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Gas-phase Basicities of Halogenotoluenes

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Proton-transfer equilibria of the type

$$XH^+ + Y \rightleftharpoons X + YH^+$$

between toluene and halogenotoluenes have been studied at 369 ± 2 K in a high-pressure, pulsed-electron-beam source. The equilibrium constants yield values of ΔG°_{369} for which a ladder of relative basicities can be constructed. The results are discussed and rationalised in terms of the combined effects of methyl and halogen substituents on the sites of protonation in the benzene ring. The results for fluorotoluenes are compared with a CNDO/2 calculation of protonated fluorotoluene structures which predicts that *p*-fluorotoluene is protonated on the methyl-bearing carbon atom.

Proton-transfer reactions between organic molecules have been studied widely both in solution and in the gas phase.[1] Since solvation energies can have a profound influence on the course of a reaction, gas-phase measurements provide the more reliable data for theoretical comparisons.[2] The study of substituent effects on protonation of the aromatic ring has received particular attention because of the large number of solution data which have been used to parameterise substituent effects in the form of 'linear free-energy relations' such as the well-known Hammett acidity functions.[3,4] This approach has also been extended to disubstituted benzene compounds and the combination of substituent effects.

The structure of these protonated molecules is of special interest, since the site of protonation gives an indication of the charge distribution in the ring and serves as a test of theoretical predictions.[5] Several experimental techniques have been used to study sites of protonation more directly. In solution, n.m.r. measurements have been successful[6] but are limited by the requirement of a super-acid medium to generate and maintain the protonated species; and in addition, there may be solvation effects. Theoretical calculations, in combination with experimental relative proton-affinity measurements, have also been employed to good effect as for the protonated xylenes.[5] In some circumstances the measurement of entropy changes in proton-transfer reactions can also provide evidence for particular structures, such as that of protonated fluorobenzene[4,7,8] in which the proton is believed to attach in the position *para* to the F atom.

This paper describes and discusses measurements of the relative basicities of toluene and some halogenotoluenes in terms of the ring-substituent effects and their influence on ring-protonation sites and compares the results with those of a CNDO/2 calculation for protonated fluorotoluenes. Relative basicity measurements by other workers have been obtained previously for the dimethylxylenes[5] and the difluorobenzenes.[7]

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The principle of the measurement is well-known.[8] If an equilibrium of the type

$$AH^+ + B \rightleftharpoons A + BH^+ \qquad \Delta H^\circ \tag{1}$$

is established and at temperature T the equilibrium constant K is measured,

$$-\boldsymbol{R}T \ln K = \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{2}$$

where $\boldsymbol{R}$ is the gas constant. Measurements at one temperature give ΔG° but measurements at several temperatures are required to determine ΔS° and $\Delta H^\circ = A_P(A) - A_P(B)$ where $A_P(X)$ is the proton affinity of X.

EXPERIMENTAL

The pulsed-electron-beam, high-pressure source attached to an MS50 mass spectrometer (Kratos Scientific Instruments Ltd) has been described previously.[8] All reactants studied were volatile liquids and mixtures of the two components required for an equilibrium measurement were accurately made up by weight from AnalaR reagents (B.D.H.). The reactant mixture was made up in a 5 dm^3 glass bulb in an oven. Methane (Matheson Gas Products, 99.9% minimum purity) was admitted to give a pressure of *ca.* 1 atm* and to this was added 10 cm^3 of SF$_6$ (Air Products Ltd, 99.9% minimum purity) and 0.05 or 0.1 cm^3 of the mixture were injected through a septum by means of a gas-tight syringe. The reaction mixture was admitted to the source through an automatic pressure regulator (Granville-Philips Ltd) to give a pressure of 1-5 Torr† measured by means of a Baratron capacitance manometer (MKS Instruments).

