Reactions of 2-Methylpropene and other Alkenes on Zinc Oxide

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Studies have been made on the hydrogenation, deuteration and exchange with deuterium of ethene, propene and 2-methylpropene on zinc oxide and Arrhenius parameters for the reactions have been determined. Some general conclusions are reached about the catalytic behaviour of alkenes on zinc oxide from these and earlier results.

Exchange occurs readily with alkenes which can dissociate to allyl intermediates but can also take place *via* the formation of vinyl intermediates with other alkenes, particularly at higher temperatures. Similar rates of alkane formation are found with different alkenes at temperatures at which the strengths of adsorption of the alkene are equivalent. The mechanism of alkane formation does not contribute to exchange of the alkene nor give rise to double-bond movement and the probable rate-determining step is the formation of adsorbed alkyl species which are then rapidly converted to alkane.

Many of the properties of zinc oxide as a catalyst for reactions of alkene such as hydrogenation or exchange with deuterium were established by Kokes and coworkers and have been reviewed by Kokes and Dent.¹ With ethene, exchange with deuterium is not observed and the addition reaction gives $C_2H_4D_2$ as the only product; the rate-determining step is the formation on the surface of the ethyl species which is then converted to ethane sufficiently rapidly so that there is little chance of it dissociating again and giving rise to exchange of the alkene. With propene, the reversible formation of adsorbed allyl intermediates is an important process giving rise to inter- and intra-molecular exchange, and in the presence of deuterium the exchange of up to five hydrogen atoms is observed together with the production of propanes having a range of isotopic content.¹⁻³ Similar allylic intermediates are thought to be involved in the isomerization of n-butenes, reactions which have been studied by a number of groups³⁻⁶ and recently by Goldwasser and Hall.⁷ Much of this work has been reviewed by John.⁸ Studies⁹ with cyclopentene and deuterium have shown that exchange of the olefinic hydrogen atoms occurs by reversible dissociation to the adsorbed cyclopentenyl species and that the formation of cyclopentane takes place by a mechanism closely allied to that for ethane formation from ethene, the rate-determining step being the production of adsorbed cyclopentyl species and the initial product being 1,2-dideuterocyclopentane.

The objective of the present work was first to study exchange and addition reactions of 2-methylpropene on zinc oxide and secondly to make some quantitative comparisons between the rates of reaction of various alkenes on the catalyst. Oyekan and Dent¹⁰ showed by infrared spectroscopy that a π -allyl species is formed readily on zinc oxide from 2-methylpropene but catalytic reactions with this alkene/oxide system have been studied only at moderately high temperatures.⁵ Most of the early studies carried out by Kokes and coworkers with ethene or propene were restricted to a

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single temperature. Thus, it was necessary to repeat some of their work using a range of temperatures to obtain Arrhenius parameters in order to be able to make adequate comparisons between the reactions of the alkenes.

EXPERIMENTAL

The zinc oxide was Kadox 25 supplied by the New Jersey Zinc Co. and it had an area of 10 m² g⁻¹ measured by nitrogen adsorption. The hydrocarbon gases were of C.P. grade and were purchased from Cambrian Chemicals Ltd. The source of the hydrogen and the deuterium and most of the experimental arrangements were as described previously.⁹

Reactions were followed in static systems either by gas-chromatographic analyses or by means of a mass spectrometer.⁹ Separation of the C_2 - C_4 hydrocarbons by gas chromatography was achieved by a 2 m column of activated alumina with 3% by weight of squalane using nitrogen as carrier gas. For ethene as reactant the column was operated at 293 K under an excess pressure of nitrogen of 138 kPa; corresponding temperatures for propene and 2-methylpropene were 348 and 368 K with excess pressures of 207 and 241 kPa, respectively.

For most experiments the pretreatment of the catalyst followed closely the main procedure used by Dent and Kokes.¹¹ The catalyst was degassed as the temperature was raised to 573 K. exposed to hydrogen (16 kPa) for 30 min with the reaction vessel opened to a cold trap in liquid nitrogen and then evacuated and the temperature raised to 723 K for 16 h.

