

On the Formation of Adduct Ions in Gas-phase Aromatic Substitution

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The evidence for the formation of adduct ions from the gas-phase reaction of charged electrophiles with aromatic substrates is critically evaluated. Experimental results concerning a few typical substrates, and a concise survey of the available data from mass spectrometric and other well established techniques, lead to the conclusion that adduct ions are indeed formed in gas-phase aromatic substitution.

GAS-PHASE aromatic substitution by simple carbocations and other charged electrophiles has been recently investigated by Morrison *et al.*^{1,2} in a triple quadrupole mass spectrometer (t.q.m.s.). From their results, obtained under particular experimental conditions, the authors draw the general conclusion that ions which act as the reactive agents in electrophilic aromatic substitution in solution *do not combine* with aromatic nuclei in the gas phase to form adduct ions of the Wheland-intermediate type. The authors further contend that any theoretical discussion of aromatic substitution which ignores the role of the solvent bears no relation to the actual situation, and conclude by suggesting that factors related to ordering of the solvent in the transition state, rather than resonance stabilization of the arenium ions, determine the course of aromatic substitution in solution.

In view of the far reaching nature of the above statements, it seems legitimate to inquire whether the experimental results support such generalizations, and to proceed to a critical comparison of the pertinent evidence accumulated on the subject during the last decade.

In essence, the authors base their argument on the failure to detect adduct ions $C_6H_5XR^+$ from the reaction of gaseous R^+ cations with aromatic substrates, C_6H_5X .

It is the purpose of this paper to evaluate the conditions prevailing in t.q.m.s. to establish whether they would allow detection of any adduct ions $C_6H_5XR^+$ formed. In addition, a few experimental examples will be given, showing that adduct ions are indeed detected in the gas-phase alkylation of typical aromatic substrates under different mass spectrometric conditions.

Finally, convincing evidence for the formation of adduct ions in a variety of gas-phase aromatic substitutions is derived from a concise survey of the large body of currently available data, obtained with mass spectrometric and other well established techniques by a number of independent workers.

EXPERIMENTAL

The mass spectra were recorded with a quadrupole mass spectrometer, model 5980 A, from Hewlett-Packard Co., connected to a 5934 A data system and operated in the chemical ionization mode.

The instrument has been previously calibrated using pure methane. The gases used were research-grade products from Matheson Co., with a stated purity exceeding 99.99 mol %. The aromatic substrates were previously analysed by g.l.c. and used without further purification.

Gaseous mixtures containing 0.01–0.1 mol % aromatic

substrate diluted with the gaseous hydrocarbon were prepared by standard vacuum techniques in carefully dried and outgassed Pyrex bulbs, and allowed to bleed into the heated (440 K) ion source through a metering needle valve. The pressure within the source was measured with a Bourdon-type mechanical gauge.

RESULTS

The CI mass spectra of benzene and toluene in C_3H_8 at 1–2 Torr are shown in Figures 1 and 2. The ionic reactant used is the $C_3H_7^+$ cation, the most abundant charged species in neat C_3H_8 at the pressure of interest.

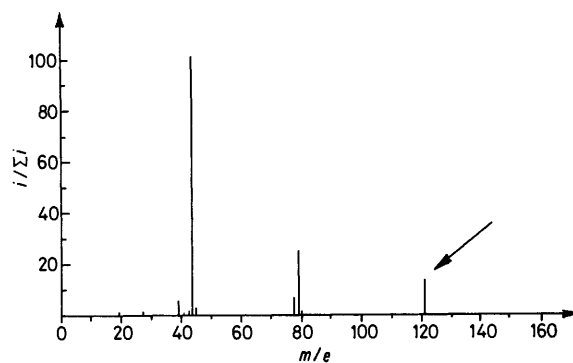


FIGURE 1 CI mass spectrum of benzene (0.01 mol %) in C_3H_8 at a total pressure of *ca.* 2 Torr. Note adduct ion $C_6H_6C_3H_7^+$ at m/e 121, and protonated benzene at m/e 79

