New York, 1978, Chapter 7.
(11) K. Levsen and H. Schwarz, *Angew. Chem., Int. Ed. Engl.*, **15,** 509 (1976).
(12) F. W. McLafferty and F. M. Bockhoff, *Anal. Chem.*, **50,** 69 (1978).
(13) J. H. McReynolds and M. Anbar, *Int. J. Mass Spectrom. Ion Phys.*, **24,** 37 (1977).
(14) E. Soltero-Rigau, T. L. Kruger, and R. G. Cooks, *Anal. Chem.*, **49,** 435 (1977).
(15) T. L. Kruger, R. G. Cooks, J. L. McLaughlin, and R. L. Ranieri, *J. Org. Chem.*, **42,** 4161 (1977).
(16) T. L. Kruger, R. Flammang, J. F. Litton, and R. G. Cooks, *Tetrahedron Lett.*, 4555 (1976).
(17) Synthesis was based on standard methods (L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Wiley, New York, 1967, p 584) and the identity of the product was checked by NMR.
(18) (a) M. S. Newman and L. K. Lula, *Tetrahedron Lett.*, 3267 (1967); (b) M. S. Newman, "An Advanced Organic Lab Course", Macmillan, New York, 1972, pp 8–41. The identity of the product was checked by NMR.
(19) (a) R. G. Cooks and T. L. Kruger, *J. Am. Chem. Soc.*, **99,** 1279 (1977); (b) D. Cameron, T. L. Kruger, and R. G. Cooks, 1977 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Papers 88 and 89; (c) R. G. Cooks, T. L. Kruger, and D. Cameron, paper presented at 25th Annual Conference on Mass Spectrometry and Allied Topics, American Society for Mass Spectrometry, Paper MF 5.
(20) G. Glish and R. G. Cooks, unpublished results.
(21) (a) M. A. Haney and R. T. McIver, paper presented at 19th Annual Conference on Mass Spectrometry and Allied Topics, American Society for Mass Spectrometry, Atlanta, Ga., 1971; (b) J. R. Hass, W. B. Nixon, and M. M. Bursey, *Anal. Chem.*, **49,** 1071 (1977); (c) R. D. Smith, D. A. Herold, T. A. Elwood, and J. H. Futrell, *J. Am. Chem. Soc.*, **99,** 6042 (1977); (d) Z. Karpas and F. S. Klein, *Int. J. Mass Spectrom. Ion Phys.*, **24,** 137 (1977); (e) M. Kumakura, K. Arakawa, and T. Sugiura, *ibid.*, **27,** 149 (1978).
(22) T. B. McMahon, *Can. J. Chem.*, **56,** 670 (1978).
(23) Given the covalent structure (b), the elimination of acetic acid should be a favorable reaction under thermal conditions existing in the high-pressure CI source.
(24) R. A. W. Johnstone and B. J. Millard, *Z. Naturforsch. A*, **21,** 604 (1966).
(25) The MIKE spectrum of the 179^+ ion generated from 2-benzylbenzyl alcohol is also identical with those shown in Figure 4. Identical MIKE spectra imply identical ion structures or sets of interconverting ion structures.[26]
(26) (a) D. H. Williams, *Acc. Chem. Res.*, **10,** 280 (1977); (b) Karsten Levsen, "Fundamental Aspects of Organic Mass Spectrometry", Verlag Chemie, Weinheim/Bergstr., Germany, 1978; (c) J. R. Haas, R. G. Cooks, J. F. Elder, Jr., M. M. Bursey, and D. G. I. Kingston, *Org. Mass Spectrom.*, **11,** 697 (1976); (c) J. R. Haas, R. G. Cooks, J. F. Elder, Jr., M. M. Bursey, and D. G. I. Kingston, *Org. Mass Spectrom.*, **11, 697** (1976); (d) F. W. McLafferty, T. Wachs, C. Koppel, P. P. Dymerski, and F. M. Bockhoff, *Adv. Mass Spectrom.*, 713 (1978).
(27) (a) V. Franchetti, B. S. Freiser, and R. G. Cooks, *Org. Mass Spectrom.*, **13,** 106 (1978); (b) M. L. Sigsby, R. J. Day, and R. G. Cooks, *ibid.*, in press.

Effect of Reaction Energetics on the Hydrogen Chemical Ionization Mass Spectra of Halobenzene Derivatives. Estimates of the Heats of Formation of Substituted Phenyl Cations

Hei-Wun Leung and Alex. G. Harrison*

Contribution from the Department of Chemistry, University of Toronto, Toronto, Canada M5S 1A1. *Received October 3, 1978*

Abstract: The H_2 chemical ionization mass spectra of the halobenzene derivatives XC_6H_4Y (X = F, Cl, Br; Y = NH_2, OCH_3, F, Cl, Br) as well as the isomeric dichloroanilines and *N,N*-dimethylanilines have been determined. The major fragmentation reactions of the protonated molecule, MH^+, produce either $YC_6H_5^{+\cdot} + X\cdot$ or $YC_6H_4^+ + HX$ depending on the identity of the halogen X and the substituent Y. In several cases the $YC_6H_4^+$ ions undergo further reaction with H_2. The formation of the odd-electron products $YC_6H_5^{+\cdot} + X\cdot$, unusual in chemical ionization mass spectrometry, is shown to result from the thermochemical stability of $YC_6H_5^{+\cdot}$ compared to $YC_6H_4^+$. The competition between the two reaction channels depends strongly on the relative stabilities of HX and $X\cdot$. From this reaction competition estimates are derived for the heats of formation of substituted phenyl cations as follows ($\Delta H_f°$ in kcal mol^{-1}): $H_3CC_6H_4^+$, 253; $H_2NC_6H_4^+$, 253; $CH_3OC_6H_4^+$, 225; $FC_6H_4^+$, 227; $ClC_6H_4^+$, 264; $BrC_6H_4^+$, 275. The estimated uncertainty in these values is ±4 kcal mol^{-1}.

