Stable Carbocations. CLII.[1] Protonation of Halophenols and Haloanisoles in Superacids

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The protonation of halophenols and haloanisoles was studied in four different superacid media: HF-SbF$_5$ (1:1 mol/mol)-SO$_2$ClF, FSO$_3$H-SbF$_5$ (1:1 mol/mol)-SO$_2$ClF, FSO$_3$H-SbF$_5$ (4:1 mol/mol), and FSO$_3$H-SO$_2$ClF at low temperature by nmr spectroscopy. O- or C-protonation was observed dependent upon the superacid media used. The structure of the formed arenium and oxonium ions was assigned based on their nmr (^{1}H and ^{19}F) spectra. Isomeric ions derived from the same precursor were also observed. Structural aspects and stability of halogenated arenium, as well as halophenyloxonium, ions are discussed in terms of hydrogen bonding and steric, resonance, and inductive effects.

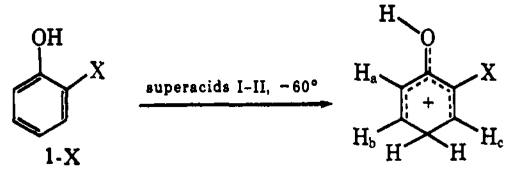
Recently, we have reported the protonation of mono-, di-, and trihydroxybenzenes and their methyl ethers in various superacid media.[3] Independently, hydroxy- and alkoxybenzenium ions have also been studied[4] and reviewed by Brouwer, *et al.*[5] The protonation (in superacid media) of haloarenes has also been investigated in our laboratory,[6] as well as by Brouwer.[7] In continuation of our studies it was of interest to undertake an investigation of the protonation of halophenols and haloanisoles in superacids. Of particular interest is the site of protonation, since phenol and anisole are both C- and O-protonated dependent on the conditions. The inductive and resonance (back-donation[8]) effects of halogens may play an important role in determining the formation of the corresponding arenium and oxonium ions in the protonation of halophenols and haloanisoles.

A systematic study of the protonation of monohalophenols and monohaloanisoles was carried out in the following four superacid systems at low temperature: (I) HF-SbF$_5$(1:1 mol/mol)-SO$_2$ClF, (II) FSO$_3$H-SbF$_5$ (1:1 mol/mol)-SO$_2$ClF, (III) FSO$_3$H-SbF$_5$ (4:1 mol/mol)-SO$_2$ClF, and (IV) FSO$_3$H-SO$_2$ClF.

Results and Discussion

The complete series of isomeric halophenols and haloanisoles was protonated in superacids I–IV. Ions observed are summarized in Table I. The nmr data of halogenated hydroxy- and methoxybenzenium ions formed under various conditions are tabulated in Table II, whereas data of the corresponding oxonium ions are summarized in Table III.

Protonation of *o*-Halophenols (1-X).—Protonation of *o*-halophenols (1-X, X = F, Cl, and Br) in superacids I and II at −60° gave the corresponding C-protonated 3-halo-4-hydroxybenzenium ions 1-Xa. The structures of ions 1-Xa can be assigned based on their nmr (^{1}H and ^{19}F) spectra (Tables II and IV). Evidence for the formation of these benzenium ions (*i.e.*, C-protonation) comes from the observed methylene absorption (δ 4.6–4.8) and the marked deshielding effect of the ortho protons (H$_b$ and H$_c$), as well as the coupling constants ($J_{H_aH_b}$ and J_{H_aF}) (Figure 1a). The meta protons (H$_a$) of ions 1-Xa are coupled to protons H$_b$. In the case of ion 1-Fa, it is also coupled to the meta F ($^4J_{HF}$ = 6.0 Hz) (Figure 1a). The pmr absorptions of the two ortho protons (H$_b$ and H$_c$) are generally more deshielded than that of H$_a$. They can be distinguished by the observed vicinal proton–proton coupling (8–10 Hz) between protons H$_a$ and H$_b$. The pmr absorptions of protons H$_b$ and H$_c$ in ions 1-Xa are a doublet of quartets and a quartet, respectively. These data indicate that the two ortho protons are coupled to each other through six bonds ($^6J_{H_bH_c}$ = 1.0 Hz). Similar results have been observed in the protonation of *o*-cresol and *o*-methylanisole.[3b] The OH pmr absorption of ions 1-Xa were not observed, presumably owing to the rapid intermolecular hydrogen exchange with the solvent system.



1-X
1-F, X = F
1-Cl, X = Cl
1-Br, X = Br

1-Xa
1-Fa, X = F
1-Cla, X = Cl
1-Bra, X = Br

The ^{19}F nmr spectrum of ion 1-Fa shows a multiplet at ϕ 129.3 (11.7 ppm deshielded from the precursor 1-F). The slight deshielding effect is mainly due to the inductive effect of the halogen. This is consistent with the assigned structure.[6] Thus, the observed fluorine shift is similar to those of the meta F in fluorobenzenium ions.[6a]

Protonation of *o*-iodophenol (1-I) and *o*-iodoanisole (2-I) in superacids I–II was not successful. Solid tar as well as iodine formation was observed. The decomposition of 1-I and 2-I is not surprising, since iodobenzene also decomposes to iodine and unidentified products under similar conditions.[9] On the other hand, iodobenzene can be readily methylated with

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[1] Part CLI: G. A. Olah and Y. K. Mo, *J. Amer. Chem. Soc.*, submitted.

[2] Postdoctoral Research Associate, 1972.

[3] (a) G. A. Olah and Y. K. Mo, *J. Amer. Chem. Soc.*, **94**, 5341 (1972); (b) *J. Org. Chem.*, in press.

[4] (a) D. M. Brouwer, E. L. Mackor, and C. MacLean, *Recl. Trav. Chim. Pays-Bas*, **85**, 109, 114 (1966); (b) T. Birchall, A. N. Bourns, R. J. Gillespis, and P. J. Smith, *Can. J. Chem.*, **42**, 1433 (1964); (c) T. Birchall and R. J. Gillespie, *ibid.*, **42**, 502 (1964); (f) C. MacLean and E. L. Mackor, *Discuss. Faraday Soc.*, **34**, 165 (1962); (e) D. M. Brouwer, C. MacLean, and E. L. Mackor, *ibid.*, **39**, 121 (1965); (f) M. P. Hartshorn, K. E. Richards, J. Vaughan, and G. J. Wright, *J. Chem. Soc. B*, 1624 (1971).

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[6] (a) G. A. Olah and T. E. Kiovsky, *J. Amer. Chem. Soc.*, **89**, 5692 (1967); **90**, 2583 (1968); (b) G. A. Olah and Y. K. Mo, *ibid.*, in press.

[7] D. M. Brouwer, *Recl. Trav. Chim. Pays-Bas*, **87**, 335, 342 (1968).

[8] G. A. Olah, Y. K. Mo, and Y. Halpern, *J. Amer. Chem. Soc.*, **94**, 3551 (1972).

[9] G. A. Olah and P. Schilling, *ibid.*, in press.

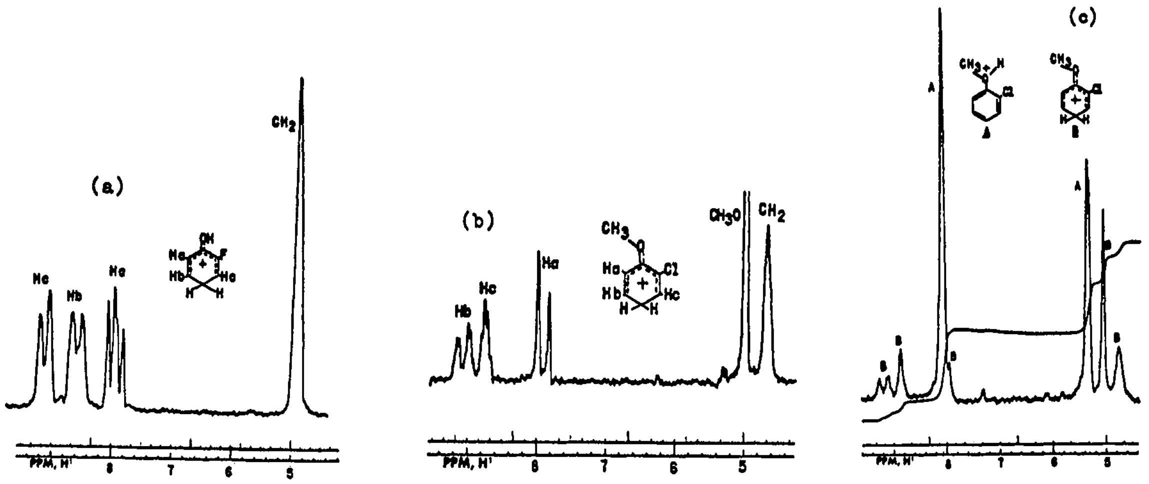


Figure 1.—Pmr spectra of 3-fluoro-4-hydroxybenzenium ion 1-Fa (a), 3-chloro-4-methoxybenzenium ion 2-Cla (b), and a mixture of ions 2-Cla and 2-Clb (c).

