Selective C−H Bond Activation with Na_2PtCl_4 in Inverted Micelles

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The selective C–H activation of *n*-heptane and methylcyclohexane with Na_2PtCl_4 under mild conditions in water in inverted micelles is described.

Introduction

The selective activation and functionalisation of aliphatic hydrocarbons is of great interest.[1,2] In particular, the transformation of aliphatic hydrocarbons under mild reaction conditions to, for example, alcohols and aldehydes presents a problem. The activation of C−H bonds is thermodynamically not a difficult process, but the selective activation of C−H bonds of specific sp^3 carbon atoms is troublesome.[3,4] The use of appropriate transition metal catalysts may alleviate this problem.[5] To date several (catalytic) reactions are known for the conversion of hydrocarbons to functionalised hydrocarbons.[1,4−7] The activation of C−H bonds has been achieved by using $[PtCl_4]^{2-}$ as the catalyst with various substrates.[8,9] Such reactions are often performed under highly acidic conditions in aqueous solutions containing CF_3COOH or H_2SO_4.[2,6,8,9] For the selective C−H activation of hydrocarbons with platinum(II), we decided to introduce a water-soluble platinum salt in an aliphatic reaction medium by means of inverted micelles. The reaction rates in water[10−13] and in biphasic systems[14] (water in oil micro-emulsions) can be increased by using inverted micelles as this increases the surface contact area between catalyst and substrate. We decided to use inverted micelles of AOT[15] as this surfactant has been well studied and is commercially available.

The incubation of inverted micelles of AOT containing a 0.20 M solution of Na_2PtCl_4 in D_2O during several hours at 353 K resulted in the selective C−H activation of the CH_3 moieties of *n*-heptane and methylcyclohexane, as witnessed by the observed H-D exchange. The use of D_2O enables a stable ^2H lock during ^{195}Pt NMR experiments and allows for the observation of the exchange of protons for deuterons in the Pt^{II}-mediated C−H activation, see below.

Water and Platinum Loading

The size and shape of inverted micelles is determined (apart from the type of surfactant, solvent, concentration) by the amount of water present in inverted micelles. The water/AOT ratio is expressed as W_0 (W_0 = $[H_2O]/[AOT]$). Variations of W_0 cause changes in the size and structure of the inverted micelles,[16] the volume of the micro-droplets, the rotational correlation time (τ_c) of the inverted micelles[17] and the water-structure in the inverted micelles.[18] Therefore, it is of vital importance to control the W_0 parameter. When performing catalysis or spectroscopy in inverted micelles, the concentration of the compound(s) of interest (catalyst and/or substrates) is an important parameter as well; it is closely related to W_0 and may influence the size and shape of inverted micelles in a similar manner. The concentration of Na_2PtCl_4 in inverted micelles may influence the maximum water loading of the inverted micelles. Therefore, the maximum platinum concentration that can be reached in a solution of inverted AOT micelles in *n*-heptane has been determined by titration,[19,20] the results of which are shown in Figure 1.

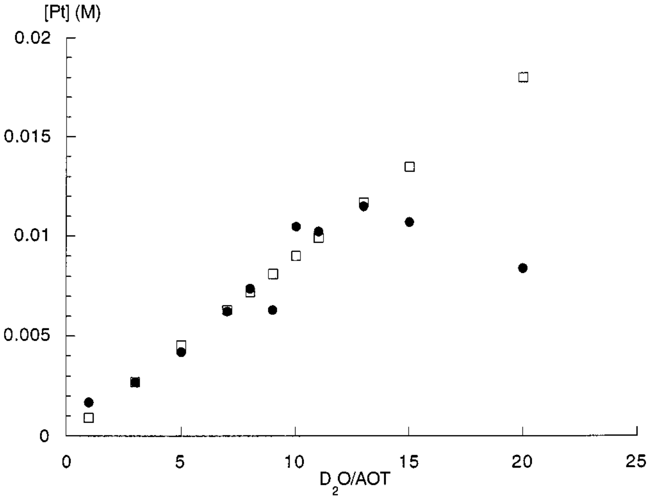

Figure 1. Titration of a solution of 0.25 M AOT in *n*-heptane with a 0.2 M solution of Na_2PtCl_4 in D_2O; filled circles are the measured platinum concentrations, open squares are the calculated concentrations

