Liquid Chromatography–Photolysis–Electrochemical Detection for Organoiodides. 2. Operative Mechanisms

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An improved high-performance liquid chromatographic detection method has been characterized for the trace determination of iodinated organic compounds. The method, which incorporates postcolumn, on-line UV irradiation prior to oxidative electrochemical (EC) detection, exploits the facile photochemical dissociation of the C–I bond to form anionic iodide and a number of solvolyzed products. Mechanistic studies for this liquid chromatography–photolysis–electrochemical detection (LC–$h\nu$–EC) approach indicate that, depending on the parent organoiodide, cationic fragments formed during photolysis may be solvolyzed by water and methanol in the mobile phase to form alcohol and ether substitution products or may undergo elimination reactions. A reaction sequence is advanced to explain differences in product yields for the iodinated organic compounds studied. The experiments demonstrate that EC response is primarily due to anionic iodide but may be influenced by the presence of solvolyzed cationic photofragments. Elucidation of photochemical detection mechanisms allows for better understanding of the basis for the enhanced selectivity available using photolysis EC detection for organoiodides, and the potential for success in future applications of this technique to the determination of organobromides and -chlorides is discussed.

In the first paper of this series, in which the use of liquid chromatography–photolysis–electrochemical detection (LC–$h\nu$–EC) for organoiodides was described (*1*), it was discovered that the new method of detection offered excellent sensitivity and enhanced selectivity for these compounds. It was important to gain an understanding of the photochemical and electrochemical mechanisms underlying the observed responsiveness of organoiodides to the photolysis EC detection approach, in order to facilitate future experiments with organobromides and -chlorides.

The photochemistry of halogenated organic compounds has been studied in some detail, primarily owing to their wide use and toxicity. At 254 nm, it is generally understood that the primary absorption process of organoiodides is localized at the C–I bond, and involves the low-lying n → σ^* transition, in both aryl and alkyl systems (*2*). This excited singlet then decays to the triplet excited state (*3*), which is sufficiently high in energy to allow for triplet homolysis of the C–I bond (estimated at 55 kcal/mol (*4*)). This homolysis forms radical pairs, and rapid electron transfer can then occur, yielding carbocation–halide ion pairs (*5–8*). From this scenario, it is understandable that organohalogens may show evidence of both ionic and radical photobehavior. While it is possible for bromine and chlorine atoms to undergo hydrogen abstraction from the solvent cage, the much less reactive iodine atom is incapable of this (*2*). Also, the greater polarizability of iodine, and the decreased charge density of the iodide anion, make the electron transfer between the initial radical pairs quite attractive. Thus, the photolytic derivatization of organoiodides

in LC–$h\nu$–EC should yield iodide and solvated cationic fragments of the parent molecules.

The fate of the cationic portion of the photolyzed organoiodides in LC–$h\nu$–EC is of interest, especially for aromatic compounds, because the generation of solvolysis products may attenuate or enhance the EC detectability of the analyte. It has been demonstrated that irradiation of primary alkyl iodides in the presence of ethanol and water leads predominantly to unsaturated products, not only at the terminus but also at internal positions (*2, 6*). Alternatively, nucleophilic trapping by solvent to form the corresponding alcohols and ethers may occur, although to a lesser extent. Similar behavior is observed for allylic halides (*9*), wherein analysis of photolytic yields has demonstrated the predominance of unsaturated products. In strained alicyclic systems (*8*), and for aromatic iodinated compounds (*4*), nucleophilic solvation products are generally produced. The formation of oxidizable nucleophilic products, such as phenol or hydroquinone, from mono- or disubstituted aromatic organoiodides, respectively, would influence the electrochemical response for the photolyzed analyte.

The experimental design described in this paper involved the use of ion, gas, and liquid chromatography in order to identify and quantitate the products formed following photolysis of organoiodides. In addition, photolysis–cyclic voltammetry (PCV) (*10*) was employed to qualitatively examine the electroactivity of photolyzed solutions. As in the experiments applying LC–$h\nu$–EC to this class of compounds, five representative analytes were chosen for study: 1-iodopentane, 1-iodo-2-propene (allyl iodide), 1,2-diiodoethane (ethylene diiodide), iodobenzene, and 1,4-diiodobenzene. It was our desire to use the results of this work to better understand the photolytic–EC detection process for organoiodides.

EXPERIMENTAL SECTION

Reagents and Materials. Standards of the organoiodide test analytes, inorganics, and possible solvolysis products were all obtained in the highest purity available from Aldrich (Milwaukee, WI), except iodopentane, which was obtained from Chem Services (West Chester, PA). Reagent grade HCl, H_3PO_4 and NH_4OH were obtained from J. T. Baker (Phillipsburg, NJ), $K_3Fe(CN)_6$ from Mallinckrodt (New York), phthalic acid from Eastman (Rochester, NY), and sodium borate from MCB (Gibbstown, NJ). High-purity He, purified H_2 and O_2, and compressed air were obtained from Yankee Oxygen (Hingham, MA), while water and methanol (MeOH) were obtained from EM Science (Cherry Hill, NJ) as the Omnisolv grade.