Ions were produced in the source by a 40 μs pulse of 400 eV electrons at 5-10 ms intervals and diffused to the ion exit slit before being accelerated towards a high-transmission grid held at a potential of between -50 and -100 V with respect to the ion source. They were then subjected to the full accelerating voltage of 8 kV and were mass-analysed in the usual way. The mass spectrometer was set to collect ions of fixed mass whilst the ion intensity was recorded as a function of time after the electron pulse, and the signal averaged on a multichannel analyser (Biomac 1000, Data Laboratories Ltd) and recorded on an X–Y recorder (Bryans model 26000). In this way, a family of curves of ion intensity against residence time were obtained for each ion of interest. Throughout this work the temperature was maintained constant at 369 ± 2 K, and was measured using a copper–constantan thermocouple.

The source could be operated in a continuous mode so that normal chemical ionisation mass spectra could be recorded.

RESULTS

CHEMICAL IONISATION SPECTRA

The methane chemical ionisation spectra of the pure compounds, obtained from mixtures of $< 0.2\%$ of compound in methane gas containing $< 0.2\%$ SF$_6$, were very similar to those reported by Harrison and coworkers.[9, 10] As examples, the spectra for toluene and *m*-fluorotoluene are shown in fig. 1.

In all cases, the protonated molecule is the most abundant ion, produced by reaction with CH_5^+ and $C_2H_5^+$. In the course of this study low-pressure experiments were performed in an ion cyclotron resonance (i.c.r.) spectrometer, using the double-resonance technique.[11] Under the i.c.r. conditions $C_2H_5^+$ appears to be the only precursor ion of the protonated species, possibly because decomposition may follow the protonation by CH_5^+, which is *ca.* 146 kJ mol^{-1} more exothermic than protonation by $C_2H_5^+$. In a high-pressure source, collisional stabilisation might allow MH$^+$, formed from reaction of M with CH_5^+, to be observed. In the fluorotoluene spectra the $m/z = 107$ ion is the second most abundant ion, and is thought to be due to reaction (3)

$$CH_5^+ + FC_6H_4CH_3 \rightarrow CH_3C_6H_4CH_3^{\cdot} H^+ + HF \tag{3}$$

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* 1 atm = 101 325 Pa. † 1 Torr = (101 325/760) (≈ 133) Pa.

producing the protonated xylene ion, in a reaction similar to that in which protonated toluene is formed in the reaction of CH_5^+ with flurobenzene. Ion cyclotron double-resonance experiments showed that CH_5^+ is indeed a direct precursor to $m/z = 107$. For all other systems the second most abundant ion in all cases was the adduct $(M+C_2H_5)^+$.

EQUILIBRIUM MEASUREMENTS

By operating the source in the pulse mode, the approach to equilibrium of reactions of the type

$$CH_3C_6H_4XH^+ + CH_3C_6H_4Y \rightleftharpoons CH_3C_6H_4X + CH_3C_6H_4YH^+ \qquad (4)$$

could be monitored, where X and Y may be H, F, Cl, Br or I. The ion intensity ratio $I(CH_3C_6H_4YH^+)/I(CH_3C_6H_4XH^+)$ is measured as a function of time, and equilibrium is assumed to have been established when this ratio becomes constant. This was verified by showing that for a given system the value of the equilibrium constant derived from these measurements was independent of the total pressure and partial pressures of reactants. No corrections were applied to observed ion intensities to minimise sampling errors which may arise at the ion exit slit.[8] A total of 15 systems were examined and experimental conditions and derived equilibrium constants are summarised in table 1.

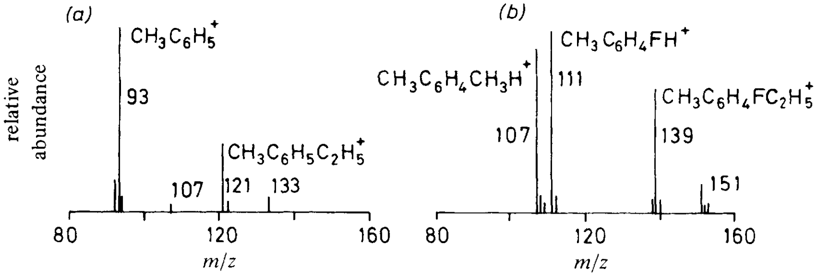


FIG. 1.—Chemical ionisation spectra of (*a*) toluene and (*b*) *m*-fluorotoluene in methane, containing < 0.2% SF_6, at 369 K and 1 Torr.

