Protonation of *p*-Methoxybenzhydryl Cations; a New Series of Indicators for Superacid Acidity Measurements by Nuclear Magnetic Resonance Spectroscopy

Dominique Touiti, Roland Jost, and Jean Sommer *
Laboratoire de Physicochimie des Hydrocarbures, Université Louis Pasteur, Institut de Chimie, 1, rue Blaise Pascal, 67000 Strasbourg, France

The behaviour of (*p*-substituted phenyl)(*p*-methoxyphenyl)methanol derivatives dissolved in superacid mixtures (HF, $HFSO_3$, or CF_3SO_3H with various proportions of SbF_5) has been studied by n.m.r. spectroscopy. Increasing the SbF_5 concentration causes drastic changes in chemical shifts due to stable *O*-protonation of the methoxy group in the highest acidity media. By using these bases as indicators for superacid acidity measurements we have shown that the acidity of these three systems does not increase as fast as previously claimed, and also that the acidity of the CF_3SO_3H–SbF_5 system remains lower than that of the $HFSO_3$–SbF_5 system in the 0—50% SbF_5 range.

The most reliable method of estimating the acidity of a strong concentrated acid solution is to measure its tendency to transfer a proton to a suitable indicator base. The unique success of the Hammett acidity function H_0[1] [equation (i)] is based mainly

$$H_0 = pK_{BH^+} - \log(BH^+/B) \qquad (i)$$

on its applicability to an extremely large range of acidity (12 H_0 units) using only one family of compounds as indicators, the so-called Hammett bases (substituted anilines). Experimental measurements of the ionization ratio (BH^+/B) are carried out by u.v. spectroscopy.

The first applications of this method in the superacid field ($H_0 < -12$)[2] were made by Gillespie,[3] using a series of aromatic nitro compounds, which gave plots of log (BH^+/B) against acidity parallel to and overlapping with those of the Hammett indicators. However, owing to the lack of weak enough bases, the measurements were limited to a very small range: up to 11 mol % SbF_5 in HSO_3F and 2 mol % SbF_5 in HF. On the other hand u.v. spectroscopy was not applicable to the triflic acid (CF_3SO_3H) system[4] because of the strong absorption bands of the acid itself.

For these reasons a number of other techniques have been suggested since. For investigation of the HSO_3F–SbF_5 ('magic acid') system up to 20 mol % SbF_5, we have used ^1H and ^{13}C chemical shift measurements as well as rotational barrier measurements by dynamic n.m.r. with protonated *p*-methoxybenzaldehyde as indicator.[5,6] Recently Gold and his co-workers[7–9] described superacid acidity measurements by dynamic n.m.r. lineshape analysis with a variety of very weak carbonyl bases. Electrochemical acidity measurements based on the pH dependence of redox potentials have been performed on various superacid systems.[10–12] The main inconvenience of the electrochemical method lies in the difficulty of knowing the exact protonation state of the electroactive forms, but the main drawback of all the foregoing methods resides in the fact that too many structurally and functionally different indicators have to be used.

In this paper we present a homogeneous family of indicators which can potentially cover the whole acidity range of the various superacid systems: the *p*-methoxybenzhydryl cations.

Results and Discussion

N.m.r. data (^1H and ^{13}C) for a large number of benzhydryl cations are available in the literature.[13,14] These ions are conveniently generated by dissolving the precursor alcohols at low temperature in superacid solution (Scheme).

In the case of *p*-methoxybenzhydryl ions we have at our disposal a family of very weakly basic indicators, the basicity of which can be controlled by suitable substitution on the phenyl rings. Protonation of these indicators (**1**) occurs on the methoxy oxygen atoms and yields the doubly charged species (**2**) (BH^{2+}) [eventually triply charged in the case of (**2f**)].

The tendency of a superacid to transfer a proton to the indicators can be estimated from the following n.m.r. parameters:

(a) the variation of the ^1H and/or ^{13}C chemical shift of the CH_3O and CH^+ groups following *O*-protonation;

(b) the variation of the barrier around the *p*-methoxyphenyl–C^+ bond.

