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A COMPARATIVE STUDY OF AN ORGANIC PHOTOREARRANGEMENT IN SOLUTION, IN THE PURE CRYSTALLINE PHASE AND IN A POLYMER FILM

Anna D. Gudmundsdottir and John R. Scheffer*
Department of Chemistry, University of British Columbia
Vancouver, V6T 1Y6, Canada

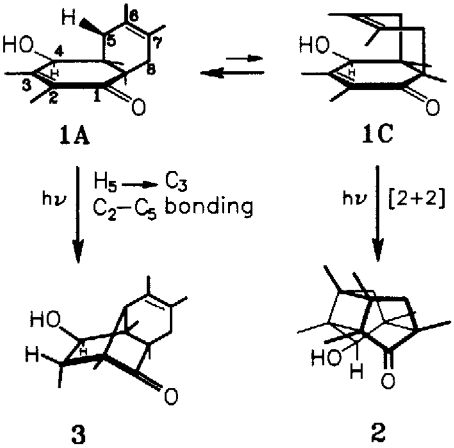
Abstract. The photochemistry of the tetrahydronaphthoquinone derivative 1, which consists of [2+2] cycloaddition in solution and hydrogen abstraction-initiated rearrangement in the solid state, has been studied in poly(methyl methacrylate) and poly(vinyl acetate) films and found to exhibit intermediate behavior that is discontinuous at the glass transition temperature.

Thin films of organic polymers containing dissolved guest molecules are readily prepared by coating glass plates or other suitable surfaces with solutions containing polymer and guest and allowing the solvent to evaporate. The guest molecules in these assemblies find themselves in unique, partially ordered environments that can be altered systematically by changing the polymer structure, tacticity, molecular weight, polydispersity and degree of cross-linking, as well as by varying the temperature above and below the glass transition temperature(s). Surprisingly, despite ease of preparation and potential significance for the fields of microlithography and photography, the use of polymer films as solvent media for carrying out photochemical transformations has received relatively little attention compared to the pure liquid and solid phases.[1] As part of our interest in the modification of chemical reactivity through the use of various organized media,[2] we have embarked on a study of the use of polymer films in organic photochemistry, and in this and the following paper we report some of our initial results.

We reasoned that, since polymer matrices have properties intermediate between liquids and solids, a good starting point would be to investigate a guest molecule whose solution and crystalline phase photochemical behavior was known to be very different. Depending on the photochemical results obtained the polymeric environment could then be classified as being more solution-like or more solid-like. An ideal candidate for study appeared to be 2,3,4aα,6,7,8aα-hexamethyl-1-oxy-4a,5,8,8a-tetrahydro-naphthoquin-4-β-ol (1, Scheme 1), whose solution and crystalline phase photochemistry has been investigated in our laboratory in some detail.[3] As outlined in Scheme 1, irradiation of this material in benzene at room temperature leads to essentially quantitative yields of the cage compound 2, whereas photolysis of crystals of 1 affords very high yields of ketol 3.[3] These results were interpreted as being due to reaction from different conformers in the different media. In the solid state, conformer **1A** is the exclusive conformer present;[4] its double bonds are improperly oriented for cycloaddition and it undergoes relatively slow excited state hydrogen abstraction to afford 3. On the other hand, the solution reaction is thought to occur through conformer 1C which is in rapid equilibrium with **1A**, and even though its equilibrium concentration is low (eclipsing), it gives rise to 2 as the exclusive photoproduct because of a relatively high rate of intramolecular [2+2] photocycloaddition (close approach of parallel double bonds).

The first polymer investigated was low molecular weight poly(methyl methacrylate) as

Scheme 1

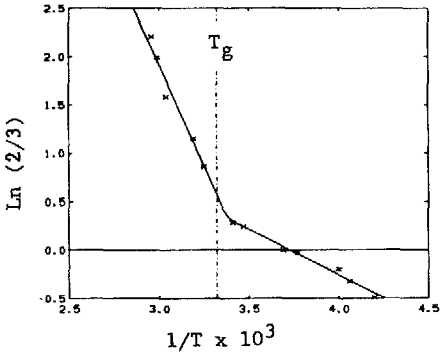


supplied by Aldrich Chemical Company; later runs employed medium and very high molecular weight PMMA with no difference in the results. Before use the polymers were freed of stabilizers and other low molecular weight impurities by dissolution in chloroform, reprecipitation by addition of methanol, suction filtration and vacuum drying. This process was repeated three times. The films were prepared by applying ca. 0.5 ml of a solution containing polymer and photoactive guest to the top of a microscope slide and distributing it evenly over the surface using a second slide as a straightedge. Typically, the solutions consisted of 1.0 g of PMMA and 70 mg of substrate in 30 ml of chloroform; identical photochemical results were obtained over substrate:PMMA ratios ranging from 1% to 40% by weight. After coating the films were air dried for 24 hours and then dried in vacuo for 48 hours at room temperature. The films so prepared had a thickness of 5-10 microns.

