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Alkali metal cation exchanged Nafion as an efficient micro-environment for oxidation of olefins by singlet oxygen

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This paper is dedicated to Prof. V. Ramamurthy on the occasion of his 62nd birthday.

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ABSTRACT

The utility of alkali metal cation exchanged Nafion beads as an efficient micro-environment for carrying out oxidation of olefins by singlet oxygen was examined with three structurally different olefins, namely, 1,2-dimethylcyclohexene (**1**), 2-methyl-2-heptene (**4**) and 2-methyl-4-phenyl-2-butene (**7**). In this report, a strategy was proposed in which the reactant and the photocatalyst are kept isolated in two different phases throughout the photoreaction and thereby enables easier separation of the products from the reaction mixture. I envisage that this approach can be synthetically useful due to the high mass balance of the photoreaction, reuse of the photocatalyst and easy handling of the reaction media. The investigated photochemical reactions also serve as probes to understand the nature of the reaction domains provided by Nafion matrix.

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1. Introduction

Hydroperoxidation of olefins is one of the most important types of reaction from the view of its synthetic applications [1–4]. Among various strategies, dye-sensitized photooxidation of alkenes involving transient singlet oxygen has been proven to be the most efficient method [5,6]. In the sensitization process, the dye molecule (while relaxing from its triplet excited state back to the ground state) transfers its energy to triplet oxygen and excites it to the singlet state. Singlet oxygen is the excited form that oxidizes electron-rich alkenes. In spite of being an economically and environmentally advantageous process, industrial scale preparation by this approach is still limited. This is due mainly to the high lability of the peroxide products [7] which complicates their separation from the photosensitizer. To overcome these complexities, the possibility of utilizing alkali ion exchanged Nafion beads as a useful micro-environment was investigated in which hydroperoxidation of olefins can be carried out using thiazine dyes as sensitizers.

Nafion is a block copolymer of tetrafluoroethylene and perfluoro-3,6-dioxo-4-methyl-7-octene containing sulfonic acid groups. When swollen in water or methanol, the solvated sulfonic

acid head groups are clustered together in solvent containing pockets of 5 nm in diameter, which are interconnected through short channels (1 nm in diameter) within the fluorocarbon matrix (Fig. 1) [8,9]. Small angle X-ray scattering and neutron scattering experiments indicate the presence of ionic clusters [10]. However details on the arrangement within these clusters have not been fully delineated. Several models have been proposed since the early 1970s to describe the manner in which the ionic groups aggregate within the polymer matrix [11]. Among them, the Mauritz–Hopfinger model, the Yeager three phase model, Eisenberg model of hydrocarbon ionomers and the Gierke network model are well known [10,12–14]. It has been established that solvent-swollen Nafion can incorporate high concentrations of aromatic hydrocarbons [15,16]. Recently we [17] have successfully demonstrated the utility of Nafion as a reaction environment for photochemical reactions. Encouraged by our previous results [17], an investigation was carried out probing whether the swelling property of Nafion could be explored to provide an efficient reaction domain for the photooxidation of olefins.

2. Results and discussion

Nafion in the H⁺ form is known to be “superacid” with a local proton concentration of ca. 1.5 M [18]. It is well known that 3°-allylic-hydroperoxide in presence of acid undergoes Hock cleavage

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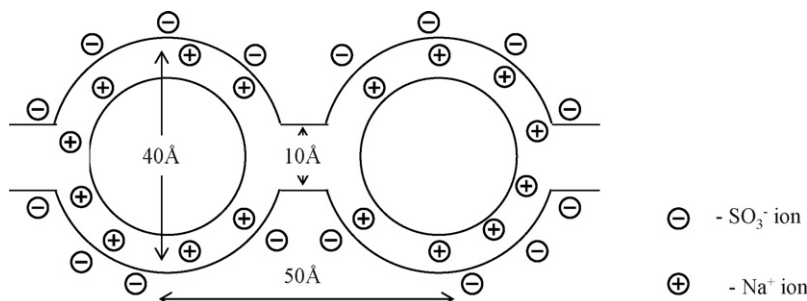
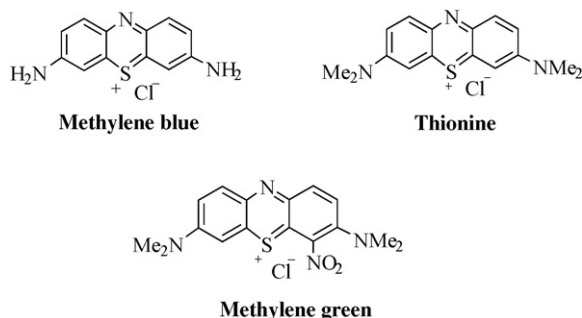


Fig. 1. Three phase cluster network model of Nafion reported in the literature [10].

to the corresponding ketones [7]. To avoid such complexities arising from the protons of Nafion, Nafion beads exchanged with Na^+ ions have been used in the present study. The protons of Nafion can be easily exchanged for Na^+ ions following the procedure as described in Section 4.

