Isotopic Exchange of Cyclic Ethers with Deuterium over Metal Catalysts

J. C. DUCHET AND D. CORNET

Département de Chimie, Université de Caen, 14032 Caen Cedex, France

The exchange reaction between deuterium and cyclic ethers (oxolane and α-methyl derivatives) has been investigated using rhodium and palladium catalysts.

The first hydrogen undergoing exchange has been found to be located on a β-carbon. This fact, and the poisoning of the exchange of cyclopentane in the presence of ether, suggest that the O atom participates in the exchange mechanism of ethers. It appears, however, that the oxygen–metal bonding occurs only during this simple exchange process; simultaneous adsorption of oxygen and a *vicinal* carbon causes hydrogenolysis of the O–C bond.

In each case multiple exchange is important. In the oxolane molecule two sets of exchangeable hydrogens are distinguished according to their reactivities, as could be expected by analogy with cycloalkanes. However, this distinction is not so clear in the exchange patterns of substituted oxolanes, since intermediate maxima are observed in these cases. It is suggested that the conformational properties of the substituted rings cause a constraint in the formation of 3,4-diadsorbed oxolanes. Thus, multiple exchange, based on α,β-process, and epimerization via the "roll-over" mechanism occur preferentially in certain parts of the molecules.

INTRODUCTION

The isotopic exchange of ethers with deuterium on metal catalysts has been the subject of relatively few studies. Clarke and Kemball (1) and Forrest and Burwell (2) have shown that aliphatic ethers and hydrocarbons undergo similar reactions: in both cases, multiple exchange is explained by an alternation between mono- and α,β-diadsorbed species. However, the exchange of the hydrogens in a carbon chain cannot propagate across an oxygen; in this respect, the O atom may be compared to a quaternary carbon.

Some uncertainty still remains about the role of the oxygen in the reaction mechanism. Clarke and Kemball described the reactive species as bonded to the metal by the oxygen and a carbon atom. But according to Forrest and Burwell, ether is adsorbed with formation of a metal–oxygen bond and this bonding prevents the adsorption of a carbon atom; therefore, exchange can only occur on those sites of the surface which are not poisoned by the oxygen.

A new problem arises with cyclic ethers, because the exchangeable hydrogens may be divided into two sets, one on each face of the ring, exactly as in cycloalkanes. Accordingly, the exchange of oxolane (tetrahydrofuran) on a rhodium catalyst was investigated by Forrest and Burwell (2). Initially, the eight hydrogens of the molecule are affected, but the exchange is clearly easier for four of them. One may wonder whether the complete exchange observed in cyclic ethers can be explained by the roll-over mechanism currently proposed for the case of cycloalkanes (3). In particular, does the oxygen atom directly participate in the species respon-
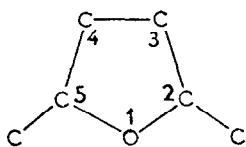
FIGURE 1.

sible for roll-over? More generally, we have attempted to elucidate the part played by the oxygen in the exchange mechanism. To this aim, four ethers have been selected: oxolane, or tetrahydrofuran (I), 2-methyloxolane (II), and the two isomers of 2,5-dimethyloxolane, namely, *cis* (III) and *trans* (IV). The one-step exchange was first examined; it is then relevant to consider the exchangeable hydrogens according to their position relative to the oxygen atom. Figure 1 shows the numbering of the carbons bearing the different hydrogens: the α hydrogens are attached to carbons 2 and 5, the cyclic β hydrogens on carbons 3 and 4; in II, III and IV, there are methyl hydrogens. When studying the multiple exchange a further distinction is made between two sets of *cis*-hydrogens (one on each side of the ring). Two metal catalysts have been used, according to their different behavior toward hydrocarbon exchange, namely, palladium, on which the roll-over mechanism is prominent, and rhodium, which is known to operate mainly by α,β-alternation.

