Electron Transfer Reactions in Organic Chemistry. IX.* Acyloxylation and/or Debromodimerization Instead of Electron Transfer in the Reaction between Tris(4-bromophenyl)ammoniumyl and Aliphatic Carboxylates

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The reaction between tris(4-bromophenyl)ammoniumyl tetrafluoroborate and carboxylate ions (acetate, pelargonate and *t*-butylcyanoacetate), in the form of their hydrogen dicarboxylate salts, was studied in acetonitrile by product and kinetic analysis. Contrary to an earlier proposal, single electron transfer is not observed. Instead, acyloxylation of the aryl group(s) is the preferred reaction mode around room temperature, whereas around 0 °C a competing process, debromodimerization of tris(4-bromophenyl)ammoniumyl, takes over. The latter reaction was not observed in dichloromethane. The mechanistic consequences of these findings for other applications of triarylammoniumyls as mediators and catalysts are briefly discussed. Also chloride ion reacted with tris(4-bromophenyl)ammoniumyl to give oxidative substitution products.

The anodic decarboxylation of carboxylates, commonly known as the Kolbe anodic synthesis,[1] can be mechanistically simulated in homogeneous medium by using very strong electron transfer (ET) oxidants, such as fluorine[2] and sulfate anion radical,[3] both employed in aqueous solution. The demand for a very strong oxidant is evident from the estimated E° of $RCOO^\cdot$, *i.e.*, 2.41 V[4] (a more recent estimate was 2.35 V)[5] *vs.* NHE*** for acetate ion [eqn. (1), R = CH_3] and 2.23 V for propionate and butyrate ion in aqueous solution (see also Ref. 1b). At one time it was suggested[6] that ET might be of the dis-

$$RCOO^\cdot + e^- \rightarrow RCOO^- \quad (1)$$

sociative type, *i.e.*, that dissociation of the C–CO_2 bond would be synchronous with transfer of the electron, in which case a much lower E° is estimated. For oxidation of acetate ion [eqn. (2), R = CH_3] it is equal to 1.55 V.[4] Subsequent work has, however, made this hypothesis less attractive,[1a] and it is now generally agreed that acetoxyl

$$R^\cdot + CO_2 + e^- \rightarrow RCOO^- \quad (2)$$

radical has a finite, although very short, life-time, the rate constant for decarboxylation being estimated to be in the region between 2×10^7 and 4×10^8 s^{-1} at 20 °C.[7,8]

It was therefore of considerable interest when it was reported[9] that tris(4-bromophenyl)ammoniumyl ($TBPA^{+\cdot}$), generated by anodic oxidation of tris(4-bromophenyl)amine (TBPA) in acetonitrile, could be used to oxidize carboxylates

*Part VIII, see Ref. 28b.

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***Normal hydrogen electrode: all potentials given in the following refer to this electrode, unless otherwise stated.

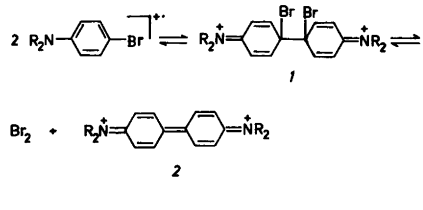
present in the electrolyte in a seemingly catalytic process, in spite of the fact that $E°$(TBPA$^{+\cdot}$/TBPA) is as low as 1.30 V. However, since $E°$(RCOO$^{\cdot}$/RCOO$^-$) is expected to decrease appreciably in transferring the components of the reaction from water to acetonitrile,[10,11] perhaps down to *ca.* 1.5 V, there did not seem to exist any intrinsic difficulty with an ET step between TBPA$^{+\cdot}$ and RCOO$^-$ from this point of view. More serious problems were raised by the product pattern from the reaction, since it deviated in a curious way from the one to be expected for a Kolbe-simulating reaction. Most products (esters) were derived from carbonium ions, in itself nothing unusual in this context,[1,6] but the remarkable feature was the apparent fragmentation of R^+ from RCOO$^-$ by one methylene group at a time, giving esters with almost all *n*-alkyl groups between CH_3 and R. Although specific fragmentations are known to take place in certain Kolbe oxidations of branched-chain acids,[12] successive one-carbon fragmentations of *n*-alkyl groups have never been observed.

We were intrigued by the possibility of using this reaction type for the indirect determination of $E°$(RCOO$^{\cdot}$/RCOO$^-$) from kinetic studies. If the reaction is of the non-bonded type, application of the Marcus theory[10,13] to a judiciously chosen set of rate/equilibrium data from RCOO$^-$/$Ar_3N^{+\cdot}$ reactions would in principle yield this kind of information.[14] Current[15] and previous[16–19] interest in the catalytic properties of triarylammoniumyls also motivated a closer study of their ET reactivity. In pursuing this goal, it soon, however, became apparent that the reaction between RCOO$^-$ and TBPA$^{+\cdot}$ cannot be of the ET type. Instead, it proceeds according to an ordinary ECE type mechanism, in which RCOO$^-$ attacks the radical cation at the nucleus to give eventually the acyloxy derivative *ortho* to nitrogen. This is a mechanism that is well known in anodic substitution of aromatics.[20] In addition, debromodimerization of TBPA$^{+\cdot}$ becomes the predominant reaction at lower temperatures in acetonitrile.

Results and discussion

Properties of tris(4-bromophenyl)ammoniumyl tetrafluoroborate. For both kinetic and product studies the preparation and previous history of the TBPA$^{+\cdot}$ salt turned out to be critical. Two methods are available for the preparation of TBPA$^{+\cdot}BF_4^-$, namely oxidation of TBPA by silver tetrafluoroborate/iodine in ether at low temperature[17] or by nitrosonium tetrafluoroborate in acetonitrile at ambient temperature.[21] The purity of the salt was checked by iodometric titration and by UV/VIS spectrophotometry; a freshly prepared sample with good kinetic behaviour should have λ_{max} at 705 and 365 nm with log ε = 4.52 ± 0.03 and 4.36 ± 0.02, respectively and log $\varepsilon \leq 0.05$ around 800 nm and in the region between 400 and 500 nm (Fig. 1, curve a). As the salt ages in the solid or in solution, a broad maximum develops around 480 nm (Fig. 1, curve b) and the absorbance around 800 nm also increases. MS analysis (direct inlet) of the aged salt (stored for six months in the solid or solution phase) shows the presence of tetra- and pentabromotriphenylamine as well as a compound with dimeric composition (corresponding to 2 TMPA$^{+\cdot}$ – 2Br). GLC analysis showed that only *ca.* 25% of the solid material was monomeric. Since coupling can take place at several sites in the same molecule, it is probable that polymers have also been formed during the ageing process.

This type of coupling reaction [eqn. (3)] is known from studies on the anodic oxidation of 4-chloro- and 4-bromo-*N,N*-dimethylaniline,[22] where, however, the fate of the bromine is not known. The same behaviour was also briefly mentioned in a study of dications of TBPA and the corresponding chloro derivative.[23] In our case, bromine interacts with TBPA$^{+\cdot}$ (or, possibly, TBPA itself, since this can be formed *via* slow oxidative hydroxylation by water adventitiously present) to give higher brominated products. We could further substantiate the nature of this process by treating a solution of TBPA$^{+\cdot}$ with hexene at 0 °C for 500 h. The detection (GLC/MS) of small amounts of 1,2-dibromocyclohexane (5%) and 1-bromo-2-fluorocyclohexane (2%) shows that bromine is slowly liberated



(3)

