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Alkali Ion Exchanged Nafion as a Confining Medium for Photochemical Reactions†

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ABSTRACT

Methanol-swollen Nafion beads were used as microreactors to control the photochemical reaction pathways. Product selectivity in three unimolecular reactions, namely, the photo-Fries rearrangement of naphthyl esters, Norrish Type I reaction of 1-phenyl-3-*p*-tolyl-propan-2-one and Norrish Type I and Type II reactions of benzoin alkyl ethers were examined. The influence of cations over the photodimerization of acenaphthylene and cross-photodimerization between acenaphthylene and N-benzyl maleimide included within Nafion were also examined. The photochemical behaviors of the above substrates were significantly altered within Nafion compared with their solution photochemistry. Of particular interest, the product distributions were found to depend on the counter cations of Nafion.

INTRODUCTION

Achieving selectivity in organic reactions continues to be one of the main goals of current research activities. In thermal reactions, the selectivity can be achieved by using suitable catalytic systems (1,2). However, due to short life times of the excited states and low energy of activation for the reactions, it is difficult to manipulate the reaction pathways in excited states. In spite of these difficulties, considerable selectivity has been achieved when photochemical reactions are conducted in solid state and in confined media (3–5). Herein, we establish Nafion, a commercial ionic polymer that possesses a confining environment and cations, as an efficient medium to enforce selectivity in photochemical reactions. Nafion is a block copolymer of tetrafluoroethylene and perfluoro-3, 6-dioxa-4-methyl-7-octene containing sulfonic acid groups. Use of Nafion as a reaction medium has previously been explored (6–11) and the results reported here further highlight the value of Nafion as a useful reaction medium.

Although the exact structure of Nafion is unknown, several models have been proposed since the early 1970s to describe the manner in which the ionic groups aggregate within the polymer matrix. Among them, the Mauritz–Hopfinger model, the Yeager three-phase model, Eisenberg model of hydrocarbon ionomers and the Gierke network model are well known (12–15). 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) (16). Small angle X-ray scattering and neutron scattering experiments indicate the presence of ionic clusters (17). However, details on the arrangement within these clusters have not been fully delineated. The protons of Nafion can be easily exchanged for alkali metal cations by treating H^+ Nafion with the corresponding aqueous hydroxide solutions. It has been established (18,19) that solvent-swollen Nafion can incorporate high concentrations of aromatic hydrocarbons. Herein we have carried out an investigation probing whether confining environment and cations of the Nafion could be utilized to achieve selectivity in photochemical reactions.

MATERIALS AND METHODS

Materials. Nafion in its protonic state was obtained from Du-Pont, Wilmington, DE. Benzoin ethyl ether (**16a**), acenaphthylene (**24**) and N-benzyl maleimide (**27**) were purchased from Sigma-Aldrich, St. Louis, MO. Benzoyl ethyl ether was recrystallized thrice from hexane. Acenaphthylene was crystallized from methanol thrice prior to use. Naphthyl benzoate (**1**), 1-naphthyl phenyl acyl ester (**6**), 1-phenyl-3-*p*-tolyl-propan-2-one (**14**) and benzoin octyl ether (**16b**) were synthesized following the procedure described in the literature (20–22). Product distributions were analyzed using a Shimadzu gas chromatograph (GC; Columbia, MD) fitted with an SE-30 column purchased from Supelco (Bellefonte, PA). Photoirradiations were carried out with a 450 W medium-pressure mercury lamp obtained from Ace glass (Vineland, NJ).

Cleaning and cation exchange procedure. Prior to the use, Nafion beads were cleaned by boiling in concentrated nitric acid for 4 h and then thoroughly washed with distilled water and finally stirred in distilled water for 24 h. The Nafion beads in Na^+ form were prepared by stirring the beads with 2 M NaOH for 24 h. Excess base was removed by stirring them in water for 24 h. Similarly Tl^+ and Cs^+ exchanged Nafion beads were prepared by treating with aqueous solutions of thallium carbonate and cesium hydroxide, respectively.

Preparation of Nafion samples. The procedure followed for all the substrates were similar and one of them is described below. A standard solution of **1** in methanol of concentration 5 mg/mL was prepared and from it 5 mL was pipetted out into a clean, dry test tube. To it, 300 mg of Nafion beads with desired cation were added and stirred for 12 h. The methanol-swollen beads were then filtered, washed with fresh methanol and dried under reduced pressure. The dry Nafion beads were then taken for irradiation.

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Abbreviations: GC, gas chromatography; Nafion, block copolymer of tetrafluoroethylene and perfluoro-3, 6-dioxa-4-methyl-oct-7-ene sulfonic acid; Type I, α-cleavage reaction of carbonyl compounds; Type II, γ-hydrogen abstraction of carbonyl compounds.