TABLE I

ION FORMATION UPON PROTONATION OF HALOGENATED PHENOLS AND ANISOLES[a]

Halogenated phenol and anisole	Ions formed in superacid system			
	I	II	III	IV
1-F	1-Fa	1-Fa	1-Fa, 1-F ⇌ 1-Fb (55%) (45%)	1-F ⇌ 1-Fb
1-Cl	1-Cla	1-Cla	1-Cla, 1-Cl ⇌ 1-Clb (60%) (40%)	1-Cl ⇌ 1-Clb
1-Br	1-Bra	1-Bra	1-Bra	1-Br ⇌ 1-Brb
1-I	Dec	Dec	1-Ia	1-I ⇌ 1-Ib
2-F	2-Fa	2-Fa, 2-F ⇌ 2-Fb (72%) (28%)	2-Fa, 2-F ⇌ 2-Fb (67%) (33%)	1-F ⇌ 1-Fb
2-Cl	2-Cla	2-Cla, 2-Cl ⇌ 2-Clb (33%) (67%)	2-Cla, 2-Cl ⇌ 2-Clb (33%) (67%)	1-Cl ⇌ 1-Clb
2-Br	2-Bra	2-Bra, 2-Br ⇌ 2-Brb (33%) (67%)	2-Bra, 2-Br ⇌ 2-Brb (30%) (70%)	1-Br ⇌ 1-Brb
2-I	Dec	Dec	2-Ia	1-I ⇌ 1-Ib
3-F	3-Fa	3-Fa	3-Fa	3-Fa
3-Cl	3-Cla	3-Cla	3-Cla, 3-Cl ⇌ 3-Clb (55%) (45%)	3-Cla, 3-Cl ⇌ 3-Clb (20%) (80%)
3-Br	3-Bra	3-Bra	3-Bra, 3-Br ⇌ 3-Brb (41%) (59%)	3-Bra, 3-Br ⇌ 3-Brb (28%) (72%)
3-I	Dec	Dec	3-Ia	3-Ia, 3-I ⇌ 3-Ib (60%) (40%)
4-F	4-Fa ⇌ 4-Fa' (75%) (25%)	4-Fa ⇌ 4-Fa' (71%) (29%)	4-Fa ⇌ 4-Fa' (88%) (12%)	4-Fa ⇌ 4-Fa' (92%) (8%)
4-Cl	4-Cla ⇌ 4-Cla' (60%) (40%)	4-Cla ⇌ 4-Cla' (60%) (40%)	4-Cla ⇌ 4-Cla' (60%) (40%)	4-Cla ⇌ 4-Cla' (70%) 4-Cl ⇌ 4-Clb (30%)
4-Br	4-Bra ⇌ 4-Bra' (60%) (40%)	4-Bra ⇌ 4-Bra' (60%) (40%)	4-Bra ⇌ 4-Bra' (60%) (40%)	4-Bra ⇌ 4-Bra' (50%) 4-Br ⇌ 4-Brb (50%)
4-I	4-Ia ⇌ 4-Ia' (50%) (50%)	4-Ia ⇌ 4-Ia' (50%) (50%)	4-Ia ⇌ 4-Ia' (50%) (50%)	4-Ia ⇌ 4-Ia' (15%) (15%) 4-I ⇌ 4-Ib (70%)
5-F	5-Fb	5-Fb	5-F ⇌ 5-Fb	5-F ⇌ 5-Fb
5-Cl	5-Clb	5-Clb	5-Cl ⇌ 5-Clb	5-Cl ⇌ 5-Clb
5-Br	5-Brb	5-Brb	5-Br ⇌ 5-Brb	5-Br ⇌ 5-Brb
5-I	Dec	Dec	Dec	5-I ⇌ 5-Ib
6-F	6-Fb	6-Fb	6-F ⇌ 6-Fb	6-F ⇌ 6-Fb
6-Cl	6-Clb	6-Clb	6-Cl ⇌ 6-Clb	6-Cl ⇌ 6-Clb
6-Br	6-Brb	6-Brb	6-Br ⇌ 6-Brb	6-Br ⇌ 6-Brb
6-I	Dec	Dec	Dec	6-I ⇌ 6-Ib

[a] For actual experimental conditions (*e.g.*, temperature), see text.

TABLE II

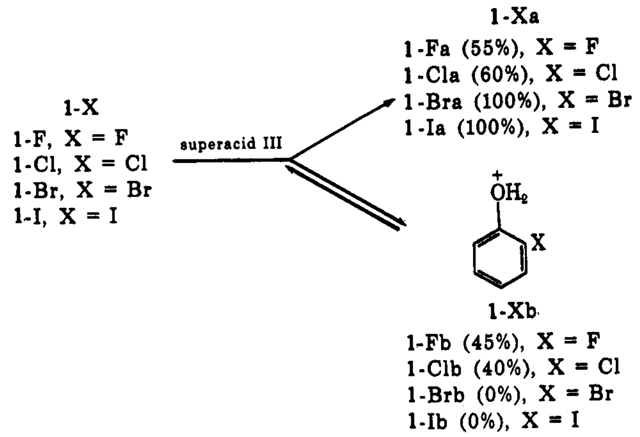
PMR DATA OF HALOGENATED HYDROXY- AND METHOXYBENZENIUM IONS[a,c]

