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FOREWORD

The study of the chemical changes consequent upon the nuclear transformation of an atom that is linked with other atoms in a molecule and surrounded by other similar or dissimilar molecules has intrigued chemists for a number of years. This interest is certainly not static but if anything is increasing. The main theme of this meeting was a discussion of the suggestions and theories that have been advanced to explain the wealth of experimental observations on the behaviour of atoms at energies and in situations not normally accessible in the laboratory. Though the subject has some practical implications in the preparation of radioisotopes, this was not an important consideration at this Symposium.

The first Symposium on hot-atom chemistry organized by the Agency was held in Prague in October 1960. Comparison of the past and the present state of the subject shows that a greater variety and sophistication of techniques are now being applied as the simpler approaches used in the past have been shown to be inadequate. Progress has been made in the understanding of the simpler gas system, but in liquids and solids there is still much to clarify. It is also of interest that for the majority of the work reported in these Proceedings a reactor was the radiation source, and in this field much experimental work still remains to be done.

The Symposium on Chemical Effects Associated with Nuclear Reactions and Radioactive Transformations was held from 7 to 11 December 1964 in Vienna, and was attended by 136 participants from 29 countries and 4 international organizations. It was organized by the International Atomic Energy Agency in co-operation with the Joint Commission on Applied Radioactivity. The publication of these Proceedings makes the content of the papers and discussion available to a wider audience than was possible at the meeting in Vienna.

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CHEMICAL STATE OF RADIOBROMINE FORMED BY THE $Rb^{85}(n,\alpha)Br^{82}$ REACTION

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Abstract — Résumé — Аннотация — Resumen

CHEMICAL STATE OF RADIOBROMINE FORMED BY THE $Rb^{85}(n,\alpha)Br^{82}$ REACTION. A study has been made of the chemical distribution of radiobromine between its higher (BrO_3^-) and lower (Br^-, Br_2, BrO^-) oxidation states produced by nuclear reaction $Rb^{85}(n,\alpha)Br^{82}$ in a number of rubidium inorganic solids.

The samples of dried Rb_2SO_4, $Rb_2S_2O_8$, $RbMnO_4$, $RbNO_3$, Rb_2CO_3 and $RbIO_3$ were irradiated with 14 MeV neutrons by a (T+d) neutron generator. It appeared that in the case of Rb_2SO_4 irradiated at room temperature or at -195°C approximately 8% of total Br^{82} activity was found in the bromate fraction, the rest following the bromide fraction. The room temperature irradiation of $RbMnO_4$ and $RbNO_3$ yielded about 1% of activity in the higher oxidation state of bromine and in the cases of $Rb_2S_2O_8$, Rb_2CO_3 and $RbIO_3$ activity could be measured only in the bromide fraction.

A small increase of the bromate activity was observed when neutron-irradiated Rb_2SO_4 was heated up to 250°C. At higher temperatures (up to 500°C) the activity passed into the lower oxidation state. The heating of the irradiated $RbMnO_4$ and $RbNO_3$ did not provoke any oxidation of bromine activity.

While in the case of $RbNO_3$ pre-irradiation γ-dose of 22 Mrad had no influence upon the distribution of bromine recoils, the analysis of Rb_2SO_4 pretreated with γ-rays (55 Mrad) gave higher bromate activity compared with the samples that before neutron irradiation had only been dried at 150°C.

In conclusion the authors stress the significance of the chemical constitution of the target compound and non-isotopic media with regard to the distribution of highly energetic Br^{82} atoms and to their inability to anneal in the rubidium compounds investigated.

ÉTAT CHIMIQUE DU RADIOBROME FORMÉ PAR LA RÉACTION $^{85}Rb(n,\alpha)^{82}Br$. Le mémoire traite de la répartition, entre ses états d'oxydation supérieur (BrO_3^-) et inférieur (Br^-, Br_2, BrO^-), du radiobrome produit par la réaction nucléaire $^{85}Rb(n,\alpha)^{82}Br$ dans des composés inorganiques solides du rubidium.

Les échantillons de Rb_2SO_4, $Rb_2S_2O_8$, $RbMnO_4$, $RbNO_3$, Rb_2CO_3 et $RbIO_3$ ont été exposés à des neutrons de 14 MeV dans un générateur de neutrons. Il est apparu que, dans le cas du Rb_2SO_4 irradié à la température ambiante ou à -195°C, environ 8% de l'activité totale du ^{82}Br se trouvaient dans la fraction bromate, le reste de l'activité ayant suivi la fraction bromure. L'irradiation de $RbMnO_4$ et de $RbNO_3$ à la température ambiante a produit environ 1% d'activité dans l'état supérieur d'oxydation du brome alors que pour $Rb_2S_2O_8$, Rb_2CO_3 et $RbIO_3$ on n'a pu mesurer l'activité que dans la fraction bromure.

