Titanium dioxide photocatalysis of adamantane

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Abstract—TiO$_2$ photocatalysis of adamantane in oxygen equilibrated MeCN yields 1- and 2-adamantanol and adamantanone with limited degradation and preference for functionalization at the 1 position, particularly in the presence of silver salts. Oxidation in CH$_2$Cl$_2$ is less selective. The oxidation of cyclohexane and cyclododecane is slower. In N$_2$-flushed solutions with Ag$^+$ as a sacrificial acceptor, products from the trapping of both 1-adamantyl radical (adamantyl methyl ketone) and cation (N-adamantylacetamide) are obtained. Furthermore, alkylation of an electrophilic alkene (isopropylidenmalononitrile) has been obtained, though in a low yield.
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1. Introduction

The selective oxidation, and more generally the activation, of the C–H bond in alkanes is a topic of continuous interest.[1] Most of the methods are based on the use of strong electrophiles, but photocatalytic methods[2] offer an interesting alternative in view of the mild conditions, which may increase selectivity. These include electron transfer or hydrogen transfer to excited organic sensitizers, such as aryl nitriles or ketones,[3] or to metal complexes[4a,b] or polyoxametallates.[4c–n] The use of a solid photocatalyst, such as the suspension of a metal oxide,[2b,5] is an attractive possibility in view of the simplified work up. Inexpensive titanium oxide is largely used for the oxidative degradation of organic pollutants,[6] including alkanes,[6e,f] in contaminated water. In this case, water and oxygen are involved in the primary photocatalytic step (Scheme 1, path *a*) and the degradation

of the hydrocarbon occurs via hydrogen abstraction by the highly reactive hydroxyl radicals and following trapping by dioxygen. The products of intermediate oxidation, such as alcohols, aldehydes or ketones are more reactive than the starting alkanes and are not accumulated to a significant extent on the way to full mineralization to carbon dioxide.[6f] However, it has been recently shown that carrying out the photooxidation in an organic medium may lead to useful yields of alcohols or ketones, as shown in the case of the TiO$_2$ photocatalytic oxidation of cyclohexane (neat or admixed with organic solvents).[7] These findings are promising and rise the question of whether an alternative mechanism is involved, i.e. direct oxidation of the organic substrate at the photocatalyst surface (Scheme 1, path *b*). We therefore further explored the TiO$_2$ photocatalysis of alkanes, with particular regard to relatively easily oxidized adamantane. We tested whether photocatalysis by using an electron acceptor other than oxygen could be used with alkanes, in view of the fact that with benzylic donors different mechanisms (see paths *c* and *d*, Scheme 1) have been shown to lead to functionalization not only via oxygenation,[8] but also via C–C bond formation.[9]
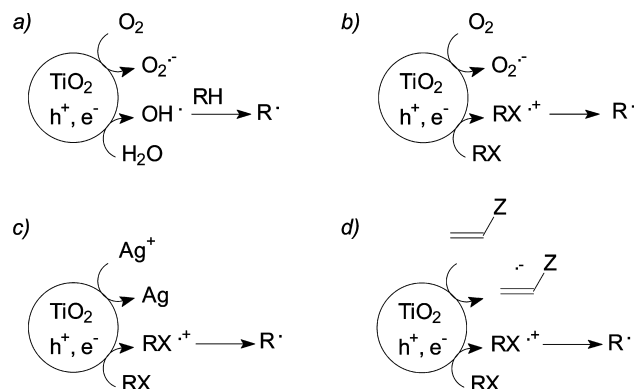
Scheme 1.

2. Results and discussion

A series of experiments were carried out at a fixed irradiation time in order to compare the effect of different conditions. As it appears from Table 1 and Scheme 1, irradiation of a suspension of TiO$_2$ (3.5 mg/mL) in a solution of adamantane (AdH, 0.01 M) in anhydrous acetonitrile for 3 h caused a 30% decomposition of the starting material that was converted to 1-adamantanol (**1**, 21% on the consumed reagent), 2-adamantanol (**2**, 2%) and 2-adamantanone (**3**, 17%), accompanied by a certain amount of the bicyclo[3.3.1]nonandione **4** (8%, Scheme 2,

Table 1. Product distribution from adamantane (0.01 M) upon 3 h irradiation in a TiO_2 suspension

