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Interaction of uranium oxides with dinitrogen tetroxide

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ABSTRACT. Data on the interaction of nitrogen oxides in different oxidation states with dinitrogen tetroxide in the temperature range 273–1073 K and in the pressure range 0.1–10 MPa are surveyed. The mechanisms of the interaction of the dissociating $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ system, liquid N_2O_4, and N_2O_4–organic solvent mixtures with uranium oxides are discussed as a function of the oxidation state of uranium, the specific surface and structure of the oxides, the state of aggregation of N_2O_4, the presence of impurities in the latter, and the presence of organic solvents. The behaviour of uranium oxides in relation to that of the other metal oxides is subjected to a comparative analysis.

The bibliography includes 91 references.

Contents

I. Introduction 728
II. Interaction of uranium oxides with liquid dinitrogen tetroxide 729
III. Interaction of uranium oxides with the gaseous dissociating $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ system 732
IV. Interaction of uranium oxides with N_2O_4–organic solvent mixtures 735

I. Introduction

The present development of chemical industry and engineering requires the use of non-traditional liquid media (non-aqueous and mixed solvents) with a wide range of varied properties. They make it possible to solve problems involving the optimisation of processes, ecological problems, the creation of waste-free technologies, etc., which are in principle impossible in aqueous solutions.

In the field concerned with the use of non-aqueous solvents, there has been in recent years the most vigorous accumulation of qualitative and quantitative data necessary for the study of the general characteristics of the behaviour of such media and for the creation of theoretical foundations for processes involving interactions in non-aqueous solvents.

Liquid dinitrogen tetroxide N_2O_4 is a typical representative of the class of non-aqueous inorganic solvents. Its physicochemical properties had been investigated previously for the purposes of preparative chemistry in the synthesis of anhydrous nitrates. A new stage in the study of the properties of N_2O_4 involved its application as an oxidant in rocket engines and later as a possible heat exchanger in atomic power stations.[1–4]

N_2O_4 is known to be a very reactive chemical substance which can exist in both liquid and gaseous states depending on the conditions. The chemical properties of N_2O_4 in different states of aggregation differ appreciably. At atmospheric pressure, N_2O_4 exists in the liquid state at temperatures in the range 261.8–294.15 K. The temperature range of the stability of liquid N_2O_4 extends to 473, 523, and 553 K and pressures of 0.5, 2.0, and 10 MPa respectively.

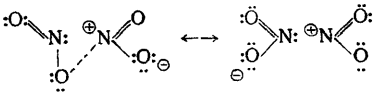
In the temperature range 263–283 K, N_2O_4 has a high density (1.470–1.515 g cm^{-3}), a low viscosity (0.468–0.599 cP),[4] and a low surface tension, amounting to 26.5 dyn cm^{-1} at 293 K and comparable to that of many volatile organic solvents. The electrical conductivity of N_2O_4 (10^{-12} Ω^{-1} cm^{-1}) is much lower than the corresponding values for liquid NH_3 and H_2O (10^{-11} at 239.6 K and 10^{-8} and 293 K).[5] The dielectric constant of liquid N_2O_4 is only 2.42 at 291 K [6] and its dipole moment is close to zero.[6]

The structures of the gaseous and solid tetroxide have been discussed in a number of studies.[7–9] According to revised data,[9] the r(N–N) distance in gaseous N_2O_4 is 0.1782 ± 0.0008 nm, r(NO) = 0.1190 ± 0.0001 nm, and ∠ONO = 135.4°. In the solid state, r(N–N) is reduced to 0.174 nm and the angle is reduced to 126°.[8] The structure of N_2O_4 has a number of features. While the N_2O_4 molecule is planar, its N–N bond length is unusually large (greater by 0.03 nm than in N_2H_4 and N_2F_2). The interatomic distances in the NO_2 groups are virtually the same as in the NO_2 molecule. The latter is consistent with the low dissociation constants of N_2O_4 at 293 K (3.43×10^{-4}–2.6×10^{-3}). It has been suggested,[10] within the framework of the valence bond method, that the greatest energy contribution to the stabilisation of the planar structure comes from the structure involving three-electron O···O bonds between the *cis*- and *trans*-oxygen atoms as a consequence of the resonance

$$O\cdot{:}O^- \leftrightarrow O\cdots O \leftrightarrow O^+{:}\,O^- \leftrightarrow O^-{:}\cdot\,O^+,$$

and

$$O^-{:}\cdot O \leftrightarrow O\cdot{:}O \leftrightarrow O^-{:}\cdot O^+.$$



Of the 21 types of ionic and covalent structures described in a N_2O_4 molecule, only one has the N–N bond, which explains, according to the author,[10] the greater bond length than the value corresponding to a single bond. The oxide N_2O_4 is capable of self-ionisation and dissociation in accordance with the schemes

$$N_2O_4 \rightleftharpoons NO_2^+ + NO_2^-,$$
$$N_2O_4 \rightleftharpoons NO^+ + NO_3^-. \qquad (2)$$

The ion pairs $[NO_2^+][NO_2^-]$ and $[NO^+][NO_3^-]$ are formed in the first stages of these processes. Since the formation of nitrites was not observed on treating metals and their salts with liquid N_2O_4,[4] it has been suggested that oxygen exchange takes place immediately after

dissociation in accordance with Scheme (3):

$$NO_2^+ + NO_2^- \rightleftharpoons NO^+ + NO_3^-. \quad (3)$$

It has been established[4,11,12] that liquid N_2O_4 interacts with alkali and many other metals (Ag, Zn, Cu, Hg). Pure N_2O_4 does not interact with the majority of metals. In order to achieve reaction, use is made of mixtures of N_2O_4 with organic solvents which are capable of increasing the dielectric constant and the degree of dissociation of N_2O_4 according to Schemes (1) and (2). In the reactions with metals, an electron is transferred from the metal atom to the NO^+ ion:

$$M + N_2O_4 \rightarrow MNO_3 + NO. \quad (4)$$

The products of the reactions of N_2O_4 with metals are nitrates as well as adducts of nitrates with N_2O_4.

