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RESEARCH REPORT NO. 183

USE OF HIGH-ENERGY RADIATION
FOR
DEGRADATION OF ENVIRONMENTAL
POLLUTANTS

By

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ABSTRACT

The purpose of this project was to explore the advantages and/or limitations of high-energy radiation treatment as a method for degrading organic pollutants, particularly aryl halides, in an aqueous medium. We have done analyses of ^{60}Co -irradiated samples and kinetic studies using pulsed electron beams. For aryl halides containing no more than two fused rings, the main products detected are those of simple halogen replacement by hydrogen, although the amount of aryl halide destroyed was always greater than the total amount of products detected. To accomplish halogen replacement by H, the reaction solvent may not be pure water but must contain a hydrogen source such as an aliphatic alcohol. The absence of such an additive, results in products of aryl radical addition to aryl halide. The necessary amount of additive required is quite small for halobenzenes. With aryl halides of three (and presumably more than three) fused rings, the radical-anion intermediates either undergo conversion to halogen-containing dihydroarenes, or lose halogen to form radicals which resist reaction with H-donating additive and thus form dimers. When aryl halides are solubilized in micelle-forming detergent solutions, the detergent molecules serve as hydrogen atom sources. Conversions are highest with cationic detergents.

DESCRIPTORS: Detoxification, Radiation, Environment

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CHAPTER I - Introduction

It is well known, that when high-energy radiation strikes matter, bound electrons are dislodged, generating electrons and cationic holes (radical cations). The energy of the initially produced electrons is still high enough to dislodge more electrons and thus "spurs" of electrons and holes are generated.¹ For common solvents, including water, the holes are radical cations of the solvent molecules and the electrons are temporarily stabilized by solvation. In the absence of solutes, the radiation chemistry of water is rather simple² and, for the most part, the durable products are harmless to biological systems. There are, after all, a limited number of possible molecules which can be built from hydrogen and oxygen alone.

When solutes are present, the possibility exists for them to react with the radiation-produced water fragments, usually the solvated electrons or radicals produced from solvent cation radicals. It has been established, that many, if not all, functionalized organic molecules present under these circumstances will capture some fraction of the solvated electrons. This produces radical anions. There then results a competition in which the radical anion of the organic molecule either transfers its electron back to a hole or undergoes some chemical change, often bond scission.³ When the solvent is water, the solvent radical cations (H_3O^+) produce hydroxyl radicals which can react with a variety of organic molecules to give hydroxyl-substituted products or products of hydrogen atom removal. Oxygen atoms can also be generated.⁴

Recently, it has been recognized that the processes mentioned above, provoked by relatively inexpensive radiation sources such as gamma-ray-producing ^{60}Co , could represent practical approaches to degrading environmental pollutants, particularly those that are resistant to biological decomposition. Getoff has studied the destruction of several low molecular weight chlorinated hydrocarbons in oxygenated water.⁵ Geringer has followed the removal of tri- and tetrachloroethylene from Vienna City water at sub-ppm levels using gamma irradiation in the presence of ozone.⁶ There have been a number of studies on radiation of aqueous and nonaqueous solutions of pesticides as discussed later. Others have studied the oxidative decomposition of aromatic hydrocarbons.⁷ The increasingly stringent limits on allowable levels of organic pollutants in drinking water⁸ coupled with the unique capacity of high-energy radiation to promote decomposition of pollutant molecules at extremely low concentrations, makes this approach seem particularly attractive.

Although there would certainly be initial public resistance to the idea of using radiation in water purification, the use of irradiation for food sterilization is gradually gaining public acceptance.⁹ Viewing the situation from a purely scientific perspective, the radiation chemistry of water is extremely simple by comparison with the complex possibilities which exist for food stuffs¹⁰ and, in principle, is more likely to be safe.

For our work, we have chosen to focus our examination on the radiation chemistry of aryl halides in aqueous systems. Aromatic compounds are often suspected as carcinogens. Aryl halides are suspected of this and a variety of environmentally

deleterious effects. Halides are resistant to the metabolic machinery of most organisms. They tend to persist in water and soil and eventually to be concentrated in certain parts of the food chain. Recently there has been considerable concern registered over dioxin which is known to be toxic at extremely low levels.¹¹ PCB's have been the target of clean-up efforts for some time. Current efforts have emphasized bioremediation.¹²

There is a moderate volume of previous work dealing directly with the radiation chemistry of environmentally hazardous aromatic halogen compounds. DDT was studied as early as 1971.¹³ Many of the DDT studies were carried out in organic solvents¹⁴ but experiments on pesticide mixtures containing DDT have been carried out in aqueous solution¹⁵ and DDT itself has been studied in aqueous solution, solubilized by detergent.¹⁶ Radiative degradation of PCBs has been studied, again mainly in organic solvents,¹⁷ but occasionally in water¹⁸ and one study showed a decreased toxicity to brine shrimp of an aqueous PCB solution after irradiation.¹⁹

Partially because of concerns over toxicity of logical target substances such as PCBs or dioxins and partially for reasons of facilitated analysis, we chose to study a structurally simple set of aryl halides. We started with naphthyl and anthryl halides because we felt that these would not only be convenient for product studies but they would also provide the option to do kinetic studies using pulsed radiation sources. We believe that information more easily obtained with these relatively simple and relatively nonhazardous compounds will be extendable to the more complex aryl halides which constitute identified environmental threats. These compounds had not been studied in

aqueous solvents. For reasons to be given in the course of our discussion, we have also done some preliminary product studies with a halophenol which could be studied in pure water and some molecules containing both halogen and labile benzylic ethers.

CHAPTER II. Research Procedures

⁶⁰Co Irradiations. Samples for ⁶⁰Co irradiation were prepared by weighing the appropriate compound or compounds into a dichromate-cleaned, ammonia-rinsed, oven-dried glass 150 mm Pyrex glass test tube. The tube was stoppered with a rubber septum which was securely wired to insure closure and to prevent slippage. For anaerobic runs deoxygenated argon gas from an Ace-Burlich inert atmosphere system, was passed into the tube through a syringe needle inserted through the septum and exited through a second, smaller diameter needle. Solvents (generally HPLC grade), previously bubbled with argon were introduced using a gas-tight syringe and the entire reaction mixture was bubbled with argon for at least ten minutes before removal of the needles and irradiation. Tubes were mounted inside of a polypropylene cylinder which was placed in the target chamber of an Atomic Energy of Canada Gamma Cell 200 ⁶⁰Co source. Radiation rates were of the order of 1000 to 1200 kilorads / min and times ranged from a few hours to two days. Reaction mixtures were analyzed directly using either a Varian Model 3700 gas chromatograph with flame ionization detection and a SE-54 coated capillary column or with a Waters High Pressure Liquid Chromatograph with a methanol-water solvent gradient, a reverse-phase C₁₆ column and UV detector. For runs employing a comparison standard, biphenyl was employed with GC analysis

and 3-nitrophenol with HPLC analysis. On some occasions, isolated materials were analyzed using a Varian 200 MHz Gemini Nuclear Magnetic Resonance Spectrometer.

Pulse Radiolysis Experiments. Pulse radiolysis experiments were carried out both at the Center for Fast Kinetics Research in Austin, TX (this system has been described earlier)²⁰ and at the Notre Dame Radiation Laboratory, Notre Dame, IN, using a LINAC accelerator. The latter system has been described in detail earlier²¹ and the procedures are those described by Chateauneuf.²²

CHAPTER III - Data and Results

Product Studies on Anthryl and Naphthyl Halides

Tables I and II compile the results of our study of products obtained from the ⁶⁰Co irradiation of various naphthyl and anthryl halides. As pointed out in the introduction, target compounds were chosen mainly for analytical convenience. However, as it has turned out, the anthryl halides show unexpected and interesting phenomena which establish some limits for the use of radiation in the removal of halogen atoms from aromatic compounds. It seems likely that these limits will also be encountered when phenyl and naphthyl halides contain radical-anion-stabilizing substituents.