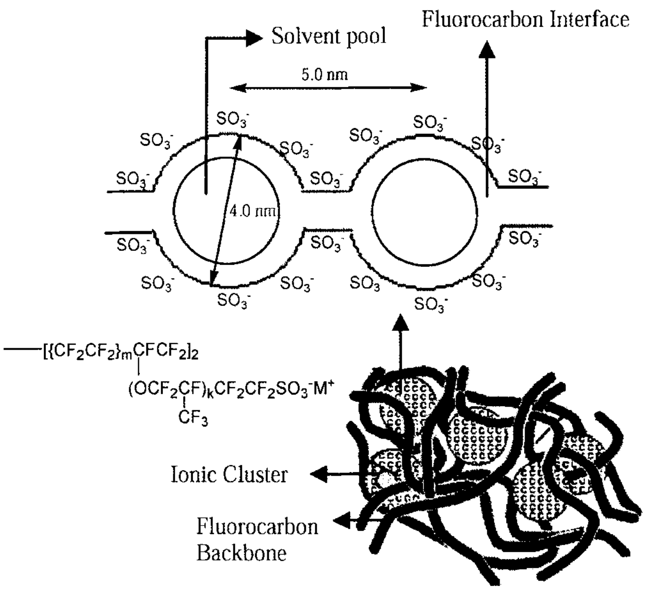


Figure 1. Ionic cluster model proposed for Nafion (12,16).

Irradiation and analysis procedure. The procedure followed for all the substrates were similar and one of these is described below. The dry Nafion beads containing the reactant molecules were taken in a sealed vial and degassed under nitrogen for 20 min and irradiated for the desired amount of time under nitrogen atmosphere using 450 W medium-pressure mercury lamp. After photolysis, the photoproducts and the unreacted starting material were extracted by stirring the beads in acetonitrile/methanol mixture (1 : 3) for 12 h. It was then filtered, washed with methanol and the combined extracts were concentrated under reduced pressure and analyzed by GC fitted with an SE 30 column. In the case of **24**, 4 h of irradiation resulted in ~10% conversion within Nafion. In the case of cross-dimerization, an equimolar mixture of **24** and **27** was irradiated for an hour to get ~20% conversion within Nafion. The loading level and the mass balance were calculated by extracting and analyzing the substrate-loaded Nafion beads before and after irradiation respectively. Above 90% mass balance was observed in all cases.

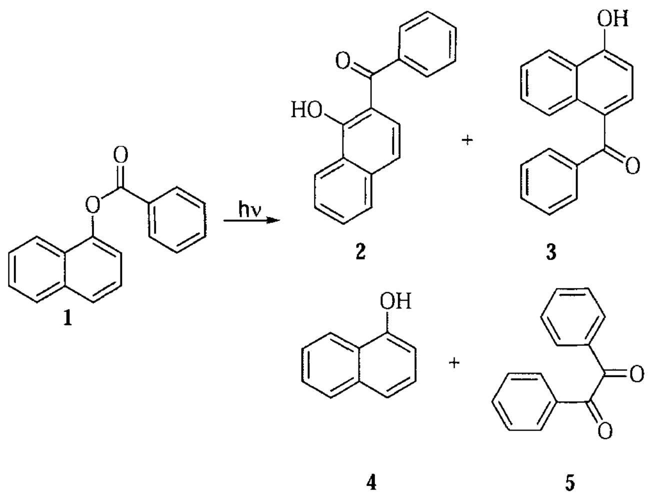
Characterization of photoproducts. Peaks in the GC traces were identified by coinjecting the authentic samples, prepared via solution irradiation. Photoproducts of **1** and **6** were isolated from their solution irradiation and spectral data were compared with literature reports (20). Among the photoproducts from **16a** and **16b**, benzaldehyde (**19**), benzil (**17**) and deoxybenzoin (**20**) were identified by comparison with commercially available samples. Photoproducts **18a** and **18b** were identified from solution reaction and spectral data were compared with literature reports (20). Photoproducts **21a**, **22a** and **22b** were isolated from reaction within Nafion and characterized using ^{1}H NMR. **21a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ1.4 (d, 3H), 5.2 (q, 1H), 5.95 (s, 1H), 7.20–7.80 (m, 10H). **22a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ1.2 (t, ^{3}H), 3.51 (q, 2H), 4.57 (s, 2H), 7.42–7.48 (m, 4H), 7.54–7.58 (m, 1H), 7.75–7.78 (m, 4H). **22b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ0.8 (t, 3H), 1.24 (m, 10H), 1.64 (m, 2H), 3.51 (t, 2H), 4.57 (s, 2H), 7.42–7.48 (m, 4H), 7.54–7.58 (m, 1H), 7.75–7.78 (m, 4H).

In the case of **14**, the photoproducts of **AA** and **BB** (Scheme 3) were commercially available (Aldrich, and Lancaster, Windham, NH). Photoproduct **AB** was identified based on the GC and mass spectroscopy fragmentation pattern. Mass spectral data *m/z* (relative intensity): 196 (M^+, 17), 105 (100), 91 (12), 77 (11).

