Combined Deuterium Nuclear Magnetic Resonance and Mass-spectrometric Studies of the Exchange Reactions of Ketones over Supported Metal Catalysts

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Deuterium NMR spectroscopy has been used in conjunction with mass spectrometry to study the exchange reaction of the ketones acetone, butan-2-one and cyclopentanone over a variety of supported metal catalysts. In many of the experiments simple, random, stepwise exchange was prevalent. However, in certain instances multiple exchange occurred. For butan-2-one and cyclopentanone this multiple exchange was essentially limited to the protons on carbon atoms adjacent to the carbonyl group, while for acetone a strong preference towards exchange into only a single methyl group was noted. Some hydrogenation to propan-2-ol accompanied the multiple exchange of acetone, with the majority of the alcohol being formed by addition of D_2 across the carbon oxygen double bond without simultaneous exchange into the methyl group, suggesting independent η_1 and η_2 adsorbed acetone surface intermediates for the exchange and hydrogenation reactions respectively.

The combination of deuterium NMR spectroscopy and mass spectrometry has already provided a much more detailed picture of exchange reactions between deuterium and hydrocarbons than could be obtained from kinetic and mass-spectrometric studies alone.^{1,2} Lately, we have extended these investigations to the ethers diethyl ether and tetra-hydrofuran.³ This allowed the 'blocking effect' of oxygen in the exchange process to be examined and also demonstrated the potential of the NMR technique when exchange was accompanied by hydrogenolysis.

Here we report results obtained from the exchange of the ketones butan-2-one and cyclopentanone over supported palladium, rhodium and iridium catalysts and for acetone over palladium, rhodium, iridium, nickel and platinum catalysts.

Earlier mass-spectrometric studies of acetone and cyclopentanone exchange over evaporated rhodium, palladium, nickel and platinum metal films^{4,5} proved difficult due to rapid exchange, extensive simultaneous hydrogenation and some additional hydrogenolysis. The observation of a marked preference for the ready incorporation of up to only four deuteriums in the exchange of cyclopentanone and a sharp 'cut-off' at D₃ in the mass-spectrometric product distribution of acetone exchanged over certain metals were, however, of particular interest. The balance of evidence at that time suggested that for cyclopentanone exchange occurred preferentially at the methylene groups adjacent to the carbonyl group rather than on one side of the ring alone, while for acetone, the exchange was concentrated in a single methyl group, but neither fact could be established with any certainty. The greater power of ²D NMR spectroscopy combined with mass spectroscopy and the generally lower exchange activity of the supported metal catalysts compared with the metal films suggested that the exchange reaction of ketones might prove the subject of worthwhile reinvestigation.

Experimental

Acetone (99.9%) and butan-2-one (99.8%), both from Aldrich Chemical Co. and cyclopentanone (99%) from BDH were further purified solely by freeze-thaw outgassing into vacuum

Materials

before use. A palladium, calcium aluminate supported catalyst, obtained from ICI, was used in the acetone and butan-2one exchange studies. In the cyclopentanone experiments a higher metal loading Pd on charcoal catalyst from Johnson Matthey was used to decrease the effect of removal of ketone by adsorption on the support. The rhodium, platinum⁶ and nickel catalysts³ were supported on silica, while the iridium catalyst⁷ was supported on γ -alumina. The metal loading of each of the catalysts is given in table 1. This range of materials is similar to that used in our preceding deuterium NMR/mass spectrometric studies.¹⁻³

In each case, the catalyst pretreatment consisted of purging the reaction vessel with flowing hydrogen and reduction at 673 K for 1 h followed by evacuation at the same temperature for 1 h and then cooling to the reaction temperature under vacuum.

Apparatus and Technique

For butan-2-one, the exchange experiments were carried out in a static reactor generally as described previously^{1,2} with an ionisation energy of 20 eV chosen for the mass-spectrometric measurements. Under these conditions, fragmentation was slight and essentially limited to loss of one hydrogen. The procedure for extracting rates of reaction, from massspectrometric product distributions, followed usual practice.^{1,2} The NMR spectra were obtained in a similar fashion to those in the earlier work^{1,2} using a Bruker WH 360 spectrometer, but taking the additional precaution of carefully drying the solvents used to prevent randomisation of the deuterium in the exchanged ketone *via* a keto/enol type mechanism.

