SHORT PAPER

J. Chem. Research (S),
2000, 522–523

Highly efficient Nafion–Ce(IV) or Nafion–Cr(III)-catalysed oxidation of polycondensed aromatic hydrocarbons with co-oxidant[†]

Takehiko Yamato* Naoki Shinoda and Tomomi Kanakogi

Department of Applied Chemistry, Faculty of Science and Engineering, Saga University,
Honjo-machi 1, Saga-shi, Saga 840-8502, Japan

A Ce(IV) or Cr(III) impregnated Nafion-K catalyst was found to be effective in promoting the dehydrogenative oxidation of polycondensed aromatic hydrocarbon with NaBrO3 as a co-oxidant.

Polycyclic aromatic hydrocarbons can be oxidised to quinones by a number of reagents, however, the operation is frequently tedious and reaction conditions are generally quite critical. Quinones have been prepared in moderate yields from chromic acid oxidation of polycyclic aromatic hydrocarbons, e.g., 1,4-naphthoquinone (18–22% yield)[1] and 9,10-phenanthrenequinone (44–48% yield).[2,3] The reaction requires either prolonged periods of standing or elevated temperatures for its completion. On the other hand, the formation of gummy precipitate and troublesome workup are serious problems arising from using chromium(VI) reagents for the oxidation of alcohols. In order to overcome these difficulties, polymer reagents such as poly(vinylpyridinium chlorochromate)[4] or poly(vinylpyridinium dichromate)[5] have been introduced. Although the purification of the final product is easy, the exchange capacity of the polymer oxidants is usually low. Furthermore, recycling of reagents requires troublesome steps of workup.

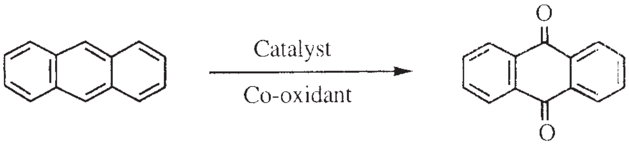
An amazing oxidising power of ceric ammonium nitrate [$(NH_4)_2Ce(NO_3)_6$; CAN] has been demonstrated by a series of oxidation reactions of organic compounds. For example, polynuclear aromatic hydrocarbons are also oxidized to quinones.[6]

On the other hand, Nozaki et al reported that *tert*-butylhydroperoxide oxidizes alcohols into the corresponding carbonyl compounds (71–98%) effectively under a Cr(III) or Ce(IV) impregnated Nafion-K catalyst, which is reusable after simple washing.[7] Recently, we have found that a Nafion-H catalyst, a perfluorinated sulfonic acid resin,[8] is effective in a wide range of liquid and gas phase reactions, including electrophilic substitutions on aromatic nuclei, transalkylations, condensations and so on.[9]

Now we report an efficient and convenient procedure for oxidation of polycondensed aromatic hydrocarbons to quinones with a Cr(III) or Ce(IV) impregnated Nafion-K catalyst using various co-oxidants, which are able to proceed quite readily, giving good to moderate yields.

Results and Discussion

Oxidation of anthracene with a Ce(IV) or Cr(III) impregnated Nafion-K catalyst was carried out in the presence of various co-oxidants. The results are compiled in Table 1. The attempted oxidation of anthracene **1** with a Ce(IV) impregnated Nafion-K catalyst using $NaBrO_3$ as a co-oxidant under MeCN refluxing for 6h gave the oxidation product, anthraquinone **2** in 14% yield, with recovery of the starting compound. Prolonging the reaction time for 24h increased the yield of **2** from 14% to 63%. Similar low yields of anthraquinone **2** were obtained by the oxidation of **1** with 30% H_2O_2/MeCN-H_2O, *tert*-BuOOH/ C_6H_6 or *m*-CPBA/ CH_2Cl_2 in spite of using a large excess of co-oxidant. These results suggested that these systems dramatically reduce the catalytic activity of the Nafion–Ce(IV) reagent and regeneration of the Nafion–Ce(IV) by oxidation with co-oxidants in the reaction system did not work well. In contrast, higher yields were obtained in the oxidation of anthracene **1** with Nafion-Cr(III) in the presence of various co-oxidants, in particular oxidation of **1** with *tert*-BuOOH as a co-oxidant in refluxing benzene furnished complete oxidation within 6h to afford anthraquinone **2** in quantitative yield. These findings strongly suggest that the Nafion–Cr(III) oxidation system is much stronger than the Nafion–Ce(IV) system. Consequently, although the yields of oxidation products are low, oxidation of anthracene with Ce(IV) or Cr(III) impregnated Nafion–K catalysts was found to be effective in promoting the dehydrogenative oxidation of polycondensed aromatic hydrocarbons with $NaBrO_3$ as a co-oxidant.