Samples were dissolved in the solutions indicated and irradiated as described in the methods section. As will be seen from the initial entries in Table I, 9-bromo- and 9-chloroanthracene (9-BrAn and 9-ClAn) behave as might be expected from literature

Table I. Product Yields from ^{60}Co Irradiation of Aryl Halides.

X-Ar	[XAr] ₀ M	Solvent	Dose Mr	Additive	Conversion ^a μmoles/mL·Mr	% in Reaction Mixture				
						XAr	HAr	Ar ₂	Other	Missing
9-BrAn	2.0	EtOH/H ₂ O 75:25 (v:v)	0.33	none	4.4	27	4.9	7.5	--	61
9-ClAn	2.2	same	0.33	none	4.6	32	2.6	2.4	--	63
1-BrNp	2.5	same	0.33	none	3.7	50	6.3	<1	--	43
1-ClNp	1.1	same	0.33	none	3.7	35	13.6	<1	--	51
9-BrAn	2.0	same	0.33	O ₂ ^b	0.9	85	<1	<1	--	15
1-BrNp	2.9	same	0.33	O ₂ ^b	<0.1	>99	<1	<1	--	<1
1-ClNp	1.6	same	0.33	O ₂ ^b	0.7	85	<1	<1	--	15
1-ClAn	5.2	same	1.10	none	2.6	45.6	<1	<1	7.0 ^d	47.4
9,10-Cl ₂ An	1.5	same	1.10	none	0.8	40.0	13.8	--	40.9 ^e	5.3
9-BrAn	9.7	MeCN	1.30	none	4.4	41.4	<1	<1	--	58.6
9-BrAn	9.7	MeCN/H ₂ O 75:25 (v:v)	1.30	none	4.3	43.2	<1	<1	--	56.8
9-BrAn	9.8	MeCN	1.30	Et ₃ N ^c	3.8	49.5	8.6	<1	--	41.9
1-BrNp	14.1	MeCN	1.30	none	3.7	66.4	9.2	<1	--	24.4
1-BrNp	14.5	MeCN/H ₂ O 75:25 (v:v)	1.30	none	1.3	88.5	1.9	<1	--	9.6

^aConversion based on loss of XAr.

^bSolution saturated with O₂ prior to irradiation.

^c[Et₃N] = 0.2 M.

^dTotal of four additional peaks detected by GC with retention times comparable to 1-ClAn. Three of these showed m/z = 214 for highest mass ion in GC/MS. This corresponds to a chlorodihydroanthracene.

^eOther products were anthraquinone, 6.3%; an isomer of 9-ClAn, 3.1%; material with GC/MS ion at m/z = 284. Appeared to contain no chlorine. Three other unidentified products totaled 23.2%.

Table II. Products from ^{60}Co Irradiation^a of Aryl Halides.

XAr	Solvent	Additive	% of GC-Observed Products ^e			
			XAr	HAr	Ar ₂	Other
9-BrAn	EtOH	none	83.5	6.8	9.7	<0.5
9-BrAn	EtOH	Et ₃ N ^d	77.5	13.5	9.0	<0.5
9-BrAn	EtOH/H ₂ O ^c	Et ₃ N ^d	44.7	34.8	11.2	9.2 ^g
9-ClAn	EtOH	none	92.7	3.4	1.4	2.5 ^h
9-ClAn	EtOH/H ₂ O ^c	none	84.3	4.1	9.6	2.0 ⁱ
9-ClAn	EtOH	Et ₃ N ^d	82.9	10.1	1.8	5.3 ⁱ
9-ClAn	EtOH/H ₂ O ^c	Et ₃ N ^d	68.7	18.0	7.5	5.7 ⁱ
9-ClAn	MeCN	none	98.9	1.1	<0.5	<0.5
9-ClAn	MeCN	Et ₃ N ^d	97.9	2.1	<0.5	<0.5
1-BrNp ^b	MeCN/H ₂ O ^f	Et ₃ N ^d	66.3	33.7	<0.5	<0.5
1-ClNp ^b	MeCN/H ₂ O ^f	Et ₃ N ^d	85.5	14.5	<0.5	<0.5
1-ClNp	MeCN/H ₂ O ^f	none	>99	<1	<1	<1

^aSamples received dose of 1.3 mR and $[\text{XAr}]_0 \cong 10$ mM except as otherwise noted.

^bThese samples received a dose of 5.06 mR. $[1\text{-BrNp}]_0 = 14.1$ mM. $[1\text{-ClNp}]_0 = 19.0$ mM.

^cEtOH: H₂O = 75:25 (v:v).

^d[Et₃N] = 0.2 M.

^eThese represent percent of total detected materials as determined by GC. Amounts "missing" were not determined for this set of experiments. See Table I.

^fMeCN: H₂O = 75:25 (v:v).

^gUnidentified long retention time material.

^hUnidentified material of slightly longer retention time than 9-ClAn. GC/MS suggests solvent substitution product.

ⁱTwo peaks of longer retention time than An₂.

suggestions. When exposure to air was scrupulously avoided, the products observed were mainly anthracene (**HAn**) and bianthryl (**An₂**) (structures in Figure 1). Yields of bianthryl were necessarily approximate, because this material was partially insoluble in the reaction solvent. The commonly accepted mechanism for this process is the sequence of eqs 1-6. With haloanthracenes it was especially important to exclude oxygen from the reaction solutions. It can be seen from entries 5-7 in Table I that saturation with O₂ effectively prevents at least the reductive part of the radiation-induced reaction from occurring. This presumably results from the ability of O₂ to react with the solvated electrons which would otherwise initiate the reactions in eqs 3-6. Considerable care was taken to exclude air in the anaerobic reactions because 9-anthryl halides in solution were slowly transformed to anthraquinone even in the absence of gamma radiation when exposed to air. This reaction is believed to be promoted by light and is observed after several days in laboratory light.



In general where the goal is to remove pollutants from aqueous systems, the formation of higher molecular weight materials will be undesirable. It seems likely that

the reduced yield of An_2 obtained in pure ethanol as contrasted with ethanol-water is reflective of the trapping of anthryl radicals by ethanol (eq 6). The data suggest that ethanol is rather inefficient at trapping 9-anthryl radicals in that a substantial amount of bianthacenyl, An_2 , is formed, even in pure ethanol. Addition of triethylamine also seemed generally to reduce the relative amount of dimer observed, but this product could not be avoided in ethanol or ethanol-water.

If the solvent is acetonitrile, both with and without water, radiolysis of 9-BrAn gave no gas chromatographically-observable products unless triethylamine was added (entries 10-12 in Table I). This suggests that, at least in this solvent, triethylamine also plays a role in the formation and/or fate of the radical anion itself, because, had the radical been formed it seems highly unlikely that it would have given an undetectable product. Moreover, we have been able to show that neither pyridine nor hydroxide ion have the same effect, thus suggesting that it is not the basicity of triethylamine that is the important factor.

To explain the effect of triethylamine in acetonitrile, we suggest the reaction sequence of eqs. 7 - 12. It is necessarily true that when gamma rays react with any solvent, the result will be the production of solvated electrons and "holes" (eq 7). If the solvent has the proper reduction potential, the electrons will produce radical anions of the solvent. In the case of acetonitrile, it has been shown that the radical anion of acetonitrile is formed and reacts by eq 8.²³ Either the solvated electron or the solvent radical anion is capable of reducing anthracene²⁴ as well as compounds of even more

negative reduction potentials. Thus, it seems certain that all of the compounds in Table I can and will be converted to radical anions in acetonitrile. The fact that neither HAn nor An₂ is obtained, presumably must mean that some species produced from the "hole" or radical cation, builds up and removes the electron from the radical anion faster than it decays (eq 9-10). We would suggest that triethylamine captures, either this species or the "hole" itself (eq 11), through its known abilities as an electron donor. Amines have, in fact, been shown to perform this function in acetonitrile.²⁵ Thus, in the presence of amines, the oxidizing species are trapped and the radical anion is allowed time to dissociate to aryl radical and halide ion (eq 4). It will be noted that for 9-ClAn, the conversion to HAn is small even in the presence of triethylamine. Perhaps, in this case, the slower rate of dissociation of the radical anion allows time for reaction with radical cations present, including Et₃N^{•+}.



