Chemical stabilization of daughter ^{99m}Tc after the β-decay in chelate systems with molybdenyl-(^{99}Mo)

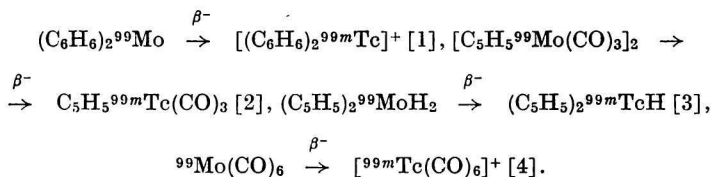ªV. MIKULAJ, ªP. RAJEC, and ᵇV. FABEROVÁ

ª*Department of Nuclear Chemistry, Faculty of Natural Sciences, Komenský University,*
801 00 Bratislava

ᵇ*J. Hronec Grammar School, 801 00 Bratislava*

Chemical consequences of the β-decay of ^{99}Mo in molecules of the type MoO_2L_2 (L is a chelating ligand) were studied. 8-Hydroxyquinoline, α-benzoinoxime, and N-benzoyl-N-phenylhydroxylamine were used as chelating agents. Kinetics of extraction of ^{99}Mo(VI) — ^{99m}Tc with chloroform solutions of chelating agents from aqueous HCl or H_2SO_4, kinetics of stripping of chelates from chloroform solutions and extractability of Tc(VII), Tc(V), and Tc(IV) were investigated. According to the results, daughter ^{99m}Tc is stabilized in oxidation degree V in high yields (80—100%). ^{99m}Tc(V) is in general unstable and its stability in the chloroform—water two-phase system depends on its ability to form chelates with chelating agents. The formation of ^{99m}Tc(V) is explained by preservation of the metal—oxygen bonds which are not much affected by phenomena accompanying the β-decay. The notable stabilizing effect on ^{99m}Tc(V) oxocation is exhibited mainly by 8-hydroxyquinoline and α-benzoinoxime. The former stabilized daughter ^{99m}Tc as a chelate of the assumed composition TcO_2Ox. Its yield (90—100%) was only slightly dependent on the aqueous phase composition.

Daughter ^{99m}Tc formed by the β-decay from ^{99}Mo bonded in an organic molecule is stabilized in a relatively high yield and the structure of the primary molecular ion is maintained if it corresponds to a stable compound of technetium. In such a case, the recoil energy of mother nuclide exhibits no marked effect on the fragmentation of the primary molecular ion. This assumption was confirmed for the following disintegrations:

$$(C_6H_6)_2{}^{99}Mo \xrightarrow{\beta^-} [(C_6H_6)_2{}^{99m}Tc]^+ [1], [C_5H_5{}^{99}Mo(CO)_3]_2 \rightarrow$$

$$\xrightarrow{\beta^-} C_5H_5{}^{99m}Tc(CO)_3 [2], (C_5H_5)_2{}^{99}MoH_2 \xrightarrow{\beta^-} (C_5H_5)_2{}^{99m}TcH [3],$$

$$^{99}Mo(CO)_6 \xrightarrow{\beta^-} [^{99m}Tc(CO)_6]^+ [4].$$

On the other hand, the knowledge of chemical consequences of the ^{99}Mo β-decay especially in two-phase systems is helpful for the proper choice of convenient systems for widely used generators of ^{99m}Tc. In general, chemical consequences of the ^{99}Mo decay can facilitate the separation of daughter ^{99m}Tc but they also can cause its undesirable retention in the separation. The latter assumption was made in a work dealing

with column generators of ^{99m}Tc [5]. Therefore the study of the chemical consequences of the ^{99}Mo decay in the extraction systems is specially interesting.

Molybdenum(VI) forms with reagents of the HL type (*e.g.* 8-hydroxyquinoline) neutral complexes of the general composition MoO_2L_2 which precipitate from aqueous solutions and can be extracted to inert solvents. Chelates of the MoO_2L_2 type have been for longer time used in analytical chemistry of molybdenum, namely in extraction procedures [6]. Among others, chelates of 8-hydroxyquinoline and its derivatives, β-diketones, α-benzoinoxime, and *N*-benzoyl-*N*-phenylhydroxylamine were studied most thoroughly. In the present work we tried to determine the chemical forms of the stabilization of daughter ^{99m}Tc formed by the β-decay from ^{99}Mo, being a part of MoO_2L_2 molecule. We chose 8-hydroxyquinoline, α-benzoinoxime, and *N*-benzoyl-*N*-phenylhydroxylamine as chelating agents. If the primary molecular ion is not fragmented after the ^{99}Mo decay, the stabilization of technetium in the form of $[^{99m}TcO_2L_2]^+$ or $^{99m}TcO_2L_2$ could be expected; *i.e.* the compounds representing atypical coordination or atypical oxidation degree of technetium should be formed.

