

Anodic Oxidations. VI. Products and Mechanism in the Electrochemical Oxidation of Toluene in Acetic Acid

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The anodic oxidation of toluene in acetic acid has been studied with potassium acetate, tetramethylammonium nitrate, and tetramethylammonium *p*-toluenesulfonate as the electrolytes. The mechanism of this oxidation was investigated by determining products, by observing rates of gas evolution, and by measuring current-anode potential relationships. The results suggest that product arises from two coexisting mechanisms—an electron transfer from the substrate in the primary process, or discharge of an anion to give a radical, which then abstracts a hydrogen atom from the substrate.

In the anodic oxidation of arenes it is common to observe products resulting from substitution on both the aromatic ring and the aliphatic side chain. For both nuclear cyanation with sodium cyanide in methanol¹⁻⁵ and nuclear acetoxylation with sodium acetate in acetic acid,⁶⁻⁸ there exists convincing evidence that electrons are transferred from the aromatic substrate in the primary process. The overall reaction entails a transfer of two electrons, which may occur in two steps so that a radical cation is a discrete intermediate, or, in a single two-electron transfer, very probably concerted with attack by the nucleophile, cyanide ion or acetate ion.

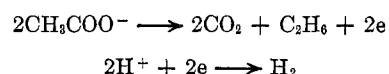
The nuclear acetoxylation reaction is accompanied by substitution of the side chain, which accounts for 28.6% of the total reaction with toluene and 50.5% of the products with ethylbenzene. There appear to be at least two discretely different mechanisms for anodic oxidation of the side chain, one in which the substrate is oxidized in the primary electrode reaction, and one in which the primary electron transfer is from either an anion or the solvent. The former type of mechanism has been demonstrated for the acetamidation reaction, usually effected with sodium perchlorate in acetonitrile,^{9,10} and the latter reaction path is followed in the side-chain methoxylation reaction.^{4,11-13} It has been suggested that this latter mechanism also prevails in the side-chain acetoxylation in the presence of nitrate ion,¹⁴ but this hypothesis is less attractive when the anion is perchlorate or even tosylate.^{7,15}

The present work is addressed to this problem of mechanism in the anodic acetoxylation of an arene sidechain. The anodic oxidation of toluene in acetic

acid has been studied with potassium acetate as the electrolyte, with tetramethylammonium nitrate as the electrolyte, with tetramethylammonium tosylate as the electrolyte, and with mixtures of the acetate and the quaternary ammonium compounds as the electrolyte. In these experiments the liquid products have been determined. In addition the composition of the gas generated during these oxidations and the rate at which it is evolved has been studied as a function of the current. As will be demonstrated, these data afford useful information as to which species undergo electron transfer at the anode and as to the relative potentials at which these oxidations occur. Finally, relationships between applied potentials and current have been studied for all three electrolytes in acetic acid, both in the absence and presence of the substrate, toluene.

Results

The electrolysis of a solution of acetate ion in glacial acetic acid results in a clean oxidation, the overall electrode reactions are almost exactly



and the coulombic yield approaches 2 mol of CO₂, 1 mol of H₂, and 1 mol of C₂H₆ per 2 F.⁸ This electrolysis will serve as a point of reference and basis of comparison for the studies to be described. An oxidation which affords, at the anode, 3 mol of gas per 2 F of charge passed will be designated as giving 100% Kolbe anode gas. If a lesser volume of gas is generated at the anode it will be designated as giving a lesser percentage of Kolbe anode gas. This arbitrary terminology will be maintained regardless of the nature of the gases formed at the anode and will refer only to the volume of gas produced. The composition of the total gas, the combination of that formed at both the anode and cathode, will, however, be given, and these data will serve as additional criteria for determining which species is being oxidized at the electrode.

