

halo derivatives, $(\text{Ph}_2\text{PN})_2(\text{NSX})$, which are very readily hydrolyzed by moisture (vide supra), the trihalide salts can be handled in air for long periods of time without hydrolysis occurring (infrared spectra). The salts **2** have also been prepared by the reaction of the 12-membered ring $(\text{Ph}_2\text{PN})_4(\text{SN})_2$ with halogens and by thermolysis of the 12-membered dication $[(\text{Ph}_2\text{PN})_4(\text{SN})_2]^{2+}[\text{Br}_3^-]_2$, whose structure has been established by X-ray crystallography.²⁰

Conclusion

The reaction of S_4N_4 with phosphorus(III) chlorides in acetonitrile provides a versatile synthesis of heterocycles containing the P_2SN_3 ring. The monofunctional heterocycle **1a** ($\text{X} = \text{Cl}$), obtained in excellent yield by this route, undergoes a number of simple substitution reactions with nu-

cleophiles. The preparation of other halo derivatives of this ring system (**1a**; $\text{X} = \text{Br}, \text{I}$) provides an unusual opportunity to compare the reactivity of sulfur-halogen bonds in similar chemical environments. The structures of **1a** ($\text{X} = \text{Cl}, \text{I}, \text{Ph}, \text{NMe}_2$) and the tendency for ring-opening reactions to occur via S-N bond cleavage will be discussed in the context of the π -electronic structure of the P_2SN_3 ring in a subsequent paper.

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Registry No. **1a** ($\text{X} = \text{Cl}$), 84247-67-6; **1a** ($\text{X} = \text{Br}$), 90133-26-9; **1a** ($\text{X} = \text{I}$), 88008-07-5; **1a** ($\text{X} = \text{Ph}$), 91948-83-3; **1a** ($\text{X} = \text{NMe}_2$), 88008-11-1; **1a** ($\text{X} = \text{NET}_2$), 89746-70-3; **1a** ($\text{X} = \text{NC}_5\text{H}_{10}$), 91948-84-4; **1b**, 91948-86-6; **1c**, 38595-77-6; $[(\text{Ph}_2\text{PN})_2(\text{SN})]^{+}\text{Br}_3^-$, 90133-25-8; $[(\text{Ph}_2\text{PN})_2(\text{SN})]^{+}\text{I}_3^-$, 91948-82-2; $[\text{Ph}_2\text{CIPNPCIPh}_2]^{+}\text{Cl}^-$, 31239-04-0; $[\text{Ph}(\text{Cl}_2)\text{PNP}(\text{Cl}_2)\text{Ph}]^{+}\text{Cl}^-$, 91948-85-5; $[(\text{H}_2\text{N})\text{Ph}_2\text{PNPPH}_2(\text{NH}_2)]^{+}\text{Cl}^-$, 2960-45-4; S_4N_4 , 28950-34-7; Ph_2PCl , 1079-66-9; PhPCl_2 , 644-97-3; PCl_3 , 7719-12-2.

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Photochemical Reduction of the Uranyl Ion with Dialkyl Sulfides

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The photochemical reduction of the uranyl ion by diethyl, di-*n*-propyl, and di-*n*-butyl sulfides has been investigated in acidified water-acetone medium by using radiations in the visible region (≥ 365 nm) from a medium-pressure mercury lamp. The photoreduction is independent of temperature. The quantum yield increases with an increase in dialkyl sulfide or hydrogen ion concentration. The plots of the reciprocal of the quantum yield vs. the reciprocal of initial dialkyl sulfide concentration are linear with intercepts on the ordinate axis. Stern-Volmer quenching constants have been calculated from luminescence measurements. It has been found that physical and chemical quenchings compete with each other. Electronic absorption spectra reveal that there is no ground-state interaction between the uranyl ion and the dialkyl sulfide. On the basis of product analysis, quantum yield of uranium(IV) formation, and Stern-Volmer quenching constants, a dynamic mechanism of oxygen atom transfer from the excited uranyl ion to dialkyl sulfide has been proposed.

