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CATALYTIC PROTIUM-DEUTERIUM EXCHANGE OF PROPANE/HYDROGEN MIXTURES

By

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Abstract

With a view to its possible use as a test reaction for low-surface-area alloy films we have studied the exchange between propane and deuterium. It is shown that the product distribution of a deuteration reaction can be described by two parameters: one expressing the kinetic inequivalence of primary and secondary hydrogen atoms in propane, the other characterizing the catalyst selectivity for multiple versus stepwise exchange.

A method is presented for the calculation of the product distribution from this two-parameter model. Calculated distributions are compared with experimental ones obtained on nickel and rhodium at low temperature.

Besides, the occurrence of important isotope effects in reactions involving considerable dedeuteration is demonstrated.

Severe self-poisoning was found at 50°C with nickel and some copper-nickel alloys. No self-poisoning was detected at -40°C. Under non-suspect conditions, the addition of copper to nickel resulted in a lowering of the catalytic activity. But under self-poisoning conditions some alloys were apparently more active than nickel.

I. Introduction

The exchange between propane and deuterium has been shown to be a valuable test reaction for comparing the catalytic properties of pure metals.¹⁾ Two types of information, characterizing the catalyst, are obtained:

- (1) the catalytic activity, expressed by the overall rate of reaction;
- (2) the selectivity for multiple *versus* stepwise exchange.

The latter is deduced by analysing the propane-isotope distribution of the reaction product. However, such an analysis is interwoven with the problem of the inequivalence of the hydrogen atoms in propane (primary and secondary hydrogen atoms) and with the isotope effects, which also influence the isotope distribution of the reaction product.

In the present work, hydrogen inequivalence and multiplicity were studied

in the reaction of light propane with deuterium, whereas for the study of the isotope effects two deuteropropanes were used.

The bulk of our work applies to the exchange on nickel films at -40°C . The reaction has also been studied in an exploratory way on copper and copper-nickel alloy films at $+50^{\circ}\text{C}$. With the reactions at 50°C attention was also paid to the tendency of the metals to promote self-poisoning rather than exchange.

Model calculations have been carried out to describe the isotope distributions arising from multiple exchange of molecules containing inequivalent hydrogen groups. The calculated distributions were compared with the results of the mainly stepwise reaction on nickel and with the mainly multiple reaction on rhodium, which was reported by KEMBALL.¹⁾ In both cases we found satisfactory agreement between calculated and observed distributions.

II. Experimental

The catalysts used were films evaporated at 10^{-10} Torr onto the inside surface of a 200-ml reactor bulb which was kept surrounded by ice during film deposition. The surface area of the film substrate amounted to approximately 200 cm^2 . After deposition the films were sintered for 16 hours at 200°C . In this period the pressure temporarily rose to 10^{-8} Torr.

For the nickel films, a helix of 0.3 mm thick spec.-pure nickel wire was used as an evaporation source. The helix consisted of 5 loops with a radius of about 2 mm. The length of the helix was about 8 mm. Spec.-pure copper was evaporated from a bud in the bend of a tantalum hair pin. Both sources were heated by passing a controlled current through them.

Alloy films were prepared with a source consisting of a nickel helix whose centre loop was entwined with spec.-pure copper wire. Since the evaporation took place mainly from the centre loop, this source could be used to prepare uniform alloy films containing up to 50% copper.

The reactor bulb was part of the bakeable ultrahigh vacuum system, which was operated by means of 75 l/s Vac Ion pump. It could be separated from the ultrahigh vacuum system by means of a glass ball-joint valve. The reaction was started by admitting 3 Torr of a purified mixture of propane and deuterium (molar ratio 1 : 9) to the entire vacuum system, with the reactor bulb at the desired temperature. After this admission the ball-joint valve was closed. The reactor was connected to a CEC 21-620 mass spectrometer by means of a Granville Phillips adjustable leak. The instrument, manufactured by Consolidated Electrodynamics Corporation, was modified in two respects. The ionizing-electron voltage was made adjustable between 12 and 86 V, and

Catalytic Protium-Deuterium Exchange of Propane/Hydrogen Mixtures

the sample bypass system was replaced by a direct duct between the adjustable leak and the cycloid tube. The pressure drop in the reactor due to sampling was less than 10% for the duration of the reaction.

The spectra were scanned intermittently. The peak heights (C_3^+ ions and masses 4, 3 and 2) were plotted as a function of time and the instantaneous spectra were obtained by interpolation. These spectra were analysed by making the usual assumptions of equal parent peak sensitivity for all isotopes and of random hydrogen loss in the fragmentation. In the reactions with pure deuterated compounds, the measured fragmentation patterns were used. The methods of analysis proved satisfactory with respect to the peak remainders at mass number 43 and the deuterium balance.

The reactant gases, deuterium and propane, were purified by passing them separately over a freshly reduced nickel catalyst, and by storing them as a mixture in a 2.5-l bulb which contained a film of about 1 gram of potassium. Deuterium was a mixture of 98.5% deuterium and 1.5% protium from Stuart Oxygen Co, propane was obtained in research grade purity from Phillips.

The monodeutero compounds (obtained from Merck, Sharp and Dohme) were purified by a potassium film and the hydrogen and deuterium used in the experiments with the labelled compounds was purified by diffusion through a heated palladium thimble.

Perfect repeatability of the reaction of propane and deuterium on the same film proved that the gas purification was sufficient.

III. Inequivalence, Isotope Effects and Multiplicity, and the Influence Thereof on the Isotope Distributions

1. Analysis of the mechanism

The simplest analysis of a propane-deuterium exchange reaction involves the following assumptions:

- (1) all eight hydrogen atoms are exchanged at the same rate;
- (2) protium atoms are exchanged at the same rate as deuterium atoms, *i.e.* there are no kinetic isotope effects;
- (3) in equilibrium of exchange, hydrogen and hydrocarbon have the same deuterium content;
- (4) only one hydrogen atom has a chance of being exchanged during one residence of a propane molecule on the catalyst surface.

On the basis of these assumptions the product distribution would be binomial:

$$d_i = \binom{8}{i} \sigma^i (1-\sigma)^{8-i} \quad (1)$$

R. JONGEPIER and W. M. H. SACTLER

In this equation d_i designates the fraction of propane molecules containing i deuterium atoms and
 σ is the mean deuterium content of the hydrocarbon:

$$\sigma = \frac{1}{8} \sum_{i=1}^8 i d_i ; \quad \sum_{i=0}^8 d_i = 1 . \quad (2)$$

Deviations of the observed distributions from the binomial ones directly indicate that one or more of the above assumptions do not hold. In the following discussions we will successively drop the assumptions 1 to 4.

If condition (1) is not fulfilled (kinetic inequivalence), the primary and secondary hydrogen atoms of propane exchange at different rates, *i.e.* adsorbed n-propyl radicals are formed at a different rate from that of the isopropyl radicals. This phenomenon is studied in Section III-2 A.

The presence of kinetic and thermodynamic isotope effects (non-validity of (2) and (3)) will be considered in Section III-2 B.

Departure from condition (4) is called multiple exchange, which implies that more than one hydrogen atom can be exchanged during one residence. For a molecule which has exchanged, *e.g.*, two hydrogen atoms during one residence on the catalytic surface, one might still visualize that:

- (a) two carbon-metal bonds were formed simultaneously, or
- (b) a mono-adsorbed structure was subsequently transformed into a bi-adsorbed structure, or
- (c) one mono-adsorbed structure has "swung over" to another mono-adsorbed one.