At atmospheric pressure, N_2O_4 exists in the liquid state up to 294 K. The brown colour of the liquid is due to the presence of nitrogen dioxide formed via the reaction $N_2O_4 \rightleftarrows 2NO_2$. With increase in temperature, the liquid is converted into a gas with the subsequent dissociation $2NO_2 \rightleftarrows 2NO + O_2$. A characteristic feature of $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ system is that individual components do not exist in a pure form,[1-3] always forming an equilibrium mixture. The system behaves as an integral whole and is characterised by its physical and thermophysical properties which have been analysed in detail.[1-3]

The forward and reverse $N_2O_4 \rightleftarrows 2NO_2$ reactions take place at very high rates even at room temperature and the equilibrium between N_2O_4 and NO_2 is established almost instantaneously. N_2O_4 dissociates via the formation of an excited $N_2O_4^*$ molecule; ΔH for the reaction $N_2O_4 \rightleftarrows 2NO_2$ at 298.16 K is 57.11 kJ mol^{-1}.[13] With increase in temperature, the rate of dissociation of N_2O_4 rises and at 430–450 K the reaction equilibrium is almost wholly displaced to the right. At higher temperatures, the reaction $2NO_2 \rightleftarrows 2NO + O_2$ takes place and its equilibrium is established in 10^{-3}–10 s depending on the temperature and pressure. With increase in pressure, the equilibrium is displaced to the left in both reactions.

Oxides of the type NO_3, N_3O_6, and N_2O_2 and the radicals NO_3^- are formed as intermediates in the system. Apart from reversible processes, there is also a possibility of irreversible processes with formation of N_2O_3, O_3, N_2, N_2O, and O_2.

II. Interaction of uranium oxides with liquid dinitrogen tetroxide

We shall consider below the interaction of uranium oxides with liquid and gaseous dinitrogen tetroxide over a wide range of temperatures and pressures, because these processes have been studied most fully.

It follows from Addison's studies that metallic uranium interacts with liquid N_2O_4 only after the addition of nitrosyl chloride[14] and alkylammonium nitrates[15] or organic solvents (ethyl acetate, methyl acetate, nitromethane, etc.[16]). The processes are completed by the formation of $UO_2(NO_3)_2.N_2O_4$, $RHN_3[UO_2.(NO_3)_3]$, or $UO_2(NO_3).mL$, where L is an organic base. It follows from a number of investigations[15,17,18] that uranium oxides either do not interact at all with liquid N_2O_4 or react with it extremely slowly.

In characterising the chemical behaviour of uranium oxides, one should note that, among metal–oxygen systems, one of the most complex is the uranium–oxygen system because of the ability of uranium to form compounds in different oxidation states and also because of the existence of oxides in several polymorphic modifications and the formation of non-stoichiometric compounds. Makarov[19] put forward the hypothesis that uranium oxides obey the general homologous U_yO_{2y+2} relation; a vanishingly small change in the chemical composition of the oxides takes place in this series with increase in y and the composition tends to UO_2. Data on uranium oxides have been surveyed by Vlasov et al.[20]

UO_3 has the largest number of polymorphic forms, the existence of seven crystalline α-, β-, γ-, δ-, ε-, ξ-, and η-forms and one amorphous form of UO_3 being known.[21-25] There is a correlation between the specific surfaces of the trioxides and their reactivities in relation to oxygen.[20,26] The following crystalline modifications of U_3O_8 have been reported in the literature: α-, α′-, β-, and γ-U_3O_8.[27-29]

$(UO_3)_{am}$ has been obtained[30,31] by heating up $UO_4.2H_2O$ at temperatures in the range 623–723 K, ε- and γ-UO_3 have been prepared by the method described by Hoekstra and Siegel,[27] and "active" UO_2 has been obtained by decomposing $UO_2C_2O_4.3H_2O$.[30] The oxides UO_2, $(UO_2)_{act}$, U_3O_8, $(UO_3)_{am}$, β-UO_3, ε-UO_3, and γ-UO_3 had the following specific surfaces (m^2 g^{-1}): 2.7, 89.0, 1.5, 9.7, 7.4, 2.8, and 0.9 respectively. Uranium oxides were brought into contact with liquid N_2O_4 in sealed tubes with stirring.[31]

When $(UO_3)_{am}$ is introduced into liquid dinitrogen tetroxide, the latter boils vigorously and the liquid acquires a blue-green colour, indicating the formation of N_2O_3. The rate of interaction of $(UO_3)_{am}$ with liquid N_2O_4 depends on the initial treatment in the synthesis of the oxide $(UO_3)_{am}$ and in the first place on the conditions under which $UO_4.2H_2O$ was heated. The presence of traces of water in the oxide has a catalytic effect on the process.

The results of chemical analysis are consistent with the presence in the final product of components having the overall compositions $UO_2(NO_3)_2.2NO_2$ and $UO_2(NO_3)_2.N_2O_4$. It has been suggested[32] that the formula of the compound be written as $NO[UO_2(NO_3)_3]$. The identification of the complex as an adduct of uranyl nitrate with dinitrogen tetroxide[15] was based on the presence in its IR spectrum of low-intensity bands in the range 1730–1770 cm^{-1} corresponding to absorption by N_2O_4.[31-34] Such an identification is not unambiguous, because bands in the range 1700–1800 cm^{-1}, corresponding to the compound absorption frequencies of NO_3^- are also manifested in the IR spectra of different nitrates.[35,36]

In order to infer the structure of the compound, its vibrational spectra were compared[37] with the spectra of potassium, rubidium, caesium, and ammonium trinitratouranylates,[38,39] which were virtually identical as regards the intensity and location of the absorption bands of the nitrate groups and the uranyl ion (Table 1).

The vibrations of the nitrate groups correspond to the symmetry point group C_{2v}, which has six bands active in the IR spectra ($3A_1 + B_1 + 2B_2$). According to the ideas of Katzin[40] and Field and Hardy,[41] the splitting of the $\nu_4-\nu_1$ bands, amounting to 270 cm^{-1}, corresponds to the bidentate binding of the nitrate groups in the compound. Its IR and Raman spectra contain a narrow moderately intense band at 2294 cm^{-1}, which is absent from the spectra of complexes incorporating alkali metals. It is characteristic of the vibrations of the nitrosonium ion.[42,43] Consequently the product of the interaction of $(UO_3)_{am}$ with liquid N_2O_4 has the same structure as rubidium, caesium, potassium, and ammonium trinitratouranylates. It undergoes purely electronic transitions in the luminescence spectra close to those of the uranylates {21 235 and 21 203 cm^{-1} for $NO[UO_2(NO_3)_3]$ and $Rb[UO_2(NO_3)_3]$ [37]}.