Recently, Nafion membrane modified with transition metal complexes has been reported as a versatile heterogeneous sensitizer for the photooxidation of olefins [19]. In this study, thiazine dyes were used as the sensitizer. Thiazine dyes aggregate [20] when incorporated into Nafion owing to high water of hydration of the medium [15,16]. Due to this complexity, thiazine dyes incorporated Nafion is less effective in generating singlet oxygen [20]. Hence an alternate strategy was used, in which, the alkenes were incorporated within Nafion and the sensitizer was kept outside in methylene chloride solution. Since methylene chloride cannot swell Nafion beads [10,12–14], the sensitizer cannot diffuse into Nafion interior. The choice of thiazine dyes as photosensitizers has been influenced by the following factors: (a) they absorb light in the visible region and photochemically generate $^1\text{O}_2$ with high quantum yield [21], (b) they are commercially available and cheap enough to be applied for industrial scale preparation, (c) sensitizer could be reused. Three different thiazine dyes (Scheme 1), namely, thionine, methylene blue and methylene green were examined for their applicability as reusable sensitizer.

In the present strategy, the olefin-loaded Nafion beads (~ 0.3 mm diameter each) were taken in dichloromethane solution of the sen-



Scheme 1. Structures of thiazine dyes used in our study.

sitizing dye and irradiated. Na^+ Nafion beads does not absorb in UV–vis region above >250 nm. Therefore direct irradiation of alkene was avoided by irradiating at wavelength >420 nm using a corning filter CS# 3-73. The dye gets excited, transfers energy to ground state triplet oxygen to produce singlet oxygen. The generated singlet oxygen is expected to diffuse readily into Nafion beads that has high permeability to molecular oxygen (6.4×10^{-12} cm mol s^{-1}) [22] and react with olefin molecules that are present inside. It has been previously established that the lifetime of singlet oxygen within air dried Nafion (contains 2–2.6 water molecules per sulfonate group) is ~ 150 μs [18]. As mentioned in Section 4, the Na^+

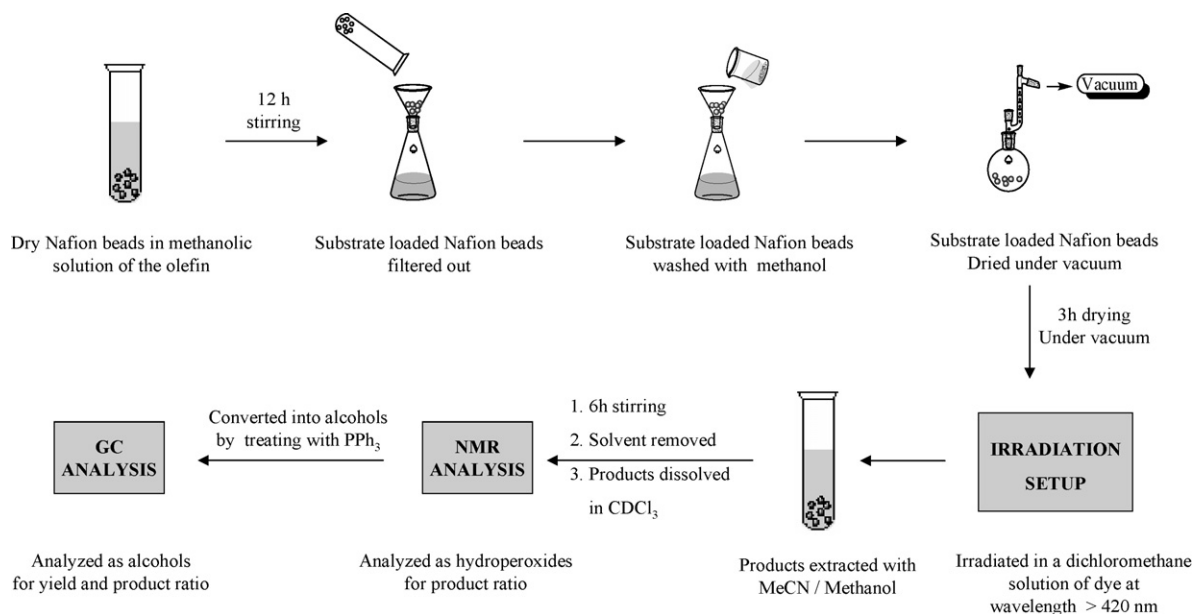


Fig. 2. Schematic representation of experimental protocol for singlet oxygen-mediated hydroperoxidation of olefins within Na^+ Nafion.

Nafion beads that were used in all the experiments contains 2% of water by weight (corresponds to 1.32 water molecules per sulfonate group), which is comparable to air dried Nafion [23]. Hence the lifetime of singlet oxygen within Na⁺ Nafion that were used in this study is expected to be ~150 μs or slightly greater than 150 μs. The diffusion co-efficient (D) of oxygen migration within Nafion is ca. $4.67 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and is independent of water content [22]. Using the Einstein equation ($\langle x^2 \rangle = 6Dt$; where x^2 is the mean square molecular displacement) [24], one can calculate that ¹O₂ can migrate approximately 200 nm within its lifetime. This implies that the diffused singlet oxygen can sample many more than 90 Nafion ionic clusters (the diameter of each ionic cluster at the experimental condition described in this study is calculated to be 2.8 nm [25]) surrounding the locus of its diffusion point. Thus the proposed strategy is expected to be an effective pathway for oxidation of olefin by singlet oxygen. Also in the proposed strategy, the sensitizer and the olefin are isolated from each other throughout the reaction and thereby separation of the sensitizer from the reaction mixture becomes much easier.