At the W_0 value where the measured concentration starts to deviate from the calculated concentration, the maximum platinum loading for the inverted micelles is reached.[21] Up to W_0 = 13 the concentration of platinum *in* the inverted micelle is 0.2 M. No precipitation of the platinum salt or exclusion of water was observed below this value. The ex-

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periments in micellar solutions have been performed at $W_0 = 10$. The orange/brown colour of the micellar solutions clearly indicates that the platinum salt is indeed dissolved in the inverted micelles. No coloration of the aliphatic solvents occurs in the absence of AOT.

^{195}Pt NMR Spectroscopy

In order to assess putative interactions between the surface of the inverted micelles and the Na_2PtCl_4, we performed a ^{195}Pt NMR study (see Table 1). As the ^{195}Pt chemical shift is very sensitive to small changes in the chemical environment of the salt, interactions between the inverted micelle and Na_2PtCl_4 are expected to appear as variations in the ^{195}Pt chemical shift. Note that a decrease of the ^{195}Pt chemical shift by 11 ppm is observed when varying the Na_2PtCl_4 concentration from 0.05 M to 0.2 M in D_2O. As we did not observe any changes of the ^{195}Pt chemical shift in inverted micelles of AOT (where the concentration is 0.2 M) relative to the chemical shift in a 0.2 M D_2O solution of Na_2PtCl_4, it can be concluded that the environment of the platinum(II) species in inverted micelles is comparable to that in D_2O solution.

Table 1. ^{195}Pt chemical shift data of Na_2PtCl_4 in inverted micelles in various solvents, $[Na_2PtCl_4] = 0.2$ M

	Solvent	[AOT][a]	$\delta(^{195}Pt)$[b]
1	D_2O[c]	–	−1614
2	D_2O	–	−1625
3	heptane	0.25	−1626
4	hexane	0.25	−1626
5	pentane	0.25	−1624

[a] AOT concentration in mols/L. – [b] $\delta(^{195}Pt)$ in ppm. – [c] 0.05 M solution.

H-D Exchange

We observe that H-D exchange of the methyl protons of *n*-heptane with deuterons from D_2O readily proceeds at 353 K in inverted micelles of AOT, as indicated by ^{2}H NMR spectroscopy and GC-MS. Stacked plots of the ^{2}H NMR spectra of 0.25 M AOT in *n*-heptane or methylcyclohexane containing 0.2 M Na_2PtCl_4 in D_2O are shown in Figure 2. Monitoring the ^{2}H NMR intensity of *n*-heptane of a micellar solution of AOT containing Na_2PtCl_4 at 353 K as a function of time, showed an increase of the integral of the methyl resonance by a factor of 2.5. Similarly, an increase of the deuterium content was observed for the methyl group of methylcyclohexane. GC-MS spectra of methylcyclohexane after H-D exchange showed a deuteration level in the isotope pattern three times higher than the natural abundance. No concomitant increase of the integral of the ^{2}H NMR resonance of the methylene protons was observed in either case. This observation is proof of the selective enrichment of the methyl groups with ^{2}H due to exchange of protons with deuterons from D_2O. Comparison with a blank experiment showed that no enrichment in deuterium of the terminal methyl groups takes place in the absence of the platinum salt. Hence, this enrichment must stem from selective C−H activation by platinum(II) followed by exchange of the proton by a deuteron from D_2O.

