Polynuclear Aromatic Hydrocarbons |Hot Paper|



Selective Oxidation of Alkyl-Substituted Polyaromatics Using Ruthenium-Ion-Catalyzed Oxidation

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Abstract: Ruthenium-ion-catalyzed oxidation of a range of alkylated polyaromatics has been studied. 2-Ethylnaphthalene was used as a model substrate, and oxidation can be performed in either a conventional biphasic or in a monophasic solvent system. In either case the reaction rates and product selectivity are identical. The reaction products indicate that the aromatic ring system is oxidized in preference to the alkyl chain. This analysis is possible due to the development of a quantitative NMR protocol to determine

Introduction

In 1953, Djerassi reported a new ruthenium tetroxide system that could be used in place of the more toxic OsO₄ for the oxidation of various organic substrates.^[1] This seminal discovery led to the introduction of an entirely new chemistry for the oxidation of organic compounds, which was later named as ruthenium-ion-catalyzed oxidation (RICO), in which RuO₄ is generated in situ by the combination of a ruthenium ion and an oxidizing agent.^[2] RICO was further developed into a practical catalytic oxidation system by Sharpless et al.,^[3] who reported that by adding acetonitrile as a co-solvent, the selectivity, as well as the activity, for the oxidation of alkenes to carboxylic acids could be improved with a much lower metal loading. Consequently, after this discovery, RICO has been reported to be effective for many reactions, including dihydroxylation of olefins,^[4] dehydrogenation of alcohols and amines,^[5] selective monooxidation of vicinal diols,^[6] ketohydroxylation,^[7] oxidative cyclization of polyenes,^[8] oxidative cleavage of double and triple bonds,^[9] oxidation of heteroatoms^[10] and oxidation of saturated hydrocarbons and aromatic hydrocarbons.^[11]

Initially, RICO was used mainly for the oxidative fragmentation of C=C bonds and aromatic compounds, which has resulted in a reputation for the chemistry being very reactive and difficult to control. Various oxidizing agents have been re-

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[b] M. Francisco ExxonMobil, Research & Engineering Company, 1545 Route 22 East Annandale, New Jersey 08801 (USA) the relative amounts of aliphatic and aromatic protons. From a systematic set of substrates we show that as the length of the alkyl chain substituent on a polyaromatic increases, the proportion of products in which the chain remains attached to the aromatic system increases. Larger polyaromatic systems, based on pyrene and phenanthrene, show greater reactivity than those with fewer aromatic rings, and the alkyl chains are more stable to oxidation.

ported to oxidize hydrocarbons; however, RICO stands apart due to its high reactivity and functional group tolerance.^[12] It has been shown that RICO occurs regioselectively at the most electron-rich C–H bond with retention of configuration.^[13] This high regioselectivity is remarkable as it is rare amongst catalytic oxidation systems. The regioselectivity of RICO has been exploited in two different research areas. The first is the oxidative fragmentation of aromatic compounds to carboxylic acids in synthetic organic chemistry,^[9b, 14] and the second is in the selective oxidation of alkylated aromatics, with aromatics oxidized to CO₂ and H₂O leaving the aliphatic chain intact terminated by a carboxylic acid group.^[2] This method is used extensively to characterize the aliphatic chain present in highly complex mixtures of substituted polyaromatic compounds.^[15] A number of papers have been published using this methodology to characterize the aliphatic chains in coal and asphaltenes.^[16] The approach is based on three hypotheses: 1) the aromatic hydrocarbons are oxidized to CO₂ and H₂O in high yield, 2) oxidation of the aliphatic portion of the compounds occurs exclusively at the carbon atoms attached to the aromatic fragment and 3) the aliphatic chain is not further oxidized. Although these hypotheses have been tested using a limited range of substrates, a detailed quantitative investigation of the hypotheses outlined above has not been reported in the literature.^[17]

In spite of the reputation for high reactivity, many researchers have tried to utilize RICO chemistry and improve its selectivity. Harris and co-workers^[11c] have reported that, using low temperatures and limiting the level of oxidant, alkyl substituted pyrenes can be converted with good selectivity to the corresponding 4,5-diones or 4,5,9,10-tetraones, although yields were generally less than 50% and no information on the oxidation of the alkyl substituents was presented.