Experimental

Chemicals, radionuclides, and instruments

8-Hydroxyquinoline, C_9H_7ON (HOx), α-benzoinoxime, $C_{14}H_{13}O_2N$ (cupron, HBO) were anal. grade (Lachema, Brno). *N*-Benzoyl-*N*-phenylhydroxylamine, $C_{13}H_{11}O_2N$ (HBPHA) was synthesized [7] and purified by recrystallization from ethanol. Chloroform, anal. grade, was freshly distilled.

Dioxo-bis(*N*-benzoyl-*N*-phenylhydroxylaminato)molybdenum(IV) chelate was prepared by the method described in [8].

For $MoO_2(C_{13}H_{10}O_2N)_2$ (552.4) calculated: 56.52% C, 3.62% H, 5.07% N; found: 56.98% C, 3.82% H, 5.01% N.

Dioxo-(8-hydroxyquinolinato)rhenium(V) chelate, $ReO_2Ox \cdot 2H_2O$, synthesized by the method of the Polish authors [9] was identified by the i.r. spectra.

The specific activity of ^{99}Mo was $100-200$ Ci kg^{-1}, in the form of aqueous solution of ammonium molybdate. ^{99m}Tc was separated from ^{99}Mo by extraction to methyl ethyl ketone [10]; after evaporation of ketone ^{99m}Tc was dissolved in a convenient solvent. ^{99}Tc was used in the form of aqueous solution of NH_4TcO_4 (The Radiochemical Centre, Amersham).

Infrared spectra were recorded on a UR-20 (Zeiss, Jena) spectrometer using the NaCl optics. Activities of ^{99m}Tc and ^{99}Mo were measured with a scintillation counter NaI(Tl) connected with a one-channel spectrometer VA-M-120 (Vakutronik, GDR) in the range of energies $0.14-0.18$ MeV. Activity of ^{99}Tc was measured with a plastic scintillator SPD-22 (Tesla, Přemyšlení).

Methods of experiments

The following properties of daughter ^{99m}Tc were studied:

1. Kinetics of extraction of aqueous solutions of ^{99}Mo$-^{99m}$Tc mixtures with chloroform solutions of chelating agents.

2. Kinetics of stripping of chloroform solutions of ^{99}MoO$_2$L$_2$ with accumulated daughter ^{99m}Tc.

3. Extraction properties of technetium in oxidation degrees Tc(VII), Tc(V), and Tc(IV).

4. Chromatographic properties of technetium.

Aqueous solutions of ammonium molybdate-(99Mo) with the equilibrium content of 99mTc were extracted with the chloroform solutions of chelating agents. Test tubes filled with equal volumes of the aqueous and organic phase (10 ml each) were shaken for 6 hours. In certain time intervals, 0.1-ml samples of both phases were repeatedly taken and from their measured activities the extraction percents of 99Mo (R_{Mo}) and 99mTc (R_{Tc}) in the organic phase were calculated from equations (1) and (2):

$$R_{Mo} = \frac{n_0}{n_0 + n_w} 100\%, \tag{1}$$

where n_0 and n_w are the counting rates of samples of the organic and aqueous phase respectively, measured 60—70 hours after separation of the phases

$$R_{Tc} = \frac{n_0\, 100 - (1 - k)\, R_{Mo}(n_0 + n_w)}{k(n_0 + n_w)}, \tag{2}$$

where n_0 and n_w are the counting rates measured immediately after separation of the phases and k is an empirical coefficient [3].

By the back extraction the labelled chelate dissolved in chloroform with accumulated 99mTc was stripped by an equal volume of diluted HCl or H_2SO_4. Samples of both phases were taken and the extraction percents of 99Mo and 99mTc in the organic phase were calculated from equations (1) and (2) similarly as in the extractions.

Technetium in lower oxidation degrees was prepared by reduction of Tc(VII) with concentrated HCl (99Tc(V)) [11] or 30% HBr (99Tc(IV)) [12]. Stock solutions of 99Tc(V) were prepared in concentrated HCl, solutions of 99Tc(IV) in 6 N-HCl. Oxidation degrees were identified by paper chromatography [11] and u.v. spectra. Extractions of 99Tc were similar to those of 99Mo.

Some extractions and strippings were carried out in an inert atmosphere; in such cases the solutions were degassed by bubbling nitrogen through them. Whatman No. 3 paper was used as a carrier for the ascending chromatography.

