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An Attempt at Enhancing the Regioselective Oxidation of Decane Using Catalysis with Reverse Micelles

**Sivaram Pradham · Jonathan K. Bartley ·
Donald Bethell · Stanislaw E. Golunski ·
Graham J. Hutchings**

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Abstract The regioselective oxidation of linear alkanes to give terminal oxidation products represents a major challenge for catalysis. A number of previous approaches have shown that confinement and encapsulation can offer an experimentally viable way forward. Against this background we have investigated the use of a system comprising gaseous oxygen, a homogenous catalyst (ammonium metavanadate) confined in an aqueous solution within reverse micelles formed in decane using bis (2-ethylhexyl)sulfosuccinate. At low conversion and at short reaction times we show that the approach does lead to a small enhancement in the selectivity to terminal products, but unsurprisingly the surfactant is more readily oxidised than decane and so the small positive effects of the micellar catalyst system are short-lived.

Keywords Decane oxidation · Regioselective oxidation · Reverse micelles

1 Introduction

The regioselective oxidation of long chain linear alkanes to produce terminal products represents a grand challenge for catalysis. In recent years there has been an increase in the production of linear alkanes from the Fischer–Tropsch synthesis and there is interest in generating new processes based on these molecules. While linear alkanes with a carbon number $>C_{10}$ can be utilised as transportation fuels in diesel, lower carbon number linear alkanes cannot similarly be used and therefore outlets have to be found for their effective utilisation, for example by isomerisation. Short chain alkanes can be functionalised by dehydrogenation either using two steps, e.g. the conversion of isobutane to methacrolein via isobutylene [1], or in a single reaction step, e.g. the conversion of butane to maleic anhydride [2]. Although two-step oxidation works well for short-chain hydrocarbons, dehydrogenation of higher carbon number alkanes can be difficult to control, with the potential for cracking or for multiple double-bond formation followed by cyclization, leading to coking and deactivation of the catalyst surface [3]. Nature has devised several strategies for the functionalisation of linear alkanes, for example by *Pseudomonas oleavorans* which regioselectively oxidises decane at the terminal carbon producing decan-1-ol [4] by encapsulating the substrate in an active site where only terminal functionalisation is possible. This biological approach has been used for the oxidation of octane to octanol [5]. Chemical catalysis has sought to emulate this specificity by using the concepts of confinement. In particular Thomas et al. [6] have shown that Mn- and Co-doped AlPOs can be effective for the regioselective oxidation of long chain alkanes. However, others have reported difficulty with reproducing the high selectivities reported in the earlier studies [7]. Recently, the mechanism by which these catalysts can activate alkanes has been described in a very elegant study by Catlow and co-workers [8], while Iglesia and co-workers [9] has shown that Mn-doped zeolites can be effective for the terminal oxidation of hexane as long as very low conversions were utilised. Hence, the central theme in all these previous studies has been to utilise confinement of the alkane. We decided to investigate a different approach based on micelles. Micelles form when two immiscible liquids, one

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S. Pradham · J. K. Bartley · D. Bethell ·
S. E. Golunski · G. J. Hutchings (✉)
Cardiff Catalysis Institute, School of Chemistry,
Cardiff University, Cardiff CF10 3AT, UK
e-mail: hutch@cf.ac.uk

of which is polar and the other is apolar, e.g. water and decane, are mixed in the presence of surfactants that have polar head groups which are soluble in the polar liquid and long apolar hydrocarbon chains which are soluble in the apolar liquid. In particular, reverse micelles form when the polar liquid is present in small amounts relative to the apolar liquid.

The concept we wished to explore was whether using reverse micelles formed in water–decane with a water soluble homogeneous oxidation catalyst could be utilised for terminal oxidation. It should be noted that the use of micelles in catalysis has been well studied for many years. For example the addition of a surfactant leads to an increase in rate, a process known as micellar catalysis [10]. Micelle systems are complex and highly fluxional [11] with micelles being formed, destroyed and reformed on a rapid timescale. Such fluxionality means that it would be difficult to expect regioselectivity to be readily achievable. However, in this study we aimed to try to exploit the dynamic ordering of decane molecules at the interface in the hope that on average the terminal methyl groups would be exposed to the oxidising species. Such a strategy would be more likely to succeed using a surfactant with linear hydrocarbon chains as the hydrophobic moiety, to maximise the possibility of decane molecules being briefly held in an extended conformation within the Stern layer by van der Waals forces. In this model study we report our findings and also demonstrate the potential problems that can be encountered with this approach since the surfactant added to stabilise the reverse micelles is likely to be more reactive than the substrate. Although we were aware of these problems at the outset, we wanted to consider whether any small but significant effects could be induced.

