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# SURVEY OF APPLICATION OF RADIATION TO PREPARATIVE CHEMISTRY

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# SURVEY OF APPLICATION OF RADIATION TO PREPARATIVE CHEMISTRY

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## SUMMARY

This report outlines the use of radiation for preparative chemistry in liquid solutions. General principles are presented and preparations involving reduction, oxidation, polymerization, and decomposition are given. The use of various solvents, water, other inorganic liquids and organic liquids for this purpose is discussed. Finally, a commentary is made on some specific applications where radiation chemistry as a preparative technique may be useful.

In general, the use of radiation primarily as a preparative tool has received little attention in the literature; thus, much of the discussion in the report is based on extrapolation of existing radiochemical data which entails some speculation. At present, the use of radiation for this purpose is limited to the preparation of laboratory quantities of high purity materials and to the synthesis of compounds that cannot be readily prepared by ordinary chemical means. An exception is when chain or autocatalytic processes are involved which result in high energy yields of product; in this case, radiation may be used for larger scale production.

## INTRODUCTION

Numerous papers on radiation chemistry have appeared in the literature. These papers are primarily concerned with the identification of short lived species formed during radiolysis, the presentation of kinetic data, and the reaction mechanisms involved. With few exceptions these reported results have not been specifically applied to actual preparation of metals and chemical compounds. This is attributed, in part, to the fact that most of these radiolysis experiments entail a relatively low radiation dose with the formation of a very small quantity of reaction product.

Several years ago we began experimental work on the preparation of metals and inorganic compounds (refs. 1 to 5) using high flux electrons from a linear accelerator. Our success in this endeavor led to the realization that the role of radiation in preparative chemistry is extremely broad, in fact too broad for us to investigate all aspects of this field.

The objective of this report is to outline in part the scope of radiation preparative chemistry as seen today, to present the principles involved and, when appropriate, to cite examples of preparations. Because of the wide range of this field this paper is limited to liquid solutions and is arranged according to the solvent employed: aqueous systems, other inorganic solvents, polar and nonpolar type organic liquids. The categories of reactions discussed include reductions, oxidations, polymerizations, decompositions, and free radical reactions. In that comparatively little has been published on the specific use of radiation for preparative chemistry in liquid systems, the results obtained from theoretical papers on radiation chemistry form the basis of most of the preparations suggested in this review. These papers are more concerned with the identification of species formed during radiolysis and the reactivities of these species than with actual preparation and isolation of a product. Some speculation on our part is necessary for the interpretation of these results in terms of preparative chemistry.

A major advantage of radiolytic preparative techniques over other commonly employed preparative methods depends on the fact that extremely reactive radicals, including strongly oxidizing and reducing species can be produced at low temperatures without the addition of reagents which would contribute to product impurity. Moreover, preparations involving radiation can be conveniently carried out at room temperature or below to minimize contamination of the product by the environment (e.g., via diffusion of container material) as well as to diminish decomposition of thermally unstable compounds.

We hope that this review will stimulate other investigators to explore the use of radiation in preparative chemistry.

## AQUEOUS SOLUTIONS

The action of ionizing radiation on water is well known (refs. 6 and 7) and may be represented as follows:

$$H_2O \rightarrow e^-_{aq} + OH\cdot + H^+_{aq} \text{ (major)} \qquad (1)$$

$$H_2O \rightarrow H\cdot + OH\cdot \text{ (minor)} \qquad (2)$$

Thus, the hydrated electron $e^-_{aq}$ is the major reducing species in irradiated water while atomic hydrogen $H\cdot$, because of the lower contribution of reaction (2) is the minor reducing species. Also formed in irradiated water are oxidizing hydroxyl radicals $OH\cdot$

and hydrated protons $H^+_{aq}$; the presence of the latter maintains the change balance. In irradiated pure water, the quantity of reducing species equals the quantity of oxidizing species and thus the net reducing and oxidizing property is essentially nil.

Irradiated aqueous systems may, however, be rendered either oxidizing or reducing by the presence of relatively small concentrations of certain additives which scavenge, respectively, the reducing or oxidizing species. The addition of a scavenger for hydroxyl radicals (e.g., primary alcohol which reacts rapidly with hydroxyl radicals but slowly with the solvated electrons and hydrogen atoms) results in a reducing system. Conversely, with the addition of a scavenger such as nitrate for the reducing species (hydrated electrons and hydrogen atoms) the system becomes a source of oxidizing hydroxyl radicals. The energy yield of product (G = atoms or molecules per 100 eV) for this radical scavenging process is limited by the amount of water decomposed by the radiation. In accord with the combined equations (1) and (2), $G(-H_2O)$ = G(reduced species) = G(oxidized species). For high energy electrons $G(-H_2O)$ is about 4.5 molecules per 100 eV (refs. 1, 3, and 8) or 1.7 moles of water decomposed per kilowatt hour of beam energy.

## Simple Reductions

The mechanism for radiolytic reduction in aqueous systems by the radical scavenging mechanism may be illustrated using ethanol ($CH_3CH_2OH$) as the scavenger for hydroxyl radicals and divalent copper ion ($Cu^{+2}$) as the species to be reduced. Ethanol reacts rapidly with hydroxyl radicals (ref. 9) to form hydroxylethyl radicals:

$$CH_3CH_2OH + OH\cdot \rightarrow H_2O + CH_3\dot{C}HOH$$

The hydroxylethyl radical is removed from the field of reaction by dimerization or dismutation (ref. 9)

$$2CH_3\dot{C}HOH \rightarrow CH_3CHOHCHOHCH_3$$

$$2CH_3\dot{C}HOH \rightarrow CH_3CHO + CH_3CH_2OH$$

The solvated electron and the hydrogen atom then reduce the metal ion in a stepwise manner (ref. 3).

$$Cu^{+2} + e^-_{aq} \rightarrow Cu^+$$

$$Cu^{+2} + H\cdot \rightarrow Cu^{+} + H^{+}$$

A disproportionation step then leads to the deposition of free copper

$$2Cu^{+} \rightarrow Cu^{0} + Cu^{+2}$$

Good hydroxyl radical scavengers for aqueous reducing systems include primary alcohols, secondary alcohols, aldehydes, and formates. The selection of an appropriate additive can be made with the aid of specific bimolecular rate constants as compiled by Anbar and Neta (ref. 10).

Pulse radiolysis studies indicate that aqueous hydrogen solutions (1500 psig $H_2$ pressure) effectively scavenge hydroxyl radicals by converting them to hydrogen atoms and hydrated electrons (ref. 11), that is,

$$H_2 + OH\cdot \rightarrow H_2O + H\cdot$$

$$H\cdot + OH^{-}_{aq} \rightarrow e^{-}_{aq} + H_2O$$

Hydrogen as a scavenger for hydroxyl radicals has the advantage that its reaction products do not introduce new species to the system such as is the case with organic scavengers. A major disadvantage of using hydrogen arises out of its low water solubility at atmospheric pressure. It has been demonstrated in our work on the deposition of copper from a water solution of copper sulfate that a saturated aqueous solution of hydrogen at atmospheric pressure does not effectively scavenge hydroxyl radicals (ref. 3). It is therefore necessary to go to high hydrogen pressure so that sufficient hydrogen concentration be maintained in solution to effectively scavenge hydroxyl radicals as they are produced by the radiation. At 1500 psig, the hydrogen concentration is about 0.08 M. The problem involved in a high pressure system is to design a window that is strong enough to withstand the high pressure and yet not so thick as to substantially inhibit the electron beam from entering the cell.

Radiolytic reducing systems for the deposition of several metals from their aqueous salt solutions have been reported (refs. 1 and 2). In general, a metal can be prepared in this manner if it does not reduce the reaction solution and if one of its lower valance salts does not precipitate from solution. The metals which may be deposited radiolytically from aqueous media are listed in table I; those metals actually prepared are given in the first column.

