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Thermal volatilisation analysis of γ-irradiated tetraphenylboron sodium

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Abstract

The effect of γ-irradiation on tetraphenylboron sodium (TPBS) has been studied by thermal volatilisation analysis (TVA) and sub-ambient TVA. When TPBS is subjected to programmed heating to 500°C under TVA conditions, benzene and hydrogen are observed as volatile products and the residue, after exposure to the atmosphere, consists of sodium carbonate and sodium tetraborate, together with some black char material. Irradiation of TPBS at ambient temperatures also leads to the formation of benzene and hydrogen and the irradiated salt gives larger amounts of benzene in the TVA experiment. It is suggested that the salt decomposes first by loss of benzene and conversion of the TPB anion to an anion with three aromatic rings, which subsequently undergoes further decomposition.

INTRODUCTION

Active fission products may be produced directly or be present in reactor fuels within a short time, as either long-lived or short-lived members of the decay chain. Their presence adds to the radioactivity problem in terms of post-irradiation handling, complete dissolution of fuel for further processing, waste disposal and decontamination procedures. Caesium-137, which comprises half of the activity in most cases, is the major concern and can be separated by precipitation as its insoluble salt with the tetraphenylborate (TPB) anion [1–3]. This solid waste, however, must also be handled carefully because the intense β- and γ-radiation from the ^{137}Cs could cause the TPB salt to decompose to form hazardous materials. No steady state γ-irradiation effects on TPB salts in the solid state are known, although studies in aqueous media under γ- and UV-irradiation have been reported [4,5].

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The present study sought to examine the effect of γ-irradiation on tetraphenylboron sodium in the solid state, using thermal analysis. The technique adopted was thermal volatilisation analysis (TVA) [6, 7] which, because of its established ability to provide access to the various types of decomposition product (non-condensable gases, condensable gases and volatile liquids, tars and waxes, and involatile residue), can give considerable information about the decomposition; in addition, sub-ambient TVA [8, 9] was used, by which technique any volatile products of thermal degradation or of γ-irradiation may be separated and identified. External ^{60}Co γ-irradiation was used to simulate the effect of ^{137}Cs.

EXPERIMENTAL

Materials

Tetraphenylboron sodium (TPBS) of 99.5% purity was obtained from Aldrich. Samples sealed in glass ampoules under vacuum (10^{-3} mbar) were irradiated at ambient temperature with γ-rays for various doses (20, 50, 100, 200 and 300 kGy) using a ^{60}Co source at the Scottish Universities Reactor Centre at East Kilbride, Scotland. The dose rate was estimated to be 10 kGy per 8 h using a Fricke dosimeter [10]. Two types of ampoules were used. For examination of the irradiated solid by TVA, simple reaction tubes were employed which could be cut open in air after irradiation. For examination of any gaseous products formed during irradiation, breakseal-type tubes were used, which could be connected to a vacuum system for separation and identification of volatile products using sub-ambient TVA [8].

Instrumental

Thermal volatilisation analysis (TVA) [6, 7] depends upon measurement of the small pressure which develops in a continuously evacuated system as a sample decomposes and as products rapidly travel to a liquid nitrogen trap. A Pirani pressure gauge placed between the heated oven containing the sample tube and the trap is used to monitor pressure changes, typically in the region 10^{-5}–10^{-2} mbar. Sample size was 50 mg and a heating rate of 10°C min^{-1} was employed. Non-condensable gases released as the sample decomposes were identified using an on-line quadrupole mass spectrometer (Leda-Mass Ltd.). Condensable gases and volatile liquids were trapped at liquid nitrogen temperature in the TVA system and could subsequently be separated in the same apparatus on the basis of volatility by controlled warm-up from −196°C to 0°C, the vaporisation of products in order of decreasing volatility also being monitored by a Pirani pressure gauge. This procedure is described as sub-ambient TVA [8, 9].

RESULTS AND DISCUSSION

Volatile irradiation products

By opening breakseal ampoules in which TPBS had been irradiated, directly into the TVA system, it was possible to identify hydrogen and benzene as volatile products of irradiation, using the on-line mass spectrometer.

Thermal volatilisation analysis of unirradiated TPBS

When TPBS is heated at 10°C min^{-1} under TVA conditions, sublimation of much of the sample occurs, but this is accompanied by decomposition which the TVA curve (Fig. 1) shows to begin at around 370°C. The decomposition produces a small amount of non-condensable gas, identified as hydrogen. Examination of the condensable volatile decomposition products by sub-ambient TVA (Fig. 2) revealed the presence of benzene only, plus traces of water.

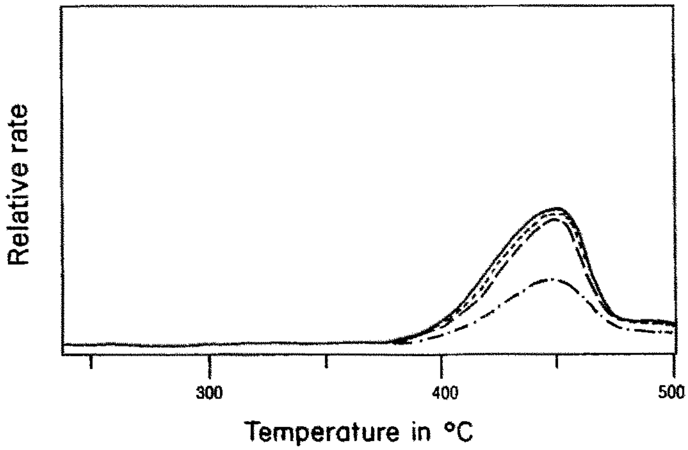

Fig. 1. TVA curve for tetraphenylboron sodium. Sample size, 50 mg; continuous evacuation; heating rate, 10°C min^{-1}. Key to Pirani traces (see refs. 6 and 7): ——, 0° and −45°C; -------, −75°C, – – –, −100°C; –·–·–·, −196°C.