The experiments with cyclopentanone and acetone were carried out in a recirculating reactor⁸ with a total volume of 1.2 dm³. This reactor was linked to a Vacuum Generators MM601 mass spectrometer and Perkin-Elmer F33 gas chromatograph. In the case of cyclopentanone, use of this reactor was necessary as the low vapour pressure otherwise limited the amount of ketone which could be collected for NMR analysis, whereas for acetone, the integral gas chromatograph proved useful in following the evolution of hydrogenation products. In other respects the techniques used were similar to those stated previously; an ionisation energy of 20 eV was found to be suitable for the mass-spectrometric work for both cyclopentanone and acetone.

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mol metal per g support	Pd	Rh	Ir	Ni	Pt
	2.5×10^{-6}	1.0×10^{-4}	2.0×10^{-5}	8.5×10^{-4}	1.0×10^{-4}
		aceto	one		
T/K	328	273	373	421	298
rate $\times 10^{-3}$	120	35	80	0.4	34
М	1.1	2.3	1.2	1.1	1.8
		butan-2	2-one		
T/K	405	371	396		
rate $\times 10^{-3}$	56	30	409		
М	1.1	1.3	1.5		
		cyclopen	tanone		
T/K	373	323	416		
rate $\times 10^{-3}$	40	3	92		
М	1.9	1.4	1.5		

Table 1. A summary of the exchange reactions studied together with the rate of reaction, expressed as mol s⁻¹ per mol metal, and the mean number of deuteriums incorporated per molecule, M

The gas charge for experiments in the static reactor was 2×10^{-4} mol of ketone and 3×10^{-4} mol in the circulating system with a 5 : 1 ratio of D₂ to ketone in each case.

Results

The range of experiments carried out is summarised in table 1 with details of the results for acetone, butan-2-one and cyclopentanone given in tables 2, 3 and 4, respectively. Generally, reaction temperatures were chosen in the range 273-423 K to produce convenient rates of reaction. The limited extent of reactions other than exchange together with the experimental emphasis on product identification rather than kinetics made the exact choice of reaction conditions of secondary importance.

Acetone

Mass spectrometric data from the exchange of acetone are given in the upper section of table 2. For each catalyst, the observed product distribution is compared with a calculated distribution (bracketed figures) based on a random, stepwise exchange.⁹ For the palladium, nickel and iridium catalysts these data show the exchange to proceed in a steady and almost stepwise fashion with no evidence for hydrogenation or hydrogenolysis of the ketone. In contrast, multiple exchange of acetone occurs over rhodium and platinum with the product distributions showing a partial break after D₃, suggesting a tendency for completion of exchange of a single methyl group.

In general the NMR spectra displayed well resolved peaks with the acetone resonances shown in fig. 1 for exchange over

the rhodium catalyst being typical of the spectra obtained. Resonances for $-CH_2D$, $-CHD_2$ and $-CD_3$ were observed at 2.03, 2.01 and 1.99 ppm, respectively, and were easily resolved with the α shift due to each additional deuterium on the same carbon atom equal to -17.5 ppb. These spectra integrate to give the percentage of deuterium in the various groupings in the exchanged acetone given in the lower section of table 2 and again suggest simple stepwise exchange of the ketone over the palladium, nickel and iridium catalysts with multiple exchange over rhodium and platinum. In addition, fig. 1 shows some hydrogenation to propan-2-ol to have occurred, with a resonance due to the alcohol CD observed at 3.83 ppm and a broader peak for -OD noted at ca. 1.5 ppm. The CH₂D, CHD₂ and CD₃ peaks of the alcoholexchanged methyl group were also found at 1.08, 1.06 and 1.04 ppm, with each peak of the methyl resonance split by a β shift of ca. -7 ppb due to a deuterium on the adjacent carbon atom. For Rh, gas chromatography indicated ca. 5% of the acetone to have been reduced with the rate of reduction being ca. one third the rate of exchange of acetone. This reduction was common to both the rhodium and platinum catalysts and was in fact the dominant reaction on the platinum catalyst with the reduction occurring at approximately twice the rate of exchange. In this instance, the NMR showed equal amount of deuterium in the OD and CD groupings, but little evidence of exchange into the methyl groups of the alcohol.

