Iodination with Electrolytically Generated Iodine(I)

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Abstract: Aromatic iodination has been accomplished by oxidizing mixtures of iodine and benzenoid hydrocarbons. The oxidations were performed potentiostatically at platinum in acetonitrile–lithium perchlorate. Monoiodoaromatic was obtained from benzene (11%), toluene (34%), xylene (50%), mesitylene (73%), anisole (19%), and triphenylmethane (15%). A competing reaction in suitable cases was side chain substitution, *e.g.*, N-*p*-xylylacetamide (12%) from xylene. This reaction was completely suppressed by performing iodine oxidation first and adding the aromatic to this mixture. This procedure produced excellent (80–100%) yields of monoiodoaromatic from benzene, toluene, xylene, and anisole. Nitrobenzene proved unreactive. Iodination involves electrophilic attack by a positive iodine species. High *ortho*, *para* to *meta* product ratios are obtained and a competition between equal amounts of toluene and benzene for this species gave twice as much iodotoluene as iodobenzene. It is proposed that N-iodoacetonitrilium ion ($CH_3C^+{=}NI$) and N-iodoacetamide are produced during iodine oxidation and that these serve as iodinating agents. This is supported by the isolation of the product acetamide, the coulometry, and cyclic voltammetry. N-Iodoacetamide was prepared and iodinates aromatics in acidified acetonitrile.

It has been demonstrated that the low ionization potential of covalently bound iodine makes the selective electrooxidation of organic iodides feasible in acetonitrile solution.[1] Alkyl iodides are oxidatively cleaved by this process eventually yielding carbonium ion products and iodine. In contrast to this anodic cleavage of the carbon–iodine bond, we report here on

$$RI \xrightarrow{-e^-} R^+ + I\cdot$$

$$R^+ + CH_3CN \longrightarrow RN\overset{+}{C}CH_3 \xrightarrow{H_2O} RNHCOCH_3$$

the anodic formation of carbon–iodine bonds. The reaction that has been discovered[2] is one of a growing number of anodic aromatic substitution reactions. Other examples include cyanation, acetoxylation, and methoxylation.[3] It will be seen, however, that important differences in mechanism and in synthetic utility exist between iodination and these other reactions.

Although electrochemical iodination has not been studied by other workers, numerous chemical iodinations have been reported. Most of these reactions involve electrophilic attack by some positive iodine species and, as expected, the reaction conditions vary considerably with the reactivity of the aromatic. The electrophilic iodine has usually been generated from molecular iodine and suitable oxidizing agents.[4] The iodinating intermediates in these reactions have for the most part not been identified. It has often been hypothesized, however, that either iodonium ion (I^+) or protonated hypoiodous acid (H_2OI^+) are involved in aqueous solutions and evidence for one or the other has been presented in several cases.[5] In strongly acidic media in the presence of oxidizing agents, evidence for IO^+, I_2^+, I_3^+, and I_5^+,[6] has been reported. Although little study of their reactivity has been undertaken, it appears that very powerful electrophilic species can be generated under such conditions.[4h,6]

The electrooxidation of iodine in acetonitrile has been studied as part of a very thorough investigation of the iodide–triiodide–iodine redox system.[7] At a rotating platinum electrode the diffusion current was found not to be a linear function of iodine concentration but did approach a limiting value of 1.2 F/g-atom at high (2×10^{-3} *M*) iodine concentrations. Millicoulometric oxidation of 0.6 μmole of iodide ion at 2.11 V[8] passed 2.8 F/mole of I^-. Assuming the conversion of iodide to iodine consumed 1.0 F/mole, this meant that iodine oxidation used almost 2 F/g-atom of I. This exhaustively electrolyzed solution was assayed for positive iodine by adding excess iodide ion. The amount of triiodide produced (0.63 μmole) indicated that only a portion of the coulombs passed in iodine oxidation were assayable as positive iodine species. These data did not lead to elucidation of the oxidation pathway. We have studied the chemistry following electron transfer and this does allow some insight into the oxidation process.