Halogenated aromatic	Ion	Superacid system, temp, °C	δ, OCH_3	δ, CH_3	δ, H_a	δ, H_b	δ, H_c	δ, OH
1-F	1-Fa	I, −20		4.8 (s,br)	7.83 (d,d), $J_{HF} = 6$ $J_{HH} = 9$	8.5 (d,br), $J_{HH} = 9$	9.0 (d,br), $J_{HF} = 10$	[b]
1-Cl	1-Cla	I, −60		4.8 (s,br)	7.90 (d,br), $J_{HH} = 8$	9.06 (d,br),	8.95 (s,br)	[b]
1-Br	1-Bra	I, −60		4.73 (t) $J_{HH} = 1$	7.80 (d), $J_{HH} = 9$	9.02 (d,q) $J_{HH} = 9, 1$	9.20 (q), $J_{HH} = 1$	[b]
1-I	1-Ia	III, −40		4.6 (s,br)	7.7 (d,br), $J_{HH} = 9$	8.9 (d,br), $J = 9$	9.3 (s,br)	12.1 (s,br)
2-F	2-Fa	I, −40	5.15 (s)	4.8 (s,br)	8.00 (d,d), $J_{HF} = 6$ $J_{HH} = 10$	8.31 (d,q) $J_{HH} = 10, 1.5$	9.16 (d,q), $J_{HF} = 10$ $J_{HH} = 1.5$	[b]
	2-Fa		5.00 (s)	4.7 (s,br)	7.90 (d,d), $J_{HH} = 10$ $J_{HF} = 6$	8.23 (d,q), $J_{HH} = 10, 1.5$	9.10 (d,q), $J_{HF} = 10$ $J_{HH} = 1.5$	[b]
2-F	⇅	II, −40						
	2-Fa′		5.20 (s)	4.7 (s,br)	7.90 (d,d), $J_{HH} = 10$ $J_{HH} = 6$	8.23 (d,q), $J_{HH} = 10, 1.5$	9.10 (d,q), $J_{HF} = 10$ $J_{HH} = 1.5$	[b]
2-Cl	2-Cla	II, −40	5.00 (s)	4.63 (t) $J_{HH} = 2$	7.90 (d), $J_{HH} = 9$	9.04 (d,q), $J_{HH} = 9, 1$	8.74 (q), $J_{HH} = 1$	[b]
2-Br	2-Bra	I, −50	4.97 (s)	4.63 (t) $J_{HH} = 2$	7.90 (d), $J_{HH} = 10$	9.04 (d,q), $J_{HH} - 10, 1$	8.97 (q), $J_{HH} = 1$	[b]
2-I	2-Ia	III, −80	4.80 (s)	4.5 (s,br)	7.8 (br)	9.0 (br)	8.6 (br)	[b]
3-F	3-Fa	I, −16		4.50 (t), $J_{HH} = J_{HF} = 3.5$	7.31 (d,d), $J_{HH} = 10$ $J_{HF} = 1.5$	7.48 (d), $J_{HF} = 10$	8.4 (m)	11.3 (br)
3-Cl	3-Cla	I, −40		4.70 (d), $J_{HH} = 2$	7.54 (d), $J_{HH} = 9$	7.70 (s)	8.73 (d,t), $J_{HH} = 9, 2$	[b]
3-Br	3-Bra	I, −40		4.70 (d), $J_{HH} = 2$	7.63 (d,d), $J_{HH} = 9, 1$	8.00 (d), $J_{HH} = 2$	8.80 (d,t), $J_{HH} = 9, 2$	[b]
3-I	3-Ia	III, −60		4.60 (d) $J_{HH} = 2$	7.50 (d,d), $J_{HH} = 10, 1$	8.30 (d), $J_{HH} = 1$	8.68 (d,t), $J_{HH} = 10, 2$	[b]
	4-Fa		4.88 (s)	4.6 (s,br)	7.4 (m)	7.4 (m)	8.3 (m)	[b]
4-F	⇅	II, −40						
	4-Fa′		4.74 (s)	4.6 (s,br)	7.4 (m)	7.4 (m)	8.3 (m)	[b]
	4-Cla		4.80 (s)	4.60 (d)	7.4 (d,br)	7.8 (s,br)	8.5 (d,br)	[b]
4-Cl	⇅	I, −30		$J_{HH} = 2$	$J_{HH} = 9$		$J_{HH} = 9$	
	4-Cla′		4.80 (s)	4.60 (d) $J_{HH} = 2$	7.7 (d,br) $J_{HH} = 9$	7.6 (s,br)	8.8 (d,br) $J_{HH} = 9$	[b]
	4-Bra		4.80 (s)	4.68 (s)	7.6 (d,br), $J_{HH} = 9$	8.2 (s)	8.5 (d,br), $J_{HH} = 9$	[b]
4-Br	⇅	I, −60						
	4-Bra′		4.80 (s)	4.68 (s)	7.8 (d,br), $J_{HH} = 9$	7.9 (s)	8.9 (d,br), $J_{HH} = 9$	[b]
	4-Ia		4.72 (s)	4.62 (d)	7.50 (d,d)	8.53 (s), $J_{HH} = 1$	8.63 (d,t)	[b]
4-I	⇅	III, −60		$J_{HH} = 2$	$J_{HH} = 10, 1$		$J_{HH} = 10, 2$	
	4-Ia′		4.72 (s)	4.62 (d) $J_{HH} = 2$	7.88 (d,d) $J_{HH} = 10, 1$	8.22 (d), $J_{HH} = 1$	8.90 (d,t) $J_{HH} = 10, 2$	[b]

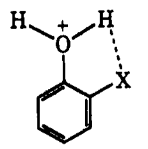
[a] Proton chemical shifts are referred to external capillary TMS in parts per million (δ). J values are in hertz. [b] OH proton is not observable owing to rapid hydrogen exchange with the solvent systems. [c] Abbreviation used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

methyl fluoroantimonate to give the methylphenyliodonium ion.[10] Thus, deiodination of iodobenzene as well as 1-I and 2-I may involve initial protonation at iodine and subsequent dehydroiodination to give the corresponding aryl cations, which would immediately arylate excess iodoaromatic compounds. Attempts to directly observe such an intermediate I-protonated species at low temperature were not successful.

Protonation of *o*-halophenols in superacid III gave C-protonated 3-halo-4-hydroxybenzenium ions (I-Xa).



However, O-protonated oxonium ions 1-Fb (45%) and 1-Cl (40%) were also formed in the protonation of 1-F and 1-Cl, respectively. The pmr spectrum of 1-F in superacid III shows, besides the absorption lines of ion 1-Fa, a multiplet at δ 7.7. This multiplet is similar to that of 1-F when protonated in superacid IV (O-protonation, see subsequent discussion). The ratio of ions 1-Fa:1-Fb can thus be determined by integration of the pmr spectrum. Similar results were also obtained when 1-Cl was protonated in superacid III. The OH proton absorptions of ions 1-Xa and 1-Xb were not observed under the experimental conditions, owing to obvious rapid exchange with the acid solvent system.



1-Xb (X = F and Cl)

The formation of oxonium ion 1-Fb (45%) and 1-Cl (40%), but not of 1-Brb and 1-Ib from 1-X (X = F, Cl, Br, and I) under identical conditions, is interesting, These data indicate that the substantial inductive effect of the electronegative fluorine and chlorine atoms in the ortho position of a benzenium ion is operative.

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(10) G. A. Olah and E. G. Melby, *J. Amer. Chem. Soc.*, **94**, 6220 (1972).

TABLE III

PMR PARAMETERS OF HALOGENATED PHENYLOXONIUM IONS[a]

Halogenated phenyloxonium ion	Superacid system and temp, °C	δ, OCH_3	δ, Aromatic	δ, OH	Remarks
1-F ⇌ 1-Fb	IV, −40		7.4 (m)	[b]	
1-Cl ⇌ 1-Clb	IV, −60		7.4 (m)	[b]	
1-Br ⇌ 1-Brb	IV, −60		7.3–7.8 (a)	[b]	
1-I ⇌ 1-Ib	IV, −80		7.3–7.8 (m)	[b]	
2-F ⇌ 2-Fb	IV, −40	4.54 (s)	7.5 (m)	[b]	
2-Clb	I, −60	5.30 (d) J_{HH} = 2	8.10 (s)	11.9 (q) J_{HH} = 2	67% with 33% C-protonation formed initially
2-Cl ⇌ 2-Clb	IV, −60	4.50 (s)	7.60 (s)	[b]	
2-Brb	II, −60	5.30 (d) J_{HH} = 2	8.0 (m)	[c]	67% with 33% C-protonation formed initially
2-Br ⇌ 2-Brb	IV, −50	4.5 (s)	7.6–7.7 (m)	[b]	
2-I ⇌ 2-Ib	IV, −80	4.60 (s)	7.3–7.9 (m)	[b]	
3-Cl ⇌ 3-Clb	III, −40		7.6 (m)	[b]	45% with 55% C-protonation
3-Br ⇌ 3-Brb	IV, −40		7.7 (m)	[b]	72% with 28% C-protonation
3-I ⇌ 3-Ib	IV, −50		7.5–7.7 (m)	[b]	40% with 60% C-protonation
4-Clb	II, −60	5.23 (d) J_{HH} = 2	7.8 (m)	12.0 (q) J_{HH} = 2	See text
4-Cl ⇌ 4-Clb	IV, −60	4.6 (s)	7.5 (m)	[b]	31% with 69% C-protonation
4-Brb	II, −60	5.23 (d) J_{HH} = 3	7.9 (m)	11.7 (q) J_{HH} = 3	10% with 90% C-protonation formed initially
4-Br ⇌ 4-Brb	IV, −50	4.60 (s)	7.6 (m)	[b]	50% with 50% C-protonation
4-I ⇌ 4-Ib	IV, −60	4.40 (s)	7.6–7.8 (m)	[b]	71% with 29% C-protonation
5-Fb	I, −20		7.8 (m)	12.0 (s)	
5-F ⇌ 5-Fb	IV, −20		7.45 (m)	[b]	
5-Clb	I, −40		7.81 (d), J_{HH} = 10 8.01 (d), J_{HH} = 10	12.3 (s)	
5-Cl ⇌ 5-Clb	IV, −60		7.3 (d), J_{HH} = 8 7.6 (d), J_{HH} = 8	[b]	
5-Brb	I, −60		7.90 (d), J_{HH} = 9 8.26 (d), J_{HH} = 9	12.7 (s)	
5-Br ⇌ 5-Brb	IV, −60		7.32 (d), J_{HH} = 8 7.78 (d), J_{HH} = 8	[b]	
5-I ⇌ 5-Ib	IV, −80		7.17 (d), J_{HH} = 8 8.00 (d), J_{HH} = 8	[b]	
6-Fb	II, −60	5.22 (d) J_{HH} = 3	7.8 (m)	12.1 (s,br)	
6-F ⇌ 6-Fb	IV, −40	4.73 (s)	7.5 (m)	[b]	
6-Clb	I, −40	5.22 (d) J_{HH} = 3	7.81 (d), J_{HH} = 9 8.03 (d), J_{HH} = 9	11.2 (q) J_{HH} = 3	
6-Cl ⇌ 6-Clb	IV, −40	4.60 (s)	7.41 (d), J_{HH} = 9 7.63 (d), J_{HH} = 9	[b]	
6-Brb	I, −40	5.22 (d) J_{HH} = 3	7.81 (d), J_{HH} = 8 8.20 (d), J_{HH} = 8	11.3 (q) J_{HH} = 3	
6-Br ⇌ 6-Brb	IV, −40	4.60 (s)	7.50 (d), J_{HH} = 9 7.90 (d), J_{HH} = 9	[b]	
6-I ⇌ 6-Ib	IV, −80	4.60 (s)	7.23 (d), J_{HH} = 9 8.00 (d), J_{HH} = 9	[b]	