This distinction, however, does not affect the product distribution. For simplicity we shall therefore describe the process in terms of (c). More generally speaking: multiplicity is treated as being due to a number of successive exchange processes during one residence. We further assume that these successive exchange steps occur by alternation of a single propane-metal bond

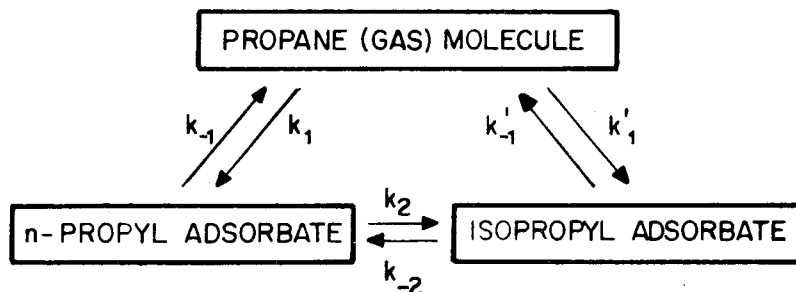


Fig. 1. Reaction scheme of propane-deuterium exchange.

Catalytic Protium-Deuterium Exchange of Propane/Hydrogen Mixtures

between neighbouring carbon atoms. The implication of multiplicity in combination with inequivalence is discussed in Section III-3.

The non-validity of assumptions (1) and (4) gives rise to the reaction scheme shown in Fig. 1.

2. Stepwise exchange with inequivalent hydrogen

(Experimental evidence of inequivalence and isotope effects)

A. Mass-spectrometric evidence

As a first approximation to the actual exchange reaction of propane and deuterium we consider the case where methyl and methyne hydrogen atoms are kinetically inequivalent, but assumptions (2), (3) and (4) are supposed to be valid; in terms of Fig. 1: k_2 and k_{-2} are negligible with respect to k_{-1} and k'_{-1} .

This kinetic inequivalence is reflected not only in the isotope distribution, but also in the composition of the monodeuteropropanes. There are two isomers of monodeuteropropane:



and



With kinetically equivalent hydrogen the concentration ratio of the isomers would be:

$$\frac{2\text{-D}_1}{1\text{-D}_1} = \frac{2/8}{6/8} = 1/3.$$

Hence, deviation from this ratio is direct evidence of the inequivalence. The isomeric composition of D_1 can be analysed mass-spectrometrically by observing the parent ion peak of D_1 ($\text{C}_3\text{H}_7\text{D}$)⁺ and the ethyl fragment peak ($\text{C}_2\text{H}_4\text{D}$)⁺ at mass numbers 45 and 30 respectively, both after correction for natural ¹³C. If there is no scrambling of the deuterium atom in the molecules in the mass-spectrometer, and if there is no isotope effect in the C-C fragmentation, then the deuterium atom of 2- D_1 is always in the ethyl fragment and the one of 1- D_1 occurs only in 50% of the corresponding ethyl fragment ions.

If the D_1 mixture contains fractions λ and μ of 1- D_1 and 2- D_1 , respectively, and if the parent peak sensitivity is equal for both, we have:

$$\begin{aligned} \lambda + \mu &= h_{45} \\ \frac{1}{2} C\lambda + C\mu &= h_{30}, \end{aligned} \tag{3 a}$$

where h_{45} and h_{30} are the peak heights due to D_1 and C is the fragmentation coefficient of $(C_2H_5)^+$ with respect $(C_3H_8)^+$ in D_0 .

In general, the three "mass-spectrometric" assumptions are not exactly valid, and we write :

$$x\lambda + y\mu = h_{30}. \quad (3\ b)$$

Measuring x and y on samples of pure 1- D_1 and 2- D_1 , we found $x=2.69$; $y=5.10$; $y/x=1.9$ instead of 2.

For the determination of λ and μ we need the peak height at mass numbers 45 and 30, which are exclusively due to D_1 . The corrections for contributions from higher isotopes, D_2 , etc., are relatively small as long as σ is low enough (see Eq. 1). In this case the corrections can be made by using the estimated isotope patterns of D_2 , etc.

The results of the determinations of λ and μ are given in Table I.

TABLE I. Isomeric Composition of D_1 in the Initial Stage of the Exchange of Propane and Deuterium on Nickel Films at -40°C

λ = fraction of 1- D_1 in D_1
 μ = fraction of 2- D_1 in D_1

D_0 conversion %	μ %	μ/λ
12.0	80.2	4.0
16.5	78.4	3.5
22.0	84.8	5.5
27.0	82.9	4.8
average	82.0	4.5

If y/x is taken to be 2.0 instead of 1.9, we arrive at $\mu/\lambda=9$, which is in agreement with KEMBALL's results.¹⁾

The reactivity ratio of secondary and primary hydrogen can be represented by a parameter P , which we will use later on in our model calculations. P characterizes the resulting rate of the reaction k'_1 , k'_{-1} with respect to k_1 , k_{-1} , i.e. the *a priori* probability of iso-adsorption over normal-adsorption. Hence:

$$\frac{P}{1-P} \approx \mu/\lambda \approx 4,$$

which differs considerably from the value corresponding to kinetically equivalent hydrogen :

Catalytic Protium-Deuterium Exchange of Propane/Hydrogen Mixtures

$$\frac{P}{1-P} = 1/3.$$

In terms of the net rates of exchange of primary (k_p) and secondary hydrogen atoms (k_s), the latter thus exchange about twelve times faster:

$$\frac{2k_s}{6k_p} \approx 4; \quad k_s = 12 k_p.$$

Assuming that the net reaction rate is controlled by the adsorption rate (reaction order in propane is unity¹⁾), and that the rate of adsorption is governed by the free energy of H-atom abstraction, we may expect that the differences between secondary and primary hydrogen are reflected in the thermodynamics of propylradical formation. The available data, which are given in Table II, are unfortunately, very inaccurate. They agree with our results in that the isoradical is slightly more stable than the normal radical.

TABLE II Standard Entropies and Enthalpies of Formation of Propyl Radicals

Species	ΔS (ref. 2)	ΔH (ref. 3)	ΔH (ref. 4)
		kcal/mole	
Isopropyl rad.	67.55 ± 0.5 e.u.	94	98.2 ± 0.6
Normal-propyl rad.	69.32 ± 0.5 e.u.	98	98.6 ± 0.6

B. Isotope effects; exchange experiments of 1-D₁ and 2-D₁ with protium-deuterium mixtures

We now consider experiments in which a monodeuteropropane reacts with a protium/deuterium mixture having the same isotopic composition as monodeuteropropane, *viz.* H : D = 7 : 1.

In the absence of a "thermodynamic" isotope effect equilibrium is indicated by an equal isotopic composition of the hydrogen atoms in propane and in molecular hydrogen, *viz.*

$$\sigma = \gamma, \quad (4 a)$$

$$\text{where } \gamma = \frac{2D_2^* + HD}{2(H_2 + HD + D_2^*)}.$$

(The symbol D_2^* stands for "molecule of deuterium" in order to avoid confusion with the symbol D_2 which stands for di-deuteropropane.)

At $\gamma = 0.125$ such a mixture would be in equilibrium from the very beginning as far as the above criterion is concerned.

However, since the deuterium should be randomly distributed over all

eight places, such a mixture will not initially be in equilibrium if we start from a well-defined monodeuteropropane, *e. g.* 1-D₁ or 2-D₁.

During equilibration, protium atoms bonded to carbon atoms will be exchanged for deuterium atoms, and deuterium atoms bonded to carbon atoms for protium atoms. In such an experiment, the σ value will temporarily depart from the initial value if the reactivity of hydrogen bonded to a primary atom is different from that of hydrogen bonded to a secondary carbon atom.

For instance, in 1-D₁ the deuterium content is $1/6=0.167$ for the six primary hydrogen atoms, but zero for the two secondary atoms. In contact with molecular hydrogen with $\gamma=0.125$ the deuterium fraction of the primary hydrogen atoms will therefore decrease and that of the secondary hydrogens will increase. As we know from the previous section that $k_p < k_s$, the overall value of σ is expected to rise initially, to pass through a maximum, and to level off at $\sigma=0.125$. The same reasoning can *mutatis mutandis* be applied to 2-D₁, having initially $\sigma_{\text{primary}}=0$ and $\sigma_{\text{secondary}}=\frac{1}{2}$. In this case σ will pass through a minimum. The curves of σ versus time as expected for this mechanism are depicted in Fig. 2.

