Sferosil) and 14 (Ketjensil) (p. 42).

The diagrams for the two catalysts are very similar. In both cases the middle free energy barrier is low at low temperature and is pushed up by increasing the temperature, without, however, becoming the highest barrier in the system.
It is interesting in the light of this finding to consider again the situation on the surface with respect to the interconversion of the two surface intermediates 1* 2*.
For the case $Z \longrightarrow 1 + E$ we derived earlier (equation 7)

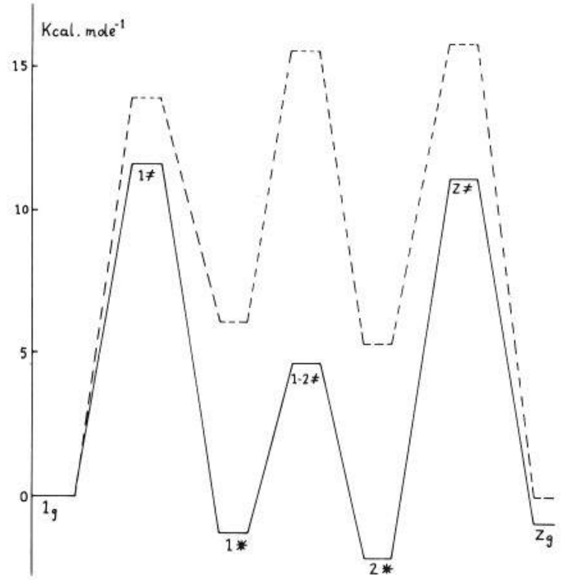

Fig. 13 The Gibbs Free Energy diagram for Sferosil at 400 and 750 K

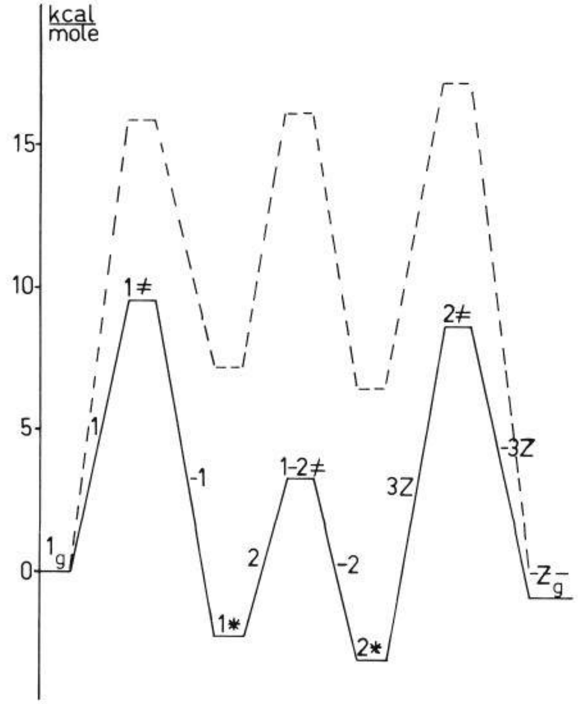

Fig. 14 The Gibbs Free Energy diagram for Ketjensil at 400 and 750 K

$$\frac{\theta_2}{\theta_1} = \frac{k_2 + k_{-1}}{k_{-2}} = K_2 \frac{1 + \alpha}{\alpha}$$

For the case $1 \longrightarrow E + Z$ we can derive along similar lines:

$$\frac{\theta_2}{\theta_1} = \frac{k_2}{k_{-2} + k_3} = K_2 \frac{\beta}{1 + \beta}$$

From the values of the parameters A, B, C and D we find that for both catalysts at low temperatures – up to about 500 K – both α and β are very much larger than unity, so that $\theta_2/\theta_1 = K_2$.

Thus at low temperature the two surface intermediates are in interconversion equilibrium and act kinetically like a single surface intermediate, similar to the carbonium intermediate. This is one explanation why Hightower and Hall (6) could use this description successfully. The same authors used a description based on first order kinetics and it might appear surprising that this was successful, in the light of our findings. However, in their study always relative rates for two feeds, one normal and one labeled, were used and in a ratio of rates the denominators of the Langmuir expressions may well cancel.