Values of ΔG° at 369 K were derived for each system and used to construct the ladder of relative gas-phase basicities shown in fig. 2. The standard state is defined as a pressure of 1 atm at 369 K, but because of the symmetry of the reactions no corrections are necessary. Values of ΔG° based on only one measurement are given in parentheses. A test of the reliability of these relative values is provided by the self-consistency of the values of ΔG° for a process derived from different thermodynamic cycles. For example, the relative basicities of toluene and *p*-fluorotoluene may be obtained from the sum of ΔG° values for (*a*) the systems *p*-fluorotoluene + toluene, *p*-chlorotoluene + *p*-fluorotoluene, *p*-fluorotoluene + *p*-chlorotoluene, giving a value of 19.8 kJ mol^{-1} or (*b*) the systems *m*-fluorotoluene + toluene, *m*-chlorotoluene + *m*-fluorotoluene, *o*-fluorotoluene + *m*-chlorotoluene, *o*-chlorotoluene + *o*-fluorotoluene, and *p*-fluorotoluene + *o*-chlorotoluene, giving a value of 19.7 kJ mol^{-1}. The maximum and minimum values of *K* measured for each system are given in table 1.

ENTROPY CHANGES

The relative gas-phase basicities given in fig. 2 differ from the relative proton affinities only by the $T\Delta S$ term. It is often assumed that the net entropy change in

TABLE 1.—SUMMARY OF RESULTS: $XH^+ + Y \rightleftharpoons X + YH^+$

	X	Y	range [X]/[Y]	no. of measure-ments	range of $K°$ measured	$\bar{K}°$	$\Delta G°$ /kJ mol^{-1}	$\Delta S°_{rot}$ /kJ mol^{-1} K^{-1}
i	*m*-F	H	1.65-5.45	8	1.3-1.65	1.5	1.2	0[a]
ii	*m*-Cl	H	3-10	4	2.6-2.8	2.7	3.0	0[a]
iii	*o*-F	H	10-41	2	62-76	69	13.0	0[a]
iv	*m*-Cl	*m*-F	0.67-1.78	3	1.53-1.94	1.89	2.0	0
v	*m*-Br	*m*-Cl	0.22-19.3	3	1.04-1.42	1.3	0.8	0
vi	*m*-Br	*o*-I	0.82	1	1.6	1.6	[1.4]	0
vii	*o*-Br	*m*-Cl	8.8-35.9	5	8.6-12.4	11	7.4	0
viii	*o*-F	*m*-Cl	3.8-15.7	3	17.8-25.1	22	9.5	0
ix	*o*-F	*o*-Br	0.74-22.6	5	1.3-2.6	2.1	2.3	0
x[c]	*o*-Cl	*o*-Br	1.0-3.8	4	5-6	> 5	[> 5.5]	0
xi	*o*-F	*p*-Br	0.07-17.1	6	1.6-2.2	1.9	2.0	between +2 and 0[b]
xii	*o*-Cl	*o*-F	0.3-0.92	2	1.9-2.5	2.2	2.4	0
xiii	*p*-Cl	*o*-F	4.1-8.4	2	6.3-6.3	6.3	5.6	between −2 and 0[b]
xiv	*p*-F	*o*-Cl	1.0-4.8	3	3.5-5.8	4.5	4.6	between −2 and 0[b]
xv	*p*-F	*p*-Cl	0.8-3.0	4	0.9-2.2	1.5	1.2	between 0 and +2[b]

[a] Assumes *para* protonation of toluene; [b] the range allows for possible *ipso* protonation of the *p*-halogenated toluenes; [c] this reaction was never observed to reach a true equilibrium in plots of I_{Y^+}/I_{X^+} against time.