In comparison with the abundant information on the reactivity of different compounds and ions toward the hydrated electron, the major reducing species in irradiated water, there is a lack of information on the products of reaction. This is especially true con-

TABLE I. - METALS WHICH MAY BE
PREPARED RADIOLYTICALLY
FROM AQUEOUS SYSTEMS

| Metals prepared | Other metals that could be prepared |
|---|---|
| Antimony | Arsenic |
| Cadmium | Bismuth |
| Copper | |
| Cobalt | Indium |
| Gold | Iridium |
| Iron[a] | Mercury |
| Lead | Osmium |
| Nickel | Rhodium |
| Palladium | Ruthenium |
| Platinum | |
| Silver | |
| Thallium | |
| Tin | |
| Zinc | |

[a] Trace amounts.

cerning the actual isolation and identification of these products. Because the hydrated electron is a reactive nucleophile, it is expected that the hydrated electron will rapidly reduce most metal ions $M^n$ in aqueous solution at least to their next lower oxidation state $M^{(n-1)}$; that is,

$$M^n + e^-_{aq} \rightarrow M^{(n-1)}$$

The exceptions to this are the alkali metal and alkaline earth ions where the redox potential of these ions is above that of the hydrated electron $E^o = 2.5$ volts (ref. 12). In addition then to the use of aqueous radiolytic reducing systems for the deposition of metals these systems may also be employed for the synthesis of metal salts in which the metal is in a lower valence state. Such preparations are particularly useful if the reduced salt is insoluble as in the deposition of copper (I) chloride (ref. 3) and mercury (I) chloride from solutions of copper (II) chloride and mercury (II) chloride, respectively. In such reactions an inert anion should be used. Many ions which have no electron vacancy such as fluoride, chloride, bromide, iodide, cyanide, cyanate, thiocyanate azide, and hydroxide are nonreactive toward hydrated electrons. Other inert anions include some oxyanions of nonmetals in their highest oxidation state, for example: sulfate, perchlorate, phosphate, and carbonate. Salts of these anions should be used when it is desirable to reduce only the cation.

Those anions that react rapidly with hydrated electrons include nitrate, permanganate, peroxydisulfate, dichromate, peroxide, chlorate, bromate, iodate, hexacyanoferrate (III), hexacyanochromate (III), and others (ref. 12). When reduction products from such anions are desired, radiolytic reduction may, in some cases, be a useful method of synthesis.

Because of its nucleophilic nature, the solvated electron also reacts rapidly with organic compounds which contain electron deficient groups on the molecule. The initial reaction of an organic molecule RH with the solvated electron $e^-_{aq}$ results in the formation of the negative entity $RH^-$ which may be an activated complex or an anion radical intermediate; that is,

$$RH + e^-_{aq} \rightarrow RH^-$$

Stable products arise out of the decay or hydrolysis of $RH^-$.

Organic compounds which are reactive toward hydrated electrons include halogenated hydrocarbons (except fluorine compounds), halogenated acids, ketones, aldehydes in the unhydrated form, conjugated compounds (butadiene, etc.), unsaturated acids (maleic, fumaric, etc.), nitro compounds, and aromatic compounds with electron withdrawing groups on the ring. Other reactive groups are thio compounds of the type C=S, disulfides (-S-S-) and peroxides (-O-O-). Some unreactive organic compounds are hydrocarbons (methane), primary alcohols (methanol), ethers (diethyl ether), ions of saturated acids (formic, acetic, succinic), and esters (ethyl acetate). Also considered as being unreactive with hydrated electrons are saturated amino acids, aromatic derivatives with electron donating groups on the ring (aniline and hydroquinone). The heterocyclic organic compounds (furan, thiophene, pyrrol, and pyrolidine) are unreactive whereas thiazole and succinimide are reactive (refs. 13 to 16).

In only a few cases have products of reaction been determined and reported. The reaction of hydrated electrons with organic halogen compounds results in dehalogenation. The reduction of both alkyl and aryl nitro compounds by hydrated electrons has been studied in some detail. Tetranitromethane ($C(NO_2)_4$) is reduced by both hydrated electrons and hydrogen atoms with the formation of the nitroform anion ($C(NO_2)_3^-$) from which nitroform ($HC(NO_2)_3$) or its sparingly soluble potassium salt could possibly be isolated (ref. 16). Thus

$$e^-_{aq} + C(NO_2)_4 \rightarrow C(NO_2)_3^- + NO_2$$

$$H\cdot + C(NO_2)_4 \rightarrow C(NO_2)_3^- + H^+ + NO_2$$

Further reduction of the nitroform anion by hydrated electrons yields nitroacetaldoxime (methazonic acid) (ref. 16).

The reduction of the aromatic nitro compound, p-nitrophenol ($HOC_6H_4NO_2$), with hydrated electrons or hydrogen atoms involves the initial formation of the transient radical anion $HO\dot{C}_6H_4NO_2^-$

$$e^-_{aq} + HOC_6H_4NO_2 \rightarrow HO\dot{C}_6H_4NO_2^-$$

$$H\cdot + HOC_6H_4NO_2 \rightarrow HOC_6H_4NO_2^- + H^+$$

The transient can become protonated to form the radical $HO\dot{C}_6H_4NO_2H$ depending on the pH of the solution. Thus

$$HO\dot{C}_6H_4NO_2H \rightleftharpoons HO\dot{C}_6H_4NO_2^- + H^+$$

Although, at a pH of 6, over 99 percent of the radicals are in the anionic form, the anion radicals do not react with each other but decay through the protonated radical to form p-nitrophenol and p-nitrosophenol ($HOC_6H_4NO$) (ref. 17).

$$2HO\dot{C}_6H_4NO_2H \rightarrow HOC_6H_4NO_2 + HOC_6H_4NO + H_2O$$

The processes described here are based on pulse radiolysis experiments where small total radiation doses are involved in the formation of infinitesimal quantities of reaction product. Because of the small quantities involved in pulse radiolysis, radiochemical reactions of organic solutes of extremely low water solubility may be studied. In scaling up radiation chemistry to high doses for the synthesis of greater amounts of product, it becomes necessary to consider only those organic solutes having appreciable solubility in water. Pulse radiolysis data only serves as a guide as to possible reaction products that could be made by large scale radiolytic reactions of organic compounds in solution. More information is needed as to reaction products formed by high dose radiolysis before a detailed discussion on radiolytic organic synthesis can be made.

## Selective Reductions

As previously indicated, two distinct reducing species, the hydrated electron and the hydrogen atom are formed in irradiated water. Because hydrated electrons generally react rapidly with positive ions it is not surprising that hydrated protons ($H^+_{aq}$) effectively scavenge hydrated electrons, converting them to hydrogen atoms (refs. 11 and 18)

$$e^-_{aq} + H^+_{aq} \rightarrow H\cdot$$

The efficiency of this conversion of course increases with decreasing pH. Conversely, hydrogen atoms react with hydroxide ions to form solvated electrons (ref. 11)

$$H\cdot + OH^- \rightarrow e^-_{aq} + H_2O$$

A system composed primarily of hydrogen atoms as the reducing species can be generated on irradiating 0.1 M perchloric acid or 0.1 M sulfuric acid containing 0.5 M methanol as a scavenger for hydroxyl radicals (ref. 19). In contrast, a system consisting primarily of hydrated electrons as the reducing species can be made by irradiating aqueous sodium hydroxide containing a suitable scavenger (e.g., methanol) for hydroxyl radicals.

