

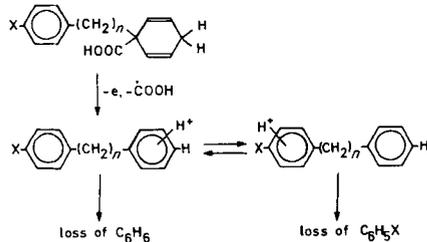
Letter to the Editor

Dear Sir

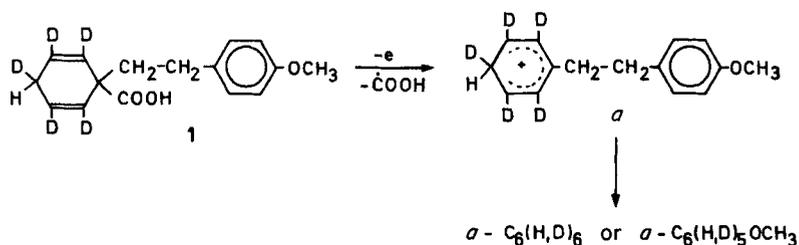
Substituent Effects on the Intramolecular Proton Transfer in ω -Phenylalkylbenzenium Ions

The rates of proton transfer reactions in bimolecular processes depend particularly on the differences in the proton affinities (PA) of the reacting species.¹ Recently, we have shown²⁻⁵ that the bimolecular proton transfer between aromatic molecules can be imitated in a mass spectrometer by an intramolecular proton migration between the two phenyl groups of ω -phenylalkylbenzenium ions (Scheme 1). These ions, with a known position of the extra hydrogen atom, arise from 1-(ω -phenylalkyl)-1,4-dihydrobenzoic acids by electron impact induced fragmentation in the ion source and react further by loss of a benzene molecule both as unstable and metastable ions.² The interannular proton exchange can be observed by the reaction of metastable ω -phenylalkylbenzenium ions specifically deuterated at one of the phenyl groups, which lose the various isotopomers of benzene if the rate of interannular hydrogen migration is faster than the rate of the fragmentation reaction.^{2,3} The results obtained with ions $C_6H_5(CH_2)_n C_6H_6^+$, $2 \leq n \leq 20$, show clearly that the proton transfer reaction has to be much faster, even in the case of a fairly long chain of 20 CH_2 groups between the aromatic rings, because a statistical distribution of deuterium labels over all aromatic positions is observed.³ The effect of different basicities of the aromatic moieties of the ω -phenylalkylbenzenium ions on the rate of the interannular proton transfer has now been studied by the introduction of substituents into one of the aromatic rings (Scheme 1; X = OCH₃, N(CH₃)₂) and by exchanging the ω -phenyl for a pyridyl group.

The mass-analysed ion kinetic energy (MIKE) spectrum and the *B/E* linked scan spectrum of the [2-(4-methoxyphenyl)ethyl]benzenium-*d*₅ ions *a* (Scheme 2) obtained in the 70 eV mass spectrum of 1-[2-(4-methoxyphenyl)ethyl]-1,4-dihydrobenzoic acid-*d*₅ **1** are shown in Fig. 1. The