Introduction

The photochemistry of the uranyl ion has received considerable attention owing to its characteristic luminescence and power to photooxidize a variety of organic substrates and inorganic ions.¹⁻³ Both intra- and intermolecular mechanisms have been proposed.^{1,3} The most important reactions of the photoexcited uranyl ion appear to be oxidations of substrates either by hydrogen abstraction⁴⁻⁷ or by electron transfer.⁸⁻¹¹ The uranyl ion can also photosensitize certain processes by energy transfer¹² or by electron transfer.¹³ Matsushima^{14,15}

has proposed an excited-state electron transfer process in the quenching of uranyl luminescence by aromatic hydrocarbons, without formation of any final redox product.

In earlier communications it has been reported that the photochemical reduction of the uranyl ion with triphenylarsine,^{16a} triphenylantimony,^{16b} triphenylphosphine,^{16c} and triphenylbismuth^{16d} proceeds via oxygen atom transfer, whereas a mechanism based on α -hydrogen abstraction has been proposed for the photoreduction of uranyl ion with alkanenitriles.¹⁷ In the present investigation, the photochemical reduction of uranyl ion with diethyl, di-*n*-propyl, and di-*n*-butyl sulfides has been studied.

Experimental Section

Uranyl acetate (BDH AnalaR) was used as received. Diethyl sulfide, di-*n*-propyl sulfide, and di-*n*-butyl sulfide were prepared and purified as reported in the literature.¹⁸ Sulfuric acid and acetone (both BDH AnalaR) were used without further purification. Deionized and doubly distilled water was used.

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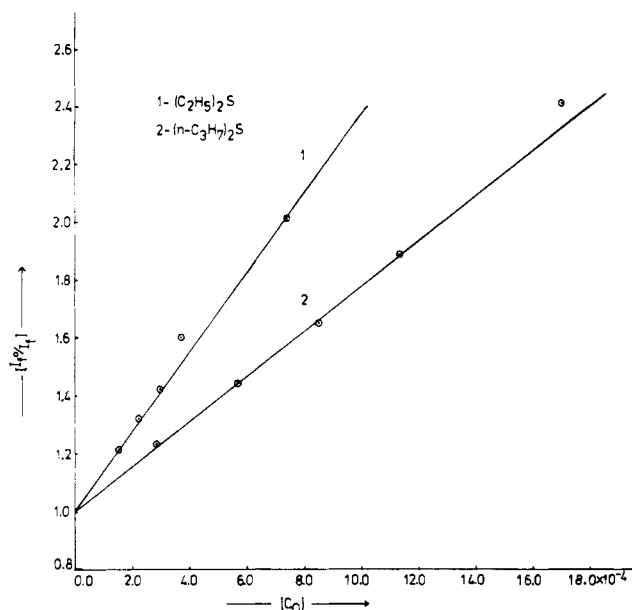


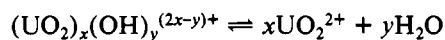
Figure 1. Stern-Volmer plots for quenching of uranyl luminescence by dialkyl sulfides.

The photolysis was carried out in a Pyrex photochemical reactor using a 125-W medium-pressure mercury lamp (Hanovia Lamps). The experimental details have been reported earlier.¹⁷ The relative intensities of uranyl emission at 516 nm were measured by means of an Aminco-Bowman spectrophotofluorometer at 418-nm excitation in acidified water-acetone solutions (1:9 by volume) containing 0.01 M uranyl acetate, 0.10 M sulfuric acid, and various concentrations of the quenchers at 25 ± 2 °C. These measurements were carried out without deoxygenation since no significant effect due to dissolved oxygen was found.

Results and Discussion

The kinetics of photochemical reduction of the uranyl ion with diethyl, di-*n*-propyl, and di-*n*-butyl sulfides has been investigated in acidified water-acetone medium (3:4 by volume) by using radiation in the visible region from a medium-pressure mercury lamp with intensities on the order of 10¹⁷ quanta/s. The rate of photoreduction with dialkyl sulfides follows the order di-*n*-butyl sulfide > di-*n*-propyl sulfide > diethyl sulfide.