Introduction

Earlier studies[1-3] of the H_2 chemical ionization (CI) mass spectra of the halobenzenes have shown that, in addition to charge transfer to the aromatic system, the mass spectra can be rationalized in terms of the fragmentation reactions 1 and 2 of the protonated molecule. The phenyl cation formed in (2) has been shown[3,4] to react further with H_2 to produce protonated benzene (reaction 3).

$$C_6H_5X{\cdot}H^+ \rightarrow C_6H_6^{+\cdot} + X\cdot \qquad (1)$$

$$\rightarrow C_6H_5^+ + HX \qquad (2)$$

$$C_6H_5^+ + H_2 \rightarrow C_6H_7^{+\cdot} \qquad (3)$$

It was observed[1,2] that the relative importance of (1) and (2) depended strongly on the identity of the halogen X and this has been rationalized in terms of the relative energetics of the two fragmentation reactions. Table I records the fractional intensities of the $C_6H_6^{+\cdot}$ and $C_6H_5^+ + C_6H_7^+$ products for the halobenzenes and compares these intensities with the standard enthalpy changes for reactions 1 and 2. The latter refer to decomposition of the ground-state protonated halobenzene and have been derived using $\Delta H_f°(C_6H_5X{\cdot}H^+)$ values derived from the proton affinities $PA(C_6H_5F)$ = 182 kcal mol^{-1},[5] $PA(C_6H_5Cl)$ = 182 kcal mol^{-1},[5] and assuming the same proton affinities for bromo- and iodobenzene. The remaining thermochemical data have been taken from ref 6 with the exception of $\Delta H_f°(C_6H_5^+)$ = 266 kcal mol^{-1}.[7]

As the data in Table I show protonated fluorobenzene and protonated chlorobenzene fragment only by reaction 2 and this is consistent with the energetics data which show this reaction to be strongly favored thermochemically. However, for the bromobenzene system ~23% of the fragmentation of MH^+ proceeds by (1) to give the benzene molecular ion and a bromine atom. This also is consistent with the thermochemistry which shows that (1) and (2) have similar energetics requirements, with (1) having a slightly higher energy requirement, consistent with its lesser importance. For protonated iodobenzene fragmentation by (1) is strongly favored thermically and this is the only fragmentation reaction which is observed.

The observation of the odd-electron products $C_6H_6^{+\cdot} + X\cdot$

0002-7863/79/1501-3168$01.00/0 © 1979 American Chemical Society

Table I. Fragment Ion Intensities in CI of Halobenzenes[a]

	$C_6H_6^{+\cdot} + X$		$C_6H_5^+ + HX$	
X	yield	$\Delta H°_{(react)}$	yield	$\Delta H°_{(react)}$
F	0	96	1.0	45
Cl	0	66	1.0	48
Br	0.23	51	0.77	48
I	1.0	36	0	49

[a] Yield as fraction of total fragment ion intensities. Thermochemical data in kcal mol^{-1}

Table II. Fragmentation and Thermochemistry in CI of Halotoluenes[a]

	$CH_3C_6H_5^{+\cdot} + X\cdot$		$CH_3C_6H_4^+ + HX$	
X	yield	$\Delta H_f°$ $(CH_3C_6H_5^{+\cdot} + X\cdot)$	yield[b]	$\Delta H_f°$ $(CH_3C_6H_4^+)$
F	0	234	1.0	<299
Cl	0	244	1.0	<266
Br	0.59	242	0.41	$\geqslant 251$
I	0.91	241	0.09	>235

[a] Yields as fraction of total fragment ion intensities. Thermochemical data in kcal mol^{-1}. [b] Yield includes $CH_3C_6H_6^+$ derived by reaction of $CH_3C_6H_4^+$ with H_2.

in proton transfer CI mass spectrometry is of considerable interest since such spectra usually are dominated by even-electon species.[8-10] The present work was undertaken in part to explore the prevalence of formation of odd-electron products in the CI mass spectra of haloaromatics. The thermochemical explanation for the halobenzene compounds lies in the stability of the aromatic molecular ion ($\Delta H_f°(C_6H_6^{+\cdot}) = 233$ kcal mol^{-1}[6]) compared to the phenyl cation ($\Delta H_f°(C_6H_5^+) = 266$ kcal mol^{-1}). The shift in reaction channel through the halogen series from fluorine to iodine results from the decreasing stability of the neutral hydrogen halide, HX, relative to the halogen atom, X·. Thus, the high stability of HF ($\Delta H_f° = -64.8$ kcal mol^{-1}[6]) compared to F· ($\Delta H_f° = 18.9$ kcal mol^{-1}[6]) is more than sufficient to compensate for the higher heat of formation of $C_6H_5^+$. However, HI ($\Delta H_f° + 6.3$ kcal mol^{-1}[6]) is not sufficiently stable relative to I· ($\Delta H_f° = 25.6$ kcal mol^{-1}[6]) to compensate for the relative thermochemical instability of $C_6H_5^+$ and formation of $C_6H_6^{+\cdot} +$ I· becomes the favored fragmentation route.

