SHORT PAPER

J. Chem. Research (S),
2002, 122–123

The Photoisomerization of *cis*- and *trans*-stilbene in ionic liquids

Carlos Lee[a,b], Gleb Mamantov[a‡], and Richard M. Pagni[a*]

[a]Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600, USA
[b]Current address: Department of Chemistry, Tennessee State University, Nashville, TN 37209, USA

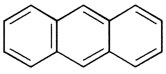
cis- and *trans*-stilbene photoequilibrate in basic *N*-butylpyridinium chloride/$AlCl_3$ via the corresponding stilbene radical cations, whereas in basic 1-ethyl-3-methylimidazolium chloride/$AlCl_3$ the hydrocarbons photoequilibrate by a different mechanism.

Keywords: stilbene, ionic liquids, photoisomerisation, photoinduced electron transfer

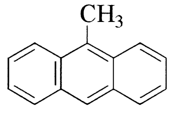
Even though molten salts have been studied for many decades, their use as solvents for organic, organometallic and catalytic chemistry has only come to the fore in the last decade or so.[1] This change in perspective occurred when molten salts were synthesised which were liquid at or near room temperature. Because many of these so-called ionic liquids (ILs) have little or no vapour pressure, they also have potential applications in the burgeoning field of green chemistry.[2] Furthermore, because solutes may be solvated differently in ILs than in traditional solvents, there is the exciting prospect of either enhanced reactivity or entirely new chemistry.

Photochemistry in ILs has been limited but the results intriguing.[3] The photochemistry of anthracene (An) in basic 1-ethyl-3-methylimidazolium chloride (EMIC)/$AlCl_3$ (55 mol% EMIC), for example, afforded the 4+4 dimer,[3b] a result identical to that seen in traditional solvents.[4] In acidic EMIC/$AlCl_3$ (55 mol% $AlCl_3$), on the other hand, where An is partially protonated (AnH^+) the photochemistry yielded a complex mixture of monomeric and dimeric products.[3b] These latter reactions were initiated by electron transfer from the singlet excited state of An (An^{*1}) to AnH^+.[3b,5]

In none of this photochemistry did the imidazolium cation serve as electron acceptor. With 9-methylanthracene (9-MeAn) as substrate, however, the results were far different.[3c] In basic EMIC/$AlCl_3$, as well as *N*-butylpyridinium chloride/$AlCl_3$ (BPC/$AlCl_3$), the photochemistry was initiated by electron transfer from the singlet excited state of the substrate (9-$MeAn^{*1}$) to the aromatic, heterocyclic cation. What differentiated the photochemistry in the two ILs is the fact that the imidazolium radical (EMI·) formed in the electron transfer reaction reduced 9-MeAn while BP·, formed similarly, did not.

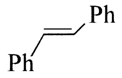


ANTHRACENE (An)

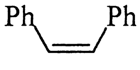


9-METHYLANTHRACENE (9-MeAn)

The photochemistry of 9-MeAn is thus quite different in character in the two ILs than the typical 4+4 cycloaddition reaction seen in most tradition solvents.[4] As shown below, the photochemistry of *cis*- and *trans*-stilbene (*c*-S and *t*-S) is also distinctive in the same two ILs.



trans-STILBENE (*t*-S)



cis -STILBENE (c-S)

The photochemistry of the two stilbenes and their derivatives has been studied extensively and is dominated by *cis–trans* isomerisation.[6] This interconversion occurs in several ways. In the singlet mechanism, direct excitation of the hydrocarbons affords singlet excited states, *c*-S^{*1} and *t*-S^{*1}, both of which twist about the ethylene double bond to a common perpendicular excited state, p^{*1}. p^{*1} undergoes a radiationless transition to ground state p^1 which then decays to *c*-S and *t*-S. On triplet sensitisation, a mechanism similar to that above but involving triplet states occurs. In this instance a perpendicular triplet excited state p^{*3} decays to ground state p^1 which then decays to *c*-S and *t*-S. Of greatest relevance to the present discussion is the isomerisation of *c*-S and *t*-S occurring through stilbene radical ions.[7,8]

It was not possible to study the photochemistry of *t*-S and *c*-S in Lewis acidic EMIC/$AlCl_3$ and BPC/$AlCl_3$. *t*-S, for example, underwent an acid-catalysed dimerisation instead. The trace HCl in Lewis acidic EMIC/$AlCl_3$ is a very strong Brønsted acid known to protonate aromatic hydrocarbons including An.[9] *t*-S is also known to dimerise in molten $SbCl_3$.[10] No such complications were observed in the basic ILs where trace HCl is not a strong Brønsted acid.

