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Novel Photochemical Behavior of Anthracene in a Room Temperature Molten Salt

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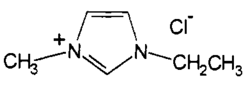
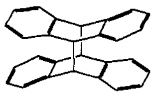
There are now available ionic mixtures which are liquid at or near room temperature.[1] The most widely studied of these consists of mixtures of 1-ethyl-3-methyl-1*H*-imidazolium chloride (EMIC) and $\mathrm{AlCl_3}$ which are liquid at room temperature over a wide range of EMIC:$\mathrm{AlCl_3}$ ratios (R).[2] By adjusting R, liquids are created which are basic ($R > 1$; $\mathrm{Cl^-}$ = base), neutral ($R = 1$; $[\mathrm{EMI^+}] = [\mathrm{AlCl_4^-}]$), and acidic ($R < 1$; $\mathrm{Al_2Cl_7^-}$ = acid) and have vastly different pCl (i.e., $-\log[\mathrm{Cl^-}]$) values.[3] Basic and acidic melts also have significantly different electrochemical windows[4] and chemical properties. HCl, for example, is a powerful Brønsted acid in acidic media, but a much weaker one in basic ones.[4,5] We wish to report the first example of a photochemical reaction in a molten salt and to show how altering the composition of this molten salt profoundly influences photochemical behavior.



EMIC

Photolysis of a 0.140 M solution of anthracene (**1**) in a basic EMIC/$\mathrm{AlCl_3}$ melt (55.0 mol % EMIC; pale yellow solution) under vacuum in a Pyrex vessel[6] afforded dimer **2** exclusively.[7] This behavior is identical to that seen for **1** in a wide variety of more traditional solvents.[8] This dimerization, in fact, is the paradigm for a photochemically allowed [4 + 4] cycloaddition reaction.[8,9] Photolysis of a 0.148 M solution of anthracene in an acidic melt containing proton (55.0 mol % $\mathrm{AlCl_3}$; green solution), on the other hand, is quite different, yielding at least 16 oxidized, neutral, and reduced monomeric and dimeric products (analytical HPLC).[10] The major products were identified as **2**–**7**, with trace amounts of 9,9′-bianthracene and 1,2,3,4-tetrahydroanthracene also being formed, as well as a fused dimer of unknown structure (**8**) but similar spectroscopically to **7**.[11] No chlorinated products or those which incorporated the EMI ring (uncharged or cationic)[12] were formed in the photoreaction.



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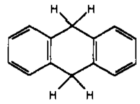

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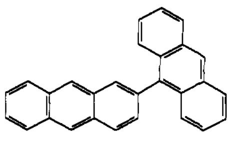

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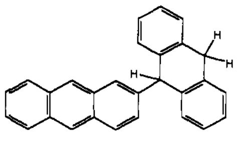

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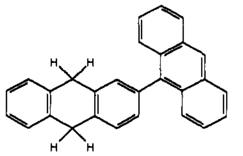

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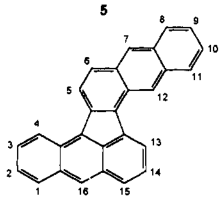

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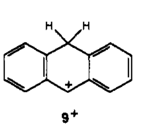

9⁺

Product yields were followed as a function of time (Table I, entries 1–3). The photoreaction is rapid initially but much slower at longer reaction times, due likely to an internal filter effect of the highly conjugated **4**, **7**, and **8** and quenching of excited states by these same species. Most of the products are also reactive as their yields go down as the reaction progresses. Only the yield of the highly oxidized **7** (and **2**) goes up as the reaction proceeds. The mass balance also decays as a function of time, suggesting the formation of oligomeric and polymeric compounds at longer reaction times. The hydrogen balance, which is a measure of the excess of reduction or oxidation in the characterized products, is small but not 0, also demonstrating the formation of missing products.