2 Experimental

2.1 Micelle Formation

The surfactant bis(2-ethylhexyl)sulfosuccinate (AOT)–decane–water reverse micelles were prepared according to the literature [12]. AOT was selected as it was considered to be one of the most effective surfactants for stabilising reverse micelles. AOT (0.418 g, Aldrich, >98%) was added to *n*-decane (9.41 g, Sigma, anhydrous, >99%), forming a clear solution after 10–15 min. A solution of ammonium metavanadate (NH_4VO_3, 0.023 g) in water (5 mL) was prepared. An aliquot of the aqueous solution of ammonium metavanadate (0.169 g) was added to the AOT in *n*-decane solution and after mixing a transparent solution was formed. The percentage composition by weight of the micelle system is:

$$n\text{–Decane} = 94.12\%,$$
$$[H_2O]/[AOT]\ \text{mol ratio} = 10$$
$$AOT = 4.18\%$$
$$\text{Water} = 1.69\%$$

The formation of the micelle system was confirmed visually by the addition of methylene blue which is a standard test [13, 14]. Methylene blue is soluble in the aqueous phase but not in decane, so if the aqueous component of the system is not present in micellar form, as happens when no AOT is added, the blue colour is visible only in small separate water droplets. Whereas, when micelles are formed the blue colour is distributed throughout the solution. It should be noted that addition of just AOT to *n*-decane also forms micelles and the charged head groups present in the core are also capable of solubilising methylene blue when added as a solid. At the concentrations tested it was found that the AOT was present above the critical micelle concentration as methylene blue was distributed throughout the solution.

2.2 Catalyst Testing

A Parr (Series 5000) Multiple Reactor System was used for decane oxidation. In a typical test, decane (9.41 g, Sigma-Aldrich; ≥99.0%) was stirred at 600 rpm with the catalyst, water and surfactant. After adding decane and the other reaction components, the reactor was flushed once with oxygen, before the O_2 pressure was increased to 15 bar. The reactor was then heated to the test temperature of 100 °C, where it was held for the required time. On completion of the test period, the reactor was cooled and de-pressurised. An internal standard (1,2,4-trichlorobenzene, 0.15 cm^3) was added to the product mixture, before a sample of the liquid (0.2 μL) was removed for analysis by GC (Varian Star 3800 fitted with a DB-WAX column). Experiments were conducted in duplicate and data are reproducible to ±2% of the quoted value. Conversion was based on the observed products. We were able in most experiments to get mass balance >90% at the low conversion levels we were operating at. The major products were identified but there are at times a number of minor products which may be due to hydroperoxide formation, and we list these as other products in the data. The focus of this investigation was on the C_{10} products.

3 Results and Discussion

The aim of these experiments is to determine if the selectivity for terminal oxidation of an alkane, in this case decane, can be enhanced through oxidation using a micelle-encapsulated water soluble homogeneous oxidation catalyst. Such a catalytic system is complex as it involves decane, oxygen, the homogeneous catalyst, the surfactant and water. Hence, before attempting to perform catalysis with the system as complicated as an active centre within a micelle, it is important to perform a number of test blank reactions to determine the contribution of each element of the system. It should be noted that in all experiments we wanted to utilise conditions giving relatively low conversions so that any effects on terminal selectivity could be maximised. This was emphasised recently in the study of Iglesia and co-workers [9] where high terminal selectivity was only observed at very low conversions.