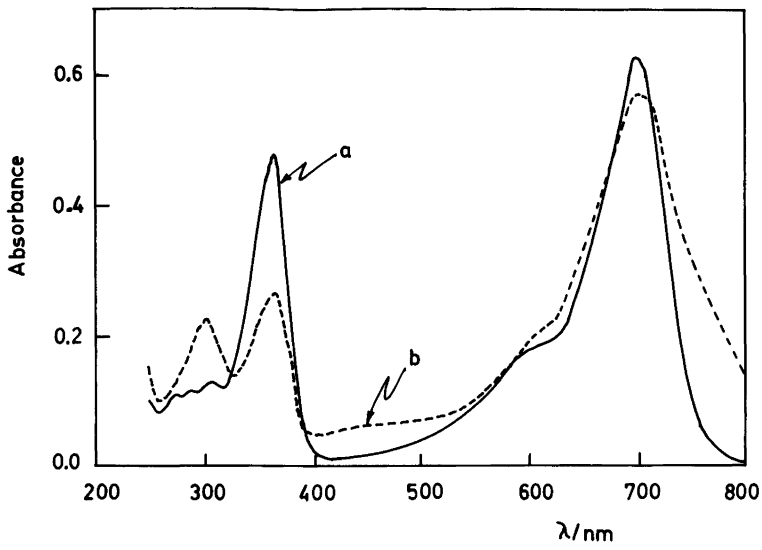


Fig. 1. UV/VIS spectra of solutions of $TBPA^{+\cdot}BF_4^-$ (0.20 mM) in acetonitrile. Curve a: Freshly prepared salt; b: Aged sample (1 month).

from $TBPA^{+\cdot}$ and trapped by the olefin. $TBPA^{+\cdot}$ derived products were free TBPA (25 %), mono- (6 %) and dibrominated TBPA (2 %). As seen from Fig. 2, the changes in the UV/VIS spectrum are qualitatively of the same nature as in the ageing process (Fig. 1); the difference resides in the rate-accelerating effect of cyclohexene, understandable in terms of removal of bromine if the second step of eqn. (3) is reversible.

Attempts to prepare $TBPA^{+\cdot}BF_4^-$ by controlled potential oxidation (1.05 V *vs.* Ag wire) of TBPA in acetonitrile/Bu_4NBF_4 led to samples of inferior quality, the maximum at 480 nm already being prominent in a freshly prepared sample. Presumably this is due to the well-known tendency of electrochemical reactions to favour bimolecular pathways due to high local concentrations of intermediates near the electrode.[24]

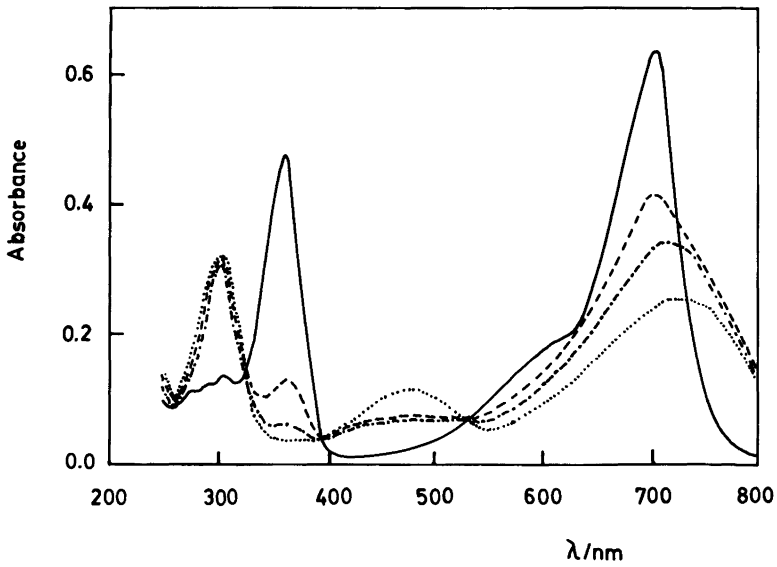


Fig. 2. UV/VIS spectra of solutions of $TBPA^{+\cdot}BF_4^-$ (16.6 mM) and cyclohexene (83.3 mM) in acetonitrile, diluted *ca.* 80 times immediately before recording the spectrum. —— Freshly prepared salt, ---- directly after addition of cyclohexene, —·—·— after 24 h, ····· after 500 h.

The effect of changing the method of preparation or ageing the salt is clearly visible in the rate determinations (see below for reactions with $RCOO^-$). The silver(I)/iodine method gives a faster-reacting salt, even when freshly prepared, and ageing also produces higher rate constants. We are not sure of the reason for the change in rate with method of preparation, but suggest that partial carbazole formation[23] (intramolecular oxidative coupling, known from earlier work and believed to occur *via* a dication intermediate) might account for the higher reactivity of the iodine generated salt. It might also be that the ageing process to produce dimers is accelerated by this method in some way.

Against this background, the NO^+ generated salt was judged to be the most well-behaved one and chosen for the kinetic studies with $RCOO^-$. All kinetic experiments were performed with freshly prepared salt (aged $\leq$1 h) showing the UV/VIS spectrophotometric specifications described above.

Product studies. Our first intention was to study in depth the reported reaction[9] between tetrabutylammonium pelargonate (nonanoate) and $TBPA^{+\cdot}$, but we encountered difficulties to obtain a well-defined salt with the composition of $Bu_4N^+\ C_8H_{17}COO^-$. We attribute this problem to the extreme tenacity by which carboxylates retain water; attempts to remove the last molecule of water gave salt preparations which contained tributylamine and dissolved in acetonitrile to give turbid solutions.

Better-behaved carboxylate salts are available in the form of homoconjugated complexes, $(RCOO)_2H^-$.[25] These can be freed completely from water and possess suitable properties for kinetic studies. Since the hydrogen diacetate salt is a well-characterized solid and the product analyses (GLC) could be most easily and accurately done with a low-molecular weight source of $RCOO^-$, our main efforts were directed toward studying the system $(AcO)_2H^-/TBPA^{+\cdot}$. In addition, pelargonate and *t*-butylcyanoacetate homoconjugates were employed, the latter being known to exhibit very characteristic behaviour upon ET (anodic or $SO_4^{-\cdot}$) oxidation[3b,26] [eqn. (4)]. Even when this reaction is performed in homogeneous medium ($SO_4^{-\cdot}$ as oxidant, $[RCOO^-] \approx 2$ M) the combined yield of products from bimolecular encounters between α-cyanoalkyl radicals is high, 30–40 %. Besides, no or very little further oxidation of α-cyanoalkyl radicals to α-cyanocarbocations takes place even under the most favourable conditions (anodic oxidation, eqn. (5)).[26,27]

To start with, all three carboxylates (used as homoconjugates, but written as $RCOO^-$ for simplicity) can be titrated cleanly at room temperature with the $TBPA^{+\cdot}$ salt according to the stoicheiometry of eqn. (6). In the acetate case the monoacetoxylated product (*3*) could be isolated in maximally 67 % yield [eqn. (6)], in addition to a diacetate in 9 % yield (as calculated for a $4e^-$ process) (Table 1). The yield of recovered TBPA was 52 %. Thus, the reaction appears to be a normal oxidative nuclear acetoxylation process, known from innumerable examples of anodic and metal ions oxidations [eqns. (7)–(9)].[28] In this type of chemistry, there is direct kinetic proof

$$\begin{array}{l} \mathrm{RCHCN} \\ \quad | \\ \mathrm{COO^-} \end{array} \xrightarrow[-CO_2]{SO_4^{-\cdot}} \mathrm{R\dot{C}HCN} \rightarrow \begin{array}{l} \mathrm{RCHCN} \\ \quad | \\ \mathrm{RCHCN} \\ \textit{meso/dl} \\ \text{ratio} \approx 1{:}1 \end{array} + \mathrm{RCH{=}\dot{C}{-}N{-}CH(CN)R} \qquad \text{isolated as the hydrated product} \qquad (4)$$

$$\mathrm{R\dot{C}HCN} \xrightarrow[\text{anode}]{-e^-,\ \text{Pt or C}} \mathrm{\overset{+}{R}CHCN} \quad \approx 0.5\,\% \qquad (5)$$