For the halonaphthalenes, XNp, radiolysis produces naphthalene, HNp, in all solvents, even acetonitrile. The dissociation of the halonaphthalene radical anions (eq 4) is appreciably faster than that for the corresponding haloanthracene radical anions

as shown both by pulse radiolysis²⁶ and by electrochemical measurements.²⁷ The absolute values of rate constants for the processes of eq 4 vary considerably as determined by the two methods. However, the former, a more direct and presumably more accurate method, gives rate constants as shown in Table III. The fact that the dissociation of BrNp^\cdot is extremely fast, adequately explains the fact that for this compound, there is no appreciable affect of additives on the yield of naphthalene. 9-BrAn^\cdot , however dissociates more slowly and is therefore subject to being oxidatively trapped before bond scission can occur. 1-ClNp , the radical anion of which dissociates at about the same rate as that of 9-BrAn^\cdot , also gives very little naphthalene on radiolysis unless triethylamine is present.

Table III. Rate Constants of Dehalogenation of the Aryl Halide Radical Anions in Aprotic Solvent²⁶

Compound	$k(\text{s}^{-1})$
1-Chloronaphthalene	7.6×10^6
1-Bromonaphthalene	$>10^9$
9-Chloroanthracene	8.3×10^5
9-Bromoanthracene	2.5×10^6

The results with 1-ClAn are different from all of the other cases in that no anthracene is produced, even in ethanol-water. This observation agrees with the fact that, in contrast to the other systems studied, the acidity of the reaction mixture does not increase on irradiation. Thus halide loss does not seem to occur. Moreover, the

only, relatively low yield, products observed appear to be dihydroanthracenes as evidenced by GC/MS data and as expected for the protonation of anthracene-type radical anions.²⁸ We will discuss this result as well as the results for **9,10-Cl₂An** in the following section.

A major question remaining from our study is that of the identity of the "missing" product or products. In the initial stages of this work, we were satisfied with the fact that gas chromatographic analysis (GC) of reaction mixtures showed mainly the expected ArH and Ar₂ type products and no significant amounts of other materials. However, as a safety check, we decided to determine absolute yields by adding a carefully measured amount of internal standard to a portion of the reaction mixture both before and after irradiation. To our surprise, in all cases, there was a significant amount of material loss which was not accounted for by the amounts of observed products. Our initial skepticism about this result has been overwhelmed by the large number of experiments which have shown this outcome. As can be observed in Table I, of the order of 50% of the starting ArX is lost but the amounts of observed products do not account for this loss. In the cases where the substrate is **ClAn** and **BrAn**, some of the material loss is accounted for by precipitated **An₂**, but with **BrNp** and **ClNp**, there is no precipitate nor is there more than a trace of **Np₂**. Therefore, we are forced to conclude that there are products formed which are not determined by GC analysis. Reinforcing this conclusion is the fact that when the reaction mixture is saturated with O₂ prior to irradiation, the recovery of starting material is at least 85%. (See entries 5-7 in Table I.)

We must then ask, what sorts of products would not be detected by GC analysis? The possibilities are: 1. high molecular weight compounds which are not sufficiently volatile to pass through the GC column, 2. low molecular weight fragments which elute with the solvent, or 3. heat sensitive materials which decompose in the GC injection port and are thus not detected. We have carried out a preliminary study of the reaction mixtures using high-pressure liquid chromatography (HPLC) rather than GC analysis. We find, first of all, that the amount of ArX lost, using HPLC is comparable to that determined by GC. Moreover, there are a number of unexplained products detected by this method. Also, not only do these products not appear when the reaction is carried out in an atmosphere of O₂, but the amount of starting compound unaccounted for in the O₂ reaction becomes insignificant. At this stage, we have not begun the process of trying to separate and identify the products observed in the HPLC runs. It is possible, and even likely, that some of these result from reactions of solvent and do not involve ArX materials. However, it seems likely that at least some of the observed materials are compounds are ArX derived materials which are not detectable by gas chromatography. Because the HPLC uses a UV absorbance detector, which responds in proportion to the molar absorptivity of the compound being detected, we cannot say anything about the amounts of products until they have been identified.

Pulse Radiolysis Experiments with Haloanthracenes

The literature reports a number of pulse radiolysis studies on 9-haloanthracenes and halonaphthalenes.^{26,29,30} It is generally agreed that these compounds are converted to radical anions which then lose halide ion. However, there have been no

product isolation studies of the type described in the previous section and, moreover, none of these studies has been carried out in aqueous or alcoholic solvents. The question then arises, for these and for other aryl halides: will the process be the same when water is present? It is well known that radical anion solutions in organic solvents are stable only when scrupulously protected from moisture. Moreover, the rate constants for protonation of some arene radical anions by alcohols have been measured.³¹ The results for anthracene are given in Table IV. It will be noted that the rate constant for protonation of anthracene in ethanol is only slightly slower than that reported (see Table III) for the dissociation of halide from 9-CIAn⁻. The protonation rate reported for methanol is faster.

To make the comparisons more apt, we undertook radiolysis measurements in aqueous alcohol solutions. Approximately 2 mM solutions of haloanthracenes in aqueous ethanol irradiated with a pulse of 4 to 10 MeV electrons produced transient absorbances which were clearly due to anthracene-type radical anions.

9-Bromoanthracene, 9BrAn

Interpretation of the data for this compound was the most straightforward of the various compounds studied. The spectrum of transients shows only a long-wavelength absorption which has a broad maximum at 680 nm and which tails beyond the range of the spectrophotometer (700 nm). This corresponds to literature spectra in other solvents.^{26,28,29} Rate data from several runs carried out in two different laboratories gave a decay rate constant for the long wavelength transient, measured at 650 nm, of $2.6 \pm$

Table IV. First-order Rate Constant for the Protonation of Aromatic Radical Anions in Aliphatic Alcohols.³¹

Alcohol	Biphenyl	Anthracene
Methanol	$17 \pm 3 \times 10^5$	$20 \pm 1.2 \times 10^5$
Ethanol	$4.4 \pm 0.4 \times 10^5$	$4.0 \pm 0.4 \times 10^5$
n-Propanol	$4.3 \pm 0.4 \times 10^5$	$3.2 \pm 0.5 \times 10^5$
iso-Propanol	$0.72 \pm 0.14 \times 10^5$	$0.47 \pm 0.08 \times 10^5$

$0.2 \times 10^6 \text{ s}^{-1}$. This rate is close to the decay rate for the solvated electron and the observation range is in the region where the solvated electron absorbs, making it possible that the decay of the solvated electron might be contributing to the process being followed. However, the fact that the decay rate was not significantly affected by changing the concentration from 0.8 mM to 5.9 mM, provided that measurements at times less than 0.1 μs after the pulse are ignored, seemed a clear indication that we were observing simple unimolecular decay of the observed transient species.