Initially, we reacted *n*-decane and oxygen in the absence of added water, surfactant or catalyst at 100 °C. The results shown in Table 1 indicate that a very low level of conversion (0.2%) is obtained even at relatively long reaction time of 24 h. This shows that the background radical autoxidation reaction is not significant under these reaction conditions. This is important as the non-catalysed autoxidation can be a significant factor in the oxidation of alkanes. Next we investigated the effect of using ammonium metavanadate (NH_4VO_3) as a catalyst under the same conditions. We selected a vanadium compound as these are known to be effective in alkane activation. NH_4VO_3 is not soluble in *n*-decane but is soluble in water (solubility = 0.84 g/100 mL water at 30 °C). In this second set of experiments we did not add water and in view of this the NH_4VO_3 remained as a solid during this experiment and in effect acted as a heterogeneous catalyst. The results are shown in Table 2. The conversion (0.02%) is very low after 4 h and it increases to 1.8% after 24 h. The terminal selectivity increases with time, perhaps indicating an induction period for this catalyst system, and was 3.7% after 24 h, comprising the C_{10} terminal alcohol and the acid products. It is therefore clear that the catalyst is having a significant effect. This is probably due to solubilisation of some of the NH_4VO_3 as water is formed as a by-product of decane oxidation.

In the experiments where we wish to utilise NH_4VO_3 as a homogeneous catalyst we clearly need to introduce low

Table 1 Oxidation of decane in the absence of catalyst

Time (h)	Conv. (%)	Selectivity (%)[a]														Mass balance (%)
		2 one	3 one	4 one	2 ol	3 ol	4 ol	1 ol	C_5 acid	C_6 acid	C_7 acid	C_8 acid	C_9 acid	C_{10} acid	Others	
8	0.01	5.8	7.4	3.8	3.9	3.4	3.2	0.0	14.3	14.8	0.0	0.0	0.0	0.0	43.5	97
24	0.2	26.8	11.6	14.8	3.1	5.2	3.0	1.4	2.5	9.2	2.2	0.2	0.4	0.7	18.9	93

Reaction conditions: 100 °C, 15 bar O_2, decane (9.41 g)

[a] One indicates decanone and 2, 3 and 4 is the carbonyl group position i.e. 2-decanone, etc.; ol indicates decanol; C_n indicates a terminal acid with n carbon number; others represent a set of minor products that are not terminal C_{10} products

Table 2 Oxidation of decane–NH_4VO_3

Time (h)	Conv. (%)	Selectivity (%)[a]														Mass balance (%)
		2 one	3 one	4 one	2 ol	3 ol	4 ol	1 ol	C_5 acid	C_6 acid	C_7 acid	C_8 acid	C_9 acid	C_{10} acid	Others	
4	0.02	59.2	9.5	16.6	4.4	4.5	5.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	85
8	0.1	15.4	14.0	22.4	5.1	3.5	5.6	0.0	3.2	3.2	1.1	1.2	1.0	2.1	24.5	95
24	1.8	13.9	11.8	20.4	4.8	3.8	6.4	0.6	3.5	1.9	3.3	3.1	2.3	3.1	21.2	95

Reaction conditions: 100 °C, 15 bar O_2, decane (9.41 g), NH_4VO_3 (0.0008 g)

[a] As in Table 1

Table 3 Oxidation of decane with water in the absence of catalyst

Time (h)	Conv. (%)	Selectivity (%)[a]														Mass balance (%)
		2 one	3 one	4 one	2 ol	3 ol	4 ol	1 ol	C_5 acid	C_6 acid	C_7 acid	C_8 acid	C_9 acid	C_{10} acid	Others	
4	0.01	28.6	12.6	20.8	6.6	5.4	15	0.0	0.0	0.0	0.0	0.0	0.0	0.0	10.8	100
8	0.02	25.9	15.8	25.8	2.9	2.5	5.0	0.0	0.0	0.0	6.3	4.7	4.8	0.0	6.3	99
24	0.4	21.1	14.5	24.4	3.2	2.1	1.4	0.6	3.0	5.3	2.1	0.4	0.8	2.2	18.8	104

Reaction conditions: 100 °C, 15 bar O_2, decane (9.41 g), H_2O (0.169 g)

[a] As in Table 1

levels of water into the reaction mixture to ensure it is solubilised. In this case the reaction will occur at the interface between the water and decane as they are immiscible. To study the effect of water, decane oxidation was carried out in presence of water alone and the results are shown in Table 3. Lower activity was observed in the presence of water (compare data in Tables 1 and 3) and hence water does not enhance the decane conversion and the conversion was found to be similar with the blank *n*-decane reaction.