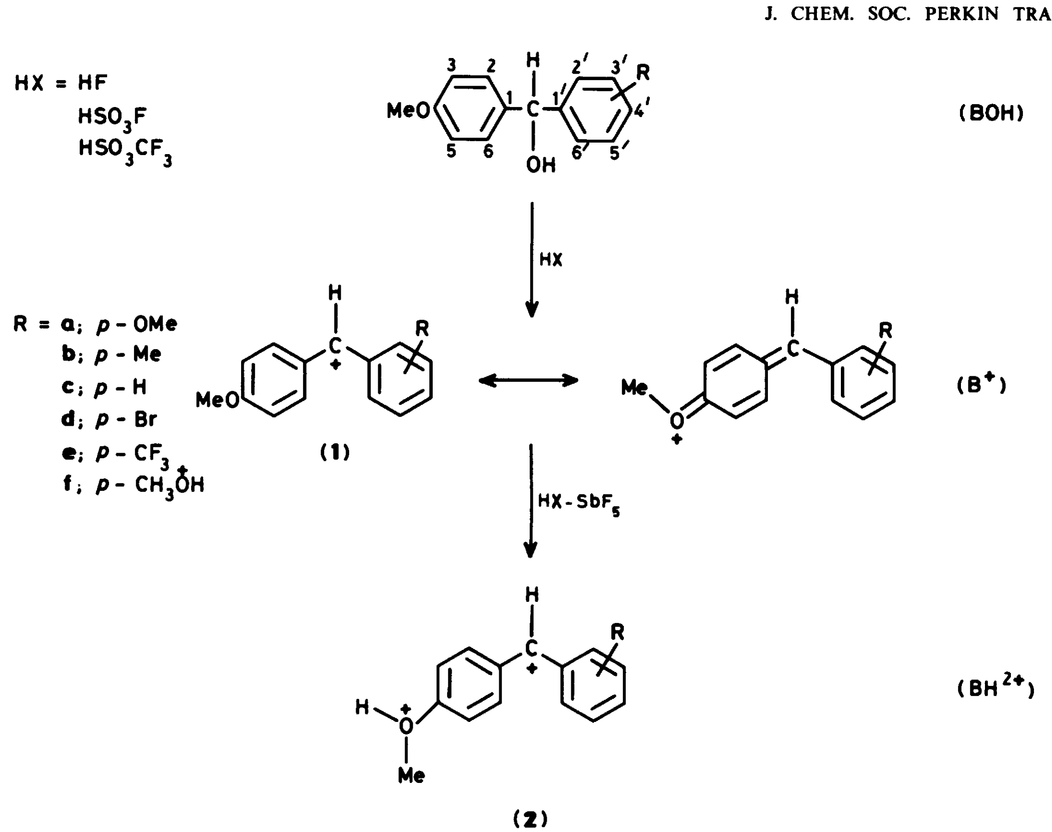
In the neat acids HF, HSO_3F, or CF_3SO_3H, protonation on oxygen is negligible as shown by the high rotational barrier around the oxygen–phenyl and the *p*-methoxyphenyl–C bonds.[15] We have demonstrated earlier the sensitivity of this type of barrier to *O*-protonation.[5] Addition of increasing amounts of antimony pentafluoride induces characteristic changes in the ^1H and ^{13}C n.m.r. spectra in accord with progressive *O*-protonation of the indicators. The concentration of SbF_5 for which full *O*-protonation is achieved depends on the relative basicity of the indicator governed by the ring substituents.

Figure 1 shows the characteristic dependence of the n.m.r. spectra of an indicator on the concentration of SbF_5 in CF_3SO_3H. In neat CF_3SO_3H at −50 °C the ^1H spectrum (a) shows the non-equivalence of the *ortho-* and also of the *meta*-protons of the methoxyphenyl ring as a consequence of restricted rotation around the methoxyphenyl–C^+ bond. At this temperature the rotation of the methoxy group around the O–phenyl bond is still fast on the n.m.r. timescale.[15] Rotation of the *p*-tolyl ring around the phenyl–C^+ bond is also fast under these conditions.