The effectiveness of this strategy was investigated with three olefins, namely, 1,2-dimethylcyclohexene (**1**), 2-methyl-2-heptene (**4**) and 2-methyl-4-phenyl-2-butene (**7**). The goals of this study are: (a) to design an efficient system for photooxidation of olefins, (b) to examine whether there is any cation-π interaction within Nafion similar to zeolite [26–38], which can template the encapsulated olefins to yield selective products. The choice of olefins were influenced by the following factors: (a) the photooxidation chemistry of these olefins has been previously established [39–45]. (b) They are structurally very different and thereby provide an opportunity to examine different modes of cation-olefin interactions within Nafion that may result in regioselectivity.

Olefin-loaded Na⁺ Nafion beads were prepared and irradiated following the procedure described in Section 4. Schematic representation of the experimental protocol and the irradiation set up used in the present study are presented in Figs. 2 and 3, respectively. Previously established photophysical studies within alkali ion exchanged Nafion using probes such as pyrene, xanthone and benzophenone within suggest that the encapsulated olefins are most likely located either within the ionic cluster or at the interfacial region between fluorocarbon backbone and ionic clusters of Nafion framework [8,9,46,47]. Previous experiments on the inclusion of probe molecules of similar kind within Nafion reported by Ramamurthy et al. [17] and me [48] also indicate that the incorporated olefins are located in the interface region closer to the ionic clusters of Nafion framework. By using the parameters reported in the literature [25], the average occupancy number of olefins per ionic cluster was calculated and presented in Table 1.

Hydroperoxidation of 1,2-dimethyl cyclohexene (**1**) was investigated first [39,40]. Reaction of **1** with singlet oxygen yielded endocyclic (**2**) and exocyclic (**3**) hydroperoxides resulting from the abstraction of H_a and H_b, respectively, as shown in Scheme 2.

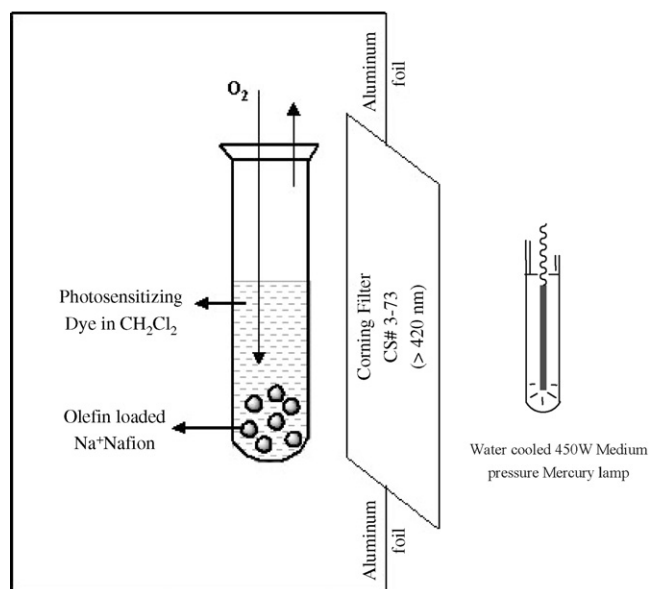


Fig. 3. Schematic representation of irradiation set up used in this study.

Table 1
Loading level of **1**, **4** and **7** in Na⁺ Nafion and average occupancy numbers

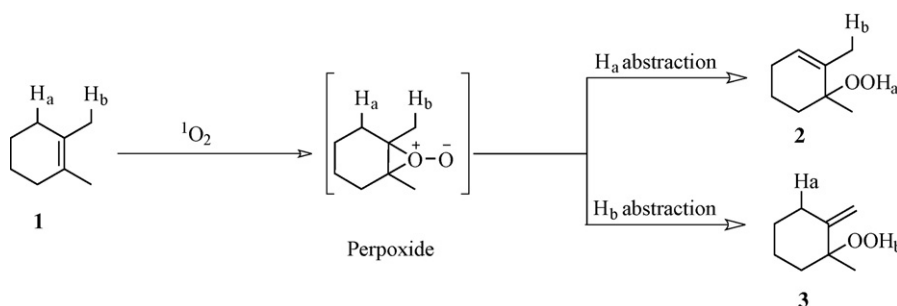
Olefins ^a	Loading level of the olefin ^b (mg/300 mg of Na ⁺ Nafion)	Occupancy number = $N_{\text{olefin}}/N_{\text{ionic clusters}}^c$
1	2.0 ± 0.2	2.3 ± 0.2
4	2.0 ± 0.1	2.3 ± 0.1
7	2.2 ± 0.1	1.9 ± 0.2

^a For structures see Schemes 2–4.

^b Loading levels were calculated by GC analysis using undecane as the internal standard. The values reported here are the mean of five independent trials ± standard deviation.