Apparatus. The design of a photolysis cyclic voltammetry (PCV) instrument for fundamental photochemical and electrochemical studies has been described (*10*). The PCV results were obtained on a glassy carbon electrode, with an Ag/AgCl reference and Pt counter electrode.

Ultraviolet spectra were obtained using a Uvicon 820 UV spectrophotometer with a Model 21 recorder (Kontron Analytical, Redwood City, CA). Ion chromatography (IC) was performed with a Model 590 solvent delivery system (Waters Corp., Milford, MA), a LiChromaDamp III pulse dampener (Handy and Harmon Tube Co., Norristown, PA), a Rheodyne 7010 injector with a 7012 filler loop and fixed volume (5-, 20-, 50-, or 200-μL) sample loops

(Rheodyne, Inc., Cotati, CA), a Vydac 302 (30 μm) 4.6 × 250 mm anion exchange column (The Separations Group, Hesperia, CA), and a high-sensitivity conductivity detector (Bio-Rad, Richmond, CA). Gradient liquid chromatography (LC) with UV detection was performed using dual 114M pumps, a 421A gradient controller, a 340 "Organizer" with 5-mL mixer and 20-μL injector, a 163 UV detector set at 230 nm, and a 427 integrator (all from Beckman, San Ramos, CA). The column used was a Waters Radial-PAK C_{18} (5 μm) 100 × 5 mm cartridge.

Gas chromatographic (GC) analyses were performed on a Varian 3700 GC-FID (Varian Corp., Walnut Creek, CA), with either a 30 m × 0.53 mm, 1.0-μm DB-WAX (poly(ethylene glycol) bonded phase) or a 30 m × 0.53 mm, 1.5-μm DB-1 (methylsilicone bonded phase) column installed (J&W Scientific, Folsom, CA). The GC was converted for capillary operation by using the "direct flash injection" and detector capillary adapters provided by J&W. The modified injector port sleeve allowed for injection (without splitting) of more than 7 μL of aqueous samples without adverse chromatographic effects.

Procedure. Photolysis cyclic voltammetry (PCV) provided a rapid method for examination of the effects of a number of experimental conditions on the generation, persistence, and behavior of products formed during irradiation of test solutes, while also allowing for voltammetric study of analytes before photolysis (10). Typical PCV operating conditions involved 6-min photolyses (unless otherwise noted), a forward scan from 0.0 V (all potentials vs. Ag/AgCl) to a positive switching potential of +1.2V, reverse scan to −0.4 V, and a supporting electrolyte of 50:50 (v:v) MeOH:0.2 M NaCl. Aliquots of the photolyzed solutions were removed from the micro-CV cell for LC, IC, or GC analysis using a microliter syringe and a short piece of Teflon tubing positioned in the base of the cell.

IC analyses for iodate (IO_3^-) and periodate (IO_4^-) in the presence of iodide (I^-) and chloride (Cl^-) incorporated a 4 mM phthalic acid (unadjusted pH 2.6) mobile phase at 1.5 mL/min, while IC separation of I^- from the large excess of Cl^- in the supporting electrolyte could be accomplished by using a mobile phase of 4 mM phthalic acid (adjusted to pH 4.5 with borate) at 2.0 mL/min. Gradient LC analysis was used for the determination of photolysis products from iodobenzene and 1,4-diiodobenzene incorporating an A solvent of 10:90 MeOH:H_2O, B solvent of 70:30 MeOH:H_2O, and a program of: hold 0% B (4 min), step to 100% B, hold 100% B (21 min), recycle to 0% B in 4 min, hold 0% B (10 min).

Capillary GC–FID (flame ionization detector) was needed for characterization and quantitation of photolysis products from iodopentane and 1,2-diiodoethane (the appropriate standards for allyl iodide were not commercially available). Injector and detector temperatures were 150 and 200 °C, respectively, with 2-μL injections, as well as a He (carrier gas) flow of 9 mL/min and H_2 and air (FID support gases) at 20 and 120 mL/min, respectively.

During product characterization for photolyzed iodopentane, the possible 1-, 2-, and 3-pentanol products, and similar methyl pentyl ethers, could be resolved by using the DB-WAX column and a temperature program of 42 °C (hold 3 min) to 150 °C at 10 °C/min. In a separate analysis, 1- and 2-pentene and pentane were adequately separated by using the DB-1 column with a temperature program of 30 °C (hold 1 min) to 200 °C at 20 °C/min. Decomposition of iodopentane in the injector port of the GC was compensated for using the LC–$h\nu$–EC system (11). Following photolysis of 1 part per thousand (ppth, mg/mL) solutions of iodopentane in supporting electrolyte, aliquots of the irradiated samples were injected onto both the LC (after 1:5 dilution) and GC systems. LC–$h\nu$–EC was used to quantitate intact iodopentane, and the molar conversion efficiency (MCE, in %) for generation of each of the products determined in photolyzed solutions was calculated as: (moles of product ÷ moles of parent compound converted) × 100.