On a observé un léger accroissement de l'activité du bromate lorsque Rb_2SO_4 exposé aux neutrons a été chauffé jusqu'à 250°C. Aux températures plus élevées (jusqu'à 500°C), l'activité est passée dans l'état d'oxydation inférieur. Le chauffage du $RbMnO_4$ et du $RbNO_3$ irradiés n'a pas provoqué d'oxydation du brome actif.

Dans le cas de $RbNO_3$, une dose gamma de 22 Mrads préalable à l'irradiation n'a eu aucun effet sur la distribution des atomes de brome de recul, mais l'analyse d'échantillons de Rb_2SO_4 préalablement exposés aux rayons gamma (55 Mrads) a montré que l'activité du bromate était plus élevée dans ces échantillons que dans des échantillons qui n'avaient été que séchés à 150°C avant exposition aux neutrons.

En conclusion, les auteurs mettent l'accent sur l'importance que présente la constitution chimique de la cible et des milieux non isotopiques en ce qui concerne la distribution des atomes de ^{82}Br de haute énergie et leur inaptitude au recuit dans les composés de rubidium examinés.

ХИМИЧЕСКОЕ СОСТОЯНИЕ РАДИОАКТИВНОГО БРОМА, ОБРАЗОВАННОГО ПРИ РЕАКЦИИ Rb^{85} (n,α) Br^{82}. Этот доклад касается химического распределения радиоактивного брома между его наивысшим (BrO_3^-) и более низкими (Br^-, Br_2, BrO^-) состояниями окисления, получаемыми в результате ядерных реакций Rb^{85} (n,α) Br^{82} в ряде неорганических твердых соединений рубидия.

Образцы высушенного Rb_2SO_4, $Rb_2S_2O_8$, $RbMnO_4$, $RbNO_3$, Rb_2CO_3 и $RbIO_3$ были облучены нейтронами с энергией 14 Мэв на нейтронном генераторе (типа T + d). Оказалось, что в случае Rb_2SO_4, облученного при комнатной температуре или при -195 °C, приблизительно 8% от общей активности брома-82 было обнаружено в броматной фракции, остальная часть сопутствовала бромидной фракции. Облучение $RbMnO_4$ и $RbNO_3$ при комнатной температуре давало примерно 1% активности, соответствующей более высокому состоянию окисления брома, хотя в случаях $Rb_2S_2O_8$, Rb_2CO_3 и $RbIO_3$ активность можно было обнаружить только в бромидной фракции.

Небольшое увеличение активности бромата наблюдалось также, когда облученный нейтронами Rb_2SO_4 нагревался до 250 °C. При более высоких температурах (до 500 °C) активность переходила во фракцию, соответствующую более низкому состоянию окисления. Нагревание облученных $RbMnO_4$ и $RbNO_3$ не вызывало никакого окисления брома.

Хотя в случае с $RbNO_3$ предварительное гамма-облучение дозой в 22 Мрад не имело никакого влияния на распределение ядер отдачи брома, анализ Rb_2SO_4 предварительно облученного гамма-лучами (55 Мрад), давал более высокую активность бромата по сравнению с образцами, которые до нейтронного облучения были только высушены при 150 °C.

В заключение авторы подчеркивают значение химического состава вещества мишени и неизотопности среды, сказывающееся на распределении высокоэнергетических атомов брома-82 и их неспособности отжигаться в исследуемых соединениях рубидия.

ESTADO QUIMICO DEL RADIOBROMO FORMADO POR LA REACCION $^{85}Rb(n, \alpha)^{82}Br$. En la presente memoria se estudia la distribución química del radiobromo entre los estados de oxidación superior (BrO_3^-) e inferiores (Br^-, Br_2, BrO^-) producidos por la reacción nuclear $^{85}Rb(n, \alpha)^{82}Br$ en cierto número de sólidos inorgánicos que contienen rubidio.

Los autores irradiaron con neutrones de 14 MeV procedentes de un generador neutrónico (T + d) muestras secas de Rb_2SO_4, $Rb_2S_2O_8$, $RbMnO_4$, $RbNO_3$, Rb_2CO_3 y $RbIO_3$. En el caso del Rb_2SO_4 irradiado a temperatura ambiente o a -195°C, aproximadamente el 8% de la actividad total del ^{82}Br aparece en la fracción bromato y el resto en la fracción bromuro. La irradiación del $RbMnO_4$ y del $RbNO_3$ a temperatura ambiente produjo alrededor del 1% de actividad en el estado de oxidación superior del bromo, mientras que en el caso del $Rb_2S_2O_8$, Rb_2CO_3 y $RbIO_3$, la actividad sólo pudo medirse en la fase bromuro.