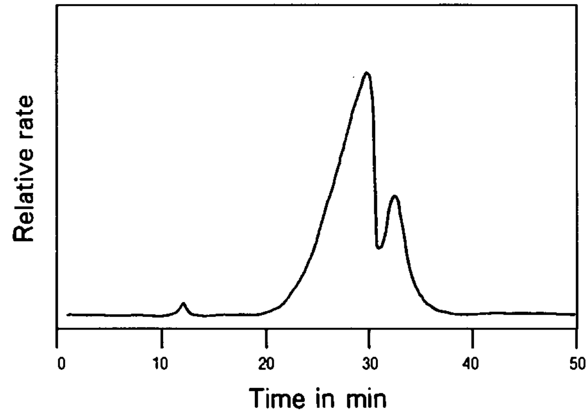

Fig. 2. Sub-ambient TVA curve for warm up from −196°C of condensable volatile degradation products of heating TPBS to 500°C in the TVA system. The major peak is due to benzene and the subsequent peak to traces of water.

Thermal volatilisation analysis of irradiated TPBS

Similar examination of samples subjected to various doses of irradiation revealed no new products, but the irradiated solid (having already lost some hydrogen and benzene as a direct result of irradiation) gave an increased yield of benzene on thermal decomposition. The irradiated TPBS also showed a slight destabilisation, as indicated by a 15° downward shift in the temperature of the rate maximum.

Examination of the cold-ring fraction and residue

In the TVA experiments, products volatile at degradation temperatures but not at ambient temperature condense out on the cooled upper part of the degradation tube (cold-ring fraction, CRF) and the involatile residue remains on the base of the flat-bottomed tube. Both of these fractions are accessible for examination by IR spectroscopy after the degradation. The spectra, shown in Fig. 3, were similar for unirradiated and irradiated TBPS samples. The CRF spectrum is identical to that of TPBS and shows that this material is simply a sublimate. The residue spectrum shows the presence of sodium carbonate and sodium tetraborate. However, because the residue is black in colour, the presence of char-like material in addition to these inorganic products is indicated. This is consistent with the yellowing observed when TPBS is irradiated, suggesting the formation of some modified structures in the solid. IR spectroscopy, however, was unable to detect these structural changes.

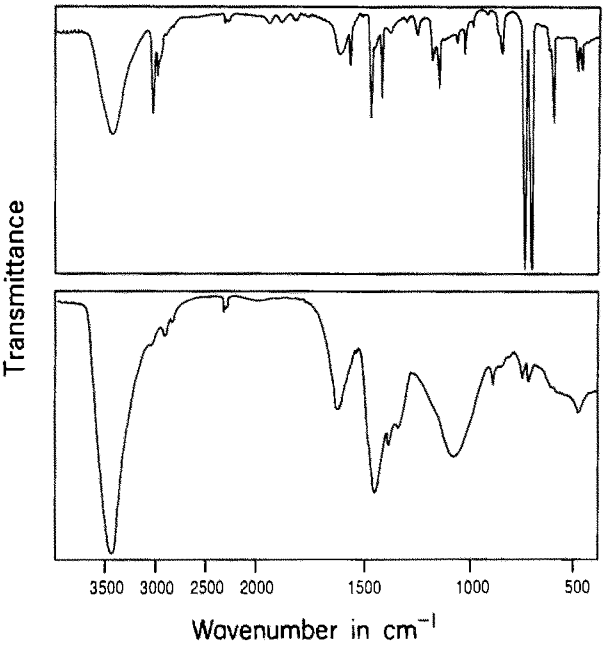

Fig. 3. IR spectra of cold-ring fraction (upper diagram) and involatile residue (lower diagram) from degradation of TPBS to 500°C in the TVA system.

Reactions during irradiation and thermal decomposition

The effect of γ-irradiation on TPBS can be explained in terms of two reactions. The first is decomposition of the $(C_6H_5)_4B^-$ anion

$$(C_6H_5)_4B^- \rightarrow (C_6H_5)_2(C_6H_4)B^- + C_6H_6$$

A similar reaction must be assumed to be induced thermally above about 370°C. This reaction explains the formation of benzene as a significant volatile product. The other volatile product, hydrogen, can be accounted for by a reaction [11, 12] of the excited state of the benzene molecule during irradiation

$$2C_6H_6^* \rightarrow H_2 + \text{radical species}$$

The radical species may be involved in the formation of the “polymeric” fraction which may be present in the char residue in the TVA experiments.

The increased benzene yield from irradiated TPBS in the TVA experiments probably results from decomposition of the $(C_6H_5)_2(C_6H_4)B^-$ anions generated during irradiation. Decomposition of this anion may also be a major route to the formation of some char during thermal decomposition, a process which must also involve some release of hydrogen, found as a thermal decomposition product. The sodium carbonate and sodium tetraborate observed in the residue of thermal decomposition imply that there is some reaction of the involatile residue of degradation with the atmosphere after the reaction tube is opened.

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