1 **2**

Table 1 Oxidation of anthracene with Nafion–Ce(IV) and Nafion–Cr(III) / Co-oxidant[a]

Run	Catalyst	Co-oxidant	Solvent	Yield of quinone[b]/%
1	Nafion–Ce(IV)	$NaBrO_3$	MeCN/H_2O	14
2	Nafion–Ce(IV)	30%-H_2O_2	MeCN/H_2O	0
3	Nafion–Ce(IV)	*t*-BuOOH	C_6H_6	15
4	Nafion–Ce(IV)	*m*-CPBA	CH_2Cl_2	18
5	Nafion–Cr(III)	$NaBrO_3$	MeCN/H_2O	20
6	Nafion–Cr(III)	30%-H_2O_2	MeCN/H_2O	20
7	Nafion–Cr(III)	*t*-BuOOH	C_6H_6	100
8	Nafion–Cr(III)	*m*-CPBABI	CH_2Cl_2	63

[a]Reaction conditions: [Oxidant]/[Anthracene]= 4:1; Nafion-Ce(IV), Cr(III): 10 wt %; Reaction temp.: reflux; Reaction time: 6h; [b]Yields were determined by GLC analysis.

When the recovered Nafion-Ce(IV) was used under the same reaction conditions, no oxidation products were obtained. This result indicates that the catalytic system which reduced Ce(III) could not regenerate Ce(IV) by $NaBrO_3$ in the system. A remarkable deactivation of catalyst was observed because regeneration of catalyst could not be achieved to the original catalytic activity. On the other hand, in the acidic media, $NaBrO_3$ smoothly oxidised the Ce(III) to Ce(IV). Similarly, in

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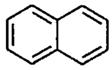
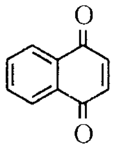
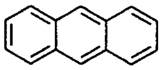
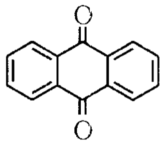
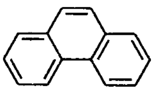
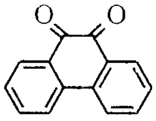
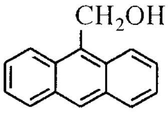
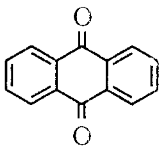
* To receive any correspondence. E-mail: yamatot@cc.saga-u.ac.jp

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 2 Oxidation of arenes with Nafion-Ce(IV)/$NaBrO_3$[a]

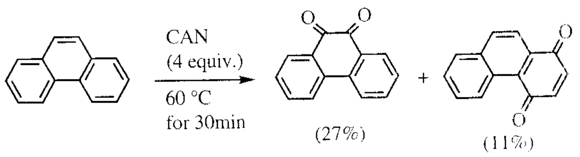
Substrate	Product	Yield[b]/%
		25
		95
		75
		95

[a]Nafion–Ce(IV), 10wt%; [$NaBrO_3$]/Substrate]=4:1; Solvent, MeCN: 1N HNO_3=7:3 v/v; Reflux for 1h. [b]Isolated yields were shown.

the acidic media the Nafion-Ce(IV) reagent could be regenerated in the present oxidation system. In fact, when the oxidation of anthracene **1** with Nafion-Ce(IV) in the presence of $NaBrO_3$ under 1 N nitric acid was carried out in refluxing $MeCN/H_2O$, the yield of the desired anthraquinone **2** increased from 14% to 95%. In the case of Nafion–Cr(III) reflux, it takes only 1h to complete the reaction to afford anthraquinone **2** in quantitative yield. Nafion–Ce(IV) or Nafion-Cr(III) were recovered simply by filtering the hot reaction mixture to give ready regeneration of the catalyst without the loss of catalytic activity. The reaction was very clean. The amount of catalyst required, as a function of the amount of anthracene **1**, was between 5 and 10 wt%. Optimum yields of anthraquinone **2** were obtained with 10 wt% of catalyst. The use of 5 wt% of catalyst gave lower yields. It was also found that the addition of 10 wt % of Nafion–H to the dual oxidation system, e.g. Nafion–Ce(IV)–$NaBrO_3$ or Nafion–Cr(III)–$NaBrO_3$ instead of nitric acid also increased the yield of anthraquinone **2** and shortened the reaction time.