[a] Proton chemical shifts are referred to external capillary TMS in parts per million (δ): s, singlet; d, doublet; q, quartet; br, broad. J values are in hertz. [b] The OH peak is not observable since it exchanges with the superacids. [c] The broad peak should be a quartet.

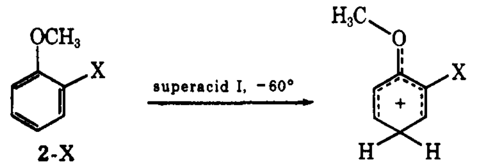
Consequently, ions 1-Fa and 1-Cla are less stable than ions 1-Bra and 1-Ia. In addition, intramolecular hydrogen bonding may be more favorable in oxonium ions 1-Fb and 1-Clb than in ions 1-Brb and 1-Ib.

In superacid IV, all the four *o*-halophenols (1-X) were O-protonated to give the oxonium ions 1-Xb.

$$\text{1-X} \xrightleftharpoons{\text{superacid IV, } -70^\circ} \text{1-Xb (X = F, Cl, Br, and I)}$$

The pmr data of oxonium ions 1-Xb in superacid IV are summarized in Table III. The aromatic proton absorptions of 1-X in superacid IV are similar to those of the precursors (in SO_2ClF), but are very much deshielded. The OH proton absorptions of 1-Xb are not observable, indicating rapid intermolecular hydrogen exchange with the solvent system.

Protonation of *o*-Haloanisoles (2-X).—*o*-Haloanisoles behave somewhat differently from *o*-halophenols in the four superacids studied. In superacid I, *o*-haloanisoles (2-X, X = F, Cl, and Br) were C-protonated to give the transoid 3-halo-4-methoxybenzenium ions



2-X
2-F, X = F
2-Cl, X = Cl
2-Br, X = Br

2-Xa
2-Fa, X = F
2-Cla, X = Cl
2-Bra, X = Br

Table IV

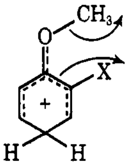
^{19}F Nmr Data of Protonated Fluorophenols and Fluoroanisoles[a]

Fluorophenol and fluoroanisole	Precursor ^{19}F chemical shift, ϕ	Superacid system, temp, °C	Formed ion	ϕ, o-F	ϕ, m-F	ϕ, p-F
1-F	141.0 (m)	I, −16	1-Fa		129.3 (m)	
		IV, −60	1-F ⇌ 1-Fb	137.8 (m)		
2-F	136.7 (m)	I, −45	2-Fa		125.9 (m)	
		II, −80	2-Fa (72%)		126.3 (br)	
			2-F ⇌ 2-Fb (28%)	131.4 (m)		
		IV, −80	2-F ⇌ 2-Fb	134.0 (m)		
3-F	112.6 (m)	I, −16	3-Fa	35.9 (m)		
4-F	130.9 (m)	I, −25	4-Fa ⇌ 4-Fa′ (75%) (25%)	32.4 (m) 45.1 (m)		
		IV, −60	4-Fa ⇌ 4-Fa′ (92%) (8%)	33.1 (m) 44.9 (m)		
5-F	125.2 (m)	I, −16	5-Fb			110.2 (m)
6-F	125.8 (m)	I, −25	6-Fb			109.3 (m)

[a] Fluorine chemical shifts are referred to external capillary CCl_3F in parts per million (δ).

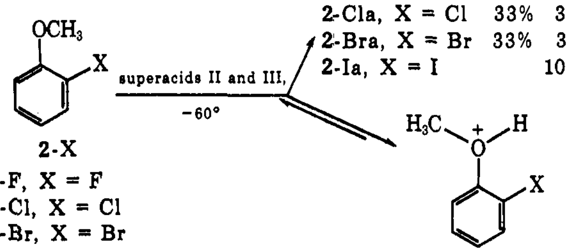
(2-Xa) exclusively. The pmr spectrum of ion 2-Cla is shown in Figure 1b.

The isomeric cisoid 3-halo-4-methoxybenzenium ions 2-Xa′ were not observed, presumably owing to unfavorable steric conditions.[4] The nmr (^{1}H and ^{19}F) spectra of 2-Xa are similar to those of 1-Xa except that an additional methoxyl proton absorption was observed in each pmr spectrum (see Table II).



2-Xa′

Both C- and O-protonated ions (2-Xa and 2-Xb) were obtained when *o*-haloanisoles (2-X) were treated in superacids II and III. The ratio of 2-Xa:2-Xb is dependent on the nature of the halogen atom and the superacids used.



2-X

2-F, X = F

2-Cl, X = Cl

2-Br, X = Br

2-I, X = I

2-Xa	superacids II	III
2-Fa, X = F	72%	67%
2-Cla, X = Cl	33%	33%
2-Bra, X = Br	33%	30%
2-Ia, X = I		100%

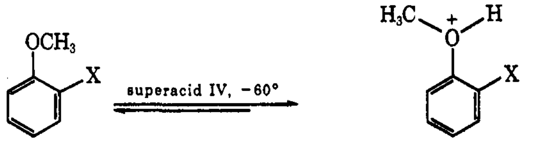
2-Xb	superacids II	III
2-Fb, X = F	28%	33%
2-Clb, X = Cl	67%	67%
2-Brb, X = Br	67%	70%

The pmr spectra of 2-F in superacids II and III are very similar. Besides the pmr absorption lines of ion 2-Fa, there is an additional singlet absorption at δ 5.20 (OCH_3). In the aromatic region an additional multiplet was also observed at δ 7.9. These data show the formation of oxonium ion 2-Fb, although the OH proton absorption is not observed (presumably owing to rapid intermolecular hydrogen exchange with the solvent system). The ratio of ions 2-Fa:2-Fb was determined from the integration of the area of the two methoxy absorptions. The ^{19}F nmr spectrum of 2-F in superacid II shows two multiplets at ϕ 126.3 (2-Fa) and 131.4 (2-Fb). The ratio of the two fluorine absorptions is identical with that of the methoxy protons. The fluorine absorption of the precursor (2-F) shows a multiplet at ϕ 136.7. Thus the slight deshielding effects in both ions 2-Fa and 2-Fb are primarily due to an inductive effect. A similar ^{19}F nmr spectrum was also observed when 2-F was protonated in superacid III.

When 2-Cl was protonated in superacid II at −60°, the pmr spectrum (Figure 1c) of the solution shows, besides the absorption lines of ion 2-Cla, a doublet at δ 5.30 (J_{HH} = 2 Hz, OCH_3), a singlet at δ 8.10 (aromatic protons), and a quartet at δ 11.9 (J_{HH} = 2 Hz, OH). These data clearly indicate the formation of oxonium ion 2-Clb. A similar pmr spectrum was also observed when 2-Cl was treated in superacid III. However, both the methoxyl and the aromatic protons of ion 2-Clb are slightly shielded from those observed in superacid II. Owing to the rapid hydrogen exchange of $>OH^+$ with the solvent system, the OCH_3 proton absorption is a singlet instead of a doublet in superacid III. *o*-Bromoanisole (2-Br) behaves very similarly to 2-Cl in both superacids II and III.

o-Iodoanisole (2-I) decomposed to unidentified products in superacid II. However, it was protonated in superacid III to give the 3-iodo-4-methoxybenzenium ion (2-Ia), together with some decomposition products. The different behavior of 2-I in superacid II and in superacid III is not yet understood.

