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Photo-Fries rearrangements of 1-naphthyl (*R*)-2-phenylpropanoate in poly(vinyl acetate) and ethyl acetate. Influence of medium polarity and polymer relaxation on motions of singlet radical pairs

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ABSTRACT

Both the regio- and stereo-chemistries of the photoreactions of 1-naphthyl (*R*)-2-phenylpropanoate have been investigated in poly(vinyl acetate) films in their glassy (at 5°C) and melted (at 50°C) states and in ethyl acetate. These results are compared with those from irradiations in polyethylene films and in *n*-hexane. The regioselectivity of the intermediate 1-naphthoxy/(*R*)-2-phenylpropanoyl radical pair combinations is much higher in both the melt and glassy states of poly(vinyl acetate) films than that in the melt state of completely amorphous polyethylene films, but the stereoselectivity of intermediate prochiral 1-naphthoxy/1-phenylethyl radical pair combinations is much lower in poly(vinyl acetate). The results emphasize the need to control the ratio between the rates of radical tumbling and translation, as well as the ratio between the rates of in-cage motions and cage-escape, if high stereo- and regio-selectivities of combination products are to be achieved. A mechanistic picture of how the radicals of the intermediate pairs are affected by and interact with the various media is advanced.

Key words: radical pair, stereoselectivity, polymer relaxation, photo-Fries.

INTRODUCTION

The rates and regio- and stereo-chemistries of radical pair combinations are known to be sensitive to local environmental effects (Porter and Krebs 1988, John 1993, Curran et al. 1995, Turro 2002, Ramamurthy and Schanze 2003). Some of these are the shapes, sizes, and flexibilities of the ‘walls’ of the reaction cages in which the combinations occur (Ramamurthy et al. 1993, Weiss et al. 1993). Others include the polarity of the cages and their ability to catalyze intersystem crossing of the radical pairs (Warrier et al. 2003). We have exploited the regiochemistry of photo-Fries reactions of aryl esters in which some decarbonylation products are formed to measure the in-cage rates of radical pair combinations (Gu and Weiss 2000). Those results provide important information about the influence of local environment on translational motions of a radical pair. Recently, we have extended that approach to develop a diagnostic system for following simultaneously the influences of time and space on radical pair combinations within reaction cages (Xu and Weiss 2003, 2005a, b, c). It is based on the fates of two related singlet radical pairs: 1-naphthoxy/(*R*)-2-phenylpropanoyl (chiral radical pair **A**) from

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Dedicated to the memory of Professor Christopher S. Foote (1935–2005), an excellent scientist and teacher and an admirer of Brasil.

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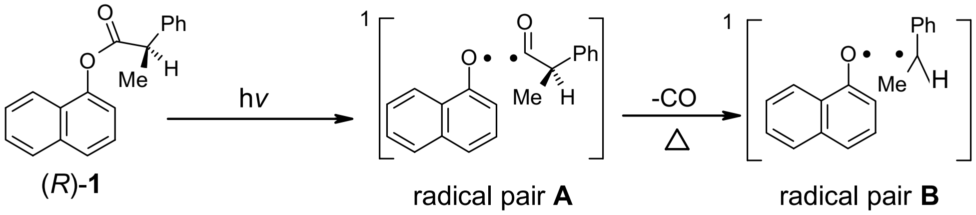


Equation 1

lysis of the excited singlet state of 1-naphthyl (*R*)-2-phenylpropanoate ((*R*)-**1**) and 1-naphthoxy/1-phenylethyl (prochiral radical pair **B**) from decarbonylation of radical pair **A** (i.e., indirectly from (*R*)-**1**) (Equation 1). Thus far, the chemistries of the combinations of *chiral* radical pair **A** and *prochiral* radical pair **B** have been investigated in relatively low polarity media such as *n*-alkanes with different viscosities (Xu and Weiss 2005a), polyethylene (**PE**) films with a wide range of crystallinities above their glass transition temperatures (T_gs) (Xu and Weiss 2005b), and the solid phases of *n*-nonadecane (Xu and Weiss 2005c). As expected, both the regio- and stereo-selectivities decrease as temperature is raised and medium viscosity is lowered (Xu and Weiss 2003, 2005a, b, c).

The high microviscosity and “templating” effects (related to low ‘wall’ flexibility from long polymer chain relaxation times) of the **PE** reaction cavities restrict radical pair movements (Gu et al. 1999, 2000a, b, Gu and Weiss 2000, 2001a, b), enabling even prochiral radical pair **B** to retain partial orientational memory of its chiral radical pair **A** precursor (Xu and Weiss 2003, 2005a, b, c). These results suggest that the rates of tumbling of a 1-phenylethyl radical and of radical pair combination are similar in these reaction cages, and both are at least comparable to the rates of relaxation of the polymeric chains constituting the **PE** cavity walls (Gu et al. 1999, 2000a, b, Gu and Weiss 2000, 2001a, b, Xu and Weiss 2003, 2005a, b, c).

