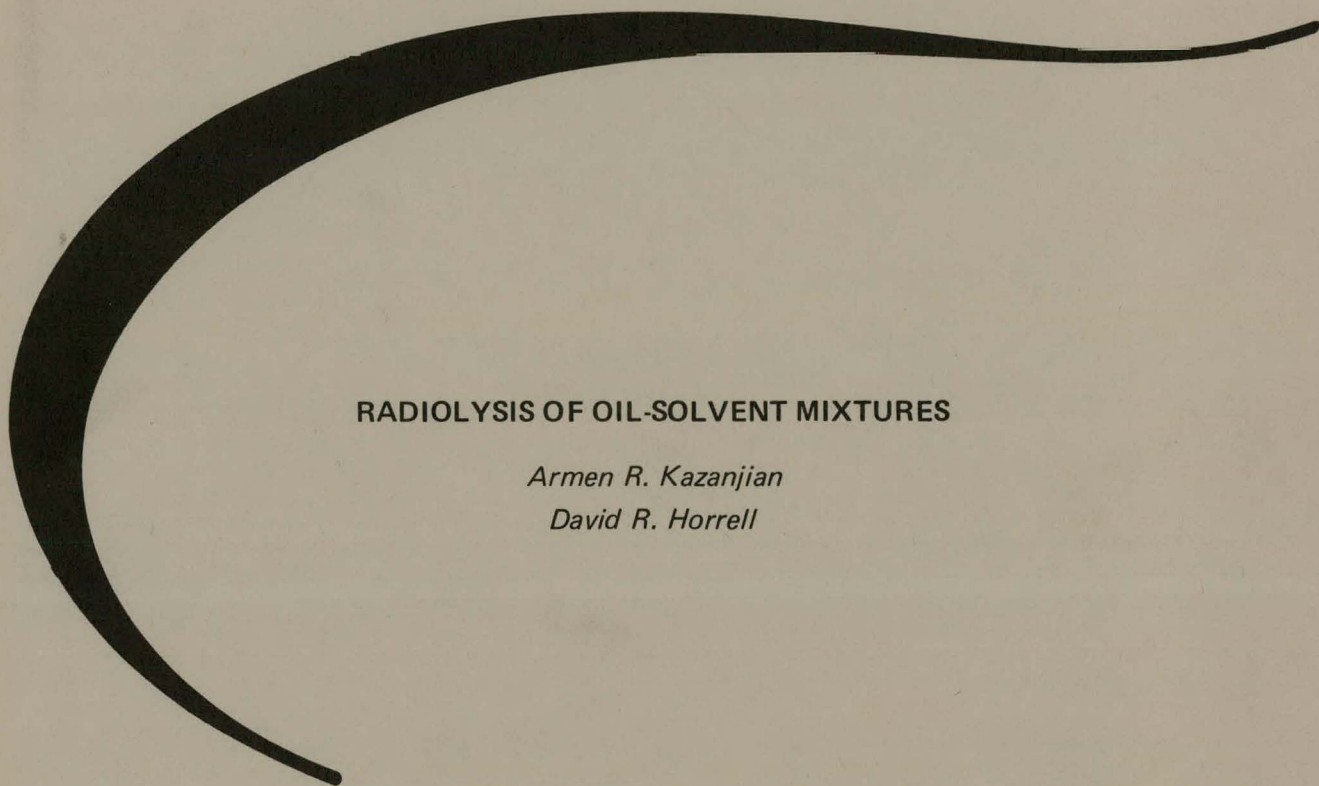191
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RADIOLYSIS OF OIL-SOLVENT MIXTURES

Armen R. Kazanjian
David R. Horrell

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THE DOW CHEMICAL COMPANY
ROCKY FLATS DIVISION
P. O. BOX 888
GOLDEN, COLORADO 80401

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CONTENTS

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Abstract. The radiolysis of trichloroethylene-dodecane and carbon tetrachloride-dodecane mixtures has been investigated. The dodecane is a substitute for saturated hydrocarbon lubricants. These solvent-lubricant mixtures are a common occurrence in the plutonium environment at Rocky Flats. Irradiations were made with gamma rays, and the total water extractable acids formed were determined over the entire range of concentrations. The acid yields were regarded as a measure of the corrosivity (toward plutonium) of the irradiated mixtures. The variation in these acid yields is explained on the basis of the radiation chemistry of the compounds. Some of the gaseous radiolysis products from 50% mixtures were identified by mass spectrometry.