EXPERIMENTAL METHODS

Products and Catalysts

The four ethers were commercial products from Schuchardt. I and II were purified by vapor-phase chromatography (VPC) (XF 1150 column) just before use. The equimolar mixture of III and IV was first fractionated by distillation using a spinning band column. In the subsequent chromatographic separation, the *cis* isomer was eluted first and was recovered with up to 1% of *trans* impurity. The *trans* isomer was obtained with a purity higher than 99.9%.

The supported rhodium and palladium catalysts had a metal content of 10%; they were obtained by impregnating the pumice support with a $PdCl_2$ or $RhCl_2$ solution, drying and reducing at 300°C in a flow of deuterium (in some cases hydrogen).

During the exchange experiments, self-poisoning occurred, but the catalyst activity and selectivity were essentially restored by deuterium treatment at 300°C: thus the same batch of catalyst could be used in many successive runs.

Apparatus and Procedure

Exchange experiments were performed in a conventional flow system, employing about 0.1 g of catalyst. The total pressure in the reactor was 760 Torr. Ether–deuterium gaseous mixtures, prepared in a thermostated saturator filled with Chromosorb, had a D_2/ether ratio equal to 30; this high value avoided isotopic dilution of the reacting deuterium, at least at low exchange levels. The reaction products were condensed at the reactor exit, then fractionated by VPC and their deuterium content was determined using an MS2 mass spectrometer. Isotopic distributions, expressed in terms of D_i (mole fraction of $OC_nH_{2n-i}D_i$ in the ether recovered after reaction) were deduced from the parent peak heights, after the usual corrections for natural isotope abundance and C–H fragmentation.

From the D_i values obtained in this way the following quantities were computed: (a) the fraction converted, $x = 1 - D_0$; (b) the average number of deuterium in the exchanged molecules, $M = \Sigma_i D_i / (1 - D_0)$, and (c) the rate of exchange, which at low exchange levels is given by $r = xF/W$ (F is the flow rate of ether, expressed in millimoles per hour, and W the catalyst mass, in grams). In the conditions of initial exchange, another quantity was also considered, namely, the fraction undergoing multiple exchange, i.e., $x' = 1 - D_0 -$

TABLE 1

Rate of Exchange of the Oxolanes

Catalyst	Ether:	I	II	III	IV
Rhodium	T (°C)	92	85	81	80
	W/F	0.121	0.033	0.018	0.029
	(g hr mM^{-1})				
	x	0.0680	0.0243	0.0268	0.0487
	r	0.561	0.735	1.453	1.679
	(mM hr^{-1} g^{-1})				
	x'	0.0413	0.0132	0.0154	0.0056
	r'	0.341	0.399	0.837	0.193
	(mM hr^{-1} g^{-1})				
	M	3.31	2.81	3.94	1.22
Palladium	T (°C)	194	200	191	195
	W/F	0.557	0.484	0.689	1.849
	(g hr mM^{-1})				
	x	0.0266	0.0478	0.0598	0.0908
	r	0.0478	0.0984	0.0868	0.0491
	(mM hr^{-1} g^{-1})				
	x'	0.0126	0.0281	0.0462	0.0193
	r'	0.0237	0.0580	0.0671	0.0104
	(mM hr^{-1} g^{-1})				
	M	1.75	2.42	5.54	2.12

D_1. From this, the rate of multiple exchange was obtained as $r' = x'F/W$.

In some runs with III and IV, the exchanged ethers were also analyzed by 60 MHz nmr spectrometry, in an effort to locate the deuterium in the reacted molecules.

RESULTS

1. REACTIVITY OF THE ETHERS

The four oxolanes, I to IV, undergo isotopic exchange at ambient temperature on rhodium, and at substantially higher temperatures on palladium. Rates of exchange for both catalysts are reported in Table 1.

The higher reactivity reported for the rhodium catalyst cannot be maintained for long periods. However, the activity loss occurring during the course of a run is by no means irreversible, since regeneration under deuterium can be repeated many times. The rates of exchange measured on rhodium increase in the sequence I < II < III, IV, while on palladium the four oxolanes react at comparable rates. However, if we consider the rates of multiple exchange r', I and IV appear to be less reactive than III on both catalysts.