Results

The feasibility of electrochemical aromatic iodination was initially explored by simply oxidizing mixtures of iodine and benzenoid hydrocarbons. The oxidations were performed at a platinum sheet anode in acetonitrile–lithium perchlorate. A cell divided into compartments for anode, cathode, and reference electrode

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[1] L. L. Miller and A. K. Hoffman, *J. Am. Chem. Soc.*, **89**, 593

[2] Preliminary results: L. L. Miller, *Tetrahedron Lett.*, 1831 (1967). (1968).

[3] N. L. Weinberg and H. R. Weinberg, *Chem. Rev.*, **68**, 449 (1968).

[4] (a) A. Kekule, *Ann.*, **137**, 162 (1866); (b) R. Elbs and A. Jaroslawzew, *J. Prakt. Chem.*, (2) **88**, 92 (1913); (c) D. E. Janssen and C. V. Wilson, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 547; (d) R. L. Datta and N. R. Chatterjee, *J. Am. Chem. Soc.*, **39**, 437 (1917); F. B. Dains and R. Q. Brewster, "Organic Syntheses," Coll. Vol. I, 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1956, p 323; (e) L. Jurd, *Aust. J. Sci. Res.*, **3A**, 587 (1950); (f) Y. Ogata and K. Aoki, *J. Am. Chem. Soc.*, **90**, 6187 (1968); (g) Y. Ogata and K. Nakajima, *Tetrahedron*, **20**, 43 (1964); (h) I. Masson, *J. Chem. Soc.*, 1708 (1938); (i) R. L. Baker and W. A. Waters, *ibid.*, 150 (1952); (j) D. H. Derbyshire and W. A. Waters, *ibid.*, 3694 (1950); (k) H. O. Wirth, O. Konigstein, and W. Kern, *Ann.*, **634**, 84 (1960); (l) J. Arotsky, A. C. Darby, and J. B. A. Hamilton, *J. Chem. Soc.*, *B*, 739 (1968).

[5] See E. Berliner, *J. Am. Chem. Soc.*, **78**, 3632 (1956), and earlier references in this series.

[6] J. Arotsky and M. C. R. Symons, *Quart. Rev.* (London), **16**, 282 (1962); R. A. Garrett, R. J. Gillespie, and J. B. Senior, *Inorg. Chem.*, **4**, 563 (1965); R. J. Gillespie and J. B. Milne, *ibid.*, **5**, 1577 (1966).

[7] A. I. Popov and D. H. Geske, *J. Am. Chem. Soc.*, **80**, 1340 (1958).

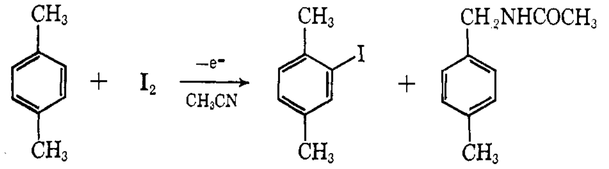
[8] All potentials measured and reported *vs.* Ag/0.1 *M* $AgNO_3$ in acetonitrile.

was employed and all oxidations were carried out potentiostatically. Work-up after oxidation at 1.6–1.7 V[8] demonstrated that iodination was indeed successful with several aromatic hydrocarbons (Table I). Although yields were not always high, the ether-soluble reaction product was fairly clean monoiodoaromatic. An interesting side reaction observed in suitable cases, *e.g.*, *p*-xylene, was side chain acetamidation or hydroxylation.