Although solutions of the hydrated electron and hydrogen atom can be made stoichiometrically equivalent, they would still differ in their reactivity. This difference in reactivity in irradiated water has been demonstrated with various organic compounds. Reactions of hydrogen atoms usually result in hydrogen abstraction, or for the case of olefinic organic compounds (e.g., allyl alcohol) in hydrogen addition (ref. 20). The hydrated electron, a nucleophilic reagent, attacks the electron difficient portion of an organic molecule with the formation of a negative ion. In aqueous monochloroacetic acid, for example, hydrogen atoms react with the chloroacetate ion ($ClCH_2COO^-$) mainly by dehydrogenation whereas the hydrated electron reaction is one of chlorine abstraction (refs. 21 and 22).

$$ClCH_2COO^- + H\cdot \rightarrow H_2 + Cl\dot{C}HOO^-$$

$$ClCH_2COO^- + e^-_{aq} \rightarrow Cl^- + \dot{C}H_2COO^-$$

The decay mechanism of the radical anions has not been established but it can be assumed that the decay of the radical anion $Cl\dot{C}HCOO^-$ results in chlorinated organic compounds while the decay of the radical anion $CH_2COO^-$ gives similar products where the chlorine is replaced by hydrogen. Possible reactions could involve dimerization.

$$2Cl\dot{C}HCOO^- \rightarrow {}^-OOCCHClCHClCOO^-$$

$$2\dot{C}H_2COO^- \rightarrow {}^-OOCCH_2CH_2COO^-$$

According to the specific rate constant compilation of Anbar and Neta (ref. 10), many metal cations are unreactive toward hydrogen atoms (e.g., $Cd^{+2}$, $Fe^{+3}$, $Ni^{+2}$,

$Sn^{+4}$, and $Zn^{+2}$). Those ions which readily react with hydrogen atoms include $Ag^{+}$, $As^{+3}$, $Cr_2O_7^{-}$, $Cu^{+2}$, $Fe(CN)_6^{-3}$, $Hg^{+2}$, $NO_2^{-}$, and $Sn^{+2}$. Advantage may be taken of the difference in reactivity of species with hydrogen atoms for selective reduction of the more reactive component in the presence of the less reactive one. Thus, in acid solution where the hydrogen atom is the major reducing agent in irradiated water, copper or silver may be selectively deposited in the presence of nickel and cadmium ions. Anions such as dichromate or hexacyanoferrate (III) may be preferentially reduced in the presence of tin (IV) and iron (III) ions.

With regard to the practical use of selective reduction in preparative chemistry, one must take into consideration that these ideas have not been tested in actual preparative work. We did find, however, that pure copper deposits preferentially from an acid solution containing both divalent copper and nickel ions (ref. 1).

## Oxidation

Aqueous oxidizing systems are attained by scavenging the reducing species in irradiated water. An aqueous system becomes a source of oxidizing hydroxyl radicals when it contains an additive which reacts rapidly with hydrogen atoms and more important, with hydrated electrons, but is relatively unreactive toward hydroxyl radicals. Additives for this purpose include silver ion $Ag^{+}$, nitrate ion $NO_3^{-}$, peroxydilsulfate ion $S_2O_8^{-2}$, permanganate ion $MnO_4^{-}$, dichromate ion $Cr_2O_7^{-2}$, chromate ion $CrO_4^{-2}$, hydrogen peroxide $H_2O_2$, nitrous oxide $N_2O$, and oxygen. $Ag^{+}$, $MnO_4^{-}$, $Cr_2O_7^{-2}$, $CrO_4^{-}$, and $O_2$ react extremely rapidly with both hydrated electrons and hydrogen atoms whereas $NO_3^{-}$, $H_2O_2$, $N_2O$ and possibly $S_2O_8^{-2}$, although highly reactive toward hydrated electrons, are somewhat less reactive toward hydrogen atoms (ref. 10).

The simplified reaction mechanism for the radiochemical oxidation (e.g., of divalent manganese ion) with nitrate ion as a scavenger may be illustrated as follows. The nitrate ion ($NO_3^{-}$) is reduced by hydrated electrons in nonacid solution to form the stable nitrite ion ($NO_2^{-}$) (refs. 9 and 23)

$$NO_3^{-} + e_{aq}^{-} \rightarrow NO_3^{-2}$$

$$2NO_3^{-2} + H_2O \rightarrow NO_2^{-} + NO_3^{-} + 2OH^{-}$$

The nitrate ion reacts relatively slowly with hydrogen atoms but in nonacid solutions, hydrogen atoms may be converted to hydrated electrons (ref. 11) which are readily scavenged by $NO_3^{-}$; thus neutral and alkaline solutions containing $NO_3^{-}$ are radiochemically oxidizing. It is then assumed that the remaining OH radicals oxidize the manganese ion ($Mn^{+2}$) to manganese (IV) oxide ($MnO_2$)

$$Mn^{+2} + 2OH\cdot \rightarrow MnO_2 + 2H^+_{aq}$$

The advantage of using either nitrous oxide, hydrogen peroxide, or oxygen is that the additive itself or its reaction products, $N_2$ or $H_2O$, do not contribute to product impurity. Hydrogen peroxide has the disadvantage in that its decomposition is catalyzed by many precipitated metal compounds especially metal oxides thereby prematurely using up the hydrogen peroxide required for scavenging. Radiolytic oxidations using nitrous oxide have been studied extensively. Its desirability for such studies is that nitrous oxide is fairly soluble in water (a saturated solution at 1 atm is about $2.5\times10^{-2}$ M) while, at the same time, efficiently scavenges hydrated electrons with the production of hydroxyl radicals (ref. 24).

$$e^-_{aq} + N_2O + H_2O \rightarrow OH\cdot + OH^- + N_2$$

Oxygen is a good scavenger for both hydrated electrons and hydrogen atoms; however, because of its low water solubility at atmospheric pressure, its use in practical synthesis from aqueous systems would be best accomplished at high pressure. This involves a high pressure apparatus similar to that mentioned previously for use with hydrogen gas.

In order to prevent reverse reactions which would generally reduce product yield (reduction of the oxidized product by hydrated electrons and hydrogen atoms), systems should be planned so that the product is removed from solution as a precipitate or a gas. In radiolytic preparations where the compound to be synthesized remains in solution during irradiation, back reactions can be minimized by employing a scavenger that reacts faster than the desired product with the reducing species in irradiated water at the concentration of each in question. In such cases, it is desirable if the spent scavenger is rendered inactive by either precipitating from solution, leaving the system as a gas, or forming an unreactive end product. Examples of removal of reaction products from the field of reaction include: $Ag^+$, and $Ag(NH_3)_2^+$ solutions where free silver precipitates; nitrous oxide solutions where nitrogen is liberated as a gas; and $H_2O_2$ and acidic $MnO_4^-$ solutions where water and $Mn^{+2}$, respectively, form as unreactive species. Several examples of radiolytic oxidation reactions are given in table II.

Because of the relatively low theoretical energy product yield afforded by reactions in aqueous systems involving the radical scavenging mechanism ($G(-H_2O) = 4.5$ molecules per 100 eV), such preparations are limited to applications where relatively small quantities of high purity metal powders and pure compounds are desired.

TABLE II. - RADIOLYTIC OXIDATION REACTIONS IN AQUEOUS SYSTEMS

| Reactant | Product | Scavenger | Radiation | Source |
|---|---|---|---|---|
| $Fe(CN)_6^{-4}$ | $Fe(CN)_6^{-3}$ | $N_2O$ | 5 MeV electrons[a] | Ref. 25 |
| $Fe^{+2}$ | $Fe^{+3}$ | $N_2O$ | 5 MeV electrons[a] | Ref. 25 |
| $Ce^{+3}$ | $Ce^{+4}$ | $N_2O$ | 5 MeV electrons[a] | Ref. 25 |
| 2-propanol | Acetone<br>$H_2O_2$ | $N_2O$ | 2.5 MeV electrons | Ref. 8 |
| Ethanol | Acetaldehyde<br>Glycol $(CH_3CHOH)_2$ | $KNO_3$ | $Co^{60}\gamma$ | Ref. 9 |
| Praseodymium(III) | Praseodymium(IV) | $N_2O$ | 5 MeV electrons[a] | Ref. 26 |
| p-nitrophenol | 1,2-dihydroxy-4-nitrobenzene | ----- | 4 MeV electrons[a] | Ref. 17 |
| $Mn(C_2H_3O_2)_2$ | $MnO_2$ | $KNO_3$ | 2 MeV electrons | (b) |
| $Na_2PbO_2$ | $Pb_3O_4$ | $KNO_3$ | 2 MeV electrons | (b) |
| $CoCl_2$+$NaNO_2$ +$NH_3$ | $Co(NH_3)_3(NO_2)_3$ | $KNO_3$ | 2 MeV electrons | (b) |

[a] Pulse radiolysis.
[b] Unpublished NASA data.

## Chain Reactions

Preparations involving chain and autocatalytic mechanisms are considerably more productive with regard to energy yield; thus, they lend themselves for preparations on a larger scale. Radiolytic chain reactions in aqueous solutions are common in organic chemistry; for example, oxidation reactions of organic compounds with oxygen (ref. 27) hydrogen peroxide (ref. 27) and nitrous oxide in strong alkaline solution (ref. 8). Chain polymerization of monomers containing olefinic bonds in aqueous systems have been studied extensively (refs. 27 and 28). We have observed (unpublished NASA data) that acrylamide in aqueous solution polymerizes to a highly viscous gelatinous material when exposed for several minutes to 2 MeV electrons at 10 microamperes beam current. The radiation furnishes ions and free radicals to initiate polymerization. Polymer dispersions in water could be produced radiochemically from solutions or dispersions of the monomer in water (an appropriate surface active agent might be required).