Exchange is accompanied by the side reactions of ring opening for every ether and, for III and IV, cis–trans isomerization. Ring opening occurs by rupture of the O–C_α bond and produces a primary or a secondary alcohol on rhodium, and an aldehyde or a ketone on palladium. Rates of exchange and ring opening are in the

TABLE 2

Isotopic Exchange of Oxolane I over Rhodium and Palladium Catalysts Initial Distributions

Catalyst	T (°C)	W/F (g hr mM^{-1})	Conversion (%)	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	M
Rh	47	0.438	3.6	28.9	27.7	10.6	14.6	5.6	5.0	2.2	5.3	2.84
Pd	194	0.557	2.7	52.4	31.8	7.9	4.9	1.5	0.7	0.4	0.4	1.75

ratio 20:1 on rhodium, and 10:1 on palladium. The epimerization observed with compounds III and IV is more pronounced on palladium than on rhodium. Its importance will be analyzed in conjunction with the exchange reaction.

2. EXCHANGE DISTRIBUTIONS

The characteristic exchange patterns are presented successively for the four ethers. In each case, D_1 is the more abundant species formed in a single act on the surface, but multiple exchange is important, and its details are considered.

a. Oxolane

The experimental distributions (Table 2) show that, on rhodium and palladium, all eight hydrogens in I may be replaced by deuterium. On palladium, the amount of species D_i decreases steadily from D_1 to D_8, whereas on rhodium a discontinuity between D_4 and D_5 indicates an easier exchange of four hydrogens. Exchange of the last four hydrogens is more pronounced on rhodium at 47°C than on palladium at 194°C.

b. 2,5-Dimethyloxolane (cis and trans)

Rhodium (Table 3). Initial distributions for the *cis* isomer have been determined at temperatures lying between 25 and 75°C. Beside the large amount of D_1, three groups of deuteroisomers may be distinguished, namely D_2–D_5, D_6–D_{10} and D_{11}–D_{12}. They are separated by secondary

TABLE 3

Isotopic Exchange of III and IV over Rhodium Catalyst Initial Distributions

Ether:	III			IV	
T (°C)	25	40	75	49	80
W/F (g hr mM^{-1}):	0.515	0.189	0.026	0.226	0.030
Isomerization (%):	0	<0.1	0.25	0.1	0.7
Conversion (%):	6.6	4.2	3.5	11.0	4.9
D_1	79.0	80.2	56.5	90.4	88.1
D_2	9.6	5.7	8.5	7.4	6.8
D_3	2.9	2.6	4.0	1.2	2.7
D_4	2.0	2.4	4.0	0.3	0.6
D_5	4.0	4.5	9.9	0.5	1.0
D_6	0.9	1.4	5.1	0.2	0.6
D_7	0.8	1.2	2.5		0.2
D_8	0.3	0.5	1.4		
D_9	0.2	0.5	2.3		
D_{10}	0.5	0.7	3.7		
D_{11}		0.2	1.1		
D_{12}		0.2	1.1		
M	1.54	1.68	2.97	1.13	1.22

TABLE 4

Isotopic Exchange of III and IV over Rhodium and Palladium Catalysts Location of Deuterium

Catalyst:	Rhodium		Palladium	
Ether:	III	IV	III	IV
T (°C):	34	50	195	195
Converstion (%):	27.0	17.5	9.6	13.7
M:	1.58	1.21	7.03	1.95
% D				
On C-2 and C-5	0	0	15	22
On C-3 and C-4	6⎱ 100[a]	8⎱ 100[a]	33⎱ 85[a]	35⎱ 78[a]
On CH_3	94⎰	92⎰	52⎰	43⎰

[a] Not entirely resolved by nmr.

maxima occurring at D_5 and D_{10}. The ratio $(D_6$ to $D_{10})/(D_2$ to $D_5)$ increases with increasing temperature; the activation energies corresponding to the formation of both groups of deuteroisomers differ by about 6 kcal mole^{-1}. Only 10 hydrogens are exchanged at 25°C and under these conditions, III is not isomerized to IV; but all 12 hydrogens are exchanged at higher temperature, with simultaneous appearance of the epimerization reaction.