In conformity with the formula $NO[UO_2(NO_3)_3]$, nitrogen was detected in the complex in the +3 and +5 oxidation states. It was determined by a standard method.[44]

Table 1. Vibrational frequencies of nitrosonium trinitratouranylate.[37]

IR	Raman	Assignment	IR	Raman	Assignment
2294	2295	ν (NO^+)	748	750	ν_3 (O_2NO^-)
1525	1522	ν_4 (O_2NO^-)	734	743	
1255	—	ν_1 (O_2NO^-)	710	714	ν_5 (O_2NO^-)
1025	1028	ν_2 (O_2NO^-)	690	—	
940	—	ν_3 (UO_2^{2+})	260	—	ν_2 (UO_2^{2+})
			250	234	
875	871	ν_1 (UO_2^{2+})	225	—	ν (U—O_2NO)
801	—	ν_6 (O_2NO^-)	210	182	δ (U—O—U)
			—	165	

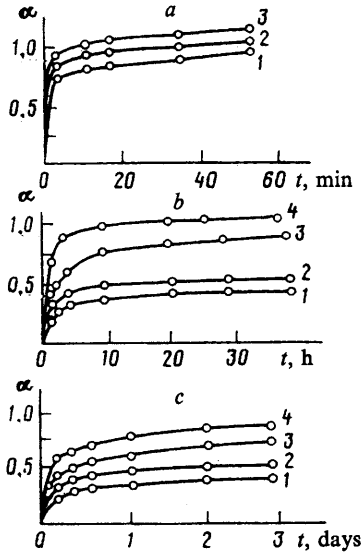


Figure 1. Dependence of the degree of conversion α of uranium trioxides $(UO_3)_{am}$ (*a*), ε-UO_3 (*b*), and γ-UO_3 (*c*) in liquid dinitrogen tetroxide on time (*t*) at different temperatures (K): *1*, 293; *2*, 323; *3*, 373; *4*, 423.

The formation of nitrosonium trinitratouranylate (NTN) on interaction of amorphous uranium trioxide with liquid N_2O_4 indicates the dissociation of the latter in accordance with Scheme (2). The reaction can be represented by the equation

$$UO_3+3N_2O_4=NO[UO_2(NO_3)_3]+N_2O_3\,. \qquad (5)$$

The product of the reactions of β-UO_3, ε-UO_3, and γ-UO_3 with liquid N_2O_4 is also NTN, but the above oxides react at a lower rate than $(UO_3)_{am}$. The properties of the oxide ε-UO_3 are closest to those of $(UO_3)_{am}$. Its degree of conversion into NTN in 1 h was 0.8 and that of ε-UO_3 was 0.25. NTN is formed from ε-UO_3 only after a month and its formation from γ-UO_3 requires more than half a year. With increase in temperature, the degrees of conversion of all the modifications of uranium trioxide in liquid N_2O_4 increase.[45] Fig. 1 illustrates the time variation of the degree of reaction of the oxides UO_3 with N_2O_4 in the temperature range 293–423 K. It is seen that the rate of reaction is especially high in the initial instant (10–30 min), after which the process gradually slows down and the time variation of α becomes almost linear. It has been observed by X-ray diffraction that the interaction is not accompanied by the formation of any intermediates.

Heterogeneous processes have been described satisfactorily by the equation $\alpha = 1 - \exp(-kt^n)$,[46] where *t* is the time and *k* and *n* are constants. (The quantity *n* indicates the region where heterogeneous reactions take place.)

Least squares treatment of the experimental data in terms of the variables $y = \lg[-\lg(1-\alpha)]$ and $x = \lg t$ yielded a slope *n* of the straight line less than 0.5 for all the modifications of uranium oxides (Table 2),[45] which corresponds to the diffusion of N_2O_4 to the surfaces of the initial uranium trioxides.

Table 2. The values of *n* and $\lg K$ for the reactions of uranium trioxides with liquid N_2O_4.

T, K	$(UO_3)_{am}$		ε-UO_3		γ-UO_3 $(UO_3)_{am}$	
	n	$\lg K$	*n*	$\lg K$	*n*	$\lg K$
293	0.46	−0.91	0.23	−5.07	0.20	−6.90
323	0.44	−0.54	0.28	−4.35	0.16	−6.23
348	0.48	−0.35	—	—	0.24	−5.13
373	0.39	−0.11	0.38	−2.73	0.19	−4.73
398	—	—	—	—	0.32	−3.80
423	—	—	0.45	−1.92	0.12	−3.68

The reaction rate constants calculated from the equation $K = nk^{1/n}$ [47] are greater by almost 5–7 orders of magnitude for $(UO_3)_{am}$ than for ε- and γ-UO_3 (Table 2).

The slopes of the $\lg K - 1/T$ relation where 0.57 ± 0.13, 3.01 ± 0.15, and 3.30 ± 0.22 for $(UO_3)_{am}$ and ε- and γ-UO_3 respectively. The empirical equations for the temperature variations of the rate constants for the reactions of the oxides with liquid N_2O_4 are as follows:[45]

$$(UO_3)_{ам}: K=10^{1.36\pm0.43}\cdot\exp-(10\,800\pm2500)/RT,$$
$$\varepsilon\text{-}UO_3: K=10^{5.20\pm0.46}\cdot\exp-(53\,300\pm2900)/RT,$$
$$\gamma\text{-}UO_3: K=10^{4.22\pm0.63}\cdot\exp-(63\,000\pm4200)/RT.$$

The lowest apparent activation energy E_A for the reaction with liquid N_2O_4 corresponded to the amorphous uranium trioxide (10.8 kJ mol^{-1}) and proved to be appreciably smaller than the energy of the dissociation of the N—N bond via the reaction $N_2O_4 \rightleftarrows 2NO_2$ (ΔH = 53.86 kJ mol^{-1} [11]). A linear relation is

observed between E_A for the formation of NTN from different uranium oxides and the specific surfaces of the latter[45] (Fig. 2). The differences between the reaction rate constants and the apparent activation energies for the reactions of the polymorphic forms of uranium trioxide with liquid N_2O_4 are probably caused by the structural features of the oxides. On passing from amorphous uranium trioxide to the crystalline modifications (β-UO_3, γ-UO_3, ε-UO_3), the quantity E_A increases by $\sim$41.8 kJ mol^{-1}. The product of the reactions of U_3O_8 and UO_2 in the temperature range 293–423 K is also NTN. The curves for the time variation of the degrees of conversion of uranium oxides indicates the acceleration of the process with increase in temperature (Fig. 3).[45] The oxide U_3O_8 is more reactive than γ-UO_3. The conversion of U_3O_8 into NTN at 293, 323, 373, and 423 K takes place after $\sim$180, 35, 5, and 1 days, while the corresponding times for UO_2 are 240, 100, 80, and 5 days. The rate of the process is limited by the diffusion of liquid dinitrogen tetroxide to the surface of uranium oxide. After 10–30 min, the rate of reaction falls owing to the formation of a layer of the reaction product on the surface of the oxide (n < 0.5) (Table 3).

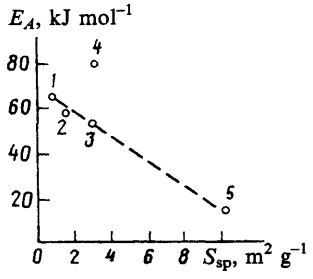


Figure 2. Dependence of the apparent activation energy E_A for the reaction of uranium oxides with liquid dinitrogen tetroxide on the specific surface of the oxide S_{sp}: *1*, γ-UO_3; *2*, U_3O_8; *3*, ε-UO_3; *4*, UO_2; *5*, $(UO)_{3am}$.