Up to this point one would expect the experiments to provide essentially the same information as already acquired in the previous section, *viz.* the ratio k_s/k_p . However, additional information can be obtained with respect to

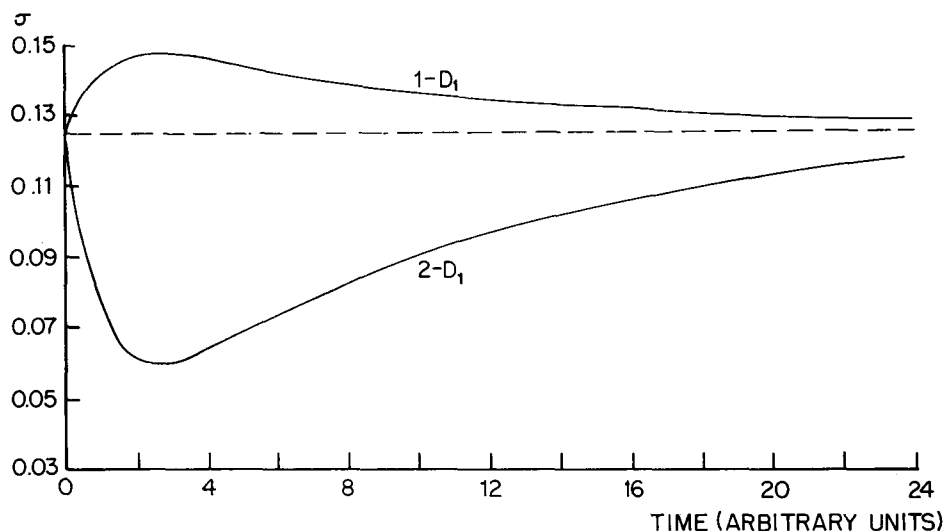


Fig. 2. Expected curves for the average deuterium content σ versus time for exchange of 1-D₁ and 2-D₁ with a 7/1 hydrogen/deuterium mixture.

Catalytic Protium-Deuterium Exchange of Propane/Hydrogen Mixtures

the isotope effects, which in these experiments are superimposed on the effect of $k_s/k_p \neq 1$.

We distinguish a thermodynamic isotope effect, which causes an equilibrium distribution for which :

$$\sigma_{\text{equilibrium}} = \beta \gamma_{\text{equilibrium}} \quad \text{with } \beta \neq 1 \quad (4b)$$

and a kinetic isotope effect, which can be defined according to :



Generally speaking, the thermodynamic isotope effect can be obtained from the equilibrium values of σ and γ , while the kinetic one can be evaluated from the initial slopes of the σ versus time curves of 1-D₁ and 2-D₁ exchange.

Before elaborating on this point it seems useful to consider the experimental results in order to gain an idea of the order of magnitude of the effects involved.

These results are represented in Fig. 3, in which σ is plotted as a function of time for two experiments. These curves immediately show that :

- (1) the initial slope of the kinetic curves is positive for 1-D₁ and negative for 2-D₁, which is an agreement with the expectation based on $k_s > k_p$;
- (2) after long reaction times σ rises above the initial value in both curves,

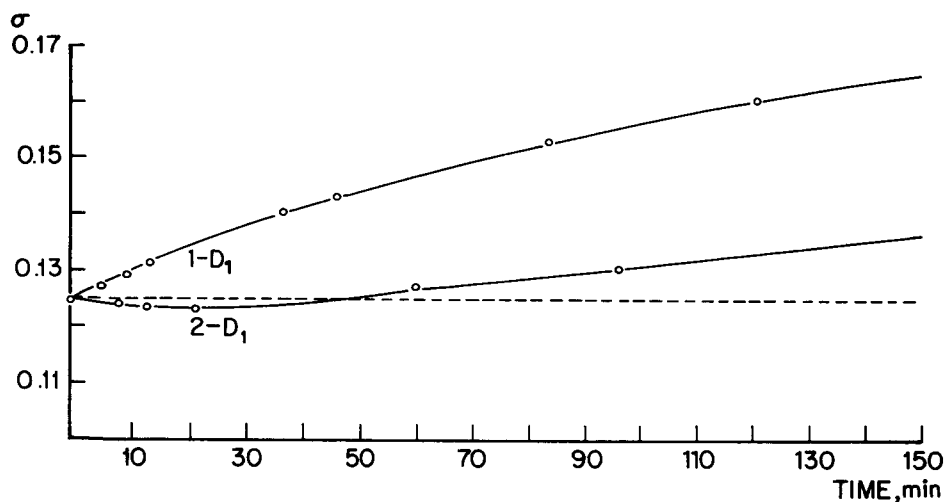


Fig. 3. Average deuterium content σ as a function of time in the exchange between 1-D₁ and 1-D₂ on nickel films at -40°C . D:H ratio = 1:7.

R. JONGEPIER and W. M. H. SACHTLER

- which indicates a non-negligible equilibrium isotope effect with $\beta > 1$;
- (3) overall equilibrium, where σ should be equal for both curves, is not attained at a reaction time of 120 minutes and a temperature of -40°C ;
- (4) the initial slopes of the two curves differ roughly in absolute value by a factor of five, which suggests the presence of an important kinetic isotope effect: $\omega < 1$ (Eq. (5)).

For a more quantitative evaluation we again assume that multiple exchange may be neglected with respect to stepwise exchange. Moreover, we assume that the exchange reaction is first-order :

$$\frac{d\sigma_p}{dt} = k_p(\sigma_p(\infty) - \sigma_p(t)). \quad (6 \text{ a})$$

In this equation σ_p is the mean deuterium content of the primary group, and

$$\frac{d\sigma_s}{dt} = k_s(\sigma_s(\infty) - \sigma_s(t)). \quad (6 \text{ b})$$

The equilibrium values for σ are given by :

$$\sigma_p(\infty) = \sigma_s(\infty) = \sigma(\infty) = \beta\gamma(\infty) = 0.125 \beta, \quad (4 \text{ a})$$

where we have assumed that hydrogen is present in such a large excess that $\gamma = 0.125$ remains unchanged.

According to Eq. (5) we define ωk_p as the rate constant for the primary group for a net dedeuteration reaction, k_p being the rate constant for the net deuteration reaction. The same kinetic isotope factor is used for the secondary groups.

As

$$\sigma = \frac{6}{8} \sigma_p + \frac{2}{8} \sigma_s, \quad (7)$$

it follows for the exchange of 1-D₁ that :

$$\frac{d}{dt} \sigma_{1-D_1} = \frac{6}{8} \omega k_p (\sigma_p(\infty) - \sigma_p(t)) + \frac{2}{8} k_s (\sigma_s(\infty) - \sigma_s(t)) \quad (8 \text{ a})$$

and 2-D₁ that :

$$\frac{d}{dt} \sigma_{2-D_1} = \frac{6}{8} k_p (\sigma_p(\infty) - \sigma_p(t)) + \frac{2}{8} \omega k_s (\sigma_s(\infty) - \sigma_s(t)). \quad (8 \text{ b})$$

When inserting the initial conditions $\sigma_p(0) = 0.167$ and $\sigma_s(0) = 0$ into Eq. (8 a), and $\sigma_p(0) = 0$, and $\sigma_s(0) = 0.5$ into Eq. (8 b), and when introducing $\sigma_p(\infty) = \sigma_s(\infty) = 0.125 \beta$ into both equations, according to Eq (4 a), then we find :

Catalytic Protium-Deuterium Exchange of Propane/Hydrogen Mixtures

$$x = \frac{\frac{d}{dt} \sigma_{1-D_1}}{\frac{d}{dt} \sigma_{2-D_1}} \Bigg|_{t=0} = \frac{-3 \frac{k_p}{k_s} \omega (0.167 - 0.125 \beta) + 0.125 \beta}{3 \frac{k_p}{k_s} 0.125 \beta - \omega (0.500 - 0.125 \beta)} \quad (9)$$

In the limiting case $k_p=0$, $\beta=\omega=1$ we would find $x=-1/3$. Although $k_p < k_s$ and isotope effects are generally assumed to be negligible, the experimental values of x appreciably differ from $-1/3$. From our four (poorly reproducible) experiments we found x values of -10 , -5.3 , -3.8 and -2.0 respectively, by combining the two 1-D₁ with the two 2-D₁ experiments in four different ways. On an average, the expected and observed x values differ by a factor of 15.

