

¹³C Spin Saturation Transfer Measurements on Protonated Aromatic Ethers. The Torsional Barrier Around the Phenyl–Alkoxy Bond

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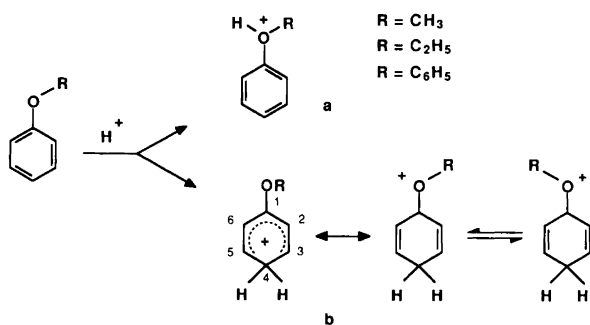
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The protonation of anisole, phenetole and diphenyl ether in superacid media at low temperature gives a mixture of both *C*- and *O*-protonated cations. The *C*-protonated forms show restricted rotation around the phenyl–alkoxy bond at low temperature. The ¹³C spin saturation transfer method has been used to obtain the free energy of activation of the torsional process (55, 54 and 49 kJ mol⁻¹, respectively) in the presence of the isomeric cations.

Alkoxy- and hydroxy-substituted carbonium ions are an important class of carbocations which occur widely as reaction intermediates and can be readily prepared in superacid media.^{1–3} As phenyl groups increase the stability of these ions, a great deal of attention has been devoted to the study of protonated phenols and alkoxybenzenes. The ambident behavior of these precursors as oxygen or carbon bases is known to be acidity and temperature dependent.^{4–11} Carbon protonation inactivates the ring toward further substitution whereas oxygen protonation changes the original *ortho/para* directing alkoxy group into a *meta* directing substituent. This property has been advantageously used in electrophilic aromatic substitution inducing high selectivities via unusual mechanistic pathways.^{12–15}

The site of protonation will also affect the rotation of the alkoxy group. In the *O*-protonated ions **a** in which the ring electrons cannot be delocalized, the torsional barrier is

very low, of the same order of magnitude as that in the free base. Carbon protonation however increases the rotational barrier around the phenyl–oxygen bond as shown in ion **b**. This type of barrier around a partial C=O double bond has been studied earlier by us and others via an experimental and theoretical approach on *p*-methoxyphenylcarbenium ions,^{16,17} hydroxycarbenium ions¹⁸ and methoxycarbenium ions.^{19–20} The activation energy of these isomerisation processes is generally measured by DNMR (line-shape analysis). However, in the case of the phenyl ethers **2** and **3**, the alkoxy cations generated by protonation are accompanied by the corresponding *O*-protonated ions in a temperature-dependent ratio. This complicates the NMR spectra and the application of the DNMR method. The spin saturation transfer method²¹ applied to ¹³C^{22,23} overcomes this difficulty easily.



Scheme 1.

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Results and discussion

Tables 1 and 2 contain the ¹³C NMR chemical shift data and the obtained energy parameters.

Protonated anisole. Both *C*- and *O*-protonated forms of anisole have been reported.² However when we dissolve anisole in FSO₃H/SO₂ClF at –60 °C, a rather weak superacid system ($H_0 = -15$),²⁴ only the *C*-protonated form **1b** is present. The value of ΔG^\ddagger at –50 °C [55(3) kJ mol⁻¹] obtained from our ¹³C spin saturation transfer experiments is in accord with the previous estimation of Brouwer⁸ who found 52.9 kJ mol⁻¹ using NMR line-shape analysis. This small difference is in agreement with a negligible solvation effect in superacid media (Brouwer used the HF/BF₃ superacid system).

Table 1. ^{13}C chemical shifts (ppm) of the *O*- and *C*-protonated alkoxybenzenes (at 220 K in $\text{HSO}_3\text{F}/\text{SO}_2\text{ClF}$).