It thus seems certain that the spectrum we observe is that of $\text{9-BrAn}^{\cdot-}$. However, despite the fact that the rate constant we determine agrees, within experimental uncertainty, with that reported for unimolecular $\text{Br}^{\cdot-}$ loss in aprotic polar solvents such as hexamethylphosphoric triamide (HMPA),²⁶ the possibility for protonation of the radical anion cannot be ignored. As will be noted in Table IV, the pseudo-first-order rate constant for protonation of anthracene by methanol is in the same range as our

observed rate of radical anion decay in ethanol-water. The identified products in our study are clearly consistent with a simple unimolecular loss of Br⁻ to give an anthryl radical which can either remove H atoms from solvent to give anthracene or dimerize as shown in eqs 5 and 6. However the fact that no products indicative of radical anion protonation were observed is not absolute proof that this process does not compete. In fact, because it is true that in product isolation studies the reaction mixture becomes appreciably acidic toward the end of the radiation period, it would seem unlikely that protonation could be avoided.

9-Chloroanthracene, 9-ClAn

Pulse radiolysis of 9-ClAn gives a long wavelength spectrum similar to that observed for 9-BrAn⁻ with an absorption maximum at 680 nm. In all of the pulse experiments with this compound there was a transient absorption which grew in after the pulse between 450 and 500 nm with a rather sharp maximum at 480 nm. It seems likely, based on literature spectra,^{32,33} that this is due to the radical anion of anthraquinone. This transient disappears if the flow of solution through the observation cell is halted and it is given a few pulses of the electron beam. This suggests that the anthraquinone is present as a trace impurity, which is consumed by the pulsing process. The 9-ClAn used was scrupulously purified by gas chromatographic separation followed by recrystallization and showed less than 0.1 % of GC measurable impurities, however it seemed extremely difficult to avoid traces of anthraquinone and it was necessary to remove it by a few pulses preliminary to the actual measurements.

The rate constant for decay of the long-wavelength absorption (measured at 650 nm) after the 480 nm transient had been removed by no-flow pulsing was ca. $3 \pm 0.5 \times 10^4 \text{ s}^{-1}$. We were concerned that the required no-flow procedure might generate enough HCl to enforce protonation (doing the pulse experiment in 20 mM HCl eliminated all transients) so we tried the experiment with triethylamine present. This did not affect the decay rate.

We conclude that the rate constant for loss of chloride ion from 9-ClAn^\cdot is $3 \pm 0.5 \times 10^4 \text{ s}^{-1}$. This is an order of magnitude slower than the protonation rate for the radical anion of anthracene in ethanol. Thus it seemed possible that protonation could account for some of this process. However, ^{60}Co radiations of this compound in ethanol-water show the same products as for 9-BrAn , so it's not obvious that radiolysis has to involve anything more than simple halide loss from the radical anion. (There is one minor, GC-observable product which has not yet been identified; but it would appear that at least the observed products of the process measured through decay of the transient absorption at 650 nm are consistent with the process being loss of halide.) Our results with this system suggest that the presence of chlorine at the 9-position of the 9-anthracene radical anion reduces the rate of protonation by comparison with unsubstituted anthracene by at least a factor of 10 which is particularly interesting in comparison with the cases which follow. It should also be noted that the rate constant we determine for this compound is more than an order of magnitude slower than reported for this process in HMPA.²⁶ This could be a solvent effect, but if so, it does not occur in the 9-BrAn case for which the value reported in the literature in HMPA²⁶ agrees

exactly with our value as well as with another literature value obtained in acetonitrile ($2.1 \times 10^6 \text{ s}^{-1}$).³⁴ Also, it appears that the measured rate constant difference between bromo- and chloronaphthalene radical anion dissociation is more than 10^2 . It seems rather unlikely that the rate difference would be less for the haloanthracene radical anions which, being more stable, should be more selective in their propensity to lose halide ions. This discrepancy with the literature remains to be resolved. However, the problems we experienced with purification of the 9-chloro compound suggest to us that small amounts of anthraquinone, which would destroy the 9-ClAn^- by electron transfer, could account for the literature numbers. In fact, our initial attempts to determine the rate constant with less rigorously purified compound gave values much closer to those previously reported.

9,10-Dichloroanthracene, 9,10-Cl₂An

The radical anion is again observed, in this case showing an absorption maximum at 680 nm. If the compound is carefully purified and O_2 is carefully excluded, the radical anion is stable over the time scale of the pulse radiolysis signal, losing less than 10% of its intensity in the first 100 μs , indicating that the rate constant for any process undergone by the radical anion was less than $1 \times 10^3 \text{ s}^{-1}$. Literature information²⁹ indicates a dissociation rate for $9,10\text{-Br}_2\text{An}^-$ of $2.7 \times 10^5 \text{ s}^{-1}$ which is 10 times slower than the monobromocompound. It would appear from our data that a second chlorine is more stabilizing than a second bromine in respect to the effect on halide dissociation, probably at least two powers of 10. Of course, it must be remembered that our data refer to a hydroxylic solvent environment, which could make a difference. We may try

to measure the rate of dissociation of **9,10-Br₂An^{•-}** in an aqueous environment. However, the extremely poor solubility of the parent compound may make this impossible.

Despite the slow rate of loss of **9,10-Cl₂An^{•-}**, product analysis shows that this compound is converted to **9-ClAn** on irradiation. This apparently means that the dissociation rate is slow but is still the dominant process. It is remotely possible that protonation of the radical anion occurs and somehow leads to **9-ClAn**, however we would not expect this to be the outcome of such a protonation. Moreover, even if this were the case, the pseudo-first-order rate constant for protonation would have to be less than 10^3 s^{-1} which is more than two orders of magnitude slower than the protonation rate reported for anthracene, even in pure ethanol (Table IV.) These data make it clear that the presence of the second chlorine in this compound has the effect of stabilizing the radical anion intermediate, both toward dissociation and toward protonation.

1-Chloroanthracene, 1-ClAn

Pulse radiolysis of this compound in 75:25 ethanol-water showed the usual transient absorption for the radical anion from ca. 580 to past 700 nm with a possible maximum at 710 nm. The decay rate constant for this transient was $1.7 \pm 0.1 \times 10^4 \text{ s}^{-1}$ at 650 nm. It is most interesting to note that no anthracene is formed when this compound is subjected to ⁶⁰Co irradiation in ethanol-water. Radiolysis mixtures contain three GC-observable products in small amounts. These appear to be dihydrochloroanthracenes by GC-MS. Although this product analysis is somewhat

tentative in lieu of isolation and detailed analysis, it is clear that (1) HAn is not formed and (2) the products which are observed have not lost chlorine. This means that the process by which the long-wavelength absorption decays is probably protonation of 1-ClAn⁻ and this takes place at a rate about 20 times slower than that reported for unsubstituted anthracene radical anion in ethanol. One curious phenomenon which we can't explain at present is a small but reproducible rate increase which occurs when triethylamine is added to the solution (a factor of 2). We cannot see why the rate of a protonation should be increased by addition of a base. Another strange phenomenon which is observed with both this compound and the dichloroanthracene is a negative absorbance which grows in at short wave lengths. For 1-ClAn, this becomes two clear minima at 405 and 430 nm. The 9,10-Cl₂An experiment gives a single minimum at 415 nm. These minima correspond exactly to triplet absorptions reported for these compounds.³⁵ The triplet seems to be produced by the lamp used for detection and apparently is present in the sample at the instant of the electron pulse. What seems to occur is that formation of triplet by the light is interrupted by the electron pulse. It is this latter phenomenon which is not presently understood. We will investigate this further.

Summary of Kinetic Data for Halonaphthalenes and Haloanthracenes

The data obtained in ethanol-water for the disappearance of the haloanthracene radical anions is summarized in Table V. It is curious that 1-ClAn⁻ seems to favor protonation relative to loss of chloride. Its rate of protonation seems to be roughly the same as that for the loss of chloride from 9-ClAn⁻ suggesting both that loss of halide from the 9-position is preferred over loss from the 1-position and that protonation of the

9-substituted compound is slowed more than for the 1-substituted compound.