proton-transfer reactions is due only to rotational symmetry changes,[12] and in many systems this is supported by experiment.[4, 8, 13] If the structures of the protonated species are known, values of $\Delta S_{\rm rot}$ may be calculated from

$$\Delta S_{\rm rot} = R \ln(\sigma_{\rm AH^+}\sigma_{\rm B}/\sigma_{\rm A}\sigma_{\rm BH^+})$$

where σ is the rotational symmetry. In the reactions listed in table 1 the maximum possible value of $T\Delta S^\circ$ is ± 2.13 kJ mol^{-1} for reactions (i)-(iii), (ix) and (xi)-(xiii), and

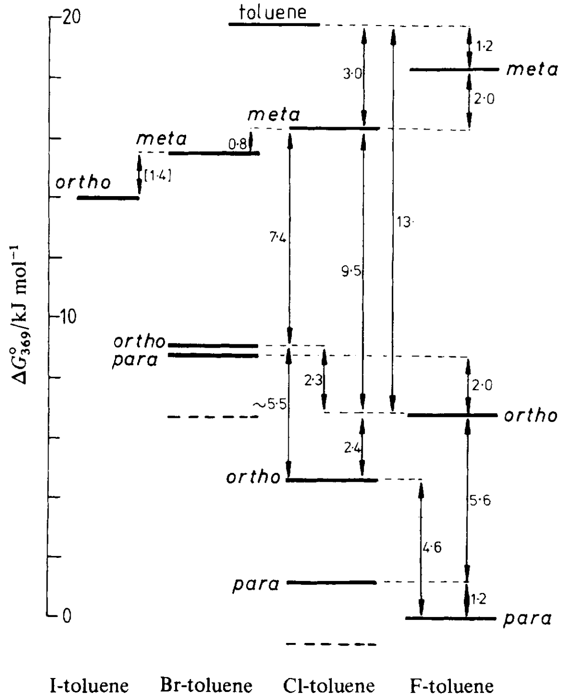


FIG. 2.—Relative basicities of toluene and the halogenotoluenes [ΔG°_{369} kJ mol^{-1} values for reactions $\mathrm{XH^+ + Y \rightleftharpoons X + YH^+}$].

is zero for all other rections because of no change in rotational symmetry. For reactions (i)-(iii) a non-zero value of $T\Delta S^\circ$ requires that protonation should occur at sites other than that *para* to the methyl group in toluene, contrary to evidence from i.c.r. experiments, theory and n.m.r. measurements in solution. For these reactions, therefore, $T\Delta S^\circ$ is probably zero. For reactions (ix) and (xi)-(xiii) a non-zero value of $T\Delta S^\circ$ implies protonation *ipso* to the methyl group; this is discussed in a later section. A ladder of relative proton affinities will differ very little from fig. 2, with the possible exceptions of the relative position of *p*-bromo- and *o*-fluoro-toluenes and *p*-chloro- and *p*-fluoro-toluenes, since these are the only pairs of compounds for which the relative gas-phase basicities are sufficiently close for $T\Delta S^\circ$ to be significant. The possible alternative positions of *p*-chloro- and *p*-bromo-toluenes are indicated by dashed lines in fig. 2. A brief study of the temperature dependence of some of these systems was inconclusive because of the onset of competing reactions at higher temperatures.

DISCUSSION

Substituent effects on the reactivity or stability of aromatic species are usually discussed in terms of charge distribution within the ring by invoking the qualitative concepts of induction, resonance and polarisation. These form the basis of the semiquantitative linear free-energy relationships, such as the Hammett substituent constants,[3] whilst a more rigorous and quantitative treatment makes use of perturbation molecular-orbital theory.[14] This theory predicts[15] that in the $C_6H_7^+$ ion the proton is attached to a specific carbon atom, which therefore exhibits a tetrahedral sp^3 valence structure (rather than its being associated with 2 or more carbon atoms), in agreement with indirect experimental evidence. A ring-bound proton will therefore act as an electron sink both through the σ and π electron systems such that the stabilizing and destabilizing effects of electron-donating and electron-withdrawing groups lead to an increase and decrease of the proton affinity of the molecule, respectively.

