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Photo-Fries Rearrangements of 2-Naphthyl Acylates as Probes of the Size and Shape of Guest Sites Afforded by Unstretched and Stretched Low-Density Polyethylene Films. A Case of Remarkable Selectivity

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We report that films of low-density polyethylene (LDPE)[1] supply sites (i.e., reaction cavities[2]) whose size, shape, and wall stiffness[2] are capable of altering drastically the reaction courses of guest molecules. Some of the factors determining the control exerted by LDPE are examined with the photo-Fries rearrangements[3] (Scheme I) of the acetyl and myristoyl esters of 2-naphthol (**1a** and **1b**, respectively).

LDPE represents a very complex family of materials which consist of (lamellar) crystalline[4] and amorphous regions which frequently contain short alkyl branches.[5] The *microscopic* properties of LDPE can be altered drastically by *macroscopic* cold-stretching, which aligns the crystalline domains along the direction of extension.[6] Although there have been several diverse studies which exploit LDPE as a constraining medium,[7] very few have examined the consequences of film stretching on the reactivity and selectivity of guest molecules;[8] the results are only suggestive and anecdotal. Of importance in this regard is an assessment of the average size, shape, and wall flexibility of the sites afforded guest molecules by unstretched and stretched films.[2]

The photo-Fries reactions of **1** proceed via homolytic scission of the acyl–oxy bond to form 2-naphthyloxy and acyl radicals as a geminal pair.[3] Our inability to sensitize the reaction with benzophenone in benzene indicates that bond scission probably occurs within the excited singlet-state manifold.[3,9] The fate of this radical pair determines the eventual photoproduct mixture.

Scheme I

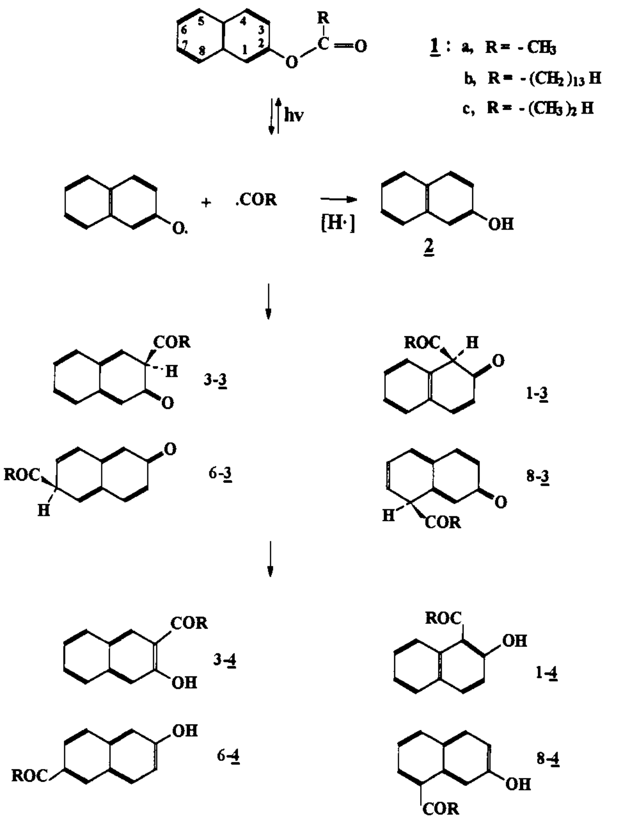

Table I. MNDO Calculations of the Free-Electron Density at the Carbon Atoms of the 2-Naphthyloxy Radical (R•) and Energies of Formation of **3c**, the Keto Isomers Expected from Irradiation of **1c**

naphthyl ring position	R•	ΔH_f of **3c** (kcal/mol)	naphthyl ring position	R•	ΔH_f of **3c** (kcal/mol)
1	0.40	−34.2	6	0.13	−19.4
3	0.06	−21.5	7	0.00	22.2
4	0.01	−20.1	8	0.10	−18.2
5	0.00	−22.2			

If cage escape is more rapid than radical recombination, an H-atom can be scavenged by the 2-naphthyloxy radical to yield 2-naphthol (**2**). Control experiments indicate that solvent molecules rather than acyl radicals may be a major source of these H-atoms:[3b] no evidence for the formation of ketenes was found in liquid media with poor H-atom donors, like *tert*-butyl alcohol. Also, the absence of alkyl 2-naphthyl ethers as photoproducts in all of the media examined indicates that decarbonylation does not compete with in-cage recombination. Loss of CO from acetyl or myristoyl radicals is expected to have activation energies which are relatively large (ca. 8–15 kcal/mol[10]) compared to the barriers from competing reactions available to the radical pairs.

If in-cage radical recombination is more rapid than cage escape, **1** or one of several keto rearrangement products (*n*-**3**) (which enolize eventually to acyl 2-naphthols, *n*-**4**) may be formed. In Table I, the MNDO-calculated free-electron density on each of the carbon atoms of the 2-naphthyloxy radical provides a crude measure of the *kinetic* probabilities of the various *n*-**4** being formed, and the energies of formation of the *n*-**3c** (from 2-naphthyl propanoate, **1c**) assess the approximate *thermodynamic* probabilities; neither parameter includes entropic factors, which may be very important in some solvent systems but should be similar in LDPE and paraffin solvents. As expected, both indicators predict that the *n*-**4** for which Lewis structures can be drawn will be favored.

