Monomer and Dimer Radical Cations of Benzene, Toluene, and Naphthalene

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Pulse radiolytic generation of monomeric and dimeric cations of benzene, toluene, and naphthalene in aqueous acid media at room temperature and their spectrophotometric characterization is discussed. Results presented include measurements of each aromatic's solubility in $H_2O-H_2SO_4$ and $H_2O-HClO_4$ media over the acidity range pH 1 to H_0 −7.0, facile oxidative generation, and real-time identification of appropriate cationic transients with respective λ_{max} (nm) and ε (M^{-1} cm^{-1}) values measured as follows: $C_6H_6^{\bullet+}$ (443, 1145 ± 75), $C_6H_5CH_3^{\bullet+}$ (428, 1230 ± 90), $C_{10}H_8^{\bullet+}$ (381, 3650 ± 225, and 687, 2210 ± 160), $(C_6H_6)_2^{\bullet+}$ (860, 2835 ± 235), $(C_6H_5CH_3)_2^{\bullet+}$ (950, 1685 ± 155), and $(C_{10}H_8)_2^{\bullet+}$ (1040, 4170 ± 320). Kinetic measurements reveal the respective formation rates of monomeric cations to be near-diffusion controlled, while the forward rate values for the dimeric species generation are marginally slower. The proton activity corrected pK_a values are found to remain between −2.6 and −1.3 for the $ArH^{\bullet+}$ species ($C_6H_6^{\bullet+}$ most acidic, $C_{10}H_8^{\bullet+}$ least acidic), while the pK_a values of $(ArH)_2^{\bullet+}$ species vary from −5.0 to −3.0 ($(C_6H_6)_2^{\bullet+}$ most acidic, $(C_{10}H_8)_2^{\bullet+}$ least acidic). In H_0 −5 in aqueous H_2SO_4, the respective stabilization energy of $(C_6H_6)_2^{\bullet+}$, $(C_6H_5CH_3)_2^{\bullet+}$, and $(C_{10}H_8)_2^{\bullet+}$ is estimated to be 16.6, 15.0, and 13.7 kcal mol^{-1}. Thus, the aqueous acid solution emerges as an alternative medium for typical radical-cationic studies, while offering compatibility for the deprotonated radical characterization near neutral pH.

Introduction

Aromatic hydrocarbon (ArH) cationic species are found and discussed in various areas such as pollution, biology, interstellar chemistry, and also in the laboratory.[1−4] Although such paramagnetic cations are chemically more reactive than the respective diamagnetic parents, a recent report on the enhancement in aromaticity hints at new characteristics.[5] In the domain of aromatic cationic species, not only the monomeric $ArH^{\bullet+}$ type but also a variety of dimers, $(ArH)_2^{\bullet+}$, are frequently cited due to their simultaneous or subsequent rapid formation, unique structures, and reactivity.[6−8] While an ArH → $ArH^{\bullet+}$ transformation generally occurs directly, further creation of the dimeric species necessitates a suitably controlled diffusive reaction: $ArH^{\bullet+} + ArH \leftrightarrows (ArH)_2^{\bullet+}$, wherein excess parent present affects the intramolecular coupling. However, to physicochemically characterize the $ArH^{\bullet+}$ or even $(ArH)_2^{\bullet+}$ radicals it becomes mandatory to impede the omnipresent and generally rapid H^+ loss (of $ArH^{\bullet+}$ to an aryl radical, $Ar^{\bullet}$). Literature survey reveals that to minimize such a deprotonation step, in almost all previous studies the radicals were created within a variety of restrictive, but dissimilar environments, e.g., frozen rare-gas matrix, organic solvents, gas phase, and within zeolites and zirconia.[9−11] Among these, the frozen matrices would also restrict any diffusive reactivity of $ArH^{\bullet+}$, including the extent of $(ArH)_2^{\bullet+}$ generation. On the other hand, uses of aprotic solvents would prevent evaluation of the acidity of a radical cation (i.e., proton transfer ability to water) and thereby may disallow any complementary study of the cationic chemistry with the respective $Ar^{\bullet}$ radical reactions, mainly evaluated in aqueous medium. Even the gas phase or other studies have limited use in such characterization studies wherein correlations to the condensed media are needed. Therefore, to suitably address such yet-unanswered topics, first a highly protic fluid medium (preferably at or near room temperature) is necessary for the creation of the radical cations. In this search for a proper but easily available reaction environment, we present the infrequently discussed,[12,13] but recently systematically characterized and quantified highly acidic $H_2O-H_2SO_4$ and $H_2O-HClO_4$ solvents[14a,b] and present the convenience and success in their use. Second, for unambiguous creation, detection, and real-time reactions of such cationic transients,[14b] additional time-resolved probing methodology is mandatory. Herein, the time-tested pulse radiolytic kinetic-spectrophotometric (PRKS) detection proved successful. Employing three representative ArH, namely, benzene, toluene and naphthalene, efficient oxidative generations of the respective $ArH^{\bullet+}$ and $(ArH)_2^{\bullet+}$ radicals, their characterizations in real-time, and measurements of relevant physicochemical properties are discussed, thus highlighting the potential applicability of this methodology for radical cationic studies in diverse fields.