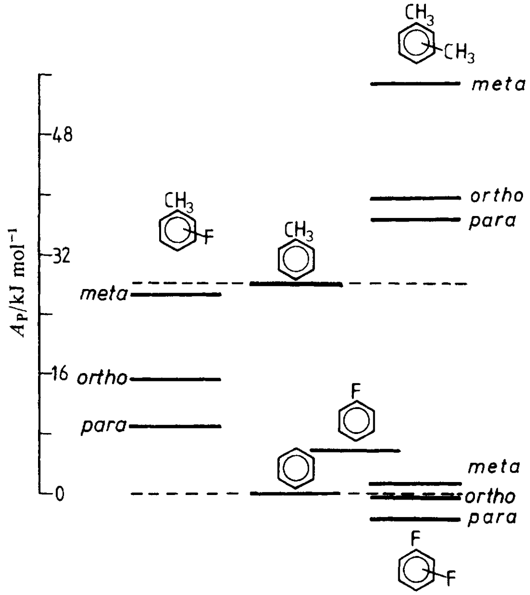


FIG. 3.—Relative proton-affinity ladder for benzene, toluene, the xylenes, the difluorobenzenes, the fluorotoluenes and fluorobenzene.

The methyl group acts only as a weak π-donor,[14-16] frequently rationalised in terms of 'hyperconjugation', and results in a significantly higher proton affinity for toluene than for benzene.[5] Halogens, on the other hand, act both as σ-acceptors and π-donors, and the relative importance of the two effects varies both with the halogen and the presence of other substituents. Thus halogens enhance both the acidity of phenol[17] and, to a lesser extent, the basicity (or more strictly, the proton affinity) of benzene,[8] the effect decreasing in the series F > Cl $\geqslant$ Br.

In the presence of these substituents, the stabilisation of the protonated molecule is greatest when protonation occurs at the ring position *para* and *ortho* to the substituent. Previous studies of proton-transfer equilibria suggest that fluorine is almost exclusively *para*-directing, whereas chlorine is less specific.[8] Quantitative molecular-orbital calculations suggest[5] that the toluene also protonates in the *para* position (see fig. 5). When two substituents are present, two points require consideration: (i) the overall effect of the two substituents and (ii) the effect of the relative positions of the two substituents. Literature values of proton affinities of xylenes and difluorobenzenes are included in the proton-affinity ladder in fig. 3, from which it is apparent that, whereas the effect of the second methyl group is to reinforce that of the first methyl group [A_{P}(benzene) < A_{P}(toluene) < A_{P}(xylenes)], the effect of a second fluorine atom is to reduce that of the first fluorine atom [A_{P}(*o*- and *p*-difluorobenzenes) < A_{P}(benzene) < A_{P}(*m*-difluorobenzene) < A_{P}(fluorobenzene)]. These trends are reproduced in the proton affinities found for fluorotoluenes in the present study. The series A_{P}(benzene) < A_{P}(toluene) > A_{P}(fluorotoluene) indicates that, whereas the introduction of a methyl group as first substituent increases the proton affinity, the introduction of a F atom as second substituent leads to a decrease. As the results in fig. 2 demonstrate, this behaviour is common to all halogens.

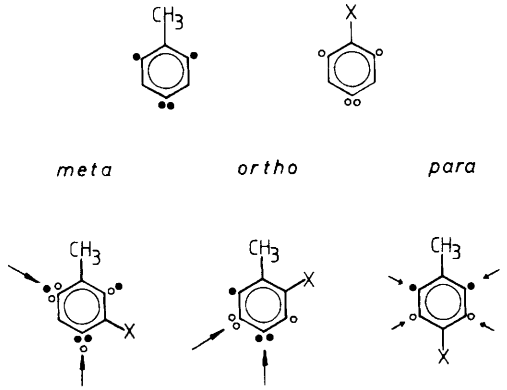


FIG. 4.—Stabilisation of positive charge on the ring in substituted benzenes: ●, preferred sites of protonation in toluene; ○, preferred sites of protonation for halogen-substituted benzene; →, expected sites of protonation in the halogenotoluenes.