Photodimers of acenaphthylene and crossdimers of acenaphthylene and N-benzylmaleimide were isolated from reaction within Nafion and characterized by comparing their spectral data with literature values (23,24).

RESULTS AND DISCUSSION

In our studies, commercially available Nafion beads in its alkali ion form were used. Previously, considerable photophysical studies within Nafion using probes such as pyrene, xanthone and benzophenone have been carried out (25–27). These studies provided information concerning the environment experienced by the organic substrates that were included within Nafion and suggest that aromatic hydrocarbons, when included in the polymer matrix, were located within the ionic cluster or at the interfacial region between fluorocarbon backbone and ionic clusters. We have investigated three unimolecular reactions, namely, the photo-Fries rearrangement of naphthyl esters **1** and **6**, α-cleavage reaction of 1-phenyl-3-*p*-tolyl-propan-2-one (**14**) and Norrish Type I and Type II reactions of benzoin alkyl ethers (**16a** and **16b**) within Nafion. Two bimolecular reactions, namely, photodimerization of acenaphthylene (**24**) and cross-photodimerization between acenaphthylene (**24**) and N-benzyl maleimide (**27**), were also examined for further understanding of the medium. The substrate of interest was included within cation exchanged Nafion beads by stirring the two in methanol. The solvent was then removed under reduced pressure to obtain dry beads. Photoirradiation of dry beads were carried out under a nitrogen atmosphere, following which the products were extracted with methanol/acetonitrile mixture and analyzed by GC.



Scheme 1.

The first reaction investigated was the photo-Fries rearrangement of naphthyl esters **1** and **6**. The choice of naphthyl system is based on the following factors: (a) Photochemical behavior of these esters has been extensively studied in isotropic solvents (28,29). (b) Attempts have been made to achieve selectivity in various media with varied success (30–33). (c) Photochemical behavior of phenyl esters within Nafion was established previously (9). (d) Because naphthyl esters give more products than the phenyl esters, they provide a greater opportunity to test the limitations of Nafion as a medium to achieve selectivity. Irradiation of **1** in isotropic solvents such as hexane, methanol and benzene resulted in four products as shown in Scheme 1. But when irradiated within alkali ion exchanged (Na^+, Tl^+ and Cs^+) Nafion, it gave a single product, 2-benzoyl-1-naphthol (**2**). The conversions and product distributions in alkali ion exchanged Nafion and in solution are presented in Table 1.

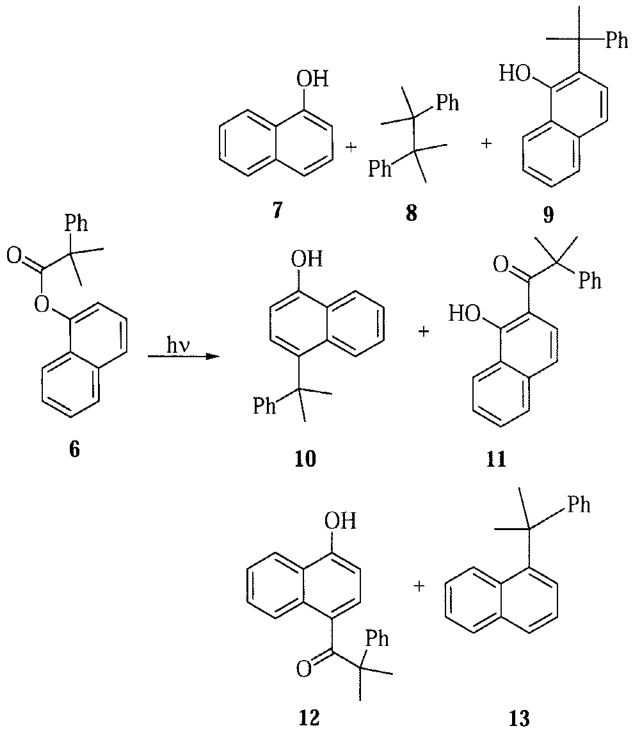
Similar to naphthyl benzoate, photolysis of 1-naphthyl phenylacyl ester (**6**) within Nafion gave a single product, 2-phenylacyl-1-naphthol (**12**), whereas the same in hexane solution yielded seven products as shown in Scheme 2 (34–39). The relative product distributions and conversions upon photolysis of **6** within Nafion and in solution are summarized in Table 2. The formation of products **3–5** upon irradiation of **1** and formation of **7–11** upon

Table 1. Relative yields of photoproducts upon irradiation of **1** in solution and within Nafion at room temperature under nitrogen atmosphere.

Medium	Irradiation time (h)	Conversion (%)	Product distribution (%)			
			2	**3**	**4**	**5**
Hexane†	6	22	60	30	7	3
Methanol†	6	25	64	26	8	2
Benzene†	6	22	76	17	6	1
Na^+ Nafion‡	1	22	>99	—	—	—
Tl^+ Nafion‡	12	29	>99	—	—	—
Cs^+ Nafion‡	12	18	>99	—	—	—

† [**1**] in solution irradiation = 1×10^{-2} M. The conversion of **1** in various media was calibrated using undecane as the internal standard.