In the weakest superacid IV, all the four *o*-haloanisoles (2-X) were O-protonated to give oxonium ions 2-Xb. The pmr data of these oxonium ions 2-Xb in

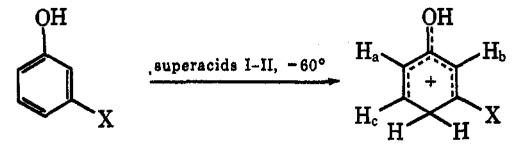


2-X

2-Xb (X = F, Cl, Br, and I)

superacid IV are summarized in Table III. The OH proton absorptions of ions 2-Xb were not observed even at the lowest possible temperature, indicating that they are rapidly exchanging with the solvent system. The ^{19}F nmr spectrum of ion 2-Fb shows a multiplet at ϕ 134.0 (2.7 ppm deshielded from 2-F in SO$_2$ClF).

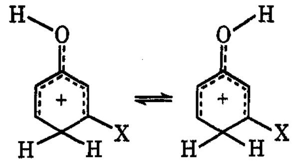
Protonation of *m*-Halophenols (3-X).—Protonation of *m*-halophenols (3-X, X = F, Cl, and Br) in superacids I–II at −60° gave the corresponding 2-halo-4-hydroxybenzenium ions (3-Xa, X = F, Cl, and Br).



3-X
3-F, X = F
3-Cl, X = Cl
3-Br, X = Br

3-Xa
3-Fa, X = F
3-Cla, X = Cl
3-Bra, X = Br

In the pmr spectra of ions 3-Xa, the OH proton either shows a broadened absorption line or is not observable. This indicates rapid equilibration of the isomeric ions



3-Xa (transoid and cisoid). Thus, the nmr (^{1}H and ^{19}F) spectra of ions 3-Xa are greatly simplified (Figures 2a and 2b).

In the pmr spectrum of ion 3-Fa, it is interesting to note that the methylene protons display a triplet at δ 4.50 ($J_{HH} = J_{HF}$ = 3.5 Hz). The triplet indicates that the two equivalent methylene protons have a similar spin–spin interaction with both ortho F and ortho H (H$_c$) in ion 3-Fa. The meta proton (H$_b$) adjacent to the ortho F shows a doublet at δ 7.48 (J_{HH} = 10 Hz). The less deshielded meta proton (H$_a$) displays a doublet of doublets at δ 7.31 ($J_{HH} = J_{HF}$ = 1.5 Hz). The further splitting is due to the five-bond H–F long-range coupling. The ortho proton shows a multiplet instead of a doublet of triplets at δ 8.4 indicating a six-bond long-range H–F spin–spin interaction.

The pmr spectra of both ions 3-Cla and 3-Bra are much simplified because of the absence of the proton–fluorine coupling as observed in ion 3-Fa. Thus, the CH$_2$ of both ion 3-Cla and 3-Ba display a doublet at δ 4.70 (J_{HH} = 3 Hz). The meta proton (H$_a$) of ion 3-Bra shows a doublet of doublets at δ 7.63 (J_{HH} = 9 and 1 Hz) while the H$_a$ proton of ion 3-Cla shows a doublet at δ 7.54 (J_{HH} = 9 Hz). These results indicate that the coupling between the two meta protons (H$_a$ and H$_b$) is larger in ion 3-Bra (1 Hz) than in ion 3-Cla (less than 0.5 Hz).

Protonation of *m*-iodophenol (3-I) in both superacids I and II was unsuccessful. It decomposed immediately even when the reaction was attempted at −90°.

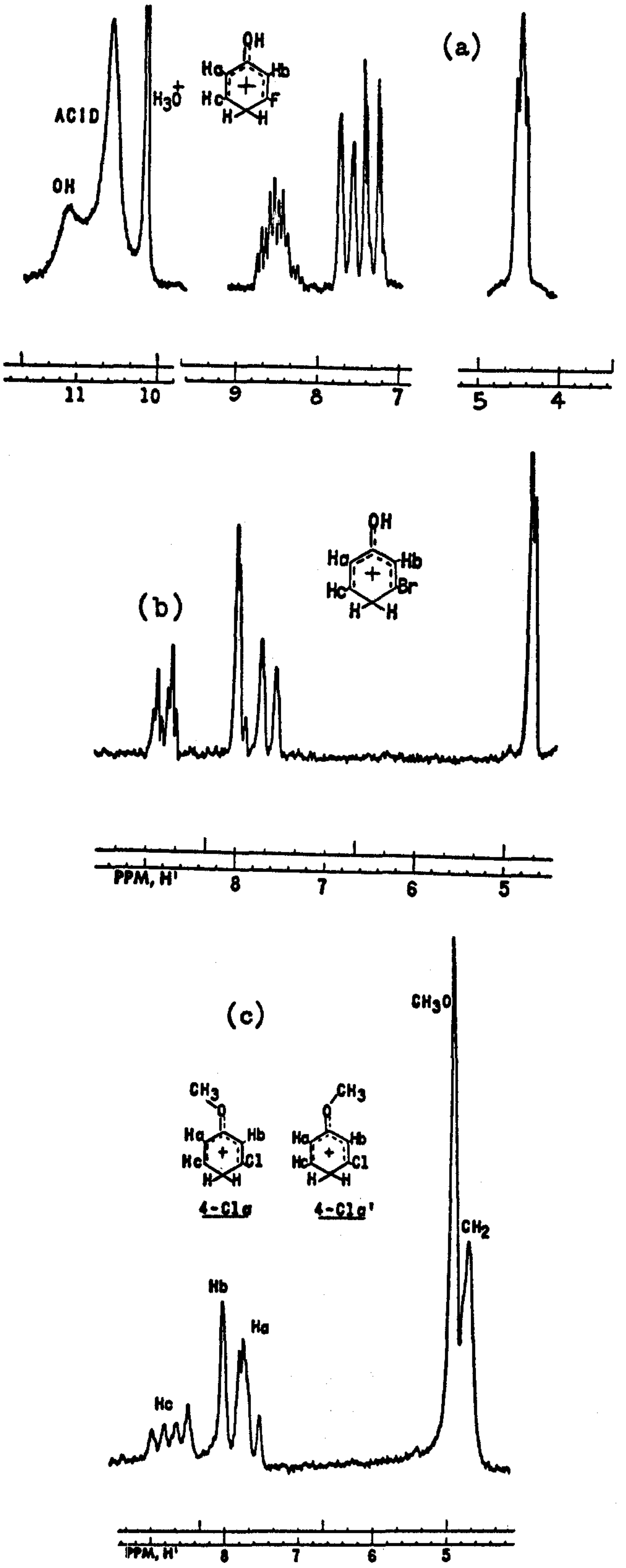
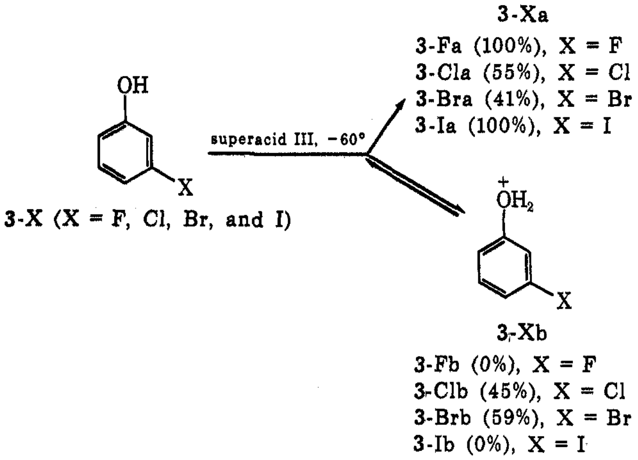


Figure 2.—Pmr spectra of ions 3-Fa (a), 3-Bra (b), and 4-Cla and 4-Cla′ (c).