The dependence of the proton affinities of isomeric disubstituted benzenes on the relative positions of the substituents is amply demonstrated in fig. 2 and 3: in each case, the proton affinities fall in the series $m > o > p$. This pattern can be understood by assuming that each substituent leads to stablisation of protonation of sites *ortho* or *para* to the substituent, the latter leading to greater stabilisation, whereas protonation in a site *meta* to the substituent is destabilising. When a site is *ortho* or *para* to one substituent and *meta* to another, stabilisation will be decreased, as illustrated in fig. 4. Only in the case of a *m*-disubstituted benzene is it possible to protonate at a site which is *ortho* to one substituent and *para* to the other, leading to maximum stabilisation and hence the highest proton affinity. In *p*-disubstituted benzenes, no free *para* position exists for protonation, and protonation at any of the unsubstituted carbon atoms is both *ortho* and *meta* with respect to the two substituents, giving the minimum stabilisation. Calculations suggest that the *para*-directing influence of the halogens is sufficiently high to make possible protonation on the methyl-bearing carbon atom. *o*-Disubstituted benzenes fall between these two cases, and the above arguments may be used to predict the site of protonation in all three isomers, as indicated in fig. 4.

Relative energies of possible structures of ring-protonated toluene and fluorotoluenes have been calculated using the CNDO/2 method.[18, 19] (Geometries used in the calculation are given in the Appendix.) For protonated toluene structures, the energies predicted by this low-level calculation are compared in fig. 5 with the results of more sophisticated calculations[5] based on the STO-3G method; there is good qualitative agreement between the two sets of relative energies. In fig. 6 are shown structures of protonated fluorotoluenes having energies which are calculated to be no more than 20 kJ mol^{-1} above that of the most stable structure. Below what is assumed to be the structure of the ground state ion in each case is given a value of ΔU calculated for the isodesmic reaction

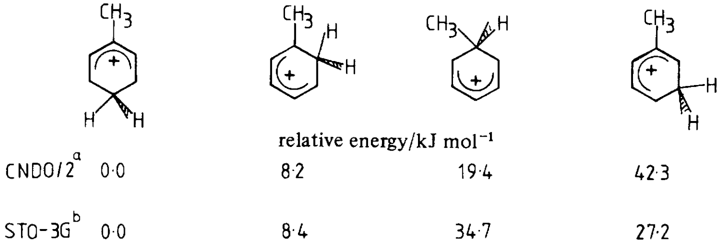
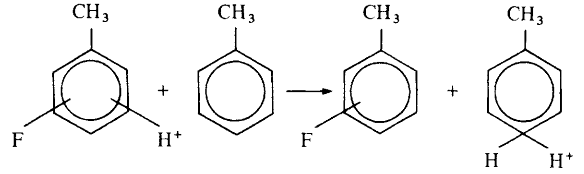


FIG. 5.—Structures of protonated toluene and their calculated relative energies (kJ mol^{-1}): (a) ref. (19), (b) ref. (5).



(5)

For comparison, experimental values of $\Delta G°$ derived from fig. 2 are also given. There is good agreement for the toluene–*m*-fluorotoluene system, and the large difference in the proton affinity of the *m*-derivative and those of the *o*- and *p*-derivatives is predicted, and although the quantitative agreement is poor, it is probably within the limits of confidence for this method.

