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Radiolysis of simple quaternary ammonium salt components of Amberlite resin

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ABSTRACT

The radiation chemical yields of gaseous products, H_2 and CH_4, in the radiolysis of dry methylammonium chloride, dimethylammonium chloride, trimethylammonium chloride, tetramethylammonium chloride and benzyl trimethylammonium chloride by γ-rays and 5 MeV helium ions have been investigated. Some of these amines are the different components of the quaternary ammonium resin Amberlite, which is a strongly basic anion exchange resin based on a polystyrene divinylbenzene copolymer. Molecular hydrogen yields with γ-radiolysis range from a high of 4.43 molecules per 100 eV for trimethylammonium chloride to 0.07 and 0.05 molecules per 100 eV for tetramethylammonium chloride and benzyl trimethylammonium chloride, respectively. Yields of methane gas are generally negligible except for trimethylammonium chloride and tetramethylammonium chloride, 0.26 and 0.02 molecules per 100 eV, respectively. Isotopic labeling studies suggest that the first step in H_2 production is the breakage of the N—H bond followed by abstraction of H$^\cdot$ atom from the methyl groups. EPR analysis shows the formation of both N and C centered radicals. A comparison is made between the radiolysis of Amberlite and its various components.

1. Introduction

Anion exchange resins have received a large amount of attention because they are used widely in the nuclear industry as a part of fuel reprocessing, waste management, and purification of reactor coolants [1]. Earlier investigations generally examined physic-chemical properties such as total exchange capacity, water retention capacity, weight loss, and similar properties that were related to the functional performance of resins [2–6]. However, exposure of anion exchange resins to ionizing radiation leads to molecular degradation releasing gaseous and other products like amines into the systems [5,6]. This radiolytic degradation might impede the separation process and can also cause serious engineering and maintenance problems. In this connection, several studies on the radiation induced decomposition of resins have reported on probable mechanisms involving radiolytic splitting of the functional groups and deterioration of the resin matrix to release basic products, amines and ammonia, on exposure to high doses [7–10].

Radiation induced decomposition studies of the anion exchange resin Deacidite FF has revealed the destruction of the strong base functional group resulting in the release of water soluble tertiary, secondary and primary amines [9]. Gamma radiolysis of aqueous solutions of benzyl trimethylammonium ions, which mimic the functional group of quaternary ammonium based resins, also reveal the cleavage of the benzyl—N bond resulting in the formation of trimethylamine as the major nitrogenous deamination product [11]. Reactions of various aryl alkyl amines have been studied in detail using pulse radiolysis techniques [12]. The results show that reductive deamination of arylalkylamines by e^-_{aq} is an important process having diffusion-controlled rate coefficients. Radiolysis of the strong basic anion exchanger resin Amberlite IRA400 in various anionic forms shows an excess production of H_2 with about 85% water weight fraction samples [13]. This enhancement in H_2 production was reported to be due to dimethylamine and trimethylamine that leached from the resin into the aqueous phase. These studies show that the presence of aliphatic amines either due to deamination or to leaching from the resin plays an important role in the radiolytic production of H_2 and other gases.

In the present work, the radiation chemical yields of gaseous products in the γ-radiolysis of different components of Amberlite, a strongly basic anion exchange resin based on polystyrene divinylbenzene copolymer, have been evaluated. These compounds include: methylammonium chloride, dimethylammonium chloride, trimethylammonium chloride, tetramethylammonium chloride and benzyl trimethylammonium chloride in the solid state. Fourier transform infrared, FTIR, Raman, and electron paramagnetic resonance, EPR, spectroscopy of the parent compounds were also performed. The results are compared with that obtained with polyethylene, and polystyrene [14] to predict what is observed in the radiolysis of Amberlite. In realistic conditions, resins

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are irradiated in association with water or aqueous solutions. All compounds examined in this work are in the dry state in order to understand the direct radiation effects induced by the deposition of energy in the resin. Indirect radiation effects can occur when water decomposition products react with the resin and the overall outcome will depend on the amount of water present. Further studies on the radiolysis of Amberlite components in association with water will be combined with the results of this work in order to understand the heterogeneous radiolysis of the resin in a practical scenario.

2. Experimental section

2.1. Materials

Methylammonium chloride, dimethylammonium chloride, trimethylammonium chloride, tetramethylammonium chloride, and benzyl trimethylammonium chloride were obtained from Alfa Aesar and used without further purification. Special care was taken in sample preparation as these amines are hygroscopic in nature. The amines were ground into uniform size and dried under vacuum at 35 °C, weighed, and placed in a drying chamber with Drierite (calcium sulfate).

2.2. Irradiations

Samples for γ-radiolysis were placed in Pyrex tubes (diameter ~1 cm, length ~10 cm), evacuated and flame sealed. Sample weights were typically between 0.5 and 1 g and the γ-radiolysis of the samples was carried out using a self-contained Shepherd 109-68 ^{60}Co source at the Radiation Laboratory of the University of Notre Dame. The dose rate was ~231 Gy/min as determined using the Fricke dosimeter [15].