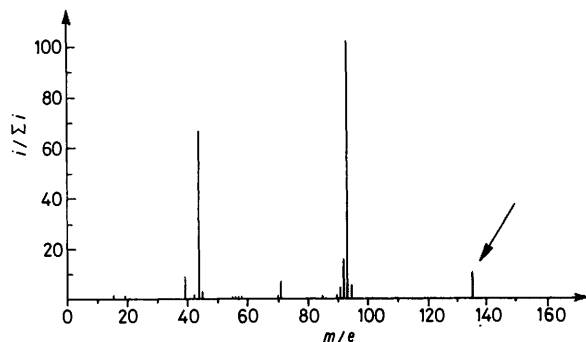


FIGURE 2 CI mass spectrum of toluene (0.01 mol %) in C_3H_8 at a total pressure of *ca.* 2 Torr. Note adduct ion $C_6H_5(CH_3)C_3H_7^+$ at m/e 135 and protonated toluene at m/e 93

The spectra reported show clearly that adduct ions $C_6H_5XC_3H_7^+$ are formed in significant yields, together with larger abundances of the protonated species $C_6H_6X^+$ from the competing Brønsted-acid reactions of $C_3H_7^+$. No propylated or protonated benzene was detected under t.q.m.s.

conditions in which a relatively inefficient charge-exchange process was the only reaction channel observed in the $C_3H_7^+-C_6H_6$ system.

Results entirely consistent with those illustrated in the Figures could have been obtained with other ionic reagents of interest, *e.g.* ethyl and allyl ions, under CI conditions. However, extension of the experiments appeared quite superfluous, since data concerning these systems are already available in the literature.

For the same reason, no special effort was undertaken to derive *quantitative* correlations, *e.g.* absolute pressure measurements, dependence of the ionic abundances on the pressure, calibration of the kinetic energy of the charged reagent, *etc.* Similar data, obtained with suitable instruments and techniques, are in fact available for a variety of systems. The experiments reported here have the limited goal of providing the reader with an unequivocal illustration that adduct ions are indeed formed and can be detected in gas-phase aromatic substitution.

DISCUSSION

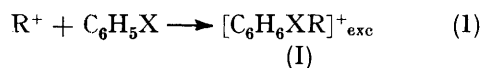
The disparity between the t.q.m.s. results and those outlined in the previous section, and more generally with a number of earlier data, can probably be reconciled by taking into account the large differences in the experimental conditions, as briefly discussed in the following paragraphs.

Excessive Energy of the Incident Ions in T.q.m.s.—Measurement of the reaction cross section as a function of the energy of the incident ions is generally significant in the study of ion-molecule reactions, and necessary when the results are used as a model for *thermal* processes in the gas phase or in solution. From the t.q.m.s. experiments, however, only a *single* cross section, measured at an energy value not explicitly stated, is reported for each process.^{1,2} Indeed, the *mean* axial component of translational energy is reported to be 0.8 eV, while the *mean spread* of energies of the primary ions in the second quadrupole, due to its radiofrequency field, is estimated from a simulation program to be <1 eV. Thus, a conservative estimate of the translational energy of the incident ions leads to values of the order of *ca.* 1 eV.* In addition, quite independently of instrumental details, the observation of *endothermic* ion-molecule reactions in t.q.m.s. unequivocally demonstrates the intervention of translationally, or otherwise, excited incident ions.† In conclusion, it appears that the ionic reagents used in t.q.m.s. are not characterized by a thermal energy spread following a Boltzmann distribution, but contain an excess of kinetic, or possibly internal energy.