At first sight it may seem surprising that at low temperature – not at high temperature – the surface intermediates are in interconversion equilibrium. We should, however, realise that at low temperature the enthalpy differences – activation energies – are determinative and the surface intermediates are hemmed in by the adjacent high activation barriers, with the result that the surface intermediates form an equilibrated pool. At higher temperature the in- and outgoing reactions are accelerated much more than the surface interconversion reactions and the former then act as a disturbing influence on the surface equilibrium.

The rates of formation of E-2-butene and 1-butene from Z-2-butene

We recall that the extensive rate data for this reaction so far have not been used, except for the change in reaction order with temperature for Sferosil. Nevertheless we were able to characterize the reaction system completely. On this basis we should now be able to predict the rates for the conversion of Z-2-butene and compare them with the observed data.

Before embarking on this exercise it is good to recall that the basis is formed by the rate data for conversion of 1-butene, measured only over a temperature interval of 100 K. Since the rates for conversion of Z-2-butene were measured over a temperature interval of almost 400 K, the exercise has the character of predictive extrapolation.

Fig. 15 to 17 show the calculated curves, together with the measured data points, for Sferosil. Fig. 15 gives the temperature dependence of ${}_{-1}k$ – the Arrhenius plot – where as we may expect the calculated curve fits the measured data well: these data were used as input. Figs. 16 och 17 show the Arrhenius plots for formation of E-2-butene and of 1-butene respectively from Z-2-butene. The curves are

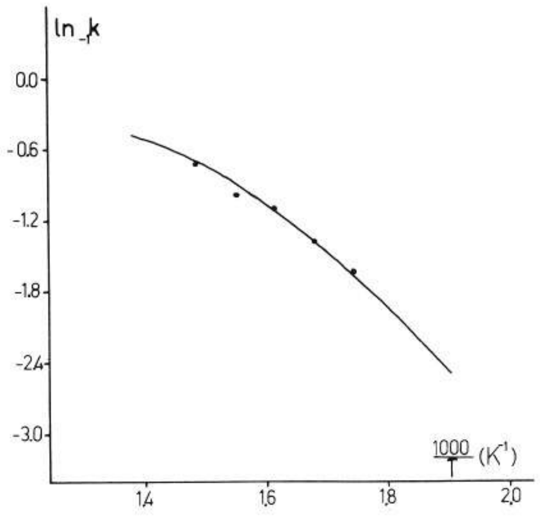

Fig. 15 Arrhenius plot $\ln_{-1}k = f(1/T)$ for Sferosil. Feed 1-butene

calculated and show a fair degree of prediction of the rate behaviour. There is some systematic deviation in the sense that the measured rates at the highest temperatures are somewhat higher than predicted. We have to bear in mind on the one hand the extended temperature interval, compared to the rate study of

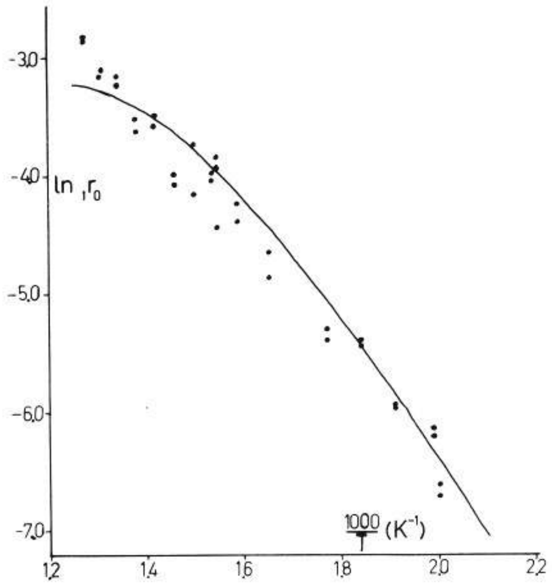

Fig. 16 Rate of formation of 1-butene from Z-2-butene on Sferosil. Drawn line computed from basic parameters, without use of the experimental data, represented by points