The photoreactions of *t*-S and *c*-S in basic BPC/$AlCl_3$ and EMIC/$AlCl_3$ were carried out in vacuum-sealed pyrex tubes using nominally 350-nm light. Both *t*-S and *c*-S absorb light above 300 nm.[11] The results of these reactions are presented in Table 1. The photochemistry in both media is dominated by *cis–trans* isomerisation of the stilbenes. In BPC/$AlCl_3$ the interconversion is particularly clean as the reaction mixture is free of other products. In EMIC/$AlCl_3$, the interconversion of the two stilbenes is the predominant reaction but other (unknown)

[‡] Deceased 12 March, 1995

[*] To receive any correspondence. E-mail: rpagni@utk.edu

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

Table 1 Photochemistry of *cis*- and *trans*-stilbene in ionic liquids

Stilbene	Solvent[a]	Time/h	Product yields/%			Other products
			c-S	*t*-S	*c*-S + *t*-S /%	
trans	BPC/$AlCl_3$	17	3.3	96.7	100	None
cis	BPC/$AlCl_3$	17	0.6	99.4	100	Trace of one
trans	EMIC/$AlCl_3$	14.5	27.1	59.5	86.6	Traces of several
cis	EMIC/$AlCl_3$	17	41.1	52.2	93.3	Two (4.3% and 1.5%)

[a] 55 mol% of heterocyclic chloride.

Table 2 Free energies (kcal/mol) of electron transfer

Stilbene	Solvent	ΔG(Singlet)	ΔG(triplet)
trans	BPC/$AlCl_3$	–31.6	+7.4
cis	BPC/$AlCl_3$	–33.0	0
trans	EMIC/$AlCl_3$	–14.3	+24.7
cis	EMIC/$AlCl_3$	–15.7	+17.3

products in small amounts are also produced. None of the minor products are stilbene dimers or reductions products, however.

The results in BPC/$AlCl_3$ are quite striking as a photostationary state (PSS) consisting of approximately 98% *t*-S and 2% *c*-S has almost been reached. A PSS which is very rich in *t*-S strongly suggests that the isomerization is occurring through the stilbene radical cations formed by photoelectron transfer from excited states of *c*-S and *t*-S to BP^+.[8] From the known excitation energies of *c*-S and *t*-S,[12] their oxidation potentials which were measured in this study, and the reduction limits of the two ILs,[3c] it is possible to calculate the free energy of electron transfer using the Rehm–Weller equation[7] (Table 2). Indeed the electron transfers from the singlet excited states to BP^+ are quite exothermic for both stilbenes. Electron transfers from the triplet states are not. A mechanism similar to that proposed in ref. 8b and shown below accounts for the results. Two features are of note: (1) the isomerisation is essentially one way, *i.e.* $c\text{-S}^{+\bullet} \rightarrow t\text{-S}^{+\bullet}$ and (2) $c\text{-S}^{+\bullet}$ is produced in two ways, by photoinduced electron transfer from $c\text{-S}^{*1} + BP^+$ and electron exchange between $t\text{-S}^{+\bullet}$ and *c*-S.

$$c\text{-S and } t\text{-S} \xrightarrow{h\nu} c\text{-S}^{*1} \text{ and } t\text{-S}^{*1}$$

$$c\text{-S}^{*1} \text{ and } t\text{-S}^{*1} + BP^+ \rightarrow c\text{-S}^{+\bullet} \text{ and } t\text{-S}^{+\bullet} + BP^\bullet$$

$$t\text{-S}^{+\bullet} + c\text{-S} \rightarrow t\text{-S} + c\text{-S}^{+\bullet}$$

$$c\text{-S}^{+\bullet} \rightarrow t\text{-S}^{+\bullet}$$

$$c\text{-S}^{+\bullet} \text{ and } t\text{-S}^{+\bullet} + BP^\bullet \rightarrow c\text{-S and } t\text{-S} + BP^+$$

Even though electron transfers from $c\text{-S}^{*1}$ and $t\text{-S}^{*1}$ to $EMIC^+$ are both calculated to be exothermic (Table 2), these do not occur in EMIC/$AlCl_3$. The product mixtures are considerably less rich in *t*-S and, unlike the reaction in BPC/$AlCl_3$, other products in small amounts are produced. The side reactions preclude a genuine PSS being attained. The photoisomerisation in EMIC/$AlCl_3$ likely proceeds via the singlet mechanism described earlier. The amount of *t*-S and *c*-S at the PSS obtained via this pathway is wavelength dependent and depends on the extinction coefficients (ϵ) of the stilbenes and the quantum yields (Φ) for their interconversion.[6] In the present circumstance where light > 300 nm was used, a PSS rich in *c*-S is expected unless the two quantum yields in EMIC/$AlCl_3$ are unusual.[6]

$$\left(\frac{t-\text{S}}{c-\text{S}}\right)_{\text{PSS}} = \frac{\epsilon_{c\text{–S}}\,\Phi_{c\text{–S}\rightarrow t\text{–S}}}{\epsilon_{t\text{–S}}\,\Phi_{t\text{–S}\rightarrow c\text{–S}}}$$

In conclusion, *c*-S and *t*-S interconvert photochemically in BPC/$AlCl_3$ and EMIC/$AlCl_3$. What differentiates the two systems are the reduction limits of the two ILs.