Conditions[a]	% Converted adamantane	% Products on reacted adamantine							
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
MeCN, O_2	30	21	2	17	8				
MeCN, O_2[b]	10	40	6	13					
MeCN, O_2, H_2O	36	23	38	8	7				
MeCN, O_2, Ag^+	5	50		14					
MeCN, O_2, H_2O, Ag^+	9	35	6						
CH_2Cl_2, O_2[c]	49	8	2	16					
MeCN, N_2	–								
MeCN, N_2, H_2O	–								
MeCN, N_2, Ag^+	6					22	14	11	
MeCN, N_2, Ag^+[b]	7					12	10	5	
MeCN, N_2, Ag^+[d]	22			1	10	7	14	2	
MeCN, N_2, H_2O, Ag^+	10	23	3			16	8	8	
MeCN, N_2, IPMN[e]	15								35
MeCN, N_2, IPMN, Ag^+[e]	15								75

[a] TiO_2 140 mg in 40 mL solution, after oxygen or nitrogen flushing; H_2O 2.5% when present; $Ag^+ = Ag_2SO_4$ 0.01 M when present.
[b] TiO_2 40 mg in 40 mL.
[c] 1-Hydroxyadamantan-2-one (4%) and some dioxygenated adamandantes (6%) also present, along with traces of 1- and 2-chloroadamantane.
[d] Prolonged irradiation, 15 h; 1,1′-diadamantane (2%) and 1-adamantanenitrile (3%) also formed.
[e] Adamantane and IPMN, 0.02 M; prolonged irradiation, 24 h.

Table 1). The products were separated by chromatography and characterized (see below for more extensive conversion). Separate experiments showed irradiation in the presence of TiO_2 converted alcohol **1** into diketone **4** and isomeric **2** into ketone **3**. The last compound reacted quite slowly under these conditions. Thus, compound **4** arose from secondary photooxidation and this applied also to part of ketone **3**. Attack at position 1 predominated over position 2 by a factor of ca. 1.5 (ratio **1**+**4**/**2**+**3**).

The use of lower quantities of TiO_2 (1 mg/mL) led to a slower reaction and increased selectively for 1-adamantanol. Both effects were induced to an even stronger degree by the addition of 0.01 M Ag_2SO_4 (ratio attack at position 1 vs. 2, 3.6). Adding 2.5% vol/vol of water, on the contrary, led to a faster reaction and a predominance of attack at position 2 leading to ketone **3** (ratio position 1 vs. 2, 0.65). Carrying out the reaction with both water and the silver salt present led to a slow reaction, with 1-adamantanol as by far the major product, isomeric alcohol **2** as the minor one and no ketone **3**.
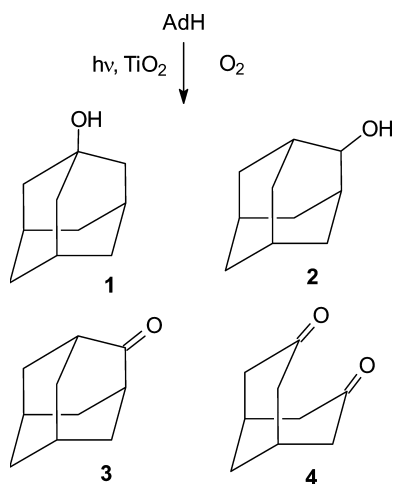
The photooxidation in anhydrous dichloromethane was the fastest of the reactions tested, though the least selective. Products **1**–**3** (the main one, 16%) were formed, along with various difunctional oxygenated products; among these 1-hydroxy-2-adamantanone, 4%, was recognized through the comparison of the mass spectrum with literature, the other ones amounted to ca. 6%. Traces of 1- and 2-chloroadamantane (GC–MS comparison with authentic samples) were also observed.

