Structures of Protonated Methyl Phenols in Antimony Pentafluoride-Fluorosulfuric Acid at —60 °C*

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The site of protonation of a series of methyl substituted phenols in 11.5 mole % SbF_5 in HSO_3F was determined using NMR spectrometry. Some substituent effects are explicable without invoking specific solvation. Protonation *para* to the hydroxy group was favored, but was blocked completely in all but one case by a *p*-alkyl group. In *para* substituted phenols, *ortho* protonation predominated. Both oxygen and ring protonation were observed for the *p*-cresol.

Due to the electron donating properties of the hydroxy group, the basicity of the aromatic ring in phenols is increased significantly. So much so that protonation on the aromatic ring and on the oxygen atom are competitive processes. Much work has been done on these ambident bases, but the position of protonation varies with substituent, temperature, and acid composition in ways not yet completely understood. As part of a larger study of the behavior of phenols and phenyl ethers in fluorosulfuric acid and its mixtures with antimony pentafluoride, we have obtained the NMR spectra of a group of methyl substituted phenols. The behavior of these compounds is the subject of this report.

The behavior of anisole in sulfuric acid was the first system studied in detail and has been the subject of some controversy, due largely to the difficulties involved in structural interpretation of uv spectra and the fact that these activated aromatic systems sulfonate rapidly.[1] In perchloric acid, both C and O protonation occur and follow different acidity functions.[2] In HF solutions, anisole undergoes both C protonation and O protonation and the ratio of C to O protonation is strongly temperature dependent.[3,4] However, in fluorosulfuric acid only C protonation is observed.[5,6] If three hydroxy or amino substituents are placed on the aromatic ring only, C protonation occurs in sulfuric or perchloric acid.[8,9] Diprotonation of the trihydroxy compounds has been observed in SbF_5/HSO_3F mixtures.[10] The presence of an alkyl group on the ring can alter the effect of the hydroxy or methoxy group. For example *p*-methylanisole in HF is protonated only on the oxygen atom,[3] contrasting to the mixed C and O protonation observed with anisole. In fluorosulfuric acid-antimony pentafluoride solutions, both protonation on the oxygen and on the ring *ortho* to the methoxy group is observed.[7,11] Furthermore the ratio of oxygen to ring protonation is sensitive to the nature of the acid as well as to temperature. As part

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* Abstracted from the Ph. D. Thesis of M. Eckert-Maksić, University of Zagreb, 1972.

TABLE I

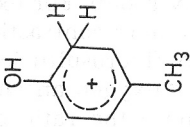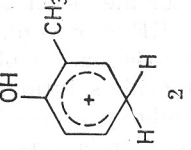Structures and NMR Spectra of Protonated Methyl Phenols in 11.5 mole % SbF₅/HSO₃F at −60 °C.

Chemical Shifts[a]

Cation	Ring Protons[b]				—CH₃[b]			$\overset{+}{\underset{H}{C}}$—CH₃	$\overset{+}{O}H_2$
	p	o	m	CH₂	p	o	m		
1a (OH, CH₃, ring-protonated)	8.70(br d) J=10 Hz	7.60[c]	7.32(d) J=10 Hz	4.47(br s)			2.37(s)		
1b (+OH₂, CH₃ para)		7.60(s)	7.60(s)		2.47(s)				
2 (OH, CH₃, ring-protonated)	8.62(d) J=10 Hz	8.40(br s)	7.42(d) J=10 Hz	4.28(br s)			2.38(s)		12.30(br)
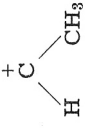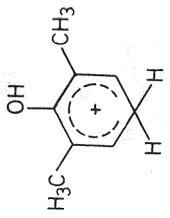
Table I — cont'd.