Methodology

To initiate the measurements, the reaction media were appropriately prepared and suitably verified to be usable. Details about the materials used and the simple experimental procedure are discussed elsewhere.[14−16] For transient generations the 7 MeV electron ns PRKS experimental facility at BARC, Trombay was employed. These were monitored over the spectral range of 250 to ∼1200 nm with a resolution of 2 nm or better, in 100 ns to almost 100 ms time scale.[17] Sample replenishment before each pulse was made with the help of a routine flow arrangement and oscilloscope traces were averaged during spectral and kinetic measurements. Polytetrafluoroethylene (PTFE) tubing was used for the entire flow system, and acid resistant Viton tubing was used

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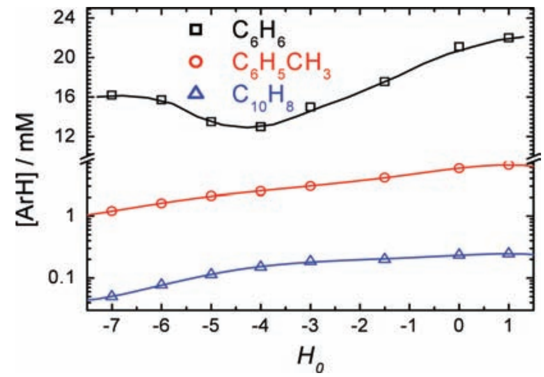

Figure 1. Saturation solubility plots of benzene (□), toluene (○), and naphthalene (△) vs. solution acidity in aqueous H_2SO_4 solution near 25 °C.

downstream for pumping in the sample solutions. A 10 mM O_2 saturated SCN^- solution was used for routine dosimetry to correlate the concentrations of the reaction-initiating radicals, taking the $(SCN)_2^{\bullet -}$ $G\varepsilon$ as 2.59×10^{-4} m^2 J^{-1} and $\varepsilon = 7650$ M^{-1} cm^{-1} at 475 nm.[14b,17,18] The reducing radicals (>98%) were scavenged with dissolved O_2, as is the standard PRKS experimental practice.[14a]

Results and Discussion

First, the compatibility and chemical stability check on C_6H_6, $C_6H_5CH_3$, and $C_{10}H_8$ in aqueous H_2SO_4 was addressed to verify the absence of sulfonation at very high acid concentrations (>15 M), as reported in some previous studies.[19] In O_2 saturated solutions, our measurements were generally restricted to an acidity of $H_0 \geq -7.0$ ($[H_2SO_4] \leq 13.8$ M)[20] wherein no significant chemical change of any of these solutes was noticed even within a few days (while a typical measurement requires <5 min). It may be noted that in $H_2O-HClO_4$ media also, even at the highest usable acid concentration of 9.3 M (H_0 −5.2),[20] these aromatics were chemically stable.