The above experiments were then repeated on nitrogen flushed slurries under otherwise identical conditions. In this case, no measurable reaction took place in 3 h in anhydrous acetonitrile or containing 2.5% water. Adding 0.01 M silver sulfate led to some reaction and gave 1-acetamidoadamantane (**5**, 22%), the main product, and 1-acetyladamantane (**6**, 14%), which were separated and recognized. Further compounds were formed, among which the main one was suggested to be 1,2-dihydroxyadamantane (**7**, Scheme 3,
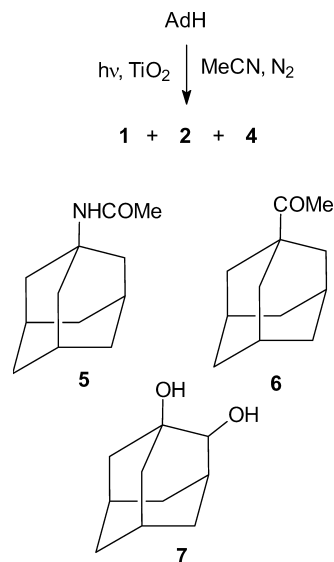

Scheme 2.

Scheme 3.

Table 1) on the basis of the GC–MS characteristics. Prolonging the reaction time led to more extensive reaction, but the product yield with respect to the converted material diminished and further compounds, which were identified as the ring-cleaved diketone **4**, 1-adamantanenitrile and 1,1'-diadamantane (GC–MS comparison with authentic samples) were detected. Using a lower amount of TiO_2 did not affect the pattern of the reaction. In nitrogen-flushed solutions, adding both Ag_2SO_4 and water enhanced the reaction rate and led to 1-adamantanol as the main product and amide **5** as the second one, accompanied by lower amounts of products **2**, **6** and **7**. As is apparent, attack at position 1 was always largely prevalent upon irradiation under these conditions (by a factor of 20 or larger).

Irradiation in the presence of cyclohexane and cyclodecane in oxygen flushed TiO_2 suspension in acetonitrile led to some oxygenation (6 and 8% conversion, respectively in 3 h) with a marked preference for the ketone with respect to the alcohol (ca. 3 to 1 in both cases) and the formation of some dihydroxylated derivative. On the contrary, in nitrogen-flushed acetonitrile no measurable reaction was detected with these alkanes also in the presence of silver sulfate.

In order to better assess the course of the non-degradative oxygenation, experiments were carried out on a larger scale (20 mmol instead of 4) in a different set up (see Section 3) with periodic monitoring in order to test the course of the reaction. In the oxygenation of adamantane the sum of identified products (**1**–**4**) remained over 50% of the consumed reagent, with a slight increase with time of the proportion of **3** and **4**. The maximum yield of the sum of these products reached 28% of the initial AdH amount at 55% conversion, and then declined slowly (Fig. 1). Under the same conditions, the yield of alcohol and ketone from cyclododecane also remained close of the half of the consumed reagent up to 50% of the conversion (e.g. 13% ketone and 4% alcohol at 35% conversion), but the reaction was ca. four times slower than with adamantane (Fig. 2). The results with cyclohexane were similar (not shown).

We then attempted functionalization by using an electrophilic alkene as the trap in the place of oxygen. Irradiation of TiO_2 suspensions were thus carried out in the presence of
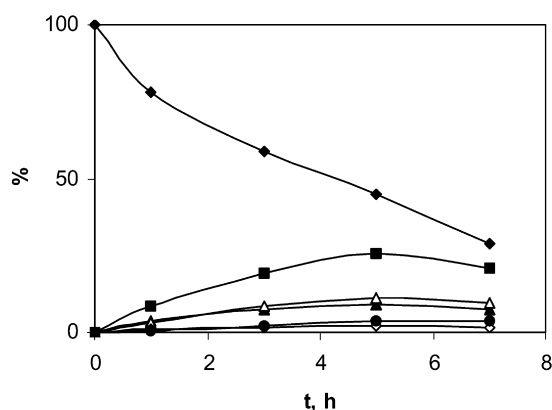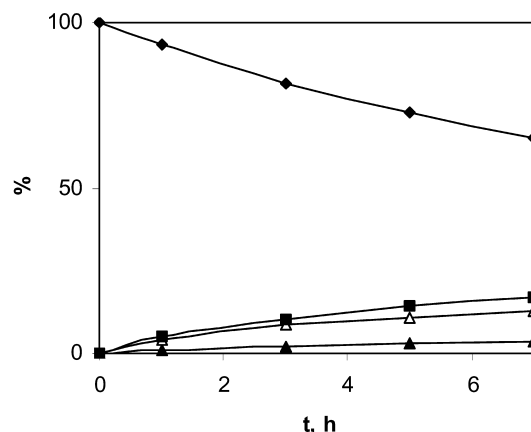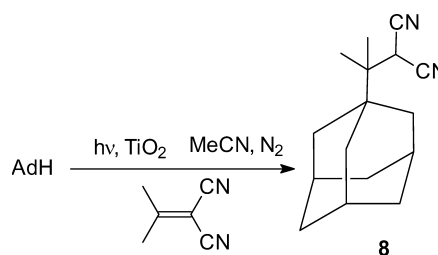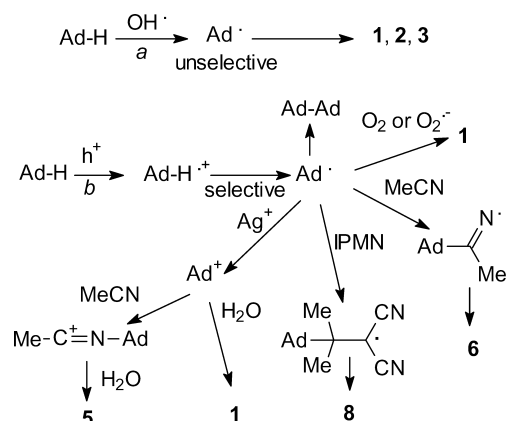
Figure 2. Degradation of cyclododecane upon TiO_2 photocalysis in oxygen equilibrated acetonitrile (◆) and formation of the cyclododecanol (▲) and cyclododecanone (△); sum of the two photoproducts (■).