‡ Loading level of **1** in Nafion samples = 1.7 mg/300 mg of Nafion.



Scheme 2.

irradiation of **6** were significantly suppressed within Nafion. In solution, the relative yields of *ortho* and *para* rearrangement products are determined by the electron densities at the *ortho* and *para* positions of the naphthoxy radicals. Evidently this is not the controlling factor within Nafion. The formation of the *para* rearrangement product requires a greater extent of motion of the radicals than that for the formation of the *ortho* product. The exclusive formation of *ortho* rearrangement product suggests that motion of the primary intermediates is significantly restricted within the polymer matrix during the reaction time scale.

The conversion of **1** and **6** within alkali ion-exchanged Nafion beads was estimated by GC analysis using undecane as the internal standard. It was observed that the product formation was approximately 10 times reduced inside heavy cation (Tl^+ and Cs^+) exchanged Nafion beads. The lower yield of products from **1** and **6** within Tl^+ and Cs^+ exchanged Nafion beads is most likely due to heavy cation effect (40) on intersystem crossing rate of the reactive singlet state. The photo-Fries rearrangements of naphthyl esters are known to take place from the singlet excited state (33). During irradiation within Tl^+ and Cs^+ exchanged Nafion beads, most likely there is a competition between intersystem crossing to the unreactive triplet state induced by heavy cations and the reaction from the excited singlet state. The inability to sensitize photo-Fries rearrangement of the naphthyl esters with benzophenone in hexane is also consistent with the general understanding that the reaction occurs exclusively from the excited singlet state (36).

With naphthyl esters (**1** and **6**) as probes, we have established that the medium is able to restrict the mobility of the singlet radical pairs generated during the course of a photoreaction. To address the question of whether Nafion can restrict the mobility of reactive intermediates even on a longer time scale, Norrish Type I reactions of 1-phenyl-3-*p*-tolyl-propan-2-one (**14**) (41,42) and benzoin alkyl ethers (**16a** and **16b**) were explored (43). These two systems fragment from their triplet excited states to yield triplet radical pairs. Under such conditions, coupling of radicals can take place only if the radical pair intersystem crosses to a singlet state or diffuses apart to form free radicals. Results discussed below on these two systems reveal that Nafion matrix provides a confining environment to reactant molecules even on a microsecond time scale.

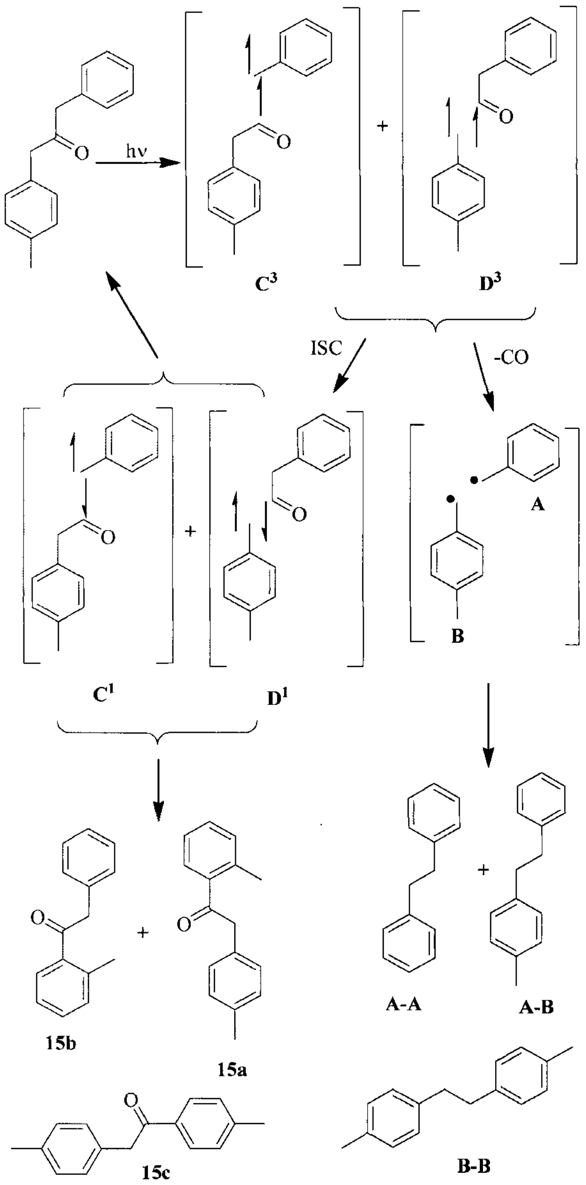
Photolysis of 1-phenyl-3-*p*-tolyl-propan-2-one (**14**) results in α cleavage to form the radical pairs $\mathbf{C}^3$ and$\mathbf{D}^3$, followed by decarbonylation to yield radicals **A** and **B** (secondary radical pair) as shown in Scheme 3 (41,42). Recombination of **A** and **B** would result in **AA**, **AB** and **BB**. If the radicals **A** and **B** are held in a cage, then the only product expected is **AB** (44). In an isotropic solvent such as hexane, the diaryl ethane products **AA**, **AB** and **BB** were formed in the ratio 1 : 2 : 1. The cage effect for the reaction was calculated according to the equation: cage effect = [**AB** – (**AA** + **BB**)]/[**AA** + **AB** + **BB**]. Product distribution in Na^+ Nafion revealed that there is a remarkable cage effect (0.84). Also, the cage effect increased with the increase in cation size present within Nafion. For example, the cage effect upon photolysis of **14** within Na^+ Nafion was 0.84 while that within Tl^+ and Cs^+ Nafion was 1. Though there is an increase in the cage effect in heavy cation exchanged Nafion, the conversion to photoproducts is low compared with that in Na^+ Nafion. The product distribution and the conversion in various reaction media are presented in Table 3. The slower reactivity within heavy cation-exchanged Nafion beads, we believe, results from heavy cation-induced intersystem crossing of the triplet geminate radical pairs $\mathbf{C}^3$ and $\mathbf{D}^3$. In the presence of heavy cations such as Tl^+ and Cs^+, most likely there is a competition between intersystem crossing of the triplet geminate radical pairs ($\mathbf{C}^3$ and $\mathbf{D}^3$) and the decarbonylation reaction as shown in Scheme 3 (45–47). The singlet geminate radical pairs $\mathbf{C}^1$