In general, substituents, Y, on the phenyl ring would be expected to influence the stability of the odd-electron $YC_6H_5^{+\cdot}$ more than the even-electron $YC_6H_4^+$ and one would anticipate that formation of odd-electron species should be more prevalent in the H_2CI of substituted halobenzenes, particularly for electron-donating substituents. In addition, the results for the unsubstituted compounds (Table I) suggest that it should be possible to obtain estimates of the heats of formation of substituted phenyl cations from observation of the preferred fragmentation channel as the halogen is varied. The thermochemical criteria indicated by the results in Table I can be stated in an equivalent fashion as follows. If $\Delta H_f°(YC_6H_4^+ + HX) < \Delta H_f°(YC_6H_5^{+\cdot} + X)$ reaction 2 will be observed, while if $\Delta H_f°(YC_6H_4^+ + HX) > \Delta H_f°(YC_6H_5^{+\cdot} + X\cdot)$ reaction 1 will be observed. If both fragmentation reactions are observed, the heats of formation of the two sets of products must be approximately equal. Since the heats of formation of HX, X·, and $YC_6H_5^{+\cdot}$ are known, estimates, or at least limits, on the heats of formation of $YC_6H_4^+$ can be derived, The major thrust of the present work is to derive estimates of the heats of formation of substituted phenyl cations. There is practically no experimental information concerning the thermochemistry of substituted phenyl cations, although the results of two separate theoretical studies recently have been published.[11,12]

Experimental Section

The chemical ionization mass spectra were obtained using a Du Pont 21-490 mass spectrometer equipped with a high-pressure chemical ionization source. The source temperature was ~160 °C and the ionizing electron energy 70 eV with the repellers held at cage potential. Liquid samples were introduced through a heated inlet system at ~150 °C while solid samples were introduced directly from a solids insertion probe. Chemical ionization mass spectra normally were determined at a H_2 pressure of ~0.5 Torr. However, for a number of systems pressure studies[3] were carried out to confirm that the $YC_6H_6^+$ product did arise by reaction of $YC_6H_4^+$ with H_2, the analogue of reaction 3.

The compounds used were commercial samples of high purity and showed no detectable impurities in their electron impact mass spectra. Reagent grade H_2 (Matheson and Co.) was used without further purification. The D_2 (Matheson and Co.) was passed through a heated palladium thimble prior to use to remove a low-level impurity of mass 28 (probably N_2).

Results and Discussion

CI Mass Spectra of Halotoluenes. $\Delta H_f°(CH_3C_6H_4^+)$. The H_2 CI mass spectra of the halotoluenes have been reported previously.[1,2] Table II summarizes the fragmentation competition for the meta isomers and gives for each halotoluene the sum $\Delta H_f°(CH_3C_6H_5^{+\cdot} + X\cdot)$. The exclusive formation of $CH_3C_6H_4^+ + HCl$ for the chlorotoluenes establishes $\Delta H_f°(CH_3C_6H_4^+) < 266$ kcal mol^{-1}, while the dominant fragmentation to form $CH_3C_6H_5^{+\cdot} +$ I· in the iodotoluenes establishes $\Delta H_f°(CH_3C_6H_4^+) > 235$ kcal mol^{-1}. From the near equality of importance of the two reaction channels for the bromotoluenes we conclude $\Delta H_f°(CH_3C_6H_4^+ + HBr) \simeq \Delta H_f°(CH_3C_6H_5^{+\cdot} + Br\cdot)$, from which we derive $\Delta H_f°(CH_3C_6H_4^+) \simeq 251$ kcal mol^{-1}. In view of the lower yield of the tolyl ion we adopt a value $\Delta H_f°(CH_3C_6H_4^+) = 253$ kcal mol^{-1}. Collisional activation studies by McLafferty and Bockhoff[13] confirm that the ion formed in the CI of halotoluenes is in fact the tolyl ion and that rearrangement to the benzyl or tropylium structure has not occurred. The experimental estimate $\Delta H_f°(CH_3C_6H_4^+) = 253$ kcal mol^{-1} is in good agreement with the calculated (STO-3G) value[11] of 254 kcal mol^{-1} but is considerably higher than the MINDO/3 estimate[12] of 236 kcal mol^{-1}. Using this lower value one would predict that only $CH_3C_6H_4^+ + HBr$ should be observed for the bromotoluene systems while the two reaction channels should be equally important for the iodotoluenes.

CI Mass Spectra of Haloanilines. $\Delta H_f°(H_2NC_6H_4^+)$. The H_2 CI mass spectra of *p*-fluoro-, *p*-chloro-, and *p*-bromoaniline are shown in Figure 1. The spectra of the ortho and meta isomers showed no significant differences with the exception that for *o*-chloroaniline the MH^+ ion signal was more intense than for the meta and para isomers.

The major fragment ion for the fluoroanilines is observed at *m/e* 92 corresponding to loss of HF from the protonated molecule. However, for both the chloro- and bromoanilines the major fragment ion, and the base peak in the spectra, is observed at *m/e* 93, corresponding to loss of a halogen atom from MH^+. Thus, the introduction of the amino substituent has made formation of the odd-electron $H_2NC_6H_5^{+\cdot} +$ Cl· products the favored fragmentation route in contrast to the halobenzenes and halotoluenes, where odd-electron products are observed only for the bromo and iodo derivatives.

The thermochemical data are summarized in Table III, from which, based on the results for chloroaniline, we derive $\Delta H_f°(H_2NC_6H_4^+) \geqslant 249$ kcal mol^{-1}. Since formation of $H_2NC_6H_4^+ + HCl$ is not the favored reaction but is still observed, the reaction would appear to have a slightly greater activation energy than the favored reaction. A reasonable es-

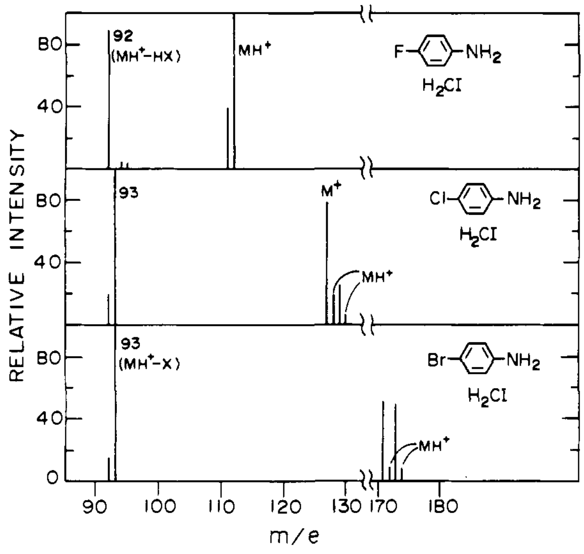


Figure 1. H_2 CI mass spectra of haloanilines.

