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The Reduction of Plutonium by Tetravalent Uranium

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In the search for substances to reduce small amounts of plutonium of higher oxidation states to Pu(III) in the presence of large amounts of U(VI), U(IV) has been tested under a number of various conditions. The use of U(IV) for reducing plutonium does not seem not to have been described previously [1].

Tetravalent uranium at concentrations $\gtrsim 0.01$ M has been found to be stable in solutions of most acids for weeks or months if air is excluded. However, the stability in HNO_3 is poor, but increases with the U(IV) concentration. Maximum stability in HNO_3 seems to be obtained around 1 M HNO_3, where about 50 % of originally 0.1 M U(IV) is reduced in a little more than

an hour at room temperature. Thus U(IV) can be used as a reducing agent even in HNO_3 solutions, provided the time of the experiments does not much exceed an hour.

In 1 M HNO_3, Pu(IV) and Pu(VI) are quantitatively (>99 %) reduced to Pu(III) by 0.1 M U(IV) within 5 min at room temperature. This effect can theoretically be used for separating uranium from plutonium in liquid-liquid extractions, if U(VI), U(IV), Pu(VI) and Pu(IV) prefer the organic phase and Pu(III) only prefers the aqueous phase [2]. The practical usefulness of this was tested in two sets of experiments.

In the first set of experiments two solutions were prepared. The organic solution consisted of methyl *iso*butyl ketone, which was 1.0 M in HNO_3 and contained Pu(IV) and Pu(VI); the aqueous solution was 0.7 M in HNO_3, 3 M in $Ca(NO_3)_2$ and contained a reductant. When these two phases are equilibrated with each other, the distribution ratio of the metals between the organic and the aqueous phases is for U(VI) 12, U(IV) ~ 10, Pu(VI) 13, Pu(IV) 9, and Pu(III) $\lesssim 0.001$ [3]; of these species thus only Pu(III) prefers the aqueous phase, and can easily be separated from the other metal ions. After the two phases had been shaken together, the amount of reduced plutonium (*i. e.* Pu(III)) was determined. Some of the results obtained with different reductants are given in the table for 5 min equilibration time.

Reducing agent	% Pu reduced
0.05 M $NH_2OH \cdot HCl$ + 0.005 M Fe^{2+}	65 ± 8
0.05 M $H_4NOSO_2NH_2$ + 0.005 M Fe^{2+}	65 ± 10
0.05 M U^{4+} in air	70 ± 10
0.05 M U^{4+} in N_2	95 ± 3

It is seen that U(IV) is equally or more effective than iron(II) plus hydroxylamine or sulfamate.

In the second set of experiments, the organic phase contained Pu(IV) as the uncharged TTA complex in 0.1 M TTA (thenoyltrifluoroacetone) in benzene, while the aqueous phase was 0.33 M in $HClO_4$ and contained U(IV). For 0.010 M U(IV), 14 % Pu had been reduced in 30 min, and 60 % in 20 h.

These experiments show the usefulness of U(IV) as a reducing agent for plutonium, either in aqueous solution or in two-phase

liquid-liquid extraction; however, in the presence of strong complexing agents for tetravalent actinides, the reduction is very slow. A more detailed account of the experiments will soon be given.

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Tritium Labelling of *p*-Aminosalicylic Acid (PAS)

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For the study of the metabolic properties of the tuberculostatic agent *p*-aminosalicylic acid* (PAS)[1], it was of importance to obtain tritium labelled PAS. In order to avoid cumbersome syntheses, the possibility of using recoil tritons for the labelling[2] was investigated.

In this method the organic compound to be labelled is mixed with a lithium salt, and the mixture is irradiated with slow neutrons. From nuclear reactions between these neutrons and ^6Li, tritium atoms with a kinetic energy of 2.7 MeV** are produced. These fast tritons are successively slowed down by collisions with surrounding atoms, which cause heavy destruction along the path of the triton, until it is finally trapped in some molecule. Since the neutron irradiation usually is carried out in a nuclear reactor, considerable destruction of the organic compound is also caused by other high energy particles present (neutrons, γ-quanta, *etc.*). The irradiated mixture will therefore contain a number of decomposition products of the original compounds, which all may be labelled with

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* Kindly supplied by A. B. Ferrosan, Malmö, Sweden.
** MeV = million electron volts.

tritons. As has been pointed out[3], the difficulty lies not in the labelling, but in the isolation of a pure product.

In our experiment, 6.0 g PAS was mixed with 0.6 g Li_2CO_3 and irradiated with a slow neutron flux of 1.4×10^{12} n/cm²/sec for 120 h (temperature $\sim 40°$ C) in the reactor at A. B. Atomenergi in Stockholm. The isolation of pure PAS from the product, which had slightly darkened during the irradiation, was made in the following manner.

The product was mixed with amyl alcohol, which dissolves PAS as well as some of the organic decomposition products but not the Li_2CO_3. After solid substances had been filtered off, the solution was shaken with an equal volume of 0.1 M $NaHCO_3$ in water.

The distribution ratio q of PAS between the two solvents is given by the equation

$$q = \frac{k_d}{1 + k_a[H^+]}$$

at pH > 3 (at lower pH another term has to be added in the denominator to correct for the amphoteric character of PAS). Since the dissociation constant[4] k_a of the carboxylic hydrogen in PAS is $10^{-4.08}$, and the distribution constant k_d of undissociated PAS between amyl alcohol and water was determined to be 36 ± 3, it is easily calculated that about 95 % of PAS goes down into the aqueous phase when this is 0.1 M in $NaHCO_3$ (pH $\sim$ 7).

The aqueous solution thus obtained was washed five times with equal portions of amyl alcohol. Since the equation above is generally valid for monobasic acids, these washings with amyl alcohol remove all organic decomposition products with $k_a < 10^{-7}$ and $k_d > 1$ (including the probable decomposition product *m*-aminophenol (MAP) with[5] $k_a = 1.3 \times 10^{-10}$ and $k_d \sim 2$). The aqueous solution was then treated in two different ways.

In *procedure A*, 0.1 M HCl was added until pH 3.8 was reached. The solution was then shaken with an equal volume of amyl alcohol. From the equation above, it can be calculated that at pH 3.8 about 95 % of PAS will be obtained in the organic phase, while a number of organic impurities are left in the aqueous phase. By this procedure all substances are removed which do not have k_a and k_d close to that of PAS.

In *procedure B*, the aqueous phase was cooled in ice, and HCl was added until a