We then reacted decane with oxygen with the surfactant, AOT, in the absence of water and catalyst. The conversion was very low after 4 and 8 h reaction, but increased to 1.1% after 24 h reaction with a terminal selectivity of 3.1% (Table 4). It is apparent that the surfactant enhances the conversion of decane slightly. In a non polar medium such

Table 4 Oxidation of decane and AOT in the absence of catalyst

Time (h)	Conv. (%)	Selectivity (%)[a]														Mass balance (%)
		2 one	3 one	4 one	2 ol	3 ol	4 ol	1 ol	C_5 acid	C_6 acid	C_7 acid	C_8 acid	C_9 acid	C_{10} acid	Others	
4	0.01	39.8	13.4	19.6	9.8	6.6	10.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	101
8	0.1	63.3	7.3	11	3.6	1.7	3.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	9.8	100
24	1.1	20.8	12.6	20.2	6.0	3.9	5.4	0.8	2.3	1.0	0.8	0.5	0.7	2.3	23.0	104

Reaction conditions: 100 °C, 15 bar O_2, decane (9.41 g), AOT (0.418 g)

[a] As in Table 1

Table 5 Oxidation of decane with NH_4VO_3 and AOT

Time (h)	Conv. (%)	Selectivity (%)[a]														Mass balance (%)
		2 one	3 one	4 one	2 ol	3 ol	4 ol	1 ol	C_5 acid	C_6 acid	C_7 acid	C_8 acid	C_9 acid	C_{10} acid	Others	
4	0.1	87.4	5.1	7.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	103
8	0.1	42.0	9.2	14.8	3.7	2.9	3.8	0.0	2.0	2.6	2.4	3.9	1.8	0.5	10.4	93
24	0.9	16.9	12.2	21.0	5.7	5.0	7.0	1.0	2.5	5.2	3.0	1.2	0.6	1.4	17.1	89

Reaction conditions: 100 °C, 15 bar O_2, decane (9.41 g), AOT (0.418 g), NH_4VO_3 (0.0008 g)

[a] As in Table 1

Table 6 Oxidation of decane with water and NH_4VO_3

Time (h)	Conv. (%)	Selectivity (%)[a]														Mass balance (%)
		2 one	3 one	4 one	2 ol	3 ol	4 ol	1 ol	C_5 acid	C_6 acid	C_7 acid	C_8 acid	C_9 acid	C_{10} acid	Others	
4	0.01	31.3	22.6	14.0	0.0	0.0	32.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	90
8	0.1	13.4	9.2	15.4	8.4	2.3	4.0	0.0	2.7	2.7	3.9	3.8	2.4	1.5	30.3	91
24	1.1	6.8	4.2	6.8	13.5	10.8	18.4	0.9	3.1	2.8	4.1	2.3	2.7	2.6	21.0	93

Reaction conditions: 100 °C, 15 bar O_2, decane (9.41 g), 24 h, NH_4VO_3 (0.0008 g), H_2O (0.169 g)

[a] As in Table 1

Table 7 Oxidation of decane in water with AOT in the absence of catalyst

Time (h)	Conv. (%)	Selectivity (%)[a]														Mass balance (%)
		2 one	3 one	4 one	2 ol	3 ol	4 ol	1 ol	C_5 acid	C_6 acid	C_7 acid	C_8 acid	C_9 acid	C_{10} acid	Others	
4	0.03	80.3	7.4	12.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	97
8	0.04	28.7	9.5	16.0	5.7	3.8	7.0	0.7	3.8	5.1	1.1	4.6	2.8	1.2	10.0	97
24	0.8	19.7	11.7	19.2	6.7	4.2	5.8	1.0	2.3	4.5	3.8	0.7	0.7	0.8	18.8	97

Reaction conditions: 100 °C, 15 bar O_2, 24 h, decane (9.41 g), H_2O (0.169 g)