^c N_{olefin} = No. of moles of olefin loaded. $N_{\text{ionic clusters}}$ = No. of moles of ionic cluster in 300 mg of Na⁺ Nafion at 2 wt% of hydration = 7.8×10^{-5} . $N_{\text{ionic clusters}}$ at our experimental condition is calculated from parameter reported in the literature [25].

The mechanism of hydroperoxidation of olefins by singlet oxygen through peroxide intermediate (Scheme 2) has been previously established [48–50]. An alternative mechanism involving exciplex intermediate (between the singlet oxygen and the olefin) was also widely discussed in the literature [51,52]. Photooxidation of **1** was carried out both in dichloromethane and within Na⁺ Nafion. After irradiation, the products and unreacted starting material were extracted from Nafion beads by stirring them in methanol followed by GC analysis (SE-30 column). First, the peroxides thus formed were analyzed as such using ¹H NMR to calculate the product distribution of peroxides. The peroxides were then converted into corresponding allylic alcohols by reacting with excess



Scheme 2. Photooxidation of 1,2-dimethyl cyclohexene (**1**).

Table 2
Product distribution upon photooxidation of olefins **1**, **4** and **7**^a

Olefins	Medium ^{b,c}	Sensitizer	Product ratio ^d (\pm S.D.)
1	CH ₂ Cl ₂	Thionine	2:3 89:11 \pm 3
	Na ⁺ Nafion	Thionine	82:18 \pm 3
	Na ⁺ Nafion	Methylene blue	80:20 \pm 4
	Na ⁺ Nafion	Methylene green	78:22 \pm 4
4	CH ₂ Cl ₂	Thionine	5:6 52:48 \pm 3
	Na ⁺ Nafion	Thionine	44:56 \pm 2
	Na ⁺ Nafion	Methylene blue	47:53 \pm 2
	Na ⁺ Nafion	Methylene green	46:54 \pm 2
7	CH ₂ Cl ₂	Thionine	8:9 46:54 \pm 2
	Na ⁺ Nafion	Thionine	47:53 \pm 2
	Na ⁺ Nafion	Methylene blue	53:47 \pm 2
	Na ⁺ Nafion	Methylene green	43:53 \pm 2

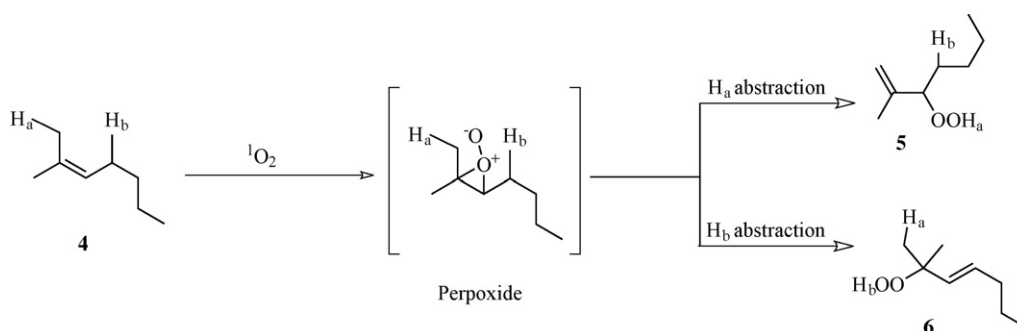
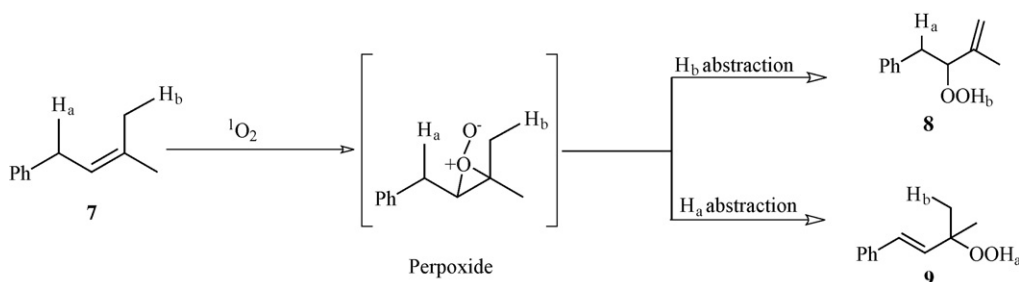
^a For structures see Schemes 1–4.^b [**1**], [**4**] and [**7**] in solution irradiation = 3×10^{-2} M.^c Loading level of **1**, **4** and **7** in Nafion samples = 2–2.2 mg/300 mg of Nafion.^d Experimental errors are within \pm 3%. The values reported here are the mean of five independent trials \pm standard deviation.

triphenylphosphine for GC analysis. This is performed to avoid any discrepancy in calculating the product ratio due to the decomposition of labile hydroperoxides [**7**] in GC column. Five independent trials were performed for each set of olefin/sensitizer within Na⁺ Nafion. The product distributions in dichloromethane and Na⁺ Nafion \pm standard deviation (S.D.) are presented in Table 2.