Eq. (9) contains three parameters, $\frac{k_p}{k_s}$, ω and β ; for k_p/k_s we insert the value of $1/12$, determined in the previous section.

KEMBALL¹⁾ found $\beta=1.228$. We believe, however, that this value is too small. From the last measured point in the experiment with 1-D₁ (Fig. 3) we conclude:

$$\beta \geq \frac{0.16}{0.125},$$

and from the absence of a maximum in the relevant curve we presume that the driving force for the dedeuteration reaction, *i.e.*:

$$(0.167 - 0.125 \beta)$$

is either negative or zero, leading to:

$$\beta \geq \frac{0.167}{0.125} = \frac{4}{3}.$$

From this reasoning it follows that the β -value nearest to KEMBALL's observations and still compatible with our experiments is $\beta=4/3$.

TABLE III Kinetic Isotope Effect at -40°C

x	ω
10.0	0.18
5.3	0.22
3.8	0.25
2.0	0.38
5	average 0.26

R. JONGEPIER and W. M. H. SACTLER

Using $k_p/k_s=1/12$ and $\beta=4/3$ we find four values for ω , depending on the observed values of x (see Table III).

We might remove the uncertainty in x by trying to evaluate ω from the isotope distributions during one experiment. *E.g.*, in the case of 2-D₁ exchange the initial rates of formation of D₀ and D₂ are given by:

$$\left. \frac{d}{dt} d_0 \right|_{t=0} = (1 - \beta r) k_s \quad (10 \text{ a})$$

and

$$\left. \frac{d}{dt} d_2 \right|_{t=0} = 6 \beta r k_p + \beta r k_s; \quad (10 \text{ b})$$

and

$$\left. \frac{\frac{d}{dt} d_0}{\frac{d}{dt} d_2} \right|_{t=0} = \frac{(1 - \beta r) \omega}{6 \beta r \frac{k_p}{k_s} + \beta r} \quad (10 \text{ c})$$

The ratios of the rates of formation of D₀ and D₂ in the two experiments with 2-D₁ were 1.24 and 1.20. The resulting ω value is 0.37.

Hence, both evaluations ((9) and (10 c)) indicate consistently that the rate constant for dedeuteration at -40°C is roughly a factor of 3 to 5 lower than the one for deuteration.

The above conclusion is a preliminary one because of possible experimental errors (ω from Eq. (9) being very sensitive to errors in k_p/k_s) and—to a lesser extent—because of our assumptions about the exchange mechanism and the nature of the isotope effects. For a more precise evaluation the influence of multiplicity can be taken into account and more complicated isotope effects might be discussed. As an instance of the latter, the reactivity of the secondary protium atom in



may be higher in comparison with that of the secondary protium atoms of



which will also give rise to a decrease in the relative rate of dedeuteration of 1-D₁.

C. Comparison of the observed isotope distributions with distributions calculated for the case of inequivalent hydrogen reactivity

The isotope distributions were calculated according to DALLINGA *et al.*⁵⁾, who established that for the assumed mechanism a binomial distribution exists

Catalytic Protium-Deuterium Exchange of Propane/Hydrogen Mixtures

in each of the two groups of hydrogen atoms. The exchange is supposed to be performed with an infinite reservoir of pure deuterium (a condition which is well approximated in practice). This condition also justifies the neglect of isotope effects, since the net dedeuteration reaction is negligible with respect to the net deuteration reaction discussed here.

The average deuterium content A of the primary groups and D of the secondary groups develop as in simple first-order reactions :

$$A(t) = 1 - \exp(-k_p t); \quad (11)$$

$$D(t) = 1 - \exp(-k_s t). \quad (12)$$

The fractions A_k of all the methyl group pairs containing k deuterium atoms, and the fractions D_j of all the methyne groups containing j deuterium atoms are now given by :

$$A_k = \binom{6}{k} A^k (1-A)^{6-k}, \quad 0 \leq k \leq 6; \quad (13)$$

$$D_j = \binom{2}{j} D^j (1-D)^{2-j}, \quad 0 \leq j \leq 2. \quad (14)$$

The propane fractions d_i , containing i deuterium atoms, can be calculated according to :

$$d_i = \sum_{k+j=i} A_k D_j. \quad (15)$$

The calculation is carried out by choosing k_p and k_s according to the previously determined ratio

$$\frac{k_p}{k_s} = \frac{1}{12}.$$

Fig. 4 shows the calculated distributions together with the experimental ones (from five experiments) and the binomial distribution from eq. (1). On the horizontal axis the conversion is indicated by the amount of light propane which has disappeared. The important conclusion from these curves is that at low conversions inequivalence can hardly be recognized from the experimental distribution curves. An experimental distribution at, *e.g.*, 40% conversion might have been interpreted as a simple stepwise process with a binomial distribution.

Whenever experimental distributions show strong deviations from the binomial curve for the highest isotopes, this is a reliable indication that multiplicity is important. The data on inequivalence are needed to enable the correct multiplicity parameter to be calculated from an experimental distribu-

R. JONGEPIER and W. M. H. SACTLER

— EXPERIMENTAL DISTRIBUTION
 -·-·- BINOMIAL DISTRIBUTION
 --- DISTRIBUTION OBTAINED FROM "INEQUIVALENT HYDROGEN"
 MODEL

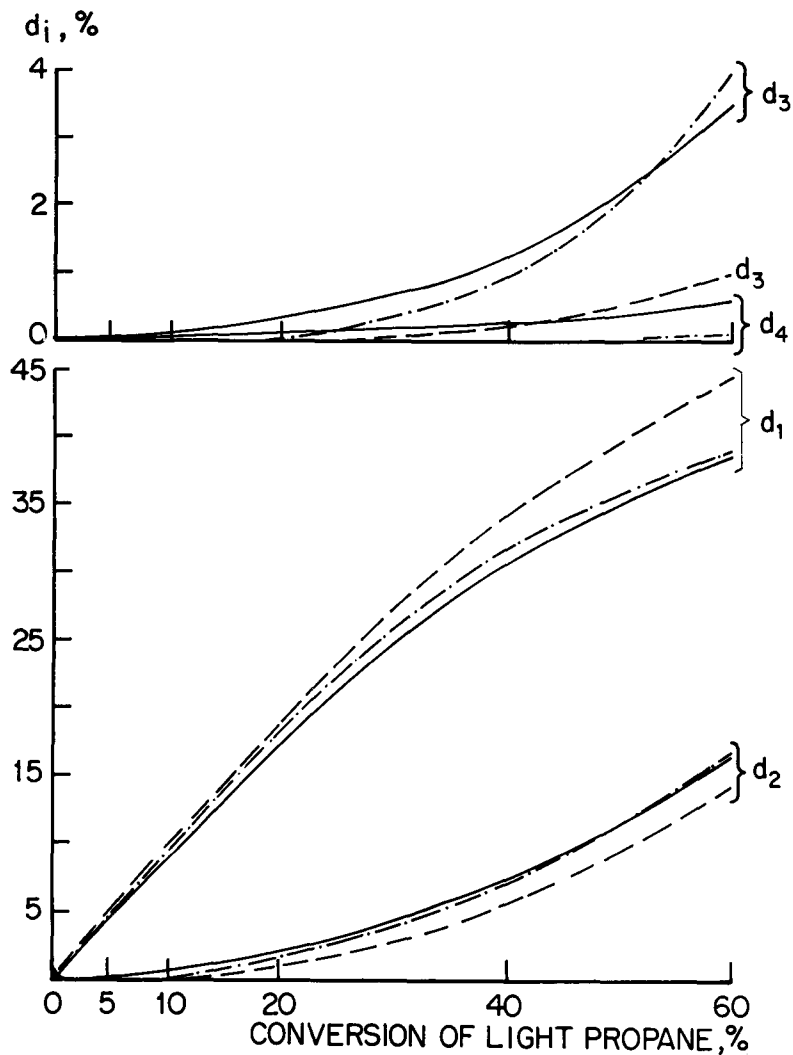


Fig. 4. Comparison of experimental isotope distributions and calculated stepwise distributions.