[a] As in Table 1

Table 8 Oxidation of decane in the reverse micelle system

Time (h)	Conv. (%)	Selectivity (%)[a]														Mass balance (%)
		2 one	3 one	4 one	2 ol	3 ol	4 ol	1 ol	C_5 acid	C_6 acid	C_7 acid	C_8 acid	C_9 acid	C_{10} acid	Others	
4	0.2	35.2	10.7	17.4	6.1	2.8	5.0	0.0	3.2	3.0	3.5	0.1	2.1	0.0	0.0	96
8	0.3	24.8	9.6	15.8	7.0	4.0	5.6	0.6	2.2	1.7	3.9	2.3	0.8	1.9	19.6	87
24	5.4	18.0	12.1	11.0	3.7	3.2	2.8	0.1	1.6	1.8	2.0	1.7	0.3	1.1	26.8	106

Reaction conditions: 100 °C, 15 bar O_2, 24 h, decane (9.41 g)

[a] As in Table 1

as decane, the AOT surfactant forms reverse micelles in which the polar head group of the surfactant is at the centre and the non polar hydrocarbon chain will be soluble in the organic phase, i.e. decane. When the solid vanadium catalyst is introduced in the decane–AOT system it will remain in the solid phase only as it is not soluble in decane–AOT. We therefore investigated the decane–AOT–NH_4VO_3 system (Table 5) in an analogous manner to the experiments we conducted with decane–NH_4VO_3 (Table 2). The conversion after 24 h increases to 0.9% but the conversion is found to be lower than the decane–NH_4VO_3 system (Table 2). The terminal selectivity was also decreased (2.4%) as compared to the decane–NH_4VO_3 system (3.7%).

The reaction was next carried out in the presence of an aqueous NH_4VO_3 catalyst in *n*-decane and the results are shown in Table 6. The conversion was very low after 4 h (0.01%) and 8 h (0.1%), but increased to 1.1% after 24 h. The decane–NH_4VO_3 system (Table 2) was found to be more active than decane–water–NH_4VO_3 system (Table 6). In this case the water is dispersed as droplets while the reaction mixture is being stirred, but there is no surfactant present to aid dispersion so the conversion is reduced. However, for the three component system, water–AOT–*n*-decane, the reverse micelles are thermodynamically stable consisting of nano-sized aqueous droplets surrounded by a monolayer of surfactant molecules. The terminal selectivity (3.1%) is similar to decane–NH_4VO_3 system (3.7%).

The next experiment involved the oxidation of decane–water–AOT, but in the absence of NH_4VO_3 and the results are shown in Table 7. Very low conversion was observed after 4 and 8 h reaction. The conversion increased with an increase in the time of reaction and reached 0.8% after 24 h. Higher selectivity to C_{10} alcohols and C_{10} ketones was observed and the terminal selectivity (1.8%, Table 7) was found to be similar after 8 and 24 h.

Having carried out all the control experiments it was now possible to carry out the reaction with the complete micelle system, i.e. decane–water–AOT–NH_4VO_3 and the results are shown in Table 8. The conversion after 4 and 8 h reaction was very low but increases after 24 h. However, the terminal selectivity increases up to 8 h (2.5%) then decreases after 24 h (1.2%). In the case of the micelle system, the conversion was relatively high after 24 h (5.4%) but the terminal selectivity is low (1.2%) compared to decane–water–AOT system without catalyst (1.8%).