The exchange pattern for IV shows less multiple exchange. D_1 is by far the major exchanged product, and a secondary maximum appears at D_5; exchange is restricted to six (possibly seven) hydrogens of the molecule, even at 80°C, but the *trans–cis* isomerization is always present.

TABLE 5

Isotopic Exchange of III and IV over Palladium Catalyst Initial Distributions

Ether:	III			IV		
T (°C):	124	154	185	155	195	
W/F (g hr mM^{-1}):	0.196	1.41	0.740	2.0	0.740	
Isomerization (%):	<0.1	0.3	0.7	0.6	3.4	
Conversion (%):	1.4	2.2	4.3	1.7	4.5	—[a]
D_1	79.1	43.8	25.3	90.4	84.3	1.5
D_2	1.4	2.7	3.5	1.8	4.9	2.3
D_3	1.4	1.8	2.5	1.2	0.7	1.9
D_4	0.7	0.9	1.4	1.2	0.7	2.1
D_5	3.6	13.4	16.6	1.2	1.6	18
D_6	5.8	23.7	23.0	1.8	2.4	28
D_7	2.9	4.9	7.1	0.6	1.6	9.8
D_8	1.4	2.2	3.0	0.6	0.2	3.4
D_9	0.7	0.4	2.8	0.6	0.2	2.7
D_{10}	1.4	0.4	3.0	0.6	0.4	4.1
D_{11}	0.7	1.8	5.5	—	1.6	13
D_{12}	0.7	4.0	6.2	—	1.6	13
M	2.15	4.13	5.07	1.38	1.76	7.42

[a] Distribution of III produced by isomerization of IV.

TABLE 6

Isotopic Exchange of II over Rhodium and Palladium Catalysts Initial Distributions

Catalyst:	Rhodium		Palladium	
T (°C):	45	85	155	200
W/F (g hr mM^{-1}):	0.378	0.033	0.712	0.484
Conversion (%);	5.7	2.4	1.9	4.8
D_1	56.2	45.5	30.4	41.4
D_2	13.2	15.3	47.4	33.1
D_3	13.4	8.7	6.7	9.5
D_4	8.4	8.7	2.1	3.3
D_5	4.0	7.0	2.1	1.0
D_6	3.0	6.6	5.2	3.9
D_7	0.5	2.1	2.1	1.9
D_8	0.5	0.8	3.1	3.3
D_9	0.4	2.9	0.5	1.4
D_{10}	0.4	2.5	0.5	1.0
M	1.81	2.82	2.45	2.42

As M is not much greater than 1, combined analysis by ms and nmr gave some information about the position of the first deuterium entering the molecule. For exchange conversions approaching 0.2, results in Table 4 indicate that this deuterium is found in positions 3, 4 or methyl, rather than on carbons 2 and 5, adjacent to the oxygen.

Palladium (Table 5). The 12 hydrogens of III are exchanged initially on palladium. The maxima that appeared at D_5 and D_{10} on rhodium are shifted to D_6 and D_{12} on palladium, except for the experiment at 124°C, where the maximum at D_{10} remains. At any temperature, the amounts of D_5 and D_6 are of comparable importance, and the $(D_2$ to $D_5)/D_6$ ratio is constant. *Cis-trans* isomerization always occurs. The exchange pattern for IV is similar to that of its *cis* isomer: the distribution extends up to D_{12} with a secondary maximum at D_6. However, the *trans* to *cis* isomerization appears to be much faster than the reverse, so that the *cis* isomer formed during the exchange of IV could be analyzed separately; ignoring the amount of D_1, the pattern is similar to that mentioned in Table 5 for the direct exchange of III.