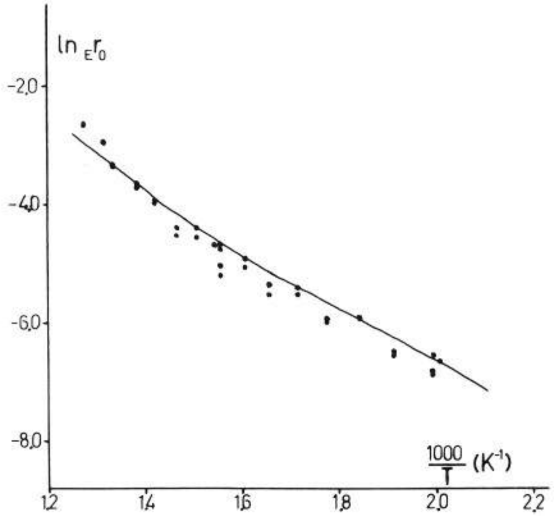

Fig. 17 Rate of formation of E-2-butene from Z-2-butene on Sferosil similar to fig. 16

conversion of 1-butene, from which the basic parameters were derived. We also recall that a basic assumption of the treatment is that the same number of active sites are operative under all conditions. Admittedly the catalysts have been preignited at the highest temperature of the rate studies. It still appears possible that at the highest temperature some extra active sites might be generated. In all the agreement for catalyst Sferosil is very fair.

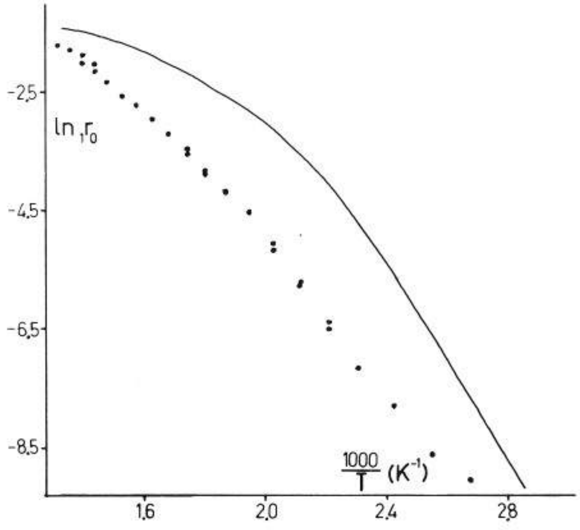

Fig. 18 Rate of formation of 1-butene from Z-2-butene on Ketjensil. Drawn line computed from basic parameters, derived from rates of isomerization of 1-butene and from selectivity in isomerization of Z-2-butene

The result for Ketjensil is less favourable, as is shown in fig. 18 in the form of the Arrhenius plot for the rates of formation of 1-butene from Z-2-butene. In the first place the predicted rates are systematically too high. Up to a temperature of about 560 K the average error factor is about 7. We now recall the interpretation we gave of the very low active site density. If there is some truth in the idea that an ensemble of e.g. three impurity atoms forms the active site, then the actual active site density should be extremely sensitive to the impurity level. A slight variation of this level between the sample used for the 1-butene isomerization study and that used for the Z-2-butene isomerization may explain the observed deviation.

In the second place there is again the deviation at high reaction temperature. After shifting the calculated curve down by a fixed amount we find again that the data points at the highest temperatures are lying systematically above the shifted predicted curve. Here the same tentative explanation as put forward for Sferosil – some further activation at the highest reaction temperatures – may be considered.

Obviously the basic reason for the observed deviations may be more fundamental. We recall that the entire treatment is based on the drastic simplifying assumptions inherent in a Langmuir type treatment: homogeneous surface, no interaction between adsorbed species. This undoubtedly must be an over-simplification, which, for the dilute catalyst systems involved in this study, may be reasonable but may still cause some systematic deviations.

The physical meaning of the assumed mechanistic model

The mechanistic model with two surface intermediates, 1* and 2*, proved a very successful approach for description of the data. Both the selectivity behaviour and the rates in their dependence on temperature could be described with very fair accuracy.

