

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

Lennart Ebersson* and Berit Olofsson

Division of Organic Chemistry 3, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden

Ebersson, L. and Olofsson, B., 1989. The Reaction between Tris(4-bromophenyl)aminium Ion and Acetate Ion *is* an Electrophilic Reaction! – Acta Chem. Scand. 43: 698–701.

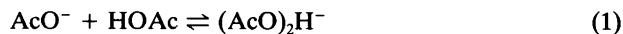
A recent claim that the reaction between acetate ion and tris(4-bromophenyl)aminium ion (TBPA⁺) is an electron transfer process, in contrast with the polar reaction demonstrated earlier between the hydrogendiacetate ion and TBPA⁺, is refuted. Product studies show that the possible products of electron 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 hexachloroantimonate, is widely used as an electron transfer (ET) catalyst or mediator.² 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.³

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.^{4,5} It is, however, no longer tenable. We have conclusively shown that TBPA⁺ in addition has both radical and electrophilic reactivity.^{6,7} The former, demonstrated in earlier work on TBPA oxidation⁸ and also for simple 4-haloaniline derivatives,^{9,10} 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(pyrrolidino)benzene.¹¹ 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⁺.^{6,7} 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 Br₃⁻ or I₃⁻. It seems that this more complex view of TBPA⁺ is now slowly beginning to penetrate the chemical community.¹²

In the reaction between acetate ion and TBPA⁺ we used the Bu₄N⁺ salt of the H-bonded [(AcO)₂H]⁻ ion as the

source of acetate¹³ 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.¹⁴ The equilibrium constant for homoconjugation [eqn. (1)] is known to be 4.7 × 10³ M⁻¹ in acetonitrile¹⁴ (85 M⁻¹ in HOAc¹⁵), so that under our reac-



tion 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 is, 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%.⁶

We were therefore surprised to find that Compton and Laing¹⁶ claimed that there is a fundamental difference between acetate and hydrogendiacetate ion in their reaction with TBPA⁺, acetate reacting via ET to give a methyl radical and CO₂ and hydrogendiacetate 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-

[#] Part XVIII in the series 'Electron Transfer Reactions in Organic Chemistry.' For Part XVII, see Ref. 1.

* To whom correspondence should be addressed.

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 $\text{H}(\text{AcO})_2^-$ was the source of acetate (see above). The experiments reported below completely rule out any hypothesis that AcO^- undergoes ET with $\text{TBPA}^{+\cdot}$.

Results

Commercial $\text{TBPA}^{+\cdot}\text{SbCl}_6^-$ (assay 86%, as determined by UV/Vis spectrometry), dissolved in acetonitrile (46 mM solution) was allowed to react with a fourfold excess of Bu_4NOAc (used as received, except for being dried over P_2O_5) 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 $< 2 \times 10^{-4}\%$ (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 Bu_4NOAc as the acetate ion source as described by Compton and Laing,¹⁶ undergoes ET to $\text{TBPA}^{+\cdot}$. Why was then 'catalytic' behaviour seen in the electrochemical experiments, as indeed was also earlier observed by Steckhan and Schmidt?¹⁷

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

Table 1. $E^{o'}(\text{RH}^{2+}/\text{RH}^+)$ [taken to be equal to $(E_{\text{pa}} + E_{\text{pc}})/2$ and $(E_{\text{pa}} - E_{\text{pc}})$] for 2-substituted TBPA derivatives, as determined by cyclic voltammetry^a at a sweep rate of 50 mV s^{-1} in acetonitrile/tetrabutylammonium hexafluorophosphate (0.1 M).

2-Substituent	$(E_{\text{pa}} - E_{\text{pc}})/\text{mV}$	$E^{o'}(\text{RH}^{2+}/\text{RH}^+)/\text{V}$ (vs. Ag/AgCl)
None	70	1.11
AcO	80	1.20
n-C ₈ H ₁₇ OCO	73	1.22
Cl	70	1.26
Br	—	1.23 ^b
CN	72	1.35

^a Also the $\text{RH}^{2+}/\text{RH}^{+\cdot}$ couple and the associated carbazole couple⁸ were seen in the cyclic voltammograms, except that the latter was not detected for the two acyloxy systems. ^b From Ref. 2.

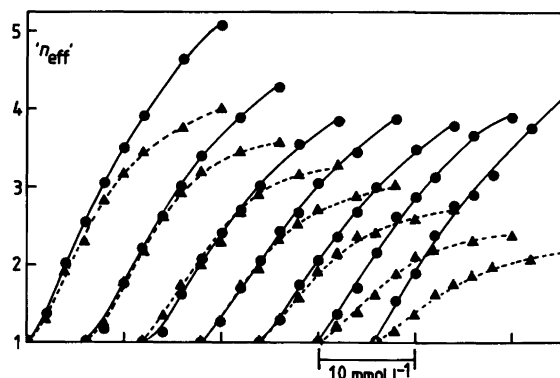


Fig. 1. Showing ' n_{eff} ' as a function of the concentration of the acetate ion species. Solid lines and circles, Bu_4NOAc ; broken lines and triangles, $\text{Bu}_4\text{N}[(\text{AcO})_2\text{H}]$. The curve pairs correspond, from left to right, to sweep rates of 25, 50, 100, 200, 400, 800 and 1600 mV s^{-1} . $[\text{TBPA}] = 3.00 \text{ mmol l}^{-1}$ 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 acetoxyated species during the sweep since the rate constants in these systems are of the order of $10^5 \text{ M}^{-1} \text{ s}^{-1}$ for the hydrogen bonded ion, $(\text{AcO})_2\text{H}^-$.⁶ It is likely that the unsolvated AcO^- ion reacts even faster with $\text{TBPA}^{+\cdot}$.