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In the present work, we set out to investigate the selectivity of RICO chemistry for alkylated aromatic compounds using NMR analysis to quantify the aromatic versus aliphatic oxidation selectivity under various experimental conditions. To achieve this, we have set out the following objectives: 1) to develop methodology to quantify the extent of aromatic vs aliphatic oxidation, 2) to establish new protocols for RICO chemistry^[6a] that allow greater control of reactivity and 3) to understand whether it is possible to manipulate selectivity by changing the reaction parameters. Against this background, we report an NMR methodology to quantify the ratio of aromatic to aliphatic protons oxidized during a reaction. This method is then applied to the products from RICO for a series of alkylated aromatics giving a quantitative estimation of the amount of aliphatic C/H oxidized relative to the amount of aromatic C/H oxidation. We report the results from the detailed investigation on the RICO of a range of substrates, including 2-ethylnaphthalene, 1-decylnaphthalene, 1-octadecylnaphthalene, 2-nonylphenanthrene, 9-octadecylphenanthrene, 1-butylpyrene, 1-decylpyrene and 1-octadecylpyrene. To our knowledge, this is the first quantification of the regioselectivity of oxidation at aliphatic and aromatic carbon using an in situ ¹H NMR technique for RICO.

Results and Discussion

Reaction quenching studies

RICO is an extremely active oxidation system and even at 295 K, the temperature routinely used in these studies, the rate of reaction was rapid. Accordingly, it is important to be able to control the reaction, especially to be able to carry out the analysis of the substrate and the reaction products as a function of time. Hence, a method was developed to guench the reaction in a simple, reliable and reproducible manner. Two strategies for effective quenching could be envisaged: deactivating or removing the catalyst, or rapidly removing the iodate oxidant. We decided to employ the latter approach using the readily oxidized sulfite ion which was introduced by adding Na₂SO₃ to the reaction mixture at the desired quench time. To test the efficacy of this approach, increasing amounts of Na₂SO₃ were added to reaction mixtures with naphthalene as the substrate and the level of naphthalene remaining after a short time was analyzed using GC. Figure 1 shows that, at ratios of sulfite/oxidant below 1, naphthalene was still oxidized after the introduction of sulfite, although the degree of oxidation decreased as the ratio of Na₂SO₃ to NalO₄ was increased. At a sulfite/oxidant ratio of 1 or greater, no oxidation of the substrate was observed. Further experiments were also performed in which a substrate was allowed to partially react before it was quenched using a stoichiometric amount of sulfite. The concentration of the substrate was then monitored over a 24 h period, and no further conversion after the addition of sulfite occurred.



Figure 1. Plot of concentration of naphthalene (**u**) remaining after quenching with Na₂SO₃ at the start of reaction (**●**) vs molar ratio of Na₂SO₃/NalO₄. Reaction Conditions: Substrate 0.195 mmol (initial number of mmol: x), NalO₄ 1.56 mmol, RuCl₃ 0.012 mmol, Na₂SO₃ 1.56 mmol, (ratio 1:1), MeCN 20 mL, H₂O 10 mL, T = 22 °C, stirring speed 500 rpm.

Oxidation of 2-ethylnaphthalene

The experimental protocol developed for large PAH systems has to cope with the low solubility of PAHs in the aqueous media suited for RICO. This resulted in the use of a biphasic reaction system for long-chain alkylated aromatics. For the smallest PAH studied, 2-ethylnapththalene, a monophasic approach could also be employed and so initial experiments on alkylated polyaromatic oxidation concentrated on 2-ethylnapththalene and a study on the effect of the solvent system was performed. Oxidation using a monophasic system also allowed us to perform experiments in an NMR tube (details in Experimental Section). Reaction products were present in both the organic and the aqueous layers. Here the organic layer analysis is presented as it gives qualitative identification of all products.

Figure 2 shows that changing the solvent system from monophasic (acetonitrile+water) to biphasic (dichloromethane+acetonitrile+water) does not alter the rate of



Figure 2. Oxidation of 2-ethylnaphthalene in monophasic (\bullet) and biphasic (\bullet) solvent system: Kinetic studies. Reaction Conditions: Substrate 0.164 mmol, NalO₄ 2.624 mmol, RuCl₃ 0.024 mmol, *T*=22 °C, stirring speed 500 rpm, DCM 16 mL, MeCN 7 mL, H₂O 7 mL or MeCN 20 mL, H₂O 10 mL.

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B B C E F B 10 20 30 Time (min)

Figure 3. Comparison of GC-MS traces from 2-ethylnaphthalene oxidation in monophasic and in biphasic solvent system. Reaction Conditions: Substrate 0.164 mmol, NalO₄ 2.624 mmol, RuCl₃ 0.024 mmol, T = 22 °C, stirring speed 500 rpm; A) DCM 16 mL, MeCN 7 mL, H₂O 7 mL; B) MeCN 20 mL, H₂O 10 mL.

oxidation of 2-ethylnaphthalene. It is also important to note that, according to GC-MS measurements, the product distribution from the monophasic system was the same as the biphasic one (Figure 3). Some minor differences are observed in the chromatograms above 21 min; however, these are associated mainly with analytical artefacts as a consequence of the high temperatures required to elute the heavy aromatic compounds. The total area for peaks eluting above 21 min was <10% of the total peak area for the major products (A–F). Hence, simplifying the reaction solvent system did not fundamentally change reaction rates or selectivity, but does simplify the product analysis. This practical advantage lead us to use the monophasic solvent system to study the oxidation of 2-ethylnaphthalene further.