The usual reaction mixture contained 1.2 kPa of hydrocarbon with a 10:1 ratio of hydrogen (or deuterium): hydrocarbon, corresponding to a charge of ca. 6 or 7×10^{19} molecules in the reaction vessel depending on the temperature used.

RESULTS

After an initial period, in most hydrogenation experiments the percentage of alkane rose steadily with time up to ca. 50% conversion and then the rate decreased as the alkene was used up. 'Initial' rates of reaction were determined either directly from the steady rate or by application of a power rate law if rates were decreasing with conversion. For application of the power rate law it was assumed that hydrogenation followed the equation

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -k_{\mathrm{r}} \left(\frac{x}{100}\right)^n \tag{1}$$

where x is the percentage of alkene present at time t, k_r is the initial rate of reaction expressed as % per unit time and *n* is the order of reaction with respect to alkene. The effects of changes in the pressure of hydrogen were ignored because most experiments were carried out with a 10:1 mixture of hydrogen: alkene. Integration of eqn (1) gave

$$x^{(1-n)} - x_0^{(1-n)} = -(1-n)k_{\rm r}t/(100)^n \tag{2}$$

where x_0 is the percentage of alkene at t = 0. If n-1 was suitably chosen plots of $x^{(1-n)}$ against time were linear and used to determine k_r , the initial rate of reaction.

A more complete analysis of the variation of the rate with alkene percentage was carried out using Langmuir isotherms for some reactions taken to more than 90% conversion but these will be described in a separate section.

ETHENE

Hydrogenation and deuteration were studied in the temperature range 247–294 K using ca. 7×10^{19} molecules of alkene in the reaction vessel. A typical experiment is shown in fig. 1, which illustrates the decrease in the rate of reaction at higher conversions and the application of eqn (2) using n = 0.3. Rates of individual experiments are reported in the Arrhenius plots in fig. 2 and the derived parameters



Fig. 1. Reaction of 1.12 kPa ethene in a 10:1 hydrogen: alkene mixture on 0.5 g zinc oxide at 294 K and the plot according to eqn (2) using n = 0.3.



Fig. 2. Arrhenius plots for the hydrogenation, \bigcirc , or deuteration, \square , of ethene.

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reaction	temp. range/K	$E/kJ \text{ mol}^{-1}$	$\log_{10}(A/\text{molecule s}^{-1}\text{ m}^{-2})$		
$C_2H_4 + H_2$	247–294	32 ± 3	21.00		
$C_2H_4 + D_2$	250-294	41 ± 2	22.27		
$(CH_3)_2C = CH_2 + H_2$	327-383	54 ± 5	22.05		
$(CH_3)_2C = CH_2 + D_2$	328-381	49 ± 3	21.45		
$(CH_3)_2C = CH_2 \text{ exc.}$	270-326	52 ± 3	23.96		
$C_3H_6 + H_2$	304-366	47 ± 5	21.78		
$\dot{C_3H_6} + \dot{D_2}$	304-364	44 ± 2	21.52		
C_3H_6 exc.	273-322	51 ± 5	23.15		
$cyclo-C_5H_8+H_2^a$	329-371	60 ± 3	23.88		
$cyclo-C_5H_8+D_9^a$	329-363	60 + 3	23.71		
$cyclo-C_5H_8 exc.^a$	324-355	82 ± 3	27.66		
$cyclo-C_6H_{10}$ exc. ^a	325-364	82 ± 5	27.00		

Table 1. Arrhenius parameters for reactions on zinc oxide

^a Results from previous work⁹ for comparison.



Fig. 3. Poisoning of ethene hydrogenation at 273 K by addition of carbon dioxide.

are given in table 1. Exchange experiments were not attempted with ethene because previous work¹² had confirmed that exchange was negligible in comparison with the addition reaction.