Table 2. Relative product distribution upon irradiation of **6** in solution and within Nafion at room temperature under nitrogen atmosphere.

Medium	Irradiation time (h)	Conversion (%)	Product distribution (%)						
			7	**8**	**9**	**10**	**11**	**12**	**13**
Hexane†	6	20	18	11	3	9	1	39	19
Methanol†	6	20	14	4	1	2	Trace	57	22
Na^+ Nafion‡	6	52	—	—	—	—	—	>99	—
Tl^+ Nafion‡	8	5	—	—	—	—	—	>99	—
Cs^+ Nafion‡	8	5	—	—	—	—	—	>99	—

† [**6**] in solution irradiation = 1×10^{-2} M. The conversions of **6** in various media were calibrated using undecane as the internal standard.

‡ Loading level of **6** in Nafion samples = 1.7 mg/300 mg of Nafion.



Scheme 3.

Table 3. Relative product distribution upon irradiation of **14** in solution and within Nafion at room temperature under nitrogen atmosphere.

Medium	Irradiation time	Conversion (%)	Product distribution (%) AA	AB	BB	Cage effect $Fc = \frac{(AB - ([AA + BB]))}{(AA + AB + BB)}$
Hexane†	15 min	42	22	53	25	0.05
Na^+ Nafion‡	15 h	56	3	92	5	0.84
Tl^+ Nafion‡	15 h	6	0	100	0	1
Cs^+ Nafion‡	1 h	9	0	100	0	1

† [**14**] in solution irradiation = 1×10^{-3} M. The conversions of **14** in various media were calibrated using undecane as the internal standard.
‡ Loading level of **14** in Nafion samples = 1.5 mg/300 mg of Nafion.

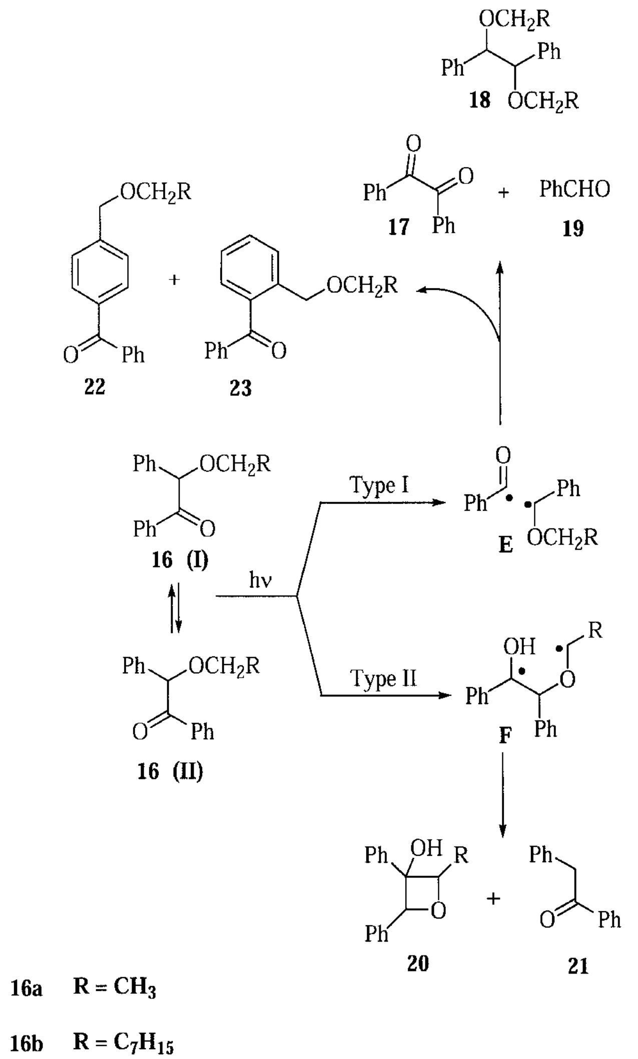
and $\mathbf{D^1}$ can recombine to yield the reactant or rearrange to form the rearrangement products (**15a–c**). Because we didn't observe any rearrangement products within Nafion, we believe that intersystem crossing of triplet radical pairs $\mathbf{C^3}$ and $\mathbf{D^3}$ exclusively regenerated the reactant and thus lowered the yield of final products.