Catalytic Protium-Deuterium Exchange of Propane/Hydrogen Mixtures

tion curve; the inequivalence parameter is preferably determined from independent data, as described in the previous section.

3. Isotope distributions resulting when both inequivalence and multiplicity are admitted

According to Fig. 1 multiplicity is introduced by allowing interconversion between adsorbed normal radicals and adsorbed iso (propyl) radicals.

We assume an infinite reservoir of pure deuterium. This is a fair approximation to our experimental conditions. As it implies that no dedeuteration takes place, it justifies neglect of isotope effects.

We start our calculations in the classical way by writing down the differential equations defining the problem (section 3. A).

In section 3 B we present another method of calculation, which proves to be more successful for the present problem: the solution from transition probabilities.

A. Solution of the differential equations

We introduce the following notations:

- $D_i A_j$ is the fraction of propane molecules containing j primary deuterium atoms and i secondary deuterium atoms;
- $D_i A_j^*$ is, analogously, the fraction of adsorbed n-propyl species having j primary and i secondary D atoms;
- $D_i^* A_j$ applies in the same way to the isopropyl radicals;
- ε is the surface concentration of normal-propyl species;
- ε' is the corresponding concentration of iso-species.

The differential equations describing this kinetic model (see Fig. 1) are:

$$\frac{d}{dt} D_i A_j = -(k_1 + k'_1) D_i A_j + k_{-1} \varepsilon D_i A_{j-1}^* + k'_{-1} \varepsilon' D_{i-1}^* A_j$$

$$i = 0, 1, 2, \quad j = 0, 1, \dots, 6 \quad (16)$$

$$\frac{d}{dt} \varepsilon D_i A_j^* = -(k_{-1} + k_2) \varepsilon D_i A_j^* + k_1 \frac{6-j}{6} D_i A_j + k'_1 \frac{j+1}{6} D_i A_{j+1}$$

$$+ k_{-2} \varepsilon' \frac{6-j}{6} D_{i-1}^* A_j + k'_{-2} \varepsilon' \frac{j+1}{6} D_{i-1}^* A_{j+1}$$

$$i = 0, 1, 2, \quad j = 0, \dots, 5 \quad (17)$$

$$\frac{d}{dt} \varepsilon' D_i^* A_j = -(k'_{-1} + k_{-2}) \varepsilon' D_i^* A_j + k'_1 \frac{2-i}{2} D_i A_j + k'_1 \frac{i+1}{2} D_{i+1} A_j$$

$$+ k_2 \varepsilon \frac{2-i}{2} D_i A_{j-1}^* + k_2 \varepsilon \frac{i+1}{2} D_{i+1} A_{j-1}^*$$

$$i = 0, 1, \quad j = 0, \dots, 6 \quad (18)$$

This system can be solved if the usual steady-state approximation⁶⁾ is introduced, and if the process starts from pure light propane. $D_0A_0=1$ at $t=0$.

The solutions for d_0 and d_1 as a function of time are given below :

$$d_0(t) = D_0A_0(t) = \exp(-kt), \quad (19)$$

$$d_1(t) = D_0A_1(t) + D_1A_0(t) = -8 \exp(-kt) + 2 \exp\left\{-kt\left(1 - \frac{1}{2} \frac{p}{1+\alpha}\right)\right\} + 6 \exp\left\{-kt\left(1 - \frac{1/6(1-p)}{1+\beta}\right)\right\}, \quad (20)$$

where :

$$\alpha = \frac{k_2}{k_{-1}\epsilon}; \quad \beta = \frac{k_{-2}}{k'_{-1}\epsilon'}; \quad p = k'_1/k; \quad k = k_1 + k'_1. \quad (21)$$

With increasing i , the expressions for d_i increase rapidly in complexity. Because of this complexity the formulae do not easily give an insight into the influence of multiplicity and inequivalent reactivity of the hydrogen groups.

The results are much better comparable when they are in numerical form. Therefore we shall try to find the solution to the problem directly by a numerical approximation.

This can be done in a very simple and elegant way by starting from a "transition scheme".⁶⁾

B. Solution from transition probabilities

This type of solution corresponds to the steady-state approximation described earlier. The rate constants in the reaction equations are now taken to be transition probabilities.

The system of the solution is as follows. First we determine what fraction of the molecules has reacted m times in a specified time interval. Secondly, we find the isotopic composition of a set of molecules which has reacted m times. Finally, we extend this calculation to cover all possible m values, corresponding to an infinitesimal description of the reaction as a function of time.

According to the definition of k in the previous section, of x molecules present a number $dx = kxdt$ react in dt seconds, *i.e.* a fraction $d\Phi$ of the molecules in the gas phase :

$$d\Phi = kdt. \quad (22)$$

After a time interval ndt the gas phase will contain a fraction $\Phi_m(n)$ of molecules having reacted m times.

If for each molecule the probability of reacting at any instant is the same and independent of the number of reactions the molecule has already

Catalytic Protium-Deuterium Exchange of Propane/Hydrogen Mixtures

undergone, $\Phi_m(n)$ is given by the binomial distribution :

$$\Phi_m(n) = \binom{n}{m} (1-kdt)^{n-m} (kdt)^m. \quad (23)$$

For convenience, we adopt an experimental time scale in which $\tau = kt$, and kdt is $\frac{\tau}{n}$.

The reaction number distribution $\Phi_m(\tau)$ at an experimental instant τ is now given by :

$$\Phi_m(\tau) = \lim_{n \rightarrow \infty} \binom{n}{m} \left(1 - \frac{\tau}{n}\right)^{n-m} \left(\frac{\tau}{n}\right)^m. \quad (24)$$

If we can give the composition of a group of molecules which has reacted m times, our problem is solved. This is done by the transition scheme.

We consider the ensemble of molecules on their way through the three steps of a reaction, taking the last two (interconversion and desorption) together. The isotope distribution of a set of molecules having reacted m times is represented by $D_i \Delta_j(m)$.

First we consider adsorption.

Adsorption

Adsorption of a $D_i \Delta_j$ molecule can give four different adsorbed species : a normal radical may be formed (probability $1-P$) by abstraction of a protium atom (probability $\frac{6-j}{6}$) or a deuterium atom (probability $\frac{j}{6}$). Likewise an adsorbed iso-radical can be the result, the molecule having lost a deuterium atom ($\frac{i}{2}$) or not ($\frac{2-i}{2}$).

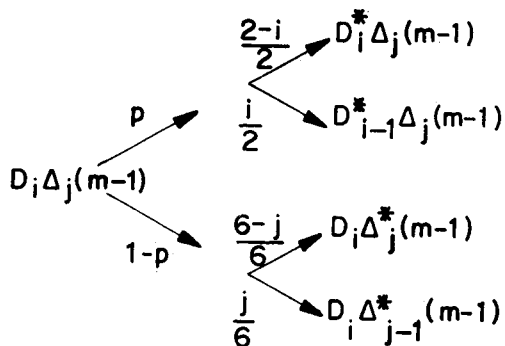


Fig. 5. Adsorption paths for an arbitrary propane isotope.

R. JONGEPIER and W. M. H. SACTLER

The possible paths of adsorption for an arbitrary molecule $D_i A_j$ are depicted in Fig. 5.