Atactic poly(vinyl acetate) (**PVAc**) is a completely amorphous polymer whose polarity is higher than that of **PE** and similar to that of ethyl acetate, even though its polymer backbone is of low polarity (Charles 1996, Stevens 1998, Ravve 2000). Common commercial **PVAc** is highly branched due to chain transfer reactions that occur during radical polymerizations of vinyl acetate. The glass transition temperature of **PVAc**, near room temperature, is much higher than the T_g of **PE** films.

Previously, McCourt and coworkers (Wang et al. 1990) have used the photo-Fries reaction to demonstrate that the distribution of a guest molecule, 2-naphthyl acetate, is non-random in the glassy state of poly(methyl methacrylate). The concentrations of 2-naphthyl acetate employed there, ca. 0.1 M (1–2 wt%), are 10–100 times larger than those of (*R*)-**1** in the current investigation. In addition, we have investigated the regiochemistry of photo-Fries rearrangements of some simple 1-naphthyl esters, including *racemic* **1**, in the glassy (at 5°C) and melted (at 50°C) states of **PVAc** films (Gu et al. 2002). The regioselectivity of the singlet radical pair **A** combinations is much greater in **PVAc** films in both states than in ethyl acetate or in hexane at comparable temperatures. The enhanced regioselectivity has been attributed to strong interactions between radicals analogous to those in radical pair **A** (or radical pair **B**) and the acetate pendent groups of **PVAc**.

Here, we report both the regio- *and* stereo-chemistries of the photoreactions of (*R*)-**1** in **PVAc** films in their glassy (at 5°C) and melted (at 50°C) states. Comparisons of these results with those from irradiations in **PE** films and in *n*-hexane and ethyl acetate (solvents of lower and comparable polarity to that of **PVAc**) provide insights into the influences of the dynamics of polymeric chain motions and solvent polarity on the radical pair combinations. Because the regiochemistry of the reactions of racemic **1** in **PVAc** have been reported previously (Gu et al. 2002), stereochemical aspects of the radical pair combinations are emphasized here. This information is of interest fundamentally–to understand the interplay between different molecular motions in confining spaces–and practically–to design media whose reaction cavities can be used for regio- and enantio-selective syntheses.

MATERIALS AND METHODS

INSTRUMENTATION

UV/Vis absorption spectra were measured on a Cary 300 Bio UV-Vis Spectrophotometer. Gas chromatography (GC) was conducted on a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector. An Alltech Scientific DB-5 (0.25μm film; 0.25 mm × 30 m) column was used to determine products purities and for periodic monitoring of reactions. HPLC analyses were carried out on a HP series 1100 liquid chromatograph equipped with an autosampler and a UV-Vis diode array detector. Columns were silica gel (5μm, 4.6 × 250 mm from Allsphere and Phenomenex) for determinations of product distributions and cyano derivatized silica (5μm, 10 × 250 mm from IBM Instruments) for semi-preparative product separations (both using mixtures of hexanes and ethyl acetate as eluting solvents). A Chiralcel OJ-H (5μm, 4.6 × 250 mm from Chiral Technologies) with hexanes and 2-propanol as eluting solvent were used for determinations of enantiomeric excesses.

MATERIALS

Hexanes, cyclohexane, ethyl acetate, dichloromethane, *n*-pentane, and 2-propanol were HPLC grade from Fisher and were used as received. Anhydrous diethyl ether (reagent grade from Fisher Scientific) was passed through a column filled with basic aluminum oxide to remove the antioxidant, 2,6-di-*tert*-butyl-*p*-cresol.

A 15-20 g portion of poly(vinyl acetate) ($\langle M_w \rangle$ ca. 83,000, d = 1.180 g cm^{-3} from Aldrich; $T_g \approx 32.5$°C (Gu et al. 2002)) was dissolved in 100 mL of CH_2Cl_2 by refluxing the mixture with stirring for 3–5 h. The solution was cooled to room temperature and slowly poured into 300 mL of stirred hexanes. The resulting white precipitate was dried in air and then under vacuum ($<$ 1 Torr) for 2–3 days. Methylene chloride solutions of **PVAc** were cast into films on clean Teflon plates. After several days of air-drying, the films were immersed in at least 3 cyclohexane aliquots during more than one week to remove any remaining additives.

The syntheses of racemic and the (R)-enantiomer of **1** and of their photoproducts have been reported previously (Xu and Weiss 2003). (R)-**1** was $>$ 99% chemically and enantiomerically pure by HPLC analyses.

GENERAL PROCEDURES FOR FILM DOPING AND IRRADIATIONS

Solutions of 2 mM (R)-**1** in ethyl acetate (containing a small amount of *n*-dodecane as an internal standard) were irradiated with the Pyrex and water filtered output of a 450W Hanovia medium pressure mercury lamp for a few seconds at 5, 23, and 50°C.

PVAc films were immersed overnight in a solution of ca. 20 mM (R)-**1** in 85/15 (v/v) *n*-pentane/diethyl ether. After being wiped gently with a hexanes-saturated tissue paper to remove any surface-occluded (R)-**1**, the films were dried under vacuum ($<$ 0.5 Torr) for $\geq$ 3 h before irradiation. The concentrations of (R)-**1** doped in the films (ca. 2–6 mmol/kg) were determined by averaging the optical densities from at least 3 UV-Vis absorption spectra measured at different positions of each film. The molecular extinction coefficient of **1** in **PVAc** at 280 nm is assumed to be 6950 M^{-1}cm^{-1}, the value in ethyl acetate (Gu et al. 2002).

