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HYDRIDE ABSTRACTION IN FSO_3H AND OTHER MEDIA - AN ELECTRON TRANSFER MECHANISM

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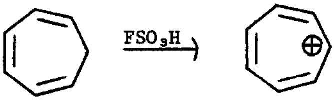
Fluorosulfonic acid (FSO_3H) and mixtures of FSO_3H and SbF_5 are among the very strongest acids known,[1] and numerous reactions occur in them that have no counterpart in other acids or solvents.[2] For example, treatment of saturated alkanes, such as isobutane, with FSO_3H-SbF_5 generates the corresponding carbenium ion by a process which is formally a hydride abstraction.[3] Some hydrogen is also produced in the reactions.

Recently we reported[4] that cycloheptatriene (1) and phenalene (3) are oxidized in FSO_3H, both in the presence and absence of SbF_5, to the corresponding carbenium ion. Remarkably, one equivalent of SO_2 and no hydrogen is produced in these reactions. SO_3 in liquid SO_2 also oxidizes these hydrocarbons. Whatever the process is by which alkanes are oxidized, the mechanism of oxidation in these latter reactions must be different.



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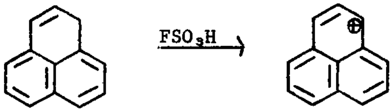

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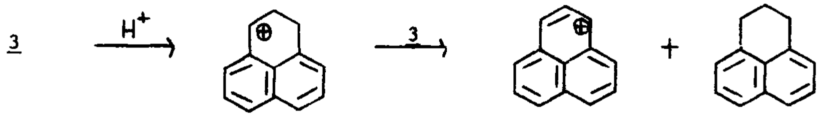
The most obvious distinction between cycloheptatriene (1) and phenalene (3) and saturated alkanes is that the first two molecules have extensive π systems and form very stable carbenium ions, while saturated alkanes do not.

We set out to test the generality of the above statement, and some of the oxidations attempted, both in FSO_3H at -78° and H_2SO_4 at room temp, are shown in Table 1. In all cases the reactions were analyzed by nmr and ion identification was based on one or more of the following: (1) independent synthesis, (2) literature nmr values, and (3) a detailed analysis of the reaction nmr.

With the exception of 1, where there is extensive polymerization, and 1,2,5,6-dibenzcycloheptatriene (9), if the ion formed, it formed cleanly; no other products were observed.[5,11] 9 underwent extensive sulfonation in both FSO_3H and H_2SO_4.

One could argue that at least for the hydrocarbons 1, 3, and 9, where there is a classic double bond, the carbenium ion is formed by protonation of the double bond to form an ion which hydride abstracts from a second molecule of hydrocarbon. The following experiments refute this: (1) if the above were correct, no SO_2 should be generated, and one equivalent of SO_2 is formed in the oxidation of 1;[4] (2) 3 is oxidized to 4 in close to 100% yield; (3) when phenalane, the neutral product of the protonation-hydride abstraction mechanism on 3, was subjected to the reaction conditions, it produced nmr signals not seen in the oxidation of 3; furthermore, phenalane was not oxidized to 4;[7] and, (4) quenching of the reaction mixture of 9 in FSO_3H produced < 1% of product which could be attributed to a protonation-hydride abstraction process.



Phenalane

TABLE 1

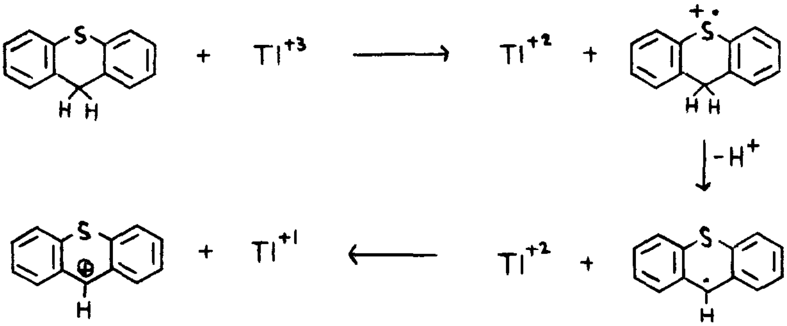
		Ion Formation in			
Compound	FSO_3H	H_2SO_4	Tl^{+3}, CF_3COOH	NO_2^+, CH_3CN	pK_{R+}
Fluorene (5)	No	No	No	No	-14[a]
Diphenylmethane (6)	No	No	No	No	-13.3[a]
Triphenylmethane (7)	No	No	No	No	-6.63[a]
7H-Benz[d,e]anthracene (8)	Yes	Yes	Yes	Yes	-6[b]
1,2,5,6-Dibenzcycloheptatriene (9)	Yes	Yes	No	Yes	-5.8[c]
Xanthene (10)	No	No	Yes	Yes	-0.84[c,d]
Thioxanthene (11)	Yes	Yes[e]	Yes	Yes	-0.21[d]
Phenalene (3)	Yes	Yes	Yes	Yes	0-2[a]
Tris(p-Anisyl)methane (12)	No	No	f	f	0.82[c]
Cycloheptatriene (1)	Yes	Yes	No	No	4.7[c]