The formation of arbitrary species from adsorption is given by:

$$D_i^* A_j(m-1) = P \frac{2-i}{2} D_i A_j(m-1) + P \frac{i+1}{2} D_{i+1} A_j(m-1); \quad (25)$$

$$D_i A_j^*(m-1) = (1-P) \frac{6-j}{6} D_i A_j(m-1) + (1-P) \frac{j+1}{6} D_i A_{j+1}(m-1). \quad (26)$$

We now have the first step in the reaction which will bring a group of molecules having reacted $(m-1)$ times to the status of having reacted m times. The next two steps, desorption and interconversion, are taken together.

Desorption and interconversion

Multiple exchange is essentially characterized by deuteration not necessarily terminating the reactive state. Alternatively, there is a definite probability of "further reaction" instead of desorption.

In our model we explicitly confine the "further reaction" to a transition of a normal-adsorbed species into an iso-adsorbed species *or vice versa*. Parameters A and B are defined for this purpose in the way indicated by Fig. 6.

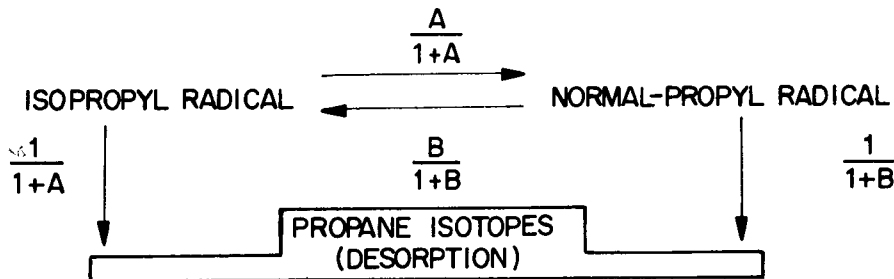


Fig. 6. Reaction paths for adsorbed species.

The transition from a normal-propyl-adsorbed species to an iso-species involves splitting off a secondary hydrogen atom, and resaturation of the primary hydrogen group by a deuterium atom. Splitting off hydrogen atoms yields a protium or deuterium loss in the same way as in adsorption.

These principles are incorporated in the transition scheme, *one element* of which is given in Fig. 7.

Thus each element (shown here is $D_i^* A_j$) is connected with two other elements in the starred state (in this case $D_{i+1} A_j^*$ and $D_{i+1}^* A_j$) and yields one

Catalytic Protium-Deuterium Exchange of Propane/Hydrogen Mixtures

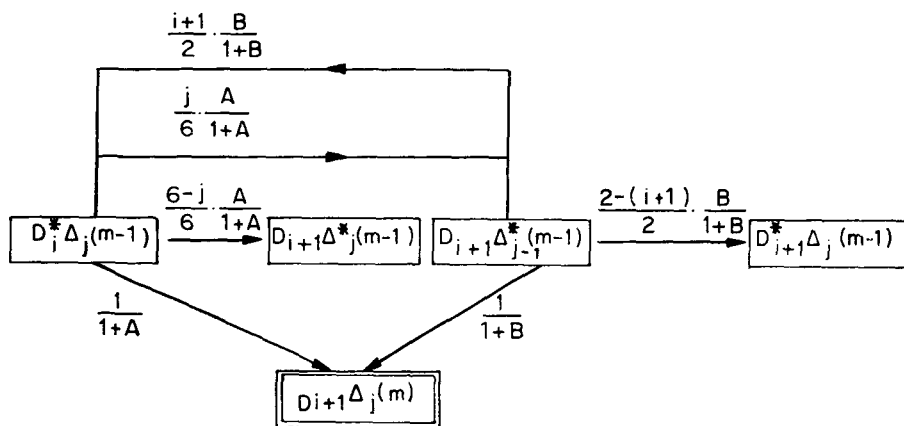


Fig. 7. Element of transition scheme.

desorbed product ($D_{i+1}A_j$).

A similar scheme can be drawn up for a normal-propyl species. The complete scheme is a network between all starred species possible. The reaction from level $(m-1)$ to m of a starred species yields two new starred species of the $(m-1)$ level and a product of the m level.

The new $(m-1)$ -level starred species give together four other starred species and again two products of the m level *etc.*, ending in $D_1^*A_6$ and $D_2^*A_5^*$, respectively, which can only be desorbed as $D_2A_6(m)$.

The probabilities of transitions from an iso-adsorbed species to other species are given by:

$$D_{i+1}A_j(m) = \frac{1+B+\frac{j}{6}A}{(1+A)(1+B)-\left(\frac{i+1}{2}\right)\frac{j}{6}AB} D_i^*A_j(m-1)$$

$$i = 0, 1, j = 0, 1, \dots, 6 \quad (27 a)$$

$$D_{i+1}^*A_j(m-1) = \frac{\frac{j}{6}\left\{1-\frac{i+1}{2}\right\}AB}{(1+A)(1+B)-\left(\frac{i+1}{2}\right)\frac{j}{6}AB} D_i^*A_j(m-1)$$

$$(27 b)$$

$$D_{i+1}A_j^*(m-1) = \frac{\left(1-\frac{j}{6}\right)\{A(1+B)\}}{(1+A)(1+B)-\left(\frac{i+1}{2}\right)\frac{j}{6}AB} D_i^*A_j(m-1),$$

$$(27 c)$$

R. JONGEPIER and W. M. H. SACTLER

and those of transitions from a normal-adsorbed species by :

$$D_i A_{j-1} = \frac{1 + A + \frac{i}{2} B}{(1 + A)(1 + B) - \frac{j+1}{6} \frac{i}{2} AB} D_i A_j^*(m-1) \quad (27 \text{ d})$$

$i = 0, 1, 2, j = 0, 1, \dots, 5$

$$D_i A_{j-1}^* = \frac{\frac{i}{2} \left(1 - \frac{j+1}{6}\right) AB}{(1 + A)(1 + B) - \frac{j+1}{6} \frac{i}{2} AB} D_i A_j^*(m-1) \quad (27 \text{ e})$$

$$D_i^* A_{j-1} = \frac{\left(1 - \frac{i}{2}\right) B(1 + A)}{(1 + A)(1 + B) - \frac{j+1}{6} \frac{i}{2} AB} D_i A_j^*(m-1) \quad (27 \text{ f})$$

By means of these formulae the isotope distributions $D_i A_j(m)$ can be calculated for any reaction starting from $D_i A_j(0)$.

From the hypothetical isotope distributions $D_i A_j(m)$ we obtain the real isotope distributions $D_i A_j(\tau)$ as a function of time or conversion :

$$D_i A_j(\tau) = \lim_{n \rightarrow \infty} \sum_{m=0}^n \Phi_m(n) D_i A_j(m). \quad (28)$$

The interpretation of τ is easy in an experiment in which light propane is deuterated :

Since $D_0 A_0(0) = 1$ (and, consequently, $D_i A_j(0) = 0$ for $i \neq 0, j \neq 0$) and $D_0 A_0(m) = 0$ for $m \neq 0$ (in consequence of $r = 1$):

$$D_0 A_0(\tau) = \lim_{n \rightarrow \infty} \sum_{m=0}^n \binom{n}{m} \left(1 - \frac{\tau}{n}\right)^{n-m} \left(\frac{\tau}{n}\right)^m \delta_{0,m} = \exp(-\tau) \quad (29)$$

$$d_0(\tau) = D_0 A_0(\tau) \text{ and } \tau = -\ln d_0. \quad (30)$$

Finally, the results are interpreted in terms of the observable quantities $d_k(\tau)$:

$$d_k(\tau) = \sum_{i+j=k} D_i A_j(\tau) \quad 0 \leq i \leq 2; \quad 0 \leq j \leq 6. \quad (31)$$

Computation of the type involved in this model can only be carried out on an electronic computer. A programme has been written which follows essentially the same lines as the procedure described here. The calculations were performed on an IBM 7094 computer.