Some experiments were also carried out on the poisoning of the hydrogenation of ethene at 273 K by carbon dioxide using a recirculating reactor similar in construction to that described by Hightower and Hall¹³ with a 4.18 cm³ doser upstream from the

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catalyst. The mean rate of reaction $(7.9 \times 10^{14} \text{ molecule s}^{-1} \text{ m}^{-2})$ determined for the hydrogenation of ethane before adding carbon dioxide was comparable with the value (8.8×10^{14}) in the static system. The influence of successive doses of carbon dioxide on the rate of hydrogenation was followed and the results obtained are shown in fig. 3. The admission of 2.29×10^{18} molecule m⁻² of carbon dioxide effectively destroyed the activity of the catalyst.



Fig. 4. Hydrogenation of 2-methylpropene on 1.0 g zinc oxide at ○, 329 and □, 383 K.

2-METHYLPROPENE

The hydrogenation and deuteration of 2-methylpropene were studied over the temperature range 327-383 K and typical reactions are shown in fig. 4. At the lower end of the temperature range some 3% conversion to 2-methylpropane occurred rapidly and this was followed by a reaction which declined over 40-60 min to a steady rate. At higher temperatures the rapid burst of reaction was followed immediately by a steady rate and the intermediate section was not discernible. The rates reported as the Arrhenius plots in fig. 5 correspond to the 'initial' rates of the steady rate of reaction. One of the hydrogenation experiments was followed by mass spectrometry using the fragment ion $C_3H_7^+$ (m/e = 43) as a measure of the alkane and the parent ion $C_4H_8^+$ (m/e = 56) as a measure of the alkene; the rate determined in this way was in agreement with rates found by gas-chromatographic analysis, as may be seen in fig. 5.

Some pressure-dependence experiments were carried out on the hydrogenation of 2-methylpropene at 383 K and the results are given in table 2. The order with respect to hydrogen was 0.9 and a four-fold change in the alkene pressure had little influence on the rate, which showed a slight maximum at the intermediate pressure of 1.12 kPa.



Fig. 5. Arrhenius plots of reactions of 2-methylpropene: ○, hydrogenation (●, measured by mass spectrometry); △, deuteration; □, exchange.

Table 2. Pressure-dependence experiments on the hydrogenation of 2-methylpropene a
383 K and of propene at 363 K

	pressure/kPa	ı	molecules hydrocarbon	initial nota		
-	(CH ₃) ₂ C=CH ₂	H ₂	$h/10^{19}$ molecule	$r/10^{14}$ molecule s ⁻¹ m ⁻²		
	1.12	5.59	5.75	2.7		
	1.12	11.2	5.75	5.5		
	1.12	22.4	5.75	8.8		
	2.24	11.2	11.5	4.6		
	0.56	11.2	2.87	3.8		
	C ₃ H ₆	H_2				
	0.6	11.2	2.95	9.7		
	1.1	11.2	5.90	12.2		
	2.2	11.2	11.8	9.2		

The amount of alkene which reacted in the rapid burst of reaction did not vary significantly with alkene pressure but was constant at ca. 1.8×10^{18} molecule g⁻¹ of zinc oxide.

The exchange reaction of 2-methylpropene with deuterium was investigated over the temperature range 270-326 K. As the exchange reaction was very much faster than the deuteration it could be followed using the appropriate peaks in the mass spectrum

without making corrections for ions formed from the deutero-alkanes. At the lower end of the temperature range the rate of exchange decreased by a factor of 2 over a period of 1-2 h but at the higher temperatures a steady rate was observed throughout the course of the reaction. The results given in fig. 5 correspond to the steady rates. The exchange process was stepwise with values of M, the mean number of deuterium atoms entering each reacting molecule, between 1.0 and 1.1; all 8 hydrogen atoms in the molecule were replaceable. Arrhenius parameters for the reactions of 2methylpropene are given in table 1.

The effects of two different pretreatments of the catalyst on the rate of hydrogenation or exchange of 2-methylpropene were examined. One was to degas the catalyst for 16 h at 723 K and the other involved the use of oxygen (16 kPa) in place of hydrogen in the standard pretreatment. Neither of these different pretreatments influenced the rate of hydrogenation at 353 K, which remained at 12.0×10^{13} molecule s⁻¹ m⁻², but in each case the amount of initial reaction was reduced to 1.5×10^{18} molecule m⁻²; likewise, neither had a significant effect on the rate of exchange at 325 K since the rate only increased by 4% to 4.53×10^{15} molecule s⁻¹ m⁻².