Butan-2-one

The results for butan-2-one exchange over the palladium, rhodium and iridium catalysts are shown in table 3. In this

Table 2. Mass-spectrometric product distributions (upper) and NMR analysis of deuterium in groupings (lower) for the exchange reactions of acetone

	Pd	Rh	Ni	Ir	Pt
D ₀	79.2 (78.4)	85.3 (71.0)	86.8 (86.8)	81.4 (80.7)	94.6 (90.9)
$\tilde{\mathbf{D}_1}$	17.9 (19.5)	6.0 (23.1)	12.0 (12.8)	16.3 (17.7)	3.1 (8.7)
D_2	2.7 (2.0)	3.5 (3.7)	1.2 (0.8)	2.1 (1.6)	1.4 (0.4)
D,	0.2 (0.1)	2.7 (0.3)	0 (0)	0.2 (0.1)	0.5 (0)
D₄	0	1.0 (0.0)	0	0 (0)	0.2 (0)
D_5	0	0.8 (0)	0	0	0.1 (0)
D_6	0	0.8 (0)	0	0	0.1 (0)
-CH ₂ D	93 (92.2)	26.8 (89.0)	95 (95.2)	88 (93.1)	47.2 (96.9)
$-CHD_2$	7 (7.6)	28.8 (10.7)	5 (4.7)	12 (6.8)	21.2 (3.1)
$-CD_3$	0 (0.2)	44.4 (0.3)	0 (0.1)	0 (0.1)	31.6 (0.0)

The bracketed figures are the calculated product distributions based on a random, stepwise exchange.



Fig. 1. ^{2}D NMR spectrum of the exchange/reduction products of acetone over Rh–SiO₂.

case no hydrogenation was observed. Slight poisoning occurred during exchange over the palladium catalyst; however, the exchange reactions were otherwise well behaved, with a tendency towards multiple exchange over the rhodium and iridium catalysts. Here, the lack of products beyond D_5 in the mass spectrometric distributions and the total absence of a resonance at $\delta = 1.2$ ppm in the NMR spectra, corresponding to exchange into the methyl group remote from the carbonyl moiety, indicate only hydrogens on carbon atoms adjacent to the carbonyl group are exchanged. Fig. 2 shows the NMR spectrum from exchange over the iridium catalyst with the characteristic chemical shifts of the adjacent methyl and methylene groups at 2.11 and 2.41 ppm, respectively, and corresponding α shifts of -18 and -27 ppb.

Table 3. Mass-spectrometric product distributions (upper) andNMR analysis of deuterium in groupings (lower) for butan-2-oneexchange

	Pd	Rh	Ir
D ₀	85.5 (85.3)	84.1 (81.6)	69.3 (64.3)
D	13.5 (13.7)	12.5 (16.9)	21.2 (29.7)
D,	1.0 (0.9)	2.5 (1.4)	7.7 (5.5)
D_3	0 (0)	0.6 (0.1)	1.5 (0.5)
D_4	0	0.2 (0)	0.3 (0)
D ₅	0	0.1 (0)	0 (0)
O-CHD-	41 (38.8)	37 (38.4)	35 (36.6)
$O-CD_2-$	0 (1.2)	8 (1.6)	12 (3.4)
$O - CH_2 D$	53 (56.3)	39 (55.3)	32 (50.3)
$O-CHD_2$	6 (3.6)	12 (4.6)	18 (9.3)
O-CD ₃	0 (0.1)	4 (0.1)	3 (0.4)

Here, the bracketed figures are the calculated distributions based on a random stepwise exchange of the five protons on carbon atoms adjacent to the carbonyl group (see text)

Cyclopentanone

Both the mass spectrometric and NMR results, given in table 4, were less reliable with this ketone since its low vapour pressure limited its gas-phase concentration. The exchange poisoned noticeably over the palladium and rhodium catalysts, but accelerated slightly with time over iridium and, in



Fig. 2. 2D NMR spectrum of butanone exchanged over the Ir– $\!\gamma\!\!-$ alumina.