When a 0.56 *M* solution of tetramethylammonium nitrate in acetic acid was electrolyzed at 400 mA, the rate of gas evolution was essentially constant with time at 15% Kolbe anode gas. The gas contained neither ethane nor methane, only trace amounts of carbon dioxide and 27% oxygen, with the remainder being hydrogen. This result was not changed detectably when 9% of the acetic acid in this solution was replaced with either acetic anhydride or water. The oxygen formed must arise from oxidation of nitrate ion, rather

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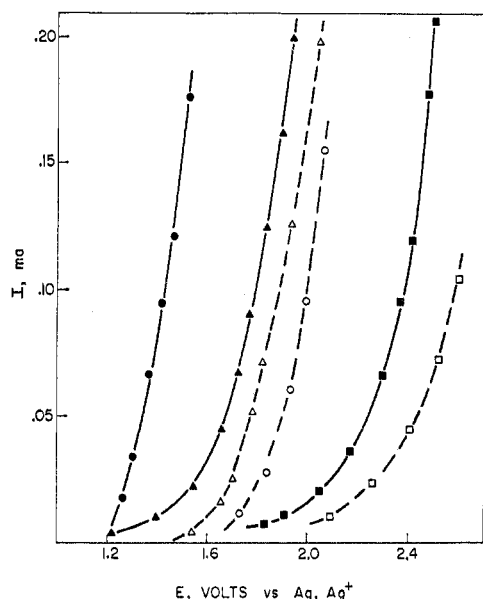


Figure 1.—Plots of electrolysis current *vs.* anode potential for solutions of tetramethylammonium nitrate (circles), tetramethylammonium *p*-toluenesulfonate (squares), and potassium acetate (triangles) in glacial acetic acid (presaturated with silver acetate), with and without added toluene. In each case measurements were first made on 50.0 ml of solution containing 0.035 mol of salt (solid lines), and then were repeated immediately after adding 2.0 ml of toluene (broken lines).

than from anodic oxidation of either water or acetic acid.

When a 0.56 *M* solution of tetramethylammonium *p*-toluenesulfonate in acetic acid was electrolyzed at 400 mA, a complex reaction, in which both the *p*-toluenesulfonate anion and acetic acid were oxidized, took place. After 48 min of electrolysis the amount of Kolbe anode gas was 7.8%. The gas composition was 1.4% methane and 14.2% carbon dioxide, with the remainder hydrogen. The coulombic yield of carbon dioxide was 8.8%. With increasing time of electrolysis both the per cent of Kolbe anode gas and the coulombic yield of carbon dioxide increase regularly. After 463 min of electrolysis the amount of Kolbe anode gas was 12.5%. At this point the gas contained 1.1% methane and 25.5% carbon dioxide, and the coulombic yield of carbon dioxide was 17.6%.

To determine relative oxidation potentials, acetic acid solutions containing both nitrate ion and acetate ion and acetic acid solutions containing both *p*-toluenesulfonate ion and acetate ion were electrolyzed and studied as a function of the current. In these electrolyses both the rates of gas evolution and the gas compositions change with time, and equilibrium between the gas composition in the solution phase and in the gas phase is not maintained. In all cases the % Kolbe anode gas starts at a high value, goes through a minimum, and then starts to rise again. A typical set of data is shown in Table I. In the remaining data to be presented only the values observed at the minimum will be given.

The results obtained on electrolysis of solutions containing both nitrate ion and acetate ion are shown in Table II. The currents are, of course, related to the anode potentials, and it is apparent from these results that as these potentials decrease, less and less acetate ion is being oxidized. It follows that nitrate ion is

TABLE I
ELECTROLYSIS OF AN ACETIC ACID SOLUTION CONTAINING
0.134 *M* TETRAMETHYLAMMONIUM NITRATE AND 0.556 *M*
POTASSIUM ACETATE AT 100 mA