PROPENE

The hydrogenation and deuteration of propene were followed over the temperature range 304-366 K. As with 2-methylpropene there was a fast initial conversion followed by a period of declining rate for as long as an hour at the lower temperatures before a steady rate was attained. At higher temperatures the period before the reaction rate settled was shorter but the percentage conversion was sufficiently large by that stage that it was necessary to derive 'initial' rates by the application of the power rate law eqn (1) using n = 0.5. The results are shown as Arrhenius plots in fig. 6 and the derived parameters are given in table 1. Some experiments were carried out with different initial pressures of hydrocarbon at 363 K; these are given in table 2 and, as with 2-methylpropene at 383 K, there was little variation in rate except for a slight maximum at the intermediate pressure.

It was possible to follow the exchange of propene with deuterium only over the temperature range 273-322 K because the complications from the accompanying deuteration which occurred at approximately one-third of the rate of exchange became too substantial at higher temperatures. Exchange was stepwise with growth of the peak in the mass spectrometer at m/e = 43 (C₃H₅D) being followed successively by rise of that at m/e = 44 (C₃H₄D₂) and then at m/e = 45 (C₃H₃D₃). Simultaneously from the start of the reaction the peak at m/e = 46 rose slowly and thus was assigned to the addition product C₃H₆D₂ and subsequently small amounts of C₃H₅D₃ and C₃H₄D₄ were formed. Corrections were made to the heights of the peaks up to m/e = 45 for fragment ions from the addition products as represented by the ions from m/e = 46 upwards and exchange rates were then evaluated from the relative amounts for C₃H₆ up to C₃H₃D₃. Rates of exchange decreased by a factor of 3 over 2 h at the lowest temperature and by a factor of 2 over 1 h at the highest temperature before attaining steady rates. A satisfactory Arrhenius plot, see fig. 6, was obtained from the steady rates and the derived parameters are given in table 1.

COMPETITIVE HYDROGENATION

The recirculating system was used to examine the competitive hydrogenation of ethene and 2-methylpropene at 294 K. The experiment started with the usual 10:1 mixture of hydrogen:2-methylpropene and after the rate of reaction had settled down, see fig. 7, a charge of ethene was admitted at 135 min. The ethene had no observable effect on the rate of reaction of the heavier alkene but its own rate of hydrogenation was slower than the usual rate of 294 K by a factor of 20. If the experiment was



Fig. 6. Arrhenius plots for reactions of propene: \bigcirc , hydrogenation; \triangle , deuteration; \square , exchange.



Fig. 7. Competitive hydrogenation of ethene and 2-methylpropene over 0.7 g zinc oxide at 294 K. The initial pressures of 2-methylpropene and hydrogen were 1.21 and 11.8 kPa, respectively, and at 135 min 0.63 kPa of ethene was added; ○, % conversion of 2-methylpropene to alkane; □, % conversion of ethene to alkane.

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conducted by admitting both hydrocarbons simultaneously with hydrogen the initial rate of ethene reaction was 4 times faster (a factor of 5 lower than the normal rate) but declined markedly as the rate of 2-methylpropene hydrogenation settled down to the steady value.

USE OF THE LANGMUIR ISOTHERM FOR ALKENE ADSORPTION

Tests were carried out to see how well the course of the hydrogenation reactions of the alkenes at the upper end of the temperature ranges could be interpreted in terms of Langmuir isotherms for alkene adsorption on zinc oxide. This seemed important as a means of achieving a better understanding of the relationship between the rate of hydrogenation and surface coverage even though the application of the power rate



Fig. 8. Plots to test the applicability of the Langmuir isotherm to alkene hydrogenation: \Box , ethene at 294 K; \bigcirc , propene at 366 K; \triangle , 2-methylpropene at 383 K; \blacksquare , cyclopentene⁹ at 363 K.

law, eqn (1), had proved a useful empirical method of estimating initial rates of alkene hydrogenation in experiments where the conversion was moderately high.