In discussing the mechanism of the interaction of uranium oxides with liquid N_2O_4, it is of interest to compare the apparent activation energies obtained from oxides having approximately the same specific surfaces but different oxidation states of uranium: ε-UO_3, U_3O_8, and UO_2 (S_{sp} = 2.8, 1.5, and 2.7 m^2 g^{-1}). On passing from the trioxide to U_3O_8 and UO_2, E_A increases and amounts to 53.3, 56.9, 75.7 kJ mol^{-1}. These data suggest that the conversion into NTN is preceded by the uranium oxidation stage. The approximate energy expenditures on the oxidation of U_3O_8 and UO_2 to the hexavalent state in liquid N_2O_4 were about 4 and 20 kJ mol^{-1} respectively. As a consequence of the oxidation of UO_2, the activation energy E_A for its interaction with N_2O_4 does not fit on the linear dependence of E_A on the specific surface of the oxide (Fig. 2).

The reactivities of the uranium oxides are probably determined not only by the state of their surfaces but also by the oxidation state of uranium in the oxide. This can be seen also in relation to amorphous UO_3 and $(UO_2)_{act}$. Although the apparent activation energy for the interaction of the oxides with N_2O_4 diminishes with increase in their specific surface, E_A for the "active" UO_2 amounted to 43.4 ± 1.88 kJ mol^{-1} compared with 10.9 kJ mol^{-1} for $(UO_3)_{am}$ despite the fact that S_{sp} for $(UO_2)_{act}$ $\simeq$ 89.0 m^2 g^{-1} [30] is almost an order of magnitude higher than for $(UO_3)_{am}$. The value of E_A for the oxidation of "active" UO_2 to the trioxide is correlated with the values obtained for the crystalline specimens.

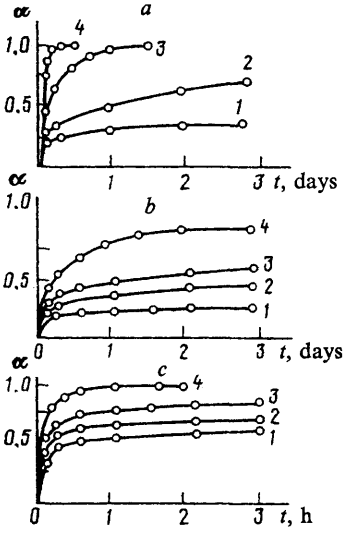


Figure 3. Time variation of the degree of conversion of the uranium oxides U_3O_8 (*a*), UO_2 (*b*), and $(UO_2)_{act}$ (*c*) in liquid dinitrogen tetroxide at different temperatures (K): *1*, 293; *2*, 323; *3*, 373; *4*, 423.

Table 3. The values of n and lg$K$ for the reactions of the oxides U_3O_8 and UO_2 with liquid dinitrogen tetroxide and the mixture of N_2O_4 with 15% of $N_2O_3^*$ in the temperature range 293–423 K.[45]

T, K	U_3O_8				UO_2				$(UO_2)_{act}$	
	n	$-\lg K$	n^*	$-\lg K^*$	n	$-\lg K$	n^*	$-\lg K^*$	n	$-\lg K$
293	0.26	4.74	0.26	5.25	0.20	5.70	0.26	5.14	0.14	3.12
323	0.35	3.73	0.35	4.06	0.17	6.01	0.22	4.98	0.23	2.14
343	0.41	3.41	0.41	3.41	0.21	5.20	0.18	5.30	0.30	1.89
373	0.51	2.61	0.48	2.67	0.29	4.43	0.29	4.80	0.24	1.64
398	0.54	2.31	0.59	2.30	0.25	4.13	0.24	4.10	0.28	0.97
423	0.46	1.78	0.49	1.76	0.35	3.18	0.29	3.35	0.35	0.75

The conversion of "active" UO_2 into NTN is completed after 48, 36, 24, and 2 h at 293, 323, 373, and 423 K respectively. The interaction of U_3O_8 and UO_2 with liquid N_2O_4 can be represented by the following schemes:

$$U_3O_8+10N_2O_4=3NO[UO_2(NO_3)_3]+4N_2O_3, \quad (6)$$

$$UO_2+4N_2O_4=NO[UO_2(NO_3)_3]+2N_2O_3. \quad (7)$$

Since dinitrogen tetroxide contains as a rule admixtures of N_2O_3, the influence of the addition of this component on the reactions was investigated. It is also seen from Eqns. (6) and (7) that N_2O_3 is a reaction product and may accumulate in the reaction mixture. In experiments with different N_2O_3 contents, it was noted that in the temperature range 293–423 K the product of the reactions of all the uranium oxides is NTN. It follows from the data in Table 3 that the introduction of 15% of N_2O_3 does not influence significantly the process kinetics in the temperature range 323–423 K. Some differences are observed at temperatures below 323 K; here the rate of reaction in the $N_2O_4-N_2O_3$ mixtures is higher than in N_2O_4 (Table 3).[48] A similar behaviour has been shown also by metallic zinc.[49] The apparent activation energies for the interaction of UO_2 and U_3O_8 with $N_2O_4-N_2O_3$ mixtures were found to be 76.48 ± 17.6 and 52.8 ± 1.63 kJ mol^{-1} respectively.[45] They are close to the values obtained for pure N_2O_4.

The increase in the rates of reaction of uranium oxides with liquid N_2O_4 in the presence of admixtures of N_2O_3 is caused by the increase in the concentrations of the NO^+ and NO_3^- ions, since N_2O_3 shows a greater tendency towards dissociation than N_2O_4. As a consequence of the dissociation of N_2O_3, according to the schemes

$$2N_2O_3 \rightleftharpoons 2NO+2NO_2 \rightleftharpoons [NO^+][NO_3^-]+2NO, \quad (8)$$

$$N_2O_3 \rightleftharpoons NO+NO_2, \quad (9)$$

$$2NO_2 \rightleftharpoons NO^+ + NO_3^-, \quad (10)$$

the amount of the reactive ion pairs $[NO^+][NO_3^-]$ as well as NO^+ and NO_3^- ions in solution increases. With increase in temperature, the degree of dissociation of N_2O_4 itself also rises appreciably and abolishes the effect of the dissociation of the added N_2O_3 observed at lower temperatures. Presumably the addition of more than 15% of N_2O_3 would also increase the kinetic parameters of the processes investigated at temperatures above 323 K, as was observed by Addison et al.[49]

Since the processes under discussion are extremely difficult to carry out in the absence of traces of water, a study has been made[31] of the influence of added H_2O on the kinetics and the composition of the reaction products. It was noted that the introduction of water appreciably increases the degree of conversion of the oxides. Thus the reaction of amorphous UO_3 in the presence of 0.2% of water is completed after 15 min and with increase in the water content the rate of reaction increases still further. The acceleration of the process has been observed also for other modifications of UO_3 as well as U_3O_8. The degree of conversion of ε-UO_3 in the presence of a water content of about 3% is 65% (45% for anhydrous ε-UO_3) and the reaction reaches completion after 20 days.