R = *t*-Bu

$$2\ \mathrm{RCOO^-} + 2\ \mathrm{Ar_3N^{+\cdot}} \rightarrow \mathrm{RCOOH} + \mathrm{Ar_3N} + \underset{\textbf{3}}{\mathrm{(4\text{-}BrC_6H_4)_2N(AcO)C_6H_3Br}} \qquad (6)$$

$$ArH \xrightarrow{-e^-} ArH^{+\cdot} \quad (7)$$

$$ArH^{+\cdot} + AcO^- \rightarrow \dot{A}r(H)OAc \quad (8)$$

$$\dot{A}r(H)OAc \xrightarrow{-e^-} \overset{+}{A}r(H)OAc \rightarrow ArOAc + H^+ \quad (9)$$

in homogeneous medium that substrates with E° up to *ca.* 2.2 V react according to the ECE mechanism with different nucleophiles.[29,30] The possibility of a Kolbe-type reaction was checked by careful analysis of the gas phase above the reaction medium; no ethane was formed, methane was positively identified but only at the limit of its detection (0.005 %), and the possible carbonium ion product, methyl acetate, was not detectable in the solution phase.

In the light of these findings, how can one then explain the demonstration of catalytic behaviour in the cyclic voltammograms of TBPA upon addition of $RCOO^-$ (pelargonate)[9]? Close inspection gives a simple answer: There is really no evidence of catalysis, only that incremental additions of $RCOO^-$ diminish the cathodic peak current to almost zero, whereas the anodic peak current grows to *ca.* twice the value of the unperturbed cyclic voltammogram of TBPA, exactly what is to be expected for an ECE mechanism according to eqns. (7)–(9)!

However, the reaction between $TBPA^{+\cdot}$ and AcO^- is not as simple as a trivial acetoxylation under all conditions. It is becoming increasingly evident that radical cation reactions are critically dependent upon temperature, aggregation between radical cations being favoured at lower temperatures, leading to a preponderance of dimerization processes.[31] Thus in acetonitrile acetoxylation predominates at 20 °C, whereas at 2–5 °C this reaction mode is suppressed in favour of formation of brominated TBPA:s (Table 1). In other words, a mechanism similar to that of the ageing procedure can be induced by treatment with AcO^- in acetonitrile at 2–5 °C, whereas the same preparation of $TBPA^{+\cdot}$ gives clean acetoxylation at 20–25 °C. To show the connection between the two reactions, the yields of recovered TBPA and combined acetates have been plotted against the combined yields of brominated TBPA:s (Fig. 3), using data of Table 1. These were chosen to represent well-behaved as well as less well-optimized preparations of the $TBPA^{+\cdot}$ salt, varying the method of synthesis and ageing period. The trend is clear: A high yield of acetate(s) is coupled to a low or zero yield of brominated product(s) or *vice versa.*

In dichloromethane at 2–5 °C, there is no sign of product reversal; acetate products are still predominant. We attribute this behaviour to the stronger ion-pairing between $TBPA^{+\cdot}$ and BF_4^- promoted in dichloromethane.[31,32]

Table 1. Products from the reaction between $TBPA^+BF_4^-$ and $Bu_4N^+(AcO)_2H^-$ under different conditions. Freshly prepared $TBPA^{+\cdot}$ salt from the Ag^+/I_2 method was used.

Solvent (temperature/°C)	Ageing period of salt/h	$[TBPA^+]/[AcO^-]$	TBPA	Yield/% Acetate(s)[a]	Brominated TBPA[b]
CH_3CN(20)	1	1:2	52	76	0
CH_3CN(20)	1	1:2	49	48	2
CH_3CN(2–5)[c]	1	1:2	31	1	30
CH_3CN(20)	24	1:2	39	8	10
CH_3CN(20)[d]	24	1:1	57	4	12
CH_3CN(20)	48	1:2	28	0	29
CH_3CN(20)	48	1:2	57	30	5
CH_3CN(20)	48	1:5	43	20	6
CH_3CN(20)	120	1:1	59	18	3
CH_3CN(20)	192	1:2	33	0	32
CH_2Cl_2(2–5)	1	1:2	49	55	4

[a]Calculated for a 2 and 4e^- process for acetate and diacetate, respectively. [b]Calculated on the assumption that 1 mol of bromine is required to substitute one position in TBPA. [c]Average of two experiments. [d]Inverse addition.

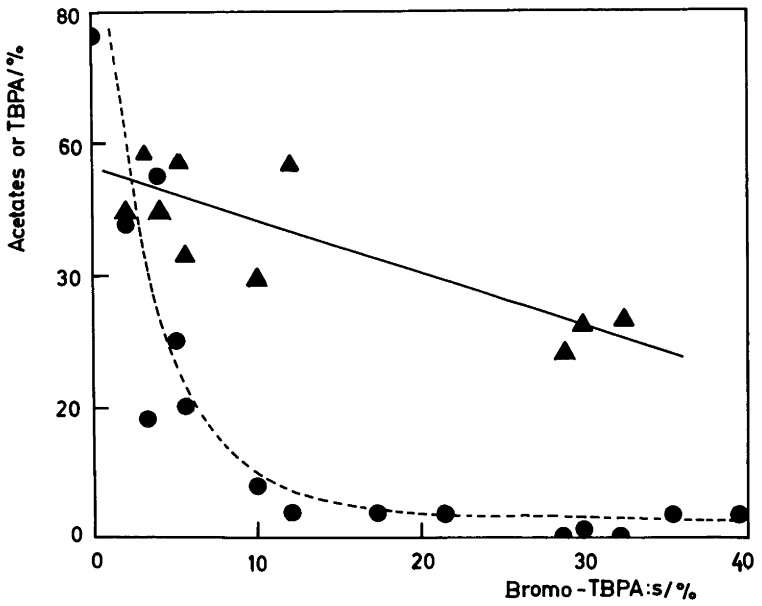


Fig. 3. Plot of yield of acetates (●) and recovered TBPA (▲) *vs.* yield of brominated TBPA:s.

The reaction between $TBPA^{+\cdot}$ and tetrabutylammonium pelargonate (which, as noted above, still contained *ca.* one molecule of water per $RCOO^-$) gave 53 % TBPA, 1.5 % Br-TBPA and 80 % pelargonic acid [*cf.* eqn. (6)]. No products of the Kolbe type were formed, a positive search for octane, octenes, hexadecane and octyl pelargonate being performed. The acyloxylation product (*3*, with $C_8H_{17}COO^-$ in the 2-position instead of CH_3COO^-) was formed in 52 and 46 % yield in acetonitrile and dichloromethane, respectively.

Table 2. Products from the reaction between $TBPA^{+\cdot}$ and Bu_4N^+ $[t\text{–}C_4H_9CH(CN)COO]_2H^-$ under different conditions. Freshly prepared $TBPA^{+\cdot}$ salt from the Ag^+/I_2 method was used throughout. $[TBPA^{+\cdot}]/[RCOO^-] = 0.5$.

Solvent (temperature/°C)	TBPA	Yield/% Brominated TBPA:(s)[a]
$CH_3CN(-40)$	31	36
$CH_3CN(20)$	41	19
$CH_2Cl_2(20)$	52	5

[a]Calculated on the assumption that 1 mol of bromine is required to substitute one position in TBPA.

The reaction between $TBPA^{+\cdot}$ and *t*-butylcyanoacetate (used as the crystalline homoconjugated complex) gave products as shown in Table 2. Qualitatively, the same behaviour as for the acetate was found: Low temperatures in acetonitrile favoured the formation of brominated TBPA:s, use of dichloromethane reduced their formation. No coupling products according to eqn. (5) were detectable (limit, ≤1 %). No acyloxylation product was detectable, and in view of the less well-behaved kinetics (see below) we did not pursue the identification of any further products at present stage.