Table V. Rate Constants for Disappearance of Haloanthracene Radical Anions in Ethanol-Water (80:20 v:v)

Compound	k(s ⁻¹)
9-BrAn ^{-•}	2.6 ± 0.2 X 10 ⁶
9-ClAn ^{-•}	3.0 ± 0.5 X 10 ⁴
1-ClAn ^{-•}	1.7 ± 0.1 X 10 ⁴ (protonation)
9,10-Cl ₂ An ^{-•}	<1 X 10 ³

Preliminary product studies in acetonitrile suggest that even when protonation is not an option, the loss of halide from the 1- or 2-position of anthracene-type radical anions is not a favorable process. Spectroscopic and theoretical studies of 9-anthryl radicals (the products of halide loss) suggest that these are simple sigma radicals with the same electronic structure as phenyl or naphthyl radicals.³⁶ It is, therefore, not clear why the 9-anthryl radical should form more readily than the 1-anthryl radical. One possible reason is the greater relief of steric congestion when the 9-substituted anthracene radical anion loses halide. However, it is not clear that this explanation is consistent with the preference for the 9-anthryl radical to give An₂ rather than HAn, the former having a rather congested structure. It would be of considerable interest to establish the actual rate difference for halide loss from 9- vs. 1-haloanthracene radical anions, but the fact that the 1-chloro compound chooses a different route of reaction prevents

comparison. It would, therefore, seem important to measure the rate of halide loss from 1-bromoanthracene radical anion which should be more disposed to cleavage. Unfortunately, this compound is not commercially available and literature syntheses are long and complex. We have devised a simple synthesis which we hope will provide a source of this compound. The synthesis of this compound will be undertaken soon.

It would appear that the steric argument mentioned above to explain the relatively rapid loss of halide from the 9-substituted anthracene radical anions must also be invoked to explain the fact that 9,9'-bianthryl, An_2 , is a major product from both 9-haloanthracenes in ethanol-water. This suggests that the 9-anthryl radical is appreciably less reactive with solvent than is 1-naphthyl radical, the latter leading to very little 1,1'-binaphthyl, Np_2 , under the circumstances of our experiments. If no alternative explanation can be found, it would appear that the steric problems for radicals localized in the 9-position of anthracene have an appreciably greater effect on the reaction with solvent than on the dimerization of two radicals.

Haloanthracenes show some structural similarity to dioxin (see Figure 1) and the fact that the 1-ClAn and 2-ClAn appear to be resistant to radiation treatment could be taken as a sign that this methodology would not work if applied to what might potentially be considered as a prime target. However, we feel fairly certain that the nonbonded electrons on the two central oxygens in dioxin would have the effect of destabilizing the radical anion and increasing the rate of halide loss. Although we noted above that the result with 9,10-Cl₂An suggests that multiple halogens will slow halide loss, it apparently

also slows the rates of alternative processes as well. As will be seen below, polyhalobenzenes and halophenols are susceptible to radiolytic dehalogenation. We suspect these are better models for compounds such as dioxin (TCDD). Our laboratories were not equipped for the handling of this highly toxic and probably carcinogenic³⁷ material and we have thus far resisted the temptation to study this class of compounds directly.

Deuterium Tracer Experiments

One way to check for the possible involvement of radical anion protonation in the formation of dehalogenated materials is to carry out the radiolysis reactions in the presence of deuterium atom sources. The results are summarized in Table VI. For the set of experiments in a solvent composed of ethanol-O-d ($\text{CH}_3\text{CH}_2\text{OD}$) and D_2O under the same conditions as described for the runs in the corresponding undeuterated solvents. We found that for radiolysis of BrNp and ClNp, the naphthalene produced contained no significant amount of deuterium. This is consistent with the reaction of eq 6 being the only significant product forming step. Because the O-H(D) bond dissociation energy is much higher than that for the C-H bond, reaction with a radical would be expected to involve only the C-H. Thus there seems no doubt that the radiolytic conversion of naphthyl halides to naphthalene involves simply formation of the naphthyl halide radical anion, dissociation to the naphthyl radical and abstraction of a hydrogen atom from a C-H bond in solvent (eqs 3,4 and 6).

To our great surprise, however, both 9-BrAn and 9-ClAn showed deuterium in the radiolysis-generated anthracene. Moreover, the amount of deuterium in each case

was almost exactly the same: 26% of one atom of D. This must mean that there are two separate paths leading to anthracene and two separate sources of the hydrogen atom which replaces the halogen, one of which involves transfer from the C-H bond in solvent and the other from the O-H bond (O-D in the tracer experiments). It seems very

Table VI. Radiolysis of Aryl Halides in Deuterium-Containing Solvents.

Aryl Halide ^a	Solvent	Product	% Of One D Atom
1-ClNp	EtOD - D ₂ O	NpH	none
1-BrNp	EtOD - D ₂ O	NpH	none
9-ClAn	EtOD - D ₂ O	AnH	26%
9-BrAn	EtOD - D ₂ O	AnH	26%
1-BrNp	CD ₃ CN - Et ₃ N	NpH	none
9-ClAn	CD ₃ CN - Et ₃ N	AnH	none

^a The aryl halide remaining unreacted was found to contain no deuterium.

unlikely that the proton transfer step occurs prior to the formation of the anthryl radical, because most mechanisms which might be envisioned, especially those involving protonation of the radical anion, should not lead to anthracene. Because the dissociation step is clearly faster for the bromo compound than for the chloro compound, there is no way that radical anion protonation could explain getting the same amount of D in anthracene produced from both precursors. As discussed above in connection with the kinetic studies carried out by pulse radiolysis, the disappearance rate for the

chloroanthracene radical anion is comparable to the rate anticipated for protonation but the corresponding bromine-containing radical anion dissociates much faster.

It thus seems clear that the 9-anthryl radical, which of course would have the same chemical reactivity whether produced from the chloro or bromo precursor, must somehow lead to both H- and D-substituted anthracene. Although, we have found examples in our own work where radiolysis-produced radicals are reduced to anions by yet undissociated precursor radical anions, the sequence of eqs 13 and 14,³⁸ such a sequence requires that the dissociation reaction (eq 13 or 4) be rather slow. While this may be possible for the chloroanthracene radical anion, it seems highly unlikely for bromo compound. Moreover, evidence for the reaction of eq 14 was obtained in a pulse experiment wherein the concentration of radical anion was relatively high immediately after the short-lived but intense burst of electrons produced by the pulse. ⁶⁰Co irradiation should produce a constant, but much lower, steady-state concentration of radical anions. Therefore to explain the deuterium incorporation result, we are forced to seek an alternative rationale.



Our current hypothesis is based on the fact that of all the haloaromatics we have looked at, only the 9-haloanthracenes give significant amounts of dimeric product. We believe that for anthryl radical in ethanol-water, this occurs via eq 5, simple dimerization

of anthryl radicals. Moreover, we suggest that this means that the reaction between ethanol (C-H bond) and anthryl radical is relatively slow at least by comparison to the reaction with naphthyl radicals or the other aryl radicals discussed in this document. It is true that in the case of chlorophenol, to be discussed below, a product is formed incorporating two substrate molecules. However the structure indicates that this is formed by reactions between aryl radicals and unreacted aryl halide molecules. Moreover, this process does not compete with hydrogen atom removal when an alcohol is present to supply C-H bonds. It seems clear that 9-anthryl radicals do react with the C-H bond in ethanol, because the yield of dimer is decreased for radiolysis in pure ethanol. However, this reaction must be relatively slow to permit anthryl radicals to build up to concentrations where radical-radical coupling becomes competitive. This being the case, we suggest that it may also be possible for anthryl radicals to react with the 1-hydroxyethyl radicals present in the reaction mixture. These 1-hydroxyethyl radicals must also find another radical with which to react in order to form stable products. Normally this would involve coupling or disproportionation of two hydroxyethyl radicals. However, under circumstances where aryl radicals are forced by an apparently slow reaction with solvent to build up in concentration, the reaction of eq 15 may become a viable competitor. As 1-hydroxyethyl radicals are also produced from the reaction of ethanol with hydroxyl and ethoxyl radicals (RO) with ethanol, this hypothesis does not depend on the reaction of eq 6 although its occurrence seems the only way to account for the undeuterated HAn which is formed. We have also found that neither HAn or HNp formed from radiolysis of the corresponding halides in CD₃CN with Et₃N present contain any deuterium. In this case, Et₃N or some species derived therefrom must be

the H-atom source.