Uranium dioxide behaves somewhat differently.[31] When the water content on the surface of the oxide is less than 1.5%, its reactivity hardly changes, whereas in the presence of larger amounts of water the process is appreciably accelerated and in the presence of 15% of water it takes place almost instantaneously. The acceleration of the process in the presence of water is probably induced by the formation of nitric acid, which activates the surface and increases the content of NO_3^- ions.

III. Interaction of uranium oxides with the gaseous dissociating $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ system

The interaction of uranium oxides with the dissociating system has been investigated under dynamic and static conditions at 293–1073 K.[50–52] In the experiments under dynamic conditions, powders of the uranium oxides were placed in a tubular furnace heated to a specified temperature. The stability of the pressure in the gas stream was achieved by maintaining liquid N_2O_4 at the boiling point (294 K) in a thermostatted cell. The contact time was 5 h in all the experiments. The interaction of uranium oxides with the gaseous dissociating system at 323–873 K and at pressures in the range 0.5–10 MPa was carried out in thick-walled glass tubes, the lower part of which was filled with liquid N_2O_4 (it was frozen with liquid nitrogen before the experiment), while uranium oxides were placed in the upper part of the tube on a special suspension. The tube was sealed off and electric furnaces were moved over its lower and upper parts. The furnace over the lower part of the tube served to ensure a constant N_2O_4 pressure during the experiment, while the necessary reaction temperature was maintained with the aid of the furnace over the upper part of the tube. (The pressure developed in the tube was calculated from the temperature dependence of the $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ vapour pressure over the liquid, as described by Nesterenko et al.[1]) At the end of the experiment, the tube was removed from the furnaces, cooled rapidly with liquid nitrogen, and then opened.

Amorphous UO_3 readily reacts in the $N_2O_4 \rightleftarrows 2NO_2$ medium at room temperature and atmospheric pressure. A 70% increase in weight is attained after 5 h under static conditions and after 3 h under dynamic conditions.[51] The changes in the rate of $(UO_3)_{am}$, the results of chemical analysis, and the results of spectroscopic studies on the product indicate that the latter is NTN. Treatment of the kinetic curves[51] yielded n close to two, which shows that the initial stages of the process take place under kinetic conditions. As the reaction product accumulates on the oxide surface, the process slows down and passes to the diffusional region (n = 0.5). With increase in temperature, the reaction also slows down. Fig. 4 illustrates the variation of the weight of the uranium trioxides with the temperature of the dissociating system for a contact time of 5 h. Curve *2* corresponding to the equilibrium process is shown for comparison. It is seen from Fig. 4 that, under equilibrium conditions, the increase in weight reaches 20–70% in the temperature range 293–423 K, after which $\Delta m/m$ falls sharply to zero. The inflections at 423 K were observed also on curves *1* and *3* and their positions are correlated with the contents of NO_2 and N_2O_4 in the gas phase. The degree of conversion of γ-UO_3 is appreciable after 5 h only close to room temperature, while at higher temperatures α did not exceed 1%.

The apparent activation energy E_A for the formation of NTN from $(UO_3)_{am}$ in the temperature range 293–423 K at atmospheric pressure, calculated by several independent equations,[53] amounted to −8.11 ± 0.83 and −7.90 ± 0.83 kJ mol^{-1}.[51] Negative values of E_A were obtained also for the reaction of sodium and potassium peroxides with the dissociating system.[54,55]

Similarly to the observation for liquid N_2O_4, the rate of reaction of gaseous N_2O_4 with $(UO_3)_{am}$ depends on the method of preparation of amorphous uranium trioxide. $(UO_3)_{am}$ specimens with specific surfaces of ~25, 10, and 5 m^2 g^{-1}, obtained by heating $UO_4.2H_2O$ at 623, 673, and 723 K, are converted into NTN after 0.5, 6, and 24 h respectively.[52]

The reactivities of other modifications of uranium trioxide in relation to the $N_2O_4 \rightleftarrows 2NO_2$ system vary in the sequence γ-UO_3 < ε-UO_3 < $(UO_3)_{am}$ and are correlated with their specific surfaces[52] (S_{sp} = 0.9, 2.8, and 9.7 $m^2\ g^{-1}$).

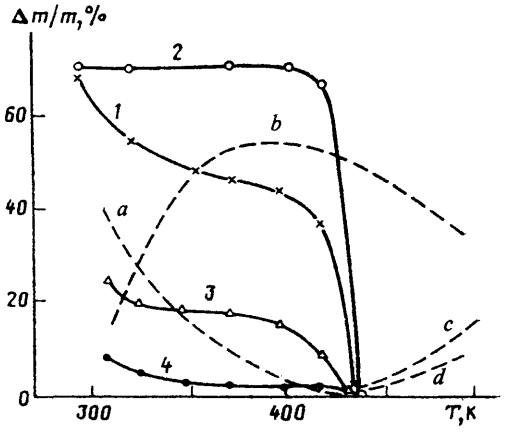


Figure 4. Weight change curves for $(UO_3)_{am}$ (curves *1* and *2*), ε-UO_3 (curve *3*), and γ-UO_3 (curve *4*) in gaseous dinitrogen tetroxide as a function of temperature at p = 0.1 MPa; contact time 5 h except for curves *1*, *3*, and *4*; *2*, specimens maintained under given conditions until the attainment of constant weight; the temperature variation of the composition of the gas phase is shown by dashed curves: *a*, N_2O_4; *b*, NO_2; *c*, NO; *d*, O_2.

The weight of uranium trioxides (Fig. 4) does not change after prolonged contact with the dissociating system at temperatures in the range 423–723 K and there is also no change in the X-ray diffraction patterns of the oxides. This constitutes the difference between the behaviour of uranium trioxides on contact with the dissociating system and that of alkali and alkaline earth metal oxides[56–61] and a series of transition and lanthanide oxides,[52,63] which form nitrides at temperatures above 423 K and the latter are stable in the range 473–673 K.