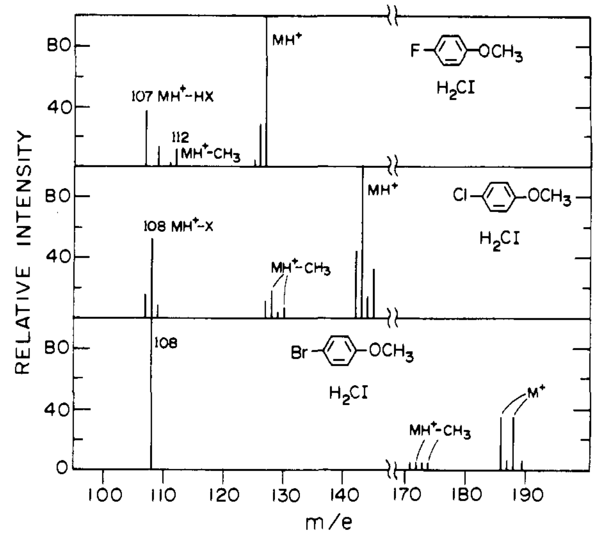


Figure 2. H_2 CI mass spectra of haloanisoles.

Table III. Fragmentation and Thermochemistry in CI of Haloanilines[a]

	$H_2NC_6H_5^{+\cdot} + X$		$H_2NC_6H_4^+ + HX$	
X	yield	$\Delta H_f°$ ($H_2NC_6H_5^{+\cdot} + X$)	yield	$\Delta H_f°$ ($H_2NC_6H_4^+$)
F	0	217	1.0	<282
Cl	0.77	227	0.23	⩾249
Br	0.90	225	0.10	>233

[a] Yields as fraction of total fragment ion intensities. Thermochemical data in kcal mol^{-1}.

Table IV. Fragmentation and Thermochemistry in CI of Haloanisoles[a]

	$CH_3OC_6H_5^{+\cdot} + X\cdot$		$CH_3OC_6H_4^+ + HX$	
X	yield	$\Delta H_f°$ ($CH_3OC_6H_5^{+\cdot} + X\cdot$)	yield	$\Delta H_f°$ ($CH_3OC_6H_4^+$)
F	0	191	1.0	<256
Cl	0.7	201	0.3	⩾223
Br	1.0	199	0	>208

[a] Yield as fraction of total fragment ion intensities. Thermochemical data in kcal mol^{-1}.

timate of $\Delta H_f°(H_2NC_6H_4^+)$ thus is 253 kcal mol^{-1}. This value is in satisfactory agreement with the calculated value[11] of 258 kcal mol^{-1} for the singlet p-$H_2NC_6H_4^+$ ion. The theoretical study[11] concluded that the triplet state was more stable than the singlet state by ~25 kcal mol^{-1}. It is obvious that the present results refer to the singlet state. Dill et al.[11] also report a higher heat of formation (by ~6 kcal mol^{-1}) for the ortho and meta isomers. No effects were observed in the CI mass spectra of the ortho and meta isomers which could be attributed to a higher heat of formation of the aminophenyl cation.

The D_2CI mass spectra of the isomeric chloroanilines also were determined. The m/e 93 base peak of the H_2 CI mass spectra shifted upward by one mass unit as expected since it now corresponds to $[MD^+ - Cl]$. The major point of interest concerns the loss of (H,D)Cl from the MD^+ ion. The ratio of intensities $[MD^+ - HCl]/[MD^+ - DCl]$ was found to be 1.9 for the ortho isomer, 0.22 for the meta isomer, and 0.50 for the para isomer. For the meta and para compounds the predominant loss of DCl indicates that for those ions fragmenting by this channel the initial protonation must be either at the halogen or at the carbon ipso to the halogen, although there is some interchange of the added proton with, presumably, the aromatic hydrogens. Although the ratio of 1.9 observed for the ortho isomer is close to the ratio of 2.0 expected for equilibrium of the added proton with the hydrogens of the amino group, it should be noted that in the D_2 CI of o-chloroanisole the $[MD^+ - HCl]/[MD^+ = DCl]$ ratio 1.3 (compared to values of 0.1 and 0.3 for the meta and para isomers) even though there are no labile hydrogens. Thus the effect of the ortho substituent is more complex and is not clearly understood.

CI Mass Spectra of Haloanisoles. $\Delta H_f°(CH_3OC_6H_4^+)$. The H_2 CI mass spectra of p-fluoro-, p-chloro-, and p-bromoanisole are shown in Figure 2. For all three compounds significant $[MH^+ - CH_3]$ ion signals are observed with weaker $[MH^+ - CH_4]$ ion signals. These were much more pronounced for the ortho isomers. For the fluoro compound the major fragmentation route involves loss of HF from MH^+, no loss of F being observed. By contrast, for the bromo compounds no loss of HBr from MH^+ is observed but rather the base peak corresponds to $[MH^+ - Br]$. As for the haloanilines, the chloro compounds represent the intermediate situation with both fragmentation reactions being observed, with loss of Cl· from MH^+ being more important.

The relative energetics are summarized in Table IV, from which it can be seen that to rationalize the reaction competition for the chloroanisoles $\Delta H_f°(CH_3OC_6H_4^+)$ must be slightly greater than 223 kcal mol^{-1}. In the following we will use a value of $\Delta H_f°(CH_3OC_6H_4^+) = 225$ kcal mol^{-1}. There are no theoretical estimates.