Summary and Conclusions Regarding Radiolysis of Anthryl and

Naphthyl Halides

By combining information from product studies, kinetic measurements and deuterium tracer studies we draw the following conclusions.

1. Halide removal by radiolysis in an aqueous medium is possible for 9-haloanthracenes and halonaphthalenes.
2. Dimer formation from the 9-anthryl radical intermediates is a significant path even with alcohol present. It is not observed in acetonitrile but reaction in this solvent requires the presence of triethylamine.
3. The presence of increased numbers of halogens attached to a given aromatic system slows halide loss. It also slows protonation.
4. Halide removal by radiolysis seems not to be possible in an aqueous environment for 1-haloanthracene and probably not for the 2-halocompound either, apparently because halide loss from the radical anion is slow and protonation becomes the dominant process.

5. Product formation from 9-haloanthracenes comes via the 9-anthryl radical. It is slow to react with ethanol and a significant fraction of the anthracene produced arises from a termination-type reaction with the 1-hydroxyethyl radical.

Product Studies on 1,2,4-Trichlorobenzene

There is presently considerable interest in the dehalogenation of PCBs and related compounds by bacteria in river sediments.³⁹ Dr. Martin Stiles of our department has been studying the reaction of polyhalogenated benzenes with certain compounds in which Ni (II) is complexed by tetraazamacrocyclic ligands. These are believed to be suitable models for "Factor 430" and other coenzymes which are believed to play a critical role in methanogenesis by Methanobacterium Thermoautotrophicum and other bacteria suspected to be involved in dehalogenation reactions.⁴⁰ Dr. Stiles finds that the products from reaction of his nickel model compound with 1,2,4-trichlorobenzene in the presence of NaBH_4 in ethanol as a source of hydrogen are p-dichlorobenzene, m-dichlorobenzene and o-dichlorobenzene in the ratio of 16:5:1 resp. We have carried out a preliminary investigation of the radiation products from this compound in ethanol and have found essentially the same ratio suggesting that both methods remove chlorine by the same mechanism. Seeing that dechlorination via the radical anion is well established as the mechanism for the radiolytic reaction, we feel that this is evidence that the Ni(II)-promoted reaction takes the same path. A product distribution for the reaction of this compound with the actual bacterium or with "Factor 430" is, to the best of our knowledge, not presently available.⁴¹

Competitive Removal of Halogen from Benzylic Ethers

An earlier study of by our research group showed that naphthylmethyl phenyl ethers and naphthyl benzyl ethers, compounds 1 through 4, could be reduced in aprotic solvents by various one electron donor compounds.⁴² The reaction mechanism was shown to involve formation of the radical anion, with the extra electron centered in the naphthalene ring. An indirect method of approximating the cleavage rates suggested that the radical anions from the two naphthylmethyl phenyl ethers, 3 and 4, underwent cleavage much faster than did those from the naphthyl benzyl ethers, 1 and 2. Recently, pulse radiolysis experiments on these compounds in acetonitrile confirmed this conclusion. The data are given in Table VII.⁴³

Table VII. Rate Constants for the Cleavage of Ether Radical Anions Measured by Pulse Radiolysis in Acetonitrile.

Ether	Rate Constant for Radical Anion Dissociation
β -NpOCH ₂ Ph (1)	$1.5 \pm 0.5 \times 10^5 \text{ s}^{-1}$
α -NpOCH ₂ Ph (2)	$1.2 \pm 0.2 \times 10^6 \text{ s}^{-1}$
β -NpCH ₂ OPh (3)	$4.0 \pm 1.0 \times 10^7 \text{ s}^{-1}$
α -NpCH ₂ OPh (4)	$> 6 \times 10^7 \text{ s}^{-1}$

Given the background of rate data for these ethers, we decided that it might be informative to introduce halogen substituents into these and related ethers and to then study the competition between ether cleavage (CH₂-O bond) and halide loss (cleavage

of C-X bond) as a way of indirectly assessing rates of halide loss and factors influencing the efficiency of such processes. For various experimental reasons, it was not possible to measure the cleavage rates for these ethers by pulse radiolysis in aqueous solvents despite the fact that we could see transient spectra which were clearly due to products of the expected cleavage reactions.

Compounds 5 through 9 were prepared by Mr. Terence Todd, a graduate student at Eastern Kentucky University under supervision of Professor Vernon Stubblefield. Preliminary data from a product study of the ^{60}Co radiolysis mixtures obtained from these compounds are shown in Table VIII.⁴⁴

As can be seen from Table VIII the predominant process in almost all cases is loss of bromine. This is as expected, given the literature rate constant for the loss of Br^- from BrNp^\cdot of $>10^9 \text{ s}^{-1}$ (see Table II). It may reasonably be assumed that the rate for cleavage of PhBr^\cdot would be as fast or faster. With the exception of compound 7 in ethanol-water and compound 6 in acetonitrile, the ratio of Br^- loss to ether cleavage is at least 10 to 1. In the ethanol-water runs, only the naphthyl 4-bromobenzyl ether, 7, shows ether cleavage. However, this compound shows only Br^- loss in acetonitrile. Ether cleavage is the predominant process for the naphthylmethyl 4-bromophenyl ether, 6, in acetonitrile, however this compound shows only Br^- loss in ethanol water. These results are considerably more complex than we had expected and we need to reproduce and to extend the experimental series before drawing firm conclusions. The fact that the rate constant for loss of Br^- from either a bromonaphthalene or bromobenzene

Table VIII. Products from the ^{60}Co Radiolysis of Bromo Ethers

Ether ^a	Solvent	Product	Yield(%)
Br- $\alpha\text{NpCH}_2\text{-OPh}$, 5	Ethanol- Water	$\alpha\text{NpCH}_2\text{-OPh}$	9.3
		Br- αNpCH_3	<0.2
		missing	24.8
$\alpha\text{NpCH}_2\text{-OPhBr}$, 6	Ethanol- Water	$\alpha\text{NpCH}_2\text{-OPh}$	1.9
		αNpCH_3	<0.2
		missing	63
$\alpha\text{NpO-CH}_2\text{PhBr}$, 7	Ethanol- Water	$\alpha\text{NpO-CH}_2\text{Ph}$	8.2
		αNpOH	ca. 3.0
		CH_3PhBr	ca. 3.0
		missing	41
BrPh $\text{CH}_2\text{-OPh}$, 8	Ethanol- Water	Ph $\text{CH}_2\text{-OPh}$	7.9
		HOPh	<0.8
		missing	20.3
Ph $\text{CH}_2\text{-OPhBr}$, 9	Ethanol- Water	Ph $\text{CH}_2\text{-OPh}$	6.7
		HOPh	<0.7
		missing	55
Br- $\alpha\text{NpCH}_2\text{-OPh}$, 5	MeCN	$\alpha\text{NpCH}_2\text{-OPh}$	5.0
		HOPh	<0.5
		Br- αNpCH_3	<0.2
		missing	7.9
$\alpha\text{NpCH}_2\text{-OPhBr}$, 6	MeCN	$\alpha\text{NpCH}_2\text{-OPh}$	2.7
		$\alpha\text{NpCH}_2\text{-X}^a$	ca. 10
		HOPhBr	ca. 10
		αNpCH_3	ca. 2
		missing	<1
$\alpha\text{NpO-CH}_2\text{PhBr}$, 7	MeCN	$\alpha\text{NpO-CH}_2\text{Ph}$	8.0
		unknown products	3.3
		αNpOH	<0.8
		CH_3PhBr	<0.2
		missing	15