Each doped **PVAc** film was placed in a septum-sealed Pyrex tube and purged with flowing N_2 gas for $>$ 45 min. It was irradiated as above for periods from a few seconds to several minutes depending on the temperature and degree of conversion sought.

Control of temperature at and above 23(±1) °C was achieved by immersing the sample tubes in a stirred water-bath in a Pyrex beaker that was heated on a hot plate. Samples in sealed tubes were immersed in a stirred ice-water bath to achieve 5(±1)°C irradiation temperatures.

DETERMINATION OF PRODUCT DISTRIBUTIONS AND ENANTIOMERIC EXCESSES

Irradiated **PVAc** films were extracted repeatedly for 2–3 h with 50–100 mL aliquots of 20/80 (v/v) *n*-pentane/diethyl ether until the last one contained no detectable UV-Vis absorbances ascribable to aromatic species. The combined extracts were divided into 2 parts in a 1/3 (v/v) ratio. One-fourth of the extracts was reduced to residue by simple distillation at ca. 50°C (hot water bath). The residue was dissolved in hexanes and analyzed by HPLC (silica column). Analyses from at least three injections were averaged to obtain the conversion and relative product distribution (Xu and Weiss 2003); the mass balance was always $>80\%$.

The remaining extract was concentrated to residue by bubbling N_2 through it. The residue was dissolved in hexanes and its components were separated on a semi-preparative HPLC column. The *ee* of the hexane solution of each separated chiral product was then determined by HPLC on a Chiralcel OJ-H column using the averaged peak area ratios of its (*R*) and (*S*) enantiomers at four different detection wavelengths with 1 or 2 injections. All of the HPLC peaks were compositionally homogeneous in that the shapes of their UV-Vis absorption spectra did not change as they were recorded at various points during the peak elution (Xu and Weiss 2003).

A small aliquot of irradiated ethyl acetate solution was analyzed by HPLC with a silica column to obtain the conversion and relative product distribution. The remaining portion was concentrated (N_2 bubbling) and the residue was analyzed as described above to determine *ee* values of photoproducts and remaining **1**.

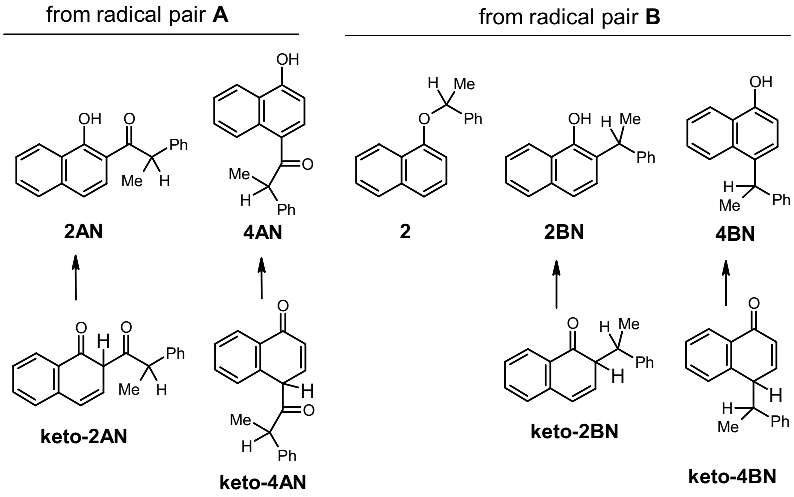
RESULTS AND DISCUSSION

COMBINATIONS OF RADICAL PAIRS A AND B FROM (*R*)-**1**. GENERAL CONSIDERATIONS

After photo-induced lysis of (*R*)-**1**, in-cage combination of radical pair **A** can reform the starting ester or form the keto intermediates of the eventually isolated photo-Fries rearrangement products, 1-[2-(1-hydroxynaphthyl)]-2-phenyl-1-propanone (**2AN**) and 1-[4-(1-hydroxynaphthyl)]-2-phenyl-1-propanone (**4AN**) (Scheme 2) (Bellus 1971, Martin 1992, Miranda 1995, Miranda and Galindo 2003a, b); tautomerization of the keto intermediates (Mori et al. 2004b) occurs rapidly on the time scale of our laboratory manipulations, even in saturated paraffins. The apparent and actual 1,3- and 1,5-sigmatropic H-shifts occur in the range of microsecond to seconds, depending strongly on the nature of the solvent, and many are intermolecular (Chiang et al. 1984a, b, Arai et al. 1994, 1995).

Alternatively, one of the radicals of the pair may escape from the cage, resulting in the eventual formation of out-of-cage products (vide infra). Finally, radical pair **A** may become singlet prochiral radical pair **B** if the 2-phenylpropanoyl radical cleaves into carbon monoxide and a 1-phenylethyl radical more rapidly than it adds to its 1-naphthoxy partner or escapes from the cage. Analogous in-cage combinations of radical pair **B** produce ether **2** as well as keto intermediates that tautomerize into 2-(1-phenylethyl)-1-naphthol (**2BN**) and 4-(1-phenylethyl)-1-naphthol (**4BN**). The structures of the keto intermediates and their enol tautomers from radical pairs **A** and **B**, as well as the directly formed ether **2** from radical pair **B**, are shown in Scheme 1.