The H_2 CI mass spectrum of m-chloroanisole showed a more pronounced $[MH^+ - HCl]$ ion signal (compared to the $[MH^+ - Cl]$ ion signal) than the other two isomers. It does not appear likely that this is an energetics effect and it may have its origin in a specific meta interaction similar to that observed in the CH_4 CI of the chloroanisoles and chloroanilines.[14]

CI Mass Spectra of Dihalobenzenes. $\Delta H_f°(XC_6H_4^+)$. Mass Spectra of $X_2C_6H_4$. Figure 3 shows the H_2 CI mass spectra of m-difluorobenzene, m-dichlorobenzene, and m-dibromobenzene. The observed spectra can be rationalized by reaction Scheme I. For difluorobenzene the MH^+ ion fragments by loss of HF to yield $FC_6H_4^+$ (m/e 95), which reacts with the reagent H_2 to give, in part, $FC_6H_6^+$ (m/e 97). Part of the latter product dissociates by loss of HF yielding $C_6H_5^+$ (m/e 77), which also is reactive with H_2 yielding $C_6H_7^+$. The spectrum of dichlorobenzene is similar with the exception that the $ClC_6H_6^+$ ion, which presumably is formed by reaction of $ClC_6H_4^+$ ($MH^+ - HCl$) with H_2, appears to be unstable and dissociates with

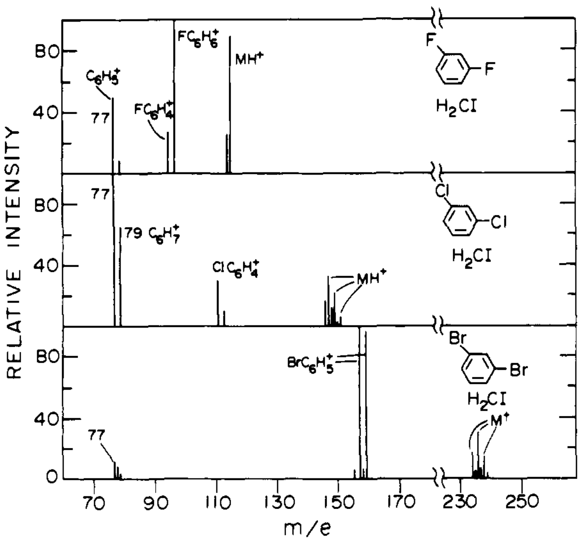
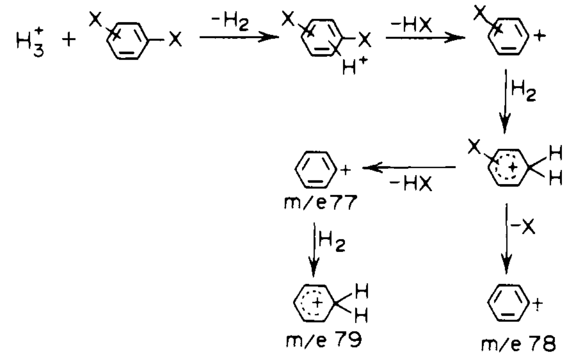


Figure 3. H_2 CI mass spectra of difluoro-, dichloro-, and dibromobenzene.

Scheme I



loss of HCl yielding $C_6H_5^+$ and $C_6H_7^+$ on reaction of $C_6H_5^+$ with H_2. Consequently, the spectrum of dichlorobenzene is dominated by $C_6H_5^+$ and $C_6H_7^+$ to a much greater extent than the spectrum of difluorobenzene.[15] No $XC_6H_5^{+\cdot}$ ($MH^+ - X$) ion signals were observed for the difluoro and dichloro compounds. On the other hand, this becomes by far the most important fragmentation reaction for the dibromobenzenes.

From the reaction competition which leads to $XC_6H_4^+$ + HX for the difluoro and dichloro compounds and to $XC_6H_5^+$ + X· for the dibromo compounds we can derive upper limits for $\Delta H_f°(XC_6H_4^+)$ for X = F and Cl and a lower limit for X = Br. The relevant data are summarized in Table V.

Mass Spectra of XX′C$_6$H$_4$. The H_2 CI mass spectra of the mixed halogen compounds *m*-chlorofluorobenzene, *m*-bromochlorobenzene, and *m*-bromofluorobenzene are shown in Figure 4. The spectra observed were independent of the relative orientation of the halogen substituents. In principle, for these compounds, four reaction channels (4-7) for fragmentation of the protonated molecule are possible.

$$XX'C_6H_4H^+ \rightarrow XC_6H_5^{+\cdot} + X'\cdot \tag{4}$$

$$\rightarrow X'C_6H_5^{+\cdot} + X\cdot \tag{5}$$

$$\rightarrow XC_6H_4^+ + HX' \tag{6}$$

$$\rightarrow X'C_6H_4^+ + HX \tag{7}$$

For the bromochlorobenzenes two reaction channels are observed (loss of Br· to form $ClC_6H_5^{+\cdot}$ and loss of HCl to form $BrC_6H_4^+$), with only a minor contribution arising from loss of HBr. There is no evidence for loss of Cl· from MH+. This is not surprising since, as the data in Table VI show, formation of $BrC_6H_5^{+\cdot}$ + Cl· is much more demanding energetically than formation of $ClC_6H_5^{+\cdot}$ + Br·. The $BrC_6H_4^+$ product ion reacts further with H_2 yielding $C_6H_6^{+\cdot}$ and $C_6H_5^+$, the latter reacting to form $C_6H_7^+$. These products also are observed in the H_2 CI of bromobenzene.[2,3] From the failure to observe significant yields of $ClC_6H_4^+$ + HBr we can derive a lower limit $\Delta H_f°(ClC_6H_4^+) > 256$ kcal mol^{-1}. Similarly, since formation of $BrC_6H_4^+$ + HCl competes reasonably effectively with formation of $ClC_6H_5^{+\cdot}$ + Br· we can derive $\Delta H_f°(BrC_6H_4^+) \geqslant 270$ kcal mol^{-1}, with the most probable value being a few kilocalories per mole greater.