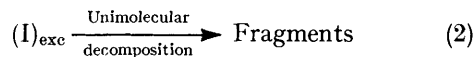
Fragmentation of Adduct Ions in T.q.m.s.—The failure to detect adduct ions in t.q.m.s. has been explained^{1,2} assuming that the ionic reagents *do not combine* with the aromatic nuclei, *i.e.* reaction (1) does not occur in the

* According to the original description of the t.q.m.s. (ref. 3), cited in ref. 1, the transverse kinetic energy of the ions ranges from 5 to 20 eV.

† For instance, charge exchange of ethyl and propyl ions with C_6H_6 has been reported. Assuming (ref. 1) the isopropyl structure for $C_3H_7^+$, its charge exchange with benzene is *endothermic* by >1 eV.



gas phase, where different reaction channels (charge exchange, disproportionation, *etc.*) are operative. However, another explanation is conceivable. Adduct ions are formed *via* (1), but their significant internal energy, arising from the intrinsic exothermicity of (1), and from the excess of energy of R^+ , causes their secondary decomposition into the observed fragments [reaction (2)].



The difference between the two hypotheses is far from trivial, in that if route (1) could only be ruled out, the alleged² fundamental mechanistic difference between gas- and liquid-phase aromatic substitution would be substantiated.

In order to ascertain whether the t.q.m.s. results provide a clearcut answer to this crucial question, one must consider the excitation level of (I), the efficiency of collisional stabilization, and the time lag between the formation of the adduct ions and their detection in t.q.m.s.

Even disregarding entirely the excess of energy of R^+ ions (see, however, the previous paragraph), the mere exothermicity of (1) is largely sufficient to cause unimolecular fragmentation of (I) before detection. For example, methylation of benzene [equation (1); $R = CH_3$, $X = H$] is characterized⁴ by an exothermicity of the order of 350 kJ mol⁻¹, and the large amount of energy released must be entirely stored in the internal degrees of freedom of the adduct ions. Such a considerable excitation energy is expected to cause fast unimolecular decomposition of (I), unless collisionally stabilized in a suitable bath gas. However, collisional deactivation is extremely inefficient in t.q.m.s. where the mean free path of the ions at the maximum working pressure, 2×10^{-4} Torr, is approximately *equal* to the length of the collision chamber.³ Under such conditions, the adduct ions from (1) are bound to undergo unimolecular fragmentation during the relatively long time, 4×10^{-5} s, required for their detection in t.q.m.s.³

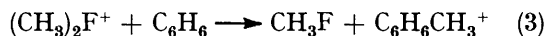
The very nature of the detected fragments, and the H-D scrambling observed in the $CH_3^+-C_6D_6$ and $CD_3^+-C_6H_6$ systems, point to formation and subsequent fragmentation of highly excited adducts.¹

In conclusion, the failure to *detect* adduct ions (I) under the specific conditions prevailing in t.q.m.s. cannot be taken as evidence against their *formation* from process (1).

Evidence Currently Available for the Formation of Adduct Ions.—Many published, and as yet unchallenged, experimental results point to the formation of a variety of adduct ions (I) in gas-phase aromatic substitution and show that these intermediates can be detected by appropriate techniques, including mass spectrometry.

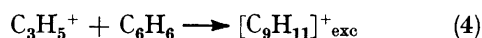
Significant yields of propylated, allylated, and especially ethylated adducts were measured as early as

1967 in the CI spectra of over 20 arenes in methane at 1 Torr.⁵ The abundance of these alkylated adducts is larger in the CI spectrum of toluene than of isomeric C₇H₈ hydrocarbons containing no aromatic ring.⁶ A significant yield of C₆H₆CH₃⁺ ions has also been measured in the i.c.r. spectra of CH₃F-C₆H₆ mixtures, arising from the typical aromatic alkylation (3) as shown in double-



resonance experiments.⁷ This clearly demonstrates that, even in the lack of collisional stabilization typical of i.c.r. experiments, adduct ions can be detected, provided the exothermicity of their formation process is not too large.*

Allylation of benzene, investigated by tandem i.c.r. mass spectrometry,⁸ provides a particularly pertinent example. At low pressures, and using excited allyl ions, no adduct ions from process (4) could be detected,



owing to their decomposition into C₇H₇⁺ ions. However, raising the pressure within the collision chamber caused a decline of the decomposition rate, allowing stabilization and detection of an increasing fraction of the adduct ions.