Increasing the SbF_5 concentration shows clearly the effects of a progressive protonation of the methoxy oxygen atom, as follows.

(*a*) Between 2 and 11 mol % SbF_5 [spectra (b) and (c)] the signals for the *meta-* and the *ortho*-protons of the methoxyphenyl ring coalesce, in agreement with partial protonation of the methoxy group. In earlier work[16] we have shown how an ionization ratio as small as 10^{-4} can affect the torsional process without affecting the chemical shifts,

(*b*) At higher SbF_5 concentration [spectra (d) and (e)] the signals of the methoxy protons and the CH^+ proton shift downfield in accord with the development of the second positive charge on the indicator *via* *O*-protonation. Despite the fact that the chemical shifts have reached their limiting values in



(2)

Scheme.

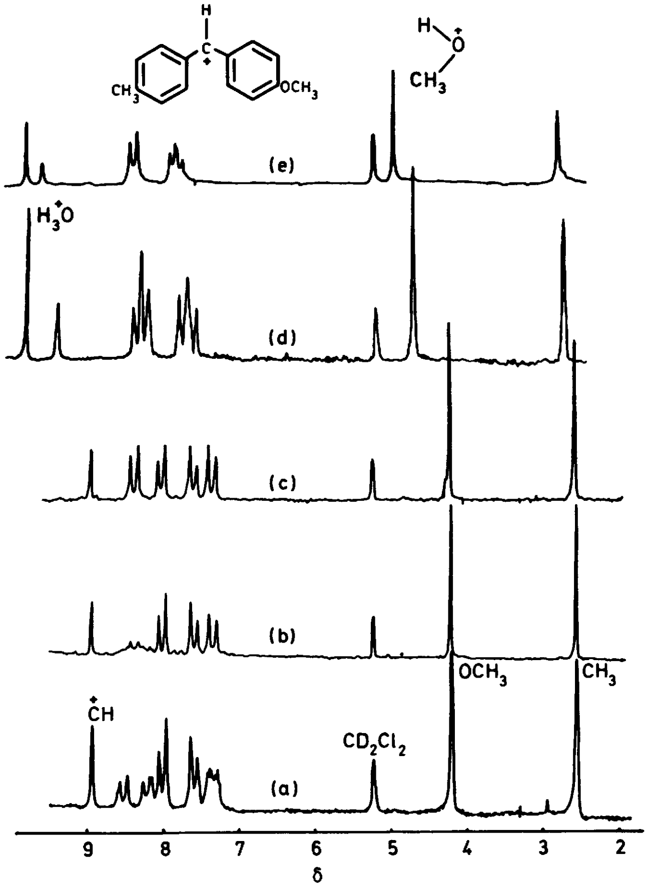


Figure 1. Changes in the proton n.m.r. spectra of the ion (**1b**) with the proportion of SbF_5 in CF_3SO_3H–SbF_5 mixtures; temperature −50 °C; % SbF_5 (a) 0, (b) 8, (c) 11, (d) 35, (e) 45

agreement with full protonation of the indicator, the lifetime of the proton on the methoxy oxygen atom is too small on the n.m.r. timescale at this temperature to allow observation of the OH proton and/or the coupling $^3J_{H,H}$.

The knowledge of the limiting n.m.r. data concerning the indicator and its protonated form allows the calculation of the ionization ratio necessary to determine the acidity of the medium.

^{13}C N.m.r. spectra show a similar dependence on the SbF_5 concentration; Figure 2 shows the limiting spectra for indicator (**1b**). The barrier to rotation around the C–C$^+$ bond is noticeable through the non-equivalence of the *ortho* (C-2, C-6) and *meta* (C-3, C-5) carbon atoms when the indicator is not protonated [Figure 2(a)]. *O*-Protonation of the indicator induces a downfield shift of the C$^+$, OCH_3, CH_3 lines as well as the equivalence of the *ortho*- and *meta*-carbon atoms due to free rotation around the C–C$^+$ bond.