For 1,2-diiodoethane, the DB-WAX column, and a temperature program of 45 °C (hold 1 min) to 150 °C (hold 3 min) at 20 °C/min, allowed for resolution of 2-iodoethanol, 2-methoxyethanol, ethylene glycol, and ethylene glycol dimethyl ether. In a fashion similar to that for iodopentane, aliquots of photolyzed solutions were injected onto the LC–$h\nu$–EC system as well, in order to quantitate intact 1,2-diiodoethane. MCEs for formation of solvolyzed products from iodobenzene and 1,4-diiodobenzene were determined by using 1 ppth solutions irradiated for 2 min.

Table I. Summary of Product Yields from Iodopentane following 6-min Irradiations

analyte	MCE,[a] %	analyte	MCE,[a] %
1-pentanol	3.15 ± 0.37	1-pentene	53.60 ± 3.95
2-pentanol	5.91 ± 0.22	2-pentene	22.18 ± 1.13
3-pentanol	9.26 ± 1.04	n-pentane	1.41 ± 0.03

[a] Molar conversion efficiency (moles of product/moles of iodopentane converted) × 100%. Mean ± standard deviation (n = 12).

A PCV study was performed to examine the voltammetric responses of 1 ppth solutions of IO_3^- and IO_4^-, before and after photolysis, for periods of irradiation between 1 and 8 min, at 1-min intervals. Aliquots were removed directly after photolysis for IC determinations of I^-, IO_3^-, and IO_4^- in the irradiated solutions. Similarly, temporal PCV analyses were performed on 1 ppth solutions of iodopentane, allyl iodide, 1,2-diiodoethane, iodobenzene, and 1,4-diiodobenzene, at 1-min intervals between 1 and 6 min. Aliquots of the photolyzed solutions were injected onto the IC for quantitation of iodide, and plots of MCE vs. irradiation time were constructed for these temporal studies.

The pH dependence of CV peak potentials and peak currents for I^- and the test organoiodides was ascertained by dissolving each of the solutes in supporting electrolyte (0.2 M NaCl for I^-) which had been adjusted to integer pH values between 3 and 10 with HCl or NaOH. IC analysis for I^- was used to establish the relationship between the yield of iodide from organoiodide precursors and the pH of the solution.

RESULTS AND DISCUSSION

Photochemical Mechanism Studies. The results of UV spectrophotometry revealed the following λ_{max} values for the test organoiodides in supporting electrolyte: iodopentane (249 nm), 1,2-diiodoethane (250, 216 nm), allyl iodide (260, 212 nm), iodobenzene (253, 219 nm), and 1,4-diiodobenzene (239 nm). Clearly, all of these compounds were capable of absorbing energy at 254 nm and were subject to the photochemical excitation–dehalogenation process outlined in the introduction.

As shown in Table I, GC characterization of the generated photolysis products indicated that nucleophilic substitution accounted for roughly 20% of the overall photolysis yield for iodopentane. Terminal and migrated elimination products were the predominant species observed, and there was also a very small yield of pentane. These results are in general agreement with those of previous workers (2, 6). However, although nucleophilic trapping of water, to form the pentanol isomers, was apparent, there was no evidence for the formation of methoxy-substitution products arising from MeOH. The CV studies of these compounds indicated that none of them exhibited oxidative response, so their generation during LC–$h\nu$–EC of iodopentane is probably of little analytical consequence.

The product analysis for 1,2-diiodoethane was not as successful as that for iodopentane. GC analyses of photolyzed solutions of 1,2-diiodoethane did not show any evidence of the expected nucleophilic substitution products or ethyl iodide. The lack of such products in the irradiated 1,2-diiodoethane samples probably means that elimination was the primary process, and it may be postulated that any ethylene so formed during the batch photolysis would probably adhere to, or diffuse through, the Teflon (poly(tetrafluoroethylene)) tubing composing the photolysis chamber. However, as with iodopentane, the generation of the elimination product in low concentrations would be expected to be somewhat inconsequential with respect to the $h\nu$–EC detection of 1,2-diiodoethane.

Table II summarizes the results of the LC analysis of photolyzed solutions of iodobenzene and 1,4-diiodobenzene. For iodobenzene, four products were generated during 2 min of photolysis, namely phenol, anisole, chlorobenzene, and

Table II. Summary of Product Yields from Iodobenzene and 1,4-Diiodobenzene Following 2-min Irradiations

substrate	product	MCE,[a] %
iodobenzene	phenol	14.16 ± 3.21
iodobenzene	anisole	35.70 ± 1.74
iodobenzene	chlorobenzene	2.62 ± 0.60
iodobenzene	fluorobenzene	43.39 ± 3.12
1,4-diiodobenzene	p-methoxyphenol	3.22 ± 0.01
1,4-diiodobenzene	p-dimethoxybenzene	0.44 ± 0.02
1,4-diiodobenzene	p-fluoroanisole	4.82 ± 0.84
1,4-diiodobenzene	p-fluoroiodobenzene	1.90 ± 0.08
1,4-diiodobenzene	iodobenzene	86.23 ± 4.48

[a] Molar conversion efficiency (moles of product/moles of parent converted) × 100%. Mean ± standard deviation ($n = 5$).

fluorobenzene. The generation of these nucleophilic products, and the lack of generation of the hydrogen abstraction product—benzene—indicates that the reaction proceeded by way of the cationic intermediate. This finding is in agreement with previous reports (4). The phenol and anisole were formed by nucleophilic solvent trapping of the cationic intermediate by water and methanol, respectively. Chlorobenzene was formed by combination of the cation with chloride present in the mobile phase as the supporting electrolyte (NaCl). The generation of fluorobenzene was unexpected but was clarified by a recent report by Batley (12) regarding the photochemical release of fluoride from Teflon used in the construction of photochemical reaction vessels. Of the four products formed from iodobenzene, phenol is the only species which contributes to the oxidative responsiveness for iodobenzene in LC–$h\nu$–EC.

