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Monsanto Chemical Company - Unit III

ABSTRACTS OF PROGRESS REPORTS

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SUMMARY OF WORK TO DATE ON VOLATILE NEUTRON SOURCE

It was proposed to prepare a volatile polonium compound which could be used alone or with another gaseous compound as a neutron source. The objective was to obtain a neutron source which would give off few neutrons in the expanded state, but when condensed would act substantially as a thick target and emit perhaps ten times as many neutrons.

Originally, polonium hexafluoride was suggested; with such a compound the fluorine atoms would constitute the target. The predicted boiling point of polonium hexafluoride is about -40°C . There was reason to believe, however, that a less relatively non-volatile fluoride would be formed rather than the hexafluoride.

Polonium alkyls were therefore proposed as alternatives. The predicted boiling point of $\text{Po}(\text{CH}_3)_2$ is about 110°C . This compound in itself would probably not be too suitable as a target material but it could be mixed with other gases such as carbon tetrafluoride, boron trifluoride, etc., as targets. As a longer range possibility, $\text{Po}(\text{CF}_3)_2$ was also suggested. This would act as its own target and would moreover have the same F/Po ratio as PoF_6 ; its boiling point could be expected to be $30^{\circ} - 60^{\circ}$ lower than that of polonium dimethyl.

Calculations were made which showed that the desired effect could be obtained either with PoF_6 or a mixture of $\text{Po}(\text{CH}_3)_2$ with a suitable target gas. Investigation of the preparation of these two compounds was therefore undertaken, and later some preliminary attempts to prepare polonium carbonyl were made.

Polonium FluoridesReaction of HF with Po Oxide (Argersinger, Coulter, Rollins)

No evidence of volatile compound formation was obtained in experiments on the reaction of Po and HF. Platinum disks containing Po were treated with aqueous HF and NH_4HF_2 . These were heated under the infra-red lamp and counted; no loss in activity was observed. Other disks were treated with gaseous HF at room temperature and heated to 150° with negative results. Negative results were also obtained in later experiments in which the residue from evaporation of a polonium solution was heated one hour on the steam bath with 48% HF, and with the reaction of gaseous anhydrous HF on a Po-Pt source which had been exposed to air to convert the Po to oxide.

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Fluorination of Po (Coulter, Leitch)

Polonium was exposed to dry fluorine in a vacuum system under a variety of conditions. While some experiments were performed by leaving source in an atmosphere of fluorine (obtained from a small cylinder), the preferred procedure was to pass fluorine (from a generator) over the source. Products were collected in refrigerated traps.

Static Fluorination

- 50 mc. on Pt wire, alternately hydrogenated and fluorinated up to 350°C.
- 60 mc. on Pt foil, alternately hydrogenated and fluorinated to 300°C.
- 65 mc. on Pt wire, hydrogenated and volatilized in fluorine atmosphere at red heat.
- 40 mc. on Ag foil, alternately hydrogenated and fluorinated to 350°C.
- 80 mc. on 60 mg. of Te (obtained by the Te process), alternately hydrogenated and fluorinated up to 400°C.
- 40 mc. on 150-200 mesh Bi powder (obtained by bismuth process), alternately hydrogenated and fluorinated up to 340°C.

Dynamic Fluorination

- 50 mc. on Pt foil, exposed to air treated with HBr and Br₂ prior to fluorination.
- 73 mc. on Pt foil thermally volatilized in H₂ and fluorinated at room temperature.
- 35 mc. thermally deposited in H₂ on a gold disk, hydrogenated, fluorinated to 250°C.
- 54 mc. of residue from evapn. of a Po-HCl solution in a Pt dish, fluorinated to 360°C.
- 111 mc. on Pt, exposed to air, heated in H₂ up to 370°C.
- 16.5 mc. on BiF₃ fluorinated at 300°C.
- 13.1 mc. on BiF₃ fluorinated at 300°C.
- 50 mc. together with a small amount of Te co-deposited on Pt foil previously electrolytically coated with Te, fluorinated at high temperature (induction furnace)
- 60 mc. on 0.25 g. Te (obtained by Te process), fluorinated up to 350°C.
- 63 mc. of residue obtained by evaporation of a Po-HCl solution in a glass boat, a small amount of Se added to residue, fluorinated to 320°C.
- 26.4 mc. together with a little Se co-deposited on a Pt electrode previously coated with Se electrolytically, fluorinated at room temperature.
- 400 mc. co-precipitated with Se, fluorinated at room temperature.