Norrish Type I and Type II reactions of benzoin alkyl ethers (**16a** and **16b**) from their triplet excited states were then investigated. In benzene, excitation of **16a** and **16b** yielded the radical pair **E** through the Type I process, which diffuses apart to form benzil (**17**) and pinacol ether (**18**) (Scheme 4). Solution irradiation of **16a** also yielded oxetenol **21** in smaller amounts (~3%) via the γ-hydrogen abstraction process (43). Photolysis of **16a** within Na^+ Nafion resulted in 31% of oxetenol (**21a**) and 42% of deoxybenzoin (**20**) via the Type II process along with 24% of the *para*-rearrangement product **22a** resulting from the Type I process. Reaction of **16a** within heavy cation exchanged Nafion beads yielded predominantly the Type II products (~85%) along with minor amounts (~15%) of the *para*-rearrangement product **22a**. In the case of **16b,** irradiation within Na^+ Nafion yielded 49% of deoxybenzoin (**20**) and 51% of *para*-rearrangement product **22b**, and reaction within heavy cation-exchanged Nafion beads resulted in 64% of deoxybenzoin (**20**) and 36% of *para*-rearrangement product **22b**.

Clearly, the photochemical behavior of **16a** (short alkyl chain) and **16b** (long alkyl chain) are altered within alkali ion-exchanged Nafion beads. Important observations to note are: (a) The Type II reaction, which is almost negligible in solution, becomes predominant within Nafion. (b) Rearrangement product **22**, which is not observed in solution, is formed in appreciable amounts within Nafion (Table 4). We believe that the formation of rearrangement product **22** within Nafion is a consequence of the restriction experienced by the geminate radical pair **E** (48,49). Preference for Type II products over Type I can be attributed to two factors: (a) Recombination of the radical pair **E** that resulted from Type I process within Nafion to yield the reactant. (b) The presence of alkoxy chain in **16a** and **16b** most likely directs the chelation of the cation to a conformer that is favorable for Type II processes.

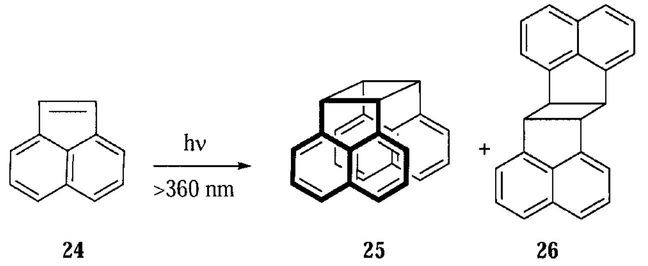
The dependence of the reactivity of **1**, **6** and **14** on the cations suggests that the substrates that are included within Nafion interact with cations. To further probe this phenomenon, photodimerization of acenaphthylene (**24**), which is known for its cation-dependent photochemistry, was examined within Nafion beads. The photochemical behavior of acenaphthylene has been extensively studied in various constrained media and in organic solvents (23,50–53). Irradiation of acenaphthylene (**24**) in solution yields *cis* (**25**) and *trans* (**26**) dimers. The ratio of *cis* to *trans* dimer depends on the nature of the excited state from which the reaction originates. Singlet excited state produces only *cis* dimer, whereas the triplet state yields both *cis* and *trans* dimers in the ratio 1 : 2.3 (23).