Elapsed time, min	% Kolbe anode gas	Gas composition		Coulombic yield	
		% C ₂ H ₆	% CO ₂	C ₂ H ₆	CO ₂
32	59.2	20.6	46.0	57.5	64.0
77	50.7	16.2	47.2	41.0	59.6
122	46.1	14.6	49.5	35.0	59.1
144	44.4	14.6	50.1	34.3	58.6
242	41.9	15.2	54.0	34.5	61.1
307	41.1	15.8	56.7	35.5	63.5
347	47.9	17.0	57.9	41.7	70.7
387	54.0	18.3	58.7	48.2	77.1
429	63.3	19.2	58.7	56.0	85.2

oxidized at a lower potential than acetate ion, but it should be noted that even at the lowest current, one that is appreciably lower than would be used in a preparative experiment, significant amounts of acetate ion are being oxidized at the anode.

TABLE II
ELECTROLYSIS OF AN ACETIC ACID SOLUTION CONTAINING
0.134 *M* TETRAMETHYLAMMONIUM NITRATE
AND 0.556 *M* POTASSIUM ACETATE

Current, mA	Elapsed time, min	% Kolbe anode gas	Gas composition		Coulombic yield	
			% C ₂ H ₆	% CO ₂	C ₂ H ₆	CO ₂
400	44	67.1	17.9	50.7	54.3	70.6
200	80	59.5	17.5	49.8	49.0	69.4
100	307	41.1	15.8	56.7	35.5	63.5
50	473	12.9	11.1	55.3	15.5	38.5

The results for a similar set of experiments with *p*-toluenesulfonate ion and acetate ion in acetic acid are shown in Table III. In this system the oxidation of acetate ion is favored at the lower potentials, but some *p*-toluenesulfonate ion is still being oxidized even at the lowest current studied. For the three anions investigated the relative order of the oxidation potentials is nitrate < acetate < *p*-toluenesulfonate.

TABLE III
ELECTROLYSIS OF AN ACETIC ACID SOLUTION CONTAINING
0.133 *M* TETRAMETHYLAMMONIUM *p*-TOLUENESULFONATE
AND 0.556 *M* POTASSIUM ACETATE

Current, mA	Elapsed time, min	% Kolbe anode gas	Gas composition		Coulombic yield	
			% C ₂ H ₆	% CO ₂	C ₂ H ₆	CO ₂
450	69	26.2				
400	75	27.0	8.8	35.3	16.1	32.1
200	96	43.7				
99	183	59.5				
50	300	63.4	19.4	45.3	56.6	65.8

Results of measurements of anode potentials as a function of electrolysis currents for acetic acid solutions of *p*-toluenesulfonate, nitrate, and acetate salts, with and without added toluene, naphthalene, or anthracene are shown in Figures 1–3. Note in Figure 1 that the addition of toluene markedly increases the anode potential required to maintain a fixed current, while Figures 2 and 3 suggest that naphthalene and anthracene are oxidized at anode potentials substantially lower than are required to oxidize the anions. Additionally, it was observed in the naphthalene case that, if the current was maintained constant at a point along the rising portion of the current–potential curve, the anode poten-

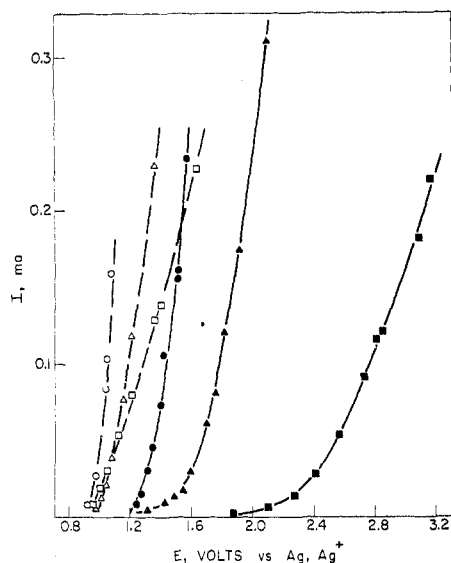


Figure 2.—Plots of electrolysis current vs. anode potential for solutions of tetramethylammonium nitrate (circles), potassium *p*-toluenesulfonate (squares), and potassium acetate (triangles) in glacial acetic acid (presaturated with silver acetate), with and without added naphthalene. In each case measurements were first made on 50.0 ml of solution containing 0.035 mol of salt (solid lines), and then were repeated after adding 3×10^{-3} mol of naphthalene (broken lines).

tial, initially quite steady, would eventually increase, over a period of several minutes, to the value obtained for the particular supporting electrolyte in the absence of the naphthalene.

