ELIMINATION BY ELECTRON BEAM IRRADIATION OF TRACE CONTAMINANTS IN GAS STREAMS

D.H Douglas-Hamilton and R.C. Slater
Avco Everett Research Laboratory Inc., Everett, Massachusetts 02149, USA.

ABSTRACT

This paper reports experimental results obtained in electron beam irradiation of few ppm concentration of vinyl chloride monomer and methyl mercaptan in various carrier gases. An ionic charge transfer process appears to result in the efficient selective destruction of the trace contaminant species.

1. INTRODUCTION

In previous work(1,2,3) methods have been developed in this Laboratory for producing stable atmospheric pressure discharges. Their adaptation to trace contaminant destruction will be discussed in this paper.

The most important process occurring in an ionized gas containing a small concentration of contaminants will be rapid charge exchange between the ionized molecules and any species present of lower ionization potential. If the contaminant gas is of lower ionization potential, then the charge will migrate to its molecules. These molecules will then recombine, generally dissociatively, thus leading to the preferential destruction of the contaminating material.

This effect has been demonstrated in the use of e-beam ionization to destroy trace quantities of methyl mercaptan, vinyl chloride monomer, benzene and hydrogen sulphide in N_2, air and argon carrier gases. The ionization potentials (I.P.) of vinyl chloride (10 eV), benzene (9.24 eV), H_2S (10.4 eV) and CH_3SH (9.44 eV) are all less than the I.P. values of all the common air constituents including argon and nitrogen.

2. EXPERIMENT

Trace contaminant destruction was accomplished by flowing an atmospheric pressure gas mixture containing a known concentration of contaminant past a continuous e-beam and analyzing for the loss of contaminant downstream from the e-beam. A schematic diagram of the experiment appears in Figure 1. The apparatus consists of three main parts: an e-beam gun, a gas flow system and diagnostics.

The 90 kV e-beam gun has been described previously.(2,3,4) The gun is housed in a high vacuum chamber and is isolated from the atmospheric pressure gas by an aluminum foil of thickness 12 μm. The maximum power output of the e-beam, calibrated calorimetrically, was 900 mW cm^{-2} emanating from a foil of area 25 cm^2. E-beam dose per unit beam current in air at NTP was also obtained calorimetrically; under these conditions ~ 50% of the beam energy incident on the gas is deposited along the 2.5 cm path length within the irradiation cell, the remainder being absorbed by the opposing wall, a 5 x 5 cm aluminum block. Qualitative dose uniformity in the plane perpendicular to the e-beam direction was observed using radiation sensitive blue cellophane.

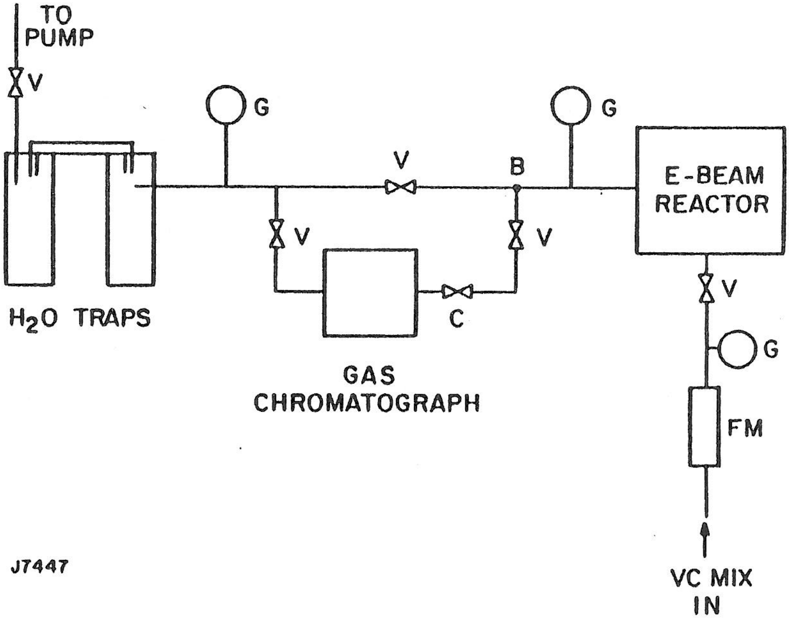

Figure 1. Experimental e-beam gas irradiator.
FM: rotameter. G: pressure gauge. V: valve.