Table I. Oxidation Products from Mixtures of Iodine and Aromatics

Aromatic	% yield Iodoaromatic	 Side chain substitution
Benzene	11	
Toluene	16 *para;* 16 *ortho;* 2 *meta*	0
p-Xylene	50	12[a]
p-Xylene[b]	66	9
Mesitylene	73	0
Anisole[c]	13 *para;* 6 *ortho;* 1 *meta*	
Anthracene	0	
Nitrobenzene	0	
Triphenylmethane	15	36[d]

[a] N-*p*-Xylylacetamide. [b] Using tetra-*n*-propylammonium fluoroborate as electrolyte. [c] Some tarry products also formed. [d] Triphenylmethanol.



It was found that all successful iodinations arise from oxidations whose current–potential and current–time behavior are essentially the same as that of iodine in the absence of aromatic substrate. This and other considerations[2] indicated that the initial oxidation of iodine controlled most of the observed chemistry.

Independent anodization of iodine in acetonitrile–lithium perchlorate followed by addition of benzenoid aromatics after the electrolysis has been discontinued was, therefore, undertaken. The yields tabulated in Table II demonstrate that benzenoids with substituents more electron releasing than hydrogen react cleanly to give high *ortho*, *para* to *meta* product ratios. The side chain substituted product found in mixture oxidations is completely absent! The same results are obtained if large amounts of iodine are partially oxidized or if smaller amounts are completely consumed. Control over the number of iodines added to each aromatic could be obtained by varying the amount of positive iodine formed and the amount of aromatic added (Table III). Extending this variation produced tetraiodo-*p*-xylene: nmr singlet δ 2.20; mass spectrum parent ion (M) = 610, fragments at M − (n)127, where n = 1–4.

Table II. Iodination Yields from a Pre-formed Agent[a]

Aromatic	% yield iodoaromatic
Benzene	96
Toluene	47 *ortho*, 47 *para*
p-Xylylene	100[b]
Anisole	56 *para*, 24 *ortho*
Nitrobenzene	0

[a] 0.5 g of I_2 oxidized completely. Excess aromatic added. Yields based on added iodine, the limiting reagent. [b] Similar yield obtained using tetrapropylammonium fluoroborate electrolyte.

Table III. Electroiodination of *p*-Xylene[a]

Coulometry, mF	% yield[b] Iodo-*p*-xylene	 Diiodo-*p*-xylene[c]	 Tetraiodo-*p*-xylene
11.5	100[d]	0	
13.2	67	25	
16.0	22	40	
23.3	0	55	2

[a] 5.5 g of iodine; 1 g of lithium perchlorate as the electrolyte; 100 ml of acetonitrile; 8.0 mmoles of *p*-xylene. [b] Percentage based on millimoles of *p*-xylene added. [c] Represents a mixture of isomers. [d] Fivefold excess of *p*-xylene added. Yield based on reacted *p*-xylene.

Examination of reaction mixtures which had only been concentrated by evaporation demonstrated the presence of acetamide. This was formed in 80% yield during *p*-xylene iodination and was also isolated from the iodination of anisole. Acetamide was characterized by its nmr, ir, and gc retention time.

In these macroscale oxidations, it was shown that the total number of coulombs passed at 1.6 V removed 1.2 electrons per iodine atom. This consumed all the iodine and left a stable, pale yellow solution. This solution instantly regenerated iodine when iodide ion was added. It also quantitatively (based on the initial amount of iodine) iodinated *p*-xylene. The rate of this reaction was demonstrated by adding iodide immediately after xylene addition. Only a trace of iodine was formed establishing that the positive iodine species reacts with xylene in seconds. The observation that slow (30 sec) addition of xylene into the solution increased the yields of polyiodo compounds seems related to this phenomenon.

