VOLATILE TECHNETIUM CARBONYL COMPOUNDS AND PROSPECTS FOR THEIR APPLICATION

G.V. Sidorenko[1], A.E. Miroslavov[1], D.N. Suglobov[1], A.A. Lumpov[1], and A.N. Yalfimov[2]

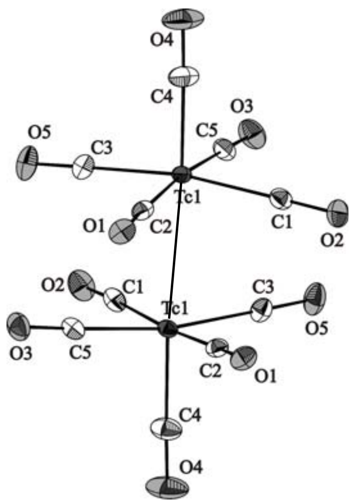
[1] Khlopin Radium Institute, Research and Production Association, Federal State Unitary Enterprise, 2-i Murinskii pr. 28, St. Petersburg, 194021 Russia

[2] Russian Research Centre for Radiology and Surgical Technologies, St. Petersburg–Pesochnyi, Russia

Chemical Forms of Volatile Tc Carbonyls

- Tc(0): $Tc_2(CO)_{10}$, $Tc_2(CO)_nL_m$, $[Tc(CO)_4]_n$?
- Tc(1+): $TcHlg(CO)_5$, $TcX(CO)_n$, $TcX(CO)_nL_m$ (X = anion, L = neutral σ-donor; n = 3–5; L = 1, 2)
- Tc(1–): $TcH(CO)_5$; $Tc(CO)_4(NO)$? (expected but not reported)
- Tc(3–): $Tc(CO)(NO)_3$? (expected but not reported)

Technetium decacarbonyl



Tc_2O_7 + CO → $Tc_2(CO)_{10}$ [Hileman et al., 1961; Hieber et al., 1961]; >200°C, >200 atm CO

$KTcO_4$ + HCOOH → no $Tc_2(CO)_{10}$; $[Tc(OH)(CO)_3]_4$ formed [our data]; >150°C, >150 atm

$Tc(CO)_6^+$ + H_2O (alkalization to pH ≥ 7) → $Tc_2(CO)_{10}$ + other products [our data]

Pentacarbonyltechnetium halides

$Tc_2(CO)_{10}$ + X_2 → $TcX(CO)_5$ and/or $[TcX(CO)_4]_2 \xrightarrow{CO} TcX(CO)_5$
[Hileman et al., 1962]

$K_2[TcX_6]$ + CO (Cu, 250–270 atm, 230–250°C) → $TcX(CO)_5$
[Hieber et al., 1965]

$KTcO_4$ + HX_{aq} + HCOOH (>100 atm, >150°C) → $TcX(CO)_5$
[under H_2: Osmanov, 1981; without H_2: Miroslavov et al., 1987]

Vacuum sublimation of pentacarbonyltechnetium halides

Vacuum sublimation:

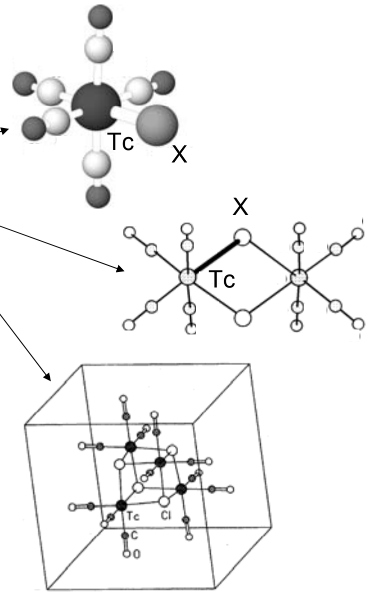
Fraction I: 60–80°C, $[TcX(CO)_5]$

Fraction II, 100–150°C, $[TcX(CO)_4]_2$

Fraction III, 230–250°C, $[TcX(CO)_3]_4$

Yield of fraction I: Cl < Br < I

Yield of fraction III: Cl > Br > I



Replacement of CO groups by neutral ligands

$$[TcX(CO)_5] + L \rightarrow [TcX(CO)_3L]_2 \text{ and/or } [TcX(CO)_3L_2]$$

Examples: L = THF, $MeOCH_2CH_2OMe$, MeCN, NH_3, Et_2NH, C_5H_5N;
$L_2 = NH_2CH_2CH_2NH_2$ (en), bipy, phen