Starting from temperatures in the range 773–823 K, uranium trioxides in the $2NO_2 \rightleftarrows 2NO + O_2$ medium lose up to 0.5% of their weight and crystallise in the form of a new phase, which was identified as $UO_{2.9}$,[29,64] while in the temperature range 873–1073 K a further weight loss is observed (by 1.8%) and U_3O_8 is formed. In contrast to $(UO_3)_{am}$, ε-UO_3 and γ-UO_3 are converted into U_3O_8, bypassing the $UO_{2.9}$ formation stage.[52]

The nature of the interaction of uranium oxides with the dissociating system in the range 423–723 K is probably determined by the properties of the intermediate products of the decomposition of NTN and in the first place of anhydrous uranyl nitrate.[16–18,37,65–69]

Vibrational spectroscopic data indicate a complex structure of anhydrous $UO_2(NO_3)_2$. The vibration frequencies $\nu_3(UO_2^{2+})$ in this compound are represented by an intense band with three maxima at 990, 980, and 965 cm^{-1}. The fully symmetrical $\nu_1(UO_2^{2+})$ vibration is manifested in the Raman spectrum by doublet bands at 903 and 895 cm^{-1}, one of the components of which (at 895 cm^{-1}) is active in the IR spectrum. The absorption of the nitrate groups in the compounds is distinguished by the greatest complexity. Simultaneously with the presence of doublet bands corresponding to the symmetry point group C_{2v} (1635, 1616 and 1235, 1220 cm^{-1}), the spectrum contains vibrations characteristic of the NO_3^- ion (1381 and 1414 cm^{-1}, Table 4). It has been suggested[37] that the structure of anhydrous uranyl nitrate probably includes at least two types of non-equivalent nitrate groups, the bands at 1414, 1381, 1235, 1220, 1635, and 1616 cm^{-1} belonging to vibrations of the test compounds and not being a result of the interaction of the substance with the material of the filler and hydrate impurities, as suggested by Vdovenko et al.[70]

Table 4. Vibrational frequencies of anhydrous uranyl nitrate.[37]

IR	Raman	Assignment	IR	Raman	Assignment
1635	—		895	903	
1616	1609		—	895	$\nu_1(UO_2^{2+})$
1450	—	ν_{as}(N=O)	798	—	
1440	—		780	—	
1414	—		756	764	$\delta(NO_3^-)$
1381	—		722	724	
1345	—		689	—	
1235	1255	ν_s(N=O)	265	—	
1220	—		255	255	$\nu_2(UO_2^{2+})$
1062	1062		235	215	
—	1010	ν(N=O)	210	199	ν(U—NO_3)
990	—		187	179	δ(U—O—U)
980	—	$\nu_3(UO_2^{2+})$	—	168	
965	—				

According to structural data,[71] discontinuous ("island type") packing with a bidentate mode of addition of nitrate groups is most characteristic of uranyl nitrate complexes of the type $M[UO_2(NO_3)_3]$ and $UO_2(NO_3)_2.2L$. The coordination number of the UO_2^{2+} ion in such compounds is six. The structure of anhydrous uranyl nitrate has been represented[65,66] by a tetragonal bipyramid with equivalent NO_3^- groups and a coordination number of UO_2^{2+} equal to four. It was shown above that this structure of anhydrous uranyl nitrate is inconsistent with the observed IR absorption of UO_2^{2+} and nitrate groups and also with the results of structural analysis. Apart from bidentate binding, in the test compounds there is probably also bridge type binding of nitrate groups, which is fairly well known for other metal nitrates.[72]

Although anhydrous $UO_2(NO_3)_2$ is formed on heating NTN, the results of different workers concerning the temperature ranges and mechanisms of the decomposition of these substances are different.[16–18,67] In particular, it has been claimed[18] that $UO_2(NO_3)_2$ is formed only within the narrow temperature range 436–438 K and that it decomposes to UO_3 in a single stage, while in another study it was assumed[16] that the formation of UO_3 is preceded by a series of intermediate stages with formation of the polymeric oxonitrates $U_2O_5(NO_3)_2$, $U_3O_8(NO_3)_2$, and $U_4O_{11}(NO_3)_2$.

The thermal stability of NTN has been investigated[37] under different atmospheres: in air, in an inert gas stream, *in vacuo*, and in the $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ medium. There are three endothermic effects at 443, 543, and 833 K on the differential thermal analysis

(DTA) curve. The first effect corresponds to the removal of nitrogen dioxide and the formation of anhydrous $UO_2(NO_3)_2$:

$$NO[UO_2(NO_3)_3] \rightarrow UO_2(NO_3)_2 + 2NO_2. \quad (11)$$

Uranyl nitrate is stable within the relatively narrow temperature range 443–473 K, above which it begins to decompose to UO_3. Special experiments involving treatment with acetone of the heat-treatment products obtained at 523, 543, and 573 K [73] (to separate the soluble uranyl nitrates from UO_3) revealed that the $U:NO_3^-$ ratio in the wash solution was 1:2, while the solid residue was UO_3. Thus NTN decomposes in a single stage with formation of uranium trioxide:

$$2UO_2(NO_3)_2 \rightarrow 2UO_3 + 4NO_2 + O_2. \quad (12)$$

In the temperature range 823–873 K, the trioxide UO_3 loses 1.9% of its weight and is converted into U_3O_8.

It has been shown[73] that $NO[UO_2(NO_3)_3]$ decomposes to uranyl nitrate in the temperature range 403–453 K in the kinetic region and takes place from the surface into the bulk of the NTN particles. The process activation energy is ~104.5 kJ mol^{-1}. In contrast to NTN, anhydrous uranyl nitrate decomposes in the diffusional-kinetic region with an activation energy of ~133.9 kJ mol^{-1}. The activation energy E_A for the decomposition of anhydrous uranyl nitrate, quoted by Klavsut',[73] is higher than the value of E_A obtained by Ondrejcin and Garrett[67] and amounts to 98.3 kJ mol^{-1}.

In the gaseous dissociating dinitrogen tetroxide at a pressure of 0.1 MPa, the thermal decomposition of $NO[UO_2(NO_3)_3]$ begins at 453–463 K. With increase in the pressure of a dissociating system, the stability of NTN rises and the limits of its stability at pressures of 0.5, 2, and 10 MPa shift to 503, 523, and 573 K. It has also been observed that NTN decomposes in the dissociating system to UO_3, bypassing the stage involving the formation of anhydrous uranyl nitrate. The presence of the latter has not been detected from the Raman spectra and from the diffraction patterns of the product maintained in the dissociating system at a temperature above 573 K and a pressure in the range 2–10 MPa.[50–52]

On decomposition of NTN and of anhydrous uranyl nitrate, the formation of intermediate oxonitrates as well as uranyl nitrates was not observed. They are not formed in the above heterogeneous processes and can be synthesised only by ligand substitution reactions.[74]

When U_3O_8 and UO_2 are treated with gaseous dinitrogen tetroxide at room temperature under dynamic conditions, the change in weight after 5 h is ~15%, while under static conditions the weight increment reaches 10% only after 24 h. The process then slows down and under static conditions its completion requires approximately half a year. The interaction with UO_2 is even slower. Under dynamic conditions, the increase in weight after 24 h is only 3%. The reaction is completed after 8–10 months. The changes in the weight of U_3O_8 and UO_2 are 73 and 80% respectively, which corresponds to the formation of NTN. The kinetics of the reactions depend on the specific surfaces of the initial specimens: U_3O_8 with S_{sp} = 13.6 m^2 g^{-1} is converted into $NO[UO_2(NO_3)_3]$ after 10 and 15 days at 293 K under dynamic and static conditions, while $(UO_2)_{act}$ is converted after 2 and 3 days respectively (S_{sp} ~ 80 m^2 g^{-1}).