For the exchange of III and IV on palladium, nmr spectra indicate no prefer-

ence for the location of the deuterium on any carbons of the ether (Table 4), but this is expected since M values are rather high.

c. 2-Methyloxolane (Table 6)

All 10 hydrogens of this molecule may be replaced by deuterium in a single act, on rhodium as well as on palladium. The exchange patterns on both catalysts differ by minor features: a break appears between D_6 and D_7 on rhodium, while palladium gives maxima at D_6 and D_8.

d. Exchange of Cyclopentane in the Presence of Oxolane

Some experiments on rhodium and palladium have been carried out with a 1:1.5 mixture of III and cyclopentane in order to estimate the extent of isotopic dilution (Table 7). The oxolane and cyclopentane are simultaneously exchanged. The ether reacts faster than the hydrocarbon and its exchange is not affected by the presence of cyclopentane. Exchange of the latter, on the contrary, is considerably slowed down by the presence of oxolane. Under these conditions, exchange of cyclopentane on palladium produces significant amounts of only D_9 and D_{10}. If we assume that species D_9 in the exchanged cyclopentane arises from isotopic dilution, i.e., the only initial product is $C_5(h,d)_{10}$ in Meyer and Burwell's nomenclature (4), then we are able to set an upper value of $b/a = 0.0222$ for the atomic ratio H/D on the surface. This in turn allows a recalculation of the distribution of III in terms of the N_i's rather than the D_i's. This calculation, presented in Table 7, shows that no significant differences are found between D_i's and N_i's. The same conclusion is also valid on rhodium. Thus the extent of isotopic dilution does not affect the position of the maxima observed in the distributions of oxolanes on any catalyst.

TABLE 7

Isotopic Exchange of III and Cyclopentane over Palladium and Rhodium Catalysts

Distri-butions	Palladium at 179°C			Rhodium at 67°C		
	C_5H_{10}	III		C_5H_{10}	III	
		Obsd D_i	Corrected N_i		Obsd D_i	Corrected N_i
D_0	99.92	97.2	97.15	99.2	94.6	94.48
D_1	—	1.60	1.64	0.16	3.6	3.68
D_2	—	0.067	0.067	0.096	0.50	0.51
D_3	—	0.035	0.036	0.11	0.16	0.15
D_4	—	0.027	—	0.095	0.25	0.21
D_5	0.003	0.29	0.26	0.28	0.45	0.49
D_6	0.004	0.38	0.41	0.013	0.13	0.13
D_7	0.005	0.15	0.14	0.006	0.079	0.088
D_8	0.005	0.046	0.049	0.006	0.031	0.021
D_9	0.012	0.027	0.029	0.006	0.067	0.061
D_{10}	0.054	0.023	0.003	0.022	0.075	0.084
D_{11}		0.096	0.090		0.040	0.045
D_{12}		0.094	0.12		0.020	0.027
H/D	0.0222^a	0.00481^b		0.0264^a	0.00488^b	

[a] Upper limit from C_5H_{10} distribution.
[b] In the exit gas, from the observed exchange.

DISCUSSION

These results permit consideration of the exchange mechanism of ethers in respect of (a) the point of first attack of the molecule (first H exchanged), and (b) the propagation of exchange to the rest of the molecule.

a. Replacement of the First Hydrogen

Experiments with III and IV reveal the mode of adsorption of ethers on the metal catalyst. In the case of rhodium, the hydrogens borne by carbons 3, 4 and methyl are much more reactive than the tertiary hydrogens. If it is assumed as proposed by Forrest and Burwell (2), that the oxygen of the ether molecule does not directly take part in the exchange mechanism, i.e., the molecule attached to the surface by the oxygen and a carbon atom is not an intermediate in the exchange sequence, it follows that the first hydrogen to be replaced by deuterium in ethers III or IV