The absorption maximum of the uranyl ion (0.005 M) in distilled water at 430 nm undergoes a hypsochromic shift on the addition of sulfuric acid that is dependent on the concentration of acid. However, the maximum does not shift beyond 420 nm when the acid concentration is 0.002 M and above. This is due to a shift of the hydrolysis equilibrium¹⁹



However, the addition of a dialkyl sulfide to the acidic uranyl solution neither shifts the position of the 420-nm absorption maximum nor changes its molar absorptivity. The Stern-Volmer plots for the quenching of uranyl luminescence by these substrates are also linear (Figure 1), thus excluding the possibility of ground-state complex formation.²⁰ These observations rule out the intramolecular quenching mechanism by the formation of the ground-state complex between the two reactants.

The uranyl luminescence region (470–580 nm) indicates that the level of the excited state of the uranyl ion to be quenched is in the range 61–49 kcal/mol, much lower than the lowest excited states of dialkyl sulfides (≈124 kcal/mol).²¹ The

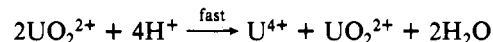
electronic energy transfer from the excited uranyl ion is a highly endothermic process, which rules out any possibility of intermolecular energy transfer from the excited uranyl ion to the sulfide. The rate of photoreduction of uranyl ion with dialkyl sulfides was found to be independent of temperature (10–30 °C). This excludes the possibility of bimolecular collisional energy transfer from the excited uranyl ion to the substrate.²⁰

The ground state of the uranyl ion is singlet, and the intense broad absorption in the UV region is attributed to the singlet-singlet transition in which uranium(VI) is excited to the lowest excited singlet state, which probably undergoes intersystem crossing to the triplet state.³ Alternatively, it is directly excited to the lowest energy triplet state by absorption in the visible region.²³ This singlet-triplet transition, which should be otherwise spin forbidden, becomes allowed in the presence of mixing between states of different multiplicity through spin-orbit coupling, which is sufficiently large in this case, due to the heavy uranium atom, to give a high efficiency for this transition. Since the triplet state has sufficient energy and a lifetime long enough for reaction,²⁴ the photochemical reactions of the excited uranyl ion occur primarily from the triplet state when it is excited with visible radiations.

The photochemical reduction of the uranyl ion by dialkyl sulfides gives uranium(IV) and the corresponding dialkyl sulfoxides, which were characterized by TLC and by IR and NMR spectroscopy. In the IR spectrum, an intense absorption appeared at 1040 cm⁻¹, which has been assigned to the >S=O stretching vibration.²⁵

Uranium(IV) produced during the course of the reaction may also absorb light and revert back to uranium(IV). Kato and Fukutomi²³ have investigated the kinetics of the photoaccelerated U(IV) → U(VI) electron-exchange reaction and have observed that radiation in the visible region (540–550 nm and ≥600 nm), absorbed by uranium(IV), is ineffective for this photoaccelerated electron-exchange reaction. A medium-pressure mercury lamp emits in the visible region high-intensity lines at only 365, 436, 546, and 571 nm, which dialkyl sulfide do not absorb. Thus, the uranyl ion is the only photoactive species responsible for the overall reaction. The photochemical reduction of the uranyl ion by dialkyl sulfides occurs most probably through the formation of an exciplex between the excited uranyl ion and the substrate.¹⁵

Uranium(V) can be detected by its absorption at 626 nm in nonaqueous solvents.²⁶ In the present investigation, however, uranium(V) could not be detected during the course of the reaction, since uranium(V), even if formed, will not be stable in the acidic reaction medium and will rapidly disproportionate to uranium(IV) and uranium(VI).¹⁷



However, the formation of dialkyl sulfoxide as one of the redox product favors the dynamic intermolecular mechanism for the photochemical reduction of the uranyl ion by dialkyl sulfides under the experimental conditions used. This involves the transfer of an oxygen atom from the excited uranyl ion to the dialkyl sulfide through the formation of an exciplex and is shown in Scheme I, where S represents the solvent molecule, Ia is the absorption of light by the reaction mixture, k_1 , k_2 , k_3 , k_4 , k_5 , k_6 , k_7 , and k_8 are the rate constants for luminescence

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Table I. Quantum Yields for Uranium(IV) Formation and Second-Order Rate Constants for Photochemical Reduction of Uranyl Ion with Dialkyl Sulfides at Different Concentrations of Substrates^a