A study using cyclic voltammetry provided qualitative evidence for this mechanism. Upon addition of incremental amounts of Bu_4NOAc in the concentration range 2–20 mM to a 3.00 mM TBPA solution in acetonitrile/ Bu_4NPF_6 (0.2 M), ' n_{eff} ' (taken to be equal to i_{pa} in the presence of acetate ion divided by i_{pa} 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 $\text{Bu}_4\text{N}[(\text{AcO})_2\text{H}]$ as the source of acetate, ' n_{eff} ' increased in the same way at lower concentrations but not nearly as much at higher concentrations (Fig. 1). For each concentration of $\text{H}(\text{AcO})_2^-$, ' n_{eff} ' decreased linearly with $\log(v/\text{mV s}^{-1})$, as exemplified in Fig. 2. This behaviour is expected on the basis of the higher nucleophilicity of AcO^- as compared with $\text{H}(\text{AcO})_2^-$ (see below). Upon addition of a thirtyfold excess of acetic acid to the final solutions containing either 20 mM Bu_4NOAc or $\text{Bu}_4\text{N}[(\text{AcO})_2\text{H}]$, the cyclic voltammogram again showed approximate one-electron behaviour, as was also noticed by Compton and Laing.¹⁶ Thus the nucleophilic reactivity of acetate ion can be suppressed far below that of $\text{H}(\text{AcO})_2^-$ by solvation by additional acetic acid molecules.

* The use of quotation marks indicates that this quotient is not strictly identifiable with n_{eff} ; for an ECE-DISP type mechanism ($n = 2$) compared with a reversible process ($n = 1$) the theoretical value of ' n_{eff} ' is 2.22, ca. 10% higher than n_{eff} . This difference does not affect our arguments.

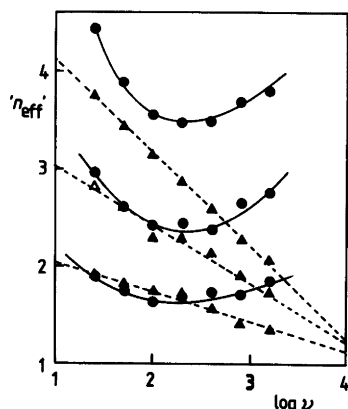


Fig. 2. Showing ' n_{eff} ' as a function of $\log(v/\text{mV s}^{-1})$ at three concentrations (from bottom to top 4, 8 and 16 mmol l^{-1}) of acetate ion species. Solid lines and circles, Bu_4NOAc ; broken lines and triangles, $\text{Bu}_4\text{N}[(\text{AcO})_2\text{H}]$. $[\text{TBPA}] = 3.00 \text{ mmol l}^{-1}$ in acetonitrile/tetrabutylammonium hexafluorophosphate (0.2 mol l^{-1}).

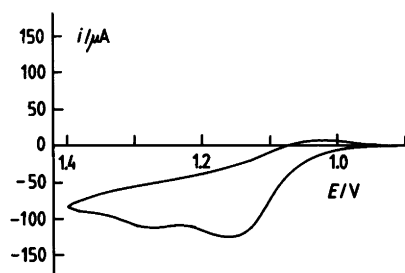


Fig. 3. Cyclic voltammogram of TBPA (3.00 mmol l^{-1}) in acetonitrile/ $0.2 \text{ M Bu}_4\text{NPF}_6$ in the presence of $6.0 \text{ mM Bu}_4\text{NOAc}$ at 800 mV s^{-1} . Reference electrode, Ag/AgCl .

At intermediate concentrations of Bu_4NOAc (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 $\text{Bu}_4\text{N}[(\text{AcO})_2\text{H}]$, although it was less distinctly visible. The anodic peak potentials of AcO^- and $\text{H}(\text{AcO})_2^-$ 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 (hydrogendiacetate ion) is known from earlier work.¹⁸

Discussion

The value of $E^\circ(\text{CH}_3\text{COO}^\cdot/\text{CH}_3\text{COO}^-)$ in aqueous media was first calculated to be 2.4 V vs. NHE¹⁹ (normal hydrogen electrode); a later estimate²⁰ 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, $\text{TBPA}^{+\cdot}$ with $E^\circ(\text{TBPA}^{+\cdot}/\text{TBPA}) = 1.3 \text{ V}$ (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 $\text{TBPA}^{+\cdot}$ 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 Laing¹⁶ are easily understandable. In the presence of 'naked' acetate ion, the slope of the $i_{\text{lim}}/v^{1/2}$ line corresponds reasonably well to $n_{\text{eff}} = 4$, i.e., at the prevailing potential two acetoxy groups are introduced into TBPA. Under conditions where the hydrogendiacetate ion is the predominant species, the $i_{\text{lim}}/v^{1/2}$ relationship is curved downwards, indicating that n_{eff} diminishes with increasing sweep rate as expected for reactions involving the less nucleophilic hydrogendiacetate 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 acetoxy radical, of the order of 10^{-9} s ,²¹ makes it impossible for the reverse reaction of eqn. (3) to manifest itself kinetically.