The proton chemical shifts of the indicators in both forms are collected in Tables 1 and 2.

When benzhydryl cations (B^+) are generated in HF, HSO_3F, or CF_3SO_3H there is good agreement amongst the proton chemical shifts of the same base in the three different acids. Moreover the ^{13}C as well as the ^1H shifts of the methoxy group show a very good correlation with $\sigma_p{}^+$ of the other substituent (Figure 3). This shows that the availability of the oxygen lone pair (*i.e.* the basicity of the indicator) can be controlled by the substitution on the second phenyl ring.

The ^{13}C n.m.r. data for the protonated benzhydryl cations (BH^{2+}) are collected in Table 3. Cations (**1a**—**d**) are fully protonated in HF—SbF_5 (less than 5 mol % SbF_5) and in 'magic acid'. Here again the chemical shifts in the three different acid systems are in good agreement despite the difference in counterions.

The indicator (**1e**) and the monoprotonated dimethoxybenzhydryl cation (**1f**) could not be protonated even in the strongest acid system tested (HF–SbF_5 1:1).

Table 1. Characteristic proton chemical shifts for cations (**1a**—**1e**)[a]

	Acid	Cation (**1a**)	(**1b**)	(**1c**)	(**1d**)	(**1e**)
δ_{MeO}	HF	4.15	4.27	4.31	4.31	4.38
	HSO_3F	4.19	4.29	4.32	4.32	4.42
	CF_3SO_3H	4.19	4.28	4.35	4.34	4.43
δ_{CH+}	HF	8.79	8.99	9.08	9.00	9.06
	HSO_3F	8.83	9.00	9.10	8.99	9.12
	←CF_3SO_3H	8.81	9.00	9.12	9.00	9.01

[a] In p.p.m. from internal CD_2Cl_2; solvent SO_2ClF; temperature −50 °C.

Table 2. ^1H N.m.r. data for cations (**2**)[a]

	Acid	Cation (**2a**)	(**2b**)	(**2c**)	(**2d**)	(**2e**)
δ_{MeO}	$HF-SbF_5$	4.71	5.04	5.06	5.05	*b*
	HSO_3F-SbF_5	4.72	4.95	5.00	5.01	*b*
	$CF_3SO_3H-SbF_5$	4.71	5.05	4.94	*b*	*b*
δ_{CH+}	$HF-SbF_5$	*c*	*c*	*c*	*c*	*c*
	HSO_3F-SbF_5	9.04	9.60	9.9	*c*	*b*
	$CF_3SO_3H-SbF_5$	9.03	9.66	9.2	*b*	*b*

[a] In p.p.m. from internal CD_2Cl_2; solvent SO_2ClF; temperature −50 °C. [b] Complete protonation was not observed. [c] The signal is covered by the acid peak.

The protonation curves of the indicators (**1a**—**d**) in HSO_3F-SbF_5 mixtures are shown in Figure 4. The decreasing basicity of the indicators corresponds to an increasing amount of SbF_5 necessary for half-neutralization. The decreasing slope of the neutralization curves when the SbF_5 amount increases shows that the variation in the acidity of the superacidic solutions is much smaller at high SbF_5 concentration. This is in agreement with all the literature data on the HSO_3F-SbF_5 ('magic acid') system whatever method has been used.[5–10] The different data now available for the acidity of this medium are presented in Figure 5. The values from different sources are in good agreement in the range 0—40% SbF_5. Despite the variety of techniques, the results yield quite compatible data.

In the light of the variety in structure and nature of the indicators used in these measurements and in our own, the question of the validity of expressing the acidity values in terms of the H_0 function must remain open. In most cases the indicators are positively charged, which means that the values should rather be expressed as H_+. However, this is a minor handicap, as several authors have demonstrated parallel and similar behaviour of the H_0 and H_+ functions.[3b,17] On the other hand, as all recent measurements show that the acidity increase becomes very small above a given amount of SbF_5, we assume that the true H_0 values will not be very different from the values quoted here. For this reason we have used averaged H_0 values from the recent literature in order to estimate the half-neutralization values for a series of our *p*-methoxybenzhydryl ions. These values are expressed in terms of the H_0 function because there is no alternative available, and have proved useful in achieving our goals in this work: (1) to try to reach the limits of superacidity; and (2) to ascertain the relative acidities of the three most used superacid systems, $HF-SbF_5$, HSO_3F-SbF_5, and $CF_3SO_3H-SbF_5$. The values obtained for our indicators (**1a**—**d**) are, respectively, −17.2, −20.0, −20.5, and −20.9.