Catalytic Protium-Deuterium Exchange of Propane/Hydrogen Mixtures

The numerical results were calculated by iteration through n (Eq. 29)) until sufficient convergence of all $d_i(\tau)$ was obtained. In the case of deuterations of D_0 a value of $n=30$ was required at 60% conversion in order to reduce the change in $d_i(\tau)$ to less than 0.01 percent in going to the next higher value of n .

Thus the range of conversions for which the distributions could be calculated in a reasonable time was limited.

If we only use $n=1$, we obtain "initial distributions" similar to those computed by ANDERSON and KEMBALL⁷⁾ in their work on the exchange distributions of ethane.

The restriction in conversion imposed on our method by practical factors is not disadvantageous, since the conversion limit is not low; besides, influences of reaction mechanisms can essentially only be observed far from equilibrium.

IV. Comparison of Calculated Distributions with Experimental Results

The method developed in Section III-3 was applied to the experimental results on nickel at -40°C . We took $P=0.85$ in accordance with our mass-spectrometric data on the reactivity ratio (Section III-2).

Since no *a priori* arguments seemed available to discuss the relation between the multiplicity parameters A and B , we took $A=B$ and tried some values of both. Excellent agreement with the experimental distributions was obtained for $A=B=0.08$ (Fig. 8). For comparison this figure also gives distributions for the case of multiple exchange with completely equivalent hydrogen atoms ($P=0.25$; $A=B=0.10$).

It thus became clear that both parameters (P , A and B) are necessary to describe the distributions observed.

Neglect of the kinetic inequivalence of hydrogen ($P=0.25$) and introduction of multiple exchange only ($A=B=0.10$) gave a reasonable fit at the very beginning of the reaction and then described d_3 and d_4 better than did any stepwise mechanism.

At higher conversions, however, differences between the observed and the calculated mechanism increased and both multiplicity and inequivalence were required to describe the results.

The isotope distributions obtained so far were calculated for only small contributions of multiple exchange. However, it seemed interesting to assess the extent to which the combined effects could explain the results obtained on metals giving extensive multiple exchange. A higher multiplicity of the reaction on nickel films could be achieved by testing at 50°C . However, at

R. JONGEPIER and W. M. H. SAGHTLER

- CALCULATED FROM $P=0.85; A=B=0.08$
 ○ CALCULATED FROM $P=0.25; A=B=0.10$ (EQUIVALENT HYDROGEN)
 x EXPERIMENTAL

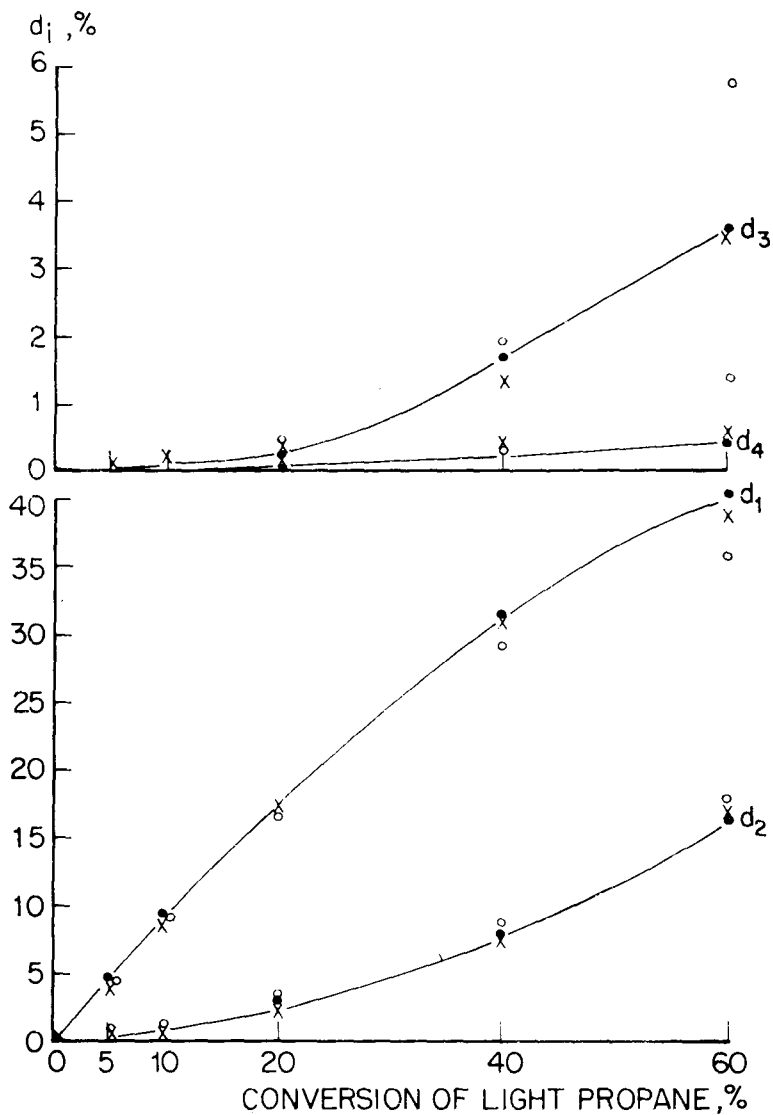


Fig. 8. Experimental distributions plotted together with distributions from the inequivalent hydrogen-multiple exchange model ($P=0.85; A=B=0.08$) and from an equivalent hydrogen-multiple exchange model ($P=0.25; A=B=0.10$).

Catalytic Protium-Deuterium Exchange of Propane/Hydrogen Mixtures

this temperature excessive self-poisoning of the reaction made it impossible to obtain reproducible isotope distributions.

We therefore compared our calculated distributions with a distribution observed by KEMBALL¹⁾ on rhodium at -24°C . This is an "initial distribution", *i.e.* all the isotope concentrations d_i are normalized with respect to the sum

$$\sum_{i=1}^8 d_i,$$

instead of to

$$\sum_{i=0}^8 d_i = 1$$

which we used.

Since d_0 was not given, we estimated the conversion $(1-d_0)$ at which the initial distribution was observed.

It seemed reasonable to assume this conversion to be about 10%, which is a compromise between the requirements "initial product" and mass-spectrometric observability.

Since we assumed the reactivity ratio between primary and secondary hydrogen to be a property of the hydrocarbon, we took again $P=0.85$. We

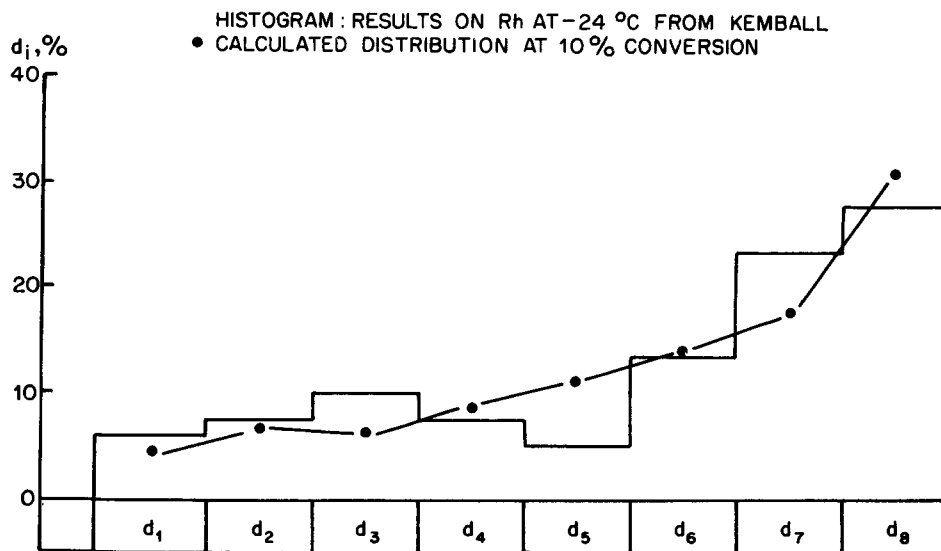


Fig. 9. Isotope distributions from propane-deuterium exchange on rhodium films at -24°C according to Kemball⁷⁾ plotted together with calculated distributions.

looked for those values of A and B which gave a good approximation of the experimental d_i curve. A reasonable fit was found with $A=B=20$. The experimental and the calculated curves are given in Fig. 9. Misfits are observed at d_3 and d_5 . These may very well be attributed to mass-spectrometric errors, which may be important with multiple exchange distributions where large fragmentation contributions have to be taken into account.