As a further guide to mechanism the products of the anodic oxidation of toluene in acetic acid were determined with tetramethylammonium nitrate as the electrolyte, with tetramethylammonium *p*-toluenesulfonate as the electrolyte, with potassium acetate as the electrolyte and with mixtures of the acetate and the nitrate and of the acetate and the *p*-toluenesulfonate as the electrolytes. In each experiment toluene (20 ml, 0.188 mol) was subjected to oxidation, and 2 F of charge per mol of the toluene present was passed through the solution. The results are assembled in Tables IV, V, and VI.

TABLE IV

PRODUCTS IN THE ELECTROCHEMICAL OXIDATION AT PLATINUM OF TOLUENE IN ACETIC ACID WITH TETRAMETHYLAMMONIUM NITRATE AS ELECTROLYTE

Current, A	0.1	1.5
Product, mol %		
Bibenzyl	3.6	3.3
Benzyl acetate	44.5	39.4
Ethylbenzene	2.2	7.4
Benzylidene diacetate	1.0	0.3
Benzaldehyde	14.9	13.1
Benzyl nitrate	22.6	27.4
<i>o</i> -Acetoxytoluene	5.8	5.5
<i>p</i> -Acetoxytoluene	5.3	3.5
% conversion	17.8	14.2
% toluene recovered	14.5	15.5

Experimental Section

Materials.—Reagent grade glacial acetic acid and toluene were both used without purification. Naphthalene was crystallized twice from ethanol before use. Anthracene was crystallized

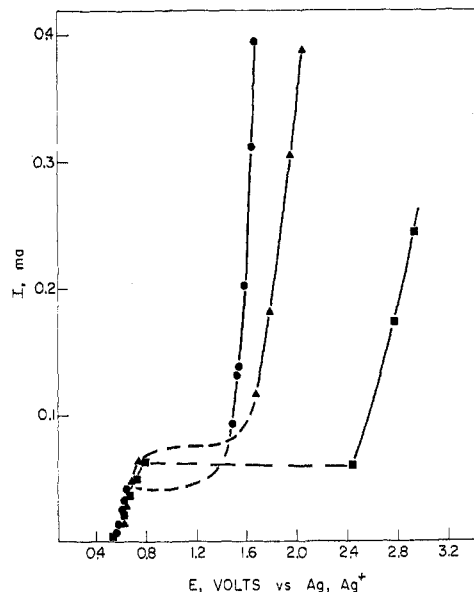


Figure 3.—Plots of electrolysis current vs. anode potential for solutions of anthracene (3.7×10^{-4} mol) in glacial acetic acid (presaturated with silver acetate), and 0.0500 mol of tetramethylammonium nitrate (circles), potassium acetate (triangles), or potassium *p*-toluenesulfonate (squares), 60-ml total solution. Broken lines indicate areas of experimental uncertainty.