Cation	Ring Protons[b]			CH_2	CH_3[b]			$\overset{+}{C}\overset{CH_3}{\underset{H}{}}$
	p	*o*	*m*		*p*	*o*	*m*	
3		8.39(s)		4.26(br s)			2.42(s)	
4		8.34(d) J=10 Hz	7.28(d) J=10 Hz	4.28(br s)		2.66(s)	2.38(s)	
5		8.16(s)	7.18(s)	4.18(br s)		2.64(s)	2.34(s)	

Table I — cont'd.
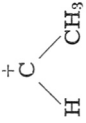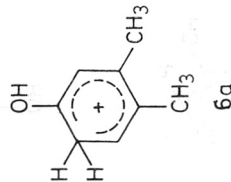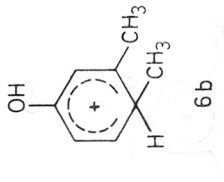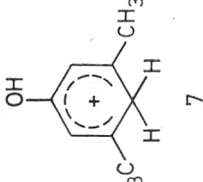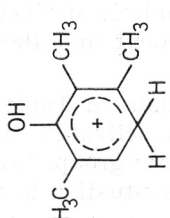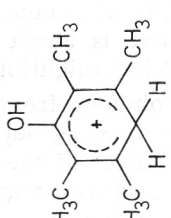
Cation	Ring Protons[b]			CH$_2$	CH$_3$[b]			$\overset{+}{C}$(H)(CH$_3$)
	p	o	m		p	o	m	
6a		7.40(s)	7.14(s)	4.26(br s)	2.78(s)		2.35(s)	
6b		8.34(br s)	7.10(s)	3.90(q) J=10 Hz		2.68(s)		1.73(d) J=10 Hz
7			7.03(s)	4.10(br s)		2.60(s)		

Table I — cont'd.

Cation	Ring Proton[b]			CH₂	CH₃[b]			$\overset{+}{C}$ with H and CH₃
	p	o	m		p	o	m	
8		8.13(s)		4.22(br s)		2.62(s)	2.34(s) 2.38(s)	
9				4.15(br s)		2.51(s)	2.31(s)	
10				3.83(q) J=10 Hz		2.56(s)	2.36(s)	1.66(d) J=10 Hz

a) Relative to Me₄N⁺ internal standard. The chemical shift of Me₄N⁺ was taken as $= -3.20$ ppm relative to TMS; s = singlet, br = broad, d = doublet, q = quartet
b) ortho, meta and para positions are relative to the ring protonated carbon
c) partially hindered by the signal of the ring protons in the oxonium ion.
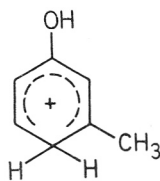
of our investigations of medium effects in superacid solvents, we have studied the behavior of a variety of substituted phenols and phenyl ethers. The behavior of methyl substituted phenols in 11.5 mole % SbF_5 in fluorosulfuric acid at —60 °C is the subject of this paper.
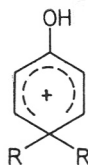
EXPERIMENTAL

Solutions were prepared by dissolving the phenol directly in 11.5 mole % SbF_5 in HSO_3F which was cooled in a dry ice-acetone bath. All operations were carried out in a dry nitrogen atmosphere. The tetramethylammonium ion was used as an internal standard and its chemical shift was taken at 3.20 ppm relative to TMS. Spectra were recorded at —60 °C using either a Varian A-60 or HA-100 spectrometer. All compounds were commercial samples purified before use. Purity of the phenols was checked by NMR.

RESULTS AND DISCUSSION

The ions formed and their spectra are given in Table I. A number of these ions have been observed in other strong acids by other workers. Cations 2, 3, and 5 have been reported in neat fluorosulfuric acid at —60 °C but no experimental details were given.[12] The NMR spectrum of phenol in neat fluorosulfuric acid at —60 °C has been studied and shows only protonation para to the hydroxy group.[13] Under the same conditions m-methylphenol gave only ring protonation, most likely ion 12.[13]

In a recent paper, Hartshorn[14] reported the behavior of phenols and anisoles having methyl groups in the 3,4, 3,5 and 3,4,5 positions in neat fluorosulfuric acid at — 50 to — 60 °C. Both ortho and para protonation of 3,4,5-trimethylphenol was observed. Only para protonation of 3,5-dimethylphenol was observed in agreement with our results. Protonation of 3,4-dimethylphenol in neat fluorosulfuric acid gave 90% ortho and 10% para protonation. This is identical to our observations in 11.5 mole % SbF_5/HSO_3F solution.