should be randomly located on any carbon since hydrocarbons reacting on rhodium show no preferential reactivity for any type of hydrogen, whether primary, secondary or tertiary (5). However, results with III and IV indicate that the reactivity of each group of hydrogens is a function of its position with respect to the oxygen atom. Thus it must be assumed that the oxygen participates in some way in the exchange mechanism. The bonding between metal and oxygen is probably the first step of ether adsorption. This surface species leads to isotopic exchange when a carbon atom becomes adsorbed, while oxygen remains attached to the surface. Our results on rhodium suggest that the carbon which is adsorbed in this exchange step cannot be an α-carbon. Simultaneous adsorption of the oxygen and a *vicinal* carbon would probably cause the rupture of the O–C bond: then hydrogenolysis occurs. As a
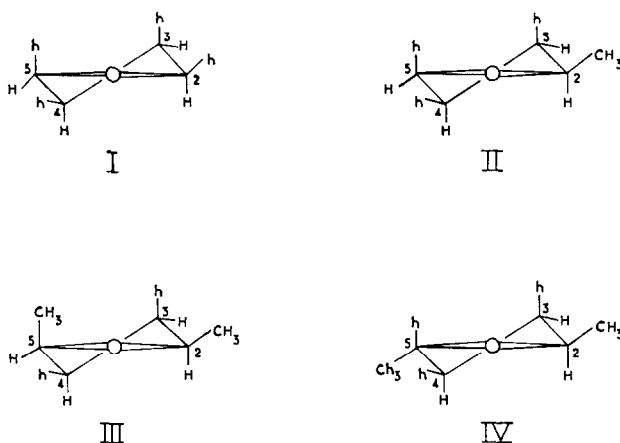
FIG. 2. Sets of hydrogen atoms in oxolanes.

result, exchange in an ether molecule cannot propagate across the oxygen.

We are led to think that on rhodium catalyst, the surface species responsible for the replacement of the first hydrogen is diadsorbed on the oxygen and a β-carbon; it is thus an α,γ-diadsorbed species. The situation is somewhat different from that found with hydrocarbons: in that case, it is established that α,γ-diadsorbed species are rather difficult to form; for instance, in the exchange of neopentane over nickel at 210°C, only a few percent of the reaction products come from an α,γ-diadsorbed intermediate (6). However, the character of the adsorption at an oxygen or at a carbon atom are essentially different, since the former does not require any bond breaking. Furthermore, the relative rates in the competitive exchange of oxolane and cyclopentane suggest that the ether is strongly held on the metal surface. This might favor the formation of an α(O), γ(C)-adsorbed species. On palladium, the location of the first hydrogen replaced in oxolane cannot be deduced from nmr analysis of exchanged III and IV ethers because M values are too high. Although the single exchange step cannot be precisely identified, it is suggested that adsorption of an ether molecule primarily occurs by metal–oxygen bonding, in view of the

similar poisoning caused in the cyclopentane exchange. Cyclopentane exchange, which would otherwise proceed at ca. 25–50°C, is completely hindered by the presence of oxolane; the latter shows no sign of decomposition at this temperature. Thus in agreement with Forrest and Burwell, we suppose that the surface is covered with ether molecules, due to the strong ether–metal linkage. As a result, hydrocarbons cannot reach the catalyst. At higher temperature (ca. 200°C) some of the ether may be dissociatively adsorbed, and the competitive adsorption between ether and hydrocarbon becomes more complicated. However, the hydrogen–deuterium equilibration remains fast, since isotopic dilution in the exchanged products is low.

Multiple exchange in the carbon chain involves adsorption of a second carbon: at this stage it is likely that the oxygen atom is no longer attached to the surface. According to this scheme, the ease of exchange propagation, i.e., the reactivity of ethers for multiple exchange, is a function of the metal–oxygen bond strength: the reactivity should decrease with increasing basicity of ethers. Such a relationship holds well for I, II and III: for instance, oxolane I, which has the highest basicity (7), appears to be less reactive than III as

judged from the values of r'. In the case of IV, steric hindrance might be the decisive factor in determining reactivity.

b. Multiple Exchange

From the above mechanism, the exchange can propagate along the carbon chain of an ether molecule only after the oxygen atom has been desorbed. Then, this propagation is similar to that encountered in saturated hydrocarbons, and the well-known mechanisms proposed for cycloalkanes, namely, interconversion between mono- and diadsorbed hydrocarbon and roll-over of the diadsorbed species, can be applied to the present oxolanes.