TABLE V

PRODUCTS IN THE ELECTROCHEMICAL OXIDATION OF TOLUENE IN ACETIC ACID WITH TETRAMETHYLAMMONIUM *p*-TOLUENESULFONATE AS ELECTROLYTE

Anode	Pt	Pt	Pt	C
Current, A	0.1	0.75	3.0	1.5
Product, mol %				
Bibenzyl	6.3	31.0	26.7	3.0
Benzyl acetate	40.3	46.8	50.9	88.8
Ethylbenzene	1.8	5.5	5.8	1.4
Benzyl alcohol	12.9	tr		
Benzaldehyde	35.7	11.9	12.0	5.6
Benzylidene diacetate	2.7	4.1	4.3	0.9
<i>o</i> -Acetoxytoluene	0.3	0.7	0.4	0.3
% conversion	19.1	10.1	9.6	14.4
% toluene recovered	37.0	38.0	38.0	39.0

TABLE VI

PRODUCTS IN THE ELECTROCHEMICAL OXIDATION OF TOLUENE AT PLATINUM IN ACETIC ACID. I, WITH POTASSIUM ACETATE AS ELECTROLYTE; II, WITH BOTH POTASSIUM ACETATE AND TETRAMETHYLAMMONIUM NITRATE AS ELECTROLYTE; III, WITH BOTH POTASSIUM ACETATE AND TETRAMETHYLAMMONIUM *p*-TOLUENESULFONATE AS ELECTROLYTE

	I	II	III
Current, A	0.75	2.0	1.0
Product, mol %			
Bibenzyl		2.0	10.5
Benzyl acetate	17.9	40.7	48.0
Ethylbenzene	21.8	22.6	22.1
Benzylidene diacetate		tr	2.2
Benzaldehyde		4.5	7.4
Benzyl nitrate		9.0	
<i>o</i> -Acetoxytoluene	29.5	12.4	2.4
<i>p</i> -Acetoxytoluene	30.8	8.8	7.3
% conversion	2.8	8.9	14.9
% toluene recovered	30.0	24.5	30.0

first from benzene and then from 1:1 benzene-ethanol. The preparation of tetramethylammonium nitrate has been described previously.¹⁶ Tetramethylammonium *p*-toluenesulfonate was prepared in 91% yield by neutralizing an aqueous solution of *p*-

toluenesulfonic acid monohydrate with an equivalent quantity of a 10% aqueous solution of tetramethylammonium hydroxide, removing the water with the water pump, and crystallizing from 2-propanol-ether, mp 252–254°. The materials used in preparing standards for determining the products formed on anodic oxidation of toluene have been described previously.¹⁶

Determination of Rates of Gas Evolution and Gas Compositions.—The reaction cell, the gas collection apparatus, and the analytical procedures used have all been described previously.³

Current–Anode Potential Relationships.—Anode potentials were measured at room temperature as a function of electrolysis current in a number of acetic acid solutions of *p*-toluenesulfonate, nitrate, and acetate salts, with and without added toluene, naphthalene, or anthracene. The anode was a platinum wire, 0.051 cm in diameter, sealed into glass with a 0.39-cm length exposed to the solution. (area \approx 0.064 cm²). The electrolysis cathode was a small piece of platinum foil. The reference cathode was a piece of silver wire, and the acetic acid used as solvent was presaturated with the slightly soluble silver acetate. Nitrogen was bubbled through the solutions before and during electrolysis. Current was supplied, in both the ascending and descending directions, by batteries, with a voltage divider circuit, and was measured with a sensitive milliammeter, while the potential of the anode relative to the reference electrode was measured with a potentiometer–galvanometer circuit. The results were independent of the sequence in which the currents were varied.

Product Studies.—The electrolysis cell consisted of a water-jacketed, 200-ml beaker fitted with a magnetic stirring bar, a thermometer, and a Teflon cover, to which were attached two platinum electrodes, 0.025 cm thick, 2.5 cm wide, immersed to a depth of 7 cm, and at a separation of 2 cm.

In a typical experiment a solution of toluene (20 ml, 0.188 mol) and 0.1 mol of the salt in glacial acetic acid (130 ml) was electrolyzed at the indicated current until 2 equiv of charge per mol of toluene had been passed through the solution. Temperature was maintained at 30° or below with water cooling. The reaction mixture was taken up in water (500 ml) and extracted first with 500 ml of ether and then with three 250-ml portions of ether. The combined ether extracts were neutralized with a slurry of sodium bicarbonate in water. The ether layer was separated and washed with saturated sodium bicarbonate solution. The aqueous layers were extracted with 250 ml of ether, and this ether extract was washed with saturated bicarbonate solution. The combined ether layers were dried over anhydrous magnesium sulfate and finally concentrated to 50 ml for analysis.