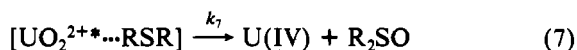
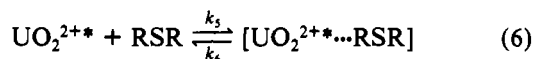
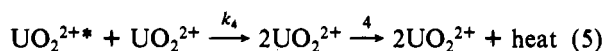
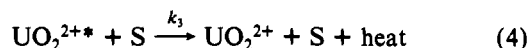
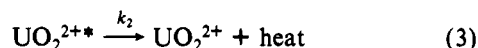
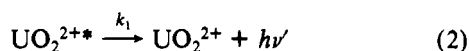
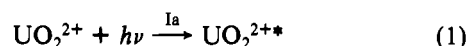
[RSR], M	quantum yield			K, M ⁻¹ min ⁻¹		
	R = C ₂ H ₅ ^b	R = n-C ₃ H ₇	R = n-C ₄ H ₉	R = C ₂ H ₅ ^b	R = n-C ₃ H ₇	R = n-C ₄ H ₉
0.0050	0.15	0.35	0.54	0.450	1.240	1.840
0.0075	0.18	0.42	0.61	0.350	1.133	1.600
0.0100	0.20	0.49	0.69	0.300	0.967	1.167
0.0125	0.23	0.54	0.76	0.275	0.900	1.033
0.0150		0.58			0.767	

^a [UO₂²⁺] = 0.005 M; [H⁺] = 0.10 M; temp = 30 °C.

^b [UO₂²⁺] = 0.0075 M for (C₂H₅)₂S.

emission, nonradiative decay, quenching by solvent, self-quenching exciplex formation, decomposition of exciplex with chemical reaction, decomposition of exciplex with the formation of uranium(IV), and nonradiative decay of the exciplex, respectively.

Scheme I



The quantum yields for the photochemical reduction of the uranyl ion to uranium(IV) at constant acid and uranyl ion concentration exhibit an increase with an increase in the concentration of dialkyl sulfides (Table I). The plots of quantum yield for uranium(IV) formation vs. initial concentration of dialkyl sulfides are linear (Figure 2). However, the values for quantum yields at constant substrate and acid concentrations are fairly constant, within experimental error, when uranyl ion concentration is varied (Table II). The quantum yields also show an increase with an increase in the concentration of sulfuric acid, at constant substrate and uranyl ion concentrations, though not linearly. This also points to the fact that the uranyl ion is not complexed with the substrate in the ground state, for addition of the acid would retard ground-state complexation, if any, and hence the quantum yield ought to fall. The values of quantum yield for uranium(IV) formation are less than unity in all cases, suggesting deactivation of the excited uranyl ion due to solvent molecules and

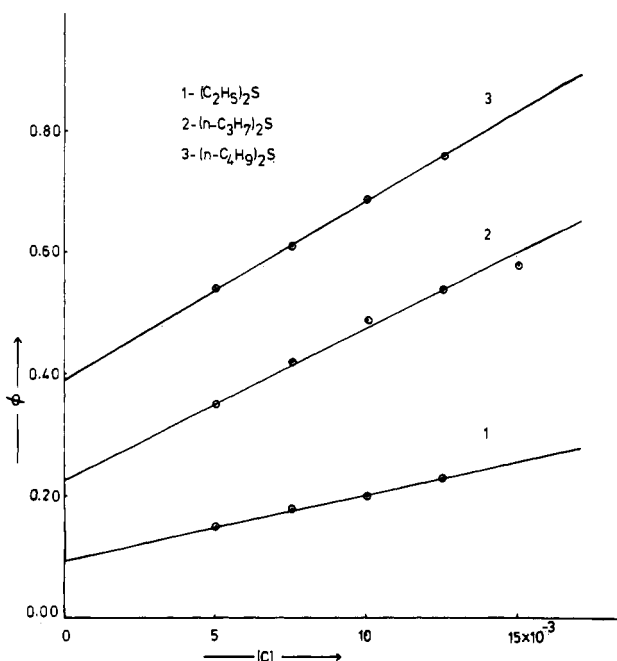


Figure 2. Plot of quantum yield for uranium(IV) formation (ϕ) vs. initial dialkyl sulfide concentration.