A measure of the solubility of the aromatics in the $H_2O-H_2SO_4$ and $H_2O-HClO_4$ solvents was essential for all subsequent quantitative correlations. These estimations were made spectrophotometrically at the respective solute absorption λ_{max} (254.6 nm for benzene, 261.7 nm for toluene, and 275.2 nm for naphthalene), and correlated to the respective aqueous medium saturation solubility. The absorbance was made against a blank medium of the same acidity (and acid). For each measurement, excess hydrocarbon was added into the medium of chosen acidity, shaken for 1 h, and later allowed to stand in a closed cell. An equilibration time of one day was judged to be adequate. During these measurements it was observed that even at the highest acidity the absorption spectral profile of each ArH remained identical with its absorption profile measured in aqueous solution. The plots in Figure 1 reveal continuous decrease of ArH saturation solubility with increasing acidity, while in the $H_2O-HClO_4$ medium (not shown as the trends were similar) such decreases were less pronounced, and at the highest acidity of 9.3 M the respective solubility remained within ≥90% of the pH 0 value. It may be noted that the solubility of C_6H_6 in $H_2O-H_2SO_4$ medium revealed an upward trend at acid concentration >8.5 M ($H_0 < -4.5$), possibly due to the onset of a protonation reaction, resulting in enhanced solvation. However, this reversal of trend did not influence the results of this study discussed later. For the PRKS measurements in aqueous acid media, respective solubility of the aromatics shown in Figure 1 proved quite adequate to reach the conclusions.

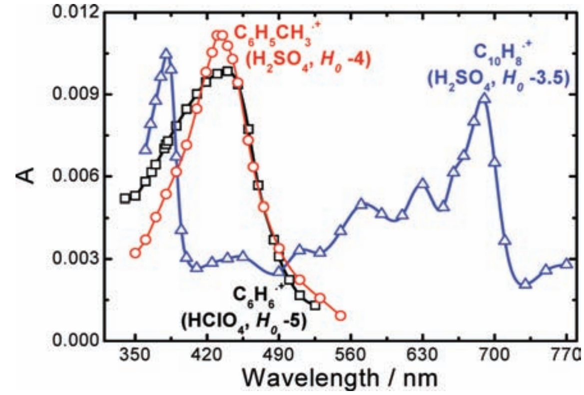

Figure 2. Absorption spectra of $ArH^{\bullet +}$ species in aqueous H_2SO_4 and aqueous $HClO_4$ solutions at various acidities and absorbed dose. $C_6H_6^{\bullet +}$ spectrum (□) from 125 μM benzene in O_2 saturated H_0 −5.0 $HClO_4$ solution irradiated with 23 Gy dose; $C_6H_5CH_3^{\bullet +}$ spectrum (○) from 140 μM toluene in O_2 saturated H_0 −4.0 H_2SO_4 solution, 26 Gy dose, and $C_{10}H_8^{\bullet +}$ spectrum (△) from 65 μM naphthalene in O_2 saturated H_0 −3.5 H_2SO_4 solution, 13 Gy dose.