Observaron un ligero aumento de la actividad del bromato cuando el Rb_2SO_4 irradiado con neutrones se calentó a 250°C. A temperaturas más elevadas (hasta 500°C), la actividad pasó al estado de oxidación inferior. El calentamiento del $RbMnO_4$ y del $RbNO_3$ irradiados no provocó ninguna oxidación del radiobromo.

Si bien la irradiación previa del $RbNO_3$ con dosis gamma de 22 Mrad no afectó la distribución de los átomos de bromo de retroceso, el análisis del Rb_2SO_4 previamente expuesto a los rayos gamma (55 Mrad) puso de manifiesto una actividad de bromato superior a la de las muestras que antes de la irradiación neutrónica sólo se habían secado a 150°C.

En conclusión, los autores subrayan la importancia de la constitución química del compuesto utilizado como blanco y de los medios no isotópicos en lo que atañe a la distribución de los átomos de ^{82}Br de energía muy elevada y a su incapacidad de regenerarse en los compuestos de rubidio investigados.

INTRODUCTION

During the last few years considerable experimental evidence has been offered concerning the chemical distribution of radiobromine created by radiative neutron capture, or by isomeric transition, in alkali bromates [1]. On the other hand, there have been few studies of the chemical effects of nuclear reactions involving a change in atomic number, in the course of which radiohalogen atoms are formed. Some attention has been paid to the effects of $S^{34}(n, p)Cl^{34}$ and $K^{41}(n, \alpha)Cl^{38}$ reactions in inorganic solids containing sulphur [2] and potassium [3], and it has been shown that practically all radiochlorine stabilizes in the reduced chemical form. The investigation of the chemical behaviour of iodine obtained by 600-MeV proton irradiation of caesium and tellurium compounds [4] has indicated that the

distribution of activity might be influenced to a great extent by degassing of the target and by integrated proton flux in the course of bombardment.

The present paper deals with the chemical states of radiobromine produced by the nuclear reaction $Rb^{85}(n,\alpha)Br^{82}$ in a number of rubidium inorganic solids. The influence of the chemical constitution of target compounds and their treatment before and after the neutron bombardment are studied with regard to the chemical distribution of radiobromine between its higher (BrO_3^-) and lower (Br^-, Br_2, BrO^-) oxidation states. Radiobromine recoils created in non-isotopic crystal lattice, in which they may be regarded as some kind of impurity, offer excellent chemical circumstances for the study of hot-atom chemistry of bromine, particularly of post-recoil annealing effects. Thermal exchange reactions that may occur when the recoils are annealed in an isotopic medium [5] are excluded. The data obtained in this work may therefore throw some new light on the features of the primary bromine recoil, and the chemical reactions taking place in the course of degradation of its energy.

SNELL [6] was the first to report that fast neutron irradiation of rubidium yields active Br^{82} by the transmutation $Rb^{85}(n,\alpha)Br^{82}$. Q energy of this reaction amounts to about 0.900 MeV [7]. By the use of an approximate expression [8] maximum recoil energy of the bromine atoms formed by 14 MeV (T+d) neutrons is calculated to be about 935 keV.

EXPERIMENTAL

Materials

Rubidium sulphate, rubidium carbonate and rubidium chloride were obtained from British Drug Houses. Rubidium nitrate was of "Merck" origin. Rubidium peroxidisulphate was synthesized by reaction of rubidium chloride and ammonium peroxidisulphate in solution [9] and recrystallized until the negative reaction on ammonia was reached. Rubidium permanganate was prepared according to Reference [10].

All salts were recrystallized from water and dried at 150°C for 2 h with the exception of rubidium peroxidisulphate because of its instability to heat. Cases of different pretreatment are mentioned later.

For degassing the rubidium sulphate sample was heated to 400°C and pumped to a pressure of about 10 mm Hg for 4 h before sealing off in a quartz ampoule.

Gamma irradiations

Gamma-ray pre-irradiation of the samples was carried out with a 200-c Co^{60} source at the position where the dose rate was 60 000 r/h.

Neutron bombardment

Neutron bombardment was carried out by 14.6 MeV neutrons, produced by $H^3(d,n)He^4$ reaction in the neutron generator of the "Ruder Bošković" Institute. Bombardments of about 3 g samples of rubidium compounds in

cadmium-wrapped polythene containers located close to the target were carried out at room temperature or at -190°C, and were of 15 h duration; the neutron flux was about 1×10^9 n/cm^2.s. The pile irradiation of a sample of rubidium sulphate was performed in a vertical graphite column of the reactor in the "Boris Kidrič" Institute, Vinča, at a neutron flux of about 5×10^{12}n/cm^2.s. The temperature did not exceed 150°C.

Thermal annealing

In the course of heating in the electric oven or in refluxed boiling liquids the solids were in contact with the atmosphere. The heated samples were chilled by dipping the stoppered tubes into liquid air.