INTRODUCTION

Solvents, such as trichloroethylene (TCE) and carbon tetrachloride (CCl_4), are frequently used to remove machining oils, such as Texaco Regal Oil A, from plutonium metal. The oil-solvent mixtures are thus subjected to the alpha particle radiation from plutonium. The radiolytic decomposition of the mixtures can lead to products which are very corrosive toward plutonium. In cases of extended exposure, significant damage to the plutonium can result from this corrosive action. A radiolytic investigation of this system was undertaken to determine the potential corrosive effects.

Regal Oil A is a complex mixture of mostly saturated long chain hydrocarbons. The radiation chemistry of such a material would be extremely complicated. Therefore, dodecane, a straight chain hydrocarbon ($C_{12}H_{26}$), was used as a substitute. Dodecane and Regal Oil A are sufficiently similar chemically to yield the same, or the same type, radiolysis products. Dodecane also has the advantage of being available in a highly pure state. Different batches of the oil could conceivably contain impurities which could completely change the radiation chemistry. However, even an analysis of the radiolysis products from the simplified system, dodecane-solvent, is very difficult, as will be discussed later.

The radiation effects on two types of mixtures, dodecane-TCE and dodecane-CCl_4, are reported here. Product yields are occasionally expressed as G values; that is, the number of molecules produced per 100 eV of absorbed energy.

Before describing the experimental results, it will be useful to report the previous work done on the individual components. The radiation chemistry of dodecane has not been investigated, but there has been extensive work done on straight chain hydrocarbons such as hexane[1] and the results can be used to predict the radiolysis products from dodecane. The primary product would probably be hydrogen with a G value of about 5. There would also be a large number of aliphatic hydrocarbons ranging from 1 to 24 carbons (the dodecane dimer) all with G values of less than 1. The analysis of all these products would be a formidable task. Irradiation of saturated hydrocarbons in the presence of oxygen also produces CO, CO_2, and probably peroxide compounds.

The radiation chemistry of trichloroethylene has been investigated at Rocky Flats. It was found that gamma irradiation of TCE under vacuum resulted in small yields of chloroacetylene (G≈0.25) and hydrogen chloride (G≈0.25), whereas irradiation in the presence of air (oxygen) produced yields (G's) in the thousands through a chain reaction. The products are dichloroacetyl chloride, phosgene, and trichloroethylene oxide, all very reactive compounds.

The radiolysis of both degassed and aerated CCl_4 has been studied using ^{60}Co radiation. The two products formed in degassed CCl_4 are chlorine (G≈0.66) and hexachloroethane, a white solid for which no yield was determined.[2]

Irradiation in the presence of air (oxygen) produces a third product, phosgene, with a G of 12.1 and increases the Cl_2 yield to a G of 3.6.[3] Irradiation of CCl_4 vapor with alpha particles also produces chlorine and hexachloroethane.[4] The G (Cl_2) was determined to be about 0.4, which is essentially the same as the yield in gamma irradiated liquid.

The mixtures studied would have other radiolysis products as well as those reported; the relative amounts depending on the concentration.

EXPERIMENTAL

Materials: The trichloroethylene used was chromatoquality, manufactured by Matheson, Coleman, and Bell.

The chromatogram showed 2 impurities, CCl_4 (0.07%) and an unknown (0.10%). Carbon tetrachloride was Baker analyzed reagent and chromatographic analysis showed less than 0.05% impurities. The dodecane used was spectroquality grade from Matheson, Coleman, and Bell, and the chromatogram showed about 0.1% impurities of unknown identity.

Irradiation: Irradiations were made with gamma rays from the Gammacell®, a source containing about 3200 curies of Cobalt-60. The approximate dose rate was 2.2×10^{17} eV/ml min (2×10^5 rads/hour). The exact value depends on the volume and position of the sample in the irradiation chamber.