Product analysis of 1,4-diiodobenzene revealed the predominant generation of iodobenzene, as well as small yields of nucleophile-trapped products. The fact that 1,4-diiodobenzene gave primarily iodobenzene, a radical-derived product, while photolyzed iodobenzene gave cationic-derived photolysis products, suggests that the electron-withdrawing substituent para to the bond homolysis site for 1,4-diiodobenzene changes the nature of the intermediate radical–radical pair. Presumably, the electron transfer from the ring carbon radical to the iodine radical is less favorable, so reaction processes open to the radical are favored and radical-derived products predominate.

The fact that methyl ether substitution products were observed for the aromatic organoiodides, yet were not evident for iodopentane, suggested that the cations generated during the photolysis process were capable of different degrees of selectivity in subsequent solvolysis. The reactivity-selectivity principle (RSP) has been invoked for many years to explain the mechanisms for generation of certain products or ratios of products during organic reactions (13, 14). The RSP states that in a series of similar reactions, the less reactive reagent (or intermediate) displays the highest selectivity. For iodopentane, it is clear that photolysis leads to alkyl cations which are stabilized by hyperconjugation. The phenyl cations formed from iodobenzene and 1,4-diiodobenzene are less stable and much more reactive than their alkyl counterparts, so iodopentane should display better selectivity than iodobenzene and 1,4-diiodobenzene. Thus, when iodopentane is photolyzed in a binary solvent consisting of an equal (volume:volume) mixture of two nucleophiles (MeOH and water), the substitution products formed should include both alcoholic and methyl ether species, in a proportion correlated to the relative nucleophilicities of the two solvents. Conversely, if the photolysis of iodobenzene and 1,4-diiodobenzene gives rise to very unstable cationic intermediates, which react at diffusion-controlled rates, the substitution products in a 50:50 MeOH:water mixture would be expected to be equally divided between phenolic and methyl ether products.

The disparity between the RSP and the results in our experiments may be rationalized by recognizing an effect known as "solvent sorting" (15). This effect is believed to exist during solvation of an analyte in a binary solvent, wherein the solvent component which best solvates the analyte will be present in the solvent shell in greater concentration than in the bulk (binary) solvent. Such changes in microscopic solvation structure can influence apparent selectivity in a reaction, giving rise to product ratios which are not in accord with the individual nucleophilicities in such binary mixtures (16). This effect may be especially important for solvent components having similar nucleophilicities (such as MeOH and water) (17). Since iodopentane, iodobenzene, and 1,4-diiodobenzene are all relatively hydrophobic, it may be postulated that solvent sorting would lead to solvent shells (before photolysis) containing higher concentrations of MeOH than the bulk solution. When cationic intermediates are formed, however, different sequences of events can be envisioned for the alkyl and aryl intermediates, due to their different stabilities.

The rate constant for exchange of solvent molecules between the bulk and solvent shell has been estimated at 10^9–10^{11} s^{-1} (15). Therefore, there is sufficient time for the stable, *polar* cationic fragments from iodopentane to reorganize the solvent shell such that it is composed predominantly of water. Although elimination is the major process for the intermediate formed, the greater shell concentration of water would lead to a predominance of alcoholic substitution products, as is observed (Table I). Thus, the results are not based solely on the nucleophilicities of water and methanol (16, 18). The formation of 2- and 3-pentanol is understandable in terms of cationic rearrangements of the initial primary species to more stable secondary aliphatic cations.

Unlike iodopentane, the cation formed from iodobenzene is highly unstable, so its distribution of substitution products should more strongly reflect a rate of reaction approaching a value which is diffusion controlled. Given the hydrophobicity of the parent analyte, solvent sorting would be expected to give rise to a predominance of anisole as the solvolysis product. It was noted that anisole could be photolyzed to form phenol, and such a process would alter the relative amounts of products observed in photolyzed solutions. This equilibrium could, in part, be responsible for the ≈15% yield of phenol from iodobenzene (Table II).

Photolysis–Cyclic Voltammetry. Under the cyclic voltammetry scan conditions chosen, I$^-$ exhibited two oxidative waves and two reductive waves, as shown in Figure 1. On the other hand, neither iodate or periodate evidenced inherent electroactivity within the experimental scan limits. When irradiated solutions of IO$_3^-$ were injected onto the IC system optimized for its detection, the peak corresponding to IO$_3^-$ decreased rapidly for irradiations between 1 and 5 min, until at 6 min the peak had been reduced to 1% of its original height. Similar study of IO$_4^-$ demonstrated more rapid degradation, in that unphotolyzed solutions were not stable to the IC conditions (displaying formation of IO$_3^-$ and a small, broad peak at slightly longer retention time). Only 4 min of irradiation was needed to reduce the peak height for IO$_4^-$ (as IO$_3^-$) to 1% of its initial level.