The NMR spectra are quite similar to reported spectra for ions having the general structures 12 and 13 prepared by protonating cyclohexadieneones[15,16]. The NMR spectra of a number of protonated anisole derivatives have also been reported[3,4,5,7,11]. Thus, there is ample precedent and the assignment of the spectra reported in Table I is straightforwad.

A number of trends are obvious from the data in Table I. Protonation tends to occur para to the hydroxy group. Two activating methyls are not sufficient to overcome the influence of the hydroxy group. However, if there is a methyl group para to the hydroxy group, the situation is altered.

The spectra of protonated 3,4-dimethylphenol show the presence of ions 6a present in about 90% and 6b present in about 10%. The behavior

of this compound is interesting for a number of reasons. With p-methylanisole in HF/BF$_3$, O-protonation occurs[3,4] while anisole gives a mixture of O and ring protonation[3]. However, anisole in HSO$_3$F is only ring protonated. p-Methyl-anisole in HSO$_3$F/SbF$_5$ mixtures gives mixtures of oxygen and ring (2-position) protonation[7,11]. Similarly, p-methylphenol gives both ring and oxygen protonation (ions *1a* and *1b*), with the ratio of oxygen to ring protonation being sensitive to the nature of the acid[17]. Thus, it seems that fluorosulfuric acid media form ring protonation more than acids based on HF. 3,4-Dimethylphenol gives ring protonation in the 2- and 4-positions in neat fluorosulfuric acid[14] as well as in HSO$_3$F/SbF$_5$ mixtures. It is quite apparent that the effect of substituents and acid on the ambient behavior of phenols and anisoles is exceedingly complicated. In more basic media, the hydroxy group is a more effective stabilizer of a cationic system due to charge dispersal to the medium through hydrogen bond formation[18,19]. Thus, one might expect to find oxygen protonation in the more basic solvent HF/BF$_3$. However, the notion that such a strong acid could serve as a hydrogen bond *acceptor* must be questioned [see however E. M. Arnett, *J. Amer. Chem. Soc.* **95** (1973) 978.]. In any case, it is clear that significant differences in the solvation of alkoxy and hydroxy substituted aromatic cations exist between HF/BF$_3$ and HSO$_3$F/SbF$_5$ solutions in several cases*. A satisfactory molecular picture of these differences has not yet been developed. Ion *6b* is of some interest. Except for hexamethyl benzene, protonation on a ring carbon bearing a methyl group is avoided. However, we have here a case in which this occurs instead of O protonation and competitive with protonation in the 2 position. It appears that protonation on a methyl bearing carbon is ca. 900 cal** less favorable than protonation on the 2 position in this case. This is a good illustration of the small energy differences separating the various basic sites on these molecules. Part of this energy difference probably lies in the fact that a tertiary C—H bond is slightly weaker than a secondary C—H bond[20]. The fact that this energy difference (865 cal) is nearly the same as the difference observed here is probably fortuitous. The fact that the equilibrium between *ortho* and *para* protonation is the same in neat FSO$_3$H and in 11.5% SbF$_5$/FSO$_3$H supports an interpretation based on intramolecular effects.

The difference in behavior of 4-methylphenol and 3,4-dimethylphenol is interesting. Why should a 3-methyl substituent hinder protonation in the 2 position? Actually, the 3-methyl group probably increases the basicity of the 4 position. Converting the 4-carbon atom from sp^2 to sp^3 will replace an eclipsed methyl-methyl interaction between the 3 and 4 methyl groups by a staggered interaction. Thus steric strain due to the 3-methyl group should destabilize the ground state of 3,4-dimethylphenol compared to 4-methyl-phenol and increase the basicity of the 4 position. This would be enough to cause a shift from a very low amount of protonation on the *para* position of the 4-methylphenol to the 10% observed in the dimethylphenol. While it is necessary to invoke solvent effects to explain the difference between the phenols and anisole, the variation within the series of phenols seems explicable without invoking specific solvent effects.