A gamma source was easier to use than an alpha source. Alpha irradiations pose a difficult handling problem because of radioactive contamination. Gamma radiation would be expected to produce the same products as alpha radiation, although in somewhat different yields. A more thorough comparison of these types of radiation is presented in RFP-1376.[5]

The irradiations were carried out in vials (in air) or sealed ampoules (under vacuum) of Pyrex glass. The exact dose rates absorbed by the ferrous sulfate dosimetry solution were 2.12×10^{17} eV/ml min for those in air, and 2.43×10^{17} eV/ml min for those under vacuum. The difference is due to different locations in the irradiation chamber. The actual doses absorbed by the dodecane-solvent mixtures varied (up to 30% from the above values) according to the compound and concentration, and are calculated on the basis of electron density.

Analysis: Product analyses after irradiation were made by different methods. The most common and successful was to determine the amount of water-extractable acid formed. This was done by shaking the irradiated solution with water and titrating the resulting acid with standard NaOH solution (phenolphthalein indicator). These acids result from the reaction of carbonyl compounds, such as acid chlorides or phosgene, with water. This type of organic compound is prevalent in these irradiations (to be discussed later) and is very reactive and corrosive. Therefore, this method provides a relative measure of the corrosivity of these irradiated solutions.

Other methods used were mass spectrometry (especially for gaseous products), infrared spectrometry, and gas chromatography. Gas chromatography was not too successful, probably because of the high reactivity of some of the radiolysis products in the column.

RESULTS

Dodecane-Trichloroethylene:

Various concentrations of dodecane-TCE were irradiated in air for 16 hours, and under vacuum for 40 hours. The total acid produced was measured and the results are shown in Figures 1 and 2. In the presence of air the acid yield from dodecane is very small, and increases with increasing TCE concentration. This is greatly so at the higher concentrations; for example, close to 100% the acid yield is enormous. It was stated that the irradiation of TCE in air produces extremely high yields. Almost any organic compound, in this case, dodecane, would inhibit the chain reaction and decrease the acid yields.

Irradiations in vacuum show that the acid yields from the pure components are very low and increase a few fold when they are mixed. There is a relatively small variation for all the intermediate concentrations.

The variation of these acid yields with irradiation time is also of interest and was determined for 50% solutions in air and in vacuum. Results are shown in Figures 3 and 4. In air, the acid production increased linearly after an initial decrease. The $G(H^+)$ calculated from the linear portion is 7.1. In vacuum, the acid production, $G(H^+) = 8.7$, is linear except at the higher doses where it decreases.

These titratable acids can be accounted for in the following way. Irradiation of dodecane in air should produce very little acid, as was found. This could result from the formation of small amounts of carboxylic acids and carbon dioxide. These compounds are soluble in water and have sharp titratable end points. As the trichloroethylene concentration is increased, the radiolysis products from TCE, dichloroacetyl chloride and phosgene, increase and contribute to the acidity:

$$CHCl_2COCl + H_2O \longrightarrow CHCl_2COOH + HCl$$

$$COCl_2 + H_2O \longrightarrow CO_2 + 2HCl$$

In vacuum, the situation is different. The acid yield in dodecane is very small and the origin of it is unknown. The acid formed in a low yield in 100% TCE is HCl. The increase in acidity at the intermediate concentrations probably is due to HCl. Chlorine atoms are formed in the radiolysis of TCE and can readily abstract hydrogen atoms from the dodecane to form HCl.