Adapting a similar procedure, 2-methyl-2-heptene (**4**) [41–43] and 2-methyl-4-phenyl-2-butene (**7**) [45] were included within Na⁺ Nafion beads and photolyzed as dichloromethane suspension in the presence of three different thiazine dyes. The olefin **4** yielded the hydroperoxides **5** and **6** upon reaction with singlet oxygen by the abstractions of respective allylic hydrogen H_a and H_b (Scheme 3). Singlet oxygen attack on the olefin **7** resulted in the formation of hydroperoxides **8** and **9** by the abstraction of H_a

and H_b, respectively as shown in Scheme 4. The product distribution upon photooxidation of olefins **4** and **7** are presented in Table 2. The reported values are the mean value of five replicates \pm standard deviation (S.D.) from the mean. The distribution of hydroperoxide products for all the olefins were determined from the integration values of the corresponding hydroperoxide proton peaks (–OOH). The product distribution was confirmed by GC analysis of the corresponding alcohols obtained by treating the hydroperoxide with triphenylphosphine. NMR data showing the peroxide peaks and GC data showing the corresponding alcohol peaks of the reaction mixture obtained upon irradiation of olefins **1**, **4** and **7** within Na⁺ Nafion using thionine sensitizer is presented in Fig. 4.

As a part of control experiments, the olefin-loaded Na⁺ Nafion (loading level \sim 2–2.2 mg) were stirred in dichloromethane solution of the sensitizer under oxygen bubbling for 3 h (dark reaction). No detectable hydroperoxides (<0.04 mg) were observed upon GC analysis. About 95 \pm 3% (S.D.) of the reactant olefin was recovered indicating that there was no side reaction in the absence of light. Also the olefin-loaded Na⁺ Nafion beads were irradiated for 1 h at wavelength >420 nm in the blank dichloromethane (without any sensitizer) under continuous oxygen bubbling. No detectable products (<0.04 mg) were observed upon GC analysis and greater than 95 \pm 2% (S.D.) of starting olefin was recovered. Also no detectable products (<0.04 mg) were observed upon GC analysis when irradiation of olefin incorporated Nafion was carried out under nitrogen bubbling (after degassing). Both the above control experiments suggest that singlet oxygen-mediated hydroperoxidation is the only reaction pathway upon irradiation of olefin-loaded Nafion beads at wavelength >420 nm. The presumption that the photogenerated singlet oxygen via photosensitization reaction of thiazine dyes in dichloromethane was further confirmed by a ‘chemical test’ by isolating products characteristic of singlet oxygen oxidation of the olefin. It has been previously reported for the olefin **1** that singlet oxygen-mediated oxidation and autooxidation via a radical pathway yield a different distribution of products [39,40]. As evident from the results (Table 2), the product obtained from photoreaction within Nafion correspond to oxidation via the singlet oxygen path-

**Scheme 3.** Photooxidation of 2-methyl-2-heptene (**4**).**Scheme 4.** Photooxidation of 2-methyl-4-phenyl-2-butene (**7**).