Rhodium. The exchange pattern of oxolane over rhodium catalyst agrees well with expectation; the "one set exchange" leads to a maximum at D_4, the "two set exchange" at D_8 (Fig. 2). In contrast to I, the initial exchange pattern of the disubstituted oxolane III does not clearly reflect the difference between the two sets of exchangeable hydrogens [10 H and 2 h (Fig. 2)]. The peaks at D_{10} and D_{12} appearing as a result of complete exchange in one or both sets are always accompanied by a larger maximum at D_5. This result indicates that exchange is particularly easy among 5 of the 10 H hydrogens. Assuming that these five hydrogens are located on the methyl carbon and on carbons 2 and 3 (or 4 and 5), the break between D_5 and D_6 means that the exchange in the set of 10 H hydrogens is subject to a new kind of constraint.

An explanation of this phenomenon can be given on the basis of conformational analysis. It is well established that the oxolane ring is puckered (8); however, the molecule does not adopt a permanent and well-defined conformation, since the puckering continuously moves around the ring. This pseudo-rotation is free for oxolane itself, whereas in substituted rings, a potential energy barrier exists. Thus,
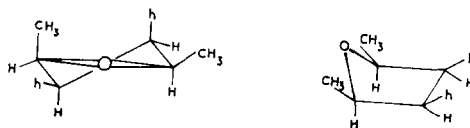

FIG. 3. Half chair and envelope forms for III.

minimal and maximal energy conformations for III correspond to nearly symmetrical ring shapes, i.e., the half chair and envelope forms (Fig. 3). The other conformations, either half chair or envelope, do not possess any symmetry elements, and their energies are intermediate.

But it is also well established that the α,β-diadsorbed species which is an intermediate in the exchange sequence of hydrocarbons can only exist in an eclipsed configuration (9). In our case, this condition is fulfilled if the oxolane ring adopts an envelope conformation in the adsorbed state. Considering compound III, the 3,4-diadsorbed species requires that the ring be in the symmetrical envelope form, at the top of the energy barrier. This species will be less probable than, for instance, a 2,3-diadsorbed species for which the corresponding envelope form is of lower energy.

It turns out that in compound III, the hydrogens on carbons 2, 3 and methyl are readily exchanged by the α,β-process, but further exchange in the H set is difficult. A break is then observed after D_5 in the exchange pattern. The importance of the pseudo-rotation barrier can be estimated from the exchange pattern recorded at various temperatures. The variation of the ratio $(D_6$ to $D_{10})/(D_2$ to $D_5)$ in compound III yields a value of 6 kcal mole^{-1}. This value is about what we expect for substituted oxolanes (8).

Another explanation could be given for the break in the exchange pattern at D_5–D_6, namely that the lone pair on the oxygen atom would tend to hold the α,β-entities on carbons 2 and 3 (or 2 and methyl). Thus, the conjugation of π electrons in the complex would possibly make

adsorption on C-3 and C-4 difficult. We do not retain this explanation, for the following reasons: (i) the effect on the exchange pattern would be similar for the series of ethers investigated, and this is not observed; (ii) from a spectroscopic study of vinyl ethers coordinated to Pt(II), it is concluded that the lone-pair oxygen electrons, while conjugated with the double bond, do not apprecialy interact with the metal (10). Thus, an extra stability resulting from conjugation, which is found, for instance, in enolate complexes is not expected here. Besides, it is not clear why a π-conjugated species would not allow the propagation of exchange across the oxygen.

The "two set exchange" in III (10 H plus 2 h), can be explained by a roll-over process as in cycloparaffins. In the present case, the "two set exchange" and epimerization occur together so that the diadsorbed species undergoing roll-over involves a tertiary and a secondary (or methyl) carbon.

Another diadsorbed species that could conceivably undergo the roll-over process is the 3,4- but as we have seen, it is formed with difficulty and so it does not appreciably contribute to D_{12} formation. In any case, the roll-over is not a favored process on rhodium, since D_{11} and D_{12} are relatively small.

The exchange pattern of IV on rhodium may be explained by the same arguments: among the 12 hydrogens of the molecule (Fig. 2), six H should be easily exchanged, but an energy barrier again makes the propagation from C-3 to C-4 difficult. This is evidenced by the maximum at D_5.