Product Analysis

Some radiolysis products from these mixtures have been mentioned previously. In addition, there are specific
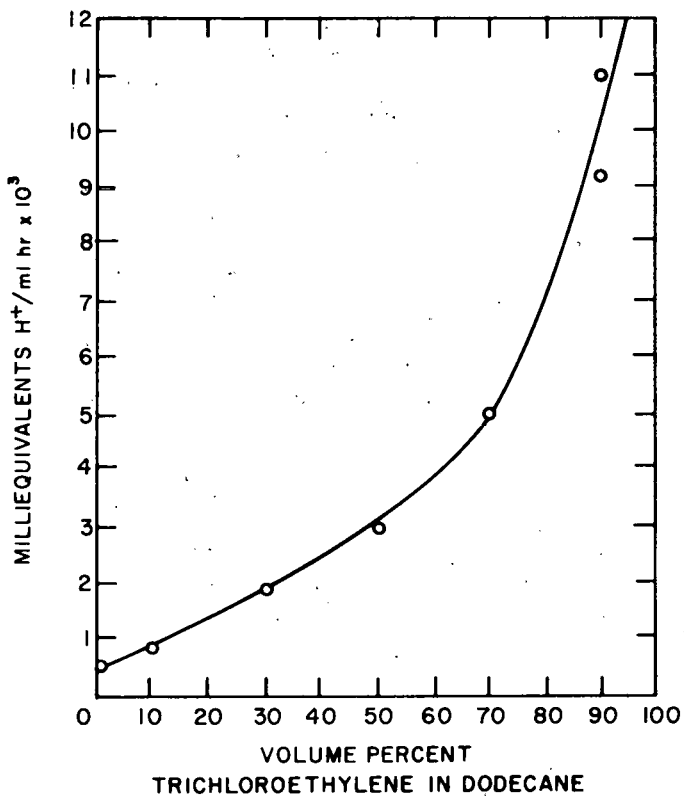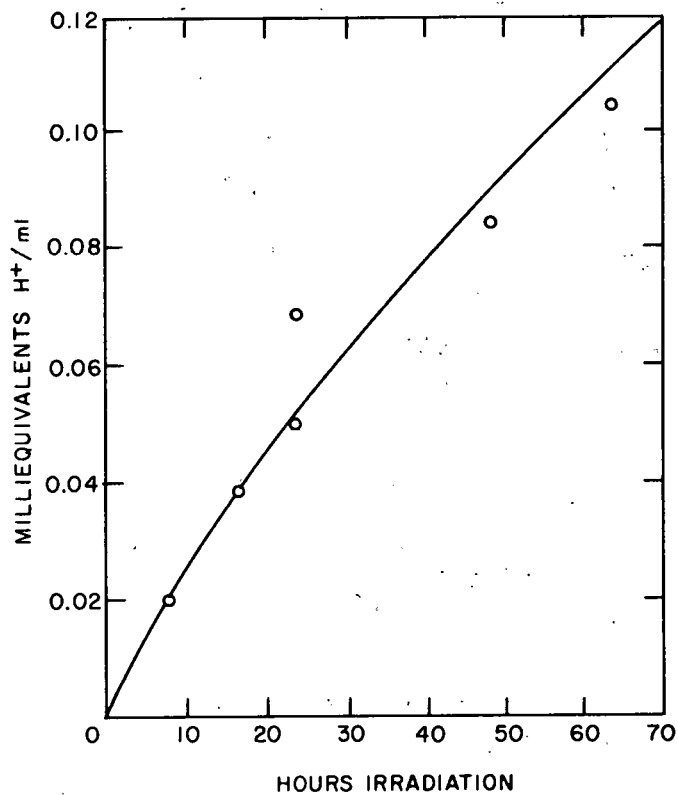
Figure 1. Acid Yield in Air.

Figure 2. Acid Yield in Vacuum.