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Table II. Photoproduct Distributions[a] from Irradiations[b] of **1** in Various N_2-Saturated Media

					photoproduct distribution				
	concn (M)	solvent	*t* (°C)	% conv	**2**	1-**4**	3-**4**	6-**4**	8-**4**[f]
1a	4.9×10^{-3}	*tert*-butyl alcohol	25	16(2)	32(1)	31(1)	11(1)	17(1)	0
1b	6.2×10^{-4}	hexane[c]	50	14(2)	85(3)	14(1)	0	1(0.2)	0
1b	(1 wt %)	heneicosane (liquid)	50	12(3)	38(3)	53(3)	0	9(2)	0
1b	6.8×10^{-4}	ethanol	25	12(1)	26(1)	62(4)	0	10(1)	0
1b	4.9×10^{-3}	*tert*-butyl alcohol	25	12(2)	0	86(4)	0	14(1)	0
1a	ca. 1.5×10^{-3}	LDPE[d] unstretched	25	12(2)	21(1)	31(1)	20(1)	28(1)	0
		LDPE[d] stretched	25	8(2)	32(2)	0	31(1)	37(1)	0
1b	5×10^{-4}–10^{-3}	LDPE[e] unstretched	25	≤7	0	0	75(2)	25(2)	0
		LDPE[e] stretched	25	≤7	0	0	92(2)	8(2)	0

[a] One standard deviation is shown in parentheses. [b] Pyrex and water filtered output of a 450-W medium-pressure Hanovia Hg arc. [c] Freshly opened Baker Spectrograde; the relative yields were dependent upon the purity and the hisotyr of the hexane employed. [d] Average of measurements on 6 films. [e] Average of measurements on 12 films. [f] Trace amounts may have been present in some experiments.

The photo-Fries rearrangements of **1a** have been examined previously,[9] but a recent study reported somewhat different results.[11] To avoid any ambiguity, the expected photoproducts from **1a** and **1b** (except 8-**4b**) were synthesized independently, and our HPLC analyses considered the molar extinction coefficient of each at the detector wavelength. Our results in isotropic media agree with those of ref 9. The almost complete absence of 8-**4** from all of the experiments and especially 3-**4b** from all of the liquid-phase experiments should be noted (Table II). Both were expected to be major components on the basis of the data in Table I. Even more remarkable is the observation that *both of the major products from liquid-phase irradiations of **1b**, **2**, and 1-**4b** are totally absent from the LDPE experiments.* In their place are found the previously undetected 3-**4b** as the major photoproduct and some 6-**4b**. The shorter chained **1a** experiences similar changes in its photoproduct distributions in LDPE, but the selectivity is less pronounced.

The results in Table II can be interpreted on the basis of the constraints imposed on molecules of **1** and their intermediates at the sites offered to them in the LDPE matrices. It is known that guest molecules are excluded from the crystalline portions of LDPE at the temperatures of our experiments.[5] The principal locations of guest molecules in unstretched LDPE are the amorphous parts and the interfacial regions between crystalline and amorphous domains.[5,12] Upon stretching of a film, guest molecules in the amorphous parts tend to translocate to the interfacial regions.[5,12] There must be a distribution of shapes and sizes associated with each site type; our photochemical results provide information about only that fraction of sites which is occupied. It is clear that the distribution is narrow and becomes narrower after a film is stretched.[12b,c]

The absence of **2** from irradiations of **1b** in LDPE films is an expected consequence of the attenuated diffusion (in effect, stiffened cavity walls) of geminate pairs of 2-naphthyloxy and myristoyl radicals in their highly viscous local environments.[7a] Slowed diffusion also increases the probability that the radical pairs will recombine to yield **1b** or an isomer of **3b**. Since the shorter acetyl radical from **1a** is able to diffuse much more rapidly in LDPE than is a myristoyl radical,[13] its escape from a 2-naphthyloxy partner will be much more rapid. Thus, the proportions of in-cage and out-of-cage reactions can be regulated in LDPE by an assidous choice of **1** chain length.

Film stretching blocks completely the formation 1-**4a** and increases the probability that radical recombination will yield 3-**3a** rather than 6-**3a**. In irradiations of **1b**, film stretching again increases the probability that radical recombination will occur at the 3-position of the naphthyl ring. In independent studies, we have found that the rates of diffusion of guest molecules are slowed by film stretching.[1] This, in part, may explain the changes in the yields of **2**.

From the preference for the more extended 3-**4** and 6-**4** photoproducts, we surmise that the average sites experienced by molecules of **1** in unstretched LDPE are somewhat cylindrical and have sufficient latitude in their narrowest dimensions to permit an acetyl group to approach the 1-position of a naphthyl ring in a bond-forming orientation from a distance which is at least the sum of the van der Waals radii of the two species. Apparently, the sites in unstretched and stretched LDPE are not large enough to permit a myristoyl radical, even in a bent conformation, to have the same approach to the 1-position. Since acyl radicals are directed preferentially by the sites to the 3- and 6-positions of the 2-naphthyloxy ring, the reaction course favors not only intermediates which are more cylindrical in shape but also the reacting species which can be contained within a somewhat cylindrical volume. This preference is exacerbated by film stretching, decreasing also the probability that an acyl radical center, created at the 2-position of a naphthyl group, will be able to migrate across the aromatic rings to the vicinity of the 6-position.

In conclusion, we have demonstrated that application of a *macroscopic* force to LDPE, resulting in film stretching, causes dramatic *microscopic* changes which influence the proportion of incage and out-of-cage reactions and the selectivity of the in-cage reactions. These changes may arise from alterations in the mole fraction of each site type occupied, the average shape and size of the sites (N.B., the conformations of the molecules residing therein), or a combination of both factors. Future work will attempt to differentiate these possibilities and to quantify their contributions.

In addition to the mechanistic importance of these observations, they have obvious synthetic potential. In fact, there is no reason to believe that other polymer formulations of LDPE (or many other polymers!) do not provide guest sites with somewhat different shapes, sizes, and wall stiffnesses.[2] The photo-Fries rearrangements of **1** are a convenient and sensitive monitor of such differences.

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