Results

8-Hydroxyquinoline and α-benzoinoxime

According to the results of extraction of technetium, in the form of TcO_4^- it is practically not extracted with chloroform solutions of 8-hydroxyquinoline (0.02 M-HOx) or α-benzoinoxime (1 × 10⁻³ M-HBO) from aqueous sulfuric acid (0.1—3 N) or hydrochloric acid (0.1—2 N), neither in trace concentrations with 99mTc nor in weighable amounts with 99Tc. The extraction percent of 99mTcO₄⁻ did not exceed 2—5% during 6 hours of extraction.

However, when the equilibrium mixture of 99Mo(VI)—99mTc was extracted with chloroform solutions of HOx or HBO from diluted H_2SO_4 or HCl, daughter 99mTc gradually passed into the organic phase and its transfer depended directly upon the transfer of 99Mo. As the kinetics of extractions are the same or alike, daughter technetium is extracted in the same way as molybdenum and its transfer does not depend on the concentration of acid (Figs. 1 and 2). Analogous results were obtained for the systems 99Mo(VI)—H_2SO_4—HOx and 99Mo(VI)—HCl—HBO.
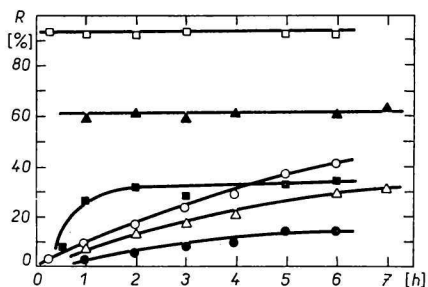
Fig. 1. Kinetics of extraction of
^{99}Mo(VI) — ^{99m}Tc with chloroform
solution of 8-hydroxyquinoline.

R — extraction percent of ^{99m}Tc or
^{99}Mo in chloroform.

○ ^{99m}Tc; □ ^{99}Mo, aqueous phase
0.1 N-HCl, initial concentrations [Mo]$_w$ =
= 2×10^{-6} M, [HOx]$_0$ = 0.02 M; △ ^{99m}Tc;
▲ ^{99}Mo, aqueous phase 0.1 N-NaCl, initial
concentration [Mo]$_w$ = 4×10^{-3} M,
[HOx]$_0$ = 0.1 M; ● ^{99m}Tc; ■ ^{99}Mo,
aqueous phase 2 N-HCl, initial concen-
tration [Mo]$_w$ = 2×10^{-6} M, [HOx]$_0$ =
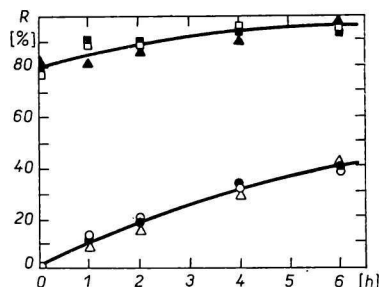= 0.02 M.

Fig. 2. Kinetics of extraction of
^{99}Mo(VI) — ^{99m}Tc with chloroform solu-
tion of α-benzoinoxime.

R — extraction percent of ^{99m}Tc or ^{99}Mo
in chloroform. Initial concentrations
[Mo]$_w$ = 8×10^{-4} M, [HBO]$_0$ = 0.01 M.
○ ^{99m}Tc; □ ^{99}Mo, aqueous phase
0.2 N-H$_2$SO$_4$; △ ^{99m}Tc; ▲ ^{99}Mo, aqueous
phase 1 N-H$_2$SO$_4$; ● ^{99m}Tc; ■ ^{99}Mo,
aqueous phase 2.5 N-H$_2$SO$_4$.

If we assume that

1. the portion of molybdenum in the organic phase is constant throughout the extrac-
tion time;

2. daughter ^{99m}Tc appearing in the aqueous phase as ^{99m}TcO$_4^-$ does not pass into
organic phase;

3. daughter ^{99m}Tc appearing in the organic phase remains there or its certain portion
is quickly (compared with the rate of its formation) and irreversibly transferred into
aqueous phase; then the expression (3) should be valid for the time dependence of the
apparent transfer of ^{99m}Tc to the organic phase (*i.e.* kinetics of the ^{99m}Tc extraction):

$$R_{\text{Tc}}(t) = \alpha R_{\text{Mo}}(1 - e^{-\lambda t}) . \tag{3}$$

In equation (3), R_{Tc} is the extraction percent of ^{99m}Tc in the organic phase at the
time t, R_{Mo} is the extraction percent of ^{99}Mo in the organic phase, ($R_{\text{Mo}}(t)$ = const),
λ is the decay constant and α is a ratio between the amount of ^{99m}Tc remaining in the
organic phase and its total amount formed in this phase during a time interval. Under
the above assumptions we can also write

$$\alpha R_{\text{Mo}} = \frac{R_{\text{Tc}}(t)}{(1 - e^{-\lambda t})} , \tag{4}$$

which enables to calculate the α value from determined R_{Tc}. The condition R_{Mo} = const
is fulfilled well for the extraction of ^{99}Mo(VI) — ^{99m}Tc with the chloroform solution of