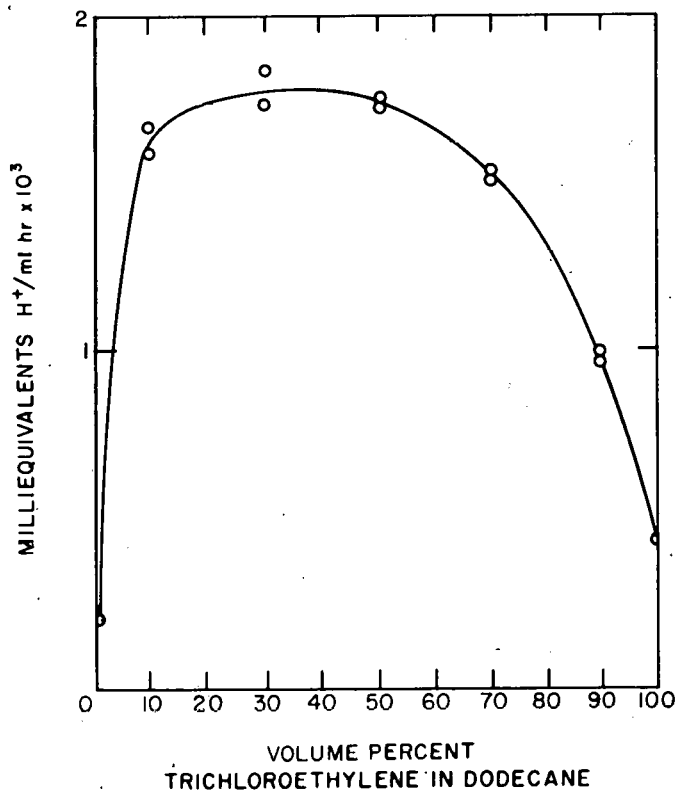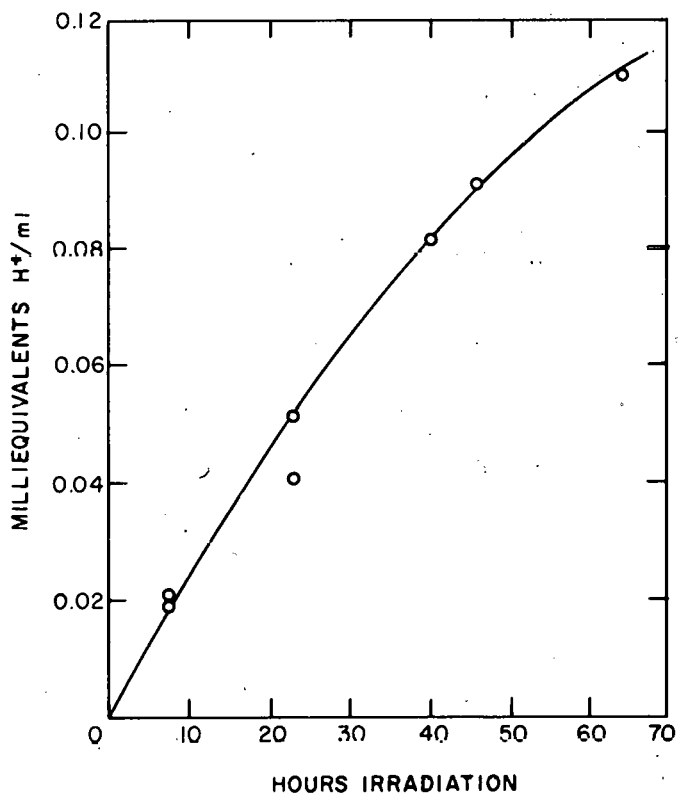Figure 3. Acid Yield in Air for 50 Volume Percent Trichloroethylene in Dodecane.

Figure 4. Acid Yield in Vacuum for 50 Volume Percent Trichloroethylene in Dodecane.

products that depend on the particular combination being irradiated. Identification of these products was made by the following methods.

Infrared spectrometry was used to analyze a 50% solution that had been irradiated for about 10 days in air. There was a large peak at 1730 cm^{-1}, caused by a carbonyl (C=O) grouping that is present in acid chlorides and carboxylic acids. There is probably more than one carbonyl containing product, but assuming the product is dichloroacetyl chloride, the amount of C=O present accounted for most of the acid production.

Mass spectrometry was used to analyze the gaseous radiolysis products. Fifty percent solutions were irradiated 48 hours in air and under vacuum and the results are summarized in Table I.

Table I. Gaseous Radiolysis Products from 50% Dodecane-TCE.

Irradiation in Air		Irradiation in Vacuum	
Product	G	Product	G
H_2	0.13	H_2	0.37
Light hydrocarbons (CH_4, C_2H_6, C_2H_4)	0.08	C_2HCl	1.25
		HCl	0.29
CO_2	0.09	Light hydrocarbons $(CH_4, C_2H_6,$	0.24
CO	0.41	$C_2H_2, C_2H_4,$	
		$C_3H_8, C_4H_{10})$	

Note:
All of these products can be accounted for from the mixture irradiated. However, the CO yield is questionable.