The e-beam irradiated flowing gas mixtures, which consisted of ppm levels of vinyl chloride monomer (VCM), methylmercaptan and hydrogen sulfide in carrier gas [commercial grade dry air (dew point = 213 K), nitrogen or argon] at near atmospheric pressure. Premixed gas samples were obtained from Matheson Corp. (U.S.A) and were used without further purification. Sample concentrations were determined by the manufacturer using a calibrated gas chromatograph (GC) traceable to the

National Bureau of Standards (U.S.A). These samples were then used as a secondary standard to calibrate the sensitivity of our own gas chromatograph [Model 1030A, Baseline Industries]. Calibration showed that the GC was accurate to better than 10% down to a concentration less than 1 ppm for both VCM and CH_3SH measurements. Below 1 ppm it is assumed to be linear. Mass flow rates between 240 and 1200 NTP cm^3 sec^{-1} were determined using calibrated rotameters.

The gas exiting from the irradiation zone was analyzed for contaminant loss and, in the vinyl chloride case, for formation of HCl. The contaminant removal was measured using the above gas chromatrograph. The Poropak P column material used was maintained at a constant 150°C. Vinyl chloride was detected using a krypton lamp detector which can photoionize compounds with ionization potentials (IP) ≤ 10.0 eV while a flame ionization detector was used for CH_3SH and H_2S. Formation of gaseous HCl was measured by passing the gas stream through two series traps containing distilled H_2O for several minutes, and then measuring the Cl^- concentration by two methods: $AgNO_3$ titration and an ion specific Cl^- electrode.

3. EXPERIMENTAL RESULTS AND DISCUSSION

We have observed effective removal of each contaminant from all the carrier gas streams investigated here. We will limit the discussion to VCM and CH_3SH removal. Typically, a few percent removal can be obtained at dose levels as low as 20 krad while we have obtained greater than 90% removal at dose levels in the several Mrad range. This range corresponds to an equivalent temperature rise in atmospheric density air of 0.2 to 60 K.

VCM removal from NTP argon (in which initial vinyl chloride concentration ($[V]_o$ = 10 and 100 ppm), nitrogen ($[V]_o$ = 100 ppm) and dry air ($[V]_o$ = 3, 10, 30, 100 and 500 ppm) was investigated using e-beam doses up to 100 Krad and a flow rate of 1300 NTP cm^3 sec^{-1}. Some of these results for VCM in argon and nitrogen are displayed in Fig. 2. Note that this data is plotted as a function of the e-beam dose D normalized to the initial VCM concentration $[V]_o$. The plots indicate the VCM removal varies exponentially with $D/[V]_o$. The slopes of these lines (N_2: 283 ppm/Mrad; Ar: 288 ppm/Mrad) are related to the specific energy required to remove a pollutant molecule. The specific energies and the interpretation of these values in terms of a charge transfer model will be discussed below.

VCM mixtures in air ($[V]_o$ = 10 ppm) were subjected to e-beam irradiation up to dose levels of 6 Mrad at flow rates from 240-1200 NTP cm^3 sec^{-1}. These data show a linear behavior at low dose (slope = 81 ppm/Mrad) similar to the argon and nitrogen data. However, the removal efficiency decreases monotonically at high dose levels in the Mrad range. About

6 Mrad is required to removed ~ 95% of the initial 10 ppm VCM stream.

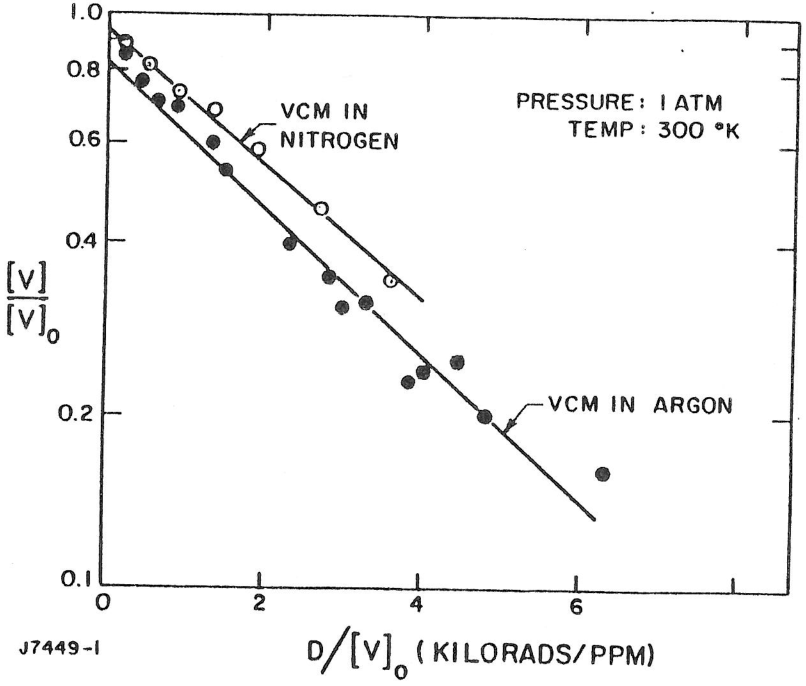

Figure 2. Fractional removal of vinyl chloride monomer by irradiation, using argon and nitrogen as carrier gases, normalized to initial concentration $[V]_0$.