While small fractions of polonium were stored from the sources in many cases, the most promising results were obtained in the fluorination of Po-Se (ratio Po/Se 1:1,100). About 0.45 of Po was co-precipitated with 0.1 gram of Se from 2M HCl solution of selenous acid by stannous chloride. The precipitate was washed with acetone and ether, dried and placed in the high vacuum system. Dry fluorine was then admitted and the products were condensed in a liquid oxygen trap. The reaction time was then about three of fluorine.

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The product was distilled back and forth from one trap to another, the movement of polonium being followed by means of the gamma counter. It was found possible to distill the polonium compound several times, although the amount distilling decreased slowly. After one or two days, however, it was no longer possible to distill the polonium and it was concluded that whatever compound was formed was decomposed by the alpha radiation. This conclusion was supported by the fact that selenium from decomposition of selenium hexafluoride was found in the traps.

It is tentatively concluded that selenium hexafluoride and probably polonium hexafluoride (if it exists) are converted to compounds of the element in a lower oxidation state by alpha bombardment. To determine the effect of alpha bombardment on such compounds as selenium hexafluoride and the polonium compound, selenium hexafluoride was condensed in a small reaction vessel and exposed to bombardment by 0.4 C of Po. A white solid was slowly deposited on the walls and after a time a red coloration appeared. Qualitative analysis after removal of volatile material showed that a considerable quantity of selenium was present. Bombardment of selenium hexafluoride in the gas phase also caused the formation of a white solid which disappeared after 24 hours. Condensation of the residual gases followed by volatilization left droplets of a liquid presumed to be SeF_4 . No significant pressure change was observed in these experiments.

Polonium Alkyls (Argersinger, Rollinson)

Reaction of Po with CH_3Br

The first experiments involved direct reaction of methyl bromide with Po, a possible reaction being: $2 \text{Po} + 2 \text{CH}_3\text{Br} = \text{Po}(\text{CH}_3)_2 + \text{PoBr}_2$. Po on a Pt source was hydrogenated and heated in CH_3Br vapor in a vacuum system. Movement of Po was followed by means of the gamma counter. At 200° about 50% of the activity was removed from the foil, but when various parts of the apparatus were analyzed it was found that, while 47.5% of the activity had been removed from the foil, most of it was on the walls of the reaction chamber. A second heating of the foil in methyl bromide failed to remove more of the activity and thus there is some evidence indicating that the reaction given above occurred, followed by decomposition of the product.

In repetitions of this experiment, with slight variations in the procedure, similar results were obtained at temperatures up to 282°C. In one experiment, about half of the activity was removed by heating to 240°C in CH_3Br ; when the foil was reheated to 305°C in CH_3Br , the total loss amounted to 93%, part of which was undoubtedly due to thermal volatilization.

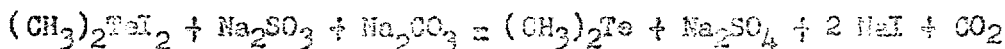
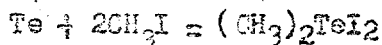
Reaction of NaPo with CH_3Br

The reaction $\text{Po} + 2 \text{Na} + 2 \text{CH}_3\text{Br} = \text{Po}(\text{CH}_3)_2 + 2 \text{NaBr}$ was considered possible. The source was 75 mc. thermally deposited on a cold finger; this was placed in the system in a stream of N_2 , the system was pumped out and filled with hydrogen at atmospheric pressure. After several

hours the system was evacuated and a film of metallic sodium was deposited on the cold finger and on the walls of the reactor by distillation of sodium from a side arm which was then sealed off. A very much smaller fraction of the activity than in the previous experiments was removed from the source and deposited on the walls of the reactor. The experiment was repeated with Po on a Pt foil. Considerable activity was removed from the foil heated in methyl bromide.