Figure 2 displays the traces obtained following 6 min of PCV of 1 ppth solutions of I$^-$, IO$_3^-$, and IO$_4^-$. The oxidative and reductive waves have very similar peak potentials and relative peak currents in these three CVs, suggesting that the same electroactive species is involved for each analyte. When this experiment was repeated and aliquots were injected onto an IC system optimized for determination of I$^-$, it was determined that I$^-$ was formed, with nearly quantitative yield, from both iodate and periodate, thereby confirming the PCV results. These findings are in agreement with those of previous
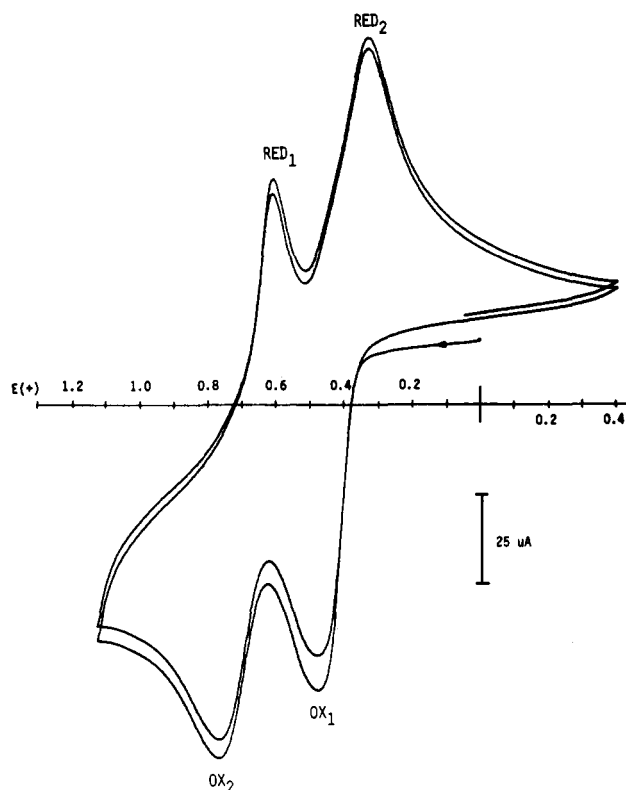
Figure 1. Cyclic voltammogram (CV) for Iodide.

Table III. FIA-EC Confirmation of Photolysis Product Experiments

lamp status	analyte injected[a]	RR (+1.0 V/+0.75 V)[b]
on	I⁻	7.62 ± 0.18
on	iodopentane	7.46 ± 0.13
on	iodobenzene	5.73 ± 0.21
off	I⁻	7.56 ± 0.16
off	phenol	1.55 ± 0.08
off	iodobenzene mix	5.04 ± 0.11
off	iodopentane mix	7.51 ± 0.09

[a] 5 ppm solutions of I⁻, iodopentane, iodobenzene, and phenol. Iodobenzene mix: 12.0 μM I⁻, 1.6 μM phenol, 4.3 μM anisole, 5.2 μM fluorobenzene. Iodopentane mix: 12.5 μM I⁻, 6.3 μM 1-pentene, 2.8 μM 2-pentene, 0.4 μM 1-pentanol, 0.8 μM 2-pentanol, 1.2 μM 3-pentanol. [b] Mean ± standard deviation (n = 10).

workers, with respect to the instability of oxygenated species of iodide when exposed to light (in the absence of strong oxidizing agents) (19).

Temporal PCV studies of the generation of electroactive species from organoiodides provided additional insight into differences in electroactivity for the products formed from alkyl and aryl iodinated compounds. As demonstrated in Figure 3, PCVs for iodopentane and I⁻ were quite similar in appearance, suggesting that the same electroactive species was being detected. PCVs for allyl iodide and 1,2-diiodoethane were also similar to that for iodide. On the other hand, the PCV for 1,4-diiodobenzene (Figure 3) displayed distinctions in response. These differences are understandable, in light of the formation of phenolic products during irradiation of aryl compounds, and similar PCV behavior was evidenced by iodobenzene.

In addition to the qualitative EC response differences delineated for the test analytes, the temporal PCV evaluations

allowed for examination of increases in electroactivity for the inherently nonelectroactive compounds, as a function of irradiation time. In Figure 4, this is aptly demonstrated for iodopentane. With increasing photolysis time, the appearance of the CV increasingly resembles that for iodide. Additionally, a plot of MCE for I⁻ generation (determined using IC) vs. irradiation time was linear for allyl iodide (MCE% = 13.96X − 10.52, where X is irradiation time (in min), correlation coefficient (r^2) = 0.969), when 1- to 8-min irradiations were incorporated. The other aliphatic organoiodides exhibited similar photolysis time–response relationships, but the aryl compounds demonstrated a quadratic relationship. This suggested that initial generation of electroactive products from aryl iodides is followed by photochemical destruction of the electroactive products to nonelectroactive forms.