One of our metal preparations, the deposition of nickel from ammoniacal nickel sulfate containing sodium hypophosphite, involved an autocatalytic process; G(Ni) for this process is greater than 10 (refs. 1 and 4). Small amounts of nickel formed initially by the reduction of divalent nickel with hydrated electrons catalyzed further nickel deposition by the thermodynamically favored reduction of $Ni(NH_3)_6^{+2}$ with hypophosphite ion. Unfortunately this autocatalytic reaction was observed only for nickel. In other cases (e.g., cobalt and cadmium) the precipitation of metals in hypophosphite solution occurred by the radical scavenging mechanism. Because of the low beam energy requirement in chain and autocatalytic processed, further investigation is warranted for this type of reaction in large scale preparations.

## NONAQUEOUS INORGANIC SOLUTIONS

### Liquid Ammonia

Liquid ammonia ($NH_3$) is an interesting solvent for radiolytic preparations because it is unreactive toward strong reducing agents. This property suggests the use of liquid ammonia systems for the radiolytic preparation of active metals as well as for the synthesis of strongly reducing compounds. Dainton, et al. (ref. 29) have made a systematic study on the radiolysis of this liquid using cobalt-60 gamma radiation. As expected, the radiation chemistry of liquid ammonia is similar to that of water. The main final products in this case are hydrogen and hydrazine ($N_2H_4$). The initial step in the radiolysis of ammonia may be represented by the equation

$$2NH_3 \xrightarrow{\text{radiation}} e^-_{sol} + NH_2\cdot + NH_4^+$$

where

| | |
|---|---|
| $e^-_{sol}$ | solvated electron in ammonia |
| $NH_2\cdot$ | amine radical |
| $NH_4^+$ | ammonium ion |

The radiolytic decomposition yield of liquid ammonia is less than that of water, $G(-NH_3) = 2.1$; this value, however, has not been verified. The use of proper scavengers as is the case with aqueous systems could render either a reducing or oxidizing condition. One can speculate that such scavengers would be the nitrogen analogue of the organic scavengers used in aquesous systems. Thus, methylamine, the analogue of methanol should scavenge the oxidizing $NH_2$ radicals in liquid ammonia just as methanol scavenges the OH radicals in irradiated water

$$2NH_3 \xrightarrow{\text{radiation}} e^-_{sol} + \cdot NH_2 + NH_4^+$$

$$\cdot NH_2 + CH_3NH_2 \rightarrow NH_3 + \dot{C}H_2NH_2$$

The amine methyl radical ($\dot{C}H_2NH_2$) would probably decay by dimerization to form the stable ethylene diamine $(CH_2NH_2)_2$ leaving the solvated electron to reduce the ion or compound $M^n$ to the next lower oxidation state $M^{(n-1)}$.

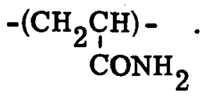
$$2\dot{C}H_2NH_2 \rightarrow (CH_2NH_2)_2$$

$$M^n + e^-_{sol} \rightarrow M^{(n-1)}$$

Likewise by using hydrazine ($N_2H_4$), the nitrogen analogue of hydrogen peroxide, added as a soluble hydrazine salt, liquid ammonia systems would be useful in oxidations for the synthesis of nitrogen containing compounds. Although the use of liquid ammonia has the disadvantage of requiring special handling, liquid ammonia may be more desirable than water as a medium for the preparation of reactive metals and compounds which reduce water but are unreactive toward ammonia. Also liquid ammonia may be utilized to advantage for the deposition of water soluble compounds which are insoluble in ammonia.

The use of liquid ammonia for the radiolytic practical synthesis of hydrazine is questionable at this time. At relatively low dose rates (1500 curies $Co^{60}$ gamma ray source) an initial yield $G(N_2H_4) = 1.1$ is obtained with 1.0 M acrylamide solution in liquid ammonia, but this yield falls rapidly with increasing dose reaching a steady-state condition $G(N_2H_4)$ = about 0.1 at high dose rates. The acrylamide scavenges solvated electrons but as the hydrazine concentration builds up at the increasing dose, hydrazine competes in the scavenging of solvated electrons and is thus destroyed. For the practical preparation of hydrazine using high radiation dose rates it would be necessary to remove the hydrazine during irradiation as an insoluble salt.

Also detected in the radiolysis of liquid ammonia is the azide ion $G(HN_3) = 0.035$ (ref. 30); however, the yield is too low for practicability. Radiation induced chain anionic polymerization of acrylamide and acrylonitrile in liquid ammonia are reported with yields $G = 10^3$ to $10^4$ (ref. 29). Because the acrylamide polymer is readily soluble in water, the repeat unit must be $-(CH_2\underset{\substack{| \\ CONH_2}}{CH})-$ . These polymerizations are more


$-(CH_2\underset{\substack{| \\ CONH_2}}{CH})-$

effectively carried out in alkaline solution. Alkaline solutions in liquid ammonia are obtained by addition of sodium amide ($NaNH_2$) or better, because of its greater solubility, potassium amide ($KNH_2$). Not too promising, at least at low dose rates are polymerizations in liquid ammonia of the monomers, methyl methacrylate, styrene, and caprolactam, but effective polymerizations of these may possibly be accomplished at high dose rate as obtained with a linear electron accelerator.

## Sulfur Dioxide

The initial reaction in the radiolysis of liquid sulfur dioxide ($SO_2$) is the formation of SO species and oxygen atoms ($O\cdot$)

$$SO_2 \rightarrow SO + O\cdot$$

These species then undergo a rapid series of reactions resulting in the formation of stable final products sulfur trioxide ($SO_3$) with a yield $G(SO_3) = 1.31$, crystalline free sulfur $G(S) = 0.65$ and small amounts of oxygen $G(O_2)$ = about 0.01 (ref. 31)

$$O\cdot + SO_2 \rightarrow SO_3$$

$$O\cdot + SO_3 \rightarrow O_2 + SO_2$$

$$2SO \rightarrow (S_2O_2) \rightarrow S + SO_2$$

The energy yield for the radiolytic decomposition of $SO_2$ is calculated to be $G(-SO_2) = 1.35$.

Radiolysis of solutions of $SO_3$ in sulfur dioxide gives a higher oxygen gas yield, $G(O_2) = 0.11$ than is obtained from pure sulfur dioxide and in addition, no free sulfur is observed in these solutions. Instead, an unstable green-blue solid is observed upon removal of the sulfur dioxide solvent. This green-blue product is probably dilsulfur trioxide ($S_2O_3$) (ref. 32). Potassium iodide (KI) in sulfur dioxide solution is radiolytically oxidized to iodine, $G(I_2) = 1.01$; some potassium bisulfate ($K_2S_2O_7$) is also produced (ref. 32). Radiolysis of sulfur dioxide containing dissolved oxygen forms $SO_3$, $G(SO_3)$ = about 2.8 (ref. 33) and from sulfur dioxide containing a small quantity of water (less than 0.5 percent) dithionic acid ($H_2S_2O_6$) is produced. As is the case with all inorganic liquids except water, there is deficiency of data on reaction products arising from the radiolysis of various solutes in sulfur dioxide. It appears, however, that liquid sulfur dioxide would be a good medium for radiochemical oxidation preparations as well as for the synthesis of sulfur compounds.

## Other Inorganic Liquids

There are other inorganic liquids such as hydrogen cyanide (HCN), hydrogen sulfide ($H_2S$), hydrogen fluoride (HF), and even fused salts which may be considered as a medium for preparative chemistry. At present, however, radiolysis data on these liquids is insufficient to warrant their discussion.

## ORGANIC SOLUTIONS

Organic liquids for inorganic preparations may, at times, be used to advantage where unreactive media are required such as for the preparation of strongly reducing metals and compounds, those which reduce water. Organic solvents are also useful for the preparation of metal organic compounds and for the synthesis of anhydrous inorganic salts.

