The Reaction between Tris(4-bromophenyl)aminium Ion and Acetate Ion is an Electrophilic Reaction!

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A recent claim that the reaction between acetate ion and tris(4-bromophenyl)aminium ion (TBPA⁺) is an electron transfer process, in contrast with the polar reaction demonstrated earlier between the hydrogeniacetate ion and TBPA⁺, is refuted. Product studies show that the possible products of electron transfer between acetate ion and TBPA⁺; methane and ethane, are formed in < 10⁻³% yield and that ring acetoxylation of TBPA, i.e., the polar process, is predominant. The demonstration of 'catalytic' electrochemical oxidation of TBPA/AcO⁻ mixtures is shown to be the result of a multi-step oxidation mechanism, due to the small difference in redox potential of TBPA and its 2-acetoxy derivative, 0.09 V.

The tris(4-bromophenyl)aminium ion (TBPA⁺), available commercially as its hexachloroantimoniate, is widely used as an electron transfer (ET) catalyst or mediator. According to common belief, the only function of this radical cation is to abstract one electron from a substrate, presumably by an outer-sphere mechanism.

This naive view remained long unquestioned, in spite of the rather extensive knowledge of the chemical reactivity of radical cations pointing to other mechanistic possibilities. It is, however, no longer tenable. We have conclusively shown that TBPA⁺ in addition has both radical and electrophilic reactivity. The former, demonstrated in earlier work on TBPA oxidation and also for simple 4-haloamine derivatives, manifests itself by ipso coupling of two TBPA⁺ radical cations at the 4-positions with subsequent loss of a brominating species and formation of a dimer. Analogous chemistry takes place in the radical-cation mediated, base-assisted debromodimerization of 1-bromo-2,4,6-tris(pyridylidino)benzene. The electrophilic reactivity results in substitution at one or several ring positions. Thus reaction between TBPA⁺ and acetate, chloride or cyanide ion gave the corresponding 2-acetoxy, 2-chloro or 2-cyano derivative of TBPA⁺. In the first-mentioned case, a diacetate was also formed in an amount corresponding to ca. 15% of the monoacetate. On the other hand, bromide or iodide ion underwent ET exclusively with regeneration of TBPA and formation of Br⁻ or I⁻. It seems that this more complex view of TBPA⁺ is now slowly beginning to penetrate the chemical community.

In the reaction between acetate ion and TBPA⁺ we used the Bu₄N⁺ salt of the H-bonded [(AcO)₂H⁻] ion as the source of acetate as it is simpler to handle compared with the extremely hygroscopic tetrabutylammonium acetate. The difficulties encountered in the purification of this material are well documented. The equilibrium constant for homocoupling [eqn. (1)] is known to be 4.7×10⁷ M⁻¹ in acetonitrile and 85 M⁻¹ in HOAc, so that under our reaction conditions (1 mM in the acetate salt in kinetic runs and ca. 15 mM in preparative runs) the distribution between 'naked' AcO⁻ and [(AcO)₂H⁻] is 37 and 63% and 11 and 89%, respectively. This, of course, a distinct disadvantage if one wants to make a detailed kinetic analysis, but this was not our intention. We wanted to show that this mixture of acetate ion species does not undergo ET with TBPA⁺ and this was easily seen by the complete absence of radical-derived products, methane and ethane, and the satisfactory yield of the 2-acetoxy derivative of TBPA, 67%, and a diacetate, 9%.

We were therefore surprised to find that Compton and Laing claimed that there is a fundamental difference between acetate and hydrogeniacetate ion in their reaction with TBPA⁺, acetate reacting via ET to give a methyl radical and CO₂ and hydrogeniacetate via the polar reaction described above. This claim was based on a rotating disc voltammetry study which indicated 'catalytic' behaviour, i.e. more than two electrons per mole of TBPA were consumed when Bu₄NOAc (commercial quality, used directly as received) was employed as the acetate ion source. Upon addition of acetic acid in incremental amounts, a stage was eventually reached when the TBPA⁺/TBPA behaved as a reversible one-electron couple (ratio of HOAc to Bu₄NOAc ca. 10). This was considered evidence that 'naked' acetate ion undergoes ET to TBPA⁺ whereas vari-
ous forms of hydrogen-bonded acetate ions react with bond formation, i.e., as nucleophiles.