Experimental

Samples were prepared in a Vacuum Atmospheres glovebox by dissolving *cis*-stilbene or *trans*-stilbene (150–250 mg) in 10–15 g of freshly prepared basic EMIC/$AlCl_3$ (55 mol% EMIC) or basic BPC/$AlCl_3$ (55 mol% BPC). Photolyses were carried out in vacuum-sealed Pyrex tubes in a Rayonet Type RS Photochemical Reaction using 350-nm lamps. After the reactions were terminated, the reaction mixtures were quenched in ice water. The aqueous layer was neutralised with NaOH (6M) and then extracted with CH_2Cl_2. Product analysis was carried out quantitatively by GC/MS (HP5890 gas chromatography and HP 5890 mass selector analyser, with a crossbonded 100% polysiloxane column).

The electrochemistry was carried out on solutions of *cis*-stilbene or *trans*-stilbene in basic EMIC/$AlCl_3$ using an Al wire in 2:1 $AlCl_3$/EMIC as reference electrode, Pt foil in bulk solution as counter electrode, and glassy carbon as the working electrode at a scan rate of 50 mV/s. $E_{1/2}$(*cis*-stilbene) = 0.972 V (irreversible), $E_{1/2}$(*trans*-stilbene) = 0.947 V (irreversible). $E_{1/2}$s were not determined in basic BPC/$AlCl_3$ but should be similar to those observed in EMIC/$AlCl_3$. The reduction limits of basic EMIC/$AlCl_3$ (–2.25 V) and BPC/$AlCl_3$ (–1.5 V) were determined previously.[3c]

This research was supported by the Air Force Office of Scientific Research.

Received 20 June 2001; accepted 9 September 2001
Paper 01/937

References

1 (a) T. Welton, *Chem. Rev.*, 1999, **99**, 2071; (b) P. Wasserscheid and W. Keim, *Angew. Chem. Int. Ed.*, 2000, **39**, 3772; (c) R. Pagni, *Advances in Molten Salt Chemistry*, ed. G. Mamantov, C.B. Mamantov, and J. Braunstein, Elsevier, Amsterdam, 1988, vol. 6, p. 211.

2 (a) M.J. Earle and K.R. Seddon, *Pure Appl. Chem.*, 2000, **72**, 1391; (b) K.R. Seddon, *J. Chem. Tech. Biotechol.*, 1997, **68**, 351.

3 (a) H.L. Chum, D. Koran and R.A. Osteryoung, *J. Am. Chem. Soc.*, 1978, **100**, 311; (b) G. Hondrogiannis, C.W. Lee, R.M. Pagni, and G. Mamantov, *J. Am. Chem. Soc.*, 1993, **115**, 9828; (c) C. Lee, T. Winston, A. Unni, R.M. Pagni, and G. Mamantov, *J. Am. Chem. Soc.*, 1996, **118**, 4919; (d) C.M. Gordon and A.J. McLean, *Chem. Commun.*, 2000, 1395.

4 D.O. Cowan and R.L. Drisko, *Elements of Organic Photochemistry*, Plenium, New York, 1976, ch. 2.

5 R.M. Pagni, G. Mamantov, G. Hondrogiannis, and A. Unni, *J. Chem. Res. (S)*, 1999, 486.

6 H. Görner and H.J. Kuhn, *Advances in Photochemistry*, Wiley-Interscience, New York, New York, 1995, vol. 19, ch. 1.

7 G.J. Kavarnos, *Fundamentals of Photoinduced Electron Transfer*, CH, New York, 1993.

8 (a) R. Searle, J.L.R. Williams, D.E. DeMeyer, J.C. Doty, *Chem. Commun.*, 1967, 1165; (b) F.D. Lewis, J.R. Petisce, J.D. Oxman, M.J. Nepras, *J. Am. Chem. Soc.*, 1985, **107**, 203; (c) Y. Kuriyama, T. Arai, H. Sakuragi, K. Tokumaru, *Chem. Lett.*, 1988, 1193.

9 (a) G.P. Smith, A.S. Dworkin, R.M. Pagni, and S.P. Zingg, *J. Am. Chem. Soc.*, 1989, **111**, 525; (b) G.P. Smith, A.S. Dworkin, R.M. Pagni, and S.P. Zingg, *J. Am. Chem. Soc.*, 1989, **111**, 5075; (c) M. Ma and K.E. Johnson, *J. Am. Chem. Soc.*, 1995, **117** 1508; (d) J.L.E. Campbell and K.E. Johnson, *J. Am. Chem. Soc.*, 1995, **117**, 7791.

10 (a) G.B. Porter and E.C. Baughan, *J. Chem. Soc.*, 1958, 744; (b) M. Hiscock and G.B. Porter, *J. Chem. Soc.*, *Perkin II*, 1972, 79.

11 H.H. Jaffé and M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy*, Wiley, New York, 1962.

12 S.L. Murov, *Handbook of Photochemistry*, Marcel Dekker, New York, 1973.