If a Langmuir isotherm applies to the adsorption of alkene and the rate of hydrogenation is directly proportional to the coverage of the surface by alkene we have dn

$$-\frac{\mathrm{d}p}{\mathrm{d}t} = k_{\mathrm{L}}\theta = k_{\mathrm{L}}ap/(1+ap) \tag{3}$$

where p is the pressure of alkene, θ is the surface coverage, k_L is a rate constant and a is a constant related to the free energy of adsorption of the alkene at the temperature of the experiment. As defined, k_L will be dependent on the hydrogen coverage of the surface and the form of eqn (3) ignores effects of changes in hydrogen pressure during

	calculated	coverage, θ_0	0.75	0.76	0.71	0.81
ion	initial rate/	k_r/k_L	0.72	0.89	0.78	0.79
alkene hydrogenat	ecule $s^{-1} m^{-2}$	Langmuir (k_L)	3.1	1.35	0.7	1.9
gmuir isotherm to	rates/10 ¹⁵ mol	initial $(k_r)^a$	2.25	1.20	0.55	1.5
cation of the Lang	free energy of	$\Delta G^{\ominus}/kJ \text{ mol}^{-1}$	- 14	-17	- 19	- 18
le 3. Appli		a/atm ⁻¹	274	275	398	383
Tab		temp./K	294	366	383	363
		reactant	C,H,	C,H,	(ĊH,),C=CH,	cyclo-C _s H _s

ergy of adsorption from the gas phase at 1 atm to	of a and the initial alkene pressure.
^b the standard free en	derived from the value
^a Rates obtained from the power rate law equation;	a half-covered surface; ^c the calculated initial coverage

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the course of the reaction on hydrogen adsorption and on alkene adsorption. Integration of eqn (3) gives

$$(1/a) \ln p + p = -k_{\rm L}t + b$$
 (4)

where b is a constant. The method of applying these equations to experimental results was to draw tangents to plots of conversion against time and hence to obtain values of dp/dt at a series of values of p. A plot of the reciprocal of dp/dt against 1/p, *i.e.* the inverse form of eqn (3), was used to derive a and the value obtained was used to plot the results for p and t according to eqn (4).

One experiment for each alkene including cyclopentene⁹ plotted in this way is shown in fig. 8. The straight lines obtained confirm the validity of the Langmuir isotherm for the adsorption of alkene on zinc oxide. Derived data from these experiments are given in table 3 and the agreement between the ratios of the initial rate: Langmuir rate $(k_r:k_L)$ and the relevant initial coverages of alkene confirm that our method of estimating initial rates was satisfactory; in each case the initial rate was lower than the Langmuir rate, which was defined for a fully covered surface, *i.e.* $\theta = 1$.

DISCUSSION

There is good agreement between our results and the rates for corresponding reactions reported in the literature for Kadox 25. We find a rate of hydrogenation of ethane at 298 K of 2.5×10^{15} molecule s⁻¹ m⁻² and the same value is calculated from the results given by Dent and Kokes¹¹ adjusted to our conditions. Our rate of deuteration of propene at 338 K is 5.3×10^{14} molecule s⁻¹ m⁻² and a value of 9.4×10^{14} in the same units is obtained from the work by Naito *et al.*³ We find a rate of exchange of propene with deuterium of 3.4×10^{14} molecule s⁻¹ m⁻² at 298 K and the data from Dent and Kokes¹⁴ give 2×10^{14} or 4×10^{14} in the same units.