It is found that the purity of the acetonitrile has an effect on the oxidation process, but apparently does not substantially change the yields of iodinated product. Two purification techniques were utilized and each gave quantitative yields of iodoxylene based on the iodine concentration before oxidation. The yields in Tables I, II, and III were obtained using damp acetonitrile which had been purified by distilling reagent grade material from permanganate, followed by redistillation under nitrogen.[9] If this was used within 2 days, the iodine oxidation mixture remained homogeneous throughout. If, however, this purified material stood for more than 2 days, iodine oxidation eventually produced a solid. A similar precipitate formed near the end of iodine oxidations in which freshly purified technical grade acetonitrile was utilized or if reagent grade acetonitrile was purified by distillation from phosphorus pentoxide and then from sodium carbonate. This solid is not necessary for

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(9) J. F. O'Donnell, J. T. Ayers, and C. K. Mann, *Anal. Chem.*, 37, 1161 (1965).

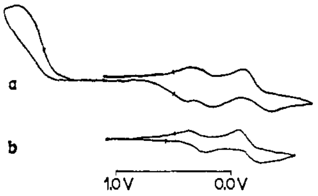


Figure 1. Cyclic voltammograms of 2×10^{-3} *M* iodine in acetonitrile purified from phosphorus pentoxide. Anodic current up. Scan rate: a, 100 mV/sec; b, 68 mV/sec.

iodination but did disappear when aromatic was added.

The nature of iodine oxidation was probed by cyclic voltammetry. The curve in Figure 1a was obtained in acetonitrile purified by the phosphorus pentoxide method, with lithium perchlorate electrolyte at a platinum working electrode. The sweep rate was 0.02 cps. Succeeding sweeps gave similar curves with E_p = 1.82 (a),[10] 0.42 (c), 0.22 (c), −0.28 (c), −0.04 (a), 0.34 (a). Background oxidation is negligible in all the experiments reported here. The curve in Figure 1b was obtained in the same solution by sweeping at 0.02 cps from 0.5 to −0.5 to 1.0 to 0.5. These peak potentials, E_p = 0.25 (c), −0.25 (c), −0.04 (a), 0.34 (a), are not a function of the dryness of the solvent up to 0.2% water. The curves in Figure 1 and 2 are typical of these obtained with this setup in that the peaks are somewhat broad, presumably due to uncompensated ir drop.

A cyclic sweep from 1.0 to 1.9 to −0.5 to 1.0 V for iodine in acetonitrile purified by the permanganate method is very similar to curves produced by iodine in phosphorus pentoxide purified acetonitrile adulterated with 0.1 ml of water. The initial anodic peak is shifted down to 1.68 V and the region from +0.5 to 0.0 V is changed. Interpretation is difficult because of the number of peaks but it appears that a new reduction peak grows in at near 0 V. In very wet solvent the 0.45-V peak is essentially absent and the ∼0.0-V peak dominates the region. A further observation is that the peak anodic current is considerably decreased in wet acetonitrile. On the second sweep a shoulder appears at about 1.3 V. This peak is much larger in wet solvent and is dependent on traversing the +0.34 (a) peak.

In order to test for the production of N-iodoacetamide, it was prepared and its cyclic voltammogram is displayed as Figure 2. This compound reacted instantly with iodide ion in acetonitrile. It was shown by nmr that it also readily iodinated anisole in the presence of trifluoroacetic acid. Mixing anisole with N-iodoacetamide in acetonitrile did not destroy the positive halogen within 1 min. Trifluoroacetic acid, however, catalyzed aromatic substitution greatly, so that immediate addition of iodide after mixing the other reagents gave no iodine.

Discussion

Oxidation of iodine in acetonitrile followed by addition of the aromatic produces quite satisfactory iodination yields of toluene, xylene, benzene, and anisole. Little attention to solvent purity or dryness is necessary and various electrolytes are suitable. It is, however, necessary to separate the anolyte and catholyte since the iodinating agent and iodine will reduce at the cathode. This method may have special application because it does not require that the aromatic be heated in strongly acidic solvents or in the presence of oxidizing agents.