Typical primary transient UV−vis absorption spectra originating from C_6H_6, $C_6H_5CH_3$, and $C_{10}H_8$ oxidation in H_2SO_4 and $HClO_4$ media (for dissimilar absorbed dose) are shown in Figure 2. In each case the respective solute concentrations were maintained below 150 μM, mainly to minimize any secondary ArH reaction with the respective transient formed. The oxidizing radical concentration was maintained in the range of 5 to 15 μM employing the appropriate dose;[17] however, due to the prevailing low solute concentrations, the maximum solute oxidation efficiency remained ≤85%. The transient absorption bands were recorded 5−8 μs after the end of the radiation pulse, when the time-resolved radical absorptions reached their maximum limit. The respective λ_{max} was observed at the following: 443 nm for C_6H_6 ($\varepsilon = 1145 \pm 75$ M^{-1} cm^{-1}), 428 nm for $C_6H_5CH_3$ ($\varepsilon = 1230 \pm 90$ M^{-1} cm^{-1}), and 381 and 687 nm for $C_{10}H_8$ (respectively $\varepsilon = 3650 \pm 225$ and 2210 ± 160 M^{-1} cm^{-1}). To estimate these ε values, detailed analyses of various kinetic traces (using a wide range of solute concentration) were necessary to record the prevailing efficiency of the oxidative reaction toward the generation of the radical cation. The concentration of the primary oxidizing radicals was obtained from the acidity (and acid)-dependent G values discussed in our previous study.[14b] Support for the monocationic nature of each transient ($ArH^{\bullet +}$) was garnered from comparisons with their previously reported absorption spectral band profiles, and respective λ_{max} values in various matrices, which matched quite well in each case.[21,22] Further support of the cationic nature of the radicals was earned from their negligible reactivity with dissolved O_2 in the reaction medium. The respective generation kinetics of the cation was estimated to be close to the diffusion controlled limit ($k > 10^9$ M^{-1} s^{-1}) in each solvent medium, taking into account the prevailing solution viscosities with respect to its acidity, especially for H_2SO_4.[23] These rate values suggest the absence of other reaction channels, save a direct one-electron oxidation in the desired direction. By employing some secondary oxidizing radicals (usable in highly acidic medium) with decreasing oxidative potency (e.g., $Cl_2^{\bullet -}$, $Br_2^{\bullet -}$, $I_2^{\bullet -}$, $C_6H_5OH^{\bullet +}$),[13b,24,25] it was observed that the targeted $C_6H_5CH_3^{\bullet +}$ and $C_{10}H_8^{\bullet +}$ species could be generated in the aqueous acid media, although at decreasing rates. On the other hand, while the $C_6H_6^{\bullet +}$ radical could be generated by using

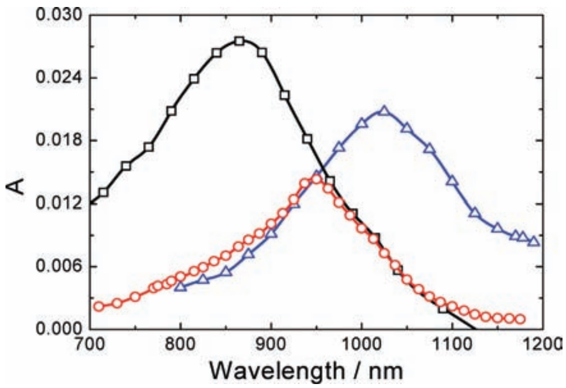

Figure 3. Absorption spectra of $(C_6H_6)_2^{\bullet+}$ (□) and $(C_6H_5CH_3)_2^{\bullet+}$ (○) measured in H_0 −6.0 O_2 saturated aqueous H_2SO_4 solutions at absorbed dose 26 Gy with 10 mM benzene or 1.2 mM toluene solution. Absorption spectrum of $(C_{10}H_8)_2^{\bullet+}$ (△) measured in O_2 saturated H_0 −5.0 aqueous $HClO_4$ solutions at absorbed dose 14 Gy with 170 μM naphthalene.

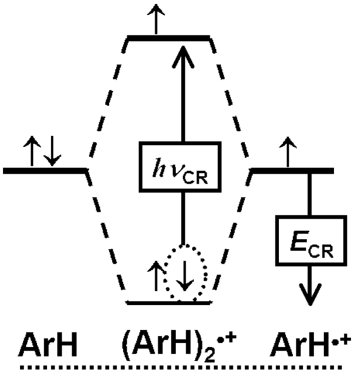

Figure 4. $(ArH)_2^{\bullet+}$ CR band MO representation. $\boldsymbol{E}_{CR} \approx 0.5 \times h\nu_{CR}$.

$Cl_2^{\bullet-}$ and $Br_2^{\bullet-}$ radicals, either $I_2^{\bullet-}$ or $C_6H_5OH^{\bullet+}$ failed to oxidize benzene. On the other hand, employing ~1 mM benzene, with either 100 μM phenol or I^-, the corresponding radical $C_6H_5OH^{\bullet+}$ or $I_2^{\bullet-}$ generation was observed to be fast, thus suggesting the $C_6H_6^{\bullet+}$ reduction potential to be higher than that of $I_2^{\bullet-}$ or $C_6H_5OH^{\bullet+}$ in the aqueous acid media, and revealing the oxidative power of various radicals as $Cl_2^{\bullet-} > Br_2^{\bullet-} > C_6H_6^{\bullet+} > I_2^{\bullet-} \approx C_6H_5OH^{\bullet+} > C_6H_5CH_3^{\bullet+} \approx C_{10}H_8^{\bullet+}$.