We strongly dispute this interpretation, on the basis that appreciable concentrations of AcO" were present in all experiments where H(AsO₂)²⁻ was the source of acetate (see above). The experiments reported below completely rule out any hypothesis that AcO" undergoes ET with TBPA⁺⁺.

**Results**

Commercial TBPA⁺⁺SbCl₅⁻ (assay 86%, as determined by UV/Vis spectrometry), dissolved in acetonitrile (46 mM solution) was allowed to react with a fourfold excess of Bu₄NOAc (used as received, except for being dried over P₂O₅) in acetonitrile (ca. 0.2 M). The yield of the 2-acetoxy derivative of TBPA was 55% and a diacetate was formed in 10% yield, based on a 2e⁻ and 4e⁻ stoichiometry, respectively. TBPA (70%) was recovered. In a separate experiment the yield of methane was determined to be <10⁻³ % (methane was positively identified by GLC but in a concentration just above the methane level in the laboratory air) and that of ethane <2×10⁻⁵ % (level of detection). In the same run, 2-acetate (35%), diacetate (7%) and recovered TBPA (61%) were found. A duplicate run gave the same result within the limits of error.

Thus preparative experiments rule out completely that acetate ion, using commercial Bu₄NOAc as the acetate ion source as described by Compton and Laing, undergoes ET to TBPA⁺⁺. Why was then 'catalytic' behaviour seen in the electrochemical experiments, as indeed was also earlier observed by Steckhan and Schmidt?

The most likely explanation is that a multi-step oxidation mechanism takes place. The 2-acetoxy compound undergoes a reversible 1e⁻ process with E°" = 1.20 V vs. Ag/AgCl, only 0.09 V above that of TBPA itself. Table 1 shows E°" values for the oxidation of a number of 2-X substituted tri(4-bromophenyl)amines in acetonitrile. The effect of introducing one acetoxy group is small, ca. 0.1 V, therefore

![Graph showing 'n" as a function of the concentration of the acetate ion species.

Fig. 1. Showing 'n" as a function of the concentration of the acetate ion species. Solid lines and circles, Bu₄NOAc; broken lines and triangles, Bu₄N[(AcO)₂]H. The curve pairs correspond, from left to right, to sweep rates of 25, 50, 100, 200, 400, 800 and 1600 mV s⁻¹. [TBPA] = 3.00 mmol l⁻¹ in acetonitrile/tetrabutylammonium hexafluorophosphate (0.2 mol l⁻¹).

"n" values larger than 2 should be expected in systems where TBPA is anodically oxidized in the presence of AcO". At relatively low sweep rates, there is enough time for formation of the 2-acetoxy compound and higher acetylated species during the sweep since the rate constants in these systems are of the order of 10⁵ M⁻¹ s⁻¹ for the hydrogen bonded ion, (AcO)₂H⁻. It is likely that the unsolvated AcO" ion reacts even faster with TBPA⁺⁺.

A study using cyclic voltammetry provided qualitative evidence for this mechanism. Upon addition of incremental amounts of Bu₄NOAc in the concentration range 2-20 mM to a 3.00 mM TBPA solution in acetonitrile/Bu₄NPF₆ (0.2 M), 'n" (taken to be equal to iₚ/iₚ, in the presence of acetate ion divided by iₚ in its absence) increased to values above 5 at low sweep rates (25 mV s⁻¹), whereas at higher rates (maximally 1600 mV s⁻¹) a value around 4 was obtained (Fig. 1). With Bu₄N[(AcO)₂]H as the source of acetate, 'n" increased in the same way at lower concentrations but not nearly as much at higher concentrations (Fig. 1). For each concentration of H(AsO₂)²⁻, 'n" decreased linearly with log(v/mV s⁻¹), as exemplified in Fig. 2. This behaviour is expected on the basis of the higher nucleophilicity of AcO" as compared with H(AsO₂)²⁻ (see below). Upon addition of a thiryfold excess of acetic acid to the final solutions containing either 20 mM Bu₄NOAc or Bu₄N[AcO₂]H, the cyclic voltammogram again showed approximate one-electron behaviour, as was also noticed by Compton and Laing. Thus the nuclophilic reactivity of acetate ion can be suppressed far below that of H(AsO₂)²⁻ by solvation by additional acetic acid molecules.