The time taken for the activity of the catalyst to reach a steady value appears to depend on the reactant and the temperature used. In our work some poisoning was observed with the two alkenes, propene and 2-methylpropene, which are known to form π -allyl species on zinc oxide but not with ethene or with cyclopentene⁹ which does not readily form allyl species. Likewise, the poisoning process was more evident at temperatures < 330 K and the time required for the catalyst to settle down to steady activity decreased with increasing temperature, as shown by the results in fig. 4. Chang et al.⁴ observed some self-poisoning of butene isomerization on zinc oxide and fig. 1 of ref. (4) shows evidence of an initial burst of activity. On the other hand, Frenial⁵ did not find any poisoning of the isomerization of but-1-ene at 570 K, but at this temperature we suggest that the type of poisoning process we observed would be completed rapidly. The initial burst of hydrogenation activity observed with 2methylpropene and also with propene may have originated from some active sites which then became poisoned very rapidly. The amount of the rapid reaction was not large and with 2-methylpropene corresponded to ca. 1.8×10^{17} molecule m⁻², *i.e.* only 1 molecule for 6 nm² of surface.

HYDROGENATION OR DEUTERATION

In this section we discuss the relative activity of the various alkenes and mechanistic ideas are treated in a later section. The temperature ranges found to be convenient for studying the reactions and the Arrhenius parameters (table 1) show the relative rates of hydrogenation of the four alkenes. The manner in which reactions taken to high conversion can be satisfactorily interpreted according to the Langmuir isotherm (fig. 8) confirms previous suggestions¹ that the rate of alkene hydrogenation is

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dependent on the coverage of the surface by adsorbed alkene. All the kinetic data on the influence of alkene pressure on the rate of reaction are consistent with this picture. Depending on the strength of adsorption of the alkene, the temperature and the pressure of gas present the rate of reaction may be zero order, fractional order or demonstrably Langmuirian. The results in table 2 which show evidence that the rate of reaction passes through a slight maximum as alkene pressure is increased and then decreases to a small extent at higher pressures are interpreted as a decrease in the ability of the hydrogen to react with alkene as the pressure of hydrocarbon is raised. The inhibition of the H_2/D_2 exchange reaction by the presence of alkene has been shown to be substantial^{1, 3, 7} and the rate is reduced by a factor > 30 at 301 K by addition of butene equivalent to the amount of H_2 or D_2 present.⁷

The results in table 3 not only confirm that the Langmuir isotherm is applicable to alkene adsorption on zinc oxide but also suggest a possible factor influencing the relative rates of hydrogenation of the alkenes. It may be significant that for each of the alkenes a similar rate of reaction (ca. 10^{15} molecule s⁻¹ m⁻²) is observed at a temperature at which the strength of adsorption is represented by a value of a of ca. 300 atm^{-1} . This could be a particular example of the general principle that effective catalysis requires an appropriate strength of adsorption. For ethene, good catalysis is found at room temperature but with larger and more strongly adsorbed alkenes higher temperatures are required in order to achieve the rate exhibited by ethene at room temperature and this rate is reached at a temperature at which the alkene has the same strength of adsorption as ethene at 294 K. The activation energies for alkene hydrogenation (table 1) seem also to conform to this picture with the value for ethene being considerably smaller than the results for the other three alkenes.

The main influence responsible for the inhibiting factor of 20 which we observed on the rate of hydrogenation of ethene due to the presence of 2-methylpropene will be competition between the alkenes for sites on the surface. Despite this inhibition the ethene still reacts many times faster than the larger alkene, showing that the latter is not eliminating adsorption of hydrogen on the surface.

Part of the explanation of the relative rates of hydrogenation of the butenes on zinc oxide may be the relative strengths of adsorption of the different isomers. Naito et al.³ gave the ratio of the rates of hydrogenation of but-1-ene: but-2-ene as 11:1 at room temperature but Goldwasser and Hall⁷ did not observe any addition reaction with either cis- or trans-but-2-ene at 301 K under conditions which gave an appreciable rate of formation of butane from but-1-ene. Chang et al.4 found that the adsorbed π -complex and the π -allyl species formed from *cis*-but-2-ene were particularly stable, which may account for the smaller rate of hydrogenation. Our results indicate that the rate of hydrogenation of 2-methylpropene is similar to that reported by Goldwasser and Hall⁷ for but-1-ene. We calculate by extrapolation a rate of reaction of 2-methylpropene at 301 K of 4.1×10^{12} molecule s⁻¹ m⁻² and the corresponding value estimated for but-1-ene is 3.5×10^{12} molecule s⁻¹ m⁻².