Monoprotonated bis-(*p*-methoxyphenyl)methylium ion (**1f**) and the *p*-CF_3-substituted indicator (**1e**) could not be protonated even in 1:1 HSO_3F-SbF_5. This shows that the acidity increase at high SbF_5 concentration is very small. If we extrapolate the graph of pK_{BH+} against σ_p^+ of the indicators (**1a**—**d**) ($pK = 3.93\sigma_p^+ - 20.57$; *r* 0.96) to the indicators (**1e**) and (**1f**) we obtain values of −22.5 and −23.0, respectively. We can then assume that the acidity of the medium does not reach these values. This shows that the H_0 values previously published for high SbF_5 concentration in HSO_3F are overestimated, despite corrections made by the authors (compare for example refs. 8 and 9). At this point it appears that we can reasonably use our indicators for relative acidity measurements of the three superacid systems.

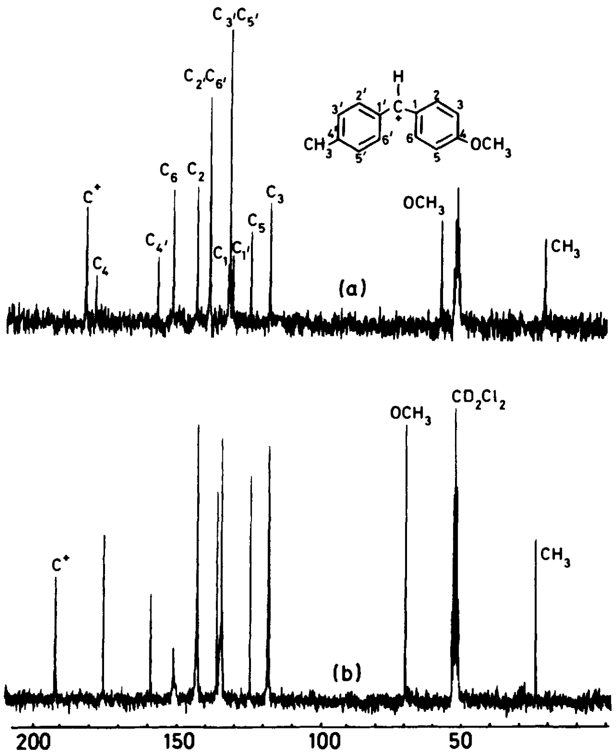


Figure 2. ^{13}C N.m.r. spectra of (*p*-methoxyphenyl)(*p*-tolyl)methylium cation generated (a) in FSO_3H-SO_2ClF, (b) in FSO_3H-SbF_5 (1:1) in SO_2ClF at −50 °C

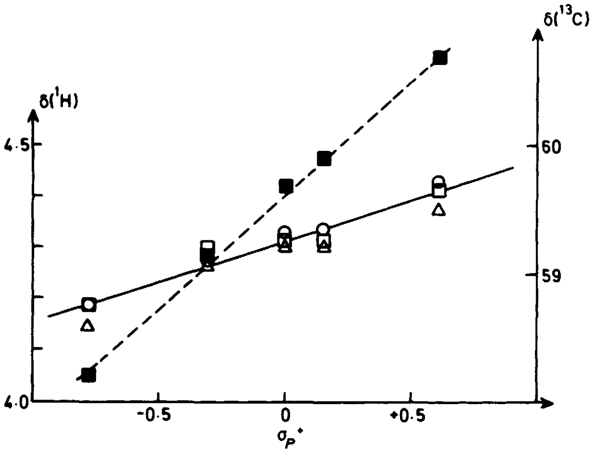


Figure 3. Correlations of methoxy proton (and carbon) chemical shifts with Brown's σ_p^+ (△ HF, □ HSO_3F, ○ CF_3SO_3H for the methoxy proton; ■ in HSO_3F for the methoxy carbon)