Special attention was focused on the selectivity of aromatic C–H versus alkyl C–H oxidation. The compounds identified using GC-MS from the oxidation of 2-ethylnapthalene are listed in Table 1. It is clear that most of the products have unoxidized alkyl chains, still attached to an oxidized aromatic ring system (Figure 3). This result is surprising for RICO, as it has been widely reported that the alkyl chain is readily oxidatively cleaved to form aliphatic carboxylic acids with the aromatic moiety oxidized to CO_2 and water.^[17b, 18]

To confirm these results, the mixture of reaction products was analyzed immediately after quenching of the reaction using 2D ¹H NMR correlation spectroscopy (COSY); a typical spectrum is shown in Figure 4. The COSY NMR spectra show coupling between protons from the CH_2 group of the alkyl region and protons from the CH_3 group, indicating that the alkyl chain is preserved. This observation is consistent with the reaction products identified by GC-MS (Table 1, Figure 3). Therefore, it is clear that during the RICO of 2-ethylnapthalene, the aromatic component can be selectively oxidized in preference to the aliphatic ethyl substituent. Table 1 also shows that partial oxidation of the aromatic system takes place and so the

 Table 1. Oxidation of 2-ethylnaphthalene in a monophasic solvent system: GC-MS product identification.^[a]

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aromatic groups are not necessarily converted to CO_2 and water. The majority of products that have the aliphatic chain intact also retain the substituted aromatic ring, so that selectivity after 4 h under our conditions appears to favor the oxidation of the unsubstituted ring of the naphthalene moiety.

In situ ¹H NMR analysis of 2-ethylnaphthalene oxidation

To quantify the aromatic versus aliphatic oxidation selectivity, an in situ time online study of the ruthenium-ion-catalyzed oxidation of 2-ethylnaphthalene was also performed inside an NMR tube as described in the Experimental Section. It is worth noting that, due to the lack of solubility of some products, reactions performed in an NMR tube were designed to give partial conversion. This was achieved by reducing the amount of oxidant and catalyst compared to the laboratory-scale experiments. In Figure 5 the ¹H NMR signals of the entire spectra are grouped into four regions; A) aliphatic region (3.51–0.53 ppm), B) olefinic region (6.98–6.43 ppm), C) aromatic region (8.63–7.51 ppm) and D) carboxylic acid/aldehyde region (10.82–10.63 ppm).

The integrated peak areas in the defined regions are proportional to the number of protons present in the reaction mixture within the assigned functionality, and so allow the relative rates of aliphatic and aromatic carbon oxidation to be measured. Integration of the peaks from a reference sample of 2-ethylnaphthalene, without acetonitrile, gave an aromatic: aliphatic ratio of 1.33 in close agreement with the 1.4

Chem. Eur. J	. :	2015, 21,	4285 – 4293
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Figure 4. Two-dimensional NMR (COSY) spectra of 2-ethylnaphthalene oxidation products in a monophasic solvent system. Reaction Conditions: Substrate 0.164 mmol, NalO₄ 2.624 mmol, RuCl₃ 0.024 mmol, T=22 °C, stirring speed 500 rpm, MeCN 20 mL, H₂O 10 mL.



Figure 5. Overlaid ¹H NMR spectra of 2-ethylnaphthalene oxidation with marked regions of integration. Reaction Conditions: Substrate 0.101 mmol, NalO₄ 20.421 mmol, RuCl₃ 0.5 μ mol, T=22 °C, CD₃CN 2 mL, H₂O 3 mL.

expected. Under reaction conditions the acetonitrile signal at 2.3 ppm will also be integrated which results in an aromatic: aliphatic ratio of 0.916. As signals from reaction products could possibly overlap with the acetonitrile peak, we decided to simply integrate the whole aliphatic region rather than attempt to explicitly exclude acetonitrile.

