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SILVER ION PERTURBATION OF OLEFIN PHOTOCHEMISTRY

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Abstract: Ag(I) catalysis and inhibition of alkene E/Z photoisomerization, and its effect on tetramethylethylene photochemistry, are reported.

The catalysis of organic photochemical reactions by metal ions has been a subject of considerable recent interest[1], prompted in part by the possible use of metal complexation as a means of amplifying light absorption in otherwise relatively transparent chromophores (as, for example, in potentially useful solar energy storage systems)[2]. Transition metals form relatively strong complexes with the otherwise weakly absorbing alkenes[3] and the perturbation of olefin photochemistry by Cu(I), for example, has been broadly studied[1]. Ag(I) has been relatively little utilized for this purpose, there being reports of (1) Ag(I)-induced photoconversion of methylenecyclohexane to 1-methylcyclohexene (mechanism unknown) followed by a Ag(I) facilitated $\pi_2 + \pi_2$ photodimerization[4] and (2) a Ag(I)-catalyzed net photoaddition of acetonitrile to norbornene (proposed to proceed via an initial photostimulated electron transfer from the alkene to the Ag(I))[5]. In this report we describe the effect of Ag(I) on alkene E/Z photoisomerization and present further observations regarding the Ag(I)-photoinitiated 1,3 hydrogen shift.

The bulk of our studies utilized 2-heptene as a prototypical aliphatic alkene, and its irradiation in the presence of silver triflate showed kinetic catalysis in both directions (i.e., $E \rightleftarrows Z$), cf. Table I. Quantum efficiencies were measured, but with no attempt to dissect the minimal UV absorbances of the Ag(I) solutions into complexed and uncomplexed components (thus "ϕ"). The results (.036 M alkene/.05 M AgOTf): $\phi_{Z\rightarrow E} = 0.025 \pm .006$ vs. "ϕ"$^{Ag(I)}_{Z\rightarrow E} = 0.056 \pm .008$ (7 pts); $\phi_{E\rightarrow Z} = 0.041 \pm .006$ vs. "ϕ"$^{Ag(I)}_{E\rightarrow Z} = 0.042 \pm .007$ (4 pts).

Note that there is a real increase in the efficiency of utilization of absorbed photons for Z, but not E, 2-heptene. The use of silica for heterogeneous photocatalysis is an area of active current interest[6], and we thus studied $AgNO_3$ deposited on SiO_2 in cyclohexane as an alternative medium[7]. Appreciable catalysis was observed with 1.7% Z→E using SiO_2 without Ag(I) vs. 30.4% Z→E with Ag(I) (23 h.). In a separate experiment, the $AgNO_3/SiO_2$/cyclohexane medium gave 17.7% Z→E vs. 11.5% for AgOTf/CH_3CN at identical amounts of Ag(I).

Table I. Ag(I) Perturbation of Olefin E/Z Photoisomerization[a]

	% Isomerization	
Alkene	with Ag(I)	Control
Z-2-heptene	45.7	9.0
E-2-heptene	5.6	1.5
Z-piperylene	18.4	8.7
E-piperylene	22.0	40.0
Z-stilbene	13.3	15.8
E-stilbene	11.6	8.2

[a] All photolyses were in CH_3CN using 254 nm light, ca. 0.04 M olefin and ca. 0.2 M AgOTf, except for the stilbenes which used .01 M olefin and 350 nm light. Times of irradiation: heptenes, 28 h; piperylenes, 2 h., stilbenes, 1 h.

There are several mechanisms by which Ag(I) may be affecting E/Z photoisomerization. One is via electron-transfer to give a more readily isomerized olefin radical-cation[8]. We do not favor this option since (1) concomitant measurements of Ag(I) to Ag(0) reduction indicate that the heptene isomerization is ~5 fold more efficient than reduction (a chain reaction is not excluded), (2) oxygen somewhat inhibits the reaction whereas oxygen catalysis was observed with Ag(I) and norbornene[5] and (3) radical-cation isomerization of stilbene promotes virtually total Z→E conversion[9], contrary to the trend we observe (cf. Table I; the photostationary state is ~50% Z).

An attractive alternative is the well-documented[10] Ag(I) promoted intersystem crossing via a heavy-atom effect. Consistent with this is our finding that when myrcene is photolyzed with Ag(I) using a Corex filter, the triplet derived fraction of the product mixture[11,12] is increased from 12.5% to 21% (it constitutes 79% of a completely triplet sensitized reaction). However the fact that Ag(I) quenches, rather than catalyzes, E-piperylene and Z-stilbene photoisomerization (cf. Table I; the pss for piperylene with Ag(I) is 68% E vs. 36% E without Ag(I)) indicates that there are appreciable distortions of the rate ratios for the decay of precursor intermediates back to the E and Z ground states. This would be expected if, for example, the triplets were not free but still complexed in some fashion with the Ag(I).

Finally, because of the report of an Ag(I) induced 1,3 shift in methylenecyclohexane[4], we looked for evidence of positional double bond isomers in the irradiated heptene, but none were observed. We therefore examined the effect of Ag(I) on the photolysis of tetramethylethylene (**TME**), since a 1,3 shift to 2,3-dimethyl-1-butene (**DMB**) is normally observed in this reaction.[13] In fact, there is indeed a >5 fold increase in **DMB** formation with Ag(I) present, with the proportion of **DMB** in the product mixture rising from 26% (without Ag(I)) to 85% (with Ag(I)) (254 nm, acetonitrile). The reaction is, however, rather inefficient: $"\phi"_{DMB}$ at 0.19 $\underline{M}$ Ag(I) = 5×10^{-4}. The excited-state origin of **DMB** formation in the photolysis of **TME** has been a subject of recent speculation.[13,14] Our observation of catalysis by Ag(I) suggests **DMB** may be formed via a **TME** triplet, a conclusion supported by our observation that **DMB** is the major product formed when **TME** is photosensitized with toluene.[15]

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12. Earlier reports of three products from the myrcene photolysis are in error; we observe four by capillary g.c., with the newly identified product being 6,6-dimethyl-2-methylenebicyclo[3.2.0]heptane, recently reported as being formed by CuOTf photocatalysis (cf. K. Avasthi, S.R. Raychaudhuri and R.G. Salomon, *J. Org. Chem.* **49**, 4322 (1984)). This product appears to have been buried under the β-pinene peak under previously employed g.c. conditions, and is formed in about a 1:2 ratio with the β-pinene.

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15. We have also noted a large solvent effect on the product distribution upon photolysis of TME in acetonitrile versus decane. This will be discussed further in our full paper.

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