Our results concerning the radiolysis of antimony (III) chloride ($SbCl_3$) solutions in dry organic liquids with the deposition of free antimony (Sb) (ref. 5) show that many common organic liquids are radiochemically reducing. The energy yield was not only dependent on $SbCl_3$ concentration but also varied widely according to the organic liquid used. The yield, G(Sb) ranged from 1.2 for 0.5 M $SbCl_3$ (the highest $SbCl_3$ concentration tested) in methanol to a zero yield for $SbCl_3$ solutions in heptanone and glycerol. In order to compare various organic liquids in terms of product energy yield for reducing radiolytic preparations it is convenient to calculate a "reducing capacity" for each liquid. The radiolytic reducing capacity (RRC) is defined by us as the ratio of the energy yield of antimony, G(Sb), from 0.25 M $SbCl_3$ initial concentration in the organic liquid to G(Sb) for the same initial concentration in methanol. These calculated RRC values for a variety of organic liquids are given in table III. Although it is believed that these RRC values for organic liquids would roughly correspond for other reductions, there is no definite evidence to support this. Thus, these values should only be used in a qualitative sense, as a guide for the selection of an organic liquid for a desired reduction. The RRC of saturated hydrocarbons is not given for the $SbCl_3$ - Sb reduction because of the limited solubility of $SbCl_3$ in these liquids; however, the product yield in other radiolytic reductions (reduction of tin (IV) chloride to tin (II) chloride in n-heptane) indicate a high RRC value for saturated straight chain aliphatic hydrocarbons. Reactions in hydrocarbon-type solvents will be discussed in the latter part of this report.

TABLE III. - PREPARATION OF ANTIMONY METAL BY

IRRADIATION OF $SbCl_3$ IN SOLUTION

[Electron energy, 2 MeV; beam current, 20 $\mu$A; dose, 0.20 coulomb; $SbCl_3$ concentration, 0.25 M.]

| Organic liquid | $RRC = \frac{G(Sb)\ \text{organic liquid}}{G(Sb)\ \text{methanol}}$ |
|---|---|
| Methanol | 1.0 |
| 1-butanol | .79 |
| Tetrahydrofuran | .79 |
| 2-propanol | .67 |
| Amyl acetate | .30 |
| Quinoline | .17 |
| Dibutyl phthalate | .15 |
| 2-methyl-2-propanol | .13 |
| Oleic acid | .13 |
| Toluene | .10 |
| Ethylbenzene | .10 |
| Acetic acid | .08 |
| 3-heptanone | 0 |
| Glycerol | 0 |

## Aliphatic Alcohols and Other Polar-Type Solvents

The high RCC values for primary and secondary alcohols, as well as the fact that considerable study has been done on the radiolysis of pure aliphatic alcohols, justify a special discussion on the radiolysis of alcohols and their application to radiochemical preparations. As would be expected for polar liquids, solvated electrons have been observed in irradiated aliphatic alcohols, $G(e^-_{sol}) = 1.0$ (ref. 34) and more recently $G(e^-_{sol}) = 1.7$ for pure ethanol (ref. 35); however, the yield of solvated electrons is too low to account for our maximum $G(Sb) = 1.2$ in primary alcohols ($G(Sb)$ of 1.2 requires a $G(e^-_{sol}) = 3.6$). This implies that a second reducing species, namely the hydrogen atom, formed during the radiolysis of primary and secondary alcohols is the major component in the reduction of $SbCl_3$ to free antimony. The importance of hydrogen atoms for radiolytic reductions in aliphatic alcohols is indicated by the high RRC values for primary and secondary alcohols (RRC = 0.67 to 1.0) compared with the relatively low RRC = 0.13 for the tertiary alcohol. Taking into account the reaction products from the radiolysis of alcohols, McDonnell and Newton (ref. 36) claim that the principal bond rupture during radiolysis occurs at the carbinal carbon atom. Rupture of this bond in primary and secondary alcohols gives rise to hydrogen atoms whereas rupture of the carbinol carbon in tertiary alcohols produces organic radicals instead. These organic radicals do not appear to be strongly reducing species or at least in sufficient abundance for the reduction of $SbCl_3$ to free antimony. The initial high yield of hydrogen gas from the irradiation of ethanol, $G(H_2)$, also implies that H· is the major reducing species (ref. 35).

By assuming that the hydrogen atom is the major reducing species the simplified reaction mechanism for radiolytic reductions in primary alcohols may be represented by the following equations:

$$RCH_2OH \xrightarrow{\text{radiation}} R\dot{C}HOH + H\cdot$$

$$2R\dot{C}HOH \rightarrow (RCHOH)_2$$

$$2R\dot{C}HOH \rightarrow RCHO + RCH_2OH$$

$$M^{n} + H\cdot = M^{(n-1)} + H^{+}$$

The major products of the radiolysis of pure ethanol are hydrogen, 2,3-butanediol, and acetaldehyde (ref. 37). The mechanism based on the results of the radiolysis of ethanol probably applies to most other alcohols (primary and secondary alcohols) in that corresponding products are presumed to be formed during radiolysis.

As mentioned before, the initial yield of hydrogen gas from the radiolysis of pure ethanol is $G(H_2) = 5.9$; the yield of hydrogen then drops off with increasing dose (ref. 35). Because most of the hydrogen gas forms as a result of extraction of hydrogen from ethanol by hydrogen atoms,

$$H\cdot + C_2H_5OH \rightarrow H_2 + CH_3\dot{C}HOH$$

the yield of hydrogen atoms is also about 5.9 atoms per 100 eV. This value of $G(H) = 5.9$ thus represents the approximate maximum reducing yield in ethanol. The actual radiolytic product yield would depend on the extent of competition for hydrogen atoms between the two reactions, the reduction of solute to form the desired product and, as shown previously, hydrogen extraction from the solvent which literates hydrogen gas. The experimental results with methanol and tetrahydrofuran show that the energy product yield increases with increasing solute concentration (ref. 5 and unpublished NASA data). This concentration dependence is believed to arise from the competing hydrogen extraction reaction. One can expect then, that increasing the solute concentration increases the probability of the solute-hydrogen atom reaction at the expense of the hydrogen extraction reaction.

The value G(H) has not been determined for most polar liquids but most probably differs somewhat for each liquid. However, the general mechanism for ethanol is probably similar for other polar liquids (e.g., tetrahydrofuran) having at least one hydrogen atom on the functional group carbon atom. For best energy products yields involving radiolytic reductions in primary alcohols, secondary alcohols, and cyclic ethers, high solute concentrations should be employed.

Because low solute concentrations are unfavorable to high product yields, it is advantageous to select a starting material (solute) and organic liquid affording high solute solubility. For radiochemical reductions involving the deposition of metals and the synthesis of lower oxidation state metal compounds, metal halides are suitable starting materials because of their good solubility in polar organic liquids. Of course, other soluble metal salts may also be used if their anion is nonoxidizing. The radiochemical reduction of higher valence metal halides in polar organic liquids is a good method for the synthesis of pure anhydrous halides of metals in a lower oxidation state. In general, because of the greater covalent character of higher valence metal halides, these compounds are more soluble in organic liquids than the ionic lower valance metal halides; thus, the reduced product forms as a precipitate which is easily removed. In the selection of an organic liquid for these preparations, one should not only consider good radiolytic reduction capacity of the liquid but also the solubility characteristics of the system, high solubility of the solute starting material and low solubility of the reduced product. In some cases special techniques required to make the solvent anhydrous are unnecessary because small amounts of water are effectively removed due to hydrolysis of the metal halide in solution. The hydrolysis product, usually an oxyhalide or hydrous oxide, is insoluble and therefore can be readily removed before irradiation.

The radiolytic deposition of metals from solutions of metal salts in polar organic liquids follows a similar mechanism as described for the preparation of lower valance metal compounds. In the preparation of metals, however, the metal salt (e.g., a halide) must be chosen so that no stable lower valent metal compound exists which would deposit instead of the free metal. Also, the use of alcohols for this purpose is limited to the deposition of those metals which do not reduce these solvents. For the preparation of the more reducing metals, tetrahydrofuran is appropriate as a solvent because it is less reactive in this respect than alcohols. In halide systems one must consider possible reaction of the metal with the hydrogen halide and alkyl halides formed as byproducts. In the radiolysis of alcohol solutions of metal halides, organic halides are produced (ref. 38) and probably some hydrogen halide.