The *cis*/*trans* dimer ratios upon irradiation of **24** in solution and within Nafion beads of various cations are presented in Table 5. The loading level of **24** in alkali ion-exchanged Nafion sample was estimated by GC with docosane as the internal standard and was calculated to be 1.7 mg/300 mg of alkali ion-exchanged Nafion beads. The *cis*/*trans* dimer ratios within the Nafion samples depended on the counter cations. For example, irradiation of acenaphthylene (**24**) included within Na^+ Nafion above 360 nm yielded predominantly *cis* dimer (*cis*/*trans* dimer ratio 28), whereas irradiation within Tl^+ and Cs^+ exchanged Nafion beads yielded the dimers with *cis*/*trans* dimer ratio 1.9 and 2.8, respectively. The dependence of *cis*/*trans* dimer ratio on the counter ions of Nafion



Scheme 4.

can be attributed to heavy atom effect (54). In the presence of heavy cations, such as Tl^+ and Cs^+, most likely, the reactive singlet state of **24** intersystem crosses to triplet, resulting in increased *trans* dimer yield. However the *cis/trans* ratio that we observed within heavy cation-exchanged Nafion was higher than the ratio obtained from triplet chemistry in solution [0.44] (23). To understand this, acenaphthylene (**24**) was loaded within Na^+ Nafion along with eosin Y, a triplet sensitizer, and irradiated above 510 nm. The triplet state thus produced within Na^+ Nafion yielded *cis* and *trans* dimers in the ratio 3.3, which is comparable with what was obtained within heavy cation-exchanged Nafion samples.



Scheme 5.

Table 4. Relative product distribution upon photolysis of **16a** and **16b** in solution and within Nafion at room temperature under nitrogen atmosphere.

Medium	Type I products (%)			Type II products (%)		Type I/ Type II
	17	**18**	**22**	**20**	**21**	
Benzoin ethyl ether (**16a**)						
Benzene†	33	64	—	—	3	32.3
Na^+ Nafion‡	<1	<2	24	42	31	0.36
Tl^+ Nafion‡	Trace	Trace	14	29	57	0.16
Cs^+ Nafion‡	Trace	Trace	17	33	50	0.20
Benzoin octyl ether (**16b**)						
Benzene†	20	80	—	—	—	Only Type I
Na^+ Nafion§	Trace	Trace	51	49	—	1
Tl^+ Nafion§	Trace	Trace	36	64	—	0.56
Cs^+ Nafion§	Trace	Trace	36	64	—	0.56

† [**16a**], [**16b**] in solution irradiation = 1×10^{-3} M.
‡ Loading level of **16a** in Nafion samples = 2.0 mg/300 mg of Nafion.
§ Loading level of **16b** in Nafion samples = 1.6 mg/300 mg of Nafion. The conversion of **16a** and **16b** in various media were calibrated using benzophenone as the internal standard.

The dominant formation of *cis* dimer from the triplet state within Nafion reflects, at least partially, the cavity control on the stereochemistry of dimer formation from acenaphthylene. In conclusion, the multiplicity of the reactive state of acenaphthylene can be controlled by varying the counter cations of Nafion.

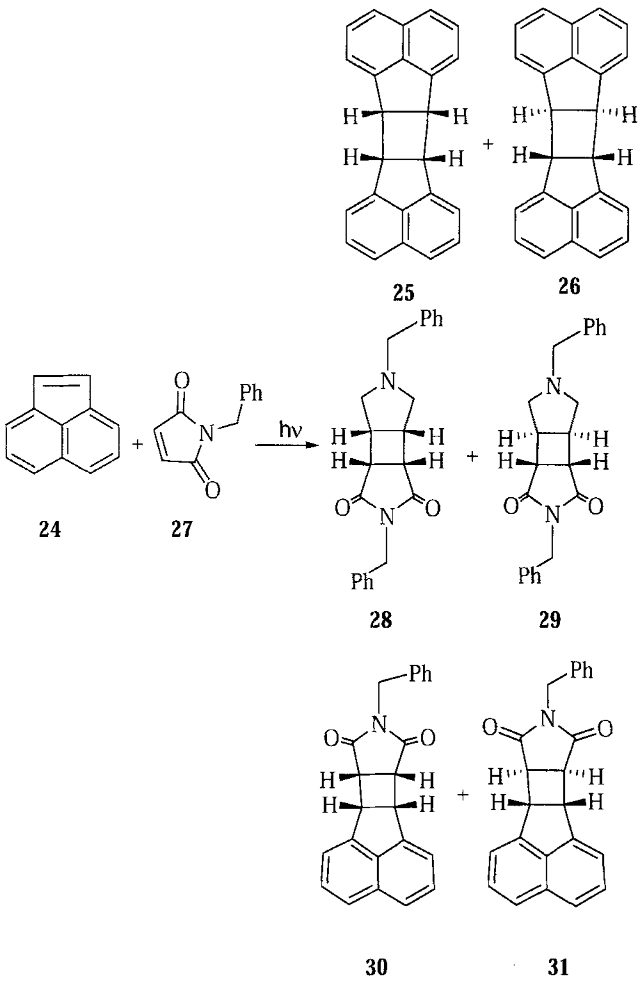
Heavy cation and confining effects of Nafion were probed with an additional system, namely cross-photodimerization between acenaphthylene **24** and N-benzyl maleimide **27** (24). N-Benzyl maleimide is found to be photochemically inactive in polar organic solvents and within alkali ion exchanged Nafion. However, irradiation of equimolar mixture of **24** and **27** in a nonpolar solvent such as hexane predominantly yielded homo *syn* dimers **25** and **28** along with minor amounts of other dimers **26, 29–31**. But in a polar medium like methanol, *syn* hetero dimer **30** and *syn* acenaphthylene dimer **25** were formed as major products upon photolysis of an equimolar mixture of **24** and **27**.