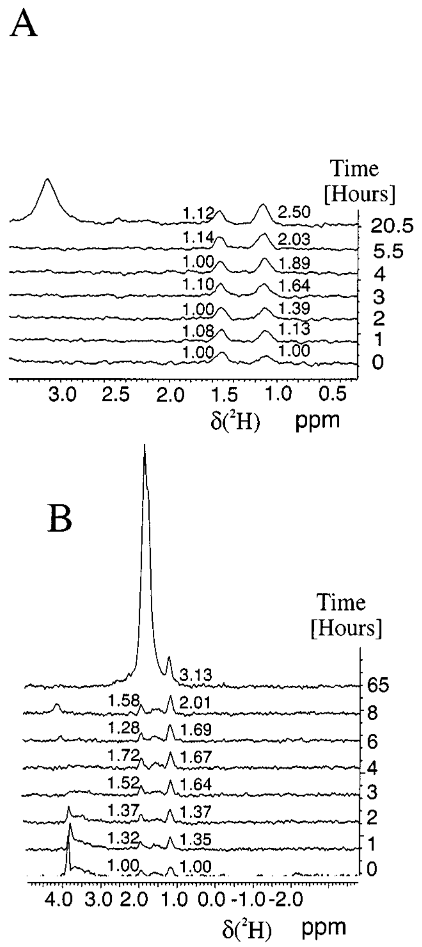

Figure 2. Stacked plots of ^{2}H NMR spectra recorded at 353 K of a micellar solution of AOT containing a 0.2 M D_2O solution of Na_2PtCl_4, demonstrating the H-D exchange in the methyl groups of *n*-heptane (A) and methylcyclohexane (B); an increase of the ^{2}H intensity of the *methyl* resonances is observed exclusively; the intensities at $t = 0$ have been arbitrarily calibrated at 1.00

This finding exemplifies the selective activation of the terminal methyl groups of aliphatic hydrocarbons in inverted micelles. Based on the total amount of platinum present in solution, we calculated that a sub-stoichiometric conversion (minimum value 10%) has been obtained so far.

After the H-D exchange had ceased, a colourless two phase system containing metallic platinum was obtained. The reason for the formation of metallic platinum is presently unknown. The signal observed at 1.5 ppm in Figure 2b might be the result of the hydrolysis of AOT, resulting in 2-ethyl-1-hexanol.

Conclusions and Outlook

The use of inverted micelles of AOT in a biphasic system of water-solubilised platinum salts in aliphatic solvents offers a very mild and selective route for the C−H bond activation of CH_3 groups in hydrocarbons. This may have interesting implications for new routes towards terminally substituted (linear) alkane derivatives.

We now aim at employing a more stable surfactant, which may increase the lifetime of the micro-emulsion. The intrinsic features of inverted micelles in biphasic systems, such as a high contact area and ease of separation of the catalyst from products, deserve further attention in connection with the activation of C−element bonds.

Experimental Section

The surfactant sodium bis(2-ethylhexyl)sulfosuccinate (AOT) was dried by azeotropically distilling the salt three times with benzene followed by drying overnight in vacuo. Solutions of inverted micelles containing Na_2PtCl_4 were prepared by the addition of 135 µL of a 0.2 M stock solution of the appropriate platinum salt in D_2O to a 0.25 M AOT stock solution in *n*-heptane or methylcyclohexane. Stirring for at least two hours resulted in yellow or brown optically transparent solutions, which are stable for several days at room temperature. The solutions of inverted micelles containing Na_2PtCl_4 (0.2 M) thus obtained were heated to 353 K in a closed NMR tube, preferably a 10 mm od, 8 mm id sapphire HP NMR tube to prevent evaporation of the solvent. The HP NMR tube has been described in detail elsewhere.[22,23] For every ^2H NMR spectrum 512 scans were acquired at 353 K using the broad band channel of a 10 mm broad band 10 MHz-121 MHz-{^1H} probe (^1H at 300 MHz). The pulse duration was 5 μs ($\approx 30°$ pulse), a 1.0 s preaquisition delay was used, during which the HOD resonance was saturated by CW irradiation.

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[19] A solution of 0.25 M AOT in *n*-heptane was titrated with a stock solution of 0.2 M Na_2PtCl_4 in D_2O. The concentration of the AOT solution used (0.25 M) is well above the critical micelle concentration of AOT, which is 0.4 mM in aliphatic solvents.[20] The platinum concentration of the solutions of inverted micelles were determined by UV/Vis absorption spectrometry at 375 nm for a number of W_0 values. A blank solution of 0.25 M AOT devoid of platinum showed no absorption at 375 nm. The extinction coefficient of the micellar solutions was calculated from the known concentration where $W_0 = 3$ and was 132 M^{-1} cm^{-1} for Na_2PtCl_4.

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