Several examples of radiolytic preparations involving alcohols and tetrahydrofuran are given in table IV. The use of radiolytic reducing organic polar liquids is certainly not limited to the preparation of metals and lower valent metal compounds. These systems should be applicable to a wide variety of other syntheses, both inorganic and organic, involving reducing reactions; these possibilities remain unexplored at this time.

TABLE IV. - PREPARATIONS INVOLVING RADIOLYTIC REDUCTION OF METAL SALT SOLUTIONS IN ALCOHOLS AND TETRAHYDROFURAN

[Radiation, 2 MeV electrons; beam current, 10 to 20 μA.]

| Metal salt | Organic liquid | Insoluble product |
|---|---|---|
| Copper(II)bromide | 1-butanol | Copper(I)bromide |
| Iron(III)chloride | Tetrahydrofuran | Iron(II)chloride[a] |
| Antimony(III)chloride | 1-butanol,<br>2-propanol, or<br>Tetrahydrofuran, | Antimony |
| Cadmium acetate | Methanol | Cadmium |
| Cadmium iodide | 1-butanol | Cadmium |
| Zinc chloride | Methanol | Zinc |

[a] A sample of our pure iron(II)chloride prepared in this system was used by Thompson and Carlson (ref. 40) as a source of $FeCl_2$ molecules for obtaining its infrared spectra.

However, our preparative work has revealed several anomalies which should be given special mention.

First, irradiation of a relatively dilute solution of $FeCl_3$ (0.25 M) in tetrahydrofuran produced $FeCl_2$ in good yield whereas with more concentrated $FeCl_3$ solutions (above 0.5 M), under similar conditions, polymerization of the tetrahydrofuran resulted and little $FeCl_2$ was deposited. This polymer on treatment with water formed an oily liquid immiscible with water. Infrared spectroscopy indicated the liquid to be polytetramethylene glycol ether, $HO((CH_2)_4O)_nH$. Second, irradiation of a dilute solution of titanium (IV) chloride in tetrahydrofuran caused the precipitation of a light blue crystalline material which rapidly hydrolyzed in moist air to a violet mass. No positive identification of the blue material has been made as yet but indications are that an organic titanium (III) chloride compound was involved.

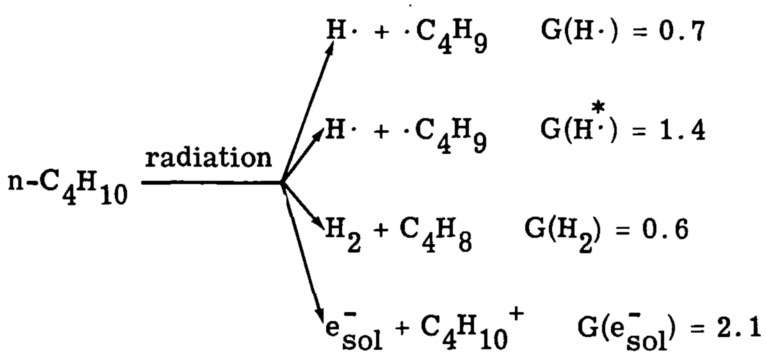
## Hydrocarbons and Nonpolar-Type Solvents

Saturated aliphatic and aromatic hydrocarbons are unreactive toward the strongest reducing reagents and provide an oxygen-nitrogen free medium for radiolytic preparations. In general, three types of radiochemical reactions concerning hydrocarbons are recognized. The first involves the reducing radicals (e.g., hydrogen atoms) in irradiated hydrocarbons as the main reactants. Reduction of the solute by these radicals takes place, for example, in the deposition of tin (II) chloride on radiolysis of a tin (IV) chloride solution in n-heptane. The second type pertains to reactions of hydrocarbon fragments formed during irradiation with the solute such as may be involved in the radiolysis of a silicon (IV) chloride solution in cyclohexane to produce the organo metallic compound, cyclohexane silicon trichloride. In the third type, the hydrocarbon may merely serve as an inert medium for the radiolytic decomposition of the solute. Such may be the case for the deposition of metals when hydrocarbon solutions of metal alkyls or metal aryls are irradiated.

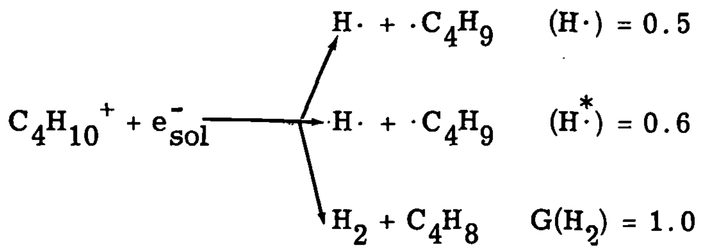
Reduction reactions. - Saturated aliphatic hydrocarbons are radiolytically reducing and, as stated previously, appear to have a relatively high radiolytic reducing capacity whereas aromatic hydrocarbons have low reducing capacity (table III). From detailed studies on the radiolysis of the straight chain hydrocarbon n-butane (refs. 40 and 41) the radiolysis mechanism will be summarized. It is assumed that the radiochemical properties of n-butane (n-$C_4H_{10}$) resembles those of other aliphatic saturated hydrocarbons especially straight chain hydrocarbons. The yield of hydrogen from the radiolysis of pure n-butane with cobalt-60 gamma rays is $G(H_2) = 4.8$. The formation of hydrogen arises from two basic processes, namely, (1) the direct excitation and ionization of the n-butane molecule and (2) neutralization of n-butane ions ($C_4H_{10}^+$) with electrons.

The reaction scheme can be represented by the following equations:

Direct excitation and ionization



Neutralization



where

| | |
|---|---|
| $H\cdot$ | scavengeable hydrogen atom |
| $H^{*}\cdot$ | precursor to nonscavengeable molecular hydrogen |
| $H_2$ | molecularly detached hydrogen molecule |

It is assumed that the same mechanism is applicable to other straight chain aliphatic hydrocarbons and that the G values for the corresponding reaction would be about the same.

The energy yield of the indicated species formed in each reaction was calculated from product yields resulting from the radiolysis of n-butane alone and in the presence of various scavengers. The reducing yield G(reducing) in irradiated n-butane, which is considerably less than the total yield of hydrogen gas, $G(H_2) = 4.8$, is the sum of the solvated electron and the scavengeable atomic hydrogen yields $(0.7 + 2.1 = 2.8)$. The remainder of the hydrogen from irradiated n-butane not available for reduction of a solute scavenger is derived from molecular hydrogen formed initially and the species $H^{*}\cdot$, the precursor to nonscavengeable hydrogen. Hopefully future work with high energy high flux irradiation of straight chain hydrocarbon systems will lend further insight as to the identification of nonscavengeable $H^{*}\cdot$.

Our preliminary experimental results on the synthesis of anhydrous $SnCl_2$, $SnI_2$, and $TiCl_3$ by radiolytic reduction of the corresponding higher valent halide $SnCl_4$, $SnI_4$, and $TiCl_4$ in n-heptane suggests that preparations from such systems are promising in terms of yield and ease of product isolation. In many cases the energy product yield appars to be appreciably higher than that determined by G(reducing) = 2.8 for n-butane No detailed explanation for this discrepancy can be given until further study is made on the high energy electron radiolysis of metal halide-straight chain aliphatic hydrocarbon systems. Several favorable characteristics found for polar organic liquid systems were also observed for aliphatic hydrocarbon systems. For example, in both cases the more ionic lower valence metal halides are less soluble and are therefore easily removed as precipitates. However, many higher valent metal halides which are soluble in polar organic liquids are insoluble in aliphatic saturated hydrocarbons; thus, the selection of metal halides is restricted to a few strongly covalent halides. Many metal halide solutions in both polar organic liquids and hydrocarbons are self dehydrating in that small amounts of water present in the solvent are eliminated by hydrolysis of the metal halide forming an insoluble hydrolysis product which can be easily removed. Our results for the radiolysis of $SnCl_4$ in n-heptane show an increasing $SnCl_2$ yield with $SnCl_4$ concentration; this same trend was observed for metal halide - polar organic liquid systems. Unfortunately, our data on the metal halide - n-heptane system cannot be correlated with that obtained for the gamma ray radiolysis of n-butane solutions of nitrous oxide and ethylene discussed earlier. The radiochemistry of hydrocarbon solutions warrants further study because they provide a medium for the radiolytic preparation of high purity, particularly oxygen and nitrogen free anhydrous metal compounds (halides) as well as for the preparation of pure metals.