Once quantitative generations and characterizations of these monomeric cations were standardized, further time-resolved studies in the presence of increasing amounts of the respective parent ArH were carried out. At higher ArH concentrations, especially at near-saturation conditions, additional secondary transient absorption bands in the near-IR were observed at 30−100 μs (inversely related to the prevailing ArH concentration) after the end of the radiation pulse. The respective broad absorption profiles are presented in Figure 3, and reveal λ_{max} values at 860, 950, and 1040 nm respectively for C_6H_6, $C_6H_5CH_3$, and $C_{10}H_8$. Assuming formation of the dimeric cationic species $(C_6H_6)_2^{\bullet+}$, $(C_6H_5CH_3)_2^{\bullet+}$, or $(C_{10}H_8)_2^{\bullet+}$ following the equilibrium reactions $ArH^{\bullet+} + ArH \leftrightarrows (ArH)_2^{\bullet+}$, the individual bimolecular (formation) rate constants were estimated to be $\leq 1.0 \times 10^9$ M^{-1} s^{-1} for C_6H_6, $\leq 6.5 \times 10^8$ M^{-1} s^{-1} for $C_6H_5CH_3$, and $\leq 3.0 \times 10^8$ M^{-1} s^{-1} for $C_{10}H_8$. Support for the dimeric transient nature was garnered from the literature report of the spectral profiles of aromatics in frozen matrices and organic solvents. Therein the absorption bands in the near-IR region have been ascribed to the respective charge resonance (CR) absorption, explained in Figure 4.[26] A few such examples are the following: γ-radiolysis in frozen 2-methylpentane generated $(C_6H_6)_2^{\bullet+}$ and $(C_6H_5CH_3)_2^{\bullet+}$ radical cations with absorption band λ_{max} at 930 and 1040 nm, while in *sec*-butylchloride glasses the respective λ_{max} are at 920 and 1020 nm.[27] In another photolytic study in frozen ArH matrix the $(C_6H_6)_2^{\bullet+}$ absorption band λ_{max} is reported at 900 nm.[28] In a different study the CR band λ_{max} of the $(C_{10}H_8)_2^{\bullet+}$ radical cation produced in flash photolysis experiments in acetonitrile is reported at 1040 nm.[29] An earlier radiation chemical study of $C_{10}H_8$ in a frozen 1:l mixture of isopentane and *n*-butyl chloride reveals the λ_{max} for $(C_{10}H_8)_2^{\bullet+}$ at 1020 nm.[30] The λ_{max} of the radiolytically generated $(C_6H_5CH_3)_2^{\bullet+}$ radical cation is reported at 1000 nm in dichloroethane solvent.[31] A comparison of these data with the three spectral plots in Figure 3 shows close matching in the respective cases, while the observed blue spectral shifts in respective λ_{max} values are expected due to the strong solvation of the transients in the highly polar aqueous acid media. For $(C_6H_6)_2^{\bullet+}$, $(C_6H_5CH_3)_2^{\bullet+}$, and $(C_{10}H_8)_2^{\bullet+}$ the respective ε values at the absorption maxima (λ_{max}) were estimated as 2835 ± 235, 1685 ± 155, and 4170 ± 320 M^{-1} cm^{-1}, considering the real-time ArH (decay) and $ArH^{\bullet+}$ (formation) profiles at the selected time window of measurement in solutions of acidity H_0 −5.0 to −6.0. (In these estimations, any radical loss reaction in an unaccounted channel(s) was considered to be negligible.)