In superacid III, both *m*-fluorophenol (3-F) and *m*-iodophenol (3-I) were C-protonated at −60° to give the corresponding 2-fluoro- and 2-iodo-4-hydroxybenzenium ions (3-Fa and 3-Ia), respectively. The pmr spectrum of 3-Ia is similar to that of ion 3-Cla. In the same superacid III, 3-Cl and 3-Br were both C- and O-protonated to give 3-Cla (55%) and 3-Clb (45%), as well as 3-Bra (41%) and 3-Brb (59%), respectively. The formation of oxonium ion 3-Clb and 3-Brb can be



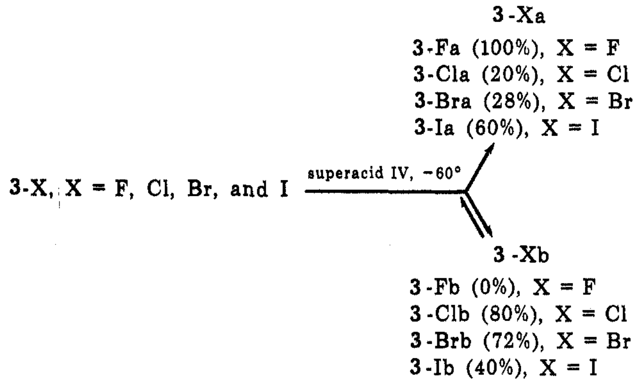
3-X (X = F, Cl, Br, and I)

3-Xa
3-Fa (100%), X = F
3-Cla (55%), X = Cl
3-Bra (41%), X = Br
3-Ia (100%), X = I

3-Xb
3-Fb (0%), X = F
3-Clb (45%), X = Cl
3-Brb (59%), X = Br
3-Ib (0%), X = I

recognized from the additional multiplets observed at δ 7.6 and 7.7, respectively, in their pmr spectra. The $^{+}OH_2$ proton absorption of ions 3-Clb and 3-Brb were not observed, indicating rapid intermolecular hydrogen exchange with the superacid system.

In superacid IV, 3-F was again C-protonated to give 3-Fa exclusively. However, both 3-Xa (X = Cl, Br, and I) and 3-Xb (X = Cl, Br, and I) were obtained when 3-X (X = Cl, Br, and I) were treated with superacid IV under similar conditions. The formation of



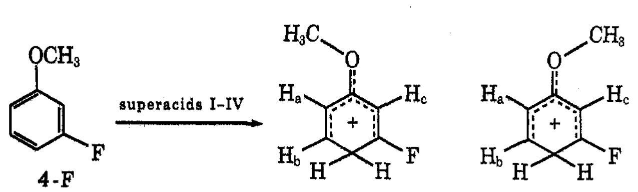
3-X, X = F, Cl, Br, and I

3-Xa
3-Fa (100%), X = F
3-Cla (20%), X = Cl
3-Bra (28%), X = Br
3-Ia (60%), X = I

3-Xb
3-Fb (0%), X = F
3-Clb (80%), X = Cl
3-Brb (72%), X = Br
3-Ib (40%), X = I

3-Xb was evidenced from the pmr multiplets of the aromatic protons. These multiplets were slightly shielded from those observed in superacid III, indicating that the equilibrium was shifting to the left (or the lifetime of 3-Xb is shortened). The ratio of ions 3-Xa:3-Xb was determined from integration of peak areas of spectra.

Protonation of *m*-Haloanisoles.—Protonation of *m*-fluoroanisole (4-F) in all four superacid systems (I–IV) gave two isomeric ions 4-Fa and 4-Fa′ in varying ratios.



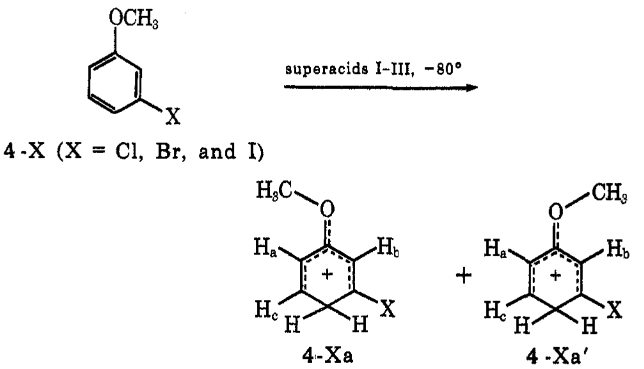
4-F

Superacid system	4-Fa	4-Fa′
I	75%	25%
II	71%	29%
III	88%	12%
IV	92%	8%

In increasingly stronger superacids a higher ratio of 4-Fa:4-Fa′ is observed. In the same superacid system, the ratio is independent of the temperature, in the range of −20 to −80°. The ratio can be determined either from the two distinct OCH_3 absorptions of 4-Fa (δ 4.88) and of 4-Fa′ (δ 4.74) or from the well-separated ^{19}F nmr absorptions at φ 33.1 (4-Fa) and 44.9 (4-Fa′). The remainder of the pmr resonance lines are not sufficiently different in ions 4-Fa and 4-Fa′. The methylene protons of both ions 4-Fa and 4-Fa′ show a broadened pmr absorption at δ 4.6. The meta protons of the ions 4-Fa and 4-Fa′ display a multiplet centered at δ 7.4 and the ortho proton shows another multiplet at δ 8.3.

The structural differentiation of ions 4-Fa and 4-Fa′ is based on their ^{19}F nmr absorptions. Ion 4-Fa has a more deshielded fluorine absorption (φ 33.1) than that of ion 4-Fa′ (φ 44.9) (Table IV). This is because the fluorine atom of ion 4-Fa is anisotropically deshielded by the nonbonded electron pair of oxygen. Similar results were observed in the protonation of *m*-methylanisole.[4]

The corresponding behavior of other *m*-haloanisoles (4-X, X = Cl, Br, and I) in superacids I–IV is slightly different from that of 4-F. Two isomeric ions (cisoid and transoid) were again observed when 4-X (X = Cl, Br, and I) were treated with superacids I–III at −80°.

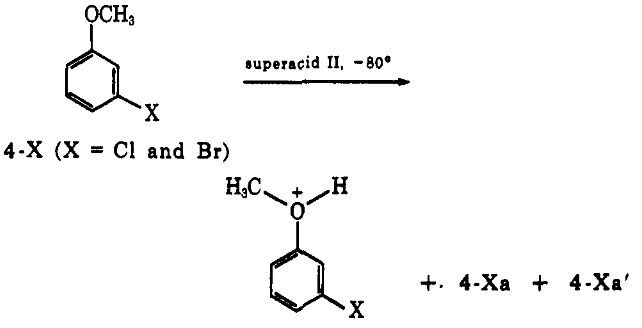


4-X (X = Cl, Br, and I)

4-Xa	4-Xa′
4-Cla (60%), X = Cl	4-Cla′ (40%)
4-Bra (60%), X = Br	4-Bra′ (40%)
4-Ia (50%), X = I	4-Ia′ (50%)

The formation of the two isomeric ions 4-Xa and 4-Xa′ can be readily recognized from the two very deshielded pmr triplet of doublets of the ortho protons (H_c). The meta protons (H_a and H_b) in ions 4-Xa and 4-Xa′ are also very much different. Owing to the anisotropy effect of the methoxy oxygen lone pair, the proton H_b in ion 4-Xa is more deshielded than proton H_a in the same ion. Similarly, proton H_a in ions 4-Xa′ is more deshielded than the corresponding H_b. The anisotropy effect is extended to the ortho proton (H_c). The ortho proton in 4-Xa is more deshielded than that in 4-Xa′ (Figure 2c). The methoxy as well as the methylene protons of both ions 4-Xa and 4-Xa′ are hardly distinguishable. Thus, the ratios of ions 4-Xa:4-Xa′ were determined from the integration of the H_c proton absorptions. Furthermore, the pmr spectra of ions 4-Xa and 4-Xa′ (X = Cl, Br, and I) are temperature dependent (similar to that of C-protonated anisole).[3,5] These data clearly indicate that the interconversion of 4-Xa and 4-Xa′ takes place through the rotation of the carbon–oxygen (C=O) partial double bond.

When 4-Cl and 4-Br were protonated carefully in superacid II at −80°, some O-protonated ions 4-Clb (10%) and 4-Brb (5%) were formed initially. Both ions **4**-Clb and **4**-Brb were transformed into C-protonated ion **4**-Cla, **4**-Cla′ and **4**-Bra, **4**-Bra′, respectively, when the solution was warmed to −20° for 1 min. The process is irreversible. It indicates that initial O-protonation is a kinetically controlled process, while C-protonation is thermodynamically controlled.