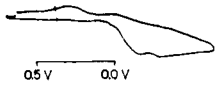
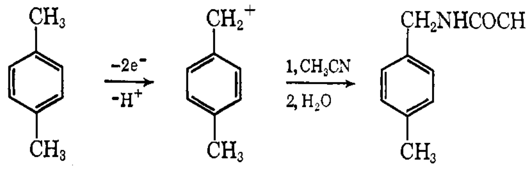


Figure 2. Cyclic voltammogram of 10^{-3} *M* N-iodoacetamide in acetonitrile. Anodic current up. Scan rate 78 mV/sec.

The improved yields using a separately formed iodinating agent seem to be a consequence of avoiding competing anodization of aromatics. In the mixture oxidations, some or all of the current is consumed *via* electron transfer from the aromatic and this process does not produce isolable iodoaromatic products. The products from the easily oxidized anthracene are instead characteristic[11] of oxidation in the absence of iodine. *p*-Xylene is of particular interest because in the mixture oxidations it produces iodoaromatic *via* iodine oxidation and side chain acetamidation apparently *via* xylene oxidation[12] as deduced from the suppression of side chain substitution with separately formed iodinating agent.



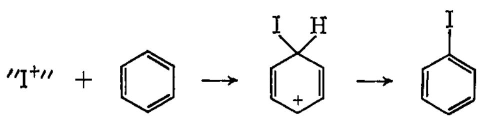
Independent iodine oxidation can also improve yields by avoiding anodization of the iodoaromatic product. This oxidation has been shown to produce diaryliodonium salts.[1] Combining electroiodination

$$\mathrm{ArI} + \mathrm{Ar'H} \xrightarrow{-2e^-} \mathrm{Ar{-}I^+{-}Ar'} + \mathrm{H^+}$$

with this coupling reaction reveals a potentially useful electrosynthesis of iodonium salts directly from iodine and aromatic hydrocarbons. Utilization of the iodinating mixture to attack olefins also appears possible.

The high *ortho*, *para* to *meta* ratios found for toluene and anisole are diagnostic for electrophilic aromatic substitution *via* the gross mechanism

$$I_2 - 2e^- \longrightarrow 2''I^{+}''$$



The unreactivity of nitrobenzene is in agreement with this mechanism as are the results of kinetic competition experiments. If an equimolar mixture of toluene and benzene is added to the iodinating mixture, twice as much iodotoluene (50% *ortho*, 50% *para*) as iodobenzene is formed. Anisole is similarly four times more reactive than toluene. This ratio is not very large and in light of the high positional selectivity and the unreactivity of nitrobenzene, seems especially low. It could be a result of a mixing phenomenon due to

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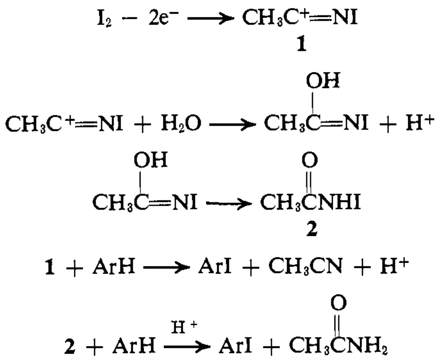
[10] (a) anodic current; (c) cathodic current.

[11] E. J. Majeski, J. D. Stuart, and W. E. Ohnesorge, *J. Am. Chem. Soc.*, **90**, 633 (1968).

[12] L. Eberson and K. Nyberg, *Tetrahedron Lett.*, 2389 (1966).

a rapid reaction rate. Alternatively, it might be explained by an indiscriminantly formed π complex which collapses selectively to a σ complex.