The presently-developed oxidation systems were further applied to other polycondensed aromatic hydrocarbons such as naphthalene and phenanthrene to afford 1,4-naphthoquinone and 9,10-phenanthrenequinone. As shown in Table 2, the present method provides good yields, easy isolation of the products, and no concomitant isomeric quinones such as 1,4-phenanthrenequinone was observed under the reaction conditions different from the direct oxidation of phenanthrene with excess of CAN.[6a] However, oxidation of 9-hydroxymethylanthracene to afford 9-formylanthracene failed. Only 9,10-anthraquinone was obtained in 95% yield.

The Cr(III) or Ce(IV) impregnated Nafion-K catalyst oxidation method succeeded in overcoming the formation of gummy precipitate and troublesome workup which are serious problems arising from using chromium(VI) reagents for stoichiometric reagents for oxidation of polycondensed aromatic hydrocarbons. Furthermore, the present oxidation method provides excellent yields, easy isolation of products, and ready regeneration of the catalyst without the loss of catalytic activity because the essential oxidaton reagent is $NaBrO_3$ as a co-oxidant.



(1)

Experimental

^1H NMR spectra were recorded at 270 MHz on a Nippon Denshi JEOL FT-270 NMR spectrometer in deuteriochloroform with Me_4Si as an internal reference. IR spectra were measured as KBr pellets on a Nippon Denshi JIR-AQ2OM spectrometer. Mass spectra were obtained on a Nippon Denshi JMS-01SA-2 spectrometer at 75 eV using a direct-inlet system. GLC analysis were carried out by Shimadzu gas chromatograph, GC-14A (conditions: Silicone OV–1, 2 m; programmed temperature rise, 12°C/min; carrier gas nitrogen, 25 cm^3/min.).

Materials: The Nafion-H catalyst was prepared from commercially available (Du Pont) Nafion–K resin, as previous described.[8,9] Preparation of Nafion–Ce(IV) or Nafion–Cr(III) was carried out following the reported procedures.[7] Nafion-Ce(IV) was prepared as follows. Nafion–K (1.1 g) was stirred with a solution of $(NH_4)_2Ce(NO_3)_6$ (1.75 g) in deionized water (30 cm^3) for 36 h at 25°C. The catalyst was filtered, washed with water (10 $cm^3 \times 5$) and dried to constant weight.

General procedure for Nafion-Ce(IV)- or Nafion-Cr(III)-catalyzed oxidation of poly- condensed aromatic hydrocarbons with co-oxidant. Typical procedure. – A mixture of anthracene **1** (178 mg, 1 mmol) and 20 mg (10 wt %) of Nafion-Ce(IV), and $NaBrO_3$ (604 mg, 4 mmol) in a mixture of acetonitrile and 1 N nitric acid (7:3 v/v) (10 cm^3) was refluxed until completion of the reaction as monitored by GLC analysis. The solid resin was filtered off and the filtrate was extracted with CH_2Cl_2 (10 $cm^3 \times 2$), washed with water (5 $cm^3 \times 2$), dried (Na_2SO_4) and condensed under reduced pressure to give anthraquinone **2** (198 mg, 95%) as a colourless solid.

Received 10 August 2000; accepted 5 November 2000
Paper 00/453

References

1 E.A. Braude and J. S. Fawcett, *Org. Synth., Coll.*, 1963, **4**, 698.
2 R. Wendland and J. Lalonde *Org. Synth., Coll.*, 1963, **4**, 757.
3 J. Muzart, *Chem. Rev.*, 1992, **92**, 113.
4 J.M.J. Fréchet, J. Warnock, and M J. Farrall, *J. Org. Chem.*, 1978, **43**, 2613.
5 (a) J.M.J. Fréchet, P. Darling, and M.J. Farrall, *J. Org. Chem.*, 1981, **46**, 1728; (b) G. Cardillo, M. Orend, and S. Sandri, J. Am. Chem. Soc., 1976, **98**, 6737.
6 (a) L. Ho, T.W. Hall, and C. M. Wong, *Synthesis*, **1973**, 206; (b) L. Ho, *Synthesis*, **1973**, 347.
7 S. Kanemoto, H. Saimoto, K. Oshima, and H. Nozaki, *Tetrahedron Lett.*, 1984, **25**, 3317.
8 G.A. Olah, P.S. Iyer, and G.K.S. Prakash, *Synthesis*, 1986, 513.
9 T. Yamato, *J. Synth. Org. Chem. Jpn.*, 1995, **53**, 487 and references therein.