Since we had experienced initial problems with the appearance of chlorinated TBPA:s in the acyloxylation experiments, the chlorine being introduced into the system *via* a commercial sample of tetrabutylammonium hydroxide strongly contaminated by chloride ion, the reaction between $TBPA^{+\cdot}$ and tetrabutylammonium chloride was studied as well. Products of oxidative chlorination, in all probability formed according to the ECE mechanism (eqns. (7)–(9), with Cl^- instead of AcO^-), were found: Cl–TBPA (49 %) and Cl_2–TBPA (11 %) in addition to recovered TBPA (56 %). As a curiosity we also noted a 2 % yield of the chlorodebromination product, presumably formed *via* an $S_{ON}2$-type mechanism.[33] Similar results were obtained from the reaction between

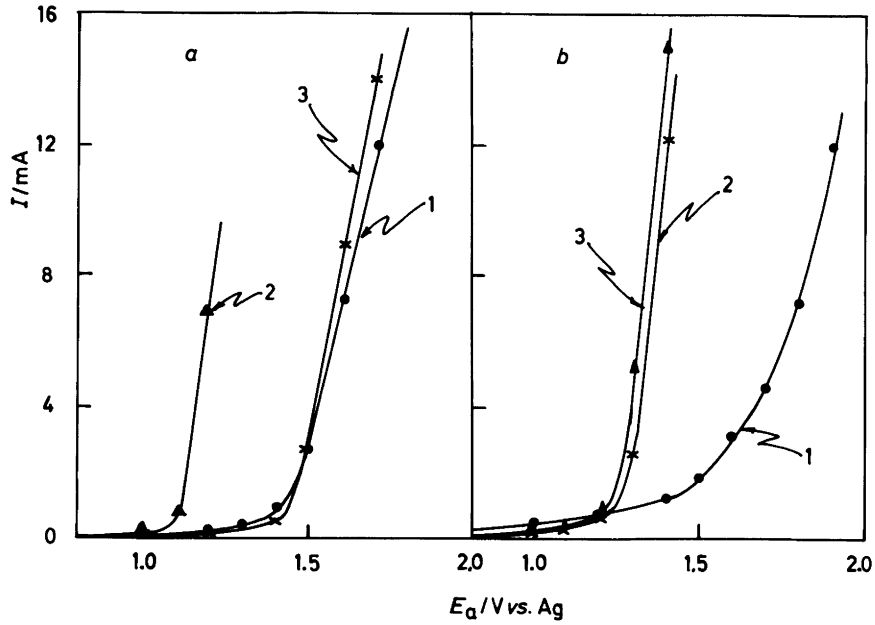


Fig. 4. Plots of *I* (mA) *vs.* E_a (V *vs.* Ag wire) for a) 6.17 mM $(AcO)_2H^-$ (curve 1), 3.00 mM TBPA (curve 2) and 6.13 mM $(AcO)_2H^-$ + 3.00 mM TBPA (curve 3) in acetonitrile at a glassy carbon anode and b) 6.17 mM $(AcO)_2H^-$ (curve 1), 3.07 mM TBPA (curve 2) and 6.22 mM $(AcO)_2H^-$ + 3.07 mM TBPA (curve 3) in acetonitrile at a platinum anode.

electrogenerated $TBPA^{+\cdot}$ in the presence of chloride ion (see Experimental).

Finally, we qualitatively noticed that $TBPA^{+\cdot}$ solutions were decolorized by addition of trifluoroacetate* and, strangely enough, trifluoromethanesulfonate ion. We do not know the reason for the latter reactivity** but found it to be in accordance with the fact that the attempts to utilize preparations of $TBPA^{+\cdot}$ trifluoromethanesulfonate for kinetic studies were thwarted by the fast decomposition (~h) of this salt in solid phase.

Electrochemical studies. We used anodic acetoxylation of TBPA for the synthesis of *3* (yield, 45 %) and in this context we also measured current/potential (CP) curves for TBPA oxidation in acetonitrile in the absence and presence of acetate ion. On glassy carbon, the electrode material employed by Schmidt and Steckhan[9] for anodic oxidation of TBPA/pelargonate mixtures, the CP curve for TBPA/AcO^- almost coincided with that of AcO^- alone (Fig. 4a), whereas on Pt it coincided with that of TBPA alone (Fig. 4b). The latter behaviour is that required to achieve acetoxylation conditions, whereas the former one would seem to indicate that co-electrolysis of TBPA and AcO^- takes place.

This would neatly explain the results of Schmidt and Steckhan who used glassy carbon in their $TBPA^{+\cdot}$ mediated oxidation of $RCOO^-$, *e.g.*, pelargonate, and in this case obtained a low yield (6 %) of octyl pelargonate (the butyl ester was also found in similar amounts but is presumably an artefact due to decomposition of tetrabutylammonium pelargonate under GLC conditions, a well-known phenomenon for tetraalkylammonium salts of nucleophilic/basic anions[35]). This would then be formed *via* the carbonium ion pathway of the Kolbe reaction [eqn. (10)]. We would also venture to guess that the R group in the RO part of the ester function has rearranged *via* R^+, at least partially. This is commonly found in such systems.[1]

*Tri-*p*-tolylammoniumyl, a weaker electrophile than $TBPA^{+\cdot}$, is known to react with trifluoroacetate ion; see Ref. 34.

**For similar cases of reactivity of nucleofugic anions, see Ref. 34a.

$$RCOO^- \xrightarrow[-CO_2]{-2e^-} CO_2 + R^+ \xrightarrow{RCOO^-} RCOOR \quad (10)$$

Kinetic studies. Since the initial aim of this project was to determine ET rate constant for the reaction between $TBPA^{+\cdot}$ and $RCOO^-$ [eqns. (11)–(12)] in the hope of being able to extract $E^\circ(RCOO^\cdot/RCOO^-)$ values *via* the Marcus treatment, the kinetics to be reported below mostly

$$TBPA^{+\cdot} + RCOO^- \rightleftharpoons TBPA + RCOO^\cdot \quad (11)$$

$$RCOO^\cdot \rightarrow R^\cdot + CO_2 \quad (12)$$

reflect the planning of such a study. Only after a long period of experimentation showing erratic results did it become evident that the mechanism given by Schmidt and Steckhan[9] [eqns. (11)–(12)] could not be correct. Instead it was deduced from subsequent product and spectroscopic studies that eqns. (7)–(9) (for acyloxylation) and (3) (for the bromination of TBPA) should represent close approximations of the molecular events taking place in these systems. It then becomes obvious that the observed rate constants (k_{obs}), determined as described below, must reflect a much more complex reaction scheme than simple ET between $TBPA^{+\cdot}$ and $RCOO^-$.

The kinetics of the reaction between $TBPA^{+\cdot}$ and $RCOO^-$ were monitored at 5.0 or 20.0 °C under pseudo-first-order conditions (ratio $[TBPA^{+\cdot}]/[RCOO^-] \leq 0.1$) at the 705 nm absorption maximum of $TBPA^{+\cdot}$; initial absorbance was between 0.2 and 0.6 and final absorbance around 0. Both the acetate and pelargonate homoconjugates behaved well under these conditions, but since the acetate salt is much easier to obtain in a defined, crystalline state, most kinetic runs were performed with acetate ion. A typical kinetic trace (digitized data, plotted by a table-top computer) is shown in Fig. 5; from this the part between *ca.* 0.25 and 2 half-lives was used to calcu-

Table 3. Observed rate constants (k_{obs}) for the reaction between $TBPA^{+\cdot}$ and $Bu_4N\ (AcO)_2\ H$ in acetonitrile at 5.0 °C, using different preparations of $TBPA^{+\cdot}BF_4^-$ after different ageing periods. The $TBPA^{+\cdot}$ salt was prepared *via* the Ag^+/I_2 method. $[TBPA^{+\cdot}]_o \approx 0.1$ mM, $[(AcO)_2H^-]_o = 1.00$ mM.