The relative percentage of protons from different regions, R_{Xr} can be calculated from Equation (1), in which we have used X

as a general subscript for A, B, C or D according to the peak of interest. I_x is the integrated area relative to TMS for the corresponding region.

$$R_{\chi} = \frac{1}{I_{\rm A} + I_{\rm B} + I_{\rm C} + I_{\rm D}} \times 100$$
 (1)

The time-on-line profiles for the relative percentage of protons are shown in Figure 6. It is clear that, in the first 100 min of reaction, there is a steady decrease in the proton signal in the aromatic region and a corresponding increase in the aliphatic region. The first data point is measured 15 mins after the initial mixing of reactants and we find an aromatic: aliphatic ratio of 0.88. Linear extrapolation of the data from the first 90 min of the reaction back to zero gives an estimate for the aromatic/aliphatic ratio of 0.91 at the start of the reaction, in good agree-



Figure 6. Normalized relative percentage amounts of protons in different environments determined by ¹H NMR spectroscopy as a function of 2-ethylnaphthalene oxidation reaction time. $\blacklozenge R_{Dr}$ acid and aldehyde; $\blacksquare R_{cr}$ aromatic; $\blacktriangle R_{Br}$ double bond; $\blacklozenge R_{Ar}$ aliphatic.

ment with the measured ratio for 2-ethylnaphthalene and acetonitrile in the absence of oxidant and catalyst. After 105 mins of reaction the observed integrated area for each region of the spectra becomes constant with time, indicating that the oxidation reaction has stopped. From this point forward the average aromatic/aliphatic ratio is 0.68, indicating a significant preference for aromatic over aliphatic oxidation in the RICO reaction. At all times the signal from protons in an olefinic or acid/aldehyde environment remains negligibly small.

The data presented in Figure 6 only shows quantification of the relative proportions of protons in different environments,



Figure 7. Absolute numbers of protons in different environments determined by ¹H NMR spectroscopy as a function of 2-ethylnaphthalene oxidation reaction time. $\blacklozenge I_c$ aromatic; $\blacksquare I_{A}$, aliphatic; $\blacktriangle I_A + I_B + I_c + I_D$, total.

rather than the total number of protons, so that the contribution of total oxidation is not taken into account. In order to provide information on the change of the total number of protons, the absolute values relative to TMS, I_{Xr} are plotted against time in Figure 7. To estimate the reduction in the total number of protons associated with organic molecules present in the sample we first extrapolated the data between 15 and 105 min back to time zero ($R^2 = 0.96$) obtaining a value of 3.36 in the arbitrary units of Figure 7. Comparing this against the value obtained at 105 min, we estimate the total absolute number of protons to be reduced by 16%. Given the spread in the data post 105 min we conclude that this is probably an upper estimate and so the contribution to the loss in proton signal from total oxidation is small. Figure 7 also shows that the reduction in total signal in the first 105 min of the experiment is due to loss of aromatic protons, while the aliphatic region of the spectrum remains largely unchanged over the time period of the experiment. This is the behavior we would expect from the products listed in Table 1, since most products show aromatic carbon oxidation and for some of the products the partial oxidation of the aromatic ring actually introduces additional aliphatic protons.

From the data presented above it is clear that RICO of 2-ethylnaphthalene, in a monophasic solvent system, leads to selective oxidation of aromatic carbon, whilst there is little or no oxidation of the aliphatic ethyl side chain. GC-MS analysis has revealed that the majority of the products identified have the ethyl chain intact (Table 1) and no products originating from oxidative cleavage of the alkyl chain were observed.

Oxidation in a biphasic solvent system

The monophasic solvent system has advantages for ease of quantification and analysis of products. However, it also has limitations, as the solubility of higher molecular weight polyaromatics is low. One of the main aims of this study is to investigate a range of alkyl-substituted polyaromatics, and study the selectivity pattern for their ruthenium-ion-catalyzed selective oxidation. To overcome the solubility problem, the more conventional biphasic solvent system, containing water, acetonitrile and dichloromethane was used. This biphasic solvent system introduces new complications for quantitative analysis because of the distribution of substrate and products between the organic and aqueous phases. We have seen that for 2-ethylnaphthalene, the change of solvent system does not affect the activity (Figure 2) or selectivity (Figure 3) of the oxidation reaction. Accordingly, with higher molecular weight polyaromatic compounds, we are able to use a biphasic solvent system and still draw comparisons with the results from monophasic oxidation of 2-ethylnaphthalene.

In the case of higher molecular weight polyaromatics, and those with longer alkyl chains, we build further on the idea of using the integrated areas from different regions of the ¹H NMR spectra to quantify the degree of regioselectivity. The electronic environment of the terminal H in a long-chain alkyl substituent of a polyaromatic compound will be affected to a lesser extent by changes due to the oxidation of the poly aromatic region, than will the protons in the ethyl group of 2ethylnaphthalene. Consequently, the terminal proton was used as an internal standard for the quantification of the RICO products of long chain alkyl aromatics in the biphasic solvent system using ¹H NMR spectroscopy. Conversely, the methylene protons of the aliphatic carbon, which are attached to the aromatic ring, will produce a triplet that is highly susceptible to any changes at the point of attachment of the aliphatic chain to the aromatic ring. This triplet signal was used for the quantification of the oxidation products in which the aliphatic chains remained intact. In addition to analysis of products using NMR spectroscopy, the conversion of the alkylated polyaromatic compounds was determined using GC.