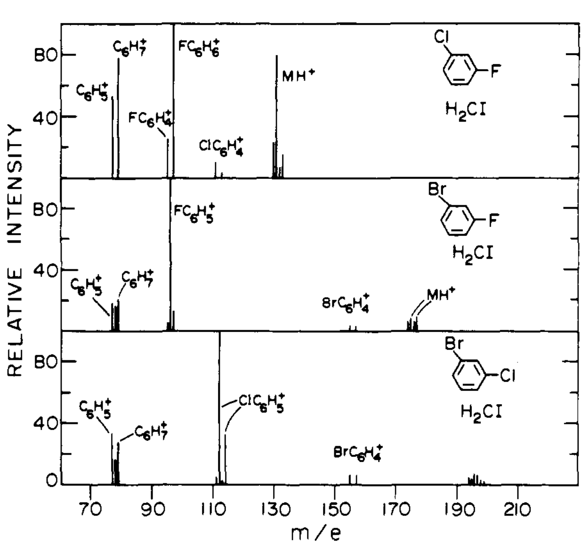


Figure 4. H_2Cl mass spectra of mixed dihalobenzenes.

Table V. Fragmentation and Thermochemistry in CI of $X_2C_6H_4$[a]

	$XC_6H_5^{+\cdot}$ + X		$XC_6H_4^+$ + HX	
X	yield	$\Delta H_f°$ ($XC_6H_5^{+\cdot}$ + X)	yield[b]	$\Delta H_f°$ ($XC_6H_4^+$)
F	0	203	1.0	<268
Cl	0	250	1.0	<272
Br	~0.8	259	~0.2	<267

[a] Yield as fraction of total fragment ion intensities. Thermochemical data in kcal mol^{-1}. [b] Yield includes further products arising from reaction of $XC_6H_4^+$ with H_2.

The H_2 CI mass spectra of the bromofluorobenzenes show $FC_6H_5^{+\cdot}$ ($MH^+ - Br$) as the base peak with only a very low yield of $BrC_6H_4^+$ ($MH^+ - Br$), although much of this product has reacted further with H_2 to produce $C_6H_5^+$, $C_6H_6^{+\cdot}$, and $C_6H_7^+$. There is very little formation of $FC_6H_4^+$ + HBr and no evidence for formation of $BrC_6H_5^{+\cdot}$ + F. The latter is not surprising since, as shown in Table VI, the formation of these products is ~40 kcal mol^{-1} less favorable than formation of $FC_6H_5^{+\cdot}$ + Br·. From the failure to observe significant yields of $FC_6H_4^+$ we can derive as a lower limit $\Delta H_f°(FC_6H_4^+) > 219$ kcal mol^{-1}. Similarly, the observation of significant yields of $BrC_6H_4^+$ leads to $\Delta H_f°(BrC_6H_4^+) \simeq 275$ kcal mol^{-1}, in reasonable agreement with the lower limit of 270 kcal mol^{-1} established from the spectra of the bromochlorobenzenes.

The H_2 CI mass spectra of the fluorochlorobenzenes show formation of $ClC_6H_4^+$ ($MH^+ - HF$), which reacts further with H_2 to yield $C_6H_5^+$ and $C_6H_7^+$, and approximately equivalent formation of $FC_6H_4^+$ ($MH^+ - HCl$), which reacts further with H_2 yielding predominantly $FC_6H_6^+$. No $FC_6H_5^{+\cdot}$ or $ClC_6H_5^{+\cdot}$ product ions are observed. Based on the thermochemistry for formation of $FC_6H_5^{+\cdot}$ we derive the upper limits $\Delta H_f°(FC_6H_4^+) < 235$ kcal mol^{-1} and $\Delta H_f°(ClC_6H_4^+) < 278$ kcal mol^{-1}. From the almost equal competition between

Table VI. Fragmentation and Thermochemistry in CI of Dihalobenzenes $XX'C_6H_4$[a]

X	X'	$XC_6H_5^{+\cdot} + X'$ yield	$\sum\Delta H_f^\circ$ [b]	$X'C_6H_5^+ + X$ yield	$\sum\Delta H_f^\circ$ [c]	$XC_6H_4^+ + HX'$ yield	$X'C_6H_4^+ + HX$ yield
Cl	F	0	240	0	213	<0.5	>0.5
Br	F	0	251	~0.6	211	<0.1	~0.4
Cl	Br	~0.6	248	0	261	<0.1	~0.4

[a] Yield as fraction of total fragment ion intensities. Thermochemical data in kcal mol^{-1}. [b] $\sum\Delta H_f^\circ = \Delta H_f^\circ(XC_6H_5^{+\cdot} + X')$. [c] $\sum\Delta H_f^\circ = \Delta H_f^\circ(X'C_6H_5^{+\cdot} + X)$.

Table VII. Thermochemistry of Substituted Phenyl Cations

Y	$\Delta H_f^\circ(YC_6H_4^+)$[a] calcd[b]	$\Delta H_f^\circ(YC_6H_4^+)$[a] exptl[c]	stabilization energy[a]
H	(266)	266	
CH_3	253	253	5
NH_2	258	253	14
CH_3O		225	4
F	221	227	−9
Cl		264	−5
Br		275	−4

[a] All data in kcal mol^{-1}. [b] From ref 11. [c] Estimated uncertainty ±4 kcal mol^{-1}.