The pH dependence of conversion of the test analytes to I⁻ was also determined using PCV. Peak currents at OX₁ (see Figure 1) for iodide were relatively constant when the analyte was dissolved in solutions having pHs at integer values between 3 and 7 (the useful range for silica-based reversed-phase LC columns). On the other hand, all of the test organoiodides exhibited a pronounced inverse linear relationship between pH and OX₁ peak currents, indicating greater yield of I⁻ when photolyses were performed on solutions having lower pHs. This effect has been noted in the literature (20, 21) and is postulated to be due to protonation of the excited organohalogen, followed by electron transfer from solvent and expulsion of the anionic halide.

Finally, the photochemical mechanisms proposed for iodopentane and iodobenzene were confirmed through the use of response ratios (RRs) generated in the FIA–$h\nu$–EC analysis of synthetic photolyzed solutions. As shown in Table III, the
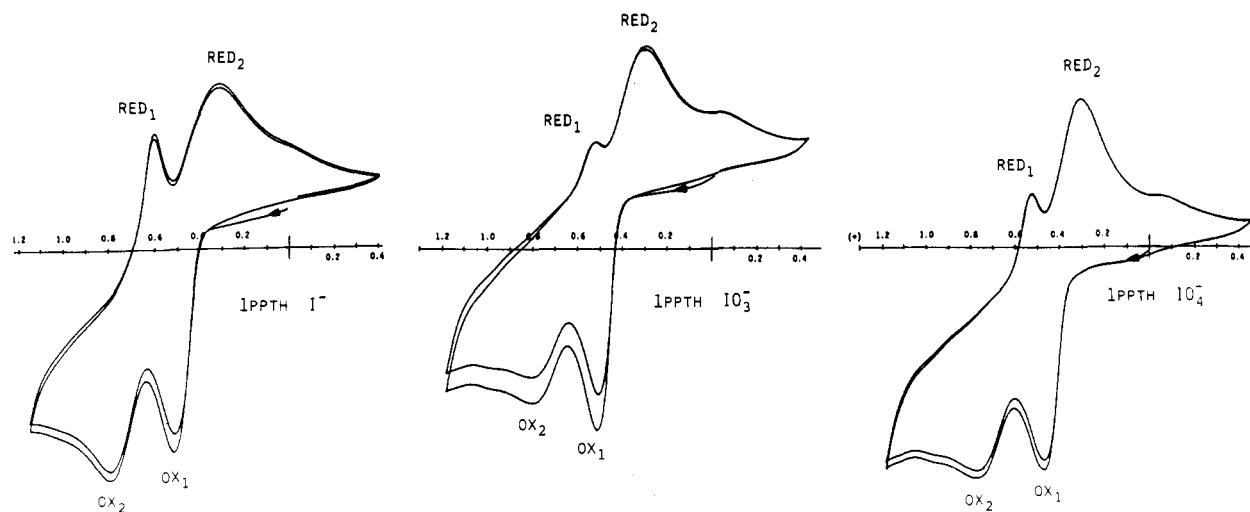

Figure 2. Photolytic–cyclic voltammograms (PCVs) for I⁻, IO₃⁻, and IO₄⁻, after 6-min irradiations.
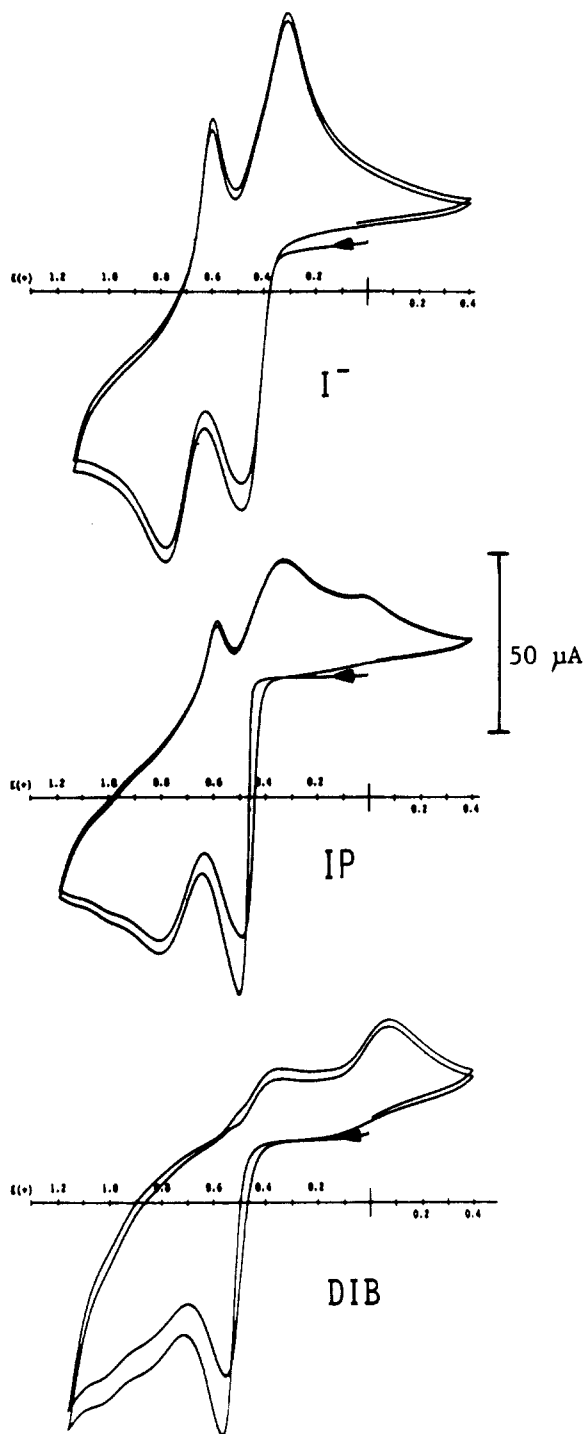
Figure 3. PCVs for I⁻, iodopentane and 1,4-diiodobenzene, after 6-min irradiations.