To demonstrate this methodology, RICO of 1-decylnaphthalene is used as an example. Figure 8 shows the ¹H NMR spectra of 1-decylnaphthalene before and after RICO for 4.5 h. The singlet at 0.9 to 0.7 ppm (region D in Figure 8) is the terminal methyl group, which is used as an internal standard. The triplet at 3.1–2.9 ppm (region A in Figure 8) is used for quantifying the amount of products with aliphatic chain substituent intact after RICO. The areas of these two peaks, for the 0 and 4.5 h samples, were calculated relative to a calibrated TMS standard and values are given in Table 2. The ratio of peak areas [Eq. (2)]

Table 2. Oxidation of 1-decylnaphthalene in a biphasic solvent system integrated area values (against TMS). Molar ratio substrate/oxidant 1:2. ^[a]					
Sample	Area A	Area D	Area ratio $r_x = A/D$	p _a [%]	
0 h 4.5 h	0.28 0.17	0.43 0.43	0.65 0.39	100 60	
[a] Reaction conditions: Substrate 0.0264 mmol, NalO ₄ 0.052 mmol, RuCl ₃ 0.0006 mmol, CDCl ₃ 2.4 mL, CD ₃ CN 1 mL, H ₂ O 1 mL, T=295 K, stirring speed 500 rpm.					

for protons A and D between the 0 and 4.5 h samples gives a measure of the percentage of products in which the aliphatic chain remains intact (p_a)

$$p_{\rm a} = (r_{4.5}/r_0) \times 100\,\% \tag{2}$$

Chem. Eur. J. 2015, 21, 4285 – 4293





significantly alter the conversion or the extent of oxidation of the alkyl chain. However, re-charging the system with additional oxidant and catalyst after 6 h during a 10 h reaction does lead to complete conversion of the substrate and practically total loss of the alkyl chain, presumably as carboxylic acid (Table 3, entry 3).

Having successfully demonstrated the quantification methodology for the RICO of an alkyl aromatic using ¹H NMR spectroscopy, our next objective was to use the methodology to understand the effect of the size of the aromatic ring moiety, the aliphatic chain length and substitution position on product selectivity. For this purpose, in addition to 1-decylnaphthalene, six other substrates with different

aliphatic chain lengths and varying numbers of fused aromatic rings were chosen for investigation using RICO. These substrates were 1-octadecylnaphthalene, 2-nonylphenanthrene, 9octadecylphenanthrene, 1-butylpyrene, 1-decylpyrene and 1octadecylpyrene for which structures are given in Table 4.

¹H NMR spectra of each substrate were measured independently before and after reaction and the peaks were grouped as

Table 4. Structures of alkyl substituted PAH compounds studied in this work.				
	Substrates	Structure		
1	1-decylnaphthalene	Grathar		
2	1-octadecylnaphthalene			
3	2-nonylphenanthrene			
4	9-octadecylphenanthrene			
5	1-butylpyrene			
6	1-decylpyrene			
7	1-octadecylpyrene	C ₁₈ H ₃₇		

Figure 8. ¹H NMR spectra of 1-decylnaphthalene before and after RICO reaction showing regions integrated as part of the NMR methodology for determining selectivity.

In Equation (2) r_x denotes the ratio of areas of region A to the area of region D for the x^{th} hour sample. For 1-decyInaphthalene oxidation it was found that 60% of the products still had the aliphatic chain attached to the ring system. This demonstrates that, through careful control of the amount of oxidant present in the reaction and the reaction temperature, the aromatic part of the molecule can be oxidized while maintaining the attached alkyl group intact (Table 3, entry 1). This is

Table select	Table 3. Effect of chain length and ring size on the RICO activity and selectivity for alkyl substituted polyaromatics. $^{\rm [a]}$							
	Substrate	Reaction time [h]	Conver- sion [%]	Preserved alky [%]				
1	1-decylnaphthalene	4.5	42	60				
2	1-decylnaphthalene	6	46	59				
3 ^[b]	1-decylnaphthalene	10	99	4				
4	1-octadecylnaphthalene	4.5	76	87				
5	2-nonylphenanthrene	4.5	73	69				
6	9-octadecylphenanthrene	4.5	62	46				
7	1-butylpyrene	4.5	80	68				
8	1-decylpyrene	4.5	90	86				
9	9 1-octadecylpyrene 4.5 81 83							
[a] Reaction Conditions: 295 K, 1000 rpm stirring speed, substrate 0.0276 mmol, $NalO_4$ 0.2065 mmol, $RuCl_3 \cdot xH_2O$ 2 µmol. [b] After reaction time 10 h, addition of extra 0.0276 mmol $NalO_4$ and 0.2065 mmol $RuCl_3 \cdot xH_2O$ after 6 h.								