Mass spectrometry was also used in attempts to identify higher molecular weight products. There was evidence for the compounds 1,2-dichlorotetradecene and tetrachloropropene. The first would be a natural addition compound of the two components, but the formation of the second compound is not easily explained.

Oxygen Consumption

Since irradiation in air involves an oxidation, it was desirable to measure the rate of oxygen consumption.

This was done by irradiating 50% dodecane-TCE mixtures in air for short periods and analyzing the residual oxygen by mass spectrometry. The results were very scattered, but the average rate of oxygen consumption was $G(-O_2) = 4.5$. This value is in accord with the rate of acid production in air, i.e., $G(H^+) = 7.1$.

Dodecane-Carbon Tetrachloride:

Various concentrations of CCl_4-dodecane were irradiated in air for 24 hours. The total acid produced was determined by titration. The results, depicted in Figure 5, show that the acid yield is very low in dodecane, increases a few fold at all intermediate concentrations, and then increases sharply at CCl_4 concentrations close to 100%. The acid yield between 10 and 90% CCl_4 is probably caused by the formation of HCl. Hydrogen chloride was not analyzed directly because it is very difficult to do. The further increase in acid yield at 100% CCl_4 can be accounted for by the formation of phosgene.

Figure 5. Acid Yield in Air.
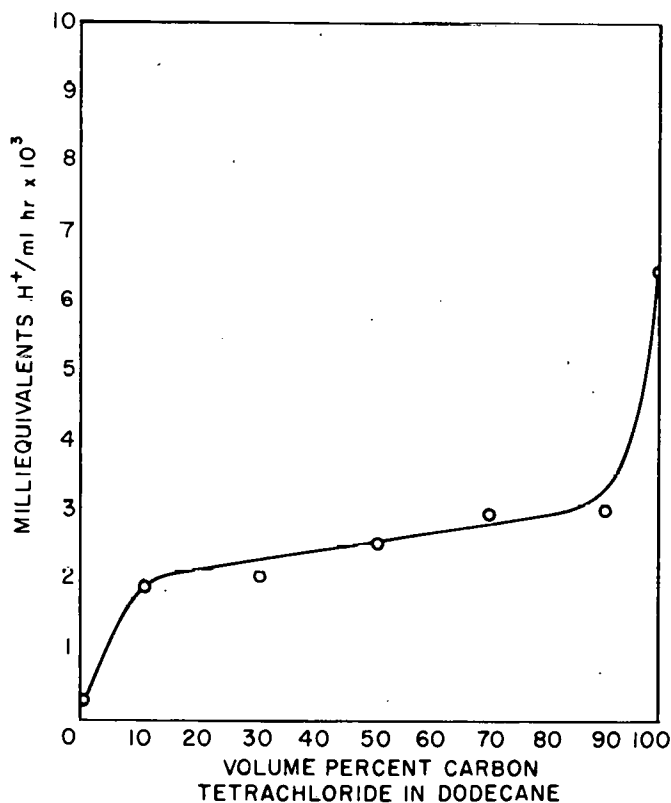
Various concentrations of CCl_4 and dodecane were also irradiated 40 hours under vacuum. The acid yields are shown in Figure 6. The results are very similar to those shown in Figure 5 (note the difference in scales) indicating the role of oxygen to be almost negligible, except at CCl_4 concentrations close to 100%. There is no phosgene formed in the absence of air and the acid yield decreases rather than increases when O_2 is present. There is still some acidity formed in 100% CCl_4 because of the formation of Cl_2:
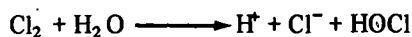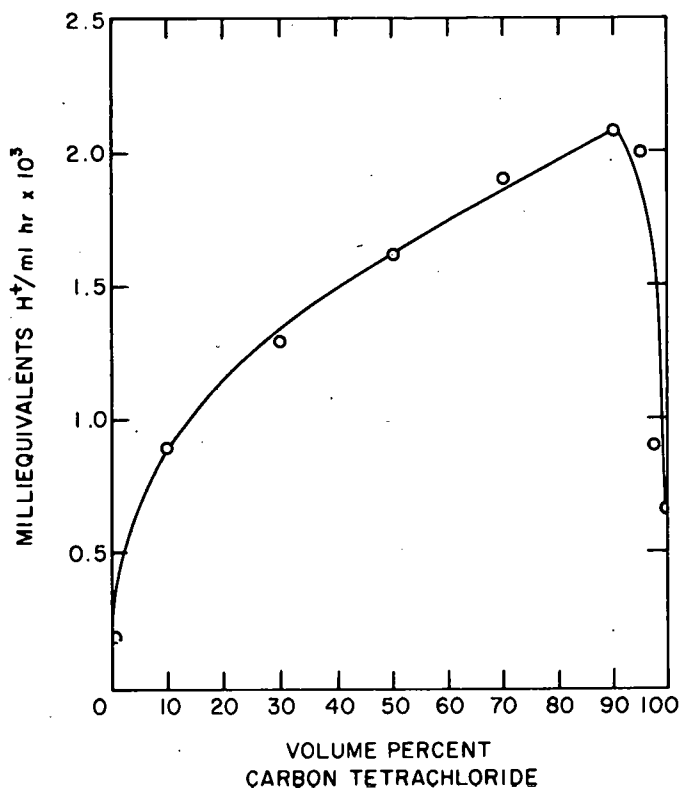
$$Cl_2 + H_2O \longrightarrow H^+ + Cl^- + HOCl$$