Moutet²² prepared electrodes coated with poly(4,4'-dibromo-4''-vinyl)triphenylamine and obtained 'catalytic' currents when Bu_4NOAc was oxidized on these. Rapid degradation of the polymer was noticed, no doubt due to acetoxylation of the rings. This system was later rediscovered,²³ 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, '≈ 95 %') was stored over P_2O_5 and otherwise used as received. $\text{TBPA}(\text{SbCl}_6)$ was of commercial quality (Aldrich, '98 %'), its radical-cation contents being checked by UV/Vis spectrophotometry immediately before use.

TBPA was recrystallized three times from heptane. Tetrabutylammonium hydrogendiacetate was recrystallized twice from ethyl acetate. Acetonitrile was of UVASOL® quality, kept over molecular sieves. Tetrabutylammonium hexafluorophosphate was recrystallized three times from ethyl acetate/hexane (7:3). 2-Substituted (AcO, C₈H₁₇OCO, 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.

Acknowledgements. We thank the National Board for Technical Development and the Swedish Natural Science Research Council for generous financial support. Drs. Ole Hammerich, University of Copenhagen and Henning Lund, University of Aarhus, are thanked for helpful comments.

References

1. Ebersson, L. and Ekström, M. *Acta Chem. Scand.* 43 (1989) 101.
2. For a review, see Steckhan, E. *Top. Curr. Chem.* 142 (1987) 1.
3. For a treatise of organic electron transfer reactions, see Ebersson, L. *Electron Transfer Reactions in Organic Chemistry*, Springer-Verlag, Heidelberg 1987.
4. Bard, A. J., Ledwith, A. and Shine, H. J. *Adv. Phys. Org. Chem.* 13 (1976) 155.
5. Hammerich, O. and Parker, V. D. *Adv. Phys. Org. Chem.* 20 (1984) 55.
6. Ebersson, L. and Larsson, B. *Acta Chem. Scand., Ser. B 40* (1986) 210.
7. Ebersson, L. and Larsson, B. *Acta Chem. Scand., Ser. B 41* (1987) 367.
8. Reynolds, R., Line, L. L. and Nelson, R. F. *J. Am. Chem. Soc.* 96 (1974) 1087.
9. Hand, R., Melichasch, M., Scoggin, D. I., Stotz, R., Carpenter, A. K. and Nelson, R. F. *Collect. Czech. Chem. Commun.* 36 (1971) 842.
10. Ahlberg, E., Helgée, B. and Parker, V. D. *Acta Chem. Scand., Ser. B 34* (1980) 187.
11. Effenberger, F. *Acc. Chem. Res.* 22 (1989) 27.
12. Engel, P. S., Hoque, A. K. M. M., Scholz, J. N., Shine, H. J. and Whitmire, K. H. *J. Am. Chem. Soc.* 110 (1988) 7880.
13. Ebersson, L. and Jönsson, L. *Acta Chem. Scand., Ser. B 40* (1986) 70.
14. Russell, C. D. *J. Electroanal. Chem.* 71 (1976) 81; see also note (16) in Hillery, P. S. and Cohen, L. A. *J. Am. Chem. Soc.* 105 (1983) 2760.
15. Clark, J. H. and Emsley, J. *J. Chem. Soc., Dalton Trans.* (1973) 2154.
16. Compton, R. G. and Laing, M. E. *J. Chem. Soc., Chem. Commun.* (1988) 1320.
17. Schmidt, W. and Steckhan, E. *J. Electroanal. Chem.* 89 (1978) 215.
18. Breitenbach, J. W., Olaj, O. F. and Sommer, F. *Monatsh. Chem.* 101 (1970) 1435.
19. Ebersson, L. *Acta Chem. Scand.* 17 (1964) 2004.
20. Pearson, R. G. *J. Am. Chem. Soc.* 108 (1986) 6109.
21. Braun, W., Rajbenbach, L. and Eirich, F. R. *J. Phys. Chem.* 66 (1962) 1591.
22. Moutet, J.-C. *J. Electroanal. Chem.* 161 (1984) 181.
23. Compton, R. G., Day, M. J., Ledwith, A. and Abu-Abdoun, I. I. *J. Chem. Soc., Chem. Commun.* (1986) 328.
24. Wright, M. E. and Jin, M.-J. *J. Org. Chem.* 54 (1989) 965.

Received March 10, 1989.