Structures observed in super-acid media using n.m.r. spectroscopy are also given in fig. 6 and for the most part agree with those predicted by the earlier qualitative arguments illustrated in fig. 4. For *p*-fluorotoluene, however, CNDO/2 calculations predict protonation in the gas phase to occur exclusively at the methyl-bearing carbon atom, *ipso*-protonation, and this may also occur for *o*-fluorotoluene. Such a structure has been observed in super-acid media only in cases in which there is no unsubstituted carbon atom available, but this difference may arise from solvation energy effects.

The most stable structures of the protonated xylenes calculated using the STO-3G method are also given in fig. 6 and indicates that *ipso*-pronation of *p*-xylene is also favoured, consistent with isotope-effect measurements.[20] It is therefore possible that *ipso*-protonation in the gas-phase is more common than observations made in super-acid media suggest, and further work is planned to investigate this possibility.

The relative basicities of *m*-derivatives lies in the sequence F > Cl > Br (see fig. 2). This order concurs with measurements of LFER constants, gas-phase acidities and proton affinities, indicating the degree of π-donation and σ-withdrawal of electrons to decrease with increasing size of the halogen substituent. It is initially surprising therefore to observe the reverse order (Br > Cl > F) for *p*-derivatives. This can be rationalised, however, by again taking account of the changing restrictions on sites

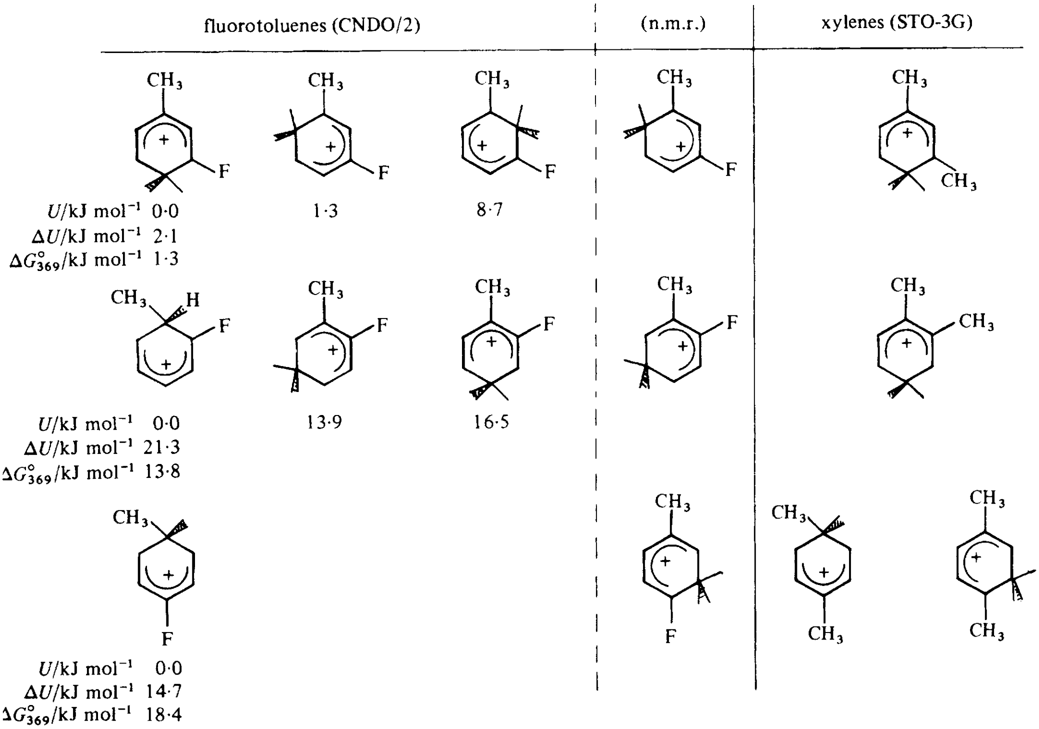


FIG. 6.—Structures of protonated fluorotoluenes in the gas phase [calculated, ref. (19)] and in super-acid media [n.m.r., ref. (6)], and the most stable calculated structures [ref. (5)] of the protonated xylenes. U: calculated relative energies, ΔU and ΔG°_{369}: see text.