The ether solutions were analyzed by vpc using a Perkin–Elmer large-diameter Golay column of 0.06-in. i.d. and 300-ft length, in which the stationary phase was Ucon polyglycol LB-550-X. The unknown solutions were compared with standards prepared from the identified components.

Discussion

Studies of the rates of gas evolution and the gas composition during anodic oxidation, in acetic acid, of nitrate ion, of acetate ion, of *p*-toluenesulfonate ion, and of mixtures of these anions indicate that the relative order of the oxidation potentials is nitrate < acetate < *p*-toluenesulfonate. This conclusion is supported by the observed current–voltage relationships (Figures 1–3) during the electrolysis of these ions in acetic acid, both with and without added substrates. It should, however, be noted that the potential scales, with the three different anions, do not necessarily bear any relationship to one another, since a different electrolyte, which would have an unknown or indeterminate effect on the potential of the reference electrode, is involved in each case. Fortunately, the potential of the reference electrode system does not change significantly as the supporting electrolyte is varied. This is demonstrated by the fact that anthracene is oxidized at a potential which is approximately invariant for the three anions (Figure 3).

Of greater significance are the changes effected in the current–voltage relationships by adding toluene to

solutions of the three anions (Figure 1). In all three cases and at all applied voltages the observed current is lower with toluene present. There is, therefore, nothing in these results that would justify the assertion that toluene is oxidized at a lower potential than any one of these three anions, not even *p*-toluenesulfonate ion. What the results do suggest is that toluene is adsorbed on the anode and that this adsorption accounts for the lower currents at any given potential. The question of which species, the anion or the toluene, undergoes electron transfer to the electrode, remains unresolved, and even the possibility that electron transfer occurs from both must be considered.

It is instructive to compare these results with comparable measurements on two substrates, naphthalene and anthracene, known to oxidize at considerably lower potentials than toluene.^{6,16–19} The current–potential curves (Figures 2 and 3) indicate that these two substrates are oxidized at potentials that are significantly lower than the potentials required for the oxidation of the supporting electrolytes, and it is highly probable that the electrochemical oxidation of naphthalene and anthracene involves electron transfer from the substrate, with a radical cation as an electrogenerated reaction intermediate.

In the measurements with naphthalene added, it was noted that, if one maintains the current constant at any point along the rising portion of the current–potential curve, the anode potential will rapidly increase (within minutes) to that value obtained for the particular supporting electrolyte in the absence of the naphthalene. This is equally true for all three supporting electrolytes, and this increase in potential occurs long before the amount of charge passed is sufficient to oxidize any significant amount of the naphthalene present in the solution.

Two facts stand out from the collected product results. The first is that, even though enough charge has been passed to permit a two-electron oxidation of all the toluene present in these reaction mixtures, large amounts of toluene can be recovered unchanged, and the actual conversion of toluene to identifiable products is always low and never attains 20%. The figures for recovered toluene are really minimum figures, since it is certain that significant amounts of toluene are entrained by the electrochemically generated gases. In terms of the charge passed, the oxidation of toluene is, thus, a side reaction rather than the major reaction.

The second fact to be noted is that the spectrum of products obtained from toluene is roughly similar for the experiments with the nitrate as the electrolyte and with the *p*-toluenesulfonate as the electrolyte, but very different when potassium acetate is the electrolyte. With the nitrate and the tosylate the products are almost entirely side-chain substitution products or side-chain coupling products. With the acetate the major products are the two ring substitution products, *o*- and *p*-acetoxytoluene.