Notes for Table VII: ^a Concentrations were 5 to 7 mM with solution volumes = 15 to 17 mL. Dose was 1.10 mR for all samples. ^b Unknown structure for X, but appears to be an attached triethylamine moiety.

radical anion is greater than 10^9 s^{-1} would seem to suggest that Br^- should be lost from all of these compounds at this extremely fast rate. If this were the case, it seems unlikely that ether cleavage would be able to compete. In fact when both groups attached to oxygen are of the single phenyl ring variety, only Br^- loss is observed. However, when one of the rings is naphthyl, the situation is apparently more complicated. For compound 5, where the Br is located in the naphthalene ring, Br^- loss still predominates, as it should if the radical anion is behaving like a simple bromonaphthalene radical anion. It might be assumed that the rate constant for cleavage at the ether linkage would be similar to that anticipated for the unsubstituted α -naphthylmethyl phenyl ether, 4, which while not measurable, would seem unlikely to be more than a power of 10 or so faster than the β -compound which was measured at approximately $4 \times 10^7 \text{ s}^{-1}$.

It would appear that when the bromine atom is attached to a phenyl ring on the opposite side of the ether linkage from an unsubstituted naphthalene ring, that either the ether cleavage is faster than that estimated for the unsubstituted ether, or that the loss of Br^- is slower than that measured for bromonaphthalene. The latter would seem reasonable at first glance in that the reduction potential of a naphthalene ring is estimated to be a full volt more positive than that of a benzene ring.⁴⁵ However, the reversible reduction potential of bromobenzene is not known with certainty⁴⁶ and it

seems likely that the σ^* orbital of the C-Br bond is lower in energy than the π^* orbital of the benzene ring.

It must be recognized that, in a radiolysis experiment, the solvated electrons produced are of sufficiently high energy to make capture by either the naphthyl or the bromophenyl moiety energetically favorable. It seems at least possible that when a bromine-substituted phenyl ring captures an electron, the electron enters the C-Br σ^* orbital and loss of Br is essentially instantaneous, faster than electron transfer to the naphthyl system. However, when the electron is captured by the naphthyl moiety, electron transfer to the remote C-Br σ^* orbital required for Br loss may be slower than ether cleavage in some cases. This would explain why only for the two compounds which contain non-bromine-substituted naphthalene rings is ether cleavage observed.

What is more difficult to explain is why for the two compounds, 6 and 7, which contain unbrominated naphthyl moieties one shows ether cleavage in acetonitrile and not in water, whereas the situation is reversed in water. If these results can be confirmed, it suggests a substantial solvation effect on the processes involved. Perhaps because σ^* radical anions are more highly localized, they are favored in hydroxylic solvents thus favoring all of the reactions which are believed to occur via this type of species. Seeing it was suggested that 2 \cdot^- undergoes cleavage via a σ^* -type transition state, the hydroxylic medium would also favor cleavage of 7 \cdot^- . In acetonitrile, π^* -type radical anions may become more accessible. In that it can be safely predicted from our pulse radiolysis work that the cleavage of 7 \cdot^- should be slow in acetonitrile, this

is consistent with the cleavage product data.

Reactions in Purely Aqueous Medium

To extend these studies to pure water required dealing with the problem of the insolubility of simple aryl halides. One possibility was to make the solutions sufficiently dilute. However in cases where this approach has been used, an extraction step preceding analysis is usually necessary and we wished to avoid this. As discussed above, there appears to be a problem with obtaining a complete material balance even when no extraction is employed. We were, therefore, reluctant to use highly insoluble materials.

One solution was to study the radiolysis of detergent solubilized arylhalides. There is a considerable literature dealing with the effect of detergent micelles on the rates of reactions of radiation-produced solvated electrons⁴⁷ as well as several papers dealing specifically with the reaction with organic halides.⁴⁸ By operating at detergent concentrations above the critical micelle concentration, it was possible to carry out radiolysis of aryl halides at concentrations comparable to the runs discussed above, but without adding organic cosolvents. We used sodium dodecyl sulfate (SDS) and hexadecyltetramethylammonium bromide (HDTB) at concentrations of 50 mM. Results for naphthyl halides are shown in Table IX.

As can be seen from the data presented, use of the cationic detergent HTDB gives higher conversions in all cases. This is consistent with kinetic studies by

Patterson⁴⁹ and others⁵⁰ which show that solvated electrons react much faster with organic electron acceptors when these are sequestered in cationic micelles than when anionic micelles are employed. Our work as represented in Table IX as well as in Table X shows that this well-documented kinetic effect translates into an increased efficiency of halogen removal.

It seemed likely from the foregoing studies that the detergent not only functioned to solubilize the aryl halide, but also served as a source of hydrogen atoms. To verify

Table IX. Radiolytic Dehalogenation of Aryl Halides in Detergent Micelles

Naphthyl Halide (conc. mM)	Dose in Mr	Detergent	% Conversion to Naphthalene	mM/Mr converted
1-BrNp (6.6)	1.33	SDS	10.1	.50
1-BrNp (6.6)	1.33	HTDB	52.3	2.6
1-BrNp (2.1)	1.29	SDS	54.4	.88
1-BrNp (2.1)	1.29	HTDB	95.5	1.6
1-BrNp (0.24)	0.076	SDS	10.6	.33
1-BrNp (0.24)	0.076	HTDB	30.2	.95
2-BrNp (11.4)	1.32	SDS	4.9	.41
2-BrNp (11.4)	1.32	HTDB	8.6	.74
1-CINp (8.4)	1.33	SDS	11.6	.73
1-CINp (8.4)	1.33	HTDB	43.5	2.7

that this was the case, we sought a substrate which could be irradiated in water alone. For our preliminary investigation we chose 4-chlorophenol, **4-ClPhOH**. This compound is readily water soluble and could be studied both in pure water and in solvent mixtures. The results are shown in Table X.

Table X. Radiolytic Dehalogenation of Chlorophenol in Water, Water-Isopropanol and Detergent Solutions

Conc. 4-ClPhOH (mM)	Additive (conc. mM)	Solvent Mixture	Phenol (yield %)	Coupled Product ^a (yield ^b)
7.8	none	H ₂ O only	<1	10
9.7	O ₂ - satd.	H ₂ O only	<1	3
8.7	SDS (50)	H ₂ O only	6.2	<1
12.1	HDTB (50)	H ₂ O only	15.2	<1
10.9	HTB (50)	H ₂ O only	6.9	2.5
10.9	HTB (9.5)	H ₂ O only	2.6	9.1
10.6	none	5% i-PrOH	5.7	<0.5
8.7	none	2.4% i-PrOH	4.1	<0.2
10.2	none	1% i-PrOH	0.57	<0.2
11.3	none	0.1% i-PrOH	1.3	0.3

^a Product **10**. ^b Relative yield only. Molar absorptivity of **10** unknown.