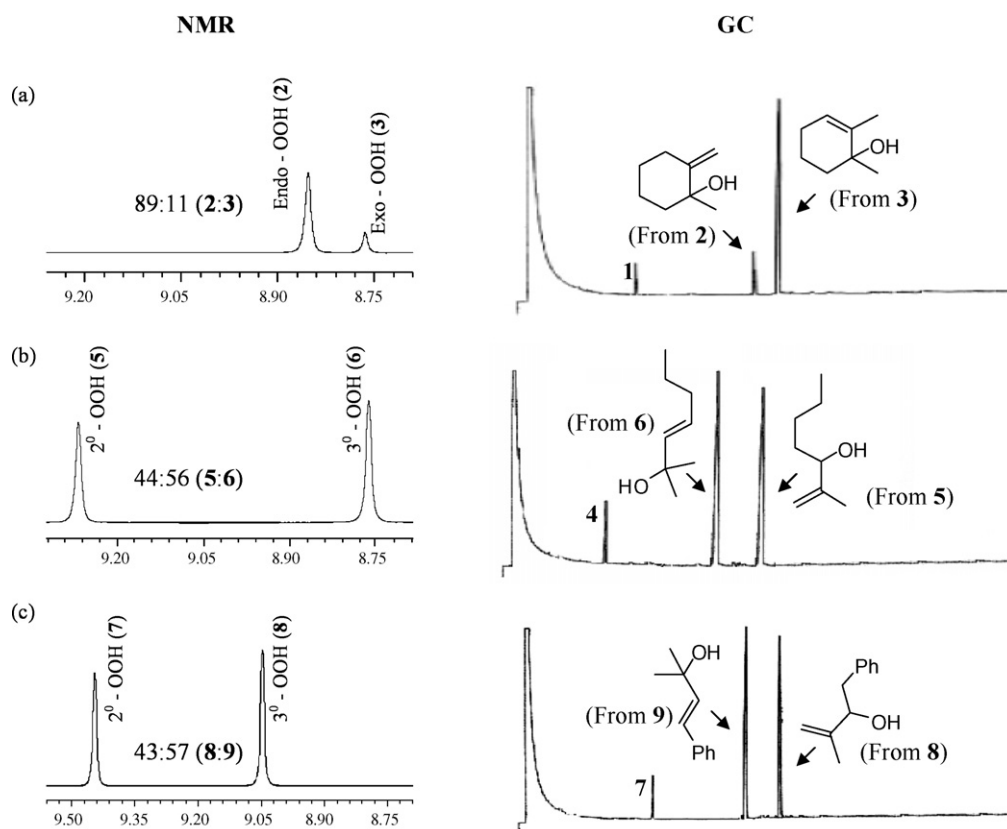


Fig. 4. NMR data showing the peroxide peaks and GC data showing the corresponding alcohol peaks of the reaction mixture obtained upon irradiation of olefins (a) 1,2-dimethylcyclohexene [1], (b) 2-methyl-2-heptene [4] and (c) 2-methyl-4-phenyl-2-butene [7] within Na⁺ Nafion using thionine sensitizer.

way. The aforementioned control experiments and “the chemical test” clearly demonstrate that the singlet oxygen generated outside Nafion can diffuse in to the fluorocarbon matrix to effect the oxidation of the encapsulated olefins.

For further understanding of the process, the following control experiments were performed. The dichloromethane solution after irradiation was analyzed to make sure that the oxidation took place within Nafion. No detectable peroxide products (<0.04 mg) were observed in dichloromethane solution. Also the extract from the photolyzed Nafion sample was analyzed by ¹H NMR and UV-vis spectroscopy. No detectable amount of the sensitizer [NMR <1 mg and UV-vis spectrometer <1 × 10⁻⁶ M (corresponds to ~0.06 absorbance at λ_{max})] was observed in the extract. The performed control experiments clearly demonstrate that the olefin and the sensitizer are kept in two different phases throughout the reaction. The mass balance (recovery) for each of the reactions was calculated by GC analysis using undecane as the internal calibration standard. The mass balance is greater than 95 ± 2% (S.D.) up to 30% conversion (five replicates) and decreases to 85 ± 3% (S.D.) at 90% conversion (five replicates) which is most likely due to further oxidation of primary photoproducts. The stability of peroxides within Nafion was then investigated. Peroxide products (isolated from the solution reaction following the procedure described in Section 4) was included within Nafion matrix, suspended in dichloromethane/dye solution and irradiated at wavelengths above 420 nm (using corning filter CS# 3-73) under continuous oxygen bubbling. The peroxides were then extracted with methanol, converted into corresponding allylic alcohols by stirring with excess triphenylphosphine and analyzed by gas chromatography using an internal calibration standard (undecane). Five replicates were performed and the recovery was found to be 85 ± 3% (S.D.).

One such sample of peroxides-incorporated Nafion was extracted with methanol without irradiating the sample. The recovery was ~94 ± 2% (S.D.) based on five independent trials. The volatile nature of peroxides is most likely responsible for their loss (6 ± 2%) in the case of thermal extraction. In the case of irradiated sample, the volatile nature of peroxides and secondary photooxidation of peroxides are probable reasons for moderate recovery (85 ± 3%). However, the ratio of peroxides remained the same both before and after the irradiation, suggesting that there was no selective decomposition of either of the peroxides within Nafion.

Statistical significance test [53] was performed between the trials for the 3 olefin/3 dyes in CH₂Cl₂ vs. Nafion. It is evident from the calculated *P*-values at 95% confidence level (Table 3) that the product distribution between free solution and Nafion is statistically significantly different for olefins 1 and 4. In the case

Table 3

P-values from statistical significance test performed between the trials for the 3 olefins/3 dyes in CH₂Cl₂ vs. Na⁺ Nafion

Olefins ^a	Medium/sensitizer	<i>P</i> -value (CH ₂ Cl ₂ vs. Na ⁺ Nafion) ^b
1	Na ⁺ Nafion/thionine	0.01
1	Na ⁺ Nafion/methylene blue	0.002
1	Na ⁺ Nafion/methylene green	0.0007
4	Na ⁺ Nafion/thionine	0.0004
4	Na ⁺ Nafion/methylene blue	0.008
4	Na ⁺ Nafion/methylene green	0.014
7	Na ⁺ Nafion/thionine	0.46
7	Na ⁺ Nafion/methylene blue	0.07
7	Na ⁺ Nafion/methylene green	0.052

^a For structures see Schemes 1–4.

^b *P*-values are calculated from Student's *t*-test using Microsoft Excel software (2003 version).