It is of special importance to define the nature of the iodinating species. Although little can be concluded about the detailed composition of the transition state leading to aromatic iodination, some conclusions can be drawn concerning the structure of the intermediate positive iodine species. As indicated in the introductory section, Popov and Geske concluded that the oxidation of iodine was complex. The observation of a nonintegral coulometric value ($n = 1.2$)[13] and purity dependent precipitates supports this viewpoint. A great deal of the available data can, however, be rationalized in terms of the scheme



$$I_2 - 2e^- \longrightarrow \underset{\mathbf{1}}{CH_3C^+{=}NI}$$

$$CH_3C^+{=}NI + H_2O \longrightarrow CH_3\overset{OH}{\overset{|}{C}}{=}NI + H^+$$

$$CH_3\overset{OH}{\overset{|}{C}}{=}NI \longrightarrow \underset{\mathbf{2}}{CH_3\overset{O}{\overset{\|}{C}}NHI}$$

$$\mathbf{1} + ArH \longrightarrow ArI + CH_3CN + H^+$$

$$\mathbf{2} + ArH \xrightarrow{H^+} ArI + CH_3\overset{O}{\overset{\|}{C}}NH_2$$

It seems likely that the initial steps involve electron transfer from the iodine–acetonitrile, donor–acceptor complex[14] to form the I(I) species **1** and/or **2**. The +1 oxidation state is supported by the coulometry in the present study[13] and the current constant.[7] The positive iodine assay[7] points to I(I) since 0.6 μmole of triiodide would be produced from a two-electron oxidation of 0.6 μmole of iodide up to I(I). The quantitative iodination of xylene also supports this postulate. Taken together these data rule out species with oxidation states less than one like I_2^+, I_3^+, and I_5^+ and stable iodine species in oxidation states higher than one. If higher states were produced, these would have to be stabilized by hydrolysis. This seems improbable because of the low water concentrations present in experiments performed with acetonitrile distilled from phosphorus pentoxide. It might also have been expected that the coulometry and/or iodinating ability would have been affected by the differences in water content if formation of HIO_2 or HIO_3 was in competition with formation of I(I) species. It may be noted that iodic acid and periodate where iodine is in high, but stable oxidation state, are quite ineffective aromatic iodinating agents. Contrastingly, in the present case, iodination is completely within seconds. An equilibrium between molecular iodine and iodine in some oxidation state higher than one could satisfy the data but can be discounted due to the lack of absorption in the visible region. Iodine with periodic acid, furthermore, requires high temperatures to achieve aromatic iodination.

Cyclic voltammetry should detect a stableI(I) species. Indeed, a comparison of Figures 1a and 1b shows that a new reducible species is formed during iodine anodization. The peaks at +0.25 (c), −0.22 (c), +0.04 (a), and +0.34 (a) are due to iodine reduction and reoxidation and are associated with the iodine–triiodide and triiodide–iodide couples.[7] The +0.45 reduction peak found in Figure 1a but not 1b is dependent on first traversing the +1.8 V anodization and is, therefore, due to the reduction of some initially formed anode product. A logical product is N-iodoacetonitrilium ion **1**. This ion should be easily hydrolyzed and we believe that this is observed. Cyclic voltammograms in wet solvent show that the relative peak height for the 0.45 (c) peak decreases and as a new peak grows in at about 0.0 V (c). Indeed, if the curve measured in "dry" acetonitrile (Figure 1a) is crudely analyzed by subtracting out the iodine reduction peaks (Figure 16), a considerable residual current remains near 0 V ($E_p \sim 0.1$). This peak is attributed to the reduction of N-iodoacetamide **2**. This contention is supported by the observed $E_p = -0.1$ for known **2**. Again, this is the most logical pathway since alkyl acetonitrilium ions readily produce alkyl acetamides.[1,15]

Both N-iodoacetonitrilium ions and N-iodoacetamide can also nicely rationalize the observed chemistry since they should be quantitatively reduced by iodide ion and could iodinate aromatics. We find that N-iodoacetamide iodinates anisole very rapidly in the presence of trifluoroacetic acid. Acid is necessary for this reaction and fortunately, 1 mole of perchloric acid is formed per mole of **2** in the electrooxidation. *Most importantly, this scheme accounts for acetamide formation during aromatic iodination.* Acetamide could also arise from acid-catalyzed hydration of acetonitrile, but does not seem to. The amount of acetamide formed is directly related to the amount of current passed and positive iodine formed. It may also be noted that acid is formed in almost all electrooxidations but acetamide is not generally formed as a product.