RRs for I⁻ and iodopentane under lamp-on conditions are significantly different than that for iodobenzene. Additionally, the RRs obtained for lamp-off injections of the synthetic photolysis product mixtures corresponded well with those observed for the parent compounds under lamp-on conditions. The small difference in RRs for iodobenzene under lamp-on conditions, and the iodobenzene synthetic mixture with the lamp off, was probably due to slight differences in the amount of phenol in the two samples. The synthetic mixture, whose composition was generated based on batch photolysis experiments, may not reflect the true proportions of products formed from iodobenzene in LC–$h\nu$–EC, since the thermodynamics in a static solution containing a high concentration of analyte may be different than those in a dilute, hydrodynamic system. However, it could be concluded that differences
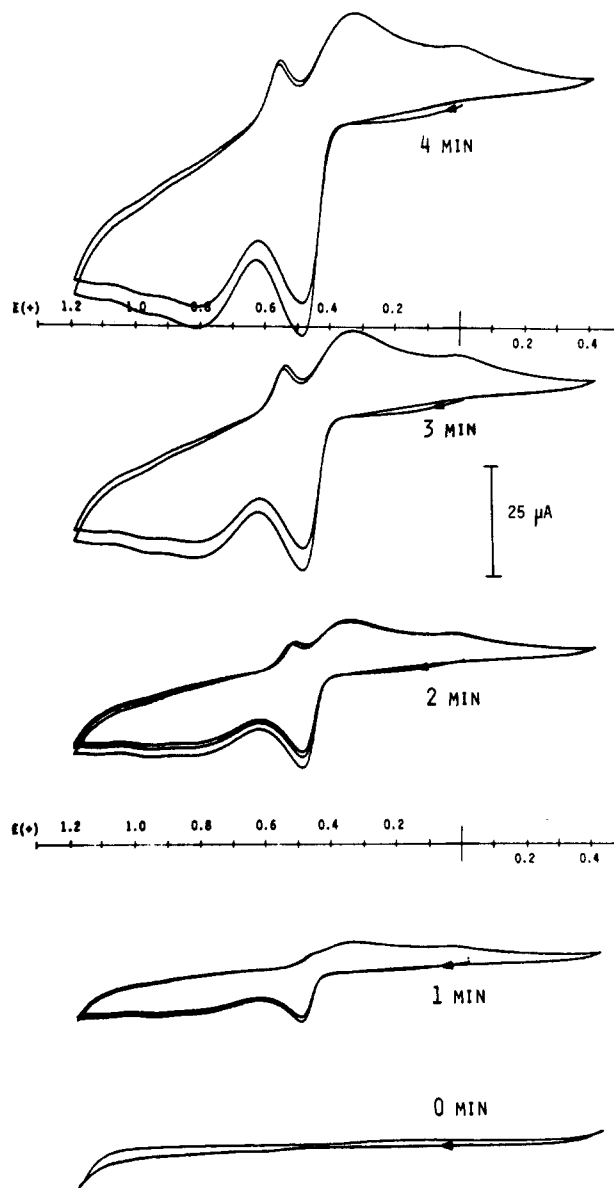

Figure 4. Temporal PCV for iodopentane.

in RRs for iodopentane and iodobenzene may be rationalized by considering differences in the amounts and identities of oxidatively electroactive species formed during photolysis of organoiodides. Additionally, the experiment demonstrated that the proper choice of working electrode potentials could facilitate the process of electrochemically distinguishing aryl and alkyl iodides.

These experiments represent the first project in a three-part program to design an improved LC detection method for organohalogens. It is envisioned that the eventual selectivity for halogenated organics using LC–$h\nu$–EC will be based on the working electrode material, mobile phase composition and pH, chromatographic retention times, electrode potentials, and lamp on/off responsiveness. It might also be possible to incorporate specific halogen–C bond selectivity into the method through the use of wavelength control (22) or by addition of photosensitizers (23) to the mobile phase. When the research program is completed, the photolytic-EC detector should offer significant improvements in the selectivity and sensitivity available during LC determinations of organohalogens.