4-X (X = Cl and Br)

4-Xb

4-Clb (10%), X = Cl

4-Brb (5%), X = Br

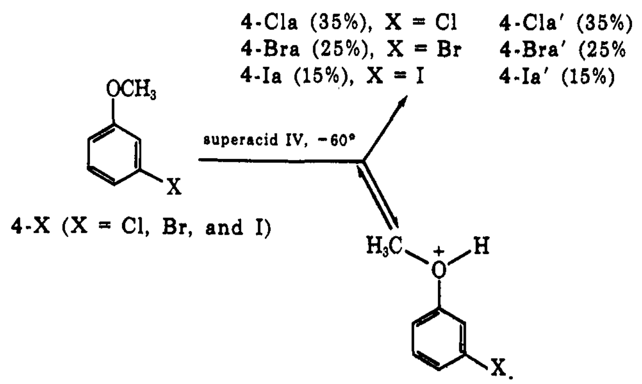
When *m*-haloanisoles (**4**-X, X = Cl, Br, and I) were protonated in superacid IV, both 2-halo-4-methoxybenzenium ions (**4**-Xa and **4**-Xa′) and oxonium ions **4**-Xb were obtained. The ratio of C- to O-protonation is dependent upon the nature of the halogens. C-protonation increases in the same order as the electronegativity of the halogens (F > Cl > Br > I). This result is in good agreement with observed degree of halogen "back-donation" in halocarbenium ions.[8] In other words, the resonance form of 2-halo-4-methoxybenzenium ion **4**-Xd arising through halogen back-donation is increasingly important with the decrease of the size of the halogen atom.

4-Xa + 4-Xa′

4-Cla (35%), X = Cl 4-Cla′ (35%)

4-Bra (25%), X = Br 4-Bra′ (25%

4-Ia (15%), X = I 4-Ia′ (15%)



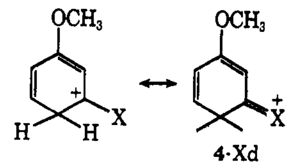
4-X (X = Cl, Br, and I)

4-Xb

4-Clb (30%), X = Cl

4-Brb (50%), X = Br

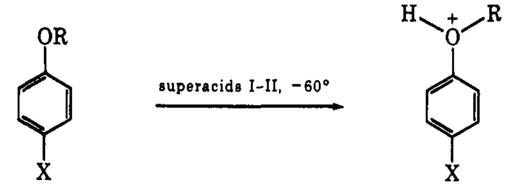
4-Ib (70%), X = I



4-Xd

The methoxy pmr absorptions of ions **4**-Clb and **4**-Brb are more shielded in superacid IV than those observed in superacid II (see Table III). The OH pmr absorptions of oxonium ions **4**-Clb and **4**-Brb were not observable even at −78°. These results indicate that the OH proton of oxonium ions **4**-Clb and **4**-Brb in IV is rapidly exchanging with the solvent system.

Protonation of *p*-Halophenols (5-X) and *p*-Haloanisoles (6-X).—*p*-Halophenols (**5**-X) and *p*-haloanisoles (**6**-X) show very similar behavior in the four superacid systems (I–IV). In either superacid I or II, the site of protonation was found to be on the oxygen atom. The $^+OH_2$ protons of O-protonated *p*-halophenols (**5**-Xb) and the $-CH_3OH^+$ proton of O-protonated *p*-haloanisoles (**6**-Xb) were directly observed in their pmr spectra (Figure 3). They are more deshielded than those of protonated alcohols[11] and ethers.[12] Obviously, the deshielding effect is caused by the inductively electron withdrawing aromatic (C_6H_4X) rings. The $^+OCH_3$ protons of all the oxonium ions **6**-Xb show a doublet at ∼δ 5.2 (J_{HH} = 3 Hz). The aromatic protons of both oxonium ions **5**-Fb and **6**-Fb are centered as a multiplet at δ 7.8 while those of oxonium ions **5**-Clb, **5**-Brb, **6**-Clb, and **6**-Brb show two doublets (or AB quartet) between δ 7.7 and 8.3 (see Table III). The multiple coupling in oxonium ions **5**-Fb and **6**-Fb must be due to the proton–fluorine interaction. The ^{19}F nmr spectra of **5**-F and **6**-F have almost identical chemical shifts at φ 125.2 and 125.8, respectively, whereas those of the O-protonated species, **5**-Fb and **6**-Fb, are both deshielded (by about 15–16 ppm) at φ 110.2 and 109.3. The relatively small deshielding (compared to those of C-protonated *o*- and *m*-fluorophenols and fluoroanisoles) indicate that back-donation by the nonbonded electron pairs of fluorine is not affecting much the deshielding for which the inductive effect is mainly responsible.



5-X (R = H)	5-Xb (R = H)
5-F, X = F	5-Fb, X = F
5-Cl, X = Cl	5-Clb, X = Cl
5-Br, X = Br	5-Brb, X = Br
6-X (R = CH₃)	6-X (R = CH₃)
6-F	6-Fb
6-Cl	6-Clb
6-Br	6-Brb

When superacid III or IV was used to protonate **5**-X and **6**-X, the $-OH_2^+$ and the $-CH_3OH^+$ protons of the corresponding oxonium ions **5**-Xb and **6**-Xb were not observed. The methoxy protons of **5**-Xb and **6**-Xb show a pmr singlet instead of a doublet. The aromatic proton absorptions of **5**-Xb and **6**-Xb are similar to those observed in superacids I–II, but are slightly shielded (Table III). Similarly, the fluorine nmr absorptions of **5**-F and **6**-F in superacids III and IV are also shielded from those observed in superacids I and II. These data indicate a rapid protonation–deprotonation equilibrium between **5**-X (**6**-X) and **5**-Xb (**6**-Xb). Consequently, the pmr absorptions of **5**-X and **6**-X are

$$\text{5-X or 6-X} \xrightleftharpoons{\text{superacids III–IV}} \text{5-Xb or 6-Xb (X = F, Cl, Br)}$$

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(11) G. A. Olah, J. Sommer, and E. Namanworth, *J. Amer. Chem. Soc.*, **89**, 3576 (1967).

(12) G. A. Olah and D. H. O'Brien, *ibid.*, **89**, 1725 (1967).

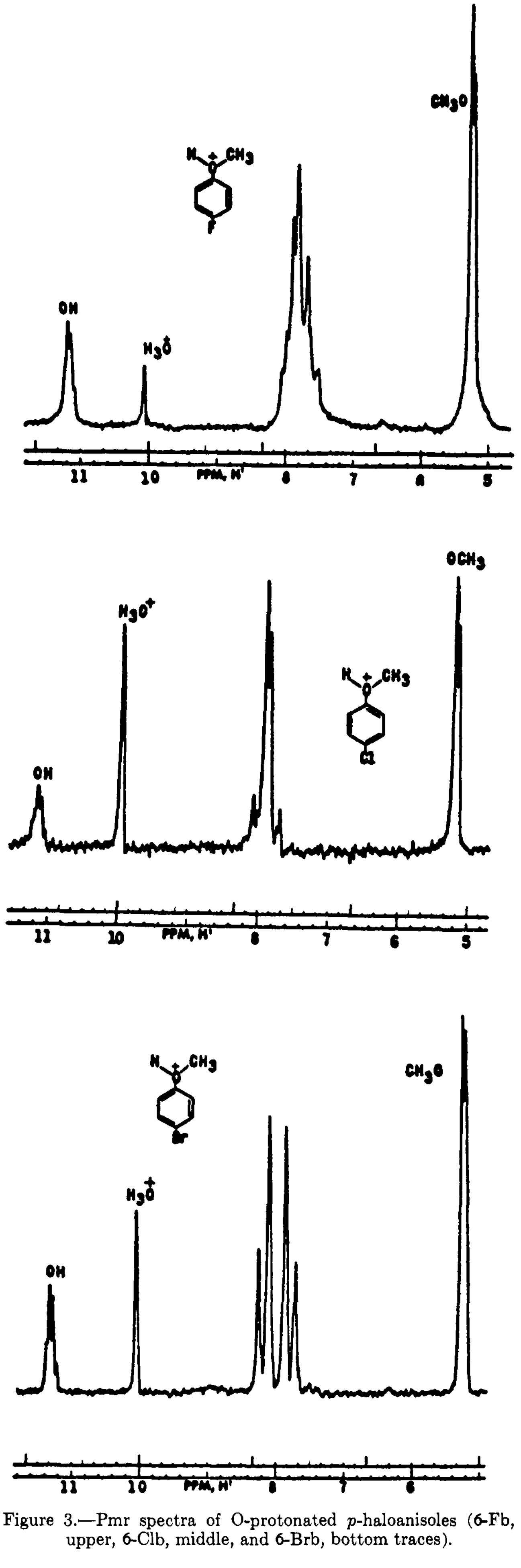
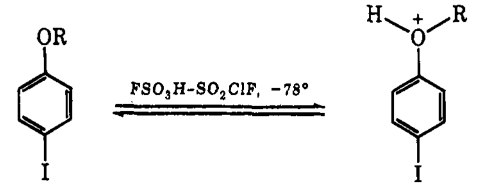


Figure 3.—Pmr spectra of O-protonated *p*-haloanisoles (6-Fb, upper, 6-Clb, middle, and 6-Brb, bottom traces).

also different in superacid III and in superacid IV. They are more deshielded in the former, indicating that the equilibria were shifting to the right or the lifetimes of the oxonium ions **5**-Xb or **6**-Xb are longer in this media.