Scheme 1



Scheme 2

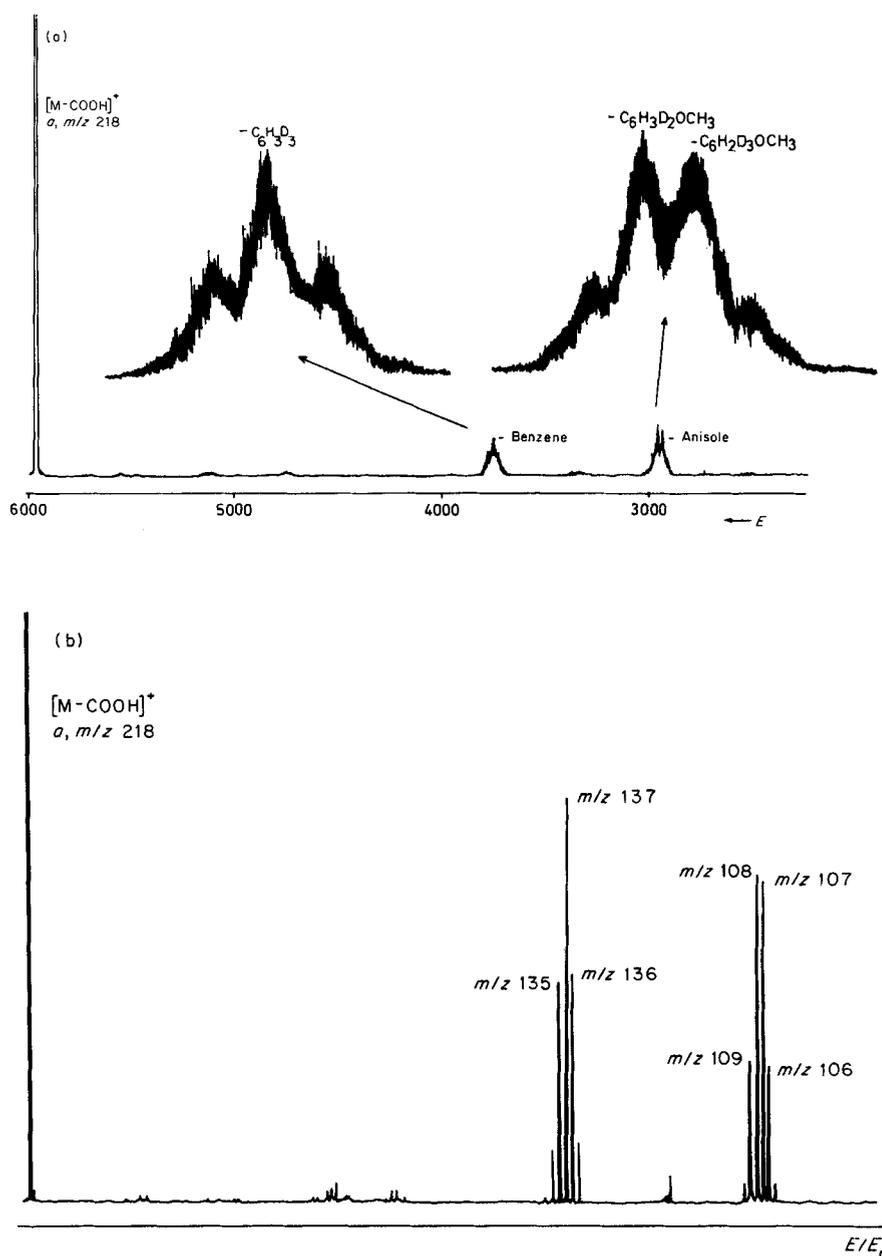
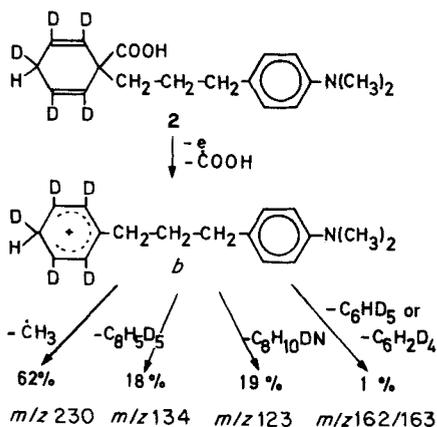
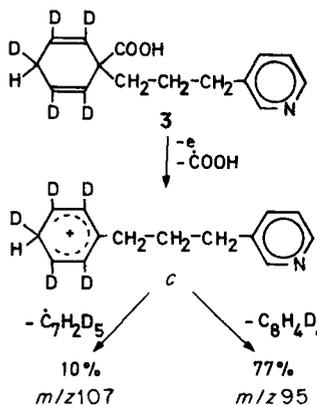


Figure 1. (a) MIKE spectrum and (b) *B/E* linked-scan spectrum of [2-(4-methoxyphenyl)ethyl]benzenium-*d*₅ ions *a* (VG ZAB-2F mass spectrometer).

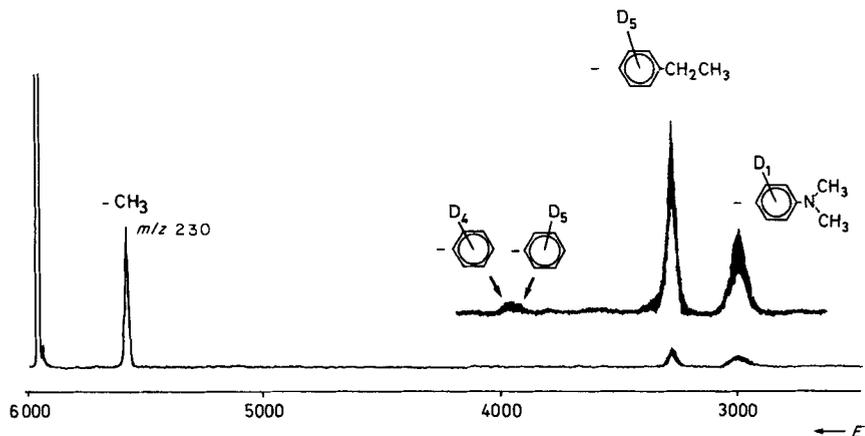
Table 1. Calculations and experimental relative abundances of anisole and benzene isotopomers formed from ions *a*