The shape of the relationship in fig. 3 between the rate of hydrogenation of ethene and added carbon dioxide shows that apart from some rather more active sites which are preferentially eliminated there is a reasonably uniform decline in catalytic activity with added gas. Of course the intercept, 2.3×10^{18} molecule m⁻², gives a maximum for the number of catalytic sites since carbon dioxide may be taken up simultaneously on sites which are not catalytically effective. In general, results for alkene adsorption correspond to an uptake of $1-2 \times 10^{18}$ molecule m⁻² on zinc oxide. Dent and Kokes¹¹ observed a saturation coverage of ca. 1.6×10^{18} molecule m⁻² of ethene, Naito et al. report the adsorption of 1.2×10^{18} molecule m⁻² of but-1-ene at 297 K and Oyekan and Dent¹⁰ found an uptake of 2.05×10^{18} in the same units for 2-methylpropene.

EXCHANGE

In this section some comparisons are made of the rates of exchange of the various alkenes using rates in molecule $s^{-1} m^{-2}$ at 325 K. 2-Methylpropene (4.0×10^{15}) reacts faster than propene (8.9×10^{14}) although the activation energies are the same. These results demonstrate that alkenes which can dissociate readily to form π -allyl species on zinc oxide undergo exchange with deuterium at appreciable rates. Cyclohexene (6.6×10^{13}) which also exchanges mainly via π -allyl intermediates⁹ reacts more slowly than propene and requires a substantially higher activation energy (table 1). Thus, there is obviously more difficulty in forming the π -allyl intermediate with the cyclic C₆ molecule. With the cyclic C₅ molecule, the formation of an adsorbed π -allyl species becomes even less significant and the exchange process is almost exclusively dependent on the reversible formation of the vinyl species leading to the replacement of the two olefinic hydrogen atoms without any accompanying double-bond movement.⁹ Although the activation energies for the exchange of cyclopentene and cyclohexene are the same, the C₅ molecule (2.4×10^{14}) reacts more rapidly by the vinyl mechanism than does the C₆ molecule by the allyl mechanism.

Comparing the relative rates of exchange and deuteration shows a range of results with the different alkenes. Exchange is faster by a factor of 100 with 2-methylpropene and by factors of 4–8 with propene or cyclopentene. Conversely, as shown previously,^{1, 2} with ethene the addition reaction occurs without evidence of accompanying exchange.

MECHANISTIC CONSIDERATIONS

Kokes and Dent¹ proposed that the rate-determining step in the addition reaction with ethene is the formation of the adsorbed ethyl, a process which is essentially irreversible because the ethyl species is quickly converted to the product ethane; the product is $C_2H_4D_2$ when deuterium is used. Our results with cyclopentene⁹ and with propene in the present work support this picture in that both alkenes gave the D_2 -alkane as the initial addition product. The Japanese workers³ have suggested that the reaction occurs by an Eley–Rideal type mechanism involving the direct addition of a gas-phase H_2 or D_2 molecule to the adsorbed alkene. But it is important to realise that the same isotopic products will result from the stepwise process as from the direct molecular addition provided that the two hydrogen or deuterium atoms which are to be added are held on Zn–O pair sites and not scrambled with other chemisorbed H or D atoms on the surface. Evidence for the existence of such pair sites was found by examining the isotopic content of the ethane molecules produced from the reaction of ethene with a mixture of H_2 and D_2 .¹

It is useful in considering the kinetic data and relative rates of exchange of different alkenes to think in terms of scheme 1 and to discuss separately non-allyl-forming alkenes and allyl-forming alkenes.

> gas alkene alkane surface (A) vinyl (5) (1) (4)(B) allyl (5) alkene (3) alkyl

> > Scheme 1.

NON-ALLYL-FORMING ALKENES

This group contains ethene and cyclopentene and for these the possible dissociated species in scheme 1 is (A) vinyl.