The dampness of the solvent is obviously important to interpretation of the nature of iodine oxidation if not the synthetic aspects of iodination. The formation of **2** demands the participation of water and formation of acid. It should be noted that the acid could lead to a reduction peak at or below 0 V.[16,17] This would lead to further complication of the voltammograms as would any instability of iodine in acetonitrile.[18] We find that the solutions are stable if dry. In wet solvent, however, considerable triiodide forms. This has no major effects on the voltammogram, but could change the nature of the oxidation to include direct conversion of triiodide to positive iodine. The possibility of using water to form hypoiodous acid or its conjugate acid, H_2OI^+, during iodine oxidation remains acceptable. If these species would reduce at near 0 V, they could explain some of the cyclic voltammetric results and would be consistent with the other observations. The formation of acetamide, however, clearly points to

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(13) The $n \sim 1.8$, measured at 2.11 V[8] and confirmed at 1.95 V in our work appears to be due to the instability of I (I) products. In particular N-iodoacetamide will be oxidized at these high potentials. This sort of product instability can also account for the extra 0.2 F/g-atom at 1.6 V.

(14) W. B. Person, W. C. Golton, and A. I. Popov, *J. Am. Chem. Soc.*, **85**, 891 (1963); R. S. Drago, B. Wayland, and R. L. Carlson, *ibid.*, **85**, 3125 (1963).

(15) J. J. Ritter and P. P. Minieri, *J. Am. Chem. Soc.*, **70**, 4045 (1948); H. Meerwein, P. Laasch, R. Mersch, and J. Spille, *Ber.*, **89**, 207 (1956).

(16) T. Osa, A. Yidiz, and T. Kuwana, *J. Am. Chem. Soc.*, **91**, 3994 (1969).

(17) We find that trifluoroacetic acid gives a reduction peak at −0.6 V.

(18) A. I. Popov and N. E. Skelly, *J. Am. Chem. Soc.*, **77**, 3722 (1955).

attack by a positive iodine species on acetonitrile and **1** and **2** provide a sufficient rationale for the observations. We consider the intermediacy of an uncoordinated I^+ or $IClO_4$ to be similarly moot.

These results are of considerable interest with respect to our earlier study of alkyl iodide oxidation. It was found that these oxidations consumed several electrons—more than could be accounted for by the observed products. It was proposed that iodine oxidation would account for the coulometry since rather high potentials were necessary. Amplification of this proposal to include positive iodine attack upon olefinic products in analogy with the aromatic iodination reported here now seems in order. It may be noted that acetamide is also formed in these alkyl iodide oxidations.

Experimental Section

Electrolysis. The electrochemical oxidations of iodine were normally carried out in acetonitrile–lithium perchlorate although acetonitrile–tetra-*n*-propylammonium tetrafluoroborate was employed in two experiments. All preparative oxidations were carried out at a controlled potential in a three-compartment glass fritted cell. The anode, or working electrode, was a platinum sheet, with an area of 625 mm^2. The cathode, or counterelectrode, was platinum gauze; the reference electrode was silver–silver nitrate (0.1 *M*) in acetonitrile. Two different cells were used in the subsequent oxidations, the difference being in the volume of the center (anodic) compartment. The particular volumes employed were 60 and 100 ml, respectively. During the oxidations, the cell was partially submerged in a water bath (room temperature) in order to regulate partially the temperature and to minimize diffusion through the glass frits. Depending upon the conditions desired, some oxidations were performed under a nitrogen atmosphere. The anolyte was stirred with a magnetic stirring bar to increase the instantaneous current.