No of salt preparation	Ageing period/h	Number of runs	k_{obs}/s^{-1}
1	1	4	16.8
2	1	5	19.6
2	200[a]	1	26
3	1	2	16.6
4	1	1	16.0
4	500[a]	1	39
5	1	1	16.0
5	700[b]	1	150
		Weighted average:[c]	17.7(2.7)

[a]Stock solution of salt, aged at 0 °C. [b]Solid salt, aged at 0 °C. [c]Only runs with freshly prepared salt.

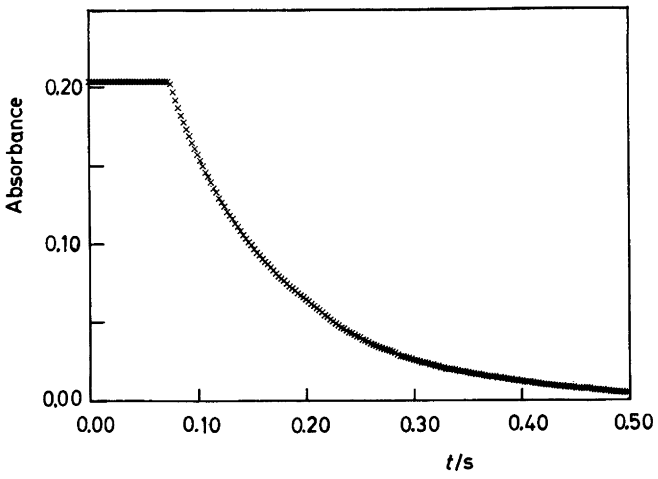


Fig. 5. Kinetic trace of the reaction between $TBPA^{+\cdot}$ (0.10 mM, prepared by the NO^+ method) and $(AcO)_2H^-$ (1.0 mM) at 5.0 °C.

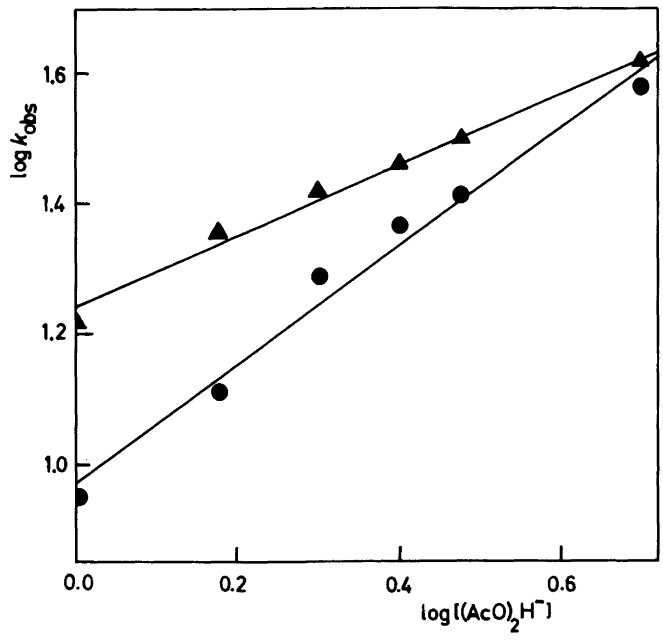


Fig. 6. Plot of $\log(k_{obs}/s^{-1})$ *vs.* $\log\{[(AcO_2)H^-]/mM\}$ in acetonitrile at 5.0 °C. Runs with Ag^+/I_2 prepared salt (▲); runs with NO^+ prepared salt (●).

late k_{obs} by fitting the data to an exponential function[28b] *via* the non-linear regression method developed by Marquardt.[36] This value generally is somewhat larger than that obtained *via* the usual $\log(A_t - A_\infty)/t$ plot (A denotes absorbance), routinely computed immediately after each run in order to check the quality of the data.

Table 3 illustrates the problems connected with the use of $TBPA^{+\cdot}$ preparations, synthesized by

Table 4. Observed rate constants (k_{obs}) for the reaction between $TBPA^{+\cdot}$ and Bu_4N $(AcO)_2H$ in acetonitrile at 5.0 °C in the presence of varying amounts of TBPA. The $TBPA^{+\cdot}$ salt was prepared by the NO^+ method. $[TBPA^+]_0 \approx 0.1$ mM, $[(AcO)_2H^-]_0 = 1.00$ mM.

[TBPA]/mM	Number of runs	k_{obs}/s^{-1} [a]
0.087[b]	2	9.5
0.11[b]	5	8.7
0.21[b]	3	9.3
1.05[c]	2	8.7
2.01[c]	2	8.4
	Weighted average:	8.9(5)

[a]Average value. [b][TBPA] after synthesis. [c]TBPA added.

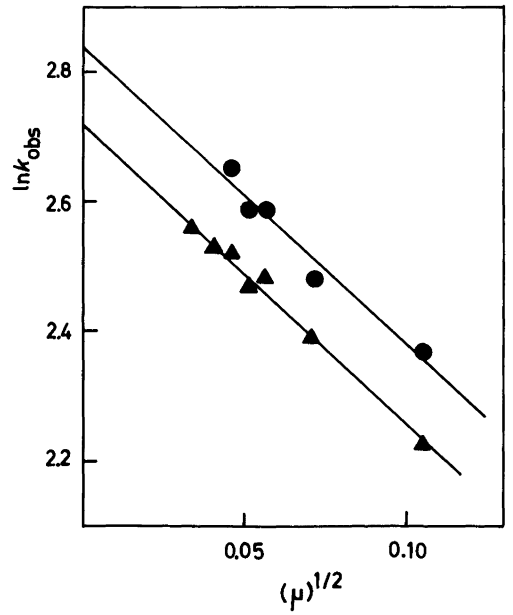


Fig. 7. Plots of $\ln(k_{obs}/s^{-1})$ *vs.* $(\mu)^{\frac{1}{2}}$ $(M^{\frac{1}{2}})$ in acetonitrile at 5.0 °C. Runs with Ag^+/I_2 prepared salt (●); runs with NO^+ prepared salt (▲).

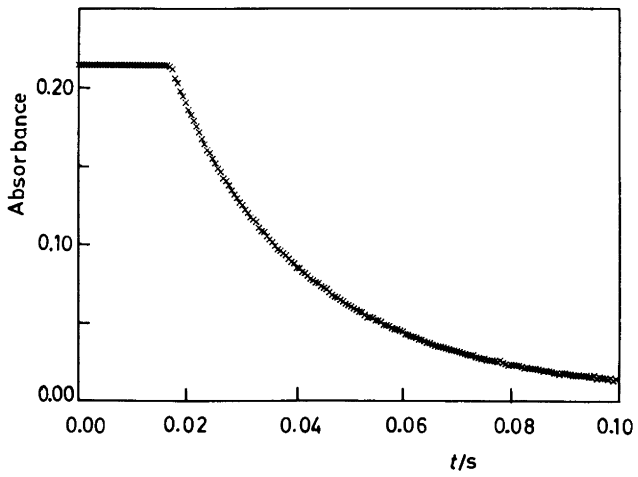


Fig. 8. Kinetic trace of the reaction between $TBPA^{+\cdot}$ (0.10 mM, prepared by the NO^+ method) and $(C_8H_{17}COO)_2H^-$ (1.0 mM) at 5.0 °C.

the Ag^+/I_2 method, aged either in solution or in solid phase. With ageing, rate constants increase strongly, presumably due to the formation of more reactive species. A dication of the type shown in eqn. (3) is a likely candidate for such an increased reactivity.