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* An exception is the behavior of p-methylanisole and p-methylphenol in HSO$_3$F/SbF$_5$ mixture. M. Eckert-Maksić, Ph. D. Thesis, Zagreb, 1972.
** 1 cal = 4.1840 J.

The other methyl substituted phenols show quite normal behavior. There is a strong tendency towards protonation *para* to the OH group except when this position is substituted. It is worth noting that even pentamethyl phenol shows no oxygen protonation.

REFERENCES

1. B. G. R a m s e y, *J. Amer. Chem. Soc.* **88** (1966) 5358 and references therein.
2. R. W. A l d e r, *personal communication.*
3. D. M. B r o u w e r, E. L. M a c k o r, and C. M a c L e a n, *Rec. Trav. Chim. Pays-Bas* **85** (1966) 109.
4. D. M. B r o u w e r, E. L. M a c k o r, and C. M a c L e a n, *Rec. Trav. Chim. Pays-Bas* **85** (1966) 114.
5. T. B i r c h a l l and R. J. G i l l e s p i e, *Can. J. Chem.* **42** (1964) 502.
6. a) C. M a c L e a n and E. L. M a c k o r, *Discuss. Faraday Soc.* **34** (1962) 195.
   b) D. M. B r o u w e r, C. M a c L e a n, and E. L. M a c k o r, *Discuss. Faraday ,Soc.* **39** (1965) 121.
7. G. A. O l a h and Y. K. M o, *J. Org. Chem.* **38** (1973) 353.
8. A. J. K r e s g e, Y. C h i a n g, and L. E. H a k k a, *J. Amer. Chem. Soc.* **93** (1971) 6167.
9. H. K ö h l e r and G. S c h e i b e, *Z. Anorg. Allg. Chem.* **285** (1956) 221.
10. G. A. O l a h and Y. K. M o, *J. Amer. Chem. Soc.* **94** (1972) 5341.
11. J. W. L a r s e n and M. E c k e r t - M a k s i ć, *Tetrahedron Lett.* (1972) 1477.
12. G. B e r t h o l o n and R. P e r r i n, *C. R. Acad. Sci. Ser. C* **2750** (1972) 645.
13. T. B i r c h a l l, A. N. B o u r n s, R. J. G i l l e s p i e, and P. J. S m i t h, *Can. J. Chem.* **42** (1964) 1433.
14. M. P. H a r t s h o r n, K. E. R i c h a r d s, J. V a u g h n, and G. J. W r i g h t, *J. Chem. Soc. B* (1971) 1624.
15. E. C. F r i e d r i c h, *J. Org. Chem.* **33** (1968) 413.
16. V. G. S h u b i n, V. P. C h z h u, A. I. R e z v u k i n, A. A. T a b a t s k a v a, and V. A. K o p t y u g, *Izv. Akad. Nauk SSSR Ser. Khim.* (1967) 2365.
17. M. E c k e r t - M a k s i ć, *Ph. D. Thesis,* University of Zagreb, 1972.
18. W. M. S c h u b e r t and R. H. Q u a c c h i a, *J. Amer. Chem. Soc.* **84** (1962) 3778; *ibid.* **85** (1963) 1278.
19. A. J. K r e s g e, Y. C h e n, L. E. H a k k a, and J. E. K o u b a, *J. Amer. Chem. Soc.* **93** (1971) 6174.
20. E. G. L o v e r i n g and K. J. L a i d l e r, *Can. J. Chem.* **38** (1960) 2367.

IZVOD

Struktura protoniranih metil supstituiranih fenola u SbF₅/HSO₃F na —60 °C

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Primjenom NMR spektrometrije određen je smjer protoniranja niza metil supstituiranih fenola u 11.5 M ⁰/₀ SbF₅/HSO₃F. Većina opaženih rezultata može se objasniti isključivo utjecajem položaja supstituenata. Favorizirano je protoniranje u *para* položaju prema hidroksi grupi osim u slučajevima *para* supstituiranih derivata. Kod *para* supstituiranih fenola dominira protoniranje u *orto* položaju jezgre. Kod p-krezola opažen je protoniranje i na kisiku hidroksi supstituenta i u *orto* položaju jezgre

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