isopropylidenmalonitrile (IPMN, 0.02 M, with adamantane likewise 0.02 M) under nitrogen. A longer irradiation time (24 h) was required for obtaining a conversion sufficient for product isolation and identification. A new product was formed and was recognized as the adduct, 2-[1-(1-adamantyl)-1-methyl)]ethylpropanedicarbonitrile (**8**, Scheme 4, Table 1). This was accompanied by traces of oxygenated products **1**–**3**, presumably arising from reaction with residual oxygen, non-negligible at long irradiation time, but not by products **5**–**7**. The same reaction carried out in the presence of silver sulfate gave a higher yield of adduct **8**, with practically none of **1**–**3**, but the conversion remained slow.

As mentioned in the introduction, the TiO_2 photocatalyzed oxidation of alkanes in water occurs exclusively with hydroxyl radicals as the active species (Scheme 1, path *a*). In organic solvents, oxidation may again occur due to the intervention of hydroxyl group at the catalyst surface. However, at least with adamantane, which is less difficult to oxidize (E_{ox} 2.7 eV vs SCE in MeCN)[10] than open chain or monocyclic alkanes, electron transfer from the alkane to photoformed holes may play a role (Scheme 1, path *b*). Alkyl radicals are then formed through an alternative path and combine with the superoxide anion formed in the reductive part of the photocatalysis. Hydroxyl radicals are less important and oxidation is not necessarily accompanied by chain degradation. Figures 1 and 2 show that nondegraded products remain around a half of the starting alkane up to 50% conversion. As one may expect, the process is more expedient with adamantane, while with oxidation-resistant monocycloalkanes the reaction is quite slow.

Figure 1. Degradation of adamantane upon TiO_2 photocalysis in oxygen equilibrated acetonitrile (◆) and formation of the photoproducts: **1** (▲), **2** (◇), **3** (△), **4** (●); sum of products **1**–**4** (■).

Scheme 4.

Scheme 5.

part adds to the solvent, MeCN. Nitriles are essentially inert to radical attack, and indeed MeCN is often used as the solvent for radical reactions. However, without access to other paths, radical addition on the nitrile moiety can occur, as previously found in the literature,[13] including an example of the adamantyl radicals from azoadamantane.[14,15] An iminyl radical results and is finally converted into 1-adamantyl methyl ketone **6** (Scheme 5).