However, even a freshly prepared salt from the Ag^+/I_2 method exhibits higher rate constants than one synthesized *via* the NO^+ method (Table 4). In the latter case, the solid salt does not need to be isolated, since the second product, nitrous oxide, can be easily removed by argon flushing. This method requires a small excess of TBPA to ensure that all NO^+ reacts, and hence it was necessary to check if TBPA influences k_{obs}. No such dependence was seen (Table 4). This constitutes further evidence against the ET mechanism [eqn. (11)], since added TBPA is predicted to decrease k_{obs} by virtue of its influence on equilibrium (11).

Fig. 6 shows the dependence of $\log k_{obs}$ upon $\log[AcO^-]$ at 5.0 °C for the two types of salt preparations, the slopes being 0.5(1) and 0.9(2) (NO^+ derived salt), respectively. At 20.0 °C, the corresponding slopes are 0.2(4) and 0.6(2), respectively.

Fig. 7 shows the effect of an added inert salt, Bu_4NBF_4, upon $\ln k_{obs}$, measured on both types of $TBPA^{+\cdot}$ salt. The slopes are negative and identical, $-4.6\ M^{-\frac{1}{2}}$, indicating that oppositely charged

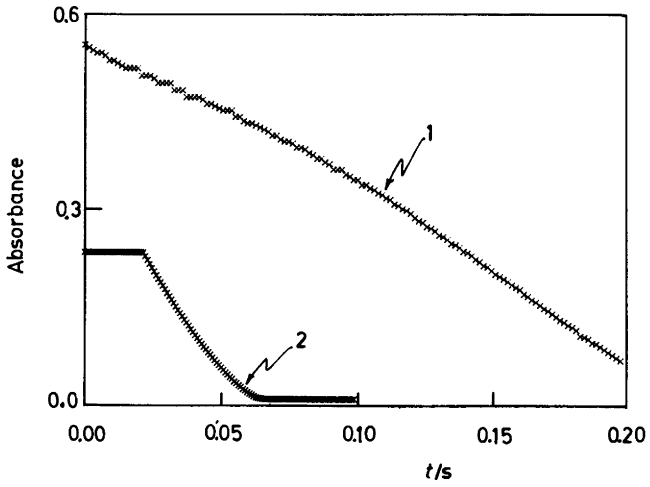


Fig. 9. Examples of kinetic traces from the reaction between $TBPA^{+\cdot}$ and $[t\text{-}C_4H_9CHCN(COO)]_2H^-$ in acetonitrile at 20.0 °C. Curve 1, NO^+ prepared salt; curve 2, Ag^+/I_2 prepared salt.

Table 5. Summary of rate constants for the reaction between $Ar_3N^{+\cdot}$ and $(RCOO)_2H^-$, expressed in second-order form.

R in $(RCOO)_2H^-$	Ar in $Ar_3N^{+\cdot}$	Temp/°C	$k_{obs}/M^{-1}s^{-1}$	
			NO^+ salt	Ag^+/I_2 salt
CH_3	4-Bromophenyl	5	8.9×10^3	1.8×10^4
CH_3	4-Bromophenyl	20	5.8×10^4	1.1×10^5
C_8H_{17}	4-Bromophenyl	5	4.4×10^4	10^5
t-C_4H_9CHCN	4-Bromophenyl	5	Not measurable	
CH_3	4-Methoxyphenyl	20.0	0.053	0.067

species are involved in the two cases as demanded by eqn. (13), the usual relationship between rate constant and ionic strength, μ; k_o is the rate constant in the absence of any salt, Z_A and Z_B are the charges of the two species, and α a constant, for acetonitrile at 5 °C equal to 1.82.[37] From eqn. (13) and the slopes above, Z_AZ_B can be calculated to be −1.3.

$$\ln \frac{k}{k_o} = 2\, Z_A Z_B\, \alpha\, \sqrt{\mu} \qquad (13)$$

Pelargonate (as the homoconjugate) was equally well-behaved kinetically *vs.* $TBPA^{+\cdot}$, as exemplified by Fig. 8, but again gave higher rate constants with the Ag^+/I_2 derived $TBPA^{+\cdot}$. On the contrary, *t*-butylcyanoacetate did not show first-order behaviour; absorbance/time curves corresponding to anything between a zero-order plot and one showing an induction period (Fig. 9) were obtained and no k_{obs} values could be calculated.

A few kinetic runs were performed with the much weaker oxidant, tris(4-methoxyphenyl)ammoniumyl (E° = 0.76 V) and $(AcO)_2H^-$ in order to test the effect of lowering the oxidation potential. The measured rate constants were *ca.* 10^6 times smaller than that of $TBPA^{+\cdot}$, and again higher rate constants were obtained for radical cation salt preparations *via* the Ag^+/I_2 method. All rate constants, expressed in second-order form to make them comparable, are summarized in Table 5.

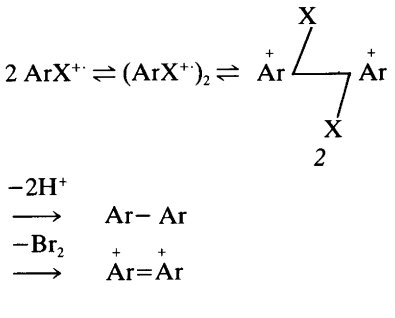
Concluding mechanistic remarks. One of the very few good Kolbe-simulating reagents in homogeneous medium is $SO_4^{-\cdot}$. Why is this so? One obvious reason is the demand for a strong oxidant, $E^\circ(SO_4^{-\cdot}/SO_4^{2-})$ being estimated at *ca.* 2.5 V in water.[10] This species can rapidly remove an electron from the difficultly oxidizable $RCOO^-$ (E° between 2.2 and 2.4 V in water) *via* an outer-sphere mechanism. Equally important is the mode of generation of $SO_4^{-\cdot}$; it is formed in very low concentration by thermal decomposition of persulfate and thus reactions between $SO_4^{-\cdot}$ and $R^\cdot$, also present in very low steady-state concentration, have very low probability of occurring. Thus radical reactions are favoured, and the carbonium ion mechanism possible in the electrochemical Kolbe reaction is not taking place.

Little is known about the reactivity of other outer-sphere oxidants of lower oxidizing power *vs.* $RCOO^-$, simply because few are available. Metal ions generally tend to accept $RCOO^-$ as ligand(s) and then the mechanism of any oxidative decarboxylation process would be of the inner-sphere variety.[38] However, two limiting cases have recently been described, involving attempts at oxidizing acetate ion by heteropoly ions.[39] Such ions are clusters of tungsten or molybdenum oxide octahedra, symmetrically arranged around a central metal ion, *e.g.*, Co(III). The central ion is completely shielded from the medium and cannot bind to any organic ligands present; only oxygens of very low basicity are exposed toward the solution.

One such ion, $Co(III)W_{12}O_{40}^{5-}$ [$E^\circ(5^-/6^-)$ = 1.0 V] was completely unchanged after heating it with an excess of acetate ion in HOAc/water (4:1) at 102 °C for 150 h.[40] Another heteropoly ion, $Ce(IV)Mo_{12}O_{42}^{8-}$ [$E^\circ(8^-/9^-)$ = 1.42 V] was completely stable toward acetate ion in HOAc/water (1:1) at 50 °C for 10 h.[28b] The latter ion instantaneously oxidized TBPA to $TBPA^{+\cdot}$ at 20 °C

in a similar medium.[41] Even if the electrostatic situation for oxidation of acetate ion by the negatively charged heteropoly ion would seem to be unfavourable in comparison to the neutral TBPA molecule, the difference is compensated for by the much harsher reaction conditions used with acetate ion.