in sharp contrast to the usual situation with RICO chemistry in which an excess of oxidant oxidizes aromatic groups completely, leaving the aliphatic chain as a carboxylic acid.^[19] Using 1decylnaphthalene as a model compound the catalytic activity was investigated for longer reaction times (entries 2 and 3, Table 3). Increasing the reaction time from 4.5 to 6 h did not

Chem. Eur. J. 2015, 21, 4285 – 4293



before; 8.50-7.50 ppm (aromatic protons), 3.40-3.20 ppm (α -Hs, CH₂) of the aliphatic chain, 2.25–2.00 ppm (β -CH₂) of the aliphatic chain, 1.91–1.90 ppm (CH₂ of the remaining chain) and 1.40–1.20 pm (terminal CH₃ group). Using the methodology discussed above, the percentage of compounds present for which the alkyl chain remains attached to a polyaromatic system after 4.5 h reaction time is summarized for each substrate in Table 3. Results for 1-decylnaphthalene after 6 h and after a 10 h experiment, in which catalyst and oxidant were recharged after 6 h, are also presented. It is evident that the amount of products with intact alkyl chain after 4.5 h of RICO, ranges from 46% for 9-octadecylphenanthrene to 87% for 1-octadecylnaphthalene. This clearly suggests that the reactivity of the alkyl chain in the RICO of alkyl aromatics is substrate dependent. We have also found that control of selectivity in RICO is possible beyond that usually seen under more forcing conditions for which, irrespective of the substrate, all of the aromatic ring system is oxidized, leaving the aliphatic chains as carboxylic acids.^[20] In our experiments this only occurs after the longer 10 h reaction times and with catalyst and oxidant refreshed after 6 h (Table 3, entry 3).

The data in Table 3 also begins to give some insight into this selective oxidation chemistry. Comparison of results from 1decylnaphthalene and 1-octadecylnaphthalene shows that the longer alkyl chain is preserved to a greater extent after oxid ation (Table 3, entries 1 and 4). This observation is further substantiated by the results of the RICO of 1-butylpyrene and 1-octadecylpyrene (Table 3, entries 7 and 9). In this case, the conversion of both molecules was practically identical, but the longer alkyl chain showed a lower susceptibility to oxidation. It is also interesting to compare the catalytic activity for a range of polyaromatic compounds that have similar lengths of aliphatic chain attached to different sizes of polyaromatic ring systems. This comparison can be made by considering the data for 1-decylnaphthalene, 2-nonylphenanthrene and 1-decylpyrene. Both the conversion and percentage of the preserved alkyl chain increase with increasing molecular weight of the ring system. Therefore, it appears that increasing the size of the ring system decreases the reactivity at the α -position for RICO.

However, we have found that the selectivity for oxidation of the alkyl group is highly dependent on the chain length, substitution position on the polyaromatic ring system and the number of fused aromatic rings. When the product distribution following the oxidation of 1-decylnaphthalene was analyzed in further detail most of the products have preserved alkyl chains. Based on the molecular formula information, obtained by GC-MS analysis, a list of possible oxidation products was proposed (Table 5). Here, two molecules are of special interest (entries 3 and 6), as they show oxidized carbon in the α -position without loss of the alkyl substituent from the aromatic ring system. This preservation of the substituent was confirmed by the ¹H NMR methodology. In the aqueous layer, decanoic acid and phthalic acid were also detected. It is believed that these products are obtained after C-C bond cleavage between the aromatic ring carbon and the α -carbon of the alkyl chain. However, the concentration of these products

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nap	hthalene.		
	Molecular formula	Mass detected (EI)	Possible structure
1	$C_{18}H_{24}O_{3}$	288	0 0 0
2	$C_{18}H_{26}O_2$	274	
3	$C_{19}H_{26}O_2$	286	
4	$C_{19}H_{26}O_3$	304	$\begin{array}{c} O & C_{10}H_{21} \\ O & C_{10}H_{27} \\ O & COOH \end{array}$

Table 5. Products observed by GC-MS following the oxidation of 1-decyl-

was small in comparison to other products found in the organic laver.