The decarbonylation process is very rapid, requiring only ca. 24 ns at 23°C in isooctane (Braun et al. 1962, Turro et al. 1983, Tsentalovich and Fischer 1994, Zhang and Nau 2000, W.M. Nau et al., unpublished data). Its rate constant (k_{-CO}) is independent of viscosity in paraffinic media (Tsentalovich and Fischer 1994, W.M. Nau et al., unpublished data) and depends only slightly on the polarity of its environment (Lunazzi et al. 1983, Tsentalovich and



Scheme 1 – Direct combination and tautomerization products from radical pairs **A** and **B**.

Fischer 1994). For instance, k_{-CO} for decarbonylation of the phenylacetyl radical at room temperature has been measured to be 5.3×10^6 s^{-1} in hexane ($\varepsilon = 1.88$), 2.6×10^6 s^{-1} in methanol ($\varepsilon = 32.7$) and 1.7×10^6 s^{-1} in acetonitrile ($\varepsilon = 37.5$) (Riddick et al. 1986, Tsentalovich and Fischer 1994). The value of k_{-CO} has not been measured in **PVAc** or in ethyl acetate. Because the relative permittivities (Riddick et al. 1986, Lindemann 1999) of isooctane ($\varepsilon = 1.94$), ethyl acetate ($\varepsilon = 6.02$), and **PVAc** films ($\varepsilon = 3.5$ at 50°C) are similar, we use k_{-CO} in isooctane for the values in ethyl acetate and **PVAc**.

As mentioned above, radicals in both of the radical pairs can diffuse from their initial solvent cages and undergo out-of-cage reactions that result in fragmentation products (**3**-**5**), radical pair **B**-like combination products (**2**, **2BN**, and **4BN** but from different original partners), and a crossed combination product, 2,3-diphenylbutane (**6**) (Scheme 2). The latter is derived from dimerization of 1-phenylethyl radicals that escape from their initial cages, and it is a clear indicator that some of the other photoproducts (N.B., **2**, **2BN**, and **4BN**) also are formed by radicals that re-encounter each other after escaping from the cages in which they were 'born'. Since **4** and **5** can be produced through other pathways besides encounter of two 1-phenylethyl radicals, we have used only **6** as a monitor of the importance of re-encounter processes by radical pairs **A** or **B** (Gu et al. 1999, Gu and Weiss 2000).

Small yields of a *decarboxylation* product, 1-(1-naphthyl)-1-phenylethane were detected also. It is produced by a concerted extrusion of CO_2 from the excited singlet state of (R)-**1** (Finnegan and Knutson 1965, 1967, Gu et al. 2001, Mori et al. 2003). In addition, abstraction of an H-atom by the constituents of radical pairs **A** and **B**, especially from the backbone of the **PVAc** polymer or from ethyl acetate, can lead to products in which a radical is attached to the polymer or solvent. Based upon our mass balances and UV-Vis absorption spectra of the films after irradiation and extraction, the yields of such products must be small and their specific structures were not explored. In addition, the relative product yields do not change when irradiations of (R)-**1** are allowed to proceed up to 30% conversion (Gu et al. 1999, 2000a). The relative yields and *ee*s of photoproducts from irradiations of (R)-**1** in **PVAc** films and ethyl acetate, as well as in completely amorphous **PE** films and *n*-hexane, are shown in Table I. The relative yields of photoproducts in Table I differ slightly from the distributions reported previously for irradiations of racemic **1** in **PVAc** and ethyl acetate (Gu et al. 2002). In large part, the disparity can be traced to a less precise method of analysis, gas chromatography, being used in the previous study.

In the absence of secondary photolytic reactions (vide infra), the regio- and stereo-chemistries of the photoreactions of (*R*)-**1** are dependent on steps in Scheme 2 up to and including the radical pair combinations yielding **2** and the keto intermediates of **2AN**, **4AN**, **2BN**, and **4BN**. Enolization should affect neither the relative yields nor the chiral centers of the photoproducts. To simplify subsequent discussions, only the final enolized products will be indicated rather than the first-formed keto intermediates.