Reaction of Te-Po with CH_3I

Another method used in an attempt to prepare polonium dimethyl was that by which tellurium dimethyl can be produced. The reactions involved in preparation of the latter are as follows:

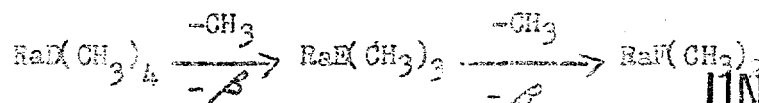


Dimethyltellurium diiodide was prepared from tellurium containing polonium. While only about half of the polonium remained with the unreacted tellurium when the reaction mixture was extracted with chloroform, the crystals of dimethyl tellurium diiodide contained only a negligible amount of polonium and therefore the second reaction was not carried out.

A variation of this approach is planned. The alkyl halide will be refluxed with a solution of $\text{Na}_2\text{Po}-\text{Na}_2\text{Te}$ formed in situ by dissolving Te-Po in a solution of "rongalite", sodium formaldehyde sulfoxylate. This may be prepared by reduction of $\text{HCHO} \cdot \text{NaHSO}_3$. Several tellurium alkyls have been prepared in this way. Khlopin and Samartzera have also reported the preparation of polonium dimethyl and polonium dibenzyl, along with the corresponding tellurium compounds, by the reaction of the alkyl sulfate with $\text{Na}_2\text{Po}-\text{Na}_2\text{Te}$.

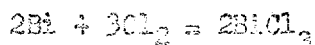
Preparation of $\text{Po}(\text{CH}_3)_2$ by the Grignard Reaction

Mortensen and Leighton obtained a volatile Po compound by the following procedure. Lead tetramethyl was synthesized from PbCl_2 containing RaDCl_2 . The gaseous products were pumped into a flask and left for a month during which RaE and RaF were formed. The gas was then pumped into a silica cell cooled to -80°C . The contents were dissolved in octane, Br_2 was added and the solution was evaporated to dryness in a vacuum. The residue, tested immediately, showed strong beta and alpha activity. The alpha activity could only have come from radium F and the conditions of the experiment show that it was in the form of a volatile compound. It was concluded that $\text{Po}(\text{CH}_3)_2$ was formed:

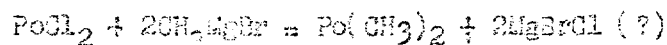
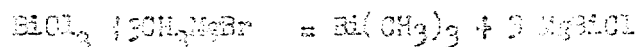
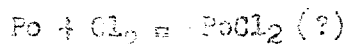


While it is planned to repeat this experiment, direct synthesis of $\text{Po}(\text{CH}_3)_2$ by the Grignard reaction was considered preferable in view of the extremely small amounts of RaD available. Active Bi has been chosen as the starting material because it is certain that its Po content is in the metallic state. The series of reactions involved is as follows:

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Active bismuth was chlorinated in an apparatus comprising a reaction tube containing the bismuth directly connected to a column, at right angles, packed with glass beads. Since the bismuth chloride must be added gradually to the Grignard solution, it was believed that this could be done by connecting the end of the collecting tower to the Grignard flask and slowly pouring the beads on which the bismuth and polonium chlorides were deposited into the solution. However, it was found that the throat of the collecting tower became clogged with bismuth chloride and it was thereafter impossible to cause the gases to pass through the tower.

Since considerable activity was carried along with the BiCl_3 smoke, this method of preparing BiCl_3 containing Po appears promising. An apparatus of improved design has therefore been constructed. It is essentially a retort whose neck will be used for the reaction tube and whose bulb will be the collector. This is to be attached to the Grignard flask through a spherical joint and the product will be transferred to the flask by refluxing with ether.