This distinction may, in fact, be an important indication of the mechanisms involved. It is difficult to see how the ring acetoxylation products, observed with

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potassium acetate as the electrolyte, could arise from a primary anodic oxidation of acetate ion to give a reactive species which subsequently attacks the aromatic ring. The acetoxy radical is too fugitive a species to make its addition to toluene a reasonable possibility, and hydrogen abstraction would occur preferentially from the side chain rather than the aromatic ring. The only alternative possibility is that these products arise from a primary electron transfer from toluene itself, either in a concerted two-electron step with acetate ion involved as a nucleophile, or in stepwise, one-electron transfers with a radical cation as an intermediate.⁶⁻⁸

This would have to be the case even though the current-anode potential curves with toluene afford no indication that this substrate is oxidized at a lower potential than acetate ion, and even though more than 90% of the charge passed is utilized in effecting the Kolbe oxidation of acetate ion to ethane and carbon dioxide. The current-anode potential curve (Figure 1) suggests that toluene may be preferentially adsorbed on the anode. Even if as little as 5% of the electron transfer occurring at the anode took place from toluene, this would be more than enough to account for the observed products. It is both plausible and probable that electron transfer from toluene does, in fact, occur at least to this limited extent, and the most reasonable mechanism for the formation of ring acetoxylation products in the anodic oxidation of toluene in this system is one that involves a direct oxidation of the toluene in the primary step.

The origin of both the benzyl acetate and the ethylbenzene in this reaction is more controversial. The ethylbenzene can arise only from cross coupling between a benzyl radical and a methyl radical. The source of the methyl radical is obvious, but the genesis of the benzyl radical is uncertain. It could be formed from the radical cation by proton transfer to a base, *e.g.*, acetate ion, or, alternatively, from toluene by hydrogen atom abstraction. The benzyl radical may also be an intermediate on the path to benzyl acetate, since the further anodic oxidation of the benzyl radical could give the benzyl cation. It is also possible that benzyl acetate is formed by the same mechanism that leads to the ring acetoxylation products. The available data afford no clear choice from amongst these possibilities.

With both the nitrate and the *p*-toluenesulfonate as electrolyte the difficulties of interpretation are compounded. The products result almost entirely from attack on the side chain, and substitution of the ring accounts for approximately 10% of the products with the nitrate and less than 1% with the tosylate. The percentage conversions are almost an order of magnitude higher than with the acetate but still very low. In these reactions the benzyl radical must be an intermediate, since significant amounts of both bibenzyl and ethylbenzene are formed, and the same uncertainty about the source of the benzyl radical that exists with the acetate electrolyte obtains in these cases as well.

If electron transfer from toluene plays an important role in the oxidation with the acetate electrolyte, it is at least an equally probable route with the *p*-toluenesulfonate, which is oxidized at a higher potential than acetate ion and cannot be dismissed in the nitrate case, even though nitrate ion is oxidized at a lower potential than acetate ion. If such electron transfer does represent the primary process in these oxidations, the failure to obtain larger amounts of ring-substituted products with these electrolytes might be attributed to the fact that the *p*-toluenesulfonate ion and the nitrate ion are poor nucleophiles compared with acetate ion and cannot participate in the concerted nuclear substitution process which has been proposed for acetate ion.^{6,7}

On the other hand, most of the charge passed in these reactions is being used to oxidize either nitrate ion or tosylate ion. A mechanism in which the primary process is discharge of the anion to form either a nitrate or tosylate radical, with subsequent hydrogen atom abstraction to form a benzyl radical, cannot be eliminated. It is possible and perhaps probable that both electrochemical routes contribute to product formation. The large increase in bibenzyl formation (from 6.3 mol % to 31 mol %) with the tosylate when the current (and hence the anode potential) is increased from 100 to 750 mA suggests that this may, in fact, be the case.

Registry No.—Toluene, 108-88-3; potassium acetate, 127-09-3; tetramethylammonium nitrate, 1941-24-8; tetramethylammonium *p*-toluenesulfonate, 3983-91-3.