RADICAL PAIR COMBINATIONS IN ETHYL ACETATE; COMPARISONS WITH RESULTS IN *n*-HEXANE

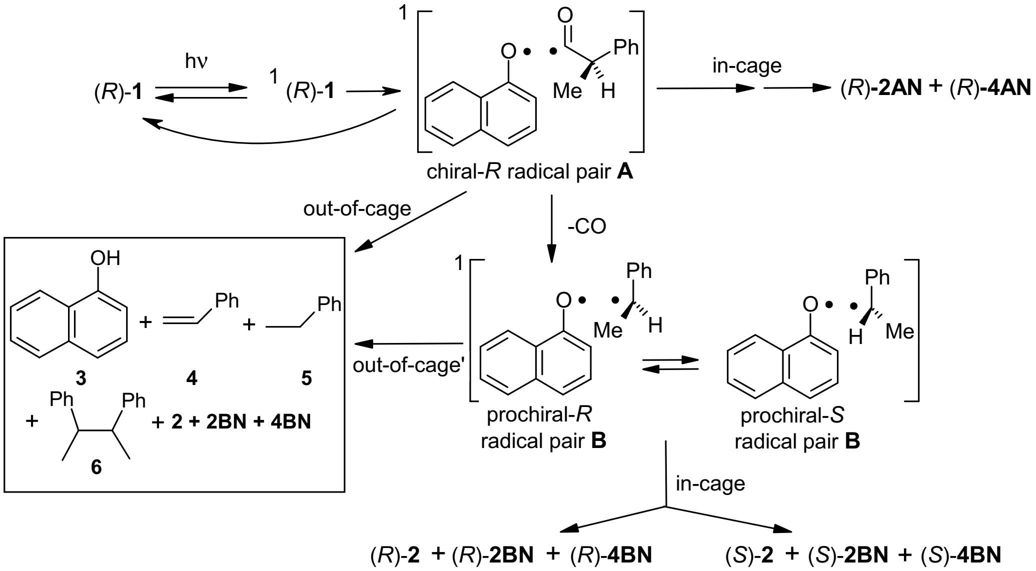
Based on the relative yields of **6** produced upon irradiation of (*R*)-**1** in ethyl acetate (Table I), **2**, **2BN**, and **4BN** are primarily from in-cage combinations of radical pair **B** at and below room temperature, but some reaction from out-of-cage encounters, especially at 50°C, occurs as well. This assertion is supported by the regio- and stereo-selectivities of combinations of radical pairs **A** and **B**.

The regioselectivity of radical pair combinations depends in part on the relative spin densities at the positions of the 1-naphthoxy radical where its partner adds (C(4) $>$ C(2) $>$ O(11); see Figure 1 for the atom numbering of **1**) (Dixon et al. 1973, Gu and Weiss 2001b), the initial orientation of the radical pair, and the degree to which the initial orientation of the radical pair is retained throughout its lifetime. The latter factor is very dependent upon the nature of the environment surrounding the radical pair.

In part because the viscosities of *n*-hexane (0.3036 cP) and ethyl acetate (0.426 cP) (Timermans 1965) are similar at 23°C, the regioselectivities of the radical pair combinations in the two solvents are somewhat similar: **2AN**/**4AN** $>>$ 1 and **2BN**/**4BN** $<<$ 1 and the **2AN**/**4AN** ratios suggest that radical pair **A** combines predominantly in-cage in both solvents (Bellus 1971, Martin 1992, Miranda 1995, Miranda and Galindo 2003a, b). The initial orientation of radical pair **A** places the radical center of 2-phenylpropanoyl closer to C(2) than to C(4) of its 1-naphthoxy radical partner (Figure 1) (Xu and Weiss 2005a). Furthermore, the much higher **2AN**/**4AN** product ratios in ethyl acetate than in *n*-hexane indicate that in-cage motions of the radicals are also mediated by their strong interactions with the polar ethyl acetate solvent (Terazima 2000, Gu et al. 2002). An additional consequence of the strong solvent-radical interactions is that cage-escape *and* the tumbling motions of radical pair **B** leading to loss of enantiomeric excess of **2**, **2BN**, and **4BN** (*vide infra*) are attenuated. The short lifetimes of the radical pairs and the high activation energy (ca. 54.4 kJ/mol (Conradi et al. 1979)) for another possible route to loss of chiral identity, internal rotation about the phenyl-benzylic C–C bond of 1-phenylethyl, precludes it from competing with combinations within a cage. Although the *ee* values of the decarbonylated products in ethyl acetate are small, they are clearly larger than those in *n*-hexane (in which *ee* values of **2**, **2BN**, and **4BN** products are virtually 0%) and indicate that, within a cage, the combination rates of radical pair **B** are comparable to the rate of tumbling of a 1-phenylethyl radical.

REGIOCHEMISTRY OF RADICAL PAIR COMBINATIONS IN PVAC FILMS AT 5 AND 50°C. COMPARISON WITH RESULTS IN AMORPHOUS PE FILMS

The absence of photoproduct **6** upon irradiations of (*R*)-**1** at 5°C (i.e., in the glassy state) and at 50°C (i.e., in the melt state) are an indicator that the combinations of both radical pairs **A** and **B** are almost exclusively in-cage in both the glassy and melt phases of **PVAc**. At both temperatures, the **2AN**/**4AN** ratios are much higher than in ethyl acetate or **PE** films. The van der Waals volume of (*R*)-**1** (ca. 254 Å^3) (Bondi 1964) is much larger than the mean free hole volume in **PVAc** both below and above the glass transition temperature (ca. 85 Å^3 at 5°C and ca. 105 Å^3 at 50°C) (Kobayashi et al. 1989). Since **PVAc** is swelled to dope (*R*)-**1** into the films, the guest molecules are sur-



Scheme 2 – Mechanistic steps in the irradiation of (*R*)-**1** emphasizing the central roles of radical pairs **A** and **B**.