Table 1

Values of αR_{Mo} for extraction of $^{99}Mo(VI)-^{99m}Tc$ with chloroform solutions of 8-hydroxyquinoline from the medium 0.1 N-NaCl (0.1 M-HOx) and 0.1 N-HCl (0.02 M-HOx)

t [hours]	0.1 N-NaCl		0.1 N-HCl	
	R_{Tc} [%]	αR_{Mo}	R_{Tc} [%]	αR_{Mo}
1	8.0	63.0	10.3	93.0
2	13.4	65.0	17.0	83.0
3	17.0	67.8	23.4	80.0
4	21.3	57.5	30.0	81.0
5	—	—	38.0	86.5
6	29.7	59.4	42.0	84.0
7	32.4	58.4	—	—
	$\bar{R}_{Mo} = 60.3\%$, $\alpha \bar{R}_{Mo} = 61.8$, $\alpha = 1.02 \pm 0.03$		$\bar{R}_{Mo} = 93.0\%$, $\alpha \bar{R}_{Mo} = 84.6$, $\alpha = 0.91 \pm 0.04$	

HOx from the medium of 0.1 N-NaCl and 0.1 N-HCl (Fig. 1). Values of αR_{Mo} at different extraction time are listed in Table 1.

Besides, if the time of extraction is long enough compared with the half life of the ^{99m}Tc decay (8—10 T, *i.e.* 50—60 hours), the time factor $1 - \exp(-\lambda t) \doteq 1$ and from equation (3) we then obtain

$$\alpha = \frac{(R_{Tc})_{\infty}}{(R_{Mo})_{\infty}}, \tag{5}$$

where the subscript ∞ stands for the portions of ^{99m}Tc and ^{99}Mo after that long enough time, *i.e.* for the equilibrium portions. The α values calculated from equations (4) and (5) are listed in Table 2.

Table 2

Mean values of α for extraction systems $^{99}Mo(VI)-^{99m}Tc$—chloroform solutions of α-benzoinoxime or 8-hydroxyquinoline

Extraction system		α	
Organic phase (chloroform)	Aqueous phase	Calculated from equation	
		(2)	(3)
	0.1 N-HCl	0.90	0.91
	2 N-HCl	—	0.90
1×10^{-3} M-HBO	0.2 N-H$_2$SO$_4$		
	1 N-H$_2$SO$_4$	0.90	—
	2.5 N-H$_2$SO$_4$		
0.1 M-HOx	0.1 N-NaCl	1.0	1.0
0.02 M-HOx	0.1 N-HCl	0.91	—
	2 N-HCl	0.91	—

Extractability of Tc in lower oxidation degrees (V and IV) with the chelating agents was investigated using ^{99}Tc nuclide. It was found that ^{99}Tc(V) (starting concentration 1×10^{-4} M) was effectively extracted with 0.1 M-HOx in chloroform from 0.02 N-HCl (90% extraction) up to 0.2 N-HCl (81% extraction) especially when the extraction was carried out in an inert atmosphere, or when the starting strongly acidic solution of ^{99}Tc(V) (in 6 N-HCl) was diluted in the course of shaking to the acidity approx. 0.6 N-HCl. Otherwise a fast oxidation or disproportionation of Tc(V) to Tc(VII) and Tc(IV) took place. Under the same conditions ^{99}Tc(IV) was not, or only very slightly, extracted. Similar results were obtained for the extraction of Tc(V) and Tc(IV) with chloroform solutions of HBO.

Extraction of Tc(V) with a chloroform solution of HOx was used for the preparation of 8-hydroxyquinolinatotechnetium(V) chelate. A solution of ^{99}Tc(V) (2 mg of technetium per 1 ml) was shaken with 10 ml of 0.1 M-HOx in chloroform and, gradually, 9 ml of water was added. The organic phase, turned to carmine red, was repeatedly washed with 1 N-HCl and distilled water. After evaporation of chloroform, a reddish substance, well soluble in chloroform, in methanol and slightly soluble in carbon tetrachloride, was obtained. This technetium oxinate was then used for measuring the i.r. spectra (Fig. 3).
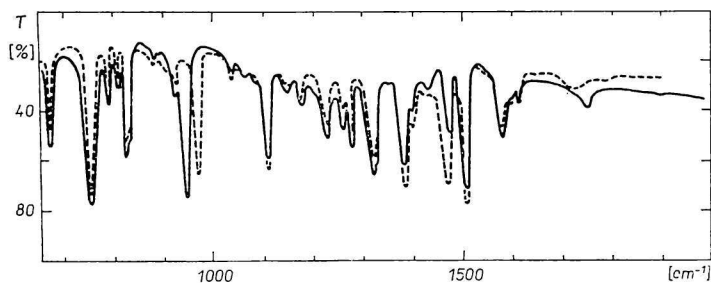

Fig. 3. Infrared spectra of dioxo-bis(8-hydroxyquinolinato)rhenium(V) and 8-hydroxy-quinolinatotechnetium(V)-(^{99}Tc) chelates (suspensions in nujol).
— — — $ReO_2O_x \cdot 2H_2O$; ——— Tc(V) oxinate.