Besides the above reaction paths, a significant fraction of the products formed in the MeCN/N_2/Ag_2SO_4 experiments arises via electron transfer to Ag^+ from the easily oxidized adamantyl radical (compare E_{ox} (*tert*-Bu·) 0.09 V vs. SCE).[16] The resulting adamantyl cation is trapped by the solvent to yield an adduct cation and N-(1-adamantanyl)-acetamide **5** from it (Scheme 5). When 2.5% water is added, on of the main products is 1-adamantanol, which is formed predominantly (10:1) with respect to the 2-isomer. Traces of 1-adamantanenitrile likewise arise by trapping of the cation by cyanide present in the solvent. Under conditions where the electron transfer path predominates in the oxidation, functionalization at position 1 is almost exclusive and involves both the radical and the corresponding cation. The reaction is slow, however, and prolonged irradiation leads to oxidation of the primary products, with formation of glycol **7** and diketone **4**.

It may be noted that overoxidation also takes a peculiar course under these conditions. Formation of doubly-oxidized, ring-cleaved diketone **4** or of dihydroxyadamantane **7** from 1-adamantanol or directly from adamantane have not been previously reported.

Finally, the reaction in the presence of a carbon-centered radical trap has also been attempted. The result is not satisfactory, since under these conditions the functionalization of adamantane proceeds sluggishly and becomes exceedingly slow at low (ca. 15%) conversions. This holds true for when electrophilic isopropylydenemalononitrile IPMN is the only additive and fills the double role of electron acceptor in the photosensitization step and of radical trap (Scheme 1, path *d*), and also when a different sacrificial oxidizer, Ag_2SO_4, is added. Nevertheless, the absence of compounds **1–7** in the presence of 0.02 M IPMN (except for traces of oxygenated compounds) is evidence for efficient scavenging of the radicals by this particularly good trap. Formation of dinitrile **8** demonstrates at least the principle that direct functionalization of alkanes by C–C bond formation is possible through heterogeneous photocatalysis.

In conclusion, the functionalization of the C–H bond in alkanes has been obtained by TiO_2 photocatalysis under mild and conditions, both through oxygen incorporating and through C–C bond forming reactions. Both oxygen and an inorganic or organic oxidant have been used as the electron scavenger. Although incomplete conversions have been obtained, yields are reasonable and the method may have some relevance in the frame of the current interest for mild alkane activation.[16] At least with P25 titanium dioxide, however, the functionalization is not easily extended to simpler alkanes, such as monocyclic derivatives.

A test for the two oxidation paths is regioselectivity in the functionalization of adamantane. Thermochemical calculations predict that single electron transfer oxidation of adamantane (Scheme 5, path *b*) is followed by deprotonation preferably from the bridgehead position, and thus leads predominantly to the 1-adamantyl radical.[10] Reactions following this path, such as anodic oxidation, ET photosensitization or ET to an oxidizing radical, such as NO_3^-, give essentially products functionalized in 1.[10,11] On the other hand, hydrogen abstraction by an electrophilic radical, such as OH·, is unselective and thus the 2-adamantyl radical is statistically favored.[2c,12] The present experiments in MeCN equilibrated with oxygen support participation of the electron transfer path. Under these conditions, the ratio for attack at position 1 vs. 2 is 1.5 with 3.5 mg/mL TiO_2, 2.1 when the reaction is made slower and more selective by using a smaller amount of photocatalyst, and 3.6 in the presence of silver salts. On the contrary, the ratio drops to 0.65 when 2.5% water is added, thus favoring the OH· path (Scheme 5, path *a*).

The photocatalyzed oxidation in dichloromethane increases the rate of reaction with respect to MeCN, but the proportion of degradation is higher and attack unselective (position 1 vs. 2, 0.5). With a less polar liquid phase, adsorption on titanium dioxide is favored and unselective hydrogen abstraction by hydroxyl groups at the irradiated catalyst surface is more effective. Traces of chloroadamantane arise from solvent trapping of the radicals. Desorption of the primary photoproducts is slower in this case and polyoxidation and degradation are more important. Thus, it is preferable to carry out the oxidation in a polar solvent such as MeCN, where adamantanols and adamantanone are accumulated to a reasonable amount in solution, minimizing skeleton degradation, and furthermore, the reaction shows some regioselectivity for position 1.