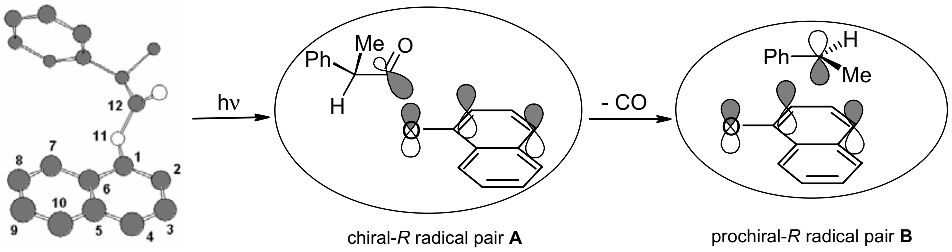


Fig. 1 – Cartoon representation of the approximate initial orientation of radical pair A produced from the excited singlet state of (*R*)-**1** and the unspecified initial orientation of radical pair B showing one of the two possible prochiralities. In the structure of (*R*)-**1** (at left), from single-crystal X-ray diffraction (Gu et al. 2001), the solid and open circles represent carbon and oxygen atoms, respectively; hydrogen atoms have not been included for clarity.

rounded tightly by many polymeric chains after removal of the solvent, so that the size and shape of the reaction cavities are defined in large part by the size and shape of (*R*)-**1**; because the relaxation processes of polymeric chains in **PVAc** films are slower, especially in the glassy state, than the rate of radical pair combinations (Angell 1995, Yoshii et al. 2000, Seymour and Carraher 2003), the initial conformation of (*R*)-**1** at the moment of its electronic excitation can have a large influence on the chemical course of product formation (i.e., there is a "templating" effect) (Weiss et al. 1993, Gu et al. 1999, Gu and Weiss 2000). In both **PVAc** and **PE** films, the greater proximity of the radical center of 2-phenylpropanoyl to C(2) than to C(4) of 1-naphthoxy immediately after the lysis of the excited singlet state of (*R*)-**1** (Figure 1) and the attenuation of motions of the radicals caused by the templating effect and high local viscosity of the reaction cages promote preferential formation of **2AN**.

The rate constants for formation of the keto intermediates of the **AN** products from radical pair

TABLE I

Relative yields (%) and enantiomeric excesses (%) of photoproducts from irradiations of (*R*)-1 in ethyl acetate, *n*-hexane,[a] and PVAc and PE[a] films at various temperatures[b].

medium	T (˚C)	**2AN**[c]		**4AN**[c]		**2**[c]		**2BN**		**4BN**		**3**	**4**	**6**	**2AN/ 4AN**	**2BN/ 4BN**
		%yield	%*ee*	%yield	%*ee*	%yield	%*ee*	%yield	%*ee*	%yield	%*ee*					
ethyl acetate	50	18.3±3.2	99	21.0±2.2	99	1.0±0.3	2	6.6±0.6	1	20.1±0.3	2	16.7±1.3	8.2±0.4	7.2±1.8	0.9	0.33
	23	36.5±4.1	99	15.5±1.3	99	1.3±0.2	2	5.9±0.8	2	18.5±0.2	3	10.3±0.7	4.0±0.7	7.4±0.6	2.4	0.32
	5	49.2±4.2	99	17.7±2.3	99	1.1±0.3	2	2.7±0.1	4	12.1±1.2	2	11.0±1.3	2.4±0.8	2.9±0.4	2.8	0.22
PVAc[d]	50	86.6±3.0	55-90[e]	2.2±1.0	99	2.6±0.2	7	1.1±0.3	5	3.1±0.2	3	3.9±0.4	0.5±0.2	0	39	0.35
[d]	5	36.7±1.3	43-70[e]	1.5±0.1	99	6.1±0.4	5	0.2±0.1	3	27.5±0.3	3	19.9±0.5	5.3±0.4	0	24	0.01
hexane	23	43.0±2.7	99	22.8±2.0	99	3.1±0.1	< 1	4.3±0.3	< 1	12.3±0.5	< 1	4.5±0.4	2.5±0.8	7.5±2.9	1.9	0.35
PE[d, f,g]	23	70.5±2.5	99	13.6±0.4	99	1.0±0.1	19	1.4±0.1	21	5.6±0.8	22[h]	5.2±0.5	0.7±0.3	0	5.2	0.25

[a] See Xu and Weiss 2005b. [b] The sum of the relative yields of all products is taken as 100%; mass balance is $>$ 80%; *ee*s of (*R*)-**1** were 99.5% before and after irradiation; the experimental error in *ee* determinations was ± 1%. [c] (*R*)-Enantiomer in excess. [d] Trace of **5** detected. [e] See text. [f] Completely amorphous **PE** films. [g] $\varepsilon \approx 2.3$ at 23 °C (Lindemann 1999). [h] $< \pm 2\%$.