There are two sections on the kinetic curves for the interaction of U_3O_8 and UO_2 with the gaseous dissociating $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ system: the initial sharp increase in the degree of conversion and the subsequent retardation of the process (Fig. 5). The value of n along the initial sections for U_3O_8 is 1.6–2.0, which corresponds to the occurrence of the process in the kinetic region. The apparent activiation energy for the formation of NTN from U_3O_8 is -10.59 ± 1.84 kJ mol^{-1} and is close to that for UO_3. As NTN accumulates on the surface of the oxide, the reaction occurs in the diffusional region (n = 0.1–0.5).

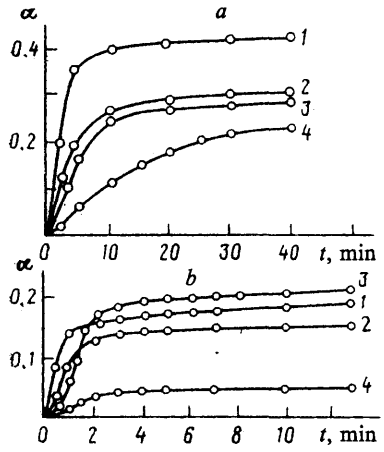


Figure 5. Variation of the degree of conversion of U_3O_8 (*a*) and UO_2 (*b*) in gaseous dinitrogen tetroxide at different temperatures (K): *1*, 293; *2*, 323; *3*, 373; *4*, 423.

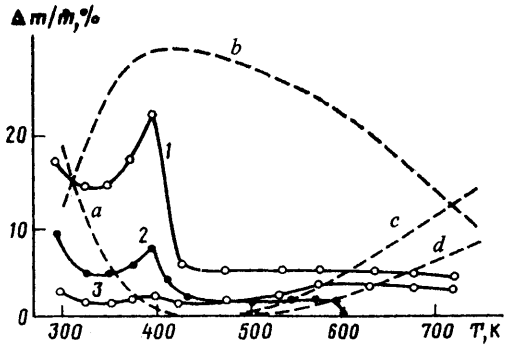


Figure 6. Weight change curves for $(UO_2)_{act}$ (curve *1*), U_3O_8 (curve *2*), and UO_2 (curve *3*) in gaseous dinitrogen tetroxide as a function of temperature at p = 0.1 MPa in the course of 5 h; the temperature variation of the composition of the gas phase is shown by dashed curves: *a*, N_2O_4; *b*, NO_2; *c*, NO; *d*, O_2.

In contrast to uranium trioxides, the temperature variation of the degrees of conversion of U_3O_8 and UO_2 is complex. When the plot of $\Delta m/m$ against T in the range 293–423 K is analysed, the presence of a very intense maximum for $(UO_2)_{act}$ and a less intense one for U_3O_8 at 393–403 K is striking (Fig. 6).[50,51] The increase in the reactivity of uranium oxides in which the oxidation state of the metal is less than 6 at 392 K is determined by the formation of

ε-UO_3 during the reaction. Its appearance has been established by X-ray diffraction. After the uranium oxides had been kept in dinitrogen tetroxide at the temperature indicated, they were treated with acetone to remove uranyl nitrates. It was found that, apart from the peaks characteristic of the initial oxides, the ε-UO_3 diffraction maxima are present on the diffraction patterns of the specimens. The presence of ε-UO_3 as an intermediate phase in the products of the reaction of U_3O_8 and UO_2 with the dissociating system shows that they react in two stages: the oxidation of U_3O_8 and UO_2 to ε-UO_3 and the subsequent formation of NTN. With increase in temperature, the rate of the first process rises and that of the second falls. The formation of the intermediate oxide ε-UO_3, which is more reactive than UO_2 and U_3O_8, accelerates the formation of NTN and induces the appearance of a maximum on the curves for the temperature variation of α. At temperatures above 423 K and a pressure of 0.1 MPa, the formation of NTN ceases as a consequence of its thermal decomposition and a sharp fall in weight is observed on the curves (Fig. 6).

In the range 453–523 K, the main product of the reaction of U_3O_8 with the dissociating system is ε-UO_3. The kinetic curves for the conversion of U_3O_8 into ε-UO_3 obtained by the present authors[51] show that the process is accelerated as the temperature rises. They are described satisfactorily by a first-order reaction equation: $\alpha = 1 - \exp(-kT)$; the activation energy is $E_A = 79.5 \pm 0.88$ kJ mol^{-1}. At temperatures above 623 K, no changes in the weight of U_3O_8 are observed although ε-UO_3 has been stated[27,75] to be stable up to 723 K. This is probably due to the phase transition from orthorhombic U_3O_8 to U_3O_8 with a hexagonal structure[76] whose properties are similar to those of hexagonal ε-UO_3.[77]

In the case of UO_2, in the range 453–523 K an increment in weight of ~1% has been observed, but the X-ray diffraction patterns of the specimens remain unchanged under these conditions.[50] This is evidence for the insertion of oxygen into the cavities of the fluorite structure of uranium dioxide with formation of the non-stoichiometric compounds UO_{2+x}, where $x = 0.20-0.34$.[78] At 623 K and above, the main phase is U_3O_8.

With increase in pressure in the system, the rate of formation of NTN increases appreciably. Thus $(UO_3)_{am}$ is fully converted into NTN after 5 h at 0.5 MPa and temperatures in the range 323–473 K and after 1 h at a pressure of 10 MPa and 473 K. The temperature range corresponding to the stability of NTN shifts at the same time to the region of higher temperatures.[52] NTN remains stable up to 503 K at a pressure of 0.5 MPa and up to 573 K at 10 MPa. The curves for the variation of the weight of U_3O_8 and UO_2 with the pressure of the dissociating system exhibit a maximum similar to that observed at atmospheric pressure.[50,51] However, the position of the maximum, corresponding to the formation of ε-UO_3, is displaced towards higher temperatures. The reactivity of uranium oxides in relation to the dissociating system follows the same sequence as at atmospheric pressure: $(UO_3)_{am} > \varepsilon\text{-}UO_3 > \gamma\text{-}UO_3 > U_3O_8 > UO_2$.[52] Consequently, with increase in the pressure of the dissociating system, the mechanisms of the reactions with uranium oxides do not change and only the rate of reaction and the thermal stability of NTN increase significantly. Above 573 K, NTN is not formed from uranium trioxides even at a pressure of 10 MPa.