		-C ₆ H ₆ R	-C ₆ H ₄ DR	-C ₆ H ₃ D ₂ R	-C ₆ H ₂ D ₃ R	-C ₆ HD ₄ R	-C ₆ D ₆ R
Anisole	Calc.	0.4	9.9	39.7	39.7	9.9	0.4
R = OCH ₃	1st FFR	2	15	34	33	14	2
	2nd FFR	1	12	37	38	11	1
Benzene	Calc.	—	2.4	23.8	47.6	23.8	2.4
R = H	1st FFR	—	6	23	42	23	6
	2nd FFR	—	3	24	46	24	3

**Scheme 3****Scheme 4**

moieties (Table 1). Thus, in spite of the considerable PA difference of 57 kJ mol⁻¹ between the aromatic groups the interannular proton transfer in metastable ions *a* is still much faster than the fragmentation.

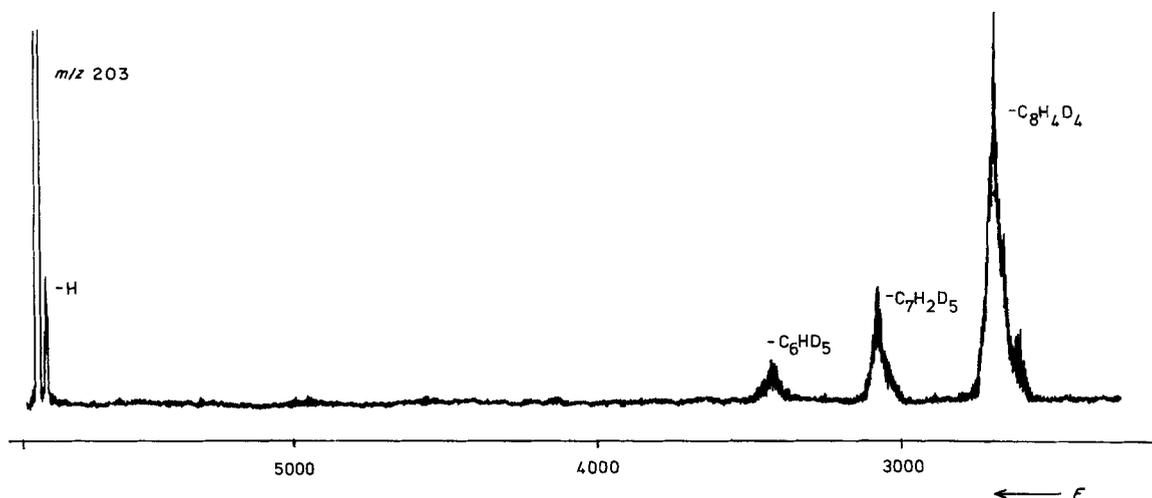
In the case of [3-(4-dimethylaminophenyl)propyl]benzenium-*d*₅ ions *b* (Scheme 3), an even larger PA difference of 167 kJ mol⁻¹ is expected for its two aromatic groups (PA (dimethylaniline) = 944 kJ mol⁻¹^{6c}). The MIKE spectrum of ion *b* differs from those of

**Figure 2. MIKE spectrum of [3-(4-dimethylaminophenyl)propyl]benzenium-*d*₅ ions *b* (VG ZAB-2F mass spectrometer).**

difference in the PAs of the methoxyphenyl group and the phenyl group in the ions *a* should correspond to the difference of 57 kJ mol⁻¹ between PA(anisole) = 834 kJ mol⁻¹^{6a} and PA(benzene) = 777 kJ mol⁻¹^{6b}.

The undeuterated analogues of ions *a* are known⁷ to lose anisole and benzene competitively in the first field-free region (1st FFR) and in the second field-free region (2nd FFR) of the ZAB-2F mass spectrometer. The relative intensities of the peaks due to the elimination of the isotopomers of benzene and anisole, respectively, clearly show complete scrambling of the H and D atoms at all ring positions of the aromatic

other ω-phenylalkylbenzenium ions^{2-5,7} by a very intense signal for the loss of a methyl radical and by an additional peak for the loss of ethylbenzene-*d*₅ (Fig. 2). The arene elimination—usually the most intense reaction—gives rise to rather small peaks only. The elimination of dimethylaniline is strongly preferred and the peak centre corresponds to the loss of dimethylaniline-*d*₁, but due to the width of the peak the elimination of small amounts (*c.* 10%) of the *d*₀- and *d*₂-isotopomers cannot be excluded. Nevertheless, the preferential losses of ethylbenzene-*d*₅ and of dimethylaniline-*d*₁, respectively, clearly demonstrate the absence of a fast reversible H/D transfer in