The helium ion irradiations were performed using the 10 MV FN Tandem Van de Graaff accelerator at the Nuclear Structure Laboratory located in the University of Notre Dame Nuclear Science Laboratory. Accelerated $^4He^{2+}$ ions of 5 MeV energy incident to the samples were generated. The window assembly and the radiation procedure are the same as reported earlier [16,17]. Energy loss of the helium ions in passing through all the windows was determined from a standard stopping power compilation [18]. The samples were irradiated with completely stripped ions at a charge beam current of about 1.5 nA. Total energy deposition was obtained from the product of the integrated beam current and the ion energy incident to the sample. The sample cell was made of quartz with a thin mica window of about 5 mg/cm^2 attached to the front for the beam entrance. The cell had inlet and outlet ports designed for purging the sample before and after irradiation.

2.3. Gas analysis

Gas chromatographic analysis of the H_2 and CH_4 was performed using a SRI 8610 apparatus equipped with a thermal conductivity detector. The chromatographic column was 6.4 mm diameter 13× molecular sieve 3 m long maintained at 70 °C. Argon or helium gases of ultra-high purity (>99.999%) were used as carrier gases in the analysis of H_2 and CH_4 gas, respectively. Following γ-irradiation each sample tube was broken in the sampling port of the gas chromatograph. An inline technique was employed to determine the H_2 production by He ion irradiation where the inlet and outlet of the sample cell are connected to the gas chromatograph by a four-way valve. Calibration was performed by injection of pure H_2 or CH_4 gas under normal conditions. The error in gas measurement is estimated to be about 5%, which includes gas measurement and manipulation.

The production of ammonia was determined using an analytic AMMONIA CHEMets kit from CHEMetrics, Inc., which employs the salicylate method of ammonia determination. Following irradiation, the sample was purged with a stream of helium gas and then bubbled through a 1 mM HCl solution trap where the ammonia was captured. A cross check of this procedure was made using a UV–visible spectrometer to get accurate absorbance values at λ_{max} = 700 nm. The concentration of ammonia was calculated on the basis of calibration performed with ammonia standard solutions in the concentration range between 0.5 ppm and 2.0 ppm of NH_3 nitrogen. Stock standard solutions of ammonia (50 ppm NH_3 nitrogen) were obtained from the Hach Company.

2.4. Spectroscopic analysis

Infrared transmittance spectra of amines were recorded using a Bruker Vertex 70 FTIR spectrometer with a resolution 4 cm^{-1} and 512 scans in the range of 400–4000 cm^{-1}. Irradiated samples were mixed with KBr powder, so that the weight fraction of the amines was about 10%. These mixtures were used to make pellets of 2 mm thickness and were then analyzed using the FTIR spectrometer. Diffuse Raman Spectroscopy was performed with a Renishaw Raman Microscope using a 12 mW 782 nm laser source with a 1200 grooves/mm rating. First derivative X-band EPR spectra at room and low temperature (77 K) were measured on a Bruker ER100 spectrometer. Samples were loaded into a fused silica EPR tube, evacuated and flame sealed. Irradiations were carried out at 77 K and then the tubes were transferred to the spectrometer without warming.

3. Results and discussion

3.1. Gas production

Radiation chemical yields, *G* values, are presented here as molecules of H_2 or CH_4 formed per 100 eV of total energy absorbed by the sample (1 molecule/100 eV = 0.104 μmol/J). The *G* values for H_2 in the γ-radiolysis of dry methylammonium chloride, dimethylammonium chloride, trimethylammonium chloride, tetramethylammonium chloride and benzyl trimethylammonium chloride were listed in Table 1. These yields vary from a low of 0.05 with the aromatic benzyl trimethylammonium chloride to 4.43 molecules/100 eV for trimethylammonium chloride. With the exception of the trimethylammonium chloride the yields of H_2 increase in the radiolysis with 5 MeV He ions because of the increased importance of intratrack reactions [19].

The yields of H_2 in the radiolysis of the methyl amines are very high and they are found to increase with increasing number of methyl groups from methylammonium chloride to trimethylammonium chloride. However in the case of tetramethylammonium chloride the H_2 yield is very low. The formation of H_2 in aliphatic compounds proceeds in two steps: first is the formation of H· atom, which is followed by an H· atom abstraction reaction [20]. Bond rupture to give the H· atom can occur at the C—H and/or N—H

Table 1
Radiation chemical yields of H_2 and CH_4 with γ-rays and 5 MeV He ions.

Amine	$G(H_2)$		$G(CH_4)$
	γ-rays	He ions	γ-rays
$CH_3N^+H_3Cl^-$	1.01	1.48	0
$(CH_3)_2N^+H_2Cl^-$	2.56	2.73	0.07
$(CH_3)_3N^+HCl^-$	4.43	2.51	0.26
$(CH_3)_4N^+Cl^-$	0.07	0.38	0.02
$C_6H_5—CH_2—N^+(CH_3)_3Cl^-$	0.05	0.19	0.00