Various structural features of these dimeric cations based on quantum chemical calculations are frequently discussed in the literature. In case of $(C_6H_6)_2^{\bullet+}$ its gas phase clustering reveals the axial C_2 geometry of the two rings to be slightly more stable than their parallel C_{2v} sandwich geometry.[32] However, other studies suggest the parallel geometry to be more stable, with an optimized distance of 3.5 Å between the two rings.[33,34] In the case of $(C_6H_5CH_3)_2^{\bullet+}$ the most stable conformer geometry is reported to result from the π-type sandwich structure, with an optimized distance of 3.59 Å between the two rings, when the two $-CH_3$ groups remain diagonally opposite to each other. On the other hand, for an overlapping conformation of the two $-CH_3$ groups,[34] the perfect hexagonal shapes of the two rings become slightly distorted to nullify the two methyl group repulsions, and an inter-ring distance of >3.6 Å is suggested.[34] However, for $(C_{10}H_8)_2^{\bullet+}$ similar structural and conformational details are not yet available in the literature.

Experimentally, the stabilization energy of a dimer radical cation is qualitatively related to the CR band in Figure 4.[35] As shown, its magnitude is close to half of the CR band peak absorption energy. Therefore, from Figure 4, the stability of the three species is found to be in the order of $(C_6H_6)_2^{\bullet+} > (C_6H_5CH_3)_2^{\bullet+} > (C_{10}H_8)_2^{\bullet+}$. At H_0 −5 in aqueous H_2SO_4, their respective E_{CR} values are estimated as 16.6, 15.0, and 13.7 kcal mol^{-1}. Previous studies also support higher stability of $(C_6H_6)_2^{\bullet+}$ vis-à-vis $(C_{10}H_8)_2^{\bullet+}$ due to reduced overlap geometry of the rings in the latter.[34,36] Additionally, the intensities of absorption bands in Figure 3 suggest that in $C_6H_5CH_3$, the presence of the methyl group reduces the overlap of the π-electron clouds of the two rings, while in C_6H_6 and $C_{10}H_8$ the extent of overlap is higher.

Lastly, qualitative measurements reveal that for each parent hydrocarbon the monomeric cation is less acidic as compared to the dimeric cation by at least 2 orders of magnitude. While the proton activity corrected pK_a values[37] range between −2.6 and −1.3 for the $ArH^{\bullet+}$ species ($C_6H_6^{\bullet+}$ most acidic, $C_{10}H_8^{\bullet+}$ least acidic), the pK_a values of $(ArH)_2^{\bullet+}$ species are found to vary from −5.0 to −3.0 ($(C_6H_6)_2^{\bullet+}$ most acidic, $(C_{10}H_8)_2^{\bullet+}$

least acidic), adopting the methodology described in detail for such estimations.[14b] The respective radical pK_a values were measured as follows. First, the peak radical absorbances at appropriate time windows, based on a fixed dose and solute concentration, were recorded in solutions of continuously varying acidity. Herein, the maximum absorbance values of the radicals were found to be dependent on changing solution viscosity[14a,23] or the related rates, which were concurrently measured. These parameters were appropriately considered to obtain plots of transient radical maximum absorbance (A) vs. solution acidity (H_0). From the first derivative of such a plot as explained in our previous study,[14b] the maximum absolute value of $\partial A/\partial H_0$ was correlated with the respective radical pK_a value. These measurements were repeated employing various solute concentrations for authentication of the measured values.

Conclusions

Convenient application of aqueous acid media with wide-ranging acid concentrations in the generation and study of aromatic radical cations near room temperature also suggests that a smooth transition in the solvent nature to purely aqueous (or later even to aqueous alkaline) is possible. In such cases any transient characteristics measured in very low to very high acidities would allow a comparison, and a complete mapping of the gradual change in transient physicochemical property, if any. Use of two different acids in this study and similar results and conclusions obtained with the use of either suggest that the nature of the acid (i.e., presence of the conjugate anion SO_4^{2-}/HSO_4^- or ClO_4^-) has no influence on these results. Thus, radical cationic studies in aqueous acid medium are now routinely possible provided the parent is soluble in and nonreactive with the particular medium in use (at least for a few minutes).

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