	Pd	Rh	Ir
D ₀	55.9 (41.6)	88.5 (79.9)	69.3 (63.9)
$\tilde{\mathbf{D}_1}$	24.6 (40.8)	6.0 (18.4)	21.2 (30.3)
D_2	10.3 (15.0)	2.7 (1.6)	7.7 (5.4)
D_3	4.9 (2.5)	1.5 (0.1)	1.5 (0.4)
D_4	3.0 (0.1)	0.8 (0)	0.3 (0)
D,	0.9 (0)	0.3	0
D_6^{a}	0.4	0.2	0
near	84 (81)	60 (95)	71 (89)
near -CD ₂ -	13 (19)	19 (5)	29 (11)
remote – CHD– ^b	3	21	0

^{*a*} No species beyond D_6 were observed. ^{*b*} Only one remote resonance was observed. The bracketed figures are calculated distributions based on a random exchange in near methylene groups.

general, the kinetics were difficult to reproduce. Some multiple exchange occurred over all three palladium, rhodium and iridium catalysts. The mass-spectrometric analysis showed no evidence for reactions other than exchange; however, the NMR spectra for both the palladium and rhodium experiments displayed a broad resonance at *ca.* 1.78-1.85 ppm, identified as D₂O. Further, non-volatile, hydrocarbon products were also noted in the catalysis line after exchange over the iridium catalyst.

In spite of these difficulties it is still evident from the data in table 4 that exchange occurs exclusively at the CH₂ group adjacent to the carbonyl group over iridium, while for palladium and especially with rhodium a resonance corresponding to deuterium at the remote CH₂ was also observed. This is illustrated in fig. 3 where the peaks at 2.13 and 2.10 ppm are the --CHD-- and α shifted --CD₂-- resonances (α shift = -26 ppb) adjacent to the carbonyl group and the smaller peak at $\delta = 1.92$ ppm is due to an isolated remote deuterium with the resonance centre shifted by a β interaction. (The population of CD₂ at the adjacent group would be too small to produce a clearly observable 2 β shift.)

Discussion

As expected, the supported metal catalysts were generally less active than the corresponding evaporated films,^{4,5} showed less tendency towards multiple exchange and differentiated more strongly between exchange and hydrogenation. As a consequence the results here were much simpler than those from the earlier evaporated film studies and the following general conclusions are immediately obvious.



Fig. 3. ^{2}D NMR spectrum of cyclopentanone exchanged over the Rh–SiO₂ catalyst.

(i) In many of the experiments multiple exchange processes were of relatively little importance as the experimental product distributions were broadly similar to those calculated for a random stepwise exchange so, in general, the exchanged ketone may be assumed to arise from relatively weakly adsorbed surface intermediates.

(ii) For butan-2-one and cyclopentanone, exchange proceeded more readily at positions adjacent to the carbonyl group, intuitively the more labile protons.

(iii) The exchange of acetone over rhodium and platinum showed much higher concentrations of D_2 - D_6 products than expected from a random stepwise exchange with a partial 'cut-off' after D_3 , indicating that the multiple exchange was to some degree concentrated in one methyl group. Here a more significant interaction of the ketone with the surface may be inferred to account for the multiple exchange.

(iv) As well as multiple exchange, the platinum and rhodium catalysts showed some reduction of acetone. Here, the selectivity strongly favoured propan-2-ol as is common for dispersed metal catalysts^{10,11} rather than propane, more characteristic of bulk metal films¹² or foils.^{13,14}

In addition to the above the combination of NMR and mass spectrometric data enables further, more detailed, analysis, allowing conclusions to be drawn as to the relative concentrations of the differently exchanged molecules present and hence the mechanism of the exchange process. How complete and reliable such an analysis can be depends on the complexity of the molecule, the number of different NMR signals which can be resolved and the degree of exchange. This will be illustrated with three examples taken from the present work.

First, the exchange of cyclopentanone over iridium proved particularly simple in that no molecules heavier than D₄ were observed in the mass spectra, and only near-CHD and near-CD₂ resonances were found in the NMR. Reconciliation of the observed NMR spectrum with the mass spectrometric results involves the realisation that, as a consequence of the NMR spectra, the d_2 signal in the mass spectra can arise only from two different forms of D₂ cyclopentanone, namely the $2,2-D_2$ and $2,5-D_2$ cyclopentanone. If the fraction of the $2,2-D_2$ D_2 compound is x then that of the 2,5 compound is simply (1 - x) and the intensity of the near-CHD resonance in the NMR must be proportional to $d_1 + 2(1-x)d_2 + d_3$, whereas that of the near CD₂ resonance is $2xd_2 + 2d_3 + 4d_4$ where d_1 , d_2 , d_3 and d_4 are the intensities in the massspectrometric product distribution. Inserting the experimental data in the two different equations gives x = 0.55 and 0.53, respectively. This indicates that although the multiple exchange over iridium would appear to involve exchange exclusively at the positions adjacent to the carbonyl group, there is no preference for either a mechanism involving repeated exchange at a single carbon (aa exchange) producing an excess of the 2,2-D₂ species or exchange on either side of the carbonyl (α - γ exchange), yielding predominantly 2,5-D₂ cyclopentanone.