Table 3. ^{13}C N.m.r. data

(a) Benzhydryl cations (**1a**—**e**)[a]

[R]	C-1	C-2	C-3	C-4	C-5	C-6	C-1′	C-2′,-6′	C-3′,-5′	C-4′	C^+	OCH_3	CH_3
OMe	130.3	145.3	119.0	174.7	119.0	145.3	130.3	145.3	119.0	174.7	179.4	58.2	
Me	133.3	144.3	118.8	179.3	121.7	152.5	131.7	139.9	132.8	157.7	182.8	59.1	22.9
H	135.2	145.7	119.5	181.2	122.4	153.8	132.5	138.6	131.5	141.3	183.2	59.7	
Br	133.8	138.6	122.7	181.0	119.7	145.2	132.7	138.9	135.0	153.8	181.6	59.9	
CF_3	*b*	137.2	123.5	179.8	120.9	146.7	*b*	136.9	127.7	155.1	184.1	60.7	

(b) *O*-Protonated cations[c]

[R]	C-1	C-2	C-3	C-4	C-5	C-6	C-1′	C-2′,-6′	C-3′,-5′	C-4′	C^+	OCH_3	CH_3
OMe	*d*	145.0	120.9	177.2	120.9	145.0	*d*	143.2	135.5	170.8	178.2	67.3	
Me	137.4	*e*	119.4	177.6	119.4	*e*	*d*	143.6	135.9	159.5	193.0	72.8	25.1
H	*d*	149.7	120.8	180.3	120.8	149.7	*d*	139.0	131.5	141.7	183.9	60.1	
Br	135.5	147.5	120.3	171.0	120.3	147.5	134.4	143.0	136.5	158.0	188.9	65.9	

[a] In $FSO_3H–SO_2ClF$, at −50 °C; reference CD_2Cl_2. [b] Quaternary carbon signals not observed due to signal-to-noise ratio. [c] In 'magic acid'–SO_2ClF, at −50 °C; reference CD_2Cl_2. [d] Not observed. [e] Coalescence.

The $HF–SbF_5$ system has been studied earlier by us.[5,6] We showed that the acidity increases strongly with a very small amount of SbF_5. However, the indicator used (protonated *p*-anisaldehyde) was still too basic and it was not possible to measure H_0 for mixtures containing more than 2% SbF_5 (H_0 −21).

Very little is known about the acidity of the $CF_3SO_3H–SbF_5$ system. Engelbrecht[18] found by conductrimetric studies in anhydrous acetic acid that CF_3SO_3H was stronger than FSO_3H. On the basis of kinetic studies, Kramer[19] has proposed a ranking of different superacid systems. An H_0 value of −13 for pure CF_3SO_3H is reported by Howells,[20] and of −14.6 by Jorgensen,[21] which seems more realistic. Recently Devynck *et al.*,[11] in a voltammetric and potentiometric study, estimated a value of the R_0 function in 1M-strong base medium (R_0 = −16).

In a first approach towards a qualitative picture of the relative acidities of these three systems, we have followed the ionization curves of the indicator (**1c**) in HF, HSO_3F, and CF_3SO_3H as a function of SbF_5 concentration. These three curves are plotted in Figure 6. The acidity level necessary for half-neutralization of the indicator (**1c**) (pK_{BH^+} −20.4) is reached with less than 7 mol % SbF_5 in HF, 23 mol % in HSO_3F, and 37 mol % in CF_3SO_3H. This gives a clear indication of the relative acidities of these three superacid systems.