Analysis

A portion of the sample amounting to 0.5 g was dissolved in 150 ml of either aqueous or 1.7 M ammonia solution containing 0.5 mmole of bromide and bromate each as carriers. Bromide was precipitated with silver nitrate. When the sample was analysed in aqueous solution, after the addition of another portion of bromide carrier, a second silver bromide precipitate was obtained. After filtration and reduction the bromate fraction was also precipitated as silver bromide. All precipitates were washed with nitric acid (1:2), water, acetone and ether, dried at 105°C and weighed for the chemical yield.

Radioactivity measurements

The filter paper with precipitate was placed in a glass tube and counted by means of a well-type scintillation counter. Decay curves were drawn for all samples and the relative activities determined from them.

RESULTS

Effect of target compound

The percentage of Br^{82} found in the bromate fraction in various rubidium crystalline compounds analysed in ammonia and/or aqueous carrier solutions is given in the last two columns of Table I. The rest of the activity followed the bromide fraction. All the samples, with the exception of $Rb_2S_2O_8$, were dried for 2 h at 150°C and irradiated at room temperature with (T+d) neutrons.

The results show a low yield of Br^{82} activity in the higher oxidation state of bromine. The Rb_2SO_4 sample gave a somewhat higher bromate fraction (7-10%) compared with other similarly pretreated rubidium compounds. In the cases of $RbNO_3$, RB_2CO_3 and RbCl, higher valency Br^{82} amounted to only a few per cent, while in the cases of $Rb_2S_2O_8$ and $RbMnO_4$ the activity could be measured in the bromide fraction only.

TABLE I

DISTRIBUTION OF Br^{82} OVER BrO_3^- AND Br^- FRACTIONS IN VARIOUS RUBIDIUM COMPOUNDS DRIED 2 h AT 150°C AND IRRADIATED WITH (T+d) NEUTRONS AT ROOM TEMPERATURE

Target	Temperature and period of heating °C min	(%) Br^{82} in BrO_3^-	
		a	b
Rb_2SO_4	No annealing	7.4 ± 0.3	10.1 ± 2
$RbNO_3$	No annealing	3.2 ± 0	1.5 ± 0.2
	100° 20	4.0	2.2
	250° 20	2.7	1.6
	60	2.6	1.5
Rb_2CO_3	No annealing	1.0 ± 0.2	0.2 ± 0.2
	100° 75	3.0	
	180	2.8	
	300° 20	0.9	
	60	1.2	
$RbMnO_4$	No annealing	0	
	180° 180	0	
$Rb_2S_2O_8$	No annealing	0	
RbCl	No annealing	0.6 ± 0.6	
	300° 20	1.6	
	60	1.4	

[a] samples dissolved in aqueous solution
[b] samples dissolved in ammonia solution

There was no significant difference between the analysis in the ammonia and the analysis in the aqueous solution.

Effect of pre-irradiation treatment

The effect of various treatment conditions before neutron bombardment has been studied on samples of Rb_2SO_4 and $RbNO_3$ (Table II).

TABLE II

EFFECT OF PRE-IRRADIATION TREATMENT ON DISTRIBUTION OF Br^{82} OVER BrO_3^- AND Br^- FRACTIONS IN RUBIDIUM COMPOUNDS IRRADIATED WITH (T+d) NEUTRONS AT ROOM TEMPERATURE

Target	Pre-irradiation conditions	Post-irradiation treatment	(%) Br^{82} in BrO_3^-	
			a	b
Rb_2SO_4	Dried 2 h at 150°C	No annealing	7.4 ± 0.3	10.1 ± 2
	Vacuum-dried 4 h at 400°C	No annealing	3.6 ± 0.5	2.9
	Containing 7.5% moisture	No annealing 200°C 20 min	2.8 ± 0.5 2.7	
	2 h at 150°C then γ 53 Mrad	No annealing 200°C 60 min	1.4 ± 0.7 3.4 ± 0.2	0
$RbNO_3$	Dried 2 h at 150°C	No annealing	3.2 ± 0	1.5 ± 0.2
	2 h at 150°C then γ 20 Mrad	No annealing 250°C 20 min		1.1 ± 0.1 0
	2 h at 150°C then γ 53 Mrad	No annealing 250°C 20 min	2.2 ± 0.1 1.7 ± 0.5	

[a] samples dissolved in aqueous solution
[b] samples dissolved in ammonia solution

Vacuum-dried Rb_2SO_4 samples and those containing about 7.5% moisture after recrystallization, showed a significant decrease in the higher valency Br^{82}.

The experimental data indicate also that besides degassing and presence of moisture, in particular pre-irradiation with cobalt-60 gamma-rays could affect the distribution of bromine recoils. It is known that the most important effect of gamma-rays in matter consists in the production of dis-