**Figure 3. MIKE spectrum of [3-(3-pyridyl)propyl]benzenium-*d*₅ ions *c* (VG ZAB-2F mass spectrometer).**

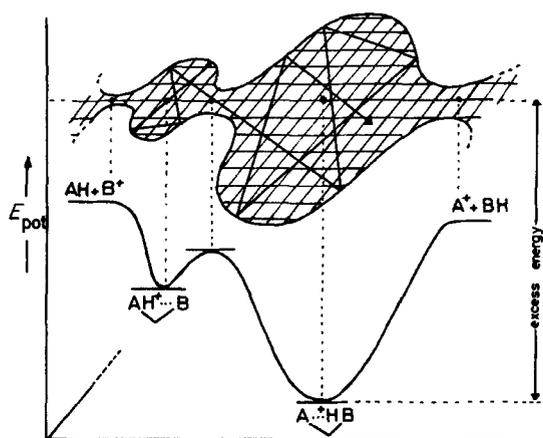


Figure 4. Schematic potential energy diagram for H exchange and fragmentation of substituted ω -phenylalkylbenzenium ions ($PA(B) > PA(A)$).

ion,^b but fragmentation mostly occurs after a single H/D transfer as depicted in Scheme 3.

The migration of the extra proton to a basic nitrogen is also expected for [3-(3-pyridyl)-propyl]benzenium- d_5 ions *c* (Scheme 4; $PA(\text{pyridine}) = 930 \text{ kJ mol}^{-1}$).^{6b} Indeed, the MIKE spectrum of *c* (Fig. 3) shows mainly the loss of styrene- d_4 and of $C_7H_2D_5$. Again, no clear indication for a fast reversible H/D transfer prior to fragmentation of ion *c* is observed. Hence, a PA difference of more than 153 kJ mol^{-1} between the aromatic groups as in ions *b* and *c* inhibits fast reversible proton exchange reactions, while a PA difference of less than 57 kJ mol^{-1} as in ion *a* has no measurable effect.

These results can be qualitatively explained by the potential energy profile for a proton exchange reaction between two different basic centres A and B in one molecule shown in Fig. 4. This reaction energy profile corresponds to the asymmetric double energy minima profile¹ known for a bimolecular proton transfer reaction. The ions *a*, *b* and *c* are generated with the

extra proton bound to the less basic group A. Thus, formation of the hydrogen-bonded complexes and proton transfer to the more basic group B are exothermic reactions which give rise to energetically excited species. The unimolecular reaction of an excited species can be described as a 'random walk' in phase space as indicated in Fig. 4.⁸ The number of microstates in phase space for a certain excess energy E depends *inter alia* on the energy difference between the excited state and ground state of an ion configuration. This difference is much larger for the more stable species with the extra proton bound to the more basic group B. Although proton transfer between A and B by an intramolecular and unimolecular reaction is reversible for energetical reasons the back transfer of the proton from B to the less basic A will be slow and cannot compete effectively with fragmentation if the energy difference between the isomeric configurations H^+A-B and $A-BH^+$ of the ion becomes large enough.

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Yours

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References

- (a) M. Jasinski and J. I. Braumann, *J. Am. Chem. Soc.* **102**, 2906 (1980); (b) D. F. Hunt and S. K. Sethi, *J. Am. Chem. Soc.* **102**, 6953 (1980).
- D. Kuck, W. Bätther and Hans-Fr. Grützmacher, *J. Am. Chem. Soc.* **101**, 7154 (1979).
- D. Kuck, W. Bätther and Hans-Fr. Grützmacher, *Int. J. Mass Spectrom. Ion Proc.*, to be published.
- D. Kuck, *Int. J. Mass Spectrom. Ion Phys.* **47**, 499 (1983).
- For related proton transfer reactions in 1, ω -diphenylalkane radical cations see D. Kuck and Hans-Fr. Grützmacher, *Z. Naturforsch.* **34b**, 1750 (1979).
- (a) Y. K. Lau and P. Kebarle, *J. Am. Chem. Soc.* **98**, 7452 (1976); (b) D. H. Aue and M. T. Bowers, in *Gas Phase Ion Chemistry*, ed. by M. T. Bowers, Vol. 2, Chapt. 9, Academic Press, New York (1979); (c) R. Walder and J. L. Franklin, *Int. J. Mass Spectrom. Ion Phys.* **36**, 85 (1980).
- (a) W. Bätther, D. Kuck and Hans-Fr. Grützmacher, *Int. J. Mass Spectrom. Ion Proc.*, in press; (b) W. Bätther, Dissertation, Universität Bielefeld (1984).
- For a recent discussion see: T. Baer in *Ionic Processes in the Gas Phase*, ed. by M. A. Almoester-Ferreira, NATO ASI Series C, Vol. 118, p. 205, Reidel, New York (1984).