N-Benzoyl-N-phenylhydroxylamine

Analogously to HOx and HBO, acidic solutions (HCl or H_2SO_4) of ammonium molybdate-(^{99}Mo) were extracted with chloroform solutions of HBPHA during 6 hours and
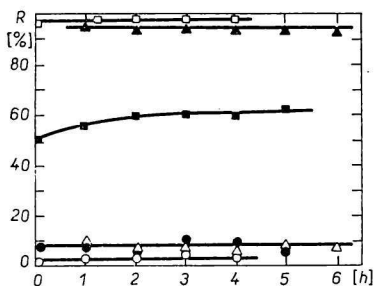

Fig. 4. Kinetics of extraction of ^{99}Mo(VI)—^{99m}Tc with chloroform solution of N-benzoyl-N-phenylhydroxylamine.

R — extraction percent of ^{99m}Tc or ^{99}Mo in chloroform. Initial concentrations $[Mo]_w = 1.5 \times 10^{-4}$ M, $[HBPHA]_0 = 3 \times 10^{-3}$ M.

○ ^{99m}Tc; □ ^{99}Mo, aqueous phase 0.1 N-HCl; △ ^{99m}Tc; ▲ ^{99}Mo, aqueous phase 1 N-HCl; ● ^{99m}Tc; ■ ^{99}Mo, aqueous phase 6 N-HCl.
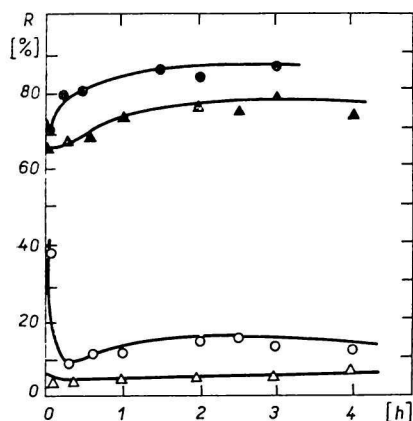
Fig. 5. Kinetics of stripping of chloroform solutions of $^{99}MoO_2(BPHA)_2 - ^{99m}Tc$. R — extraction percent of ^{99m}Tc in chloroform. Distribution of ^{99}Mo is not marked. Initial concentration $[MoO_2(BPHA)_2]_0 = 1.5 \times 10^{-4}$ M.
△ decay in solid chelate, aqueous phase 2 N-HCl; ○ decay in chloroform solution, aqueous phase 0.02 N-HCl (inert atmosphere); ▲ decay in solid chelate, initial concentration $[HOx]_0 = 0.1$ M, aqueous phase 0.02 N-HCl (inert atmosphere); ● decay in chloroform solution, initial concentration $[HOx]_0 = 0.1$ M, aqueous phase 0.02 N-HCl.

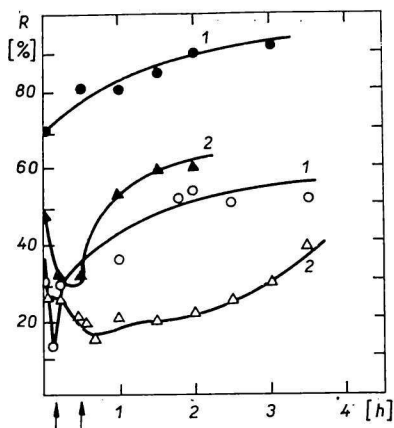*Fig. 6.* Kinetics of stripping of chloroform solutions of $^{99}MoO_2(BPHA)_2 - ^{99m}Tc$ with 0.02 N-HCl in an inert atmosphere. R — extraction percent of ^{99m}Tc in chloroform. Distribution of ^{99}Mo is not marked. Initial concentrations $[MoO_2(BPHA)_2]_0 = 1 \times 10^{-4}$ M, $[HOx]_0 = 0.1$ M. HOx added after 10 minutes (*1*) and 30 minutes (*2*) of shaking.
○, △ decay in solid phase; ●, ▲ decay in chloroform solution.

portions of ^{99}Mo and ^{99m}Tc in the organic phase were calculated from equations (*1*) and (*2*). The course of extraction from solutions of sulfuric acid and hydrochloric acid was similar (Fig. 4). Although in this case daughter ^{99m}Tc was formed in the organic phase, it passed relatively quickly (if compared with the rate of formation) into the aqueous phase, its portion in chloroform did not depend upon the portion of ^{99}Mo in the organic phase and remained constant throughout shaking. Paper chromatography of aqueous phase was carried out (eluent 0.2 N-HCl) and ^{99m}Tc was identified only in the oxidation degree VII.