<table>
<thead>
<tr>
<th>2-Substituent</th>
<th>(E°₂⁻−Eϕ lay)/mV</th>
<th>E°&quot;(RH²⁺/RH)/V (vs. Ag/AgCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>70</td>
<td>1.11</td>
</tr>
<tr>
<td>AcO</td>
<td>80</td>
<td>1.20</td>
</tr>
<tr>
<td>n-C₄H₉OCO</td>
<td>73</td>
<td>1.22</td>
</tr>
<tr>
<td>CI</td>
<td>70</td>
<td>1.26</td>
</tr>
<tr>
<td>Br</td>
<td>72</td>
<td>1.23</td>
</tr>
<tr>
<td>CN</td>
<td>72</td>
<td>1.35</td>
</tr>
</tbody>
</table>

Also the RH²⁺/RH⁺⁺ couple and the associated carbazole couple were seen in the cyclic voltammograms, except that the latter was not detected for the two acyloxy systems. From Ref. 2.

Fig. 2. Showing 'n-eff' as a function of \( \log(\text{v/mV s}^{-1}) \) at three concentrations (from bottom to top 4, 8 and 16 mmol l\(^{-1}\)) of acetate ion species. Solid lines and circles, Bu\(_4\)N\(\text{AeO}_2\)H; broken lines and triangles, Bu\(_4\)N(\(\text{AeO}\)\(_2\))\(\text{H} \) \[ \text{[TBPA]} = 3.00 \text{ mmol l}^{-1} \] in acetonitrile/tetraethylammonium hexafluorophosphate (0.2 mol l\(^{-1}\)).

Fig. 3. Cyclic voltammogram of TBPA (3.00 mmol l\(^{-1}\)) in acetonitrile/0.2 M Bu\(_4\)NPF\(_6\) in the presence of 6.0 mM Bu\(_4\)NOAc at 800 mV s\(^{-1}\). Reference electrode, Ag/AgCl.

At intermediate concentrations of Bu\(_4\)NOAc (4–12 mM), a second anodic peak, 90 mV (average value at 200 and 400 mV s\(^{-1}\)) more anodic than that of TBPA itself, was easily discernible (Fig. 3) at sweep rates \( \geq 200 \text{ mV s}^{-1} \). This presumably originates from oxidation of the monoacetate. The same phenomenon appeared in the runs with Bu\(_4\)N[(\(\text{AeO}\)\(_2\))\(\text{H} \)], although it was less distinctly visible. The anodic peak potentials of AcO\(^-\) and H(\(\text{AeO}\)\(_2\))\(^-\) under the same conditions were 1.63 and 1.99 V, respectively, and it was ascertained that the contribution to the current due to these species was negligible in the potential range of TBPA oxidation. The increase in oxidation potential of acetate ion upon addition of acetic acid, including the role of the 1:1 complex (hydrogenacetate ion) is known from earlier work.\(^{18}\)