Table VIII. H_2 CI Mass Spectra of Dichloroanilines

dichloroaniline	MH^+ [a]	$M^{+\cdot}$ [a]	$MH^+ - Cl$[a]	$MH^+ - HCl$[a]
3,5-	7.4	28.8	40.6	23.2
3,4-	9.7	25.7	36.6	27.9
2,3-	36.7	14.8	32.3	16.3
2,4-	20.5	26.6	41.4	11.6
2,5-	18.9	31.1	40.2	9.7
2,6-	39.3	28.4	26.9	5.4

[a] All intensities as percent of total additive ionization.

the two reaction channels observed we can state that $\Delta H_f^\circ(FC_6H_4^+ + HCl) \simeq \Delta H_f^\circ(ClC_6H_4^+ + HF)$, from which $\Delta H_f^\circ(FC_6H_4^+) \simeq \Delta H_f^\circ(ClC_6H_4^+) - 43$ (kcal mol^{-1}). To summarize the arguments derived from the dihalobenzenes, the results indicate a value $\Delta H_f^\circ(BrC_6H_4^+) \simeq 275$ kcal mol^{-1}. For $\Delta H_f^\circ(FC_6H_4^+)$ the results establish a lower limit of 219 kcal mol^{-1} (bromofluorobenzene) and an upper limit of 235 kcal mol^{-1} (chlorofluorobenzene) leading to a most probable value of 227 ± 4 kcal mol^{-1}. For $\Delta H_f^\circ(ClC_6H_4^+)$ the results provide an upper limit of 272 kcal mol^{-1} (dichlorobenzene) and a lower limit of 256 kcal mol^{-1} (chlorobromobenzene) leading to a most probable value of 264 ± 4 kcal mol^{-1}. The theoretical work of Dill et al.[11] provides $\Delta H_f^\circ(FC_6H_4^+)$ values of 221 kcal mol^{-1} for the para isomer, 224 kcal mol^{-1} for the meta isomer, and 226 kcal mol^{-1} for the ortho isomer. Our result, which does not distinguish between the isomers, is in reasonable agreement with the theoretical values.

Stabilization Energies of Phenyl Cations. The thermochemical data derived in the present work are summarized in Table VII and compared with the heats of formation for the para isomer calculated by Dill et al.[11] The estimated uncertainty in the present heat of formation data is ±4 kcal mol^{-1} The final column of the table records the energy of stabilization of the phenyl cation by substituent. These have been determined from the standard enthalpy change for the reaction

$$YC_6H_4^+ + C_6H_6 \rightarrow YC_6H_5 + C_6H_5^+ \qquad (8)$$

A positive value indicates a stabilizing effect relative to H, while a negative value indicates a destabilizing effect of the substituent relative to hydrogen. The present experimental estimates for the heats of formation of the substituted phenyl cations are in quite good agreement with the (STO-3G) calculated values, lending credence to our basic assumption that the competition between the reaction channels is determined by the relative activation energies which are calculable from heats of formation. The stabilization energy calculations show that the NH_2 group strongly stabilizes the phenyl cation, the CH_3 and CH_3O groups stabilize the phenyl cation to a lesser extent, while the three halogen substituents, F, Cl, and Br, all destabilize the phenyl cation. Because of the uncertainties in the heats of formation of the halophenyl cations the apparent order of destabilization by the halogens cannot be considered significant. For a detailed discussion of the stabilization energies in terms of π and σ effects the reader is referred to Dill et al.[11]

H_2 CI Mass Spectra of Dichloroanilines and *N,N*-Dimethylchloroanilines. The H_2 CI mass spectra of these two series of compounds were determined, although no attempts were made to derive heats of formation of substituted phenyl cations owing to the absence of the appropriate thermochemical data. The spectra are presented here because they provide further examples of the formation of odd-electron product ions in proton transfer chemical ionization and because they exhibit some interesting structural features.

The major features of the H_2 CI mass spectra of the six isomeric dichloroanilines are summarized in Table VIII, where the intensities are listed as a percent of the total additive ionization. There is considerable charge transfer from H_3^+ to the aromatic system forming $M^{+\cdot}$, as well as proton transfer forming MH^+. As was observed for the chloroanilines, two fragmentation channels for MH^+, loss of Cl· and loss of HCl, are observed, with the former accounting for 60–80% of the total fragmentation. It is clear that the stability of the odd-electron chloroaniline molecular ion relative to the chloroaminophenyl cation is sufficient to make formation of the odd-electron fragmentation products the energetically favored fragmentation channel for MH^+. There was no evidence for further reaction of the MH^+-HCl fragment ion with H_2. This is in contrast to the dichlorobenzenes, where complete dehalogenation occurs through reaction of the chlorophenyl cation with H_2, but in accord with the results for the haloanilines, where the aminophenyl cations are quite unreactive toward H_2. It is evident that the amino substituent plays the dominant role in determining the reactivity of the chloroaminophenyl cation. A further interesting observation is that the MH^+ ion is of greater abundance when there is at least one chlorine substituent ortho to the amino group (last four entries of Table VIII) and is particularly abundant when the substituents have a 1,2,3 arrangement (2,3-dichloroaniline and 2,6-dichloroaniline). These observations can be rationalized in terms of internal solvation of the added proton by substituents ortho to the substituent protonated, although it is not evident whether the protonation occurs at the chloro or amino position. As noted above, the MH^+ intensity also was greater for *o*-chloroaniline than for the meta and para isomers.

The H_2 CI mass spectra of the three *N,N*-dimethylchloroanilines are shown in Figure 5. For all three isomers the charge-transfer product $M^{+\cdot}$ is the base peak. For the ortho isomer the major fragment ions observed correspond to [M −

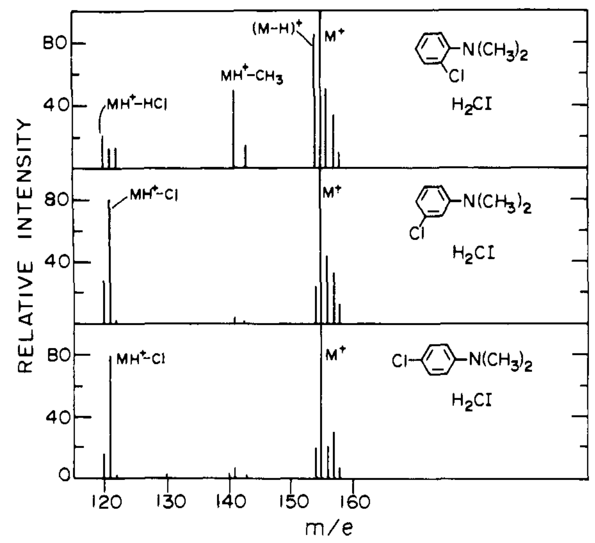


Figure 5. H_2 Cl mass spectra of isomeric *N*,*N*-dimethylchloroanilines.