Ion	C-1	C-2	C-3	C-4	C-5	C-6	Others
1a	Not observed						
2a^a	150.2	131.9	120.0	131.0	120.0	131.9	85.7 (CH ₂) 13.2 (Me)
3a^a	154.2	131.8	119.9	129.8	119.9	131.8	
3a^b	156.0	132.4	119.9	128.2	119.9	132.4	
1b^a	192.0	127.0	175.4	40.3	168.8	121.1	
2b^a	190.0	127.1	174.6	40.0	168.1	121.4	74.0 (CH ₂) 13.8 (Me)
3b^a	190.7	127.0	176.6	41.5	72.3	122.4	119.4 (C ₃ , C ₅) 131.2 (C ₂ , C ₆) 151.6 (C ₁) 131.3 (C ₄)
3b^b	192.4	128.4	178.0	42.7	173.8	123.7	121.4 (C ₃ , C ₅) 133.2 (C ₂ , C ₆) 153.2 (C ₁) 131.3 (C ₄)

^a25.14 MHz, internal reference CD_2Cl_2 $\delta = 53.8$ ppm. ^b100 MHz, external reference TMS.

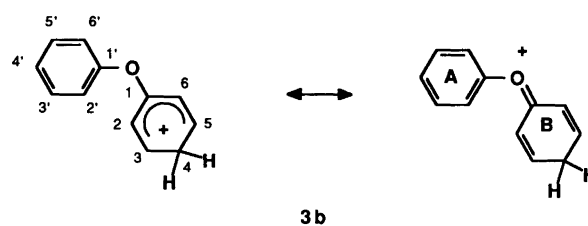
 Table 2. ΔG^\ddagger values for the torsional barrier in *C*-protonated alkoxybenzenes.

Ion	Observed C atom	Irradiated C atom	I_0/I_∞	T_1/s	k/s^{-1}	$\Delta G^\ddagger/\text{kJ mol}^{-1}$ ^a	Mean value
1b (223.2 K)	C ₂	C ₆	0.55	1.20	0.68	54.8	55(3) ^b
	C ₆	C ₂	0.43	1.72	0.77	54.6	
	C ₅	C ₃	0.52	1.10	0.83	54.5	
	C ₃	C ₅	0.70	1.15	0.37	56.0	
2b (220.7 K)	C ₂	C ₆	0.41	1.11	1.30	53.1	54(3) ^b
	C ₆	C ₂	0.56	1.30	0.60	54.4	
	C ₅	C ₃	0.51	0.96	1.00	53.5	
	C ₃	C ₅	0.45	1.22	0.97	53.6	
3b (205.7 K)	C ₂	C ₆	0.74	0.35	1.00	49.7	49(4) ^b
	C ₆	C ₂	0.68	0.40	1.18	49.5	
	C ₅	C ₃	0.67	0.38	1.30	49.3	
	C ₃	C ₅	0.46	0.31	3.79	47.5	

^aCalculated from the Eyring equation. The rate constant k is obtained by $k = (I_0/I_\infty - 1)/T_1$ where I_0 and I_∞ are the intensities of one carbon in the absence and presence of irradiation of the other. ^bError estimated from the standard deviations of T_1 and I_0/I_∞ .

Protonated ethyl phenyl ether. The ^{13}C NMR spectrum of phenetole in $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$ at -53°C shows clearly the presence of both *O*- and *C*-protonated ions (**2a** and **2b**). The relative amount of these two ions is temperature dependent, the *C*-protonated form being favored at higher temperature. The spin saturation transfer spectra are shown in Fig. 1. The ΔG^\ddagger value obtained for the barrier around the phenyl–oxygen bond in ion **2b** [54(3) kJ mol^{-1}] is slightly lower than in ion **1b**. Despite the error in ΔG^\ddagger which is of the same order of magnitude, the difference observed in the barrier height is consistent with the rates of solvolysis of the *p*-chloromethyl derivatives of anisole and phenetole as studied by Baddeley²⁸ and the basicity of these two aromatic ethers estimated by Arnett.²⁹ It is generally admitted that the small increase in inductive effect of the alkyl group is compensated by a repulsive interaction between the *ortho* hydrogens and the ethyl group in the planar ground state.

Protonated diphenyl ether. The ^{13}C NMR spectrum of diphenyl ether in $\text{HFSO}_3/\text{SO}_2\text{ClF}$ at 60°C is displayed in Fig. 2. It shows the presence of both *O*- and *C*-protonated forms (**3a** and **3b**). Stable *C*-protonation under slow exchange conditions, as shown by the methylene peak at 42.7 ppm, yields two non-equivalent phenyl rings A and B. The NMR spectrum is in accordance with a fast rotation of ring A around the C–O bond whereas the rotation of ring B



Scheme 2.