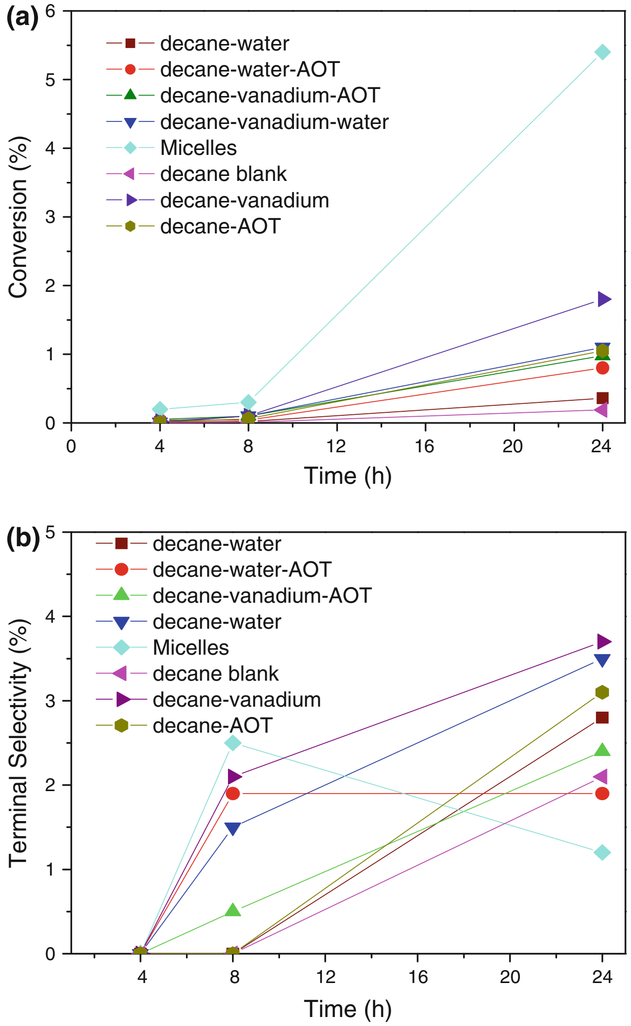

Fig. 1 Effect of reaction time on **a** conversion and **b** terminal selectivity

Comparison of all the data is shown for conversion and terminal selectivity in Fig. 1. It is clear that the most active catalysis is observed in the micelle system. However it is important to contrast the effect of conversion on

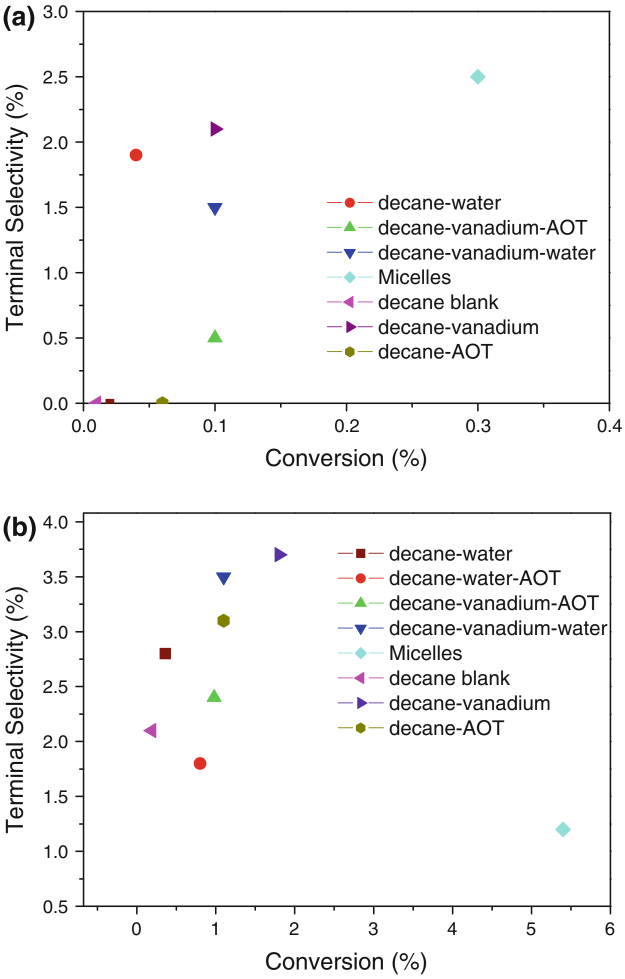

Fig. 2 Conversion vs. terminal selectivity after **a** 8 h, **b** 24 h

selectivity, as selectivity in alkane oxidation is a function of conversion [12] and these data are shown in Fig. 2. It is clear that after 8 h reaction the highest terminal selectivity is observed with the micelle system, but this effect is lost at longer reaction times. Detailed analysis of the reaction mixture showed that AOT was unstable and only 3% (based on nmr spectroscopy of the product) of the initial concentration remained at the longest reaction time. Tests for micelle stability using methylene blue showed that the micelles were not stable at 24 h but remained sufficiently intact at a reaction time of 8 h. Hence, although we were able to demonstrate that the oxidation of decane in a micelle system can enhance terminal selectivity slightly, the inherent non-stability of the micelles, caused by the higher reactivity of AOT for oxidation relative to decane, means that this is not a practical approach for a solution to this complex problem.

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