The anode potential was controlled by means of a Model 61RS Wenking potentiostat from Brinkman Instruments. During the course of the reaction, the potential was also monitored on a Simpson vacuum tube voltmeter. Coulometry was performed by plotting the current-time curve and weighing the appropriate area of paper. At 1.6 V, 1.2 ± 0.1 mF/mg-atom of iodine were passed. The products were worked up by evaporating the solvent, adding ether, and washing this mixture with water and aqueous thiosulfate. This was followed by drying with magnesium sulfate and evaporation of the ether. The concentrated ether solutions were analyzed by vapor phase chromatography (Hewlett-Packard Model 5750). A 5 ft × 0.25 in. column of 3% Se 30 on 100/120 Varaport 30 run at 110° achieved the desired separations. Further structural varification and *ortho*, *meta*, *para* ratios of the products were determined by nmr.

For the cyclic voltammetry studies of iodine in acetonitrile–lithium perchlorate solution, a two-compartment glass fritted cell was used exclusively. The electrodes employed were a platinum foil or bead anode, a stainless steel cathode, and a silver–silver nitrate (0.1 *M*) reference electrode. A function generator Model 225a from Exact Electronics was used to drive the Wenking potentiostat in a triangular mode. The sweep rate was varied from 0.25 to 0.01 V/sec in different experiments. The recorder employed during these cyclic experiments was a Model F-80A X–Y recorder from Varian Instruments.

Reagents. Acetonitrile (400 ml), reagent and practical grade, was purified from potassium permanganate (15 g) and sodium carbonate (10 g). Sulfuric acid (2–3 drops) was then added to the acetonitrile and allowed to stand overnight. Following this, the acetonitrile was filtered and redistilled under a nitrogen atmosphere. This procedure yielded solvent too wet to dry by storage over molecular sieves.

Drier acetonitrile could be obtained by distillation from phosphorus pentoxide followed by distillation of a center cut from anhydrous sodium carbonate. The final cut was stored over Type 4A Molecular Sieves.

Lithium perchlorate, anhydrous reagent (G. F. Smith), was used as obtained or dried at 110° if anhydrous conditions were employed. All other reagents were used as obtained.

Tetraiodo-*p*-xylene. The oxidation of iodine was run as previously described using 5.5 g of iodine, with 23.3 mF being passed over a period of 4 hr. The solution was worked up in the usual manner. Upon evaporation of the ether solution, the resulting solid was redissolved in 95% ethanol for the purpose of recrystallization. The recrystallized solid melted at 209–210°. Structural assignment was made on the basis of the mass spectrum (AEI-MS12) and nmr spectrum. To facilitate interpretation of the mass spectrum, heptatacosafluorotributylamine ($C_{12}F_{24}N$) was used as an internal standard. The molecular (parent) ion occurred at an *m*/*e* 610, with principal fragment ions occurring at *m*/*e* 483, 356, 229, and 102. Nmr spectrum showed a single absorption at 2.2 ppm (δ). *Anal.* Calcd: C, 15.7; H, 0.98. Found: C, 17.18; H, 1.23.

N-Iodoacetamide was prepared by the method of Boismenu.[19] Iodine (7 g) was added successively to a solution of acetamide and 100 ml of ethyl acetate in 0.2–1.0-g amounts with constant stirring. After each amount of iodine was added, enough silver oxide was added to decolorize the solution. The total time required for the addition of all the iodine was 30 hr. Care was taken throughout the reaction to assure that all the silver oxide was being used by observing that only the yellow silver iodide could be seen. Upon filtration of the reaction mixture and evaporation, then washing of the N-iodoacetamide with 3–4 ml of $CHCl_3$, white crystals were obtained, mp 140°. The nmr showed a singlet at τ 8.06 (1 H) and a singlet 7.86 (3 H). The ir in CH_3CN showed bands at 3195, 1665, and 1242 cm^{-1}.

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[19] E. Boismenu, *C. R. Acad. Sci., Paris*, **153**, 948 (1912).