Alkane formation occurs by steps (1), (3), which is rate-determining, and (4). Since

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step (4) is faster than step (3) the back reaction from adsorbed alkyl to adsorbed alkene is omitted and the formation of alkyl plays no part in alkene exchange or double-bond movement. Alkene exchange may occur by steps (5) and (6) dependent on how fast these are in relation to step (3). Clearly with cyclopentene, which exchanges some 4-8 times faster than it forms cyclopentane, steps (5) and (6) take place more readily than step (3). With ethene, the absence of any detectable exchange of the alkene at the comparatively low temperature at which the addition reaction takes place is probably a consequence of a difference in activation energy between exchange and addition. In other words, we are suggesting that the activation energy of the exchange of ethene by steps (5) and (6) is likely to be nearer the value of 82 kJ mol^{-1} found for cyclopentene exchange than to the value of 41 kJ mol⁻¹ observed for the deuteration of ethene by step (3). Steps (5) and (6) only become important with ethene in the absence of added H_2 or D_2 and they can lead to the scrambling reaction between C_2H_4 and C₂H₄ which has been observed^{2, 15} under these circumstances and which greatly reduces the chance of steps (3) and (4) occurring.

Alkane formation from both ethene¹⁶ and cyclopentene⁹ showed a kinetic dependence of ca. 0.5 order with respect to hydrogen (or deuterium) pressure and both showed a 'normal' primary kinetic isotope effect of ca. 1.5 for $k_{\rm H}/k_{\rm D}$ for cyclopentene⁹ at 350 K and 2.3 for ethene at room temperature.¹⁶ We can easily relate the half-order kinetic dependence on hydrogen to the rate-determining step (3) by assuming that most of the hydrocarbon is present on the surface as alkene and that reaction takes place between the adsorbed alkene and a relatively weakly adsorbed hydrogen atom.

ALLYL-FORMING ALKENES

In this group we consider primarily propene and 2-methylpropene but cyclohexene could also be included. The dominant dissociated species in scheme 1 will be (B) allyl, although a smaller quantity of vinyl species may also form. The infrared and adsorption studies reviewed by Kokes and Dent¹ suggest that a substantial fraction of the sites on the surface will be occupied by allyl species and a lower fraction by undissociated alkene. We believe that the difference between the two groups of alkenes in the proportion of the surface occupied by adsorbed alkene is important and gives rise to some of the different kinetic effects observed with the allyl-forming alkenes. Both propene and 2-methylpropene show 'abnormal' kinetic isotope effects for the addition reaction; at 323 K, $k_{\rm D}/k_{\rm H} = 1.5$ for propene and 2.7 for 2-methylpropene. Also the addition reaction with 2-methylpropene is nearly first order in hydrogen in contrast to the half-order found with the non-allyl-forming alkenes. The kinetic results for the allyl-forming alkenes can be rationalised if one assumes that the ratio of adsorbed alkene: adsorbed allyl is proportional to the square root of the hydrogen pressure and that the adsorbed allyl occupies the major fraction of the sites. The rate-determining step for the addition reaction is still step (3) involving the union of a weakly adsorbed hydrogen atom $(\propto p_{\rm H_2}^{\rm t})$ with the adsorbed alkene, giving rise to an overall first-order dependence on hydrogen. We suggest that the abnormal kinetic isotope effect arises because the equilibrium between adsorbed allyl and adsorbed alkene is shifted towards adsorbed alkene when deuterium is used in place of hydrogen.

But the dominant reaction with the allyl-forming alkene is exchange with deuterium which takes place substantially more rapidly than the addition reaction especially with 2-methylpropene. It follows that steps (5) and (6) and also steps (1) and (2) are faster than step (3). The results in table 1 show that the activation energies for exchange of propene and 2-methylpropene are similar and significantly less than the value for cyclopentene in keeping with the greater rate of exchange found with the allyl-forming

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alkenes. Cyclohexene does not exchange nearly as readily as the other allyl-forming alkenes and also exhibits a higher activation energy but these differences presumably result from the restrictions on allyl dissociation associated with the C_6 ring.

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