In contrast to the reactions at atmospheric pressure, at $p > 0.5$ MPa in the temperature range 573–723 K the oxides $(UO_3)_{am}$ and ε-UO_3 undergo a phase transition with formation of the most stable modification γ-UO_3, which loses oxygen at a temperature above 773 K with formation of the oxide $UO_{2.9}$ and then U_3O_8.

γ-UO_3 is obtained under the same conditions as U_3O_8. The phase having the composition $UO_{2.9}$ is formed during the oxidation of U_3O_8 at temperatures in the range 623–723 K at a pressure of 0.5 MPa. In the temperature range 723–873 K and in the pressure range 0.2–10 MPa, uranium trioxides and UO_2 are converted into U_3O_8. However, at pressures above 2 MPa in the temperature range 573–673 K, the γ-UO_3 phase was detected in reaction products. It was absent at the same temperatures and atmospheric pressure.

IV. Interaction of uranium oxides with N_2O_4–organic solvent mixtures

We noted above that liquid N_2O_4 does not interact with the majority of metals. In order to achieve such reactions, mixtures of liquid N_2O_4 with organic solvents are employed. The chemical behaviour of dinitrogen tetroxide is associated with the characteristics of its electronic structure. Each atom in N_2O_4 has *p* orbitals perpendicular to the plane of the molecule and forming a system made up of six π molecular orbitals in which 12 electrons can be accommodated. N_2O_4 has only eight electrons in its molecular orbitals, as a result of which it exhibits the properties of an acceptor capable of accepting two pairs of electrons. The tetroxide N_2O_4 does not show a tendency to react with metals. On the other hand it forms readily molecular complexes with electron-donating solvents.[79] It has been noted[80] that, as the electron-donating properties of the solvent are enhanced, the absorption maximum $\lambda_{max}(N_2O_4)$ in the range 330–340 nm diminishes and the extinction coefficient of the complex formed increases. According to Solov'ev et al.,[81] in weak organic bases at high concentrations of N_2O_4 the latter exists mainly as undissociated molecules. Only at low N_2O_4 concentrations does the homolytic dissociation $N_2O_4 \rightleftarrows 2NO_2$ occur and the concentration of NO_2 becomes comparable to that of N_2O_4. The thermodynamic parameters of the homolytic dissociation reactions of N_2O_4 in CS_2, $CHCl_3$, CCl_4, $SiCl_4$, and n-hexane depend little on the nature of the solvent.[81] On the other hand, in strong organic bases the heterolytic dissociation $N_2O_4 \rightleftarrows NO^+ + NO_3^-$ takes place.[79]

The introduction of an organic solvent increases the dielectric constant of N_2O_4, promoting the formation of ion pairs. The processes can be represented by the following scheme:

$$m\,L + N_2O_4 \rightleftharpoons (L)_m \cdot N_2O_4 \rightleftharpoons [L_mNO^+]\,[NO_3^-]. \qquad (13)$$

Since the N_2O_4 molecule can accept two electron pairs in its orbitals, *m* is as a rule equal to two.

Adducts of the nitrates of the corresponding metal with N_2O_4 or with the solvent are formed in mixed solvents: $M(NO_3)_2.N_2O_4$ and $M(NO_3)_2.nL$. The former complexes are usually nitrosonium compounds in the solid phase, like nitrosonium trinitratouranylate.

In the reactions of metallic uranium and its oxides with mixtures of N_2O_4 and organic solvents, the solvent was evaporated in order to obtain the final products. As a result, NTN was formed from mixtures of N_2O_4 with nitromethane and nitrobenzene whereas adducts of uranyl nitrate with two molecules of the organic base, namely $UO_2(NO_3)_2.2L$, were obtained with solvents such as CH_3CN, $(CH_3)_2CO$, $(C_2H_5)_2O$, $(CH_3)_2NCOH$, and $(CH_3)_2SO$.[14,16,82]

We may note that the formation of uranium(IV) compounds was not observed as a result of the reaction, only uranyl complexes being detected in the reaction products. Thus, as has been observed for gaseous and liquid N_2O_4, in mixtures of N_2O_4 with organic solvents the

first stage of the reaction is the oxidation of uranium to the hexavalent state:

$$U + 2\,[NO^+]\,[NO_3^-] \rightarrow UO_2^{2+} + 2\,N_2O_3. \quad (14)$$

Since NTN is formed only in the case of nitromethane and nitrobenzene, its formation cannot be accounted for by the high dielectric constant of the solvent, which is responsible according to Addison and co-workers,[82–84] for the heterolytic dissociation of N_2O_4. Indeed, adducts formed by the addition of two molecules of the solvent to uranyl nitrate are obtained in the reactions with acetonitrile, dimethylformamide, and dimethyl sulphoxide, which have higher dielectric constants (ε = 38.0, 36.1, and 44.5) than nitromethane and nitrobenzene (35.9 and 34.8 respectively).

The formation of the adducts agrees well with the increasing electron-donating capacity of the solvent. On passing from nitromethane and nitrobenzene to stronger bases, i.e. acetone, diethyl ether, dimethylformamide, and dimethyl sulphoxide, their donor numbers increase correspondingly: 2.7, 4.4, 17.0, 19.2, 26.6, and 29.8.[85] Thus the complexes $UO_2(NO_3)_2.N_2O_4$ for solvents having a low electron-donating capacity probably exist in solutions of N_2O_4. Their composition is better reflected by the formula $UO_2(NO_3)_2.N_2O_4$ than by $UO_2(NO_3)_2.2NO_2$, because the degree of the dissociation $N_2O_4 \rightleftarrows 2NO_2$ in liquid N_2O_4 is 140–500 times smaller than in the gas phase owing to the "cage" effect of the liquid.[86] In solution, the stability of the complex is apparently achieved via the stable isomer O_2N-NO_2,[87] which behaves as a bidentate neutral ligand. As the complex passes to the solid phase, the stability of this isomer diminishes and it is converted into the $ON-NO_3$ isomer with formation of a nitrosonium compound. The equilibrium in the heterolytic dissociation of liquid N_2O_4 has been displaced[88–91] by adding alkylammonium nitrates or nitrosyl chloride.

In terms of its electron-donating properties, N_2O_4 is probably close to nitrobenzene and stronger bases can compete with N_2O_4, displacing it from the inner coordination sphere of UO_2^{2+}.

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