Another source of metallic polonium is also available, namely, a foil on which polonium has been deposited electrolytically and which has been assayed for purity in the usual way. It is proposed to hang such a foil in an atmosphere of chlorine in the Grignard flask and then prepare the Grignard reagent in the flask after it has been swept out with dry nitrogen. It is expected that the polonium treated in this way will be converted to an anhydrous chloride which should react with the Grignard reagent. In connection with this experiment it will be interesting to weigh such a foil before and after chlorination to get some idea as to what chloride is formed.

Reaction of Free Radicals with Po

The reaction of free alkyl radicals with metallic Po appears to be a promising method of preparing polonium alkyls and work along this line is still in progress. It has been shown by Paneth, Rice, and others that free alkyl radicals, obtained by thermal decomposition of various organic compounds, are capable of reacting with metals in thin films to form metal alkyls. The apparatus comprises a reservoir for the appropriate organic compound, a quartz tube a short region of which is surrounded by an electrical furnace capable of giving temperatures as high as 1200°C , traps for condensing the products, and a pumping system capable of giving a high pumping speed. While lead tetramethyl was used by Paneth and other investigators originally, Rice and co-workers have found that many organic compounds, such as aldehydes, ketones, hydrocarbons, etc. may be used.

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Volatile Neutron Source

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The reservoir is charged with an appropriate free radical source, e.g., acetone, a pellet of the desired metal is placed in the end of the quartz tube next to the traps, and the system is evacuated. A metallic mirror is formed on the wall of the quartz tube by heating the metal carefully with a flame and distilling the mirror down the tube to the desired position; since traces of oxygen inactivate most metallic mirrors, it is sometimes desirable to form the mirror in a hydrogen atmosphere. The furnace is started and allowed to reach the temperature required for thermally cracking the organic compound. Next the stopcock communicating with the reservoir is opened, which allows the organic vapor to pass through the heated zone and over the metallic mirror into the traps. If the pumping speed is high enough and if the mirror is not too far from the end of the heated zone, the free radicals (of half-life about 0.006 sec.) formed by thermal decomposition will pick up the metal in the form of metal alkyl which will be condensed in the trap; thus, the course of the reaction can be followed by observing the rate at which the metallic mirror disappears.

Many metals have been used in such experiments, including Bi, Sb, As, Hg, Pb (mirrors of which can also be formed by decomposition of lead tetramethyl), etc. In general the simplest alkyl is formed with cold mirrors; if the mirror is warmed, in some cases more complex alkyls are formed and sometimes no reaction occurs. It is interesting to note that the antimony analog of cacodyl was first prepared by the action of free radicals on antimony when numerous attempts to prepare it by the usual procedures had failed.

A system for studying the action of free radicals on polonium was constructed and tested with Te mirrors and acetone. After several difficulties had been overcome, it was found possible to remove tellurium mirrors rapidly with free methyl radicals from acetone vapor. Next polonium which had been thermally deposited on a cold finger was placed in the apparatus so that the end of the cold finger was the same distance from the furnace as had been the Te mirrors. Gamma counts showed that about 85% of the Po was removed in five hours by the action of free methyl radicals from acetone vapor. Analysis of the contents of various parts of the apparatus showed that the removal was 70% and that 44% was collected in the liquid air trap.

It was then found that the pumping speed was in the range $18-78 \times 10^5$ cm/sec., which is about 1,000 times that recommended by Paneth and Rice. Thus the acetone vapor was in contact with the hot zone of the reaction tube for the very short time of 2×10^{-6} seconds, which is too short. A larger electrical furnace was therefore installed and the experiments were repeated. In one experiment with Te, a mirror one centimeter long and eleven centimeters from the end of the furnace was removed in less than a minute.

A new source (polonium thermally deposited on a cold finger) was introduced and exposed to the free methyl radicals from acetone vapor. Gamma counts showed that 92% of the activity was removed in about 15 minutes. In this experiment, 2 traps were used, the first being refriger-

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ated during the reaction. After the reaction was complete, the acetone containing polonium was distilled from one trap to the other and it was found that considerable activity could be transferred by distillation although the amount decreased with each consecutive distillation. Analysis of the contents of various parts of the apparatus showed that 97% of the activity had been removed from the source, 59% being in the traps.