of protonation. As we have seen, potential sites of protonation are relatively unhindered by either substituent of the *m*-halogenotoluenes, but in the *p*-derivatives the prime site (in *para* positions) is blocked, the free carbon atoms all being in positions *meta* to one or other of the substituents. The restrictions on site of protonation, which appear to be quite rigid for fluorine, become progressively relaxed for chlorine and bromine,[8] such that we would expect stabilisation of positive charge at these *meta* positions to increase in the observed sequence Br > Cl > F. As is usual the *o*-derivatives fall in between yielding a sequence I > Br > F > Cl.

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APPENDIX

The following values of lengths (Å) and angles were used in the calculations:

6-membered ring (taken as perfect hexagon in all cases)	C—C	1.40
	C(sp^2)—H	1.08
	C(sp^2)—H	1.33
exocyclic	C—C	1.52
C—H in all CH_3		1.09
At sp^3 carbon (*i.e.* the protonated position) exocyclic	C—H	1.09
	C—C	1.52

The ring plane bisected the tetrahedral angle (109° 28′). A CH_3 group in the ring plane was arranged so that one hydrogen was on one side of the ring and the other two symmetrically placed on the other: in structures with CH_3 at the protonated position, this arrangment was tilted out of the ring plane by 54° 44′.

[1] E. Caldin and V. Gold, *Proton Transfer Reactions* (Chapman and Hall, London, 1975).
[2] R. W. Taft, *NATO Adv. Study Inst. Ser., Ser. B*, 1979, **40**, 271.
[3] J. Hine, *Structural Effects on Equilibria in Organic Chemistry* (Wiley and Sons, New York, 1975).
[4] Y. K. Lau and P. Kebarle, *J. Am. Chem. Soc.*, 1976, **98**, 7452.
[5] J. L. Devlin, J. F. Wolf, R. W. Taft and W. J. Hehre, *J. Am. Chem. Soc.*, 1976, **98**, 1990.
[6] G. A. Olah and Y. K. Mo, *Adv. Fluorine Chem.*, 1973, **7**, 69.
[7] K. G. Hartmann and S. G. Lias, *Int. J. Mass Spectrom. Ion Phys.*, 1978, **28**, 213.
[8] D. K. Bohme, J. A. Stone, R. S. Mason, R. S. Stradling and K. R. Jennings, *Int. J. Mass Spectrom. Ion Phys.*, 1981, **37**, 283.
[9] A. G. Harrison and P. Lin, *Can. J. Chem.*, 1975, **53**, 1314.
[10] H. Leung and A. G. Harrison, *Can. J. Chem.*, 1976, **54**, 3439.
[11] G. C. Goode, A. J. Ferrer-Correia and K. R. Jennings, *Int. J. Mass Spectrom. Ion Phys.*, 1970, **5**, 229.
[12] S. G. Lias, *NATO Adv. Study Inst. Ser., Ser. B*, 1979, **40**, 223.
[13] R. Yamagni and P. Kebarle, *J. Am. Chem. Soc.*, 1976, **98**, 1320.
[14] For a recent example see: A. Pross, L. Radom and R. W. Taft, *J. Org. Chem.*, 1980, **45**, 818.
[15] W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, 1972, **94**, 6901.
[16] W. J. Hehre, L. Radom and J. A. Pople, *J. Am. Chem. Soc.*, 1972, **94**, 1496.
[17] G. Kemister, A. Pross, L. Radom and R. W. Taft, *J. Org. Chem.*, 1980, **45**, 1056, and references therein.
[18] J. A. Pople and G. A. Segal, *J. Chem. Phys.*, 1966, **44**, 3289.
[19] J. Burdon, personal communication (Department of Chemistry, University of Birmingham).
[20] J. F. Wolf, J. L. Devlin, D. J. DeFrees, R. W. Taft and W. J. Hehre, *J. Am. Chem. Soc.*, 1976, **98**, 5097.

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