A can be calculated approximately using the decarbonylation rate of 2-phenylpropanoyl (k_{-CO}) in isooctane (see above) and the relative yields of the **AN** and **BN** products (Equation 2) (Gu and Weiss 2000). Using this method, $k_{2AN} = (0.8 - 1.3) \times 10^9$ s^{-1} for **2AN** and $k_{4AN} = (2.1 - 3.3) \times 10^7$ s^{-1} for **4AN** in **PVAc** films at 50°C. Although it is possible to perform similar calculations using the data from experiments in **PVAc** at 5°C, the numbers have questionable physical meaning because the events leading to photoproducts in the glassy state are stochastic in nature (Wang et al. 1990). By comparison, from data obtained in unstretched, completely amorphous **PE** films (Xu and Weiss 2005b), $k_{2AN} = (0.5 - 1.2) \times 10^9$ s^{-1} at 60°C and $(2.2 - 3.7) \times 10^8$ s^{-1} at 23°C and $k_{4AN} = (1.3 - 3.0) \times 10^8$ s^{-1} at 60°C and $(4.2 - 7.1) \times 10^7$ s^{-1} at 23°C. The ranges of values are due to our uncertainty about the origin of 1-naphthol (**3**). If all of **3** is from 1-naphthoxy radicals within radical pair **A** (see out-of-cage route in Scheme 2), [**3'**] = 0 in eq 2 and the larger value is applicable; if **3** emanates from 1-naphoxy radicals of radical pair **B** (see out-of-cage' route in Scheme 2), [**3'**] is the same as the total yield of **3** and the lower value is more correct. Since **3** is probably produced via both routes, the rate constants should take intermediate values.

Regardless, the values clearly demonstrate (1) that $k_{2AN}$is significantly larger than k_{4AN} in each of the films, (2) that k_{2AN} is almost the same in the two films at comparable temperatures, and (3) that the rate of formation of **4AN** is slowed much more in the melt of **PVAc** than in amorphous **PE**. The latter observation may be attributed to an additional factor that retards radical motions within **PVAc** cages—strong dipole-dipole interactions of the radicals with surrounding acetate pendent groups (Terazima 2000, Gu et al. 2002). Apparently, the much smaller motions required to bring the radical center of a 2-phenylpropanoyl radical to a position where it can form a bond with C2 of its 1-naphthoxy within radical pair **A** is not affected by the polarity of its environment to the same extent as when the bond is made at the more distant C4. However, formation of **2AN** requires the radicals of radical pair **A** to move at least 3.1 Å with respect to each other (Xu and Weiss 2005b).

$$k_{2AN} \approx \frac{k_{CO} \times [2AN]}{[2] + [2BN] + [4BN] + [3']} \qquad (2a)$$

$$k_{4AN} \approx \frac{k_{CO} \times [4AN]}{[2] + [2BN] + [4BN] + [3']} \qquad (2b)$$

Contrary to the results noted for combinations of radical pair **A**, combinations of radical pair **B** favor **2** and **4BN** in both the glassy and melt states of **PVAc** (Table I). The decreased yield of **2BN** is most striking in the glassy state at 5°C where exceedingly long relaxation times of the polymer chains must amplify inhomogeneities of reaction cavities—reaction cavities may be described better in the glassy state stochastically rather than as an ensemble average (Wang et al. 1990). In the glassy state of the polymer, the motions of long chain segments become very slow and have time constants, on the order of 100 s (Angell 1995, Yoshii et al. 2000, Seymour and Carraher 2003), that are much longer than submicrosecond time scales for combination of the radical pairs. Therefore, only motions involving very short chain segments and pendent groups can facilitate the movement of radicals leading to their combination. As a consequence, radicals are still capable of reorientation, but they can move only short distances over relatively long periods. Those 2-phenylpropanoyl radicals that live long enough to lose CO (leading to radical pair **B**) must be 'born' from excited singlet states of (R)-**1** whose conformations are locked by the glassy reaction cavities into positions which do not promote **AN**-type product formation. We suspect that the long lifetimes of the ensuing radical pair **B** here compensates for the lack of radical mobility. The net result is that memory of the initial positions of radical pair **A** is lost in radical pair **B** and electronic considerations prevail in the eventual combination events.

Polarity changes cannot be responsible for these observations because the yield of **2AN** decreases dramatically between 50 and 5°C in **PVAc** but increases significantly over the same temperature change in ethyl acetate. The large increase in the yield of 1-naphthol (**3**) at 5°C in **PVAc** is also consistent with a large fraction of the radical pairs being unable to move easily in their glassy reaction cages (Wang et al. 1990, Gu et al. 2002). The very slow radical movement in **PVAc** films at 5°C provides the 1-naphthoxy radical more opportunities for hydrogen abstraction (principally from the polymer) to form photoproduct **3** and make the 2-phenylpropanoyl radical less likely to combine at the C(2) position of 1-naphthoxy at 5°C than at 50°C, even though decarbonylation of the 2-phenylpropanoyl radical is also slowed significantly at 5°C (Turro et al. 1983). At this point, we view the very small **2BN**/**4BN** ratio in **PVAc** at 5°C as another indication that the glassy states increases templating effects and the distribution of cage types experienced by the radical pairs.