While the results of this experiment appeared very promising, the following questions arose:

1. Whether the activity was partly removed by thermal volatilization, since the acetone vapor was found to coat the cold finger considerably;
2. Whether the decomposition of the polonium compound evident in the distillations is due to reaction of polonium with acetone or perhaps moisture;
3. Whether carbon monoxide, formed in the thermal decomposition of acetone along with free methyl radicals, is capable of removing polonium under the experimental conditions.

Some data regarding the first question were obtained by running a blank experiment with a thermocouple inserted in the cold finger (containing no polonium) with all other conditions the same as in the experiment described. The tip of the cold finger was found to be at 306°C ; the outside was probably considerably higher. The temperature dropped with distance from the tip to 53°C at a distance of eight centimeters. It was therefore decided that in future experiments with polonium the cold finger would be cooled by circulating cold water through it.

To avoid the ambiguities indicated in 2 and 3, the apparatus was modified so that ethane would be used as a source of free radicals. A large flask is used as the reservoir. This communicates with the hot end of the reaction tube through a very fine capillary drawn to a size such that the rate of flow of ethane is small enough to permit the pumping system to maintain the desired low pressure. Preliminary experiments with a Po-Pt source were unsuccessful because of one or more of the following reasons: the foil was an old one and although it was hydrogenated for some time, it is probable that the Po was not completely reduced; no free radicals were formed or they were formed in insufficient amount; finally, free radicals in sufficient amount were formed but failed to react with the polonium.

Tests with tellurium mirrors gave negative results and it was found that the inlet capillary was too small to admit a sufficient amount of ethane. When this difficulty was corrected, the apparatus was again tested with tellurium mirrors which were removed by the free radicals from ethane. In these experiments not only did the tellurium mirrors disappear but there was definite evidence that they disappeared due to compound forma-

ation since a considerable amount of a yellow-orange product was condensed in the liquid air trap; this is presumably dimethylditelluride which has already been prepared by this technique by Rice and Dooley; its melting point is -19.5°C .

This material could be distilled readily between the traps, one of them at room temperature and the other refrigerated. Some of it was isolated in a separate system comprising a trap, flask and manometer. Its vapor pressure at room temperature was found to be about 240 mm.

Attempts will now be made to prepare polonium alkyls by this procedure. It is to be noted that any product formed will be in contact only with ethane, and perhaps small amounts of other hydrocarbons formed by secondary reaction, which are chemically inert and not likely to react with polonium as was suspected in the case of acetone. Moreover, the first trap will be cooled with a trichloroethylene-dry ice bath, as in the experiments with tellurium, which allows most of the excess ethane to pass through; it was also observed that the excess ethane could be partially removed from the tellurium product by fractional distillation.

Since there is a possibility that any polonium compound formed may be unstable because of alpha particle bombardment, investigation of the stability of the tellurium alkyl in the presence of alpha radiation from polonium is in progress, in an attempt to obtain some evidence as to the stability of the bonds involved in these compounds.

Polonium-Carbon Monoxide System - (Leitz)

Several investigators have studied the preparation of COS and COSe and preliminary work on COTe has been done. These compounds were prepared by the action of carbon monoxide on the element. It has also been reported that polonium is more easily volatilized in carbon monoxide than in several other gases. A study of the polonium-carbon monoxide system therefore appeared desirable.

A reaction line was set up with provisions for heating polonium sources in carbon monoxide freed of carbon dioxide and oxygen. While quite large fractions of the polonium could be moved from the source to the walls of the reaction chamber by this technique, the temperature required was quite high, i.e., up to red heat (with induction furnace).

This method appears to be of little promise as far as preparation of volatile Po compounds is concerned. However, the results seem to indicate that CO was not responsible for the movement of Po in the experiments with free methyl radicals from acetone; both temperature and CO pressure were lower in the latter.

Carl L. Rollinson

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