We have also studied the protonation of *p*-iodophenol (**5**-I) and *p*-iodoanisole (**6**-I) in the four superacid systems (I–IV). When **5**-I and **6**-I were treated with superacids I–III at −78°, only tar formation and liberation of iodine were observed. The decomposition of **5**-I and **6**-I in superacids I–III is similar to those of **1**-I and **2**-I (see previous discussion). However, both **5**-I and **6**-I were O-protonated in FSO_3H-SO_2ClF (IV) at −78°. The pmr spectra of **5**-I and **6**-I in FSO_3H-SO_2ClF are similar to those of **5**-X (X = Cl and Br) and **6**-X (X = Cl and Br) in the same medium. Thus, in oxonium ions **5**-Ib and **6**-Ib the hydroxyl protons are intermolecularly exchanging with the superacid systems.



5-I, R = H
6-I, R = CH$_3$
5-Ib, R = H
6-Ib, R = CH$_3$

Conclusion

The site of protonation of halophenols and haloanisoles was found to be dependent upon the four superacids (I–IV) used as well as the nature of the halogen atoms. In general, C-protonation of halophenols and haloanisoles to give the corresponding halogenated hydroxy(methoxy)benzenium ions was achieved in the strongest superacid I, while O-protonated oxonium ions were formed in the weakest acid IV. Since OH and OCH_3 are stronger activating groups than halogen atoms, protonation of rings always takes place at the position para to the hydroxy or methoxy group. In the case when the para position is substituted by a halogen atom (*e.g.*, *p*-halophenols), no C-protonation was observed. Instead the corresponding O-protonated oxonium ions were formed, even in superacid I.

The nature of the halogen atoms plays an important role in the formation of halogenated hydroxy(methoxy)-benzenium ions (**1**-Xa–**4**-Xa). Protonation of *o*-halophenols (**1**-X) in superacid III is particularly interesting. **1**-Br and **1**-I were completely C-protonated in superacid III at −60°, while **1**-F and **1**-Cl were both C- and O-protonated. These results reflect the strong negative inductive effect of fluorine and chlorine atoms, respectively. O-Protonation to give oxonium ions **1**-Fb and **1**-Clb is favored through involvement of hydrogen bonding (**1**-Xb). In the case of *m*-halophenols (**3**-X), complete C-protonation was found when **3**-F and **3**-I were treated with superacid III. Under identical conditions, **3**-Cl and **3**-Br were only partially C-protonated. These results indicate that resonance effects (halogen back-donation) stabilize ion **3**-Fa the most, while ion **3**-Ia is inductively more favorable than related ions **3**-Xa (X = F, Cl, and Br). Thus, ions **3**-Cla and **3**-Bra have lesser resonance stabilization than that of ion **3**-Fa and at the same time are destabilized inductively much more than ion **3**-Ia.

o-Halophenols (**1-X**) were completely C-protonated in superacid II, while their methyl ethers (**2-X**) were only partially C-protonated. These data show that a hydroxy group is better in stabilizing arenium ions than an alkoxy group. Similar results have been observed in the case of other hydroxy- and alkoxybenzenium ions.[3a]

The present study of the protonation of halophenols and haloanisoles in varying superacid media also gives useful information relating to the electrophilic aromatic substitution of these compounds. The site of electrophilic attack in substitution reactions in general should parallel those observed in protonation of halophenols and haloanisoles. Kinetic *vs.* thermodynamic control can be responsible for O- or C-substitution. The former, however, is generally reversible through intermolecular displacement (exchange) reactions.[13]

Experimental Section

Materials.—All the halophenols and haloanisoles were commercially available in high purity and were used without further purification. Antimony pentafluoride (Allied Chemical Co.) was refluxed overnight while passing a stream of dry nitrogen through it. The material was then twice distilled (bp 150°). Fluorosulfuric acid (Allied Chemical Co.) was distilled (bp 160–164°) before use. Hydrogen fluoride was obtained from Baker Chemical Co. Sulfuryl chloride fluoride was obtained from Allied Chemical Co.

Preparation of Ions.—Superacid solutions were prepared by mixing antimony pentafluoride and HF or FSO_3H at −78° in Teflon bottles in the concentrations indicated. The resulting solutions were then diluted with sulfuryl chloride fluoride. Ions for nmr studies were prepared by adding 30–40 mg of the aromatic compound (dissolved in SO_2ClF) to 1 ml of the above superacid solution (at −78°). Upon warming, while stirring or shaking, a clear solution was obtained. After nmr study, solutions were quenched (as previously described)[14] and starting halophenols and haloanisoles were recovered (as indicated by nmr, ir, and glc studies) showing that no side reactions took place, other than described.

Nmr Spectra.—A Varian Associates Model A-56/60A nmr spectrometer equipped with a variable-temperature probe was used for ^1H and ^{19}F nmr spectra. Both ^1H and ^{19}F coupling constants are believed accurate to ±0.1 Hz. Unless otherwise indicated, proton chemical shifts (δ) are from an external capillary of TMS. Fluorine chemical shifts (ϕ) are from an external capillary of CCl_3F.

Registry No.—**1**-F, 367-12-4; **1**-Cl, 95-57-8; **1**-Br, 95-56-7; **1**-I, 533-58-4; **2**-F, 321-28-8; **2**-Cl, 766-51-8; **2**-Br, 578-57-4; **2**-I, 529-28-2; **3**-F, 372-20-3; **3**-Cl, 108-43-0; **3**-Br, 591-20-8; **3**-I, 626-02-8; **4**-F, 456-49-5; **4**-Cl, 2845-89-8; **4**-Br, 2398-37-0; **4**-I, 766-85-8; **5**-F, 371-41-5; **5**-Cl, 106-48-9; **5**-Br, 106-41-2; **5**-I, 540-38-5; **6**-F, 459-60-9; **6**-Cl, 623-12-1; **6**-Br, 104-92-7; **6**-I, 696-62-8.

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The Copper-Catalyzed Additions of Diazo Esters to 2,4-Hexadienes

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Decomposition of ethyl diazoacetate with copper powder in the presence of *trans,trans-*, *cis,trans-*, and *cis,cis-*2,4-hexadiene afforded the eight isomeric ethyl 2-methyl-3-propenylcyclopropanecarboxylates which were separated by preparative glpc. The structures of the isomeric products were established on the basis of their spectral properties and from correlations based on thermolysis and ozonolysis results. The additions took place with a general preference for the orientation of the carboethoxy group trans to the propenyl group. The stereoselectivity of the reaction is discussed.

The addition reactions of carbenes and carbenoids have proven to be of great synthetic utility;[2,3] in particular the copper-catalyzed addition of diazoacetic ester to olefins has allowed the synthesis of numerous cyclopropanecarboxylic acids.[4] In conjunction with a study of their thermochemistry,[5] we required a series of "maximally labeled"[6] vinylcyclopropanes whose stereochemistry was known with certainty so that firm conclusions could be made on the mechanism and stereochemistry of their thermal rearrangements. With these objectives in mind we embarked on a study of the addition of alkyl diazo esters to the isomeric 2,4-hexadienes.

Results

The general procedure for the addition reactions involved adding a mixture of diazo ester in the appropriate diene to a slurry of copper powder (activated by preliminary washing with acetic acid) in the diene. Products were purified by vacuum distillation and the isomers were separated by preparative glpc. Isolated yields in the preparative runs ranged from 51 to 59%.

Product distributions (Table I) were determined by glpc analysis of the crude reaction mixture and were invariant throughout the course of the reaction, indicating that there was no product interconversion. These data are only slightly different from those ob-

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