Table 4Chemical yield and product distribution upon photooxidation of the olefin **1** in the presence of pre-used sensitizer solution^a

Medium ^b	Sensitizer	Product ratio ^d			Chemical yield ^{c,d}		
		1st use 2:3	2nd use 2:3	3rd use 2:3	1st use	2nd use	3rd use
Na ⁺ Nafion	Thionine	82:18 ± 4	80:20 ± 3	79:21 ± 3	97 ± 1	94 ± 2	96 ± 2
Na ⁺ Nafion	Methylene blue	80:20 ± 1	83:17 ± 3	80:20 ± 2	96 ± 2	93 ± 3	98 ± 1
Na ⁺ Nafion	Methylene green	78:22 ± 2	80:20 ± 2	82:18 ± 3	95 ± 3	97 ± 2	95 ± 2

^a For structures see Schemes 1 and 2.^b Loading level of **1** in Nafion samples = 2.0 mg/300 mg of Nafion.^c Nafion samples were irradiated for 45 min and the chemical yield were calculated from GC analysis using undecane as internal standard.^d Experimental errors are within ±3%. The values reported here are the mean of five independent trials ± standard deviation.

of **7**, no statistically significant difference between free solution and Nafion was observed. It has been previously established by Ramamurthy and Li [26], Clennan and Sram [54], Stratakis and Froudakis [55] and Tung and coworkers [56] that regioselectivity could be altered by complexation of alkenes to alkali metal cation and thereby preventing access to selective allylic hydrogen. Similar cation–substrate interaction might be the reason for the observed small difference in the case olefins **1** and **4**. In the case of **7**, the presence of phenyl ring may lead to different kind of substrate–cation interaction (phenyl ring π electrons–cation interaction instead of olefin π –cation interaction) which may result in no regioselectivity. However the difference in product distribution upon irradiation of olefins **1** and **4** within Nafion compared solution photochemistry [39–45] is too low to conclude anything. Henceforth no model for the type substrate–cation interaction within Nafion that explains can be proposed at this point of time.

Of particular interest low regioselectivity was observed in the products formation upon photooxidation of olefins **4** and **7** within Na⁺ Nafion compared to zeolite. It has been established in organic solvents that the singlet oxygen adds to a trisubstituted olefin from the more substituted side and yield equal amounts of both secondary and tertiary hydroperoxides [5]. However within zeolite, as shown by Ramamurthy and coworkers [21,45], the olefins are preorganized (unlike in organic solvent) through cation– π interaction and thereby facilitates the singlet oxygen attack from less substituted side resulting in selective formation of secondary hydroperoxides. The present study clearly suggests that there is no preference for any particular alignment of olefins within Nafion prior to attack of singlet oxygen. This is probably due to the weak cation– π interaction which is not strong enough to freeze the alkenes in any preferred conformation within Nafion. This is most likely due to appreciable amount of hydration resulting from residual water molecules (1.32 water molecule per sulfonate group) at our experimental condition (2% of water by weight) [25]. Nafion is well known for its highly hydroscopic nature [57]. As reported in the literature [18], the Nafion should be dried in high vacuum (10^{-3} Torr) at 120 °C for 2 days to get rid of most of the residual water molecules. At such harsh conditions, the incorporated olefins decompose to yield various thermal products (not characterized). Due to poor stability of the olefins at such conditions, olefin-loaded Nafion beads were dried under medium vacuum at room temperature. Following the procedure described in Section 4, moderately dry Nafion samples slightly better than air dried Nafion (2.6 molecules per sulfonate group) [23] could be prepared without decomposing the incorporated olefins. The product distribution within Na⁺ Nafion did not change with degree of conversion, demonstrating that the peroxide product is fairly stable within Nafion. As a part of the control experiments, the chemical yield and the product distribution upon photolysis of olefin **1** in the presence of pre-used sensitizer solutions were examined. As evident from Table 4, the effectiveness of the reused photo-

sensitizer and the product distribution there from remained the same.

3. Summary

Dye-sensitized photooxidation of olefins **1**, **4** and **7** were efficiently carried out in within micro-environment of Nafion. The singlet oxygen that was generated outside the 'Nafion matrix' could diffuse through the fluorocarbon wall to effect oxidation. The yield of peroxide products was high (>95%) at appreciable conversion (~30%) and appreciable (~85%) at high conversion (>90%). The peroxides were fairly stable inside Nafion matrix and could be easily separated out from the photosensitizer. Of particular interest, the sensitizer can be reused. Overall, I envisage that the proposed strategy could be synthetically useful for industrial scale preparation of compounds requiring hydroperoxidation. Also, the investigated photoreactions serve as probes to understand the nature of the reaction domains provided by Nafion matrix.

4. Experimental

4.1. Materials

Nafion beads in its H⁺ form were obtained from DuPont. 2-Methyl-2-heptene and 1,2-dimethylcyclohexene were purchased from Sigma–Aldrich. 2-Methyl-4-phenyl-2-butene were synthesized and purified as per the procedure reported in the literature [45].