The synthesized dioxo-bis(*N*-benzoyl-*N*-phenylhydroxylaminato)molybdenum(VI)--(^{99}Mo) chelate with accumulated daughter ^{99m}Tc was dissolved in chloroform and stripped with diluted HCl or H_2SO_4. In the second series of experiments, solutions of the labelled chelate were stripped after standing for 2—3 days in the dark so that daughter ^{99m}Tc was formed in solutions. Since lower oxidation degrees of technetium at low concentration, especially Tc(V), are known to oxidize easily to Tc(VII), further strippings were carried out in an inert atmosphere and 8-hydroxyquinoline was added to the chloroform solution of chelate at the start of stripping (Fig. 5). During further strippings, 8-hydroxyquinoline was added after 10 and 30 minutes of shaking (Fig. 6).
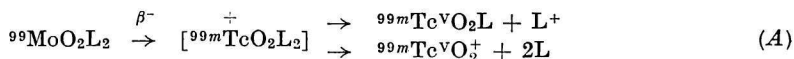
Discussion

8-Hydroxyquinoline and α-benzoinoxime

HOx, HBO as well as HBPHA form with Mo(VI) chelate compounds of the MoO_2L_2 type, easily extracted with chloroform. The composition of the extractable Mo(VI) chelates was confirmed for HOx [13, 14], HBPHA [15] and it was also assumed for HBO [16].
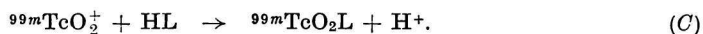
A possible interpretation of the kinetics of extraction of the $^{99}Mo(VI)-^{99m}Tc$ mixture with chloroform solutions of HOx and HBO (Figs. 1 and 2) is that daughter ^{99m}Tc formed by the β-decay of ^{99}Mo existing in the chemical form of $^{99}MoO_2Ox_2$ or $^{99}MoO_2(BO)_2$ is stabilized in the form of extractable chelate compounds, contrary to ^{99m}Tc formed in the oxidation degree VII by the decay of $^{99}Mo(VI)$ in the aqueous phase. TcO_4^- obviously does not form chelate compounds and thus cannot be extracted with the chloroform solution of a chelating agent. After French authors [17], $^{99m}Tc(VII)$, i.e. $^{99m}TcO_4^-$, is the only form of stabilization of technetium formed by the $^{99}Mo(VI)$ decay in acidic, neutral as well as alkaline aqueous solutions. The yield of chelated ^{99m}Tc (100α, %) did not depend markedly upon the concentration of acid in the aqueous phase when the α portions were calculated from the course of extraction or from the established equilibrium state (Table 2). The quantity αR_{Mo} remained constant in the course of extraction (Table 1), which confirmed the validity of equation (3) as well as the above-stated assumptions.

A high degree of extraction of $^{99}Tc(V)$ from $0.02-0.6$ N-HCl with chloroform solutions of HOx or HBO, in contrast to the low extraction of Tc(VII) and $^{99}Tc(IV)$, corroborates the stabilization of daughter ^{99m}Tc just in the oxidation degree V. Also according to *Kuznetsov et al.* [18], Tc(VII) and Tc(IV) are not extracted with the chloroform solution of HOx from solutions at pH 7—10 N-HCl even after 10 hours of extractions. Infrared spectra of technetium oxinate obtained from the chloroform layer after extraction with HOx and those of $ReO_2Ox \cdot 2H_2O$ were much alike (Fig. 3). The absorption band at 1100 cm^{-1} is characteristic of metal oxinates, that at 968 cm^{-1} in the spectrum of rhenium oxinate is close to the wavenumber value corresponding to rhenium oxo-compounds (vibrations of the $Re=O$ bond; see [19], p. 405). Analogously, the band at 946 cm^{-1} in the spectrum of technetium oxinate may be attributed to the vibration of the $Tc=O$ bond. In both the spectra no absorption was observed in the region about 3400 cm^{-1}, characteristic for OH groups.