Equimolar mixture of **24** and **27** were loaded within alkali ion-exchanged Nafion beads and dried under reduced pressure prior to irradiation. Using gas chromatographic techniques with docosane as the internal standard, the loading levels of **24** and **27** in 300 mg of Na^+ Nafion were calculated to be 1.0 mg and 1.1 mg, respectively. When irradiated within Na^+ Nafion, it yielded *syn* hetero dimer (**30**) as the major product. The product distributions in

Table 5. Relative yields of photoproducts upon irradiation of **24** in solution and within Nafion at room temperature under nitrogen atmosphere.

Medium	Irradiation wavelength (nm)	**25/26** [*cis/trans*] ratio
THF†	360	26
Na^+ Nafion‡	360	28
Tl^+ Nafion‡	360	1.9
Cs^+ Nafion‡	360	2.8
Methanol/eosin Y§	510	0.44
Na^+ Nafion/eosin Y‡	510	3.3

† [**24**] in solution irradiation = 6.4×10^{-3} M.
‡ Loading level of **24** in Nafion samples = 1.7 mg/300 mg of Nafion.
§ [**24**] in triplet sensitization in methanol = 0.6 M; [eosin Y] = 4×10^{-3} M.



Scheme 6.

solution and within Nafion beads of various cations are presented in Table 6. Product distribution almost remained the same within Na^+ Nafion when studied at various irradiation wavelengths from 270 to 400 nm at ~20% conversion. However, upon prolonged irradiation (>12 h) at wavelengths <300 nm, the acenaphthylene dimer gradually reverted back to the starting material leaving more hetero dimer in the reaction mixture (55). We believe that the preference for hetero dimers over homo dimers within Na^+ Nafion network is probably due to a weak charge-transfer complex formation between the excited state of acenaphthylene and ground-state N-benzyl maleimide. The hetero to homo dimer ratio decreased upon photolysis of **24** and **27** (1 : 1) within heavy cation-exchanged (Tl^+ and Cs^+) Nafion beads. To account for this, the triplet state of **24** was produced within Na^+ Nafion using a triplet sensitizer (eosin Y) in the presence of an equimolar amount of **27**. The product distribution upon triplet sensitization within Na^+ Nafion is very similar to that obtained within Tl^+ and Cs^+ exchanged Nafion samples (Table 6). The above results indicate that formation of hetero dimer is less favored from acenaphthylene (**24**) triplet state compared with that from excited singlet state.

Table 6. Relative yields of photoproducts upon irradiation of equimolar mixture of **24** and **27** in solution and within Nafion at room temperature under nitrogen atmosphere.

Medium	Irradiation wavelength (nm)	Product distribution (%)						Hetero/homo dimers
		25	**26**	**28**	**29**	**30**	**31**	
Hexane†	360	59	4	31	—	4	2	0.06
Methanol†	360	43	2	2	—	53	Trace	1.17
Na^+ Nafion‡	360	16	6	—	—	71	7	3.5
Tl^+ Nafion‡	360	26	7	4	—	44	21	1.85
Cs^+ Nafion‡	360	28	10	2	—	47	13	1.5
Na^+ Nafion eosin Y§	510	38	22	0	—	30	10	0.7

† [**24**], [**27**] in solution irradiation = 6.4×10^{-3} M.

‡ Loading level of **24** in Nafion samples = 1.0 mg/300 mg of Nafion; loading level of **24** in Nafion samples = 1.2 mg/300 mg of Nafion.

§ Loading level of eosin Y in Na^+ Nafion sample = 0.02 mg.

CONCLUSION

In conclusion, remarkable product selectivity was obtained during the photo-Fries rearrangement of naphthyl esters **1** and **6** within alkali ion-exchanged Nafion beads as a result of restricted motion of the reactive intermediates within Nafion. Selectivity obtained in the case of 1-phenyl-3-*p*-tolyl-propan-2-one (**14**) and benzoin alkyl ethers (**16a** and **16b**) reveals the ability of Nafion matrix to impose restriction on reactive intermediates even on longer lifetimes. This work also illustrates that the cations of Nafion can play an important role in altering the excited-state behavior of the substrates included within the ionic clusters of Nafion. The yield of product formation in the case of **1**, **6** and **14** were significantly altered within heavy cation-exchanged Nafion beads. The multiplicity of excited state of acenaphthylene was altered by careful choice of counter cations of Nafion. Also, the product distribution in cross-dimerization between acenaphthylene and N-benzyl maleimide was significantly altered in the cationic environment of Nafion compared with solution photochemistry.

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