Other adducts demonstrated by mass spectrometry include C₁₂H₁₁⁺ and C₁₄H₁₅⁺ ions from the arylation of benzene and toluene with C₆H₅⁺ and C₇H₇⁺ ions,⁹ and acetylated adducts from the reaction of C₂H₃O⁺ ions with alkylbenzenes.¹⁰ In general, the relative abundance of the ionic adducts increases at higher pressures, owing to the increasing efficiency of collisional stabilization. Accordingly, it is not surprising that techniques other than mass spectrometry, but otherwise well established, such as radiolytic and nuclear decay methods,^{11,†} characterized by a much wider range of accessible pressures, have provided kinetic and mechanistic evidence for the formation of adduct ions of the Wheland-intermediate type. The processes studied include gas-phase aromatic alkylation,^{4,12-27} acetylation,^{28,29} halogenomethylation,⁷ and halogenation.³⁰⁻³²

Conclusions.—There is no reason to doubt that the results reported by Morrison *et al.*,^{1,2} in particular their failure to detect C₆H₅XR⁺ adduct ions, correctly reflect the situation prevailing in the collision region of the t.q.m.s. However, the relevance of such negative evidence to the general problem concerning the formation of adduct ions in gas-phase aromatic substitution cannot be asserted with the same degree of confidence. In fact, adduct ions (irrespective whether they are the Wheland

* Exothermicity of reaction (3) can be evaluated from the methyl cation affinity of benzene and methyl fluoride to be ca. 184 kJ mol⁻¹, *cf.* ref. 7. Owing to the formation of a CH₃F molecule, the energy released is only partially available to the internal degrees of freedom of the adduct.

† Contrary to the belief expressed in ref. 1, the stabilization of excited adducts in the gases studied by radiolytic or nuclear-decay techniques does not involve three-body collisions on the walls, but in the bulk of the gas, exactly as in the collision chamber of a mass spectrometer operated at sufficiently high pressures.

type, or otherwise) could hardly be detected in t.q.m.s., even if actually formed, owing to the fast fragmentation caused by the large exothermicity of the formation process, enhanced by the intervention of excited reactant ions, and not appreciably prevented by collisional deactivation. Consequently, the failure to detect C₆H₅XR⁺ adducts does not prove, *per se*, the inability of the R⁺ ions to combine with aromatic nuclei, even under the specific conditions prevailing in t.q.m.s.

A fortiori, it seems unwise to extrapolate from the negative evidence from low-pressure t.q.m.s. experiments to gas-phase aromatic substitution in general in order to deny the role of adduct ions, and to draw generalized inferences on the mechanism of orientation in liquid-phase reactions. It would seem that such a broad extrapolation does not adequately take account of the fact that the gas phase encompasses a multiplicity of reaction environments, characterized by an enormous range of kinetically and mechanistically significant features. In this context, the lack of consistency noted¹ between the t.q.m.s. results and those obtained⁴ at much higher pressures (by at least five orders of magnitude) can be readily rationalized and could provide a reason for caution.

From the above considerations, it seems fair to conclude that the t.q.m.s. results, considered within their own domain of validity, do not conflict with, or detract from, the ample and unchallenged evidence accumulated in recent years. The evidence shows that C₆H₅XR⁺ adduct ions (i) are actually formed in gas-phase aromatic substitution, (ii) can be (and have been) detected under suitable conditions by a variety of techniques, and (iii) yield, following deprotonation, neutral products corresponding to those expected from Wheland-type intermediates, in particular from the crucial standpoint of the isomeric composition.

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