The proposed mechanism (Scheme 1) predicts that the 2:3 product ratio should be temperature and/or viscosity dependent. In methanol, however, no temperature dependence was observed from +20 to -60 °C; only in ethylene glycol at -10 °C (viscosity 65 cp) did photoproduct 3 start to appear in the gas chromatographic traces. It was striking, therefore, to find that irradiation of enone 1 in the PMMA matrix at room temperature gave equal amounts of photoproducts 2 and 3. The temperature dependence of this process was measured not in PMMA (T_g = 114 °C) but rather in poly(vinyl acetate) (T_g = 28 °C) so as to be able to assess the effect of passing through the glass transition temperature. The results of these measurements, plotted as ln(2/3) vs 1/T, are shown in Figure 1. This indicates qualitatively that in PVA the 2:3 ratio increases more rapidly above the glass transition temperature than below it. The data can be fitted by two reasonably good straight lines of different slope that meet at the glass transition temperature.

A relatively strightforward explanation of these results is that the viscous polymer matrix exerts a strongly restrictive influence on the topochemically demanding process of conformational isomerization, both in the ground state and the excited state. As Lewis has pointed out,[5] under these conditions the Curtin-Hammett principle no longer applies and the photoproduct ratios reflect the ground state conformer populations. This interpretation is

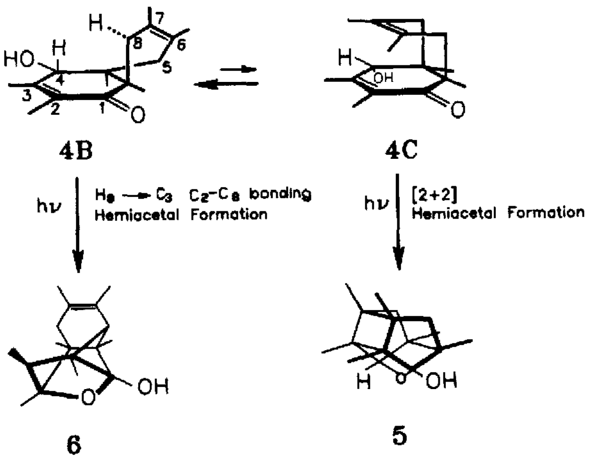
Figure 1. Temperature Dependence of Photoproduct Ratio in Poly(vinyl acetate) Films.



consistent with the observed overall temperature dependence in that lower temperatures would tend to favor the lower energy conformer **1A** and thus lead to greater amounts of photoproduct 3. The reduced sensitivity of the product ratios to temperatures below T_g compared to those above can be ascribed to a matrix-derived topochemical restriction of the motions required for conformational isomerization; above T_g the free volume increases more rapidly with temperature and such restrictions are eased.

We also investigated the polymer matrix photochemistry of the 4-α-ol epimer of enone 1. Previous studies from our laboratory had shown that photolysis of this material (4, Scheme 2) in solution affords the intramolecular [2+2] photocycloaddition product 5, presumably through conformer 4C.[3] Compound 4 crystallizes in conformation 4B, the controlling factor being the preference for the hydroxyl group to lie in the pseudoequatorial position.[4] Intriguingly, crystals of enone 4 proved to be photochemically inert.[3] In polymer films, however,

Scheme 2



enone **4** was far from inert; irradiation in PMMA at 20 °C led to a mixture of compounds **5** (20%) and **6** (80%).[6] Photoproduct **6** corresponds to the product expected (but not observed) from photolysis of **4B** in the solid state; such a reaction has been observed for an analogue of **4** that lacks methyl groups at C(6) and C(7).[3] The present results thus indicate that the lack of reactivity of enone **4** in the solid state is most likely due to a crystal lattice packing effect that is not present in the polymer matrix. Our original suggestion[3] that the lack of reactivity of **4b** in the solid state is due to a C(3)···H(8) distance that lies just outside the sum of the van der Waals radii of carbon and hydrogen is probably not correct. As was the case with enone **1**, the product ratios obtained from irradiation of **4** in polymer films proved to be temperature dependent. A plot of ln (**5**/**6**) vs 1/T in PMMA (the only polymer investigated) was approximately linear with a slope of *ca*. -3×10^3 K.

In summary, we have demonstrated that polymer matrices are useful reaction media for reducing the rates of conformational interconversions to the point that alternative chemical processes that are normally too slow to be observed in solution become competitive. This leads to chemical consequences that in some cases mimic those observed in the solid state, and in others, where the crystal is unreactive for some reason, afford completely new products.

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6. Photoproduct **6**, mp 163-165 °C, exhibited the following spectral features: IR (KBr) 3448 cm^{-1} (OH); NMR ($CDCl_3$) δ 0.87 (s, 3H), 0.88 (d, 3H, J = 8 Hz), 0.97 (s, 3H), 1.01 (s, 3H), 1.76 (d, 1H, J = 20 Hz), 1.85 (s, 1H), 1.87 (q, 1H, J = 8 Hz), 1.94 (d, 1H, J = 20 Hz), 2.59 (s, 3H), 2.66 (s, 3H), 2.78 (s, 1H, exchangeable), 3.32 (s, 1H); mass spectrum m/e (rel intensity) 248 (M^+, 1.3), 187 (66.3), 134 (67.2), 119 (100); Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.63; H, 9.73. These data are in complete agreement with the spectra reported in reference 3 for the analogous photoproduct that lacks methyl groups on the double bond and whose structure was proved by X-ray crystallography.

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