(a) Experimental value cited in Ref. 8; (b) Computed from MO theory by the method described in Ref. 8; (c) Experimental value cited in Ref. 9; (d) See Ref. 10; (e) See Ref. 11; (f) This reaction was not run.

If the above mechanism does not occur, can the results be explained by direct hydride abstraction? As can be seen in Table 1, there is no obvious correlation between ion stability (pK_{R+}) and whether the hydride abstraction occurs. Because there should be a correlation between ion stability and rate of direct hydride abstraction,[12] such a process seems unlikely here.[13]

Because all the molecules which are oxidized in FSO_3H and H_2SO_4 have large π systems, the oxidizing agent is behaving either as an electron acceptor or as an electrophile, and there should be nothing unique about FSO_3H, H_2SO_4 or SO_3 in this regard. Indeed, as seen in Table 1, the hydride abstractions also occurred with $NO_2^+BF_4^-$ in CH_3CN and $Tl(O_2CCF_3)_3$ in CF_3COOH.[14,19]With the exception of 9, if the ion formed, it formed cleanly; no other products were observed. Treatment of 9 with NO_2^+ did generate the ion, but other unidentified products were also formed. 9 also reacted with Tl^{+3}, but no ion was formed here. Because of the diverse nature of the oxidants used, this fact reenforces the unlikelihood of a direct hydride transfer mechanism.

In view of Kochi's demonstration of the formation of radical cations in the thallation of electron rich aromatics,[15] the generation of the radical cation of 9,9-dimethylthioxanthene in H_2SO_4,[16]and the electrochemical oxidation of thioxanthene[17] and cycloheptatriene,[18] an electron transfer mechanism, as shown below for Tl^{+3}, represents an attractive explanation for most of these "hydride" abstractions.



Further work to probe into the mechanism of these reactions is now in progress.[20]

References and Notes

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(5) In those cases where hydride abstraction did not occur, protonation was usually observed in FSO_3H at -78° and sulfonation in H_2SO_4 at room temp. 12 underwent a cleavage in FSO_3H to give anisole and 4,4'-dimethoxybenzhydryl carbenium ion.[6]

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(7) If phenalane had been oxidized to 4 (and SO_2), a combination of this oxidation and the protonation-hydride abstraction mechanism could explain our earlier results.

(8) A. Streitwieser, "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N.Y., 1967, p. 365.

(9) D. Bethel and V. Gold, "Carbonium Ions, An Introduction", Academic Press, Inc., New York, N.Y., 1967, Chapter 4.

(10) J. Degani, et al., Boll. Sci. Fac. Chim. Ind. Bologna, 23, 243 (1965); Chem. Abst., 63, 13050g (1965).

(11) Some sulfonation is observed in the reaction of 11 in H_2SO_4: H. L. Shine and L. Hughes, J. Org. Chem., 31, 3142 (1966).

(12) N. C. Deno, G. Saines, and M. Spangler, J. Amer. Chem. Soc., 84, 3295 (1962).

(13) A constant steric requirement must hold for the members of a series; this is not known here. This conclusion also depends on the rate of competitive processes, such as sulfonation and carbon-carbon bond clevage, which are not known.

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(18) D. H. Geske, J. Amer. Chem. Soc., 81, 4145 (1959).

(19) It is interesting that xanthene is oxidized by Tl^{+3} and NO_2^+ but not by FSO_3H and H_2SO_4. Xanthene is protonated on one of the benzene rings in FSO_3H at -78°.[6] The lack of oxidation in FSO_3H and H_2SO_4 may be due to the much more negative pKa expected for protonated xanthene.

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