H]$^+$, which may arise either by H_2 loss from MH^+ or by direct hydride obstruction by $H_3^{+\cdot}$, and to the odd-electron $ClC_6H_4NHCH_3^{+\cdot}$ ion, arising by methyl radical loss from MH^+. The loss of the chlorine substituent is of only minor importance with loss of HCl from MH^+ being more prominent than loss of Cl· from MH^+. For the meta and para isomers the formation of both $[M - H]^+$ and $MH^+ - CH_3$ is of greatly reduced importance, the major fragment ion observed corresponding to the odd-electron *N*,*N*-dimethylaniline molecular ion arising by loss of Cl· from the protonated molecule. Thus, for this system as well, the major fragmentation reactions of the protonated molecule involve formation of odd-electron products. The enhanced formation of the $MH^+ - CH_3$ product by the ortho substituent also is observed for the haloanisoles where the $MH^+ - CH_3$ product is much more significant for the ortho isomer than for the meta and para isomer. This rather strong ortho effect can be rationalized if one assumes that for the ortho-substituted compound protonation occurs at the substituents to give, effectively, a disolvated proton. Loss of CH_3 from this species can readily yield the respective halophenol or haloaniline odd-electron molecular ion. Such disolvation cannot occur when the substituent is meta or para and formation of $MH^+ - CH_3$ is greatly reduced.

Acknowledgment. The authors are indebted to the National Research Council of Canada for financial support and to Professor F. W. McLafferty for communication of results (ref 13) prior to publication.

References and Notes

(1) A. G. Harrison and P.-H. Lin, *Can. J. Chem.*, **53,** 1314 (1975).
(2) H.-W. Leung and A. G. Harrison, *Can. J. Chem.*, **54,** 3439 (1976).
(3) H.-W. Leung, H. Ichikawa, Y.-H. Li, and A. G. Harrison, *J. Am. Chem. Soc.*, **100,** 2479 (1978).
(4) M. Speranza, J. M. S. Henis, M. D. Sefcik, and P. P. Gaspar, *J. Am. Chem. Soc.*, **99,** 5583 (1977).
(5) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **98,** 7320 (1976).
(6) H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data, Suppl. 1*, **6** (1977).
(7) H. M. Rosenstock, J. T. Larkins, and J. A. Walker, *Int. J. Mass Spectrom. Ion Phys.*, **11,** 309 (1973).
(8) G. Arsenault in "Biochemical Applications of Mass Spectrometry", G. R. Waller, Ed., Wiley-Interscience, New York, 1972.
(9) E. H. Field in "Mass Spectrometry", A. Maccoll, Ed., MTP Review of Science, Butterworths, London, 1972, Chapter 5, p 149.
(10) F. H. Field in "Ion-Molecule Reactions", Vol. 1, J. L. Franklin, Ed., Plenum Press, New York, 1972.
(11) J. D. Dill, P. v. R. Schleyer, and J. A. Pople, *J. Am. Chem. Soc.*, **99,** 1 (1977). The values of $\Delta H_f°(YC_6H_4^+)$ reported in this study are relative to a $\Delta H_f°(C_6H_5^+) = 270$ kcal mol^{-1}. To compare with the present work where $\Delta H_f°(C_6H_5^+) = 266$ kcal mol^{-1} has been used the calculated values of $\Delta H_f°(YC_6H_4^+)$ have been reduced by 4 kcal mol^{-1}.
(12) C. Cone, M. J. S. Dewar, and D. Landman, *J. Am. Chem. Soc.*, **99,** 372 (1977).
(13) F. W. McLafferty and F. M. Bockhoff, *Org. Mass Spectrom.*, in press.
(14) H. W. Leung and A. G. Harrison, presented at the 25th Annual Conference on Mass Spectrometry, Washington, D.C., June 1977.
(15) Because of the numerous sequential reactions with H_2 (Scheme I) the spectra of dichloro- and difluorobenzene are strongly dependent on the reagent gas pressures and ion-source residence time. For example, the spectrum for $Cl_2C_6H_4$ in Figure 4 was recorded at a lower H_2 pressure than the spectrum reported previously[3] where $C_6H_7^+$ was observed as the base peak.

ESR Evidence for a Biradical Dimer Initiator in Diacetylene Polymerization

Y. Hori[†] **and L. D. Kispert***

Contribution from the Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama 35486. *Received December 14, 1978*

Abstract: Single-crystal monomers of 5,7-dodecadiyne-1,12-diol bis(phenylurethane) X-ray irradiated at 77 K give rise to an ESR spectrum at 77 K consisting primarily of lines due to radical pairs along with some weaker lines due to $S = 1/2$ radicals. The radical pair is a biradical of a diacetylene dimer with $D = 732$ G and $E = 26.5$ G and appears to be the initiator of solid-state polymerization of X-ray irradiated TCDU crystals at low conversion.

Introduction

Single crystals of disubstituted diacetylene monomers are capable of producing highly perfect crystals of conjugated polymers by solid-state polymerization.[1-5] Initiation may be by heat, light, or high-energy radiation. The 1,4-addition polymerization of diacetylene single crystals leads to two possible mesomeric structures, I and II. Examples of structures I[6] and II[7,8] have been studied by X-ray diffraction and Raman spectroscopy.

$$\underset{\text{I}}{—(R)C{=}C{=}C{=}C(R)—} \qquad \underset{\text{II}}{{=}(R)C—C{\equiv}C—C(R){=}}$$

The solid-state polymerization mechanism of diacetylene single crystals has become of considerable interest in the past

---

[†] Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, Japan.

0002-7863/79/1501-3173$01.00/0 © 1979 American Chemical Society