In particular in the case of d_8 it can be shown that the normal procedure of pattern calculation leads to a serious underestimation of the experimentally observed d_8 . This is due to the fact, that—according to the literature⁸⁾—the contribution of d_8 to mass 52 (the parent peak of d_6) is about half the value which would be expected when using the random fragmentation assumptions. Similar effects in d_6 and d_7 may account for errors in d_5 and d_3 .

Fig. 10 demonstrates the influence of multiplicity and different reactivity on the isotope distributions at 10% conversion. The different reactivity gives

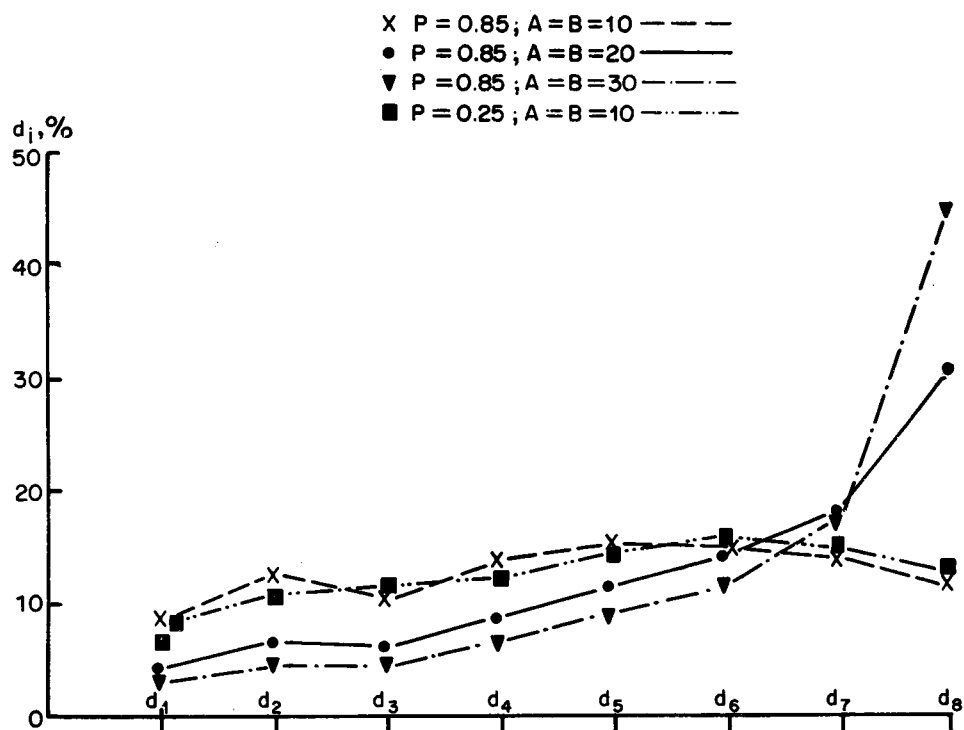


Fig. 10. Isotope distributions at various values of the parameters A , B and P at 10% conversion. $P=0.25$: equivalent hydrogen atoms.

Catalytic Protium-Deuterium Exchange of Propane/Hydrogen Mixtures

rise to a weak maximum at d_2 .

This qualitatively corresponds to the general observation⁹⁾ that the isotope distribution of propane after multiple exchange consists of two parts: one with a weak maximum between d_0 and d_4 and a steeply rising branch from d_6 to d_8 . The pronounced minimum often observed in the mid-region of d_4 does not show up in calculations. Hence it is expected to be due to mass-spectrometric errors, especially to erroneous assumptions concerning the fragmentation patterns as stated above.

Exchange on copper, nickel and copper-nickel alloys

The test reaction was exploratively carried out on copper and some copper-nickel alloy films at -40°C and 50°C . No exchange was observed on copper at -40°C , *i. e.* the rate on this metal was less than 10^{10} molec./ $\text{cm}^2\cdot\text{s}$. The addition of copper to nickel resulted in a decrease in the activity from about 10^{13} molec./ $\text{cm}^2\cdot\text{s}$ to 10^{12} for alloys containing up to 40% copper.

The results, although scattered, indicate that the alloying of nickel with copper does not enhance the catalytic activity as is sometimes reported.

The exchange distributions obtained from the alloy experiments were indistinguishable from those observed on nickel at -40°C .

When testing at 50°C , observations were completely different: at this temperature the nickel films were rapidly inactivated by self-poisoning, so that hardly any exchange was found to take place, whereas the rate on copper seemed to be higher than that on nickel. The initial rate at 50°C was found to be higher for some alloys than for copper and nickel.

As maxima in the activity pattern of alloys have been reported with respect to several catalytic reactions (see *e. g.* EMMETT's recent article on this matter¹⁰⁾), we wish to stress that in the present work such maxima were unequivocally related to self-poisoning *i. e.* absent in the absence of self-poisoning.

The rates and product distributions at 50°C do not allow detailed discussion because of the severe self-poisoning occurring at this temperature. Nevertheless, the qualitative observation may be made that the maximum in the "activity pattern" was accompanied by a minimum multiplicity. It seems therefore that multiplicity is connected with the tendency of propane to poison the catalyst. This can be understood from the self-poisoning being a decomposition of propane at the surface, resulting in the deposition of carbonaceous residues. This process is initiated by the formation of several bonds between a propane molecule and the surface. If for a fraction of these adsorbed entities all bonds are hydrogenated, high multiplicity is observed.

Our results at 50°C seem to indicate that alloying with copper decreases the tendency of nickel to self-poisoning and to multiple exchange.

R. JONGEPIER and W. M. H. SACTLER

It seems that the number of bonds which one propane molecule forms with the surface increases with the nickel content of the alloy. This concept also checks with our incidental observations that metal cracking takes place at 160°C on nickel films, whereas this reaction does not occur at temperatures below 220°C with alloys containing 10 to 40% copper.

The above discussion of the reaction on alloys is a tentative one, since experimental reproducibility was poor in the catalytic experiments on alloy films. Errors due to small amounts of impurities or a slight non-uniformity in the composition of alloy film surfaces cannot at present be excluded.

V. Conclusions

Experimental results on the exchange of propane and deuterium over nickel and rhodium films can be analysed and the underlying mechanism can be understood by means of the scheme given in this paper. It appears that isotope effects, although numerically large, can be neglected under the conditions used in many experiments (large excess of deuterium).

The kinetic inequivalence of primary and secondary hydrogen atoms has little influence on the isotope distribution at low conversion, but analysis of the two D_1 isomers initially formed shows that the rate constants for these two are different. For a reliable calculation of multiplicity from distribution curves, this result must be taken into account.

When nickel films are prepared under good ultra-high vacuum conditions, the rates at -40°C are high enough to study the exchange between propane and deuterium on films obtained after sintering.

The present results also reveal that the effect of self-poisoning in this reaction is very important. In consequence, data obtained at 50°C could not be used for a reliable analysis of reaction parameters other than those connected with the formation of carbonaceous residues.

The activity pattern for copper-nickel alloys observed at non-suspect conditions does not exhibit a maximum. But under conditions where self-poisoning is predominant, some alloys are apparently more active than nickel. This apparent maximum therefore seems to result from a competition of the activities for the test reaction and for the production of carbonaceous residues.

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Catalytic Protium-Deuterium Exchange of Propane/Hydrogen Mixtures

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