The position of substitution of the alkyl chain on the ring system also exerts an influence on reactivity and product selectivity. This influence has been probed by oxidation of 9-octadecylphenanthrene for comparison with results from 2nonylphenanthrene. The alkyl chain in the case of 9-octadecylphenanthrene is attached to the position that is most likely to be attacked by RuO₄, according to the idea of a preference for the double bond which leads to the minimum loss of aromaticity on oxidation.^[12b,21] The percentage of preserved α -H for the 9-substituted phenanthrene is considerably lower than that for the substituent at the 2-position (Table 3, entries 5 and 6). Indeed, it appears from the conversion data that for 9-octadecylphenanthrene the p_a number can be accounted for purely on the basis of unreacted substrate. Nevertheless, it has been found that the product from the oxidation of this substrate still contains preserved alkyl chain oxidized in the α -position as shown by MS analysis (Table 6).

Using an electron ionization MS method molecular ion peaks at m/z 462 and 444 were detected and assigned to structures of compounds having oxidized but preserved alkyl chains. Moreover, a strong peak from unreacted substrate was also detected. Using electrospray ionization, positive peaks at m/z 463 and 445 were determined, which can be assigned to structures in entries 2 and 4 in Table 6, respectively. 9-Bromophenanthrene was found even in the starting material and it is probably a substrate from the 9-octadecylphenanthrene synthesis. These data suggest that there are only two products obtained in this reaction. Using the developed NMR methodology it was only possible to quantify unreacted substrate, because the signals from products corresponding to the α -H are not present for these α -carbon oxidized products. In addition β -H atoms that become α -H atoms after oxidation are significantly shifted in the NMR spectra due to the presence of the C=O group and are outside the integration region.

Chem.	Eur.	J.	2015.	21.	4285 -	4293



Table 6. Possible products of 9-octadecylphenanthrene oxidation and contamination.					
	Molecular formula	Mass detected (EI)	Possible structure		
1	$C_{14}H_9Br$	256	Br		
2	$C_{32}H_{44}O_2$	462	C ₁₈ H ₃₅		
3	$C_{32}H_{46}$	430	C18H37		
4	$C_{32}H_{44}O$	444	С ₁₇ Н ₃₅		

From the above results it is clear that the amount of alkyl chain that is preserved under RICO depends on the ring size, the length and the location of the attached aliphatic chain. This is an important result from this work, because in the characterization of coal and asphaltenes, it has always been assumed that all of the aromatic components are consumed with alkyl chains ending up as aliphatic acids. This assumption may be true for long alkyl chains in an excess of oxidant, but not necessarily so for shorter alkyl chains, as has been presented in the case of 2-ethylnaphthalene oxidation. Mechanistic investigations are in progress to find the rationale behind this trend.

Conclusion

Historically, it has always been assumed that the aromatic regions of alkylated polyaromatic compounds are oxidized mainly to CO₂ and H₂O by RICO chemistry and the aliphatic chain remains as the corresponding carboxylic acid. Based on the data reported in this paper this assumption does not always hold, and RICO chemistry may be used in a more selective manner to oxidize the aromatic regions of these molecules leaving the alkyl substituents unmodified and still attached to the ring system. A quantitative NMR protocol has been developed to determine the relative amount of aliphatic and aromatic protons resulting from the RICO of alkyl-substituted polyaromatic compounds, which may also find applications with other oxidation approaches to substituted aromatic systems. The reaction products under the relatively mild conditions employed here are highly dependent on the aliphatic chain length, substituent position and size of the polyaromatic ring system which also affect the degree of conversion.

Here we have shown that RICO chemistry can be used in a selective way to reduce the aromaticity of alkylated

polynuclear aromatics while preserving aliphatic chain substituents. These findings may also lead to the improvement in the processing of heavy fractions of oil to preserve carbon number while increasing process ability.

Experimental Section

Materials and equipment

All the chemicals used were of high purity, purchased from commercial sources or supplied by ExxonMobil and were used without further purification. Commercial materials were acetonitrile (99.95% Fisher Scientific), dichloromethane (99.5% Fisher Scientific), deuterated chlorobenzene (99.8%D), deuterated acetonitrile (98%D, Goss), H₂O (HPLC grade Sigma-Aldrich), NalO₄ (>99% Sigma-Aldrich), RuCl₃·xH₂O (98% Aldrich), 2-ethylnaphthalene (99%, Sigma-Aldrich). 1-Octadecylnaphthalene, 1-decylnaphthalene, 2-nonylphenanthrene, 9-octadecylphenanthrene, 1-octadecylpyrene, 1-butylpyrene and 1-decylpyrene were of >95% purity and were supplied by ExxonMobil.