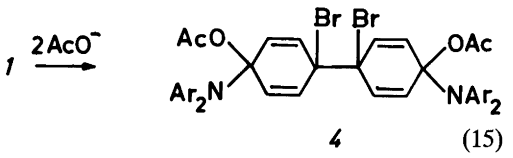
From this we conclude that $TBPA^{+\cdot}$ cannot react with acetate or alkanecarboxylates according to an outer-sphere mechanism, and this is borne out by the experimental results. At 20 °C in acetonitrile, or generally in dichloromethane, acyloxylation of the aromatic nucleus takes place, a well-known and thoroughly explored reaction since the mid-sixties. Mechanistically, such reactions are of the ECE type [eqns. (7)–(9)], and it is pertinent to note that many substrates of considerably higher E° than TBPA (such as naphthalene with $E^\circ = 2.08$ V) for many years have been assumed to react nucleophilically with acetate ion



(14)

and not with electron exchange. There is no reason why TBPA should behave differently.

While the acyloxylation process represents a well-trodden path, the competing dimerization/bromination reaction, although known as a phenomenon, has some unusual features. It is not common to find an almost complete switch in mechanism over a temperature range of merely 15°, but this is what the data of Fig. 3 indicate. Effenberger[31a] found similar behaviour in the chemistry of mesitylene radical cation; over *ca.* 20° a switch from biaryl coupling to side-chain substitution took place. This behaviour was ascribed to complex formation between two $ArH^{+\cdot}$, strongly favoured at low temperature [eqn. (14)], with loss of 2 H^+ in the last step and thus inducing



(15)

biaryl coupling. Our results are analogous, and it is only the presence of two bromine groups at the coupling sites [eqn. (14), X = Br)] that presents some unusual mechanistic problems. The first coupling product [*1*, see eqn. (3)] is formally a bromine adduct of a diphenoquinonebisiminium ion* (*2*), and in principle such a species would be a good example of a species containing "positive bromine" and thus capable of brominating other molecules, as it for example does with TBPA (Tables 1 and 2) or added cyclohexene.

The acceleration of this reaction by acetate ion can be understood either in terms of extensive loading of *1* by electron-withdrawing groups (*4*), thus further increasing the propensity to lose bromine [eqn. (15)], or, more likely, by removal of Br^+ from *1* by acetate ion to give AcOBr which is an excellent brominating agent. Effenberger *et al.*[41a] have described a similar case in which acetone acted as a Br^+ acceptor.

The kinetic results are, as already mentioned, reflections of the rather complex interplay between the ECE and coupling mechanisms. The activation parameters that can be formally calculated from the data of Table 5 already tell us that a complex kinetic scheme must be involved: ΔH^+ is *ca.* 20 kcal mol^{-1} while ΔS^+ comes out at *ca.* 30 e.u., hardly a reasonable value for a simple bimolecular encounter between two oppositely charged ions.

Implications for other work. The most important conclusion of the experimental work described here is that $TBPA^{+\cdot}$ does not undergo ET with $RCOO^-$; instead its *electrophilic* properties manifest themselves through the wellknown acyloxylation process. A second mode of reactivity, favoured in polar medium at lower temperatures, involves formation of a dimeric dication (*1*), capable of brominating other species present and producing othere dicationic species, such as *2*.

The former conclusion contradicts a preliminary positive judgement of the feasibility of ET between $TBPA^{+\cdot}$ and pelargonate,[10] based on the

*Ions of type *2* are relatively stable[42] and the corresponding salts can be isolated.[43]

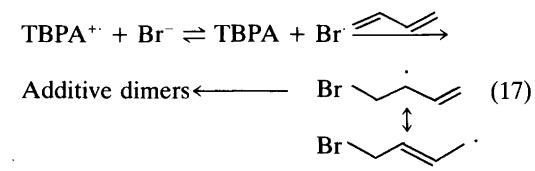
Marcus treatment. This involved an estimate of the ET rate constant, for which the most critical parameters are the E° values of the redox couples involved. Here lies the major uncertainty in the choice of $E^\circ(RCOO^{\cdot}/RCOO^-)$ for acetonitrile, since the free energies of transfer from water to acetonitrile of the species of the reaction defining the standard potential [eqn. (16)] are not very well known. According to the best available data,[44] the two ionic species of eqn. (16) are much less stable in acetonitrile than in water, free energies of transfer being presently estimated at *ca.*

$$CH_3COO^{\cdot}(aq) + \tfrac{1}{2}\,H_2(g) \rightarrow CH_3COO^-(aq) + H^+(aq) \qquad (16)$$

14 and 11 kcal mol^{-1}* for acetate ion and the proton, respectively. With these parameters, $E^\circ(AcO^{\cdot}/AcO^-)$ in acetonitrile could be estimated to be as low as 1.3 V.[11]

We have no entirely satisfactory explanation for the discrepancy between theory and experiment that has now emerged, but suggest that one reason may be that the conditions for the low E° values estimated for oxidation of acetate ion in acetonitrile are never reached in experimental situations due to the extremely strong hydration ability of $RCOO^-$. In this respect $RCOO^-$ is similar to fluoride ion.[45] Here one also can notice the recent,[5] high value of $E^\circ(AcO^{\cdot}/AcO^-) = 2.35$ V, estimated for acetonitrile/water (4:1). To avoid the experimental problems connected with this behaviour, we used homoconjugated ions, for which it is known in the acetate case that their oxidation potential is 0.1–0.2 V higher than that of the solvated ion.[46]

The results reported above may have some relevance for mechanistic discussions of the application of $TBPA^{+\cdot}$ and related triarylammoniumyls as mediators and catalysts. Their mediating or catalyzing effect has generally been assumed to depend on their ET reactivity, as in the carboxylate case, and other modes of action, such as hydrogen atom transfer, have been ruled out.[47] As an example, high ET activity of $Ar_3N^{+\cdot}$ toward substrates with >1 V higher redox potentials has often been postulated, as in the oxidation of benzylic[47] and allylic[48] alcohols, and benzylic esters.[49] By analogy with the carboxylate case, we doubt that these reactions involve non-bonded ET; instead mechanisms involving electrophilic and/or radical reactivity of $Ar_3N^{+\cdot}$ should be contemplated. Since moreover the favourite catalysts contain 4-bromo substituents, the complexities introduced by eqn. (3) cannot be ignored, especially in polar media. The latter possibility lies for example close at hand in the $TBPA^{+\cdot}$ mediated bromination of butadiene to form additive dimers, assumed to occur *via* eqn. (17).[50]



(17)

Finally, a recently[51] described electrode coating of poly(4,4′-dibromo-4″-vinyl)triphenylamine which was suggested to catalyze the anodic oxidation of $RCOO^-$, most likely derives its short-lasting effect from reactions similar to those of eqns. (7)–(9), *i.e.*, the aryl groups of the polymer are acyloxylated and thus the film rapidly loses its "catalytic" effect.

Other uses of $TBPA^{+\cdot}$ as an ET catalyst are not marred by the same problems as the reactions commented upon above, even though recent work[52] on catalyzed Diels-Alder reactions would seem to suggest some restraint in the acceptance of ET mechanisms.

Experimental

General methods. UV spectra were obtained with a Cary 219 UV/VIS spectrophotometer. ^{1}H NMR spectra were recorded on a Varian XL-300 MHz instrument. Mass spectral analysis was carried out on a Finnigan 4021 instrument at 70 eV using a GLC inlet.

GLC analysis was carried out by using a Varian 1400 gas chromatograph, equipped with an HP-3380A integrator, on either a 2 m×3 mm Porapak P column for the analysis of methane and ethane or a 2 m×3 mm 3% OV-101 on Chromosorb Q column. Yields on the latter column were determined using bimesitylene as internal standard, calibrated against authentic samples of TBPA, formed products, expected Kolbe-type products and *3*. The identification of the products was based on GLC/MS comparison with authentic samples (only GLC/MS for mono- and di-

*Earlier estimates were 3.3 and 6.9 kcal mol^{-1}.

halogenated and bisacetoxylated TBPA). The 2-nonanoyloxy derivative of TBPA was analyzed on an HP 5380A gas chromatograph, equipped with an HP 18850 integrator and a glass insert in the injection port (column, 0.5 m×1.8 mm glass-lined 5 % OV-1701 on Chromosorb W), using triphenylene as an internal standard. Methane and ethane were analyzed by injection of a sample of the gas phase above the solution and the concentration determined by comparison with a calibration curve. Iodometric titration was performed on a Mettler DL-40 Memo Titrator.

