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Photoinduced Electron Transfer Reactions of Anthracene in $CF_3SO_3H-CF_3CO_2H$†

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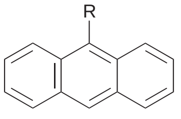
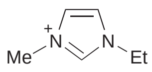
Photolysis of anthracene in a mixture consisting of 2% CF_3SO_3H in CF_3CO_2H (w/w), where anthracene is partially protonated, gives a mixture of oxidized, neutral and reduced monomeric and dimeric products, initiation of this chemistry being photoinduced electron transfer from anthracene to protonated anthracene.

Two types of Brønsted superacids are known: those consisting of fluorine-containing Brønsted acids with or without Lewis acids[1] such as $HF-SbF_5$ and the less well known bromine- and chlorine-containing room temperature molten salts such as HCl (1 atm) in $AlCl_3$–l-ethyl-3-methylimidazolium chloride (EMIC; excess $AlCl_3$),[2–4] (1 atm) in $AlCl_3$–EMIC (excess $AlCl_3$ buffered with LiCl or NaCl),[5] and $HBr-AlCl_3-Me_3SBr$.[6] Because the two types of superacids have high acidity and low basicity/nucleophilicity in common, it should be possible to observe the same organic chemistry in both. One in fact can adjust the acidity of a mixture of CF_3SO_3H and CF_3CO_2H so that the same, complex photochemistry of anthracene (An) **1a** occurs in it as in the room temperature molten salt: HC1 in $AlCl_3$–EMIC.



1a R = H
1b R = Me



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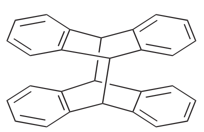

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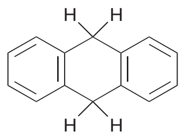

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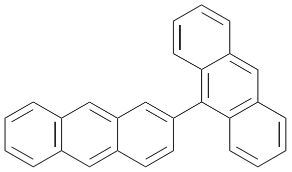

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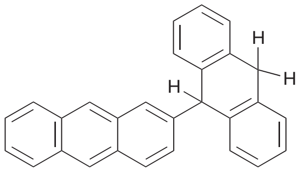

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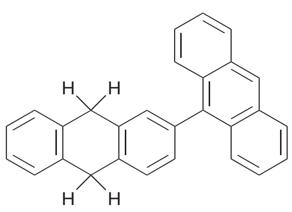

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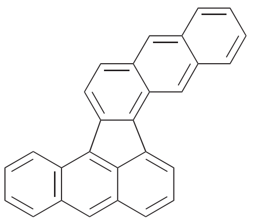

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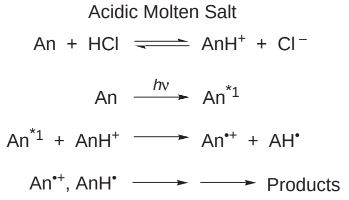
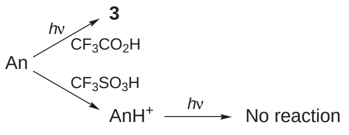
Consider first the following published results. The photochemistry of 9-methylanthracene **1b** in degassed basic EMICl–$AlCl_3$ (55 mol% EMIC), which contains EMI^+ (**2**), Cl^- and $AlCl_4^-$, is initiated by electron transfer from the singlet excited state of **1b** to **2**.[7] The photochemistry of the less easily oxidized An in the same medium, on the other hand, affords the 4 + 4 dimer **3** exclusively,[8] a result identical to that previously observed in numerous other solvents.[9] Photochemistry of An in acidic EMIC–$AlCl_3$ (55 mol% $AlCl_3$), which contains **2**, $AlCl_4^-$ and $Al_2Cl_7^-$, a powerful Lewis acid, takes an entirely different course affording a series of oxidized, neutral and reduced monomers and dimers: **3**–**9**.[8] This latter chemistry is initiated by electron transfer from the singlet excited state of An, not to EMI^+ but to protonated anthracene (AnH^+), which is formed by protonation of An by trace amounts of HCl in the molten salt (Scheme 1).[8] This unusual set of products arises by a series of bimolecular coupling, hydrogen-transfer, and electron-transfer reactions. Reaction of $An^{\cdot +}$ with solvent components does not occur here because there are no good bases in the acidic medium with which $An^{\cdot +}$ can react. Instead $An^{\cdot +}$ reacts with itself, An and species derived from them.