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Registry No. I⁻, 20461-54-5; IO₃⁻, 15454-31-6; IO₄⁻, 15056-35-6; 1-iodopentane, 628-17-1; allyl iodide, 556-56-9; 1,2-diiodoethane, 624-73-7; iodobenzene, 591-50-4; 1,4-diiodobenzene, 624-38-4.

LITERATURE CITED

(1) Selavka, C. M.; Krull, I. S. Anal. Chem., preceding paper in this issue.
(2) Kropp, P. J.; Poindexter, G. S., Plenta, N. J.; Hamilton, D. C. J. Am. Chem. Soc. 1976, 98, 8135.
(3) Nagaoka, S.; Takemura, T.; Hiraoaki, B. Bull. Chem. Soc. Jpn. 1985, 58, 2082.
(4) Sharma, R. K.; Kharasch, N. Angew. Chem., Int. Ed. Engl. 1968, 7, 36.
(5) Kropp, P. J.; Jones, T. H.; Poindexter, G. S. J. Am. Chem. Soc. 1973, 95, 5420.
(6) Poindexter, G. S.; Kropp, P. J. J. Am. Chem. Soc. 1974, 96, 7142.
(7) McNeely, S. A.; Kropp, P. J. J. Am. Chem. Soc. 1976, 98, 4319.
(8) Fery-Forgues, S.; Paillous, N. J. Org. Chem. 1986, 51, 627.
(9) Cristol, S. J.; Lee, G. A. J. Am. Chem. Soc. 1969, 91, 7554.
(10) LaCourse, W. R.; Selavka, C. M.; Krull, I. S. Anal. Chem. 1987, 59, 1366.
(11) Selavka, C. M. Ph.D. Thesis, Northeastern University, 1987.

(12) Batley, G. E. Anal. Chem. 1984, 56, 2261.
(13) Ta-Shma, R.; Rappoport, Z. J. Am. Chem. Soc. 1983, 105, 6082.
(14) Johnson, C. D. Tetrahedron 1980, 36, 3461.
(15) Harris, J. M.; Clark, D. C.; Becker, A.; Fagan, J. F. J. Am. Chem. Soc. 1974, 96, 4478.
(16) Karton, Y.; Pross, A. J. Chem. Soc., Perkin Trans. 2 1977, 1860.
(17) McClelland, R. A.; Banait, N.; Steenken, S. J. Am. Chem. Soc. 1986, 108, 7023.
(18) Ritchie, C. D. J. Am. Chem. Soc. 1975, 97, 1170.
(19) Haimovich, O.; Treinin, A. Nature (London) 1965, 207, 185.
(20) Fery-Forgues, S.; Paillous, N. J. Org. Chem. 1986, 51, 627.
(21) Smothers, W. K.; Schanze, K. S.; Saltiel, J. J. Am. Chem. Soc. 1979, 101, 1895.
(22) Butler, L. J.; Hintsa, E. J.; Lee, Y. T. J. Chem. Phys. 1986, 84, 4104.
(23) Nelleborg, P.; Lund, H.; Eriksen, J. Tetrahedron Lett. 1985, 26, 1773.

Real-Time Library Search of Vapor-Phase Spectra for Gas Chromatography/Fourier Transform Infrared Spectrometry Eluents

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A gas chromatography/Fourier transform infrared spectrometry (GC/FT-IR) data collection/library search system is described which provides infrared spectral characterization of gas chromatographic eluents during separation. Parallel computing and multitasking are employed to arbitrate data acquisition and library search functions based on priority assignment. Various methods are described for increasing the efficiency of real-time library searching. The qualitative analysis capability of the system is established for a synthetic alcohol mixture. Real-time search results for unknown composition hydrocarbon and flavor mixtures are described. It is determined that the signal-to-noise ratios of GC/FT-IR eluent spectra are an important factor in the reproducibility and quality of real-time library search identification.

The importance of combining complementary structure specific detection methods with gas chromatography for complex mixture analysis is well established. A great deal of effort has been expended to develop routine gas chromatography/infrared/mass spectrometer analysis systems (GC/IR/MS) (1–7). The effectiveness of GC/IR/MS analysis is heavily dependent on the method selected for interpreting infrared and mass spectrometric information obtained during chromatographic separation. Initial GC/IR/MS identifications were performed by manually comparing library search results obtained from infrared and mass spectrometric data (1, 2). This method was time-consuming and often required days for complete data evaluation. Williams et al. subsequently proposed several schemes for automating GC/IR/MS data evaluation (8, 9). Recently, an automated GC/IR/MS data evaluation procedure based on library search comparisons was reported (5). This automated analysis system was tested by using a 17-component synthetic mixture. Gas chromatographic separation of the 17 components required 25 min but the total analysis time (including chromatographic separation) was 140 min. These results indicate that current limitations of GC/IR/MS analysis systems lie in available data reduction methods.

GC/IR or GC/MS data reduction is usually considered an off-line function. As such, gas chromatographic separation must be completed prior to initiating spectral interpretation procedures. However, real-time data evaluation can be achieved by using parallel processing data acquisition hardware (10). In this paper, we describe a GC/FT-IR mixture analysis system incorporating real-time (during the separation) library searching for chromatographic eluents. Analysis