Next, the exchange of butan-2-one may be treated in a similar way. Here the exchange is again limited to hydrogens on carbons adjacent to the carbonyl group, but now five resolved NMR signals can be observed. This places fewer restrictions on the possible exchanged butanones and it transpires that there are six parameters representing the fractions of the different possible molecular species to be evaluated. Here, unfortunately, the experimental data do not allow the equations to be solved analytically. If however, the extent of exchange is small, satisfactory approximate solutions can be obtained for molecules containing few deuterium atoms as the calculations are then most sensitive to these species. Table 5 compares the results of such calculations for D_1 and

Table 5. Comparison of product distributions of D_1 and D_2 butan-2-ones from NMR with the calculated distributions based on a random exchange of hydrogens on carbon atoms adjacent to the carbonyl group (see text)

compound	Pd at	Rh at	Ir at	random
	405 K	371 K	396 K	distribution
$D_{1} \begin{cases} CH_{3}CHDCOCH_{3} \\ CH_{3}CH_{2}COCH_{2}D \end{cases}$	0.43	0.48	0.52	0.40
	0.57	0.52	0.48	0.60
$D_{2} \begin{cases} CH_{3}CD_{2}COCH_{3} \\ CH_{3}CHDCOCH_{2}D \\ CH_{3}CH_{2}COCHD_{2} \end{cases}$	0	0.20	0.20	0.10
	0.56	0.42	0.37	0.60
	0.44	0.38	0.43	0.30

 D_2 butan-2-ones with those for exchange assuming a random, stepwise exchange over the palladium, rhodium and iridium catalysts. As mentioned previously, only hydrogens on carbon atoms adjacent to the carbonyls are considered exchangeable. For palladium, comparison with the random distribution shows all these hydrogens to be equally labile, whereas both rhodium and iridium exchange the CH₂ group faster. Multiple exchange is not restricted to hydrogens on one side of the carbonyl group with any of the three catalysts. This result is similar to that observed with cyclopentanone.

Finally, for acetone, where in certain instances the exchange reaction was accompanied by partial reduction to propan-2-ol, analysis of the distribution of deuterium in both the exchange and reduction reaction products proves possible.

First, although similar in mass to the exchanged acetone, the presence of propan-2-ol presents no difficulties to obtaining the mass-spectrometric product distribution of the exchanged ketone since at almost all ionisation energies the alcohol efficiently fragments to the minus-methyl ion. Consequently, the mass spectrometric product distribution and NMR data may be analysed together to give information about the exchanged ketone even in the presence of substantial amounts of alcohol or exchanged alcohol. This analysis is of most interest for the reaction over the platinum and rhodium catalysts where simple inspection of the MS product distribution indicates multiple exchange to be prevalent. Here the most fruitful way to rationalise the mass spectrometric and NMR data is to fit the observed NMR intensities to calculated intensities based on different multiple exchange mechanisms and the observed mass spectrometric product distribution. Two different multiple exchange mechanisms may be envisaged,⁴ one involving random multiple exchange across both methyl groups (RME), the other, repeated exchange on a single methyl group (SGME) followed by exchange of the second methyl. Again if $d_1, d_2 \dots d_6$ are the intensities in the mass spectrometric product distribution then the D_1 species contributes d_1 to the CH_2D resonance equally by both mechanisms but for the D₂ species RME gives $6/5 d_2$ towards CH₂D resonance and $4/5 d_2$ towards the CHD_2 , whereas SGME is assumed to give 100% CHD_2COCH_3 and so contributes $2d_2$ to the CHD_2 peak intensity, and so forth for d_3 through to d_6 . The calculated NMR intensities for each mechanism are compared with the experimental values in table 6. For both rhodium and platinum the calculations show that the high relative intensity of the CD₃ signal can be reproduced only by the SGME mechanism; however, in neither case does this mechanism alone satisfactorily account for the observed NMR spectra. The incorporation of a deuterium isotope effect does produce a minor shift in the calculated distribution towards the desired goal; however, the NMR intensities are still not adequately reproduced in calculations based on any single exchange mechanism taken in isolation. For rhodium, a combination