Reactions involving fragments. - Reactions of hydrocarbon solvent fragments with free radicals from an inorganic solute produced by radiolysis in some cases result in organic derivatives. Several suggestions as to application of these reactions for organometallic synthesis appear in the literature; however, extensive work in this field appears to be lacking. Irradiation of certain inorganic covalently bonded halides of the less metallic elements in hydrocarbon solution leads to the formation of an organometal halide (ref. 42)

$$RH + MX_n \rightarrow HX + RMX_{n-1}$$

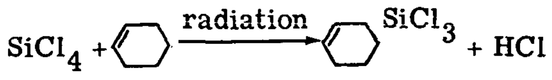
The results reported by Henglein (ref. 42) on the radiolytic preparation of several organo-phosphorus compounds using high energy, high flux electrons from a Van de Graff generator are shown in table V. Good yields of organo-phosphorus compounds of the type $RPCl_2$ are obtained on irradiation of 50:50 volume percent $PCl_3$ and hydrocarbon. The organo-phosphorus dichloride remains in the residue after unreacted $PCl_3$ and hydrocarbon are removed by distillation. Also reported in the same paper is the radiolysis of mixtures of silicon tetrachloride with cyclohexane, cyclohexene, and hexene-1. In all cases the corresponding organic silicon trichloride was obtained; however, the yields are lower by a factor of nearly two than in the corresponding reactions

TABLE V. - RADIOLYTIC PREPARATION OF ORGANO-PHOSPHORUS COMPOUNDS

[Radiation, 3-MeV electrons; solution, 30 ml of 50:50 volume percent $PCl_3$ in hydrocarbon.]

| Hydrocarbon | Weight of nonvolatile products, g | G($PCl_3$+RH consumption), molecules/100 eV | Composition of nonvolatile products, wt. % | | | | |
|---|---|---|---|---|---|---|---|
| | | | RCl | $P_2Cl_4$ | $RPCl_2$ | $R_2$ | Residue |
| Cyclohexane | 81 | 6.8 | 3 | 2 | 50 | 2 | 43 |
| n-heptane | 63 | 5.7 | 2 | 2 | 45 | 2 | 49 |
| Cyclohexene | 104 | 12 | 7 | 1 | 40 | 5 | 47 |
| Hexene-1 | 120 | 16 | 3 | 2 | 20 | 75 | |
| Benzene | 17 | 2.0 | 5 | 5 | 40 | 5 | 45 |
| Ethylbenzene | 25 | 2.7 | 4 | 2 | 30 | 5 | 59 |

of $PCl_3$. The authors suggest that acids of the type RSiO(OH) could be obtained by hydrolysis of the organo-silicon trichloride in cold water. The radiolysis of the silicon tetrachloride ($SiCl_4$), cyclohexene mixture is represented by the following equation:



Based on these findings it is possible to speculate that organic compounds of this type could be radiochemically synthesized from hydrocarbon mixtures of other covalent halides of the less metallic elements. These would include the halides of germanium, boron, and sulfur.

Decomposition of solute. - In certain radiochemical preparations the overall function of the solvent, that is, saturated hydrocarbons, may be that of an inert medium in which radiolytic decomposition of the solute occurs. This appears to be the case in the radiolytic deposition of metal from metal alkyl and metal aryl solutions in the nonreducible organic liquids such as saturated hydrocarbons and ethers. This type of process which does not depend on the reduction potential of a reducing species generated in the irradiated solvent (e.g., hydrogen atoms) allows the deposition of the most electropositive metals to take place. Recently reported results on the formation of free lithium from the photolysis of solutions of lithium aryls (ref. 43) supports speculation that most active metals can be radiolytically prepared. Ultraviolet irradiation of the lithium aryls, phenyllithium or 2-naphthyllithium, in ethyl ether solution resulted in the deposition of lithium metal in good yield according to the equation

$$2C_6H_5Li \rightarrow 2Li + (C_6H_5)_2$$

where $(C_6H_5)_2$ is biphenyl. Apparently in such cases the metal-carbon bond is sensitive to radiation; thus, rupture of this bond occurs resulting in the formation of free lithium. The photolytic decomposition of other alkyl and aryl metal compounds in unreactive organic liquids has been reported. Ultraviolet irradiation of tetramethyl lead, $Pb(CH_3)_4$, and tetraphenyl lead, $Pb(C_6H_5)_4$, solutions in 2,2,4-trimethylpentane, benzene, or hexane results in the precipitation of metallic lead (ref. 44). Similarly, the photolysis of mercury diphenyl $Hg(C_6H_5)_2$ and lead tetraphenyl in isopropyl benzene solution caused the deposition of mercury and lead, respectively (ref. 45). Triphenyl bismuth, $Bi(C_6H_5)_3$, a compound which is easily purified by distillation is a good starting material for the preparation of pure bismuth. Free bismuth is produced by photolysis of triphenyl bismuth in organic aromatic liquids (ref. 46). Our results (unpublished NASA data) show that a good yield of bismuth powder is obtained when a 10-percent solution of triphenylbismuth in dibutyl ether is exposed to high flux 2-MeV electrons. Under similar conditions we found that a somewhat poorer yield of finely divided lead was deposited by radiolysis of 5 percent tetramethyl lead in n-heptane. In all probability, other high purity metal powders would be deposited by high energy electron irradiation of their alkyl or aryl derivatives in hydrocarbon or ether solution. These would include the preparation of aluminum, cadmium, and zinc from solutions of triphenylaluminum, $Al(C_6H_5)_3$; dibutylcadmium, $Cd(C_4H_9)_2$; and diphenylzinc, $Zn(C_6H_5)_2$, respectively.

Besides alkyl and aryl metal compounds, radiolytic decomposition of other metal compounds in solution may possibly be employed for the preparation of pure metals. In this respect metal carbonyls may be of interest for the preparation of certain metals, for example, chromium, nickel, and tungsten, respectively, from solutions of chromium hexacarbonyl, $Cr(CO)_6$; nickel tetracarbonyl, $Ni(CO)_4$; and tungsten hexacarbonyl, $W(CO)_6$.

Alkyl and aryl compounds of silicon apparently radiolytically decompose to form carbosilanes rather than free silicon. Irradiation of pure liquid tetramethylsilane, $Si(CH_3)_4$, with 50-kilovolt X-rays forms, in addition to hydrocarbons, carbosilane products (ref. 47) such as $(CH_3)_3SiCH_2Si(CH_3)_3$, $(CH_3)_3SiCH_2CH_2Si(CH_3)_3$, and $CH_3CH_2Si(CH_3)_3$ with corresponding yields of $G = 1.2$, 1.2, and 0.6. It is expected that carbosilanes would also form from radiolysis of $Si(CH_3)_4$ in hydrocarbon solution; they should also form if high energy electron radiation were used instead of X-rays. Because of the somewhat similar chemistry of silicon, boron, germanium, and tin, we may speculate that carboboranes, carbogermanes, and possibly carbostannanes could be synthesized from the appropriate alkyl and aryl derivatives.

## Other Organic Solvents

Oxidizing reactions. - Liquid organic halides, particularly those which contain no hydrogen atoms, are radiolytically oxidizing. Thus, irradiated carbon tetrachloride $CCl_4$ is oxidizing in that it is a source of chlorine atoms. Gamma irradiated pure $CCl_4$ forms chlorine gas and hexachloroethane $C_2Cl_6$ as major products with a yield $G =$ about 0.7 (refs. 48 and 49). For simplicity, the radiolytic decomposition of $CCl_4$ may be represented as follows:

$$2CCl_4 \rightarrow 2Cl\cdot + 2\dot{C}Cl_3$$

$$2Cl\cdot \rightarrow Cl_2$$

$$2\dot{C}Cl_3 \rightarrow C_2Cl_6$$

In a recent paper (ref. 50) on the cobalt-60 gamma radiolysis of bromine and iodine solutions in $CCl_4$, the bromine and iodine were radiolytically oxidized to bromine chloride, BrCl, and iodine chloride, ICl, respectively. For $CCl_4$ the yield of scavengeable chlorine G(Cl·) is 8.3 atoms per 100 eV which should represent the maximum oxidation equivalent for $CCl_4$.