We should now consider what can be the physical meaning of the surface intermediates. We discussed already that the conventional carbonium intermediate, (7) of which we must assume that there is only one for the butenes because of the higher stability of the secondary carbonium ion, cannot serve our purpose. Another intermediate which has been proposed (8) for the interconversion of the linear butenes is an allylic one, formed by donation of one H to a Lewis site. Since the allylic grouping must be expected to be straight with respect to the axis through the three carbon atoms, for the butenes again there would be only one single surface intermediate. Therefore also this mechanism cannot describe the maximum in n(T).

π-bonding of an olefinic double bond to a sufficiently acidic surface proton has been proposed (9, 10). This clearly would lead to a mechanism with three different surface intermediates, derived from the three butene isomers, as already proposed qualitatively in fig. 2, since adsorbed Z- and E-2-butene will have different structure. We might envisage the conventional secondary carbonium intermediate as a transition state for interconversion between the three surface intermediates (11) as shown in fig. 19.

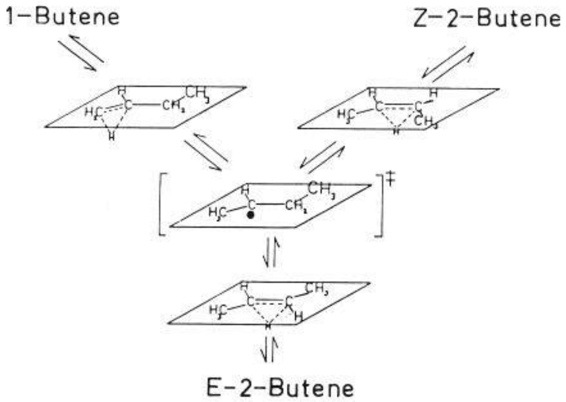

Fig. 19 Mechanism with three intermediates, identified as the three π-bonded proton complexes

Now how do we bridge the gap between this mechanism and the simpler 2-intermediate one, which proved so successful to describe the kinetic data? For this we see two possibilities. If we assume the surface proton to be sufficiently acidic, then we might imagine that the π-electrons of the adsorbed 2-butenes are withdrawn to such an extent from between the olefinic carbon atoms that rotation around the $C = C$-axis becomes easy enough. Then the difference between the two adsorbed 2-butenes will disappear and the mechanism of fig. 19 will degenerate to the one we used in the kinetic analysis. Obviously at low temperature the free energy barrier between all three intermediates will be relatively unimportant and in that temperature range the system will behave kinetically like a one-intermediate system.

There is, however, a further possibility which recalls to us the limitations of kinetics in mechanistic study. Earlier we mentioned already that the 3-intermediate mechanism leads to a very complex rate equation, which however, can be derived along similar lines as we did for the 2-intermediate case. As we may expect, the equations we used are simply degenerations of this complex rate equation. Now it appears plausible to assume that this complex equation will retain the salient properties of the 2-intermediate equation, so that we may confidently expect that also this mechanism will lead to a maximum in n(T), even though this is not easy to demonstrate mathematically.

Some final remarks

In the general introduction we expressed regret that the application of kinetics in the elucidation of catalytic mechanism has declined in recent years to almost non-existence. We hope that the second example has demonstrated that kinetic studies still deserve a place under the catalytic sun.

We again stress the point that kinetics focus attention on those intermediates on the surface, which are actually involved in the catalytic reaction. The main drawback of spectroscopic identification of intermediates is that often there is no possibility to ensure that the intermediates one sees have any relevance for the catalytic act. In the case of the butene interconversion there may well be a hundred different intermediates – e.g. polymers – which are simply dead ends, not contributing to the catalytic pathway.

If there is truth in our finding that the density of catalytically active sites on the surface is extremely low, then the findings with perdeuterated catalysts (12, 13), a very low incorporation of deuterium in the products, finds a natural explanation, because obviously this small number of sites, even though initially deuterated, will immediately be protonated in their first participation in the catalytic act and no further deuteration of products will occur.

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