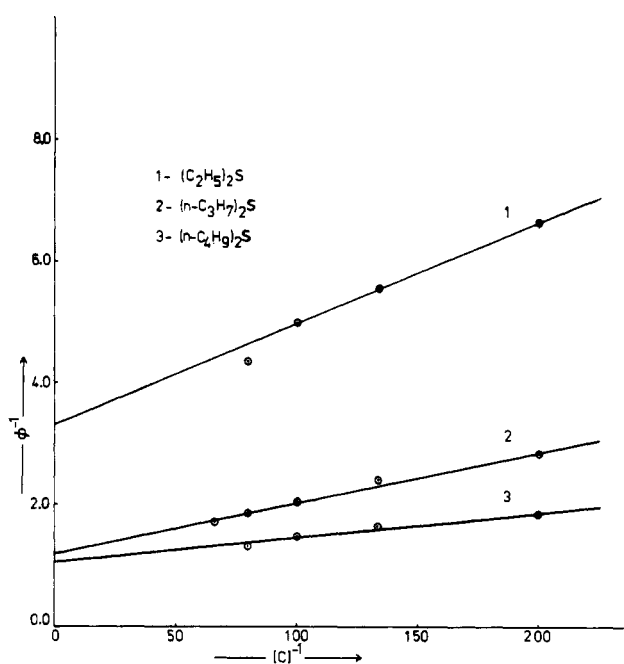


Figure 3. Plot of reciprocal of quantum yield for uranium(IV) formation (ϕ^{-1}) vs. reciprocal of [dialkyl sulfide].

other deactivation steps like self-quenching and luminescence emission in addition to the nonradiative decay.

Assuming steady-state conditions for the intermediate species [UO₂²⁺]* and the exciplex [UO₂^{2+*}...RSR], the

Table II. Quantum Yields for Uranium(IV) Formation and Second-Order Rate Constants for Photochemical Reduction of Uranyl Ion with Dialkyl Sulfides at Different Concentrations of Uranyl Ion^a

(C ₂ H ₅) ₂ S ^b			(n-C ₃ H ₇) ₂ S			(n-C ₄ H ₉) ₂ S		
[UO ₂ ²⁺], M	quantum yield	K, M ⁻¹ min ⁻¹	[UO ₂ ²⁺], M	quantum yield	K, M ⁻¹ min ⁻¹	[UO ₂ ²⁺], M	quantum yield	K, M ⁻¹ min ⁻¹
0.0065	0.18	0.350	0.0030	0.31	1.133	0.0040	0.54	2.067
0.0075	0.18	0.350	0.0040	0.34	1.267	0.0050	0.54	1.840
0.0085	0.20	0.400	0.0050	0.35	1.240	0.0060	0.55	1.933
0.0095	0.22	0.475	0.0060	0.35	1.267	0.0070	0.57	1.933

^a [RSR] = 0.0050 M; [H⁺] = 0.10 M; temp = 30 °C. ^b [(C₂H₅)₂S] = 0.0075 M.

Table III. Quantum Yields for Uranium(IV) Formation, Second-Order Rate Constants (K), and Stern-Volmer Quenching Constants (K_{sv}) for Photochemical Reduction of Uranyl Ion with Dialkyl Sulfides

RSR	quantum yield	K , M ⁻¹ min ⁻¹	K_{sv} , M ⁻¹
(C ₂ H ₅) ₂ S	0.18	0.350	1367
(<i>n</i> -C ₃ H ₇) ₂ S	0.35	1.240	780
(<i>n</i> -C ₄ H ₉) ₂ S	0.54	1.840	

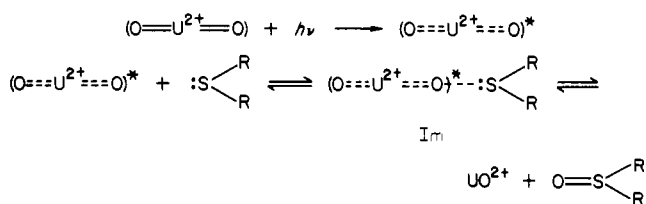
quantum yield of uranium(IV) formation (ϕ) is related to the various rate constants by eq 9. The plots of the reciprocal of