Other experiments using a higher initial VCM concentration, $[V]_0$ = 100 ppm, indicate that HCl is the major chlorine bearing product in e-beam irradiated VCM/air mixtures. About 75 ± 24 mole percent of the initial chlorine in VCM is recovered as Cl^- in the downstream water traps. In addition, mass spectral and gas chromatographic data indicate negligible chlorinated hydrocarbons in the exhaust stream.

CH_3SH removal from nitrogen carrier was investigated over a dose range and flow rate range comparable to the VCM experiments. The data obtained is plotted in Fig. 3. The low dose CH_3SH data also scales exponentially with $D/[M]_0$, where $[M]_0$ is initial mercaptan concentration, with a slope comparable to the argon/VCM and nitrogen/VCM data. Greater than 99% removal of CH_3SH (10 ppm) is obtained for e-beam doses around 5 Mrad. It is also observed that the 10 ppm and

100 ppm data lie on a single universal curve, showing that contaminant removal scales as a function of $D/[M]_o$. At low fractional dose the fraction remaining varies exponentially with $D/[M]_o$.

It can be shown that this exponential dependence is predicted if a reaction inhibitor is formed as the contaminant is destroyed. If a molecule competing with the original contaminant for ions or free radicals (whichever accomplish its destruction) is formed, then the destruction efficiency will decrease linearly with contaminant fraction remaining. This leads to the observed exponential dependence of the remaining contaminant fraction on normalized dose.

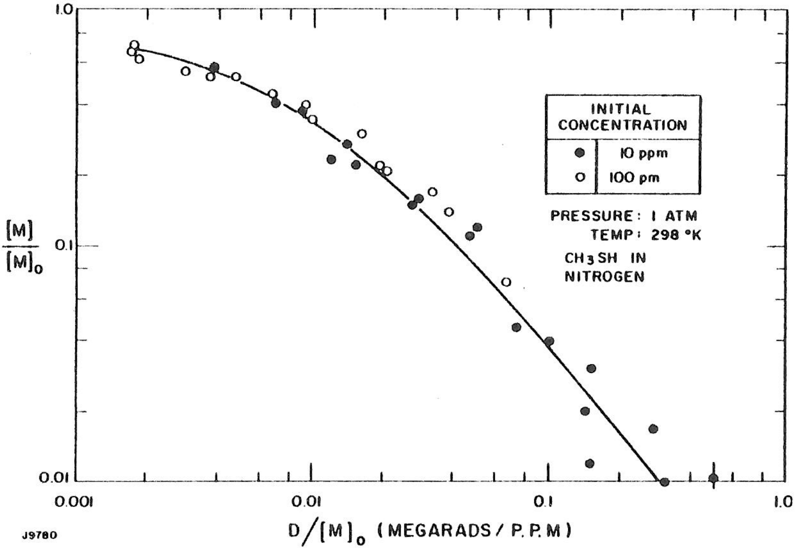

Figure 3. Fractional removal of methyl mercaptan by irradiation, using nitrogen as carrier gas, normalized to initial concentration $[M]_o$.

For the case of VCM removal we find that

$G(N_2) = 9.2 \pm 0.6$

$G(Ar) = 13 \pm 0.7$

$G(Air) = 2.7 \pm 0.26$

The high values of G especially in argon and nitrogen indicate that several VCM molecules are being removed for each ionization event in the carrier gas. The most likely mechanism which can explain these values (at least for the VCM case) is to assume that removal is initiated by positive ion charge transfer down to VCM, e.g:

$$Ar^+ + C_2H_3 \rightarrow C_2H_3Cl^+ + Ar$$

followed by a series of ion aggregation reactions of the type:

$$C_2H_3Cl^+ + C_2H_3Cl \rightarrow (C_2H_3Cl)_2^+$$

which remove one additional VCM molecule for each ionization event. Reactions of this type have been observed in mass spectrometer studies.(5) The eventual removal of the aggregated ion is assumed to occur by dissociative electron recombination, e.g.

$$(C_2H_3Cl)_N^+ + e^- \rightarrow \text{products}$$

For CH_3SH removal from N_2 we find $G \sim 12$. As in the case of VCM removal, several molecules are being destroyed per ionization event. It is probable that the mechanism for CH_3SH removal is similar to that for VCM removal.

4. CONCLUSION

The use of e-beam irradiation to remove trace quantities of CH_3SH, C_2H_3Cl, H_2S and C_6H_6 from N_2 and Ar has been demonstrated. The high efficiency of this process leads to potential applcation in detoxifying gas streams, and in deodorizing exhalations from pulp mills, rayon production and other fields. A particular advantage exists in large volume, low concentration gas streams, in which high efficiency is required.

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