Reactions of chlorine atoms from irradiated $CCl_4$ with various solutes, even gases, may be used for a variety of preparations including the fixation of molecular nitrogen. Radiolytic nitrogen fixation from nitrogen solutions in $CCl_4$ or in tetrachloroethylene $C_2Cl_4$ have been observed (ref. 51). The results of cobalt-60 gamma irradiation of nitrogen solutions in $CCl_4$ or $C_2Cl_4$ under static conditions with different nitrogen pressures above the solution shows that the nitrogen fixation yield G($-N_2$) increases with increasing pressure, ranging from about 0.08 at 1 atmosphere pressure to about 0.2 at 100 atmospheres $N_2$ pressure. Cyanogen chloride CNCl was identified among the products of radiation synthesis. At 120 atmospheres $N_2$ pressure above the solution ($30^\circ$ C), the yield of CNCl for both $CCl_4$ and $C_2Cl_4$ is estimated to be G(CNCl) = 0.12. If the generally unreactive gas $N_2$ reacts with radiochemically generated chlorine atoms, then one can assume that other more active substances would be reactive. It is therefore anticipated that under these conditions one could readily synthesize phosgene, $COCl_2$ and sulfuryl chloride, $SO_2Cl_2$, respectively, from carbon monoxide, CO, and sulfur dioxide, $SO_2$.

Several interesting radiolytic synthesis involving nitric oxide, NO, and organic polyhalides are reported by Hanglein (ref. 52) which represent preparations using high flux and high energy, 3-MeV electrons. During radiolysis, NO gas was continuously pumped through the liquid by means of a frit at the base on the reaction vessel. Irradiation of a NO - $CCl_4$ mixture produced trichloronitrosomethane, $CCl_3NO$, in addition to nitrosyl chloride, NOCl, and free chlorine. Using 450 grams of $CCl_4$, 22 grams of $CCl_3NO$ could be prepared in one batch. The value of G($CCl_3NO$) is about 4.2 at 10 microamperes electron beam current; the yield decreases slightly with increasing beam current. This is explained by depletion of NO in the reaction zone. Under similar conditions but using trichlorobromomethane $CCl_3Br$ instead of $CCl_4$, $CCl_3NO$ is formed in a higher yield (G($CCl_3NO$) = 5.2). Other products include free bromine and nitrosyl bromide NOBr. No dichlorobromonitrosomethane, $CCl_2BrNO$ was found thus indicating that the C-Br bond is preferentially dissociated by the radiation. Following this trend with organic polyhalides, C-I bond rupture should occur more readily than with the C-Br bond. The nitroso group should replace iodine preferentially in polyhalides containing also chlorine and bromine. It then should be possible to prepare a variety of nitroso chlorides, nitroso bromides, and nitroso compounds containing both chlorine and bromine. The position of the more easily replaceable halide in the polyhalide molecule should be the same as the nitroso group in the final product. It may be conceivable to introduce radiolytically more than one nitroso group in an organic polyhalide containing several iodine atoms. The likelihood of preparing nitro compounds by irradiating an organic halide (e.g., an alkyl iodide) and nitrogen dioxide $NO_2$ has not as yet been ascertained; however, this synthesis would be an interesting one to study.

Other organic liquids no doubt could be used in preparations involving radiolytic oxidation. One such compound is tetranitromethane $C(NO_2)_4$; however, data on this compound for radiochemical synthesis is lacking.

Acid producing reaction. - The decomposition of chloroform $CHCl_3$ with cobalt-60 gamma radiation results in the formation of hydrogen chloride: G(HCl) = 11.4 with no observable yields of hydrogen or chlorine (ref. 49). A variety of alkyl chlorides, $C_2Cl_6$, $CH_2Cl_2$, $C_2HCl_5$, $CCl_4$, and $C_2H_2Cl_4$, are also produced (ref. 53). It appears that irradiated alkyl polychlorides containing hydrogen form hydrogen chloride HCl in the absence of strong reducing agents; thus, chloroform $CHCl_3$ when irradiated becomes a source of HCl, a Lewis acid which can react with a Lewis base to precipitate the corresponding salt. For example, the irradiation of $CHCl_3$ containing ammonia $NH_3$ forms insoluble ammonium chloride $NH_4Cl$ (ref. 54). Application of such systems would be of interest in the preparation of anhydrous chlorides or hydrochlorides of bases such as amines, hydrazines, and phosphines. By analogy, irradiated bromoform $CHBr_3$ would be a possible source of hydrogen bromide.

Chain oxidation reactions. - The results of a systematic study of oxidative radiolytic synthesis involving the metal tin with alkyl halides has been reported (ref. 51). Using gamma radiation, dibutyltin dibromide, $(C_4H_9)_2SnBr_2$, is prepared by the radiolysis of a vigorously stirred mixture of finely divided pure tin powder and n-butyl bromide, $C_4H_9Br$.

$$2C_4H_9Br + Sn \rightarrow (C_4H_9)_2SnBr_2$$

The reaction apparently proceeds by a chain mechanism as evidenced by the abnormally high product yield, $G = 10^3$ to $10^4$ molecules per 100 eV. The reaction rate is proportional to the square root of the dose rate and stops as soon as radiation is terminated; therefore, the reaction is not self-perpetuating. Nevertheless, because of their high product yields, synthesis involving any type of chain reactions become practical for the preparation of large amounts of product.

Based on these results for the radiation induced tin-alkyl halide reaction, one can consider similar reactions of alkyl and aryl halides with other metals such as aluminum, lead, and magnesium. In reactions of magnesium and alkyl or aryl halides in a suitable solvent, difficult Grignard reactions could be initiated or even propagated with radiation.

# CONCLUDING REMARKS

In this report we have described the scope of radiation preparative chemistry in liquids as we see it today. Many liquids ranging from water to nonpolar organic compounds may be used. Various types of reactions, decomposition, polymerization, redox and so forth, may be accomplished using radiation leading to a diversity of products: pure metals, compounds, and even polymers.

## Radiation Source

Our work on radiation preparative chemistry made use of high energy electrons, 2 MeV, from a sophisticated linear accelerator. Due to its high cost of operation we have limited our preparations to laboratory quantities. The use of such an accelerator may be practical for large scale preparations if a chain or autocatalytic mechanism is involved; however, for preparations relating to less productive chemical mechanisms, the use of a simpler, low cost accelerator would be far more practical for preparations on a large scale. An accelerator of lower electron voltage may suffice for this purpose.

## Special Applications

An interesting possibility of radiolytic preparative techniques is the coating of a substrate with a metal. The substrate in this case could be a powdered material or a single solid object. In several experiments using aqueous systems we have radiolytically deposited metals (lead and platinum) on powdered silica and alumina. In a few cases we were able to form an adherent metal (nickel) mirror on glass. It appears that the more adherent coatings are obtained under conditions favoring the formation of extremely fine metal powders in the colloidal range. Pretreatment of the substrate also influences particle adhesion. Metals deposited radiochemically from solutions of low ionic activity (weak electrolytes) are submicron and tend to form colloids. For example, a colloidal lead-aqueous suspension is radiolytically produced from aqueous lead acetate (weak electrolyte) while, under similar conditions, a conglomerate of lead forms from the strong electrolyte, aqueous lead perchlorate.

A technique, based on pure speculation, is the use of radiation chemistry for the epitaxial growing of single crystals. By placing a seed crystal at a proper location in the solution (near the reaction zone as determined by the beam width and beam penetration) the newly formed crystallites produced during irradiation could orient themselves on the seed crystal. A low radiation dose rate causing gradual deposition of product would be advantageous for single crystal growth.

Another interesting aspect of preparative radiation chemistry is synthesis at extremely low temperature where reaction rates are too low for ordinary chemical methods. The use of radiation to propagate such reactions would allow the preparation of thermally unstable compounds which can exist only at reduced temperature.

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Cleveland, Ohio, March 8, 1973,
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