$$\frac{1}{\phi} = \left[1 + \frac{k_6 + k_8}{k_7} \right] \times \left[\frac{k_1 + k_2 + k_3[S] + k_4[UO_2^{2+}]}{k_5[RSR]} + 1 \right] \quad (9)$$

quantum yield vs. the reciprocal of the initial dialkyl sulfide concentration are linear, with intercepts on the ordinate axis (Figure 3). The linearity of these plots shows that the mechanisms of photoreduction are similar with each of the substrates. The intercepts are also greater than unity in all cases, which is in agreement with eq 9. The linear ϕ^{-1} vs. $[RSR]^{-1}$ plots also support the intermolecular mechanism since a mechanism based on intramolecular energy transfer would show deviation from linearity in the above plots as reported in the photolysis of uranyl nitrate-lactic acid system at pH 3.5.¹⁰

The Stern-Volmer plots for the quenching of uranyl luminescence by diethyl and di-*n*-propyl sulfides are linear (Figure 1). The values of the Stern-Volmer quenching constants (K_{sv}) for these substrates are 367 and 780 M⁻¹, respectively (Table III). Matsushima and co-workers,^{14,20} on comparing the quantum yields for uranium(IV) formation with Stern-Volmer quenching constants, deduced that physical and chemical quenchings compete with each other in the case of certain alcohols. In the present investigation, the quantum yield for uranium(IV) formation is greater with di-*n*-propyl sulfide than with diethyl sulfide (Table I) whereas an opposite trend is observed in the K_{sv} values. So it becomes evident that physical and chemical quenchings compete with each other and di-*n*-propyl sulfide is a more efficient chemical quencher of uranyl luminescence than diethyl sulfide.

The chemical quenching leads to the formation of uranium(IV) and the corresponding dialkyl sulfoxide as the redox products via the formation of an intermediate (Im). The oxygen atom acts as a bridge between the excited uranyl ion and sulfur and thus facilitates atom transfer.



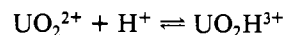
The redox intermediate (Im) finally decomposes to yield UO₂²⁺ (uranium(IV)) and the corresponding dialkyl sulfoxide.

Excitation results in a progressive weakening of the U–O bonds,⁴ and the bond distances in the excited uranyl ion are longer than those in the ground state.²⁷ Moreover, the uranyl ion is a stronger oxidizing agent in the excited state ($E_0 = +2.6$ V) than in the ground state ($E_0 = 0.05$ V).³

In the highest occupied molecular orbital (HOMO) of uranyl ion, composed of uranium 5f or 6d and oxygen 2p atomic orbitals, most of the electron density is located on the oxygen atom. The two lowest unoccupied molecular orbitals (LUMO's) are mainly uranium 5f molecular orbitals.²² The electron density on the uranium atom should be increased with photoexcitation, and the effective charge on the uranium atom will decrease.²⁸ Thus, the oxygen atom of the uranyl moiety will be more labile in the excited state than in the ground state, which would promote the atom-transfer mechanism. However, the unpaired electron on the oxygen atom in the excited uranyl moiety may also be a key factor in its enhanced reactivity.

In the photochemical reduction of uranyl ion with dimethyl sulfoxide in 5 M sulfuric acid medium, an oxygen atom transfer from the excited uranyl ion to dimethyl sulfoxide has been proposed.²⁹ Also for the photochemical reactions ($\lambda = 436$ nm) of UO₂²⁺ with SO₂ or O₃, an oxygen atom transfer mechanism has been proposed.³⁰

The increase in the rate of photoreduction and quantum yield (ϕ) with an increase in sulfuric acid concentration can be attributed to (a) increased lifetime of the excited uranyl ion in the presence of SO₄²⁺ (H₂SO₄),³¹ (b) higher oxidizing power of the protonated uranyl ion, (c) longer lifetime of the protonated uranyl ion in the excited state, and (d) change in the nature of species present.³² It appears that the protonated uranyl ions are formed through a fast equilibrium:



These ions have a stronger oxidizing power in the excited state than the unprotonated uranyl ions.³³

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Registry No. UO₂²⁺, 16637-16-4; (C₂H₅)₂S, 352-93-2; (*n*-C₃H₇)₂S, 111-47-7; (*n*-C₄H₉)₂S, 544-40-1; uranium(IV), 16089-60-4.

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