Scheme 1

If one is to observe the same photochemistry of An in a Brønsted acid as occurred in the acidic molten salt, one requires a medium that is poorly nucleophilic and will sustain a low concentration of AnH^+. The pK_a, of AnH^+, which is 3.2 in HF,[10] −9.1 in MeCN,[11] and −9.2 in HCl (1 atm)–EMIC–$AlCl_3$ (acidic),[2,3] provides some guidance in the choice of acid. A mixture of CF_3CO_2H, with $H_0 = -2.7$, and CF_3SO_3H, with $H_0 = -14.0$, with an H_0 between −2.7 and −14.0[12] in fact provides the appropriate acidity and nucleophilicity.



Scheme 2

Photolysis of a degassed solution of An in CF_3CO_2H (very faint pink coloration); which contains no AnH^+ (^1H NMR; UV–VIS), proceeds in the classic manner to afford the 4 + 4 dimer **3** exclusively (Scheme 2). As there is no AnH^+ in the CF_3CO_2H, there is no electron acceptor available to initiate the photochemistry observed in the acidic molten salt. Photolysis of a solution of An in

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† This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

‡ Deceased March 12th, 1995.

Table 1 Product distribution from the photolysis of anthracene in $CF_3SO_3H-CF_3CO_2H$[a] and acidic EMIC–$AlCl_3$[b]

	Relative product yield(%)						
Solvent	**4**	**5**	**6**	**7**	**8**	**9**[c]	**3**
$CF_3SO_3H-CF_3CO_2H$[d]	36.2	23.3	5.4	11.7	1.6	14.8	7.0
EMIC–$AlCl_3$	32.2	30.0	10.1	6.6	4.4	7.9	8.8

[a] Photolyzed for 28 h; 52% of An consumed. The material balance was 25.7%. [b] Photolyzed for 24 h; 60.4% of An was consumed. The material balance was 22.7%. [c] An unknown condensed product similar in structure to **8**. [d] 9,9′-Bianthracene and two other unknown dimeric products were also formed in this reaction.

CF_3SO_3H (deep green coloration), which contains AnH^+ and no An (^1H NMR), on the other hand, yields no photoproducts; An is recovered quantitatively on workup. In this case the electron acceptor (AnH^+) is present but the donor (An) is absent.

$$\text{An, AnH}^+ \xrightarrow[CF_3SO_3H-CF_3CO_2H]{h\nu} \textbf{3–9}$$

Scheme 3

The pK_a of AnH^+ in $CF_3SO_3H-CF_3CO_2H$ clearly lies between −2.7, where An is unprotonated, and −14.0, where An is completely protonated. When the ^1H NMR and UV–VIS detection limits of An and AnH^+ are taken into account {1% An in CF_3SO_3H (^1H NMR) and 0.1% AnH^+ in CF_3CO_2H (UV–VIS [$\varepsilon(AnH^+) \approx 1 \times 10^4$ $dm^3\,mol^{-1}\,cm^{-1}$])}, the pK_a range is narrowed to between −5.7 and −12.0. Thus, photolysis (Scheme 3) of a degassed, pale green solution of An in 2% CF_3SO_3H–98% CF_3CO_2H (w/w), which has $H_0 = -8.1$[12] and contains both An and AnH^+, yields **3**–**9**, the same products as found in acidic EMIC–$AlCl_3$, and a couple of other minor products (Table 1). The distribution of products in $CF_3SO_3H-CF_3CO_2H$ is very similar to that found in the molten salt (Table 1). Because the molten salt reaction was conclusively shown to be initiated by electron transfer from An^{*1} to AnH^+,[8] the reaction in $CF_3SO_3H-CF_3CO_2H$ must begin in the same way. The subsequent sequence of bimolecular coupling, hydrogen- transfer and electron-transfer reactions must be similar as well.

Because many aromatic hydrocarbons have basicities similar to that of An,[13] photoelectron transfer between an aromatic hydrocarbon and its conjugate acid should be a common reaction in strong acids.

Experimental

The CF_3SO_3H and CF_3CO_2H were of the highest purity and used as received. The acid solutions, *ca.* 0.1 M in An, were deoxygenated by purging with dry N_2 and photolyzed in a Rayonet reactor using 3500 Å lamps. Work-up of the reactions and separation, identification and quantitation of products were identical to that found in the Supplementary Material of ref. 8.

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