Materials. Tris(4-bromophenyl)amine was prepared as described by Baker *et al.*[53] and recrystallized three times from heptane.

Tris(4-methoxyphenyl)amine was synthesized *via* an improved method for substituting aromatic halogen against methoxy described by Bacon and Rennison.[54] The recipe was scaled up by a factor of six and gave the methoxy derivative in 90 % yield (96 % purity, with 4 % of bis(4-methoxyphenyl)phenylamine, as analyzed by GLC/MS). Two recrystallizations from heptane gave a pure sample of white crystals, m.p. 96–97 °C (lit.[55] 94.5 °C).

The triarylammoniumyl tetrafluoroborates were prepared by treatment of the triarylamine with $AgBF_4/I_2$, as described by Barton *et al.*[17] In order to remove all traces of AgI, the dichloromethane solution was filtered through Hyflo Super-Cel before it was poured into dry ether. The radical cation contents were determined iodometrically, and UV spectra were found to be in good agreement with published data.[56,57] The radical cations were also prepared by treatment of the triarylamines with $NOBF_4$ in acetonitrile,[21] where the radical cation concentrations were determined spectrophotometrically at 705 ($TBPA^{+\cdot}$) and 720 nm, respectively. After dilution the solutions were used directly for kinetic measurements. The results are summarized as follows: $TBPA^{+\cdot}BF_4^-$, yield from Ag^+/I_2 method *ca.* 50 % with a purity of 96–98 %; yield from $NOBF_4$ method 55 %, λ_{max} in acetonitrile (ε), 705 (3.2×10^4) and 365 nm (2.4×10^4). Tris(4-methoxyphenyl)ammoniumyl tetrafluoroborate, yield from Ag^+/I_2 method 95 % with a purity of 96–98 %; yield from $NOBF_4$ method 100 %, λ_{max} in acetonitrile (ε), 720 (2.9×10^4) and 375 nm (1.5×10^4).

Tetrabutylammonium hydrogendicarboxylates were prepared according to the method described for the acetate salt.[28b] The *t*-butylcyanoacetate/acid complex had m.p. 95.5–97 °C and was used without recrystallization.

Acetonitrile (Baker HPLC reagent) was stored in the dark and used without further purification (extensively purified solvent did not change its behaviour in kinetic runs). Dichloromethane (Merck zur Rückstandsanalyse) was dried and stored over 3 Å molecular sieves. All other chemicals were of highest commercial quality avilable.

Kinetic runs. Measurements with $TBPA^{+\cdot}$ solutions were performed in a thermostatted stopped-flow spectrophotometer (2 mm cell path), HI-TECH SF-3L with control unit SF-3C and data display and storage system DSF-3 from HI-TECH Scientific Ltd., Salisbury, England. The system was connected to an HP-9835A tabletop computer for control of the measurements and storage of the transmittance/time readings. After thermal equilibration, the solutions were mixed and the transmittance at 705 nm monitored. For calculation of rate constants, see text.

With tris(4-methoxyphenyl)ammoniumyl solutions measurements were performed in a thermostatted cuvette holder of the Cary 219 spectrophotometer, interfaced to an HP-85 microcomputer. Five hundred μL of the acetate solution were placed in a cuvette (2 mm cell path) in the thermostatted cell compartment. After thermal equilibration, the reaction was initiated by addition of prethermostatted radical solution (150 μL), the absorbance at 720 nm being recorded as a function of time. Normally, 200 absorbance/time readings were collected. The calculation of rate constants was carried out as for $TBPA^{+\cdot}$ runs.

Preparation of (2-acetoxy-4-bromophenyl)-bis(4-bromophenyl)amine. A 0.1 M solution of Bu_4NBF_4 in acetonitrile (75 ml) containing 3 mM TBPA and 6 mM $Bu_4N(AcO)_2H$ was electrolyzed under Ar at 20 °C by using a Pt anode (10 cm^2) and Pt cathode (wire) in a three-compartment cell at a constant current of 10 mA (anode potential 1.13–1.20 V *vs.* Ag wire). After passage of 2F/mol of TBPA the solvent was evaporated. The residue was extracted three times with diethyl ether and the combined extracts washed with saturated sodium hydrogen carbonate solution, dried and evaporated. GLC analysis showed that about 60 % of the amine had been consumed and

given acetoxylated amine (*3*) in 45 % yield and a trace of bisacetoxylated amine. The procedure was repeated three times and the combined product mixtures were subjected to flash chromatography on a silica gel column with ethyl acetate/light petroleum (5:95) as the eluent. This gave *3* of 95 % purity, m.p. 94–96 °C. MS: *m/z* (relative intensity), 540(M^+), 541(3.5), 539(4.0), 537(2.0), 499(8.1), 497(9.7), 495(5.0), 419(1.5), 417(2.8), 415(1.5), 339(2.2), 337(2.5), 260(8.2), 76(17), 43(100). ^{1}H NMR (acetone-d_6): 1.82 (s, CH_3); 6.95 and 7.45 (H2 and H3 in 4-BrC_6H_4); 7.42, 7.47 and 7.17 (H3, H5 and H6 in 2-acetoxy-4-bromophenyl; J_{35} = 2.4 Hz, J_{56} = 8.5 Hz).

Reactions with TBPA$^{+\cdot}$; product studies. Solutions of chloride or the carboxylate/acid complex (1 or 0.5 mmol in 10 mL of acetonitrile) were thermostatted at the desired temperature. A solution of TBPA$^{+\cdot}BF_4^-$ (0.5 mmol in 20 mL of acetonitrile) was added dropwise with stirring. The blue radical cation solution was immediately decolourized and turned yellow-brown. The reaction mixture was evaporated and the residue extracted with ether. The organic phase was washed with saturated sodium hydrogen carbonate solution, dried and analyzed by GLC. The 2-nonanoyloxy derivative of TBPA was isolated by flash chromatography of the ether solution on a silica gel column, using ethyl acetate/light petroleum (5:95) as the eluent. MS: *m/z* (relative intensity), 638 (M^+), 639(0.29), 637(0.38), 499(8.7), 497(10.1), 495(3.9), 419(1.8), 417(2.6), 415(1.0), 339(1.6), 337(1.5), 260(6.4), 71(18), 69(16), 57(46), 55(40), 43(100). ^{1}H NMR (acetone-d_6): 0.88 (triplet, CH_3); 1.25 (–$(CH_2)_5$); 1.38 (CH_2 β to –COO^-); 2.1 (CH_2 α to COO^-); 6.95 and 7.45 (H2 and H3 in 4–BrC_6H_4); 7.42, 7.47 and 7.14 (H3, H5 and H6 in 2–C_8H_{17}COO–4–Br–Phenyl; J_{35} = 2.3 Hz, J_{56} = 8.5 Hz).

Reactions between TBPA$^{+\cdot}$ and $(AcO)_2H^-$ in which analyses for ethane and methane were performed, were conducted as above in a two-necked flask of a volume of 100 mL, equipped with a pressure-equilibrated dropping funnel (the total volume of the system was 230 mL) and a rubber septum. After the end of the reaction, samples of the gas phase were with-drawn by a gas-light syringe and analyzed by GLC (see above). The methane/ethane content was determined from calibration curves, made up using known amounts of the gases in the same apparatus and under the same conditions as used for the actual reactions.

Current/potential curves. These (see Fig. 4) were determined in an undivided cell with a Pt or glassy carbon anode of area 10 cm^2, a Pt cathode and an Ag wire as reference electrode, using an AMEL model 552 potentiostat. After each potential setting, the current was allowed to stabilize (1 min) before reading.

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