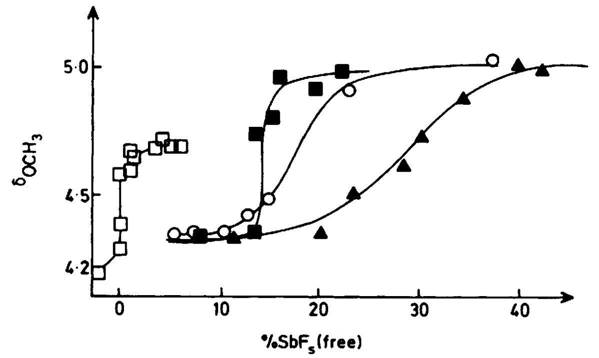


Figure 4. Methoxy ^1H chemical-shift variation of cations (**1a**—**d**) with the concentration of SbF_5 in $HFSO_3$ [□ (**1a**), ■ (**1b**), ○ (**1c**), ▲ (**1d**)]

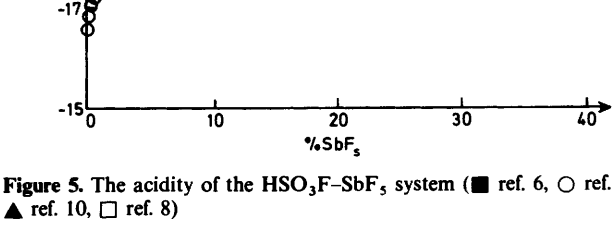


Figure 5. The acidity of the $HSO_3F–SbF_5$ system (■ ref. 6, ○ ref. 3, ▲ ref. 10, □ ref. 8)

Conclusion

In order to measure acidities over the whole superacid range in the three different acids we must synthesize a larger number of indicators of the same family with varying basicity in order to obtain better overlapping of the protonation curves. This work is in progress.

Experimental

Syntheses.—The diphenylmethanols were synthesized by the Grignard method, from *p*-bromoanisole and the appropriate *p*-substituted benzaldehyde. The *p*-CF_3 compound was obtained from 1-bromo-4-trifluoromethylbenzene and *p*-anisaldehyde. The bis-(*p*-methoxyphenyl)methanol was commercially available (Aldrich). The alcohols were purified by recrystallization from methanol–water before use.

SbF_5, $HFSO_3$, and CF_3SO_3H were triply distilled in all-glass apparatus and stored in Nalgene bottles. SO_2ClF was prepared as described by Cueilleron *et al.*[22]

The $HSO_3F–SbF_5$ mixtures are relatively stable and can be kept for long periods in Teflon bottles. The triflic acid–SbF_5 mixtures, especially those with high SbF_5 concentrations, are not stable for long, and were freshly prepared before each series of protonations.

Protonations.—The protonations were carried out at temperatures lower than −80 °C, in the apparatus described by Ahlberg *et al.*[23] SO_2ClF was used as solvent. The solutions of the cations were more or less coloured and fairly stable at low temperature.

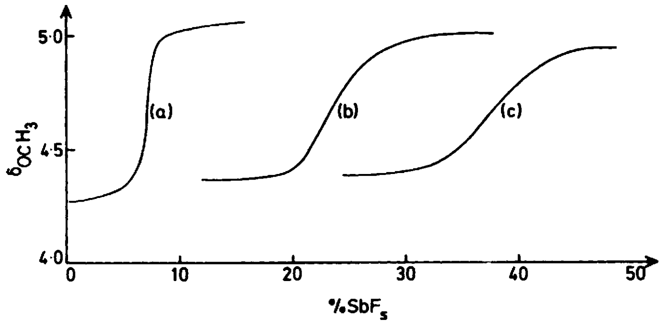


Figure 6. Methoxy ^1H chemical-shift variation of cation (**1c**) with the concentration of SbF_5 in (a) HF, (b) FSO_3H, and (c) CF_3SO_3H

N.m.r. Measurements.—The ^1H n.m.r. spectra were recorded at −50 °C with a WH 90 Brüker spectrometer in the Fourier transform mode. The ^{13}C n.m.r. spectra were obtained with an SY 200 Brüker spectrometer at −50 °C. A DEPT experiment[24] was performed with the cation (**2b**) in order to facilitate the assignment of the signals.

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