Catalytic oxidation reactions were performed at atmospheric pressure in a 50 mL glass round-bottomed flask with a jacket connected to a thermostat (Julabo F25-ME Refrigerated/Heating Circulator) fitted with a water pump to maintain the desired temperature of 295 K. The reaction mixture was stirred using a magnetic bar (500 rpm). For reactions performed on a smaller scale, a 5 mL round bottom flask maintained at 295 K was used with the same stirring speed.

Product identification was carried out by GC-MS analysis with reference to the standard library of compounds supplied with the instrument.

Ruthenium-ion-catalyzed oxidation in monophasic and biphasic solvent systems

Reactions using a monophasic solvent system employed a glass reactor that was charged with 2-ethylnaphthalene (25.6 mg, 0.164 mmol) dissolved in acetonitrile (20 mL). An aqueous solution of NalO₄ (300 mg, 1.403 mmol in 10 mL H₂O) and solid RuCl₃·xH₂O (2.5 mg, 0.012 mmol) were added to this solution, and this was considered as the starting point of the reaction. For GC-MS analysis, reactions were quenched by adding aqueous Na₂SO₃ (0.1 mL, 0.176 g, 1.403 mmol in 6 mL H₂O) to a 0.5 mL sample of the reaction liquor.

For reactions in a biphasic solvent system, dichloromethane (16 mL) acetonitrile (5 mL) and water (5 mL) were used.^[6a] The ratio of substrate/oxidant/catalyst was the same as in the monophasic solvent system (0.164:1.403:0.012). For GC-MS analysis, samples were withdrawn and analyzed from both immiscible layers. For NMR analysis, all products were extracted using DMSO after previous evaporation of solvents.

Gas chromatography/mass spectrometry analysis

For qualitative analysis, GC-MS was used. Analyses were performed using a Waters GCT Premier instrument fitted with an Agilent HP-5 MS column (0.25 mm×0.25 μ m×30 m) with helium as the carrier gas (1 mL min⁻¹) and a temperature program from 303 K to 563 K. Mass spectra of the unknown compounds were compared against the NIST mass spectral database. Standards of the compounds identified were then injected into the GC-MS so that comparison of their retention time with those of the components in the reaction mixture could be used to confirm assignments. Reaction mix-



tures were also analyzed quantitatively using a Varian gas chromatography, system fitted with a VF-5HT column (0.25 mm \times 30 m) and a flame ionization detector (FID). Helium was used as the carrier gas. The GC oven temperature was increased from 343 to 683 K at a heating rate of 20 Kmin⁻¹.

In situ NMR studies on the oxidation of 2-ethylnapthalene

All ¹H NMR spectra were acquired on a Bruker 500 MHz DPX system equipped with a 5 mm autotune broad band probe. Water suppressed NMR spectra were acquired over 32 scans using the Bruker pulse sequence *zgpr*. A power level of 53.5 db was employed for water pre-saturation, in conjunction with a relaxation delay of 5 s and an acquisition time of 1.638 s.

An aqueous solution of NalO₄ (90 mg, 0.421 mmol in 3 mL H₂O) was added to a solution of 2-ethylnaphthalene (15.8 mg, 0.101 mmol) in CD₃CN (2 mL), and the mixture stirred for 1 min. 0.7 mL of this reaction mixture was transferred to an NMR tube fitted with a calibrated glass insert containing a TMS standard. After recording the ¹H NMR spectra of the solution (0 h sample), RuCl₃·xH₂O (20 μ L, 0.105 mg, 0.5 μ mol) was added to the NMR tube and ¹H NMR spectra were recorded every 15 min over an 8 h period.

Small-scale ruthenium-ion-catalyzed oxidation in a biphasic solvent system for NMR analysis

An aqueous solution of NalO₄ (44 mg, 0.206 mmol in 1 mL H₂O) was added to a solution of substrate (0.028 mmol in 2 mL CDCl₃ and 1 mL CD₃CN) were placed in a round-bottomed flask, and the mixture was stirred for 1 min. A 0.6 mL portion of the organic layer was transferred to an NMR tube containing a calibrated glass insert and 0.3 mL of CD₃CN. The content of the tube was subsequently analyzed using ¹H NMR spectroscopy and the spectra labelled as reaction time 0 h. An aqueous solution of RuCl₃·xH₂O (20 μ L, 2 μ mol) was then added to the round-bottomed flask and stirring was commenced. After the requisite time, a 0.6 mL portion of the organic layer was transferred to an NMR tube containing a calibrated TMS glass insert, 0.3 mL of CD₃CN was added and the ¹H NMR spectra recorded. For conversion data, the sample (0.2 mL) was mixed with a 20 μ L aliquot of 2-butanol and injected into the GC immediately after NMR analysis.

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