It follows from the above-said that after the decay of ^{99}Mo in the $^{99}MoO_2Ox_2$ or $^{99}MoO_2(BO)_2$ molecules, daughter ^{99m}Tc is stabilized in the form of a chelate oxo-complex of $^{99m}Tc(V)$. Chemical consequences of the β-decay of Mo(VI) in dioxo-chelates are determined primarily by the change of an electric charge of the central atom while the recoil energy does not play an important role, analogously to the behaviour observed at molecular compounds of molybdenum [1—4]. In general, the dioxo group in chelates of the MoO_2L_2 type acts as a central pseudoatom which is caused by the strong $M-O$ bond. Chelate complex of $^{99m}Tc(V)$ may appear due to the fragmentation of a primary molecular ion

$$^{99}MoO_2L_2 \xrightarrow{\beta^-} [^{99m}TcO_2L_2]^{\div} \rightarrow \begin{array}{l} ^{99m}Tc^VO_2L + L^+ \\ ^{99m}Tc^VO_2^+ + 2L \end{array} \qquad (A)$$

The fragmentation is followed by chelation of the ^{99m}Tc dioxo-cation by an exchange reaction with non-active MoO_2L_2 (B) or with chelating agent (C) if it is present in excess

44

$$2\ ^{99m}TcO_2^+ + MoO_2L_2\ \rightarrow\ 2\ ^{99m}TcO_2L + MoO_2^{2+}, \tag{B}$$

$$^{99m}TcO_2^+ + HL\ \rightarrow\ ^{99m}TcO_2L + H^+. \tag{C}$$

Dioxo-compounds of Re(V) are liable to protonization [19, p. 407]; it is proved *e.g.* by the existence of two Re(V) oxinates, $ReO_2Ox \cdot 2H_2O$ and $ReO(OH)Ox_2$ [9]. Thus for chelates of Tc(V) a similar reaction cannot be excluded either

$$TcO_2L + HL\ \rightarrow\ TcO(OH)L_2.$$
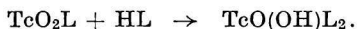
According to the report [20] on experiments with stripping of chloroform solutions of $^{99}MoO_2Ox_2$ with accumulated daughter ^{99m}Tc, the chelated ^{99m}Tc remained in the organic phase even when 6 N-HCl and 6 hours of shaking of the phases were applied. It corroborates an extraordinary kinetic inertness of the oxinate complexes of daughter ^{99m}Tc.

N-Benzoyl-N-phenylhydroxylamine

Kinetics of extraction of the $^{99}Mo(VI) - ^{99m}Tc$ mixture with chloroform solutions of HBPHA from solutions of HCl as well as H_2SO_4 (Fig. 4) was different from the extraction made by chloroform solutions of HOx and HBO (Figs. 1 and 2). When using HBPHA, daughter ^{99m}Tc, although being generated in the organic phase, very quickly passed into aqueous phase compared with the rate of its formation and its portion in the organic phase did not depend on the portion of $^{99}Mo(VI)$. Since ^{99m}Tc was found in the aqueous phase only in oxidation degree VII by paper chromatography, *i.e.* in the form of $^{99m}TcO_4^-$, it is doubtful whether the assumptions of the stabilization of daughter ^{99m}Tc in molybdenyl-(^{99}Mo) chelates is applicable also to $^{99}MoO_2$ (BPHA)$_2$. It concerns mainly the formation of ^{99m}Tc in oxidation degree V. We utilized the ability of HOx to stabilize unstable Tc(V) and made strippings of the synthesized chelate $^{99}MoO_2(BPHA)_2$ with accumulated ^{99m}Tc in the presence of HOx and in an inert atmosphere. The influence of HOx upon the course of stripping was convincing (Fig. 5), and its explanation follows from the properties of Tc(V) and HOx found in the first part of this work. After the β-decay of ^{99}Mo in the $^{99}MoO_2(BPHA)_2$ molecule as well as in the oxinate and α-benzoinoxinate chelates, daughter ^{99m}Tc is formed in oxidation degree V but $^{99m}Tc(V)$ is not stabilized by the chelating agent and on the contact of chloroform solutions with aqueous phase it is stripped and relatively quickly oxidized to $^{99m}Tc(VII)$.

The last conclusion was confirmed by experiments where HOx was added in the course of stripping, 10 and 30 minutes after the organic and aqueous phase were brought into contact (Fig. 6). The addition of HOx in the 30th minute of stripping (the decay of ^{99}Mo in the solid chelate) did not increase practically the portion of ^{99m}Tc stripped in the aqueous phase, *i.e.* nearly all daughter $^{99m}Tc(V)$ was already oxidized to $^{99m}Tc(VII)$. Oxidation of ^{99m}Tc formed by the decay in the solid phase was remarkably faster than in the case of ^{99m}Tc accumulated in chloroform solution of chelate which stabilizes $^{99m}Tc(V)$ to a certain extent. It should be noted that the increase of the R_{Tc} portion occurring after approx. 30 minutes of stripping in the presence of HOx is characteristic of the chemical consequences of the β-decay in $^{99}MoO_2Ox_2$ chelate and it corroborates the following exchange reaction taking place at the excess of HOx

$$^{99}MoO_2(BPHA)_2 + 2HOx\ \longrightarrow\ ^{99}MoO_2Ox_2 + 2HBPHA.$$
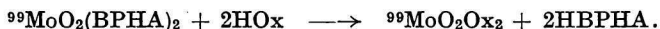
Thus the increase of R_{Tc} after $30-60$ minutes of stripping is typical for $^{99}MoO_2Ox_2$ (Fig. 2).