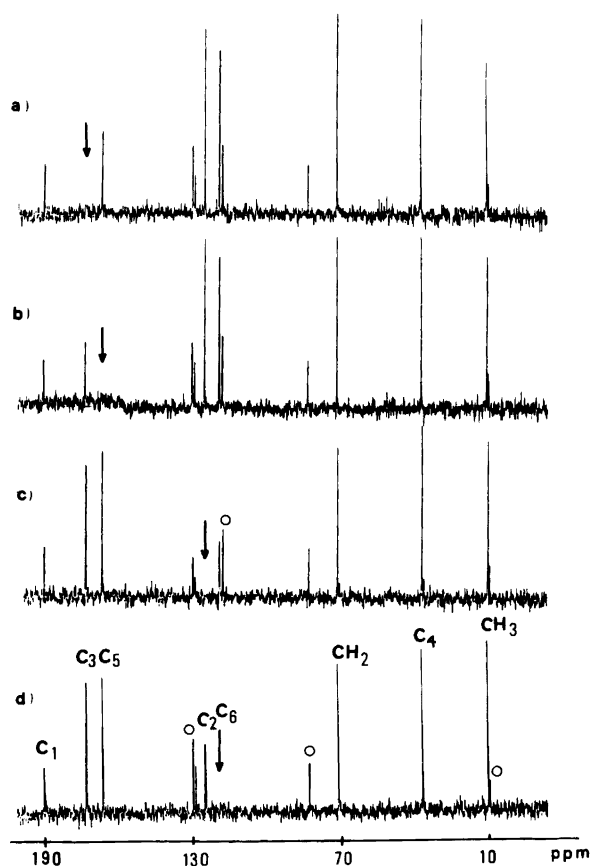
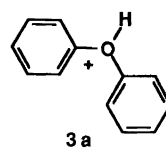


Fig. 1. ^{13}C spin saturation transfer experiments on C-protonated ethyl phenyl ether (ion **1b**) at -53°C : (a) irradiation of carbon C-3; (b) irradiation of carbon C-5; (c) irradiation of carbon C-2; (d) irradiation of carbon C-6. O = O-protonated ion.



Scheme 3.

appears slow on the NMR time scale: the two *ortho* and the two *meta* carbons are non-equivalent by approximately 7 ppm. The ΔG^\ddagger value [$49(4) \text{ kJ mol}^{-1}$] is significantly lower than in the first two compounds. This is easily rationalized on the basis of both steric and electronic effects as expressed by the lower σ_{R} value (0.36) of the phenoxy group as compared with the alkoxy groups (0.44 and 0.43, respectively).²⁵⁻²⁷

In 1964, Birchall,⁵ using 60 MHz ^1H NMR spectroscopy, was not able to observe the O-protonated ion, even at -85°C . Our ^{13}C NMR spectra obtained at 25.14 and 100 MHz clearly show the presence at -50°C of the O-protonated phenyl ether (**3a**) which presents a very simple pattern due to the symmetry of the ion. The ^{13}C NMR spectrum of this ion consists of only four lines, because internal rotation of the two equivalent phenyl rings is fast on the NMR time scale.

Protonation of t-butyl phenyl ether. Our attempts to study the rotational barrier in protonated t-butyl phenyl ether failed due to fast protolytic cleavage of the precursor under superacidic conditions. Even at -120°C we obtained only the cleavage products, the t-butyl cation and protonated phenol.