This unusual photochemistry must be initiated by an electron-transfer reaction. One possible electron acceptor is $\mathrm{EMI^+}$, but this is not correct. First of all, $\mathrm{EMI^+}$ did not function as an electron acceptor in the photochemistry of **1** in the basic melt, nor does it in the photoreaction of **1** in $\mathrm{CH_3CN}$ saturated with EMIC, where **2** is formed quantitatively. The electron acceptor is, in fact, the anthracenium ion **9⁺**,[13] formed by protonation of **1** with trace amounts of HCl in the melt,[14] and it is more easily reduced electrochemically than is EMIC (eqs 1–3).[14] Even the

$$\mathbf{1} + \mathrm{HCl} \rightleftarrows \mathbf{9}^+ \tag{1}$$

$$\mathbf{1} + \mathbf{9}^+ \xrightarrow{h\nu} \mathbf{1}^{\bullet+} + \mathbf{9}^{\bullet} \tag{2}$$

$$\mathbf{1}^{\bullet+} + \mathbf{9}^{\bullet} \twoheadrightarrow \text{products} \tag{3}$$

most rigorously purified melts contain traces of HCl. In the first three photoreactions described in Table I, there is approximately 3% of **9⁺** present in each solution. When the HCl content of the melt is deliberately increased by the addition of EMIC·HCl,[14] the content of **9⁺** increases to 26% (Table, entry 4). When this solution is irradiated, the photochemistry is somewhat different than the previously described cases, but it is exclusively redox in

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[1] Hussey, C. H. In *Advances in Molten Salt Chemistry*; Mamantov, G., Mamantov, C., Eds.; Elsevier: Amsterdam, 1983; Vol. 5, p 185.

[2] (a) Wilkes, J. S.; Levisky, J. A.; Wilson, R. A.; Hussey, C. L. *Inorg. Chem.* **1982**, *21*, 1263. (b) Fannin, A. A., Jr.; Floreani, D. A.; King, L. A.; Landers, J. S.; Piersma, B. J.; Stech, D. J.; Vaughn, R. L.; Wilkes, J. S.; Williams, J. L. *J. Phys. Chem.* **1984**, *88*, 2614.

[3] Hussey, C. L.; Scheffler, T. B.; Wilkes, J. S.; Fannin, A. A., Jr. *J. Electrochem. Soc.* **1986**, *133*, 1389.

[4] Smith, G. P.; Dworkin, A. S.; Pagni, R. M.; Zingg, S. P. *J. Am. Chem. Soc.* **1989**, *111*, 525.

[5] Smith, G. P.; Dworkin, A. S.; Pagni, R. M.; Zingg, S. P. *J. Am. Chem. Soc.* **1989**, *111*, 5075.

[6] A Rayonet reactor with 3500-Å lamps was used as the light source.

[7] The reaction mixtures were quenched with water under argon and products extracted into methylene chloride.

[8] (a) Cowan, D. O.; Drisco, R. L. *Elements of Organic Photochemistry*; Plenum: New York, 1976; Chapter 2. (b) Becker, H.-D. *Chem. Rev.* **1993**, *93*, 145 and references cited therein.

[9] Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag: Weinheim, Germany, 1970.

[10] An uncharacterized condensation chemistry also occurs in the absence of light, but the reaction is much slower than the photochemical reaction.

[11] The products were separated by column chromatography, prep TLC, and prep HPLC and characterized spectroscopically. Known samples of **2**, 9,9′-bianthracene, and 1,2,3,4-tetrahydroanthracene were available. The spectra of some other products were available in the literature. 2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ) oxidation of the reduced products gave the corresponding aromatic hydrocarbons.

[12] The aqueous solution formed during reaction workup, which contains $\mathrm{EMI^+}$ and other ionic organic compounds, was evaporated and the residue subjected to SIMS. Only $\mathrm{EMI^+}$ was detected.

[13] The electron transfer from arene excited states including that of anthracene to diaryl- and triarylmethyl carbocations is known and is very fast: Johnston, L. J.; Kanigan, T. *J. Am. Chem. Soc.* **1990**, *112*, 1271. Samanta, A.; Gopidas, K. R.; Das, P. K. *Chem. Phys. Lett.* **1993**, *204*, 269.

[14] Carlin, R. T.; Trulove, P. C.; Osteryoung, R. A. *Electrochim. Acta* **1992**, *37*, 2615.