Figure 6. Acid Yield in Vacuum.

Figure 7. Acid Yield in Air for 50 Volume Percent Carbon Tetrachloride in Dodecane.

Figure 8. Acid Yield in Vacuum for 50 Volume Percent Carbon Tetrachloride in Dodecane.

The acid yields as a function of radiation exposure were also determined for 50% solutions in air and in vacuum. Figure 7 shows a least-squares fit of all the data points. There is some scatter at the longer exposures. The G value calculated from this line is $G(H^+) = 13.6$. Figure 8 shows the results of the irradiations in vacuum. The G value calculated from these data is $G(H^+) = 8.0$. These values are consistent with the results from the previous work; that is, acid yields are somewhat higher than those in vacuum.
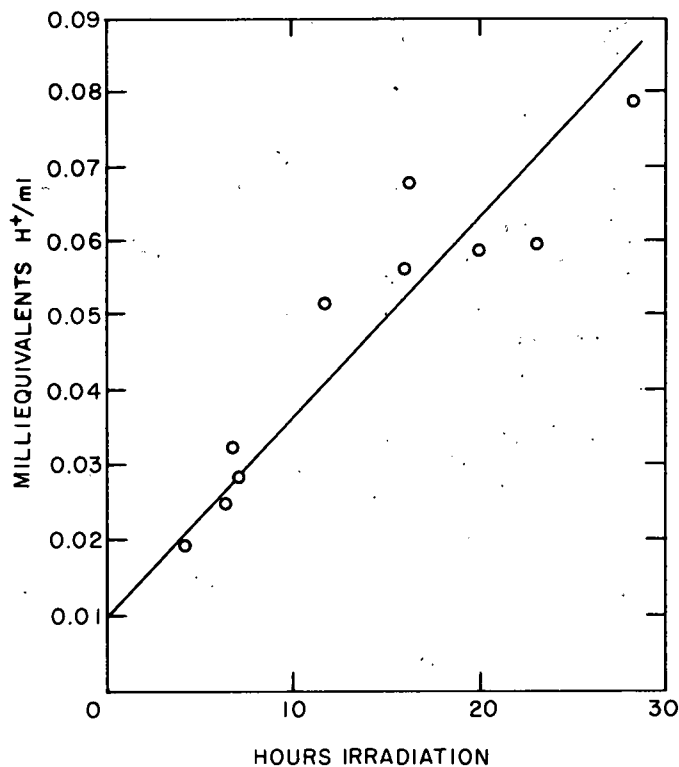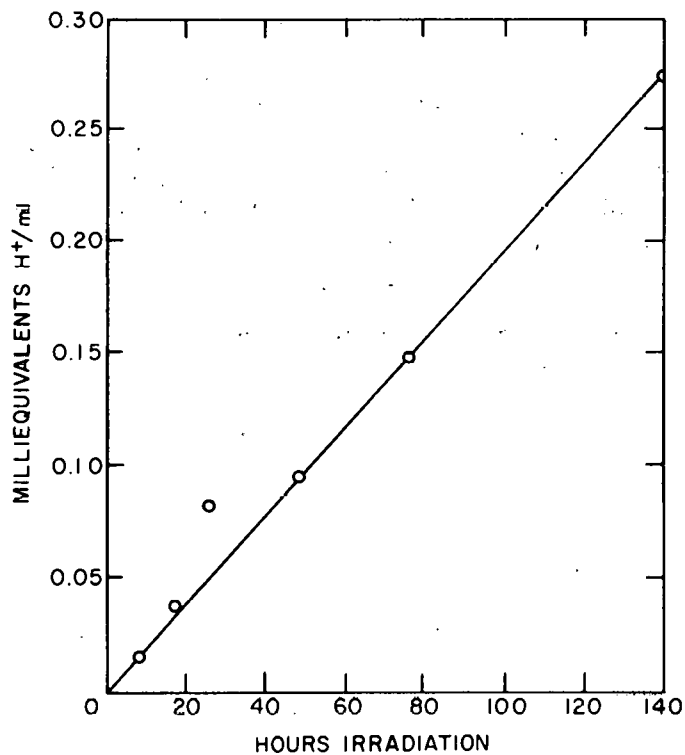
Product Analysis