We would like to underline here that one drawback of

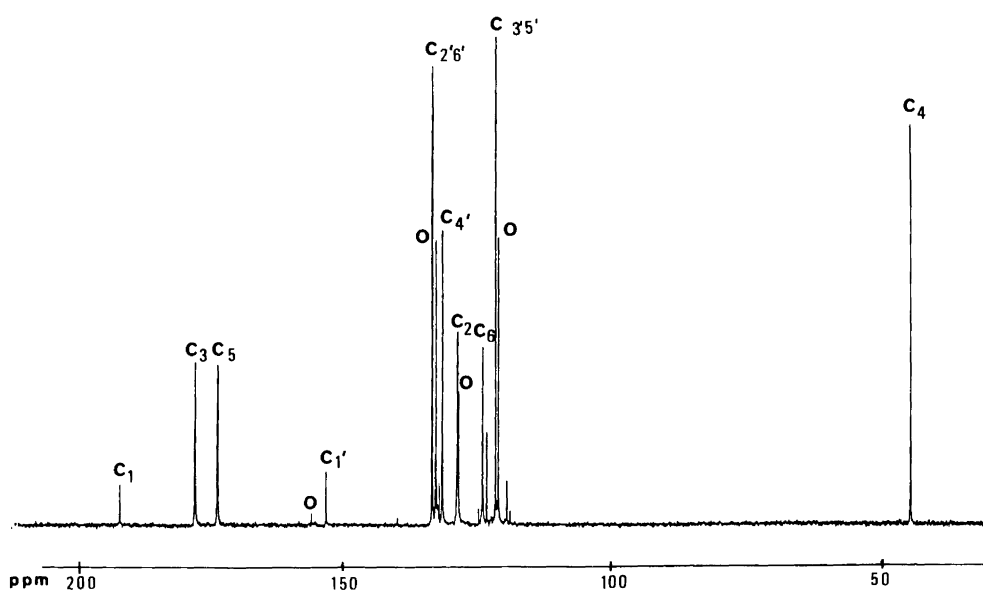


Fig. 2. 100 MHz ^{13}C NMR spectrum of protonated diphenyl ether in $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$ at -65°C (O = ion **3a**, C = ion **3b**).

the ^{13}C spin transfer method is the narrow temperature range under which the experiments can be carried out. In order to obtain the most accurate results, the ratio of the peak intensity with saturation and intensity without saturation should lie between 0.4 and 0.8, which is only observed in a small temperature domain. This can be a large handicap when comparing two systems for which the ΔG^\ddagger measurements have to be made at quite different temperatures. Our values for *C*-protonated anisole and phenetole were obtained at nearly the same temperature. The value for the *C*-protonated phenyl ether was obtained within a fifteen-degree interval, but our earlier studies on the rotational barriers in stable ions in superacid media, as measured via DNMR³⁰ in a large temperature range have shown that the ΔS^\ddagger value in these processes is rather low (around $20 \text{ J mol}^{-1} \text{ K}^{-1}$). On the other hand, the fact that the ^{13}C spin transfer measurements are made at temperatures much below those necessary for DNMR studies can be a real advantage for the study of unstable reaction intermediates.^{16,31}

Experimental

Anisole and diphenyl ether are commercially available and were used without further purification. Ethyl phenyl ether was prepared by the Williamson synthesis, starting from phenol and ethyl iodide. *t*-Butyl phenyl ether was prepared from isobutene according to Baddeley.²⁸

Preparation of ions. The ions were synthesized directly in 5 mm NMR tubes using the ion generation apparatus described in Ref. 32. The general method was as follows: ca. 30 mg of the ether dissolved in ca. 100 mg of CD_2Cl_2 were added to and rapidly mixed with, at temperature below -65°C , a 0.4 ml solution of $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$ (1:1 v/v). When the solution was mixed it became pale yellow and transparent.

Spectra and ^{13}C spin transfer saturation experiments. The 25.14 MHz ^{13}C NMR spectra were obtained with a JEOL FX 100 pulse spectrometer equipped with a 5 mm variable temperature $^1\text{H}/^{13}\text{C}$ dual probe, external Li lock, quadrature phase detection and a multi-irradiation unit. For protonated diphenyl ether, 100 MHz ^{13}C spectra were obtained on a Bruker AM 400 spectrometer.

The assignment of the lines of *C*-protonated anisole has already been made by Olah.² The values reported (with CS_2 as the reference) match with ours. *C*-protonated phenetole exhibits a pattern which is close to the former spectrum. Assignment of the lines of the *O*-protonated ion is (1) facilitated by the relative ratio of the two isomers, which is temperature dependent, and (2) based on the usual charge delocalization pattern. The assignment of the lines of protonated diphenyl ether is then straightforward. In this latter case, the recording of 100 MHz ^{13}C spectra supports the assignments.

The multiple-irradiation experiments were performed as

previously described.¹⁶ Care was taken to use a pulse repetition time $>5 T_1$.

The spin-lattice relaxation times were obtained with the progressive saturation method using the pulse sequence ($\tau, 90$) for protonated anisole and phenetole, and the inversion recovery method with the pulse sequence (180, $\tau, 90$) was applied to protonated diphenyl ether. The T_1 measurement sequences were analysed off line through a three-parameter optimization program.

The temperature was monitored before and after each spin-transfer experiment by use of a methanol thermometer.³¹

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