Table 6. Comparison of observed and calculated NMR CX₃ resonance intensities based on single group multiple exchange (SGME) and random multiple exchange (RME) mechanisms together with a best fit for rhodium based on a combination of the two mechanisms with SGME : RME = 2

		observed	SGME	RME	best fit
Rh	$\begin{cases} CH_2D\\ CHD_2\\ CD_3 \end{cases}$	26.8 28.8 44.4	21.0 25.4 53.6	39.1 34.6 26.3	27.0 28.5 44.5
Pt	$\begin{cases} CH_2D\\ CHD_2\\ CD_3 \end{cases}$	47.2 21.2 31.6	34.7 32.3 33.0	56.0 28.6 15.3	

of the two multiple exchange mechanisms yields a fit which converges to within 1% of the observed intensities for all three resonances when SGME/RME = 2.0. For platinum, a similar combination of the two mechanisms fails to yield an acceptable fit, suggesting the inclusion of a third, possibly stepwise, exchange mechanism to produce an accurate fit; however, once again, the SGME mechanism would clearly have to feature highly in the exchange process.

This strong asymmetry in the exchange of an otherwise symmetric molecule requires the involvement of an asymmetric surface intermediate in the exchange process. In the original work over evaporated films,⁴ an adsorbed acetone radical, multiply bonded to the surface via both a methyl group and the carbonyl (I), was suggested to account for the exchange into predominantly one methyl;⁴ however, a more recent and perhaps more plausible surface species, presenting the correct geometry to allow exchange into a single methyl group, is η_1 (O) acetone (II). This mode of bonding of adsorbed acetone has been observed directly on Pt(111) between 120 and 185 K by electron energy loss spectroscopy (EELS)^{15,16} and is one of only two general classes of coordination of acetone in organometallic chemistry.¹⁷ In the EELS study the plane of the molecule was shown to lie essentially perpendicular to the metal surface with the molecule weakly bound via one of the oxygen lone pairs, yielding a geometry placing one methyl remote from the surface and the other immediately adjacent, thereby allowing rapid multiple exchange with surface D atoms perhaps via an $\alpha \gamma$ intermediate (III), a feature of the exchange activity of saturated hydrocarbons over rhodium and to a lesser extent platinum catalysts.2,6



When attempting to study the propan-2-ol formed during the acetone exchange, the fortuitous fragmentation which prevents the alcohol interfering with the ketone mass spectrometric product distribution prevents observation of the exchanged alcohol. Under favourable circumstances an estimate of the propan-2-ol product distribution can be obtained from the alcohol 'pseudo-parent' minus-methyl fragment;¹⁸ however, in these experiments this too is masked by the acetone fragment-ion signal. However, the NMR still yields

Table 7. Relative intensities of the peaks in the methyl resonance of the exchanged acetone and alcohol from the exchange of acetone over the rhodium catalyst.

	CH ₂ D	CHD ₂	CD ₃
methyl group in acetone	26.8	28.8	44.4
normalised to 100	23.1	28.9	48.0

useful data on the exchanged alcohol. First, for the exchange over rhodium, the ratio of the integrated intensities of the peaks in the acetone and alcohol methyl resonances, shown in table 7, are broadly similar, apparently suggesting a common intermediate in the exchange and hydrogenation reactions.

Comparison of the intensities of the alcohol CD and methyl resonances (fig. 1), however, indicates formation of the alcohol largely by direct addition of D₂ across the carbon oxygen double bond without simultaneous exchange into the methyl. This pattern is borne out on the platinum catalyst where a substantial alcohol CD resonance is observed in the NMR with no obvious sign of exchange into the methyl group. This behaviour suggests that the small amount of methyl-exchanged alcohol in fact derives from previously exchanged acetone and that, while the exchange activity results from η_1 acetone, the hydrogenation activity derives from a second form of adsorbed acetone, almost certainly η_2 (O, C) acetone (IV), believed to be important both from the early work on evaporated films⁴ and, once again, EELS studies of acetone adsorbed on Pt(111) at temperatures >185 K.15,16

$$\frac{O-C}{I} \leq CH_3$$

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