Efforts were made to identify the individual radiolysis products. Most of these products, such as $COCl_2$ and Cl_2 formed in CCl_4, and HCl formed in the mixtures. are very difficult to analyze directly because of reactivity. Infrared analysis of a 50% solution that had been irradiated for 1 month showed a large peak at 1750 cm^{-1}, indicating a C=O group. As was their case for the TCE-dodecane mixture, the compound or compounds associated with this carbonyl group could account for most of the observed acidity.

Mass spectrometric analysis was made of the gaseous products from a 50% solution that had been irradiated under vacuum. Results are summarized in Table II.

Table II. Gaseous Radiolysis Products from 50% Dodecane-CCl_4.

Product	G
H_2	0.36
HCl	0.10
CH_4	0.01
C_2H_6, C_4H_8,	trace
C_4H_{10}, C_6H_{12}	amounts

CONCLUSIONS

The relative amounts of potentially corrosive products resulting from the irradiation of oil-solvent mixtures have been determined. Although there are practical consequences of this work to plutonium corrosion, they are not discussed because the actual production conditions under which the radiation-induced corrosion would occur are too variable to define.

The materials with the greatest corrosion potential are the pure solvents when irradiated in air. Although this is particularly true of TCE, it should be noted that the TCE used in this study did not contain any stabilizing additives. The commonly used solvent, Alk-Tri® (a product of The Dow Chemical Company), contains an additive, diisopropylamine, which substantially decreases the rate of acid production in the initial radiation stages. The addition of dodecane to these solvents decreases the acid yield greatly.

The situation is different when the materials are irradiated in the absence of air. Under these conditions the pure solvents produce little acid, but the irradiation of a mixture increases the acid yield a few fold. This phenomenon is most likely caused by the formation of HCl from the two components.

An important corrosion factor that has not been mentioned is the formation of hydrogen in dodecane. Irradiation in air or in vacuum will produce a significant amount of hydrogen, G$\approx$5. The amount of hydrogen does not appear in the acid yields, but is known to corrode plutonium by the formation of a hydride.

REFERENCES

1. H. A. Dewhurst, *J. Am. Chem. Soc., 83,* 1050 (1961).

2. T. H. Chen, K. Y. Wong, and F. J. Johnston, *J. Phys. Chem., 64,* 1023 (1960).

3. Z. Spurny and I. Janovsky, *Nature, 190,* 624 (1961).

4. W. Mund, P. Huyskens, and J. Debaisieux, *B CZAR BELG, 41,* 929 (1955).

5. A. R. Kazanjian and A. K. Brown, Radiation Chemistry of Materials used in Plutonium Processing, USAEC RFP-1376, Rocky Flats Division, The Dow Chemical Company, September 4, 1969.