A further variation is the use of a silver cation as a sacrificial acceptor in the place of oxygen (Scheme 1, path *c*). The reaction is slower in this case, but selectivity for position 1 is high (the ratio 1 vs 2 is >10, in all the experiment in N_2-flushed slurry, see Table 1). As for the chemical paths, when oxygen is excluded, no obvious radical trap is present. The relatively persistent adamantyl radical in part dimerizes (traces of 1,1-diadamantane are formed, see Table 1) and in

3. Experimental

Reagents. Degussa P25 titanium dioxide was dried in a oven at 110°C for 24 h and acetonitrile was distilled from calcium hydride and stored over molecular sieves. The chemicals used were either commercial compounds or were prepared according to published procedures, as in the case of dinitrile IPMN.[17]

Irradiations. A 140 mg sample of titanium dioxide (or a lower amount, see Table 1) was weighted in a round bottomed Pyrex tube (2.4 cm internal diameter, 14 cm height). A solution of adamantane or other alkanes (0.01 or 0.02 M) with the appropriate additives in MeCN or CH_2Cl_2 (40 mL) was added. The tube was sealed with a serum cap and the mixture sonicated for 1 min. Two needles were inserted and either oxygen or purified nitrogen was passed through the solution for 15 min with magnetic stirring. One to four of such tubes were put in the center of four 15 W phosphor-coated lamps (40 cm length, 350 nm center of emission) and irradiated while maintaining a slow flux of gas and magnetic stirring. The reaction course was monitored by GC. The suspension was then filtered over a 0.2 μm porosity filter under vacuum. Samples were either directly analyzed or rotary evaporated and taken up to a fixed volume for quantitative determination (see below). Several batches were reunited, evaporated and chromatographed.

The most abundant compounds were isolated by silica gel chromatography (cyclohexane–ethyl acetate mixtures as the eluant). 1- and 2-Adamantanol (**1**, **2**), adamantanone (**3**) and 2-(1-adamantyl)-etanone (**6**) were identified by comparison of their GC/MS and NMR spectra with commercial authentic samples. *N*-(1-Adamantyl)acetamide (**5**) was identical to a previously obtained sample[10] and bicyclo-[3.3.1]nonan-3,7-dione (**4**) was recognized on the basis of the comparison of spectroscopic characteristics, in particular of ^1H, ^{13}C (DEPT) NMR spectra with a literature report.[18]

2-[1-(1-Adamantyl)-1-methyl)]ethylpropanedicarbonitrile (**8**), colorless solid, mp 66–67°C; analysis C 79.5, H 9.3, N 11.2 %, calculated for $C_{16}H_{22}N_2$, C 79.29, H 9.15, N 11.56%; ^1H NMR (CDCl$_3$) δ 1.2 (s, 6H, CH$_3$), 1.6–1.8 (m, 12H, CH$_2$), 2.1 (br, s, 3H, CH), 3.75 (s, 1H, α-CH); ^{13}C NMR (CDCl$_3$) δ 21.0 (CH$_3$), 28.2 (CH), 30.2 (CH), 36.3 (CH$_2$), 36.6 (CH$_2$), 37.6, 43.0, 113.4 (CN); IR (melt) 2251 cm^{-1}; MS, *m/e* 242 (M$^+$, 4%), 177 (10), 135 (100).

In other cases, the amount was too low for a preparative separation and the compound was identified by comparison of the GC/MS characteristics with that of authentic samples, either of commercial origin (1- and 2-chloroadamantane, 1-adamantenenitrile) or prepared through a known method (1,1-diadamantane).[19] The identification of 1, 2-hydroxy-adamantane (**7**) was suggested on the basis of the MS fragmentation that distinguished it from other isomers.[20] 1-Hydroxyadamantan-2-one was likewise recognized by comparing GC/MS data with the literature.[21]

The yields were determined by GC on the basis of calibration curves using dodecane or cyclododecane as the internal standards. Gas chromatographic analyses were carried out by using an HP 5890 apparatus with a 0.3 mm×30 m capillary column with a flame ionization detector. Gas chromatography/mass spectrometry determination was performed using an HP 5970B instrument operating at a ionizing voltage of 70 eV, connected to an HP 5890 instrument equipped with the same column as above.

Larger scale irradiations were carried out with a suspension of TiO_2 (0.7 g) in MeCN (200 mL) in an immersion well apparatus fitted with a Pyrex-filtered, water-cooled medium pressure mercury arc (150 W). The suspension was magnetically stirred and flushed with oxygen during irradiation. GC analysis and preparative chromatographic separation were carried out as above.

Acknowledgements

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