Palladium. On the palladium catalyst, the absence of a maximum at D_4 in the exchange of oxolane suggests that roll-over is an easy process. However, this is not absolutely convincing since multiple exchange is very limited in that case. The ease with which roll-over occurs is better demonstrated by the similar exchange distributions obtained for the two isomers

III and IV. The new D_6 maximum observed for III means that, when five H hydrogens on one side of the molecule are exchanged (3 on methyl, 1 on C-2 and 1 on C-3), one more hydrogen reacts before the molecule is desorbed. It is likely that this sixth hydrogen to be exchanged is the h atom borne by carbon 3. If this location of the reactive hydrogens is correct, it then becomes clear that roll-over of the molecule is easier than the propagation of exchange from C-3 to C-4, which implies overcoming the pseudo-rotation barrier. In fact, the constant ratio $D_6/(D_2$ to $D_5)$ indicates that the extra activation energy associated with roll-over is very small. This difference with the case of hydrocarbons may be due to a substantially higher reaction temperature.

c. Exchange of 2-Methyloxolane

Similar distributions are observed on both catalysts, with a maximum or a break at D_6. For the palladium catalyst, the same explanation can be given as in the case of the dimethyloxolanes; the six reactive hydrogens are identified as 5 H and 1 h (Fig. 2) because roll-over is relatively easy. The secondary maximum at D_8 would result from the extension of the H-set exchange to the hydrogens on C-4 and C-5: again, this is consistent with an appreciable energy barrier associated with a C-3, C-4-diadsorbed ether. The same explanation may be repeated for the exchange mechanism on rhodium, although on this catalyst, results with III and IV have shown that roll-over and C-3, C-4-propagation are two processes of comparable difficulty: roll-over is probably easier in the case of II than for the dimethyl compounds due to less steric hindrance.

CONCLUSION

From these exchange reactions of oxolanes, we conclude that the first step of ether adsorption on a metal catalyst is the formation of an oxygen–metal bond. This

bonding is probably maintained during a single exchange step, but should be broken for multiple exchange to occur in the carbon ring. An α,β-diadsorbed ether with oxygen and a *vicinal* carbon simultaneously adsorbed can only lead to hydrogenolysis of the O–C bond.

Multiple exchange based on the α,β-diadsorbed species is very sensitive to molecular geometry: the eclipsed conformation required for such a species makes the propagation of exchange from C-3 to C-4 relatively difficult. In addition to these processes, roll-over is revealed by *cis–trans* isomerization reactions. On palladium, roll-over is much easier than C-3, C-4-propagation whereas the α,β-process seems favored on rhodium.

REFERENCES

1. Clarke, J. K., and Kemball, C., *Trans. Faraday Soc.* **55**, 98 (1959).
2. Forrest, J. M., and Burwell, R. L., *J. Phys. Chem.* **63**, 1017 (1959).
3. Burwell, R. L., and Schrage, K., *J. Amer. Chem. Soc.* **88**, 4549 (1966).
4. Meyer, E. F., and Burwell, R. L., *J. Amer. Chem. Soc.* **85**, 2881 (1963).
5. Anderson, J. R., and Baker, B. G., "Chemisorption and Reactions on Metallic Films," Vol. 2, p. 104. Academic Press, New York, 1971.
6. Kemball, C., and Kempling, J. C., *Proc. Roy. Soc., Ser. A* **329**, 391 (1972).
7. Arnett, E. M., and Wu, C. Y., *J. Amer. Chem. Soc.* **84**, 1684 (1962).
8. Buys, H. R., Altona, C., and Havinga, E., *Tetrahedron* **24**, 3019 (1968).
9. Burwell, R. L., Shim, B. K. C., and Rowlinson, H. C., *J. Amer. Chem. Soc.* **79**, 5142 (1957).
10. Wakatsuki, Y., Nozakura, S., and Murahashi, S., *Bull. Chem. Soc. Japan* **44**, 786 (1971).