Several important conclusions can be drawn from this preliminary data. As with the simple aryl halides, it is apparent that the presence of cationic micelles facilitates the dehalogenation process. It also seems clear that the micelles are serving as a source of hydrogen atoms. It will be noted that when the solvent is pure water, with no additives, the first entry in Table XI, the product is not the simple dehalogenated phenol but rather an adduct involving two chlorophenol molecules. Nor is this product the result of radical-radical coupling as observed with 9-haloanthracenes but still contains one chlorine atom. We have isolated a sufficient amount of this material to allow analysis by nuclear magnetic resonance spectroscopy (NMR) and are reasonably certain that the compound is 2-(4'-hydroxyphenyl)-4-chlorophenol, **10**. It seems likely that this compound comes from the reaction of 4-hydroxyphenyl radicals with 4-chlorophenol followed some sort of hydrogen transfer process. The envisioned mechanistic sequence is indicated in Figure 2. Interestingly, when we ran the reaction in water using hexyltrimethylammonium bromide (HTB), as contrasted with micelle-forming hexadecyltrimethylammonium bromide, the adduct species, **10**, is still evident even when the concentration of HTB is 50 mM. It would appear that 4-hydroxyphenyl radicals formed in micelles, don't make it out, and react almost exclusively by H-atom abstraction from the micellar chains. We also explored the question of how low the concentration of an H-atom donor could be and still prevent adduct formation. From Table X, it is clear that even at 0.1%, isopropanol prevents adduct formation to a large extent. It appears to be significantly superior in this function by comparison to HTB when the two are compared at concentration levels comparable to that of chlorophenol.

CHAPTER IV. Conclusions

The work described in this report establishes ground work for further research which may lead to a justification for the use of high-energy radiation sources for the degradation of harmful pollutants in water. The present study focuses on the reactions of aryl halides, but the principles outlined should apply to other types of organic pollutants as well. We would expect the analogies to aliphatic halides such as halomethanes and haloethanes to be straightforward. Extensions to organic compounds which lack a dissociable group should be possible, but will probably require the employment of oxidizing additives.

For aryl halides, it has been established that radiation in aqueous solution in the absence of oxygen results in dehalogenation. Based on the studies carried out to date, haloaromatics with two or less fused aromatic rings will undergo replacement of halogen by hydrogen, provided that a hydrogen source is present. The O-H bond in water is too strong to permit water molecules to serve in this capacity. Results in a limited series suggest that aliphatic alcohols and amines can serve this function. For chlorophenol, it was shown that the amount of hydrogen source need only be present in concentration comparable to that of the halogen compound. For halogen compounds solubilized by detergent micelles, the detergent molecules apparently provide the hydrogen source. These results suggest that most compounds containing simple aliphatic C-H bonds will serve. When no hydrogen source other than water is present, the intermediate radical anions formed through reaction of the aryl halide with water will still undergo halide loss,

however, the aryl radical produced will seek out and add to another aromatic molecule in preference to removing H-atoms from water molecules. This circumstance is probably undesirable in that the major product will be of higher molecular size and complexity than the original target molecule. In principle, it would seem to be possible in very pure water, to make halobiphenyls from halobenzenes. However, the water sample would have to be scrupulously free of all aliphatic organic materials (detergents, soluble carbohydrates, alcohols, etc.) to force this outcome.

For aryl halides with more than two fused rings, e.g. the halogenation products from polynuclear aromatic hydrocarbons, the situation becomes somewhat more complicated. From the limited series that we have studied, it would appear likely that for compounds with more than three fused rings, the radical anions formed will not eject halide. This conclusion may be drawn from the fact that dehalogenation rates become increasingly slower in the series phenyl, naphthyl, anthryl. Moreover, we have found that even for anthryl halides, the 1-chlorine-substituted compound undergoes ring reduction without halogen removal. While this would not prevent eventual removal of halide, it would require application of a higher radiation dose in order to complete the ring reduction process prior to halide removal. For 9-anthryl halides the reduction process is complicated by the apparent relative stability and persistence of the radical generated. In this case only, we observed formation of substantial quantities of Ar_2 -type compounds. We also found other evidence that these radicals are less reactive than aryl radicals generated from naphthyl and phenyl halides. We also found evidence that halide loss from the intermediate radical anion will be slowed when multiple halogen

substituents are present, but this does not prevent the radiolytic removal of halogen from taking place, probably because protonation is also slowed by multiple halogen substitution. We showed that dehalogenation of trichlorobenzene is practical. Interestingly we found the same pattern of halogen removal from 1,2,4-trichlorobenzene as has been observed with a compound used to model biological agents.

Compounds which incorporate both halogen substituents and other labile moieties will probably still exhibit some halide loss on radiolysis. We have studied an interesting series of halogen containing benzyl-type ethers and have found that halogen removal is either the exclusive or the preferred product. The pattern of this competition was extremely interesting and deserving of further study.

One important but somewhat troubling result of this work was the demonstration that there very likely are products formed in radiolysis of aryl halides which do not show up in simple gas chromatographic analysis of products. Although the positive aspect of this is that the destruction of these compounds is more extensive than hitherto recognized, the significance of this finding for water purification purposes can not be assessed without further study to reveal the identity of the missing compounds.

In summary, we have shown that radiation treatment is potentially a powerful and potentially noninvasive method for degrading organic material in aqueous solution. Further work will be necessary before a quantitative picture of all of the processes involved is available.

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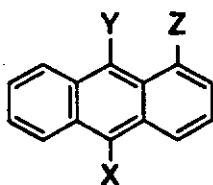
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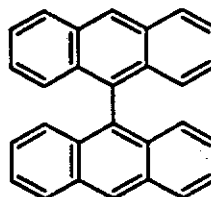
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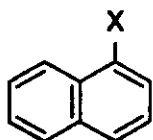
Figure 1. Structures of Compounds Studied.



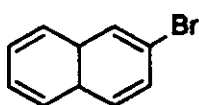
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 X = Cl; Y, Z = H **9-ClAn**
 X = Br; Y, Z = H **9-BrAn**
 X, Y = Cl; Z = H **9,10-Cl₂An**



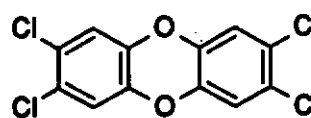
An₂



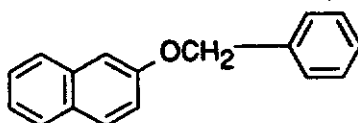
X = Cl **1-ClNp**
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 X = H **HNp**



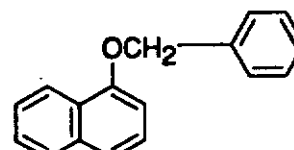
2-BrNp



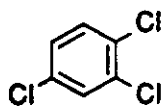
TCDD (dioxin)



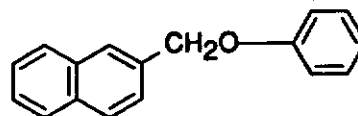
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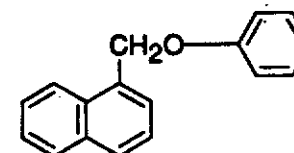
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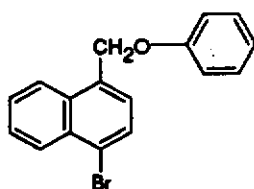
1,2,4-trichlorobenzene



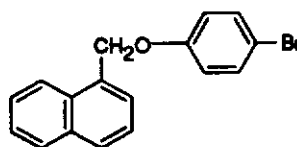
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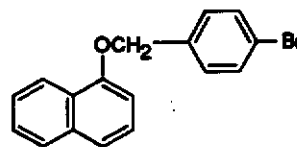
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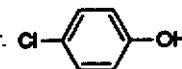
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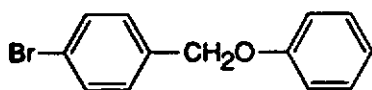
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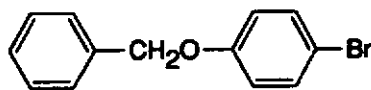
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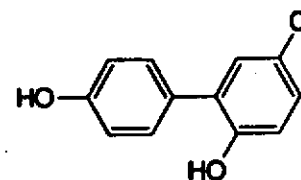
4-ClPhOH



8



9



10