**Discussion**

The value of \( E'(\text{CH}_3\text{COOO}'/\text{CH}_3\text{COO}^-) \) in aqueous media was first calculated to be 2.4 V vs. NHE\(^{19}\) (normal hydrogen electrode); a later estimate\(^{20}\) was lower, 2.04 V (NHE). Since the acetate ion is strongly solvated in water, transfer to acetonitrile lowers the above \( E' \) value by ca. 0.6 V. This brings it into a region where, in principle, \( \text{TBPA}^{2+} \) with \( E'(\text{TBPA}^{2+}/\text{TBPA}) = 1.3 \text{ V (NHE)} \) would seem to be able to undergo outer-sphere ET from acetate ion. It is therefore not unreasonable per se that earlier workers assumed that ET took place. The absence of radical-derived products (methane and/or ethane from acetate ion) however rules out this possibility, and the formation of substitution products of TBPA shows that indeed nucleophilic attack by acetate on \( \text{TBPA}^{2+} \) occurs. Since the successively formed acetate products have closely spaced peak potentials, multi-step oxidation is observed, thus simulating 'catalytic' behaviour. There is no qualitative difference between the extremes of a naked acetate ion and one strongly solvated by acetic acid, but naturally, the nucleophilic reactivity is significantly reduced in the latter case.

In the light of the above findings, the rotating disc voltammetric data given by Compton and Laing\(^{16}\) are easily understandable. In the presence of 'naked' acetate ion, the slope of the \( i_{\text{pa}}/v^{1/2} \) line corresponds reasonably well to \( n_{\text{eff}} = 4 \), i.e., at the prevailing potential two acetoxo groups are introduced into TBPA. Under conditions where the hydrogenacetate ion is the predominant species, the \( i_{\text{pa}}/v^{1/2} \) relationship is curved downwards, indicating that \( n_{\text{eff}} \) diminishes with increasing sweep rate as expected for reactions involving the less nucleophilic hydrogenacetate ion. The finding that these data can be quantitatively analyzed in terms of an EC' mechanism of the pre-equilibrium type [eqns. (2)–(4)] must be fortuitous since the extremely short lifetime of the acetoxo radical, of the order of \( 10^{-9} \text{ s} \),\(^{11}\) makes it impossible for the reverse reaction of eqn. (3) to manifest itself kinetically.

Moutet\(^{21}\) prepared electrodes coated with poly(4,4'-dibromo-4'- vinyl)triphenylamine and obtained 'catalytic' currents when Bu\(_4\)NOAc was oxidized on these. Rapid degradation of the polymer was noticed, no doubt due to acetoxylation of the rings. This system was later rediscovered,\(^{22}\) and again 'catalytic' oxidation of acetate ion was claimed, degradation now being explained in terms of attack by methyl radicals. An additional synthesis of the monomer has recently been published,\(^{24}\) but extreme difficulties in its purification were claimed.

**Experimental**

**Materials and methods.** Tetrabutylammonium acetate (Fluka AG, \( ^{\sim} 95 \% \) ) was stored over \( \text{P}_2\text{O}_5 \) and otherwise used as received. TBPA+BrCl was of commercial quality (Aldrich, \( ^{\sim} 98 \% \) ), its radical-cation contents being checked by UV/Vis spectrophotometry immediately before use.
TBPA was recrystallized three times from heptane. Tetra-butylammonium hydrogendiaacetate was recrystallized twice from ethyl acetate. Acetonitrile was of UVASOL® quality, kept over molecular sieves. Tetra-butylammonium hexafluorophosphate was recrystallized three times from ethyl acetate/hexane (7:3). 2-Substituted (AcO, C₆H₅CO, Cl, CN) derivatives of TBPA were available from previous studies.⁶,⁷

Cyclic voltammetry was performed with Ar protection using the BAS-100 instrument from Bioanalytical Systems, Inc., West Lafayette, Indiana, USA, using an Ag/AgCl electrode as the reference electrode. The analytical procedures and precautions necessary to ensure high quality of TBPA⁺⁺ salts have been described earlier.⁶

The product studies were made as described in our previous work,⁶ except that the concentrations of the reactants were kept higher, sometimes even under conditions where some of the radical cation salt remained undissolved before the reaction was initiated. The analysis of gaseous products was performed on runs conducted in a flask of ca. 50 ml free volume.

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References


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