The results of experiments with extraction of ^{99}Tc in oxidation degrees VII, V, and IV at rather high concentration of HBPHA (0.1 M in chloroform) from diluted H_2SO_4

showed that the degree of extraction of ^{99}Tc increased with the increasing concentration of the acid (0.2 — 6 N-H_2SO_4) and decreased in the order ^{99}Tc(VII), ^{99}Tc(V), and ^{99}Tc(IV) when the concentration of H_2SO_4 did not change. *Fouché* [21] studied thoroughly the mechanism of extraction of $HReO_4$ and $HTcO_4$ from $HClO_4$ and HCl media. He concluded that in both cases the compounds of the type $HTCO_4 \cdot HBPHA$ are extracted. The mechanism of extraction of the lower oxidation degrees of Tc requires more detailed study.

Study of the chosen chelate systems with molybdenyl shows that after the β-decay ^{99}Mo in the molecule of the MoO_2L_2 type the daughter ^{99m}Tc is stabilized in the case of HOx and HBO as oxo-chelates of ^{99m}Tc(V). They are analogous to Re(V) chelates and for Tc(V) they have been unknown till now. We succeeded in obtaining the chelate of this type by a modified extraction process using HOx. In the case of HBPHA the primary molecular ion is fragmented and generated ^{99m}Tc(V) is oxidized to ^{99m}Tc(VII) in aqueous phase. The proposed mechanism of the stabilization (*A*) of daughter ^{99m}Tc may be valid also for other chelate compounds of the MoO_2L_2 type.

References

1. Baumgärtner, F., Fisher, E. O., and Zahn, U., *Chem. Ber.* **94**, 2198 (1961).
2. Baumgärtner, F., Fisher, E. O., and Zahn, U., *Naturwissenschaften* **49**, 156 (1962).
3. Mikulaj, V., Macášek, F., and Kopunec, R., *Chem. Zvesti* **27**, 23 (1973).
4. Nefiodov, V. D. and Mikulaj, V., *Radiokhimiya* **15**, 846 (1973).
5. Cífka, J. and Veselý, P., *Radiochim. Acta* **16**, 31 (1971).
6. Busev, A. I. and Rodionova, T. V., *Zh. Anal. Khim.* **26**, 578 (1971).
7. Shome, S. C., *Analyst* (London) **75**, 27 (1950).
8. Sinha, S. K. and Shome, S. C., *Anal. Chim. Acta* **24**, 33 (1961).
9. Przywarska-Boniecka, H. and Jeżowska-Trzebiatowska, B., *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **13**, 67 (1965).
10. Fadeeva, M. S., Pavlov, O. N., and Bakunina, V. V., *Zh. Neorg. Khim.* **3**, 165 (1958).
11. Shukla, S. K., *J. Chromatogr.* **21**, 92 (1966).
12. Ossicini, L., Saracino, F., and Lederer, M., *J. Chromatogr.* **16**, 524 (1964).
13. Bantysh, A. N., Dobizha, E. V., and Knyazev, D. A., *Zh. Neorg. Khim.* **12**, 2165 (1967).
14. Atovmyan, L. O. and Sokolova, Yu. V., *Zh. Strukt. Khim.* **12**, 851 (1971).
15. Bantysh, A. N., Knyazev, D. A., and Levina, O. V., *Zh. Neorg. Khim.* **9**, 2142 (1964).
16. Hoenes, H. J. and Stone, K. G., *Talanta* **4**, 250 (1960).
17. Ferradini, C., Carlier, R., Genet, M., and Pucheault, J., *Radiochim. Acta* **12**, 1 (1969).
18. Kuznetsov, V. I., Gudish, L. S., Rudenko, N. P., and Khadi Kadom Avad, *Radiokhimiya* **11**, 240 (1969).
19. Cotton, A. F. and Wilkinson, G., *Advanced Inorganic Chemistry*. Part 3. (Russian translation.) Mir, Moscow, 1969.
20. Hudák, V., *Diploma Thesis*. Faculty of Natural Sciences, Komenský University, Bratislava, 1969.
21. Fouché, K. F., *J. Inorg. Nucl. Chem.* **33**, 857 (1971).