STEREOCHEMISTRY OF RADICAL PAIR COMBINATIONS IN GLASSY AND MELT PHASE PVAC FILMS. COMPARISON WITH RESULTS IN AMORPHOUS PE FILMS

The formation of a large amount of (S)-**2AN** can be attributed to the enhanced restrictions to motions within the reaction cages in the glassy and melt phases of **PVAc** films. Analogous loss of enantiomeric purity of **2AN** has been observed during irradiations of (R)-**1** in **PE** films with relatively high crystallinities (unlike the **PE** film employed here) (Xu and Weiss 2005b). It can be traced to protraction of the lifetime of keto-(R)-**2AN**, increasing the probability of its excitation (Jiménez et al. 1997, Mori et al. 2004a) and reversible intramolecular γ-H-atom abstraction at the chiral center (i.e., a secondary reaction analogous to the first step in the Norrish-Yang reaction (Yang and Elliott 1969, Stephenson et al. 1971)) before tautomerization to (R)-**2AN** can occur. An analogous intramolecular H-abstraction upon excitation of keto-**4AN** is not possible for steric reasons, and **4AN** remains enantiomerically pure under all of the irradiation conditions we have explored. The range of *ee*s for **2AN** from **PVAc** films reported in Table I is a consequence of somewhat different irradiation times, fluxes, and conversions of (R)-**1** in the several experiments conducted.

Based on the *ee* values for **2**, **2BN**, and **4BN** (Table I), the stereoselectivity of radical pair **B** combinations in both **PVAc** films and ethyl acetate is much lower than in **PE** films. Thus, although the reaction cages of **PVAc**, especially in its glassy state, have stiffer walls than the cages of the **PE** films, they are unable to afford higher stereoselectivity in products from prochiral radical pair **B** combinations. As noted above, the regiochemical results suggest that the absolute rates of both translational and tumbling motions (leading to interconversion of the prochiral-*R* and prochiral-*S* radical pairs **B**; Scheme 2) are slowed in **PVAc** films. However, the relative retardation of tumbling by the 1-phenylethyl radical must be less within the reaction cages of **PVAc** than those of **PE**.

CONCLUSIONS AND COMMENTS ON THE INFLUENCE OF ENVIRONMENT ON THE FATES OF RADICAL PAIRS

Radicals such as those in radical pairs **A** and **B** are more polarizable than their parent species (i.e., molecules produced by adding an H-atom to the radical site). As a result, they diffuse more slowly, especially in polar media where dipole-dipole and H-bonding interactions may be important (Terazima 2000). The magnitude of the decreased mobility depends on several factors, including the properties of the solvent and the radicals, and the characteristics of the radical motions. In addition, the slower relaxation processes of polymeric chains in **PVAc** films than in **PE** films affect the chemistry of radical pair combinations. For these reasons, the regioselectivity of radical pair **A** combinations is much higher in both the melt and glassy states of **PVAc** films than that in completely amorphous **PE** films at 23°C (i.e., in their melt state, far above T_g), but the stereoselectivity of prochiral radical pair **B** combinations is much lower in **PVAc**. In addition, even though reaction cavities of glassy **PVAc**, with their stiffer walls, control better the regiochemistry of radical pair combinations than those of melt **PVAc**, they do not control as well the stereochemistry. This behavior is reminiscent of the stiffer reaction cages within the interfacial regions of partially crystalline **PE** films, where radical pair combinations are less stereoselective than in the amorphous cages of the same film (Xu and Weiss 2003, 2005a, b, c).

From a synthetic standpoint, the results obtained here emphasize the need to control the relationship between the rates of radical tumbling and translation, as well as the relationship between the rates of in-cage motions and cage-escape, if high stereo- and regio-selectivities are to be achieved. It should be possible eventually to tune the important factors that modulate the motions of the radicals (N.B., the polarity and physical state of the medium, the shape, size and electronic properties of radicals themselves, and temperature) to maximize the yields of regio- and stereo-isomers of desired products. The research performed here contributes to our understanding how to reach that goal.

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RESUMO

A régio- e a estereoquímica das fotoreações de (R)-2-fenilpropanoato de 1-naftila foram investigadas em filmes de poli (acetato de vinila) nos estados vítreo (5°C) e fundido (50°C) e em acetato de etila. Estes resultados foram comparados aos obtidos em filmes de polietileno e em *n*-hexano. A regioseletividade das combinações de pares radicalares intermediários 1-naftoxi/(R)-2-fenilpropanoila é muito maior nos estados fundido e vítreo do poli (acetato de vinila) do que no estado fundido de filmes de polietileno, mas a estereoseletividade das combinações de pares de radicais intermediários proquirais 1-naftoxi/(R)-2-fenilpropanoila é muito menor em poli (acetato de vinila). Os resultados enfatizam a necessidade de se controlar a relação entre as taxas de tombamento e de translação de radicais, assim como a relação entre as taxas dos movimentos no interior da gaiola ou de escape da gaiola, se for desejado atingir estéreo- e regioseletividades elevadas. Propõe-se um quadro mecanístico a respeito de como os radicais dos pares intermediários são afetados pelos vários meios e interagem com eles.

Palavras-chave: par de radicais, estereoseletividade, relaxação de polímeros, foto-Fries.

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