4.2. Instrumentation

The NMR data were acquired on a 400 MHz Varian Unity INOVA system with an autoswitchable probe operating at 25 °C. Chemical shifts for ¹H NMR were referenced to internal solvent peak (CDCl₃ δ 7.26 ppm) and were reported relative to tetramethylsilane. The pulse sequence used was "s2pul" (standard Varian pulse sequence) with the following parameters: number of scans = 8; spectrometer frequency (sfrq) = 400.154; acquisition time (at) = 1.998 s, number of data points (np) = 25,582, sweep width (sw) = 6402 Hz; transmitter power (tpwr) = 60 dB, relaxation delay (d1) = 1 s, transmitter offset frequency (tof) = 392.8 Hz, decoupler power (dpwr) = 43 dB. GC data were obtained using Shimadzu 17A series gas chromatograph fitted with an SE-30 column. The following conditions were used for GC analysis of the photoproducts: injection port temperature = 225 °C; detection port temperature = 250 °C; temperature program (olefin **1** and **4**): initial temp., 40 °C; initial time, 5 min; rate, 5 °C/min; final temp., 220 °C; final time, 10 min; temperature program (olefin **7**): initial temp., 60 °C; initial time, 5 min; rate, 5 °C/min; final temp., 240 °C; final time, 10 min. GC–MS data were collected using Varian Saturn 2100 GC/MS system fitted with SE-30 column. The parameters used for the GC part were as

follows: injection port temperature = 200 °C; detection port temperature = 270 °C; temperature program (olefin **1**, **4** and **7**): initial temp., 50 °C; initial time, 5 min; rate, 5 °C/min; final temp., 270 °C; final time, 10 min. UV–vis absorption were measured in Shimadzu UV–vis scanning spectrophotometer UV-2101PC with the following set parameters: start (nm) = 850; stop (nm) = 210 nm; UV–vis scan rate (nm/min) = 12000.00; UV–vis data interval (nm) = 1.25; UV–vis ave. time (s) = 0.0125.

4.3. Cleaning and cation exchange procedure

Prior to the use, Nafion beads were cleaned by boiling in concentrated nitric acid for 4 h. It was then thoroughly washed with distilled water and finally stirred in distilled water for 24 h. The Nafion beads in Na⁺ form were then prepared by stirring the clean beads with 2 M NaOH for 24 h. Excess base was then removed by stirring in water for 24 h.

4.4. Preparation of Nafion samples

The procedure followed for all the substrates are similar and one of them is described as below. A standard solution of **1** in methanol of concentration 5 μL/mL was prepared and from it, a 5-mL aliquot was placed into clean dry test tube. To it, exactly 300 mg of Na⁺ Nafion beads were added and stirred for 12 h. The methanol-swollen beads were then filtered, washed with fresh methanol and dried under medium vacuum (10⁻² Torr) for 6 h. Moderately dry Nafion beads (2% water by weight which corresponds to 1.32 water molecules per sulfonate group [25]) slightly better than air dried Nafion beads (2.6 water molecules per sulfonate group) [23] were obtained.

4.5. Photolysis and extraction procedure

Alkene-loaded Nafion beads suspended in dichloromethane solution of the sensitizer (ca. 10⁻⁴ M) was taken in test tube closed with septa and irradiated using a 450-W medium pressure mercury lamp fitted with a corning filter CS# 3-73 (>420 nm) with continuous bubbling of oxygen. Thiazine dyes, namely, thionine, methylene blue and methylene green were used as singlet oxygen sensitizer. Alkenes **1**, **4** and **7** were irradiated for 45 min to get ~30% conversion within Nafion. For higher conversion (>90%), the samples were irradiated for 2–3 h. After photolysis, the Nafion beads were separated from the solution and the photoproducts were extracted by stirring the beads in acetonitrile/methanol mixture (1:3) for 12 h. The beads were filtered off, washed with methanol and the combined extracts were concentrated under reduced pressure the reaction residue was taken for photoproduct analysis.

4.6. Analysis of photoproducts

First the residue was dissolved in deuterated chloroform and analyzed as such using ¹H NMR for examining the distribution of peroxide products in the reaction mixture. The distribution of hydroperoxide products for all the olefins were determined from the integration values of the corresponding hydroperoxide proton peaks [Olefin **1**; exo -OOH 88.77 ppm, endo -OOH 88.84 ppm, Olefin **4**; 3°-OOH 88.76 ppm 2°-OOH 89.26 ppm, Olefin **7**; 3°-OOH 89.05 ppm 2°-OOH 89.45 ppm]. The peroxides were then converted into the corresponding alcohols and analyzed using GC fitted with SE-30 column. The product distribution calculated from GC are within ±2% from that calculated from NMR analysis. The mass balance of the photosensitized oxidation and the chemical yield were calculated from GC analysis using undecane as the internal standard. The alcohol products from the photosensitized oxidation of

alkenes **1**, **4** and **7** were isolated from a preparative scale photoreaction, characterized by GC-MS, ¹H NMR and the spectral data of alcohol products are consistent with the literature reports [39–45].

4.7. Testing the stability of peroxides within Nafion

Using thionine as sensitizer, 12.5 μL of the alkene in acetonitrile was irradiated for 1 h with continuous bubbling of oxygen. Acetonitrile was evaporated and the resulting mixture was dissolved in hexane and passed through 3 cm silica column to remove the sensitizer. The resulting colorless solution containing peroxides was divided into two parts. Undecane was added to the first part to estimate the initial amount of hydroperoxides, analyzed as the alcohols by GC analysis to avoid any complexities. The second part was loaded into Na⁺ Nafion, irradiated at wavelength 420 nm under condition identical to alkene oxidation (with sensitizer and oxygen flow). The peroxides were then extracted from Nafion and analyzed as the alcohols by GC analysis. The stability of peroxides were estimated by comparing the amount of peroxide before and after the reaction.

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