0002-7863/93/1515-9828$04.00/0

Table I. Product Distributons from the Photolysis of Anthracene in Acidic Melts[a]

entry	reaction time (h)	ratio of **1** to protonated **1**[b]	% of **1** consumed	yield[c] (%)							material balance (%)[e]	hydrogen balance (%)[f]
				3	**4**	**5**	**6**	**7**	**8**[d]	**2**		
1	0.5	29:1	12.7	24.5	19.4	12.1	2.3	0	13.7	0	72.0	4
2	24	29:1	60.4	7.3	6.8	2.3	1.5	1.0	1.8	2.0	22.7	8
3	48	29:1	64.2	6.2	4.6	2.4	1.3	3.1	1.3	2.4	21.3	–4
4	48	2.9:1[g]	73.6	2.5 (2.8)[h]	0	0	0	9.0	0	0	14.2	–6
5	24	1:0[i,j]	15.4	1.9	0	0	0	0	0	2.5	44.4	

[a] 0.148 M solution (2.35 mmol of **1** in 21.0 g of melt (55.0 mol % $AlCl_3$) which has a density of 1.32 g/mL[2b] photolyzed in Pyrex under argon. [b] Based on the extinction coefficient of protonated anthracene (Zingg, S. P.; Dworkin, A. S.; Sølie, M.; Chapman, D. M.; Buchanan, A. C., III; Smith, G. P. *J. Electrochem. Soc.* **1984**, *31*, 1602 and ref 4–5) and the equilibrium constant for the reversible protonation of anthracene[14] using dilute solutions of anthracene in the melt. [c] For monomeric products: (mmol of product/mmol of consumed **1**) × 100. For dimeric products: (mmol of product × 2/mmol of consumed **1**) × 100. [d] An unknown fused product similar to **7**. [e] [(Σmmol of monomeric products + 2Σmmol of dimeric products)/mmol of consumed **1**] × 100. [f] (mmol of H added to reduced products – mmol of H lost from oxidized products)/(mmol of H added to reduced products + mmol of H lost from oxidized products) × 100. [g] HCl in the melt increased by the addition of EMIC·HCl.[14] [h] Yields of 1,2,3,4-tetrahydroanthracene. [i] HCl removed from the melt by addition of excess methylaluminum sesquichloride.[14] [j] GC/MS of the product mixture revealed the presence of methylanthracene(s) (8%), 9,10-dimethylanthracene (1%), and chloroanthracene(s) (2%).

nature, giving largely the highly oxidized and reduced products **7** and 1,2,3,4-tetrahydroanthracene. This reaction is clearly farther along the cascade of oxidation and reduction reactions than are the previous three examples. When the HCl is deliberately removed by addition of excess methylaluminum sesquichloride,[14] the overall reaction is slower than when HCl is present, and the redox chemistry is largely suppressed (Table I, entry 5).[15]

The essential difference in the photochemistry of **1** in the basic and acidic molten salts is due to the different in acidity of HCl in the two media. In the basic melt, HCl is insufficiently acidic to protonate **1**, and the photochemistry proceeds in the normal manner. In the acidic medium, however, HCl, now a powerful Brønsted acid, protonates **1** to form a small amount of **9**$^+$, which function as an electron acceptor, thus diverting the chemistry of **1** into an entirely new channel. Photolysis of **1** in H_2O also generates **1**$^{\bullet+}$,[16] which reacts rapidly with the nucleophilic H_2O.[16,17] In the acidic molten salt, there are no good nucleophiles with which **1**$^{\bullet+}$ can react. Only **1** or products or transients derived from **1** can serve this purpose. As a result, the chemistry is dominated by bimolecular electron transfer, hydrogen transfer, and coupling reactions. The present chemistry is reminiscent of that described by Smith *et al.* for **1** in molten $SbCl_3$, which is also poorly basic, at elevated temperatures.[18] In that case, the electron transfer is driven thermally by the reversible reduction of Sb(III). Thermally and photochemically driven electron-transfer reactions in poorly basic solvents should yield other unusual chemical transformations.

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Supplementary Material Available: Experimental details and characterization of the products (4 pages). Ordering information is given on any current masthead page.

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(15) The interpretation of this fact is complicated by the fact that products are formed here which contain Cl and CH_3 (from excess $Me_3Al_2Cl_3$).

(16) Sigman, M. E.; Zingg, S. P.; Pagni, R. M.; Burns, J. H. *Tetrahedron Lett.* **1991**, 5737.

(17) Wirz, J., unpublished results.

(18) (a) Poutsma, M. L.; Dworkin, A. S.; Brown, L. L.; Benjamin, B. M.; Smith, G. P. *Tetrahedron Lett.* **1978**, 873. (b) Dworkin, A. S.; Poutsma, M. L.; Brynestad, J.; Brown, L. L.; Gilpatrick, L. O.; Smith, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 5299. (c) For a related case, see also: Keszthelyi, C. P. *Electrochim. Acta* **1981**, *26*, 1261.