Vacuum sublimation behavior:

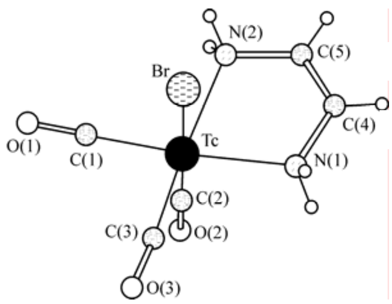
Full loss of L: O donors, MeCN, NH_3 → $[TcX(CO)_3]_4$

Partial loss of L: Et_2NH, C_5H_5N

Retention of L: en, bipy, phen

Structure of $TcBr(CO)_3{\cdot}en$

Vacuum sublimation at 200–220°C



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Halogen replacement: monodentate anions

TcHlg(CO)$_5$ + KCH$_3$COO (donor solvent) → Tc(CH$_3$COO)(CO)$_3$·*x*(solvent)

TcHlg(CO)$_5$ + AgY → TcY(CO)$_5$ + AgHlg (Y = CF$_3$COO, ClO$_4$)

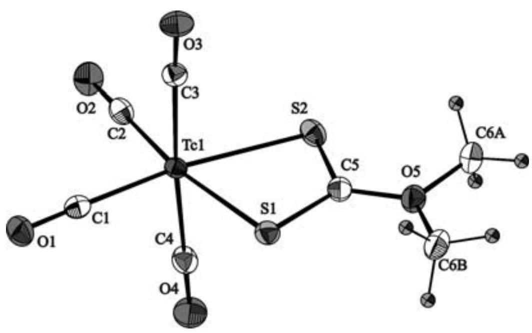
Tc(CF$_3$COO)(CO)$_5$: volatile but unstable to decarbonylation

Halogen replacement: bidentate anions

TcHlg(CO)$_5$ + M^{I}Y (donor solvent) → TcY(CO)$_3$·solvent

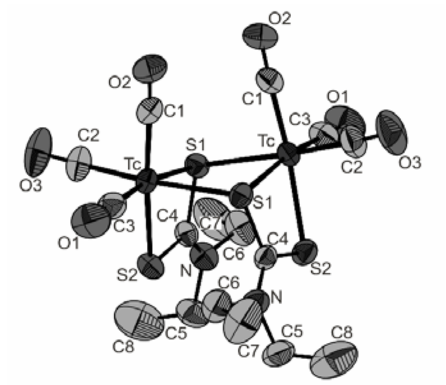
TcHlg(CO)$_5$ + M^{I}Y (inert solvent) → TcY(CO)$_4$

Y = β-diketonate, Et$_2$NCS$_2$, MeOCS$_2$

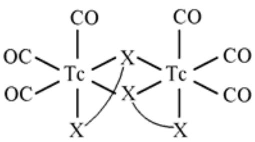


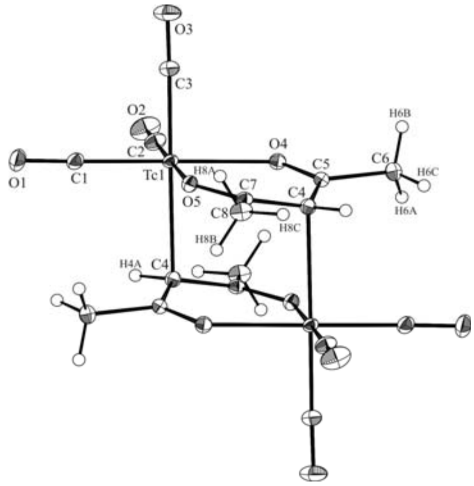
Molecular structure of Tc(MeOCS$_2$)(CO)$_4$ (with disordered Me groups)

Dimers $[TcY(CO)_3]_2$ (Y = bidentate anion)



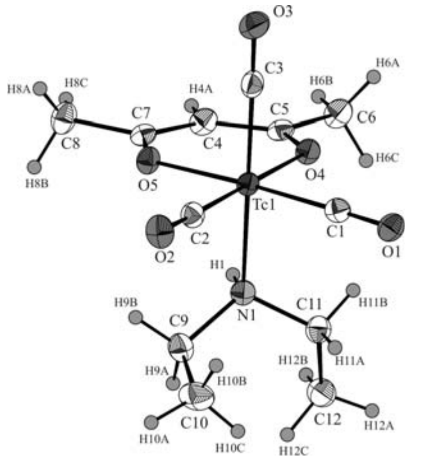
$[Tc(Et_2NCS_2)(CO)_3]_2$, “common” dimer;
topology:

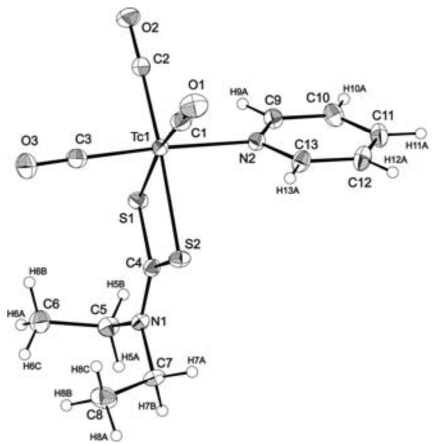




$[Tc(MeCOCHCOMe)(CO)_3]_2$:
“cage” dimer

Halogen replacement: bidentate ligands + neutral σ donor, $[TcY(CO)_3L]$

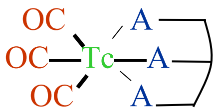




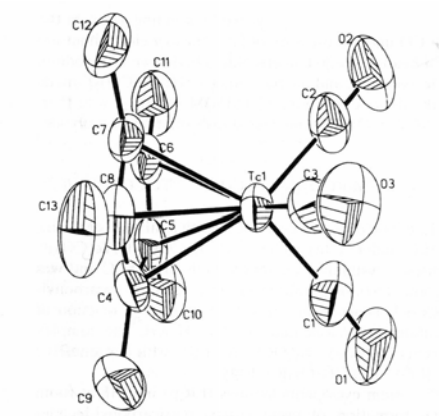
$[Tc(MeCOCHCOMe)(CO)_3(Et_2NH)]$ $[Tc(Et_2NCS_2)(CO)_3(C_5H_5N)]$

One-step synthesis from $TcCl(CO)_5$ with Y = $CF_3COCHCOAlk$:
$TcCl(CO)_5 + HY + Et_2NH \rightarrow [TcY(CO)_3(Et_2NH)]$

Halogen replacement: tridentate ligands



$TcCl(CO)_5$ + NaCp/THF → $TcCp(CO)_3$



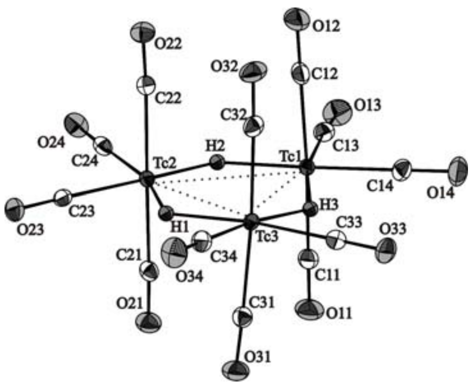
Structure of $Tc(C_5Me_5)(CO)_3$ [Raptis et al., 1991]

Technetium carbonyl hydrides

$Tc_2(CO)_{10}$ + Na-amalgam → $[Tc(CO)_5]^-$; acidification → $TcH(CO)_5$ [Hileman et al., 1962]

$Tc(CO)_4^-$ + $BH_3{\cdot}THF$ (THF, CO, room temperature) → $[Tc_3H_3(CO)_{12}]$ [Alberto et al., 1996]

$Tc(CO)_6^+$ + H_2O (alkalization to pH ≥ 7) → precipitate; heating → $[Tc_3H_3(CO)_{12}]$ + other products [our data]



Molecular structure of $[Tc_3H_3(CO)_{12}]$ [our data]; Alberto et al., 1996: similar molecular structure but different crystal packing

Solution and gas-phase IR spectra of technetium carbonyls (ν_{CO}, cm^{-1})

Compound	Solution (solvent)	Gas
$[TcI(CO)_5]$	2143 w, 2053 s, 2022 w, 1997 m (CCl_4)	2061 s, 2005 m
$[TcBr(CO)_5]$	2150 w, 2057 s, 2025 w, 1994 m (CCl_4)	2062 s, 2000 m
$[TcBr(CO)_3]_4$	2049, 1950 ($CHCl_3$)	2063, 1982
$[TcCl(CO)_3]_4$	2041, 1944 ($CHCl_3$)	2065, 1984
$[TcBr(CO)_3(en)]$	2039, 1942, 1905 ($CHCl_3$)	2049, 1965, 1919
$Tc_2(CO)_{10}$	2064 m, 2017 s, 1983 m (hexane)	2069 m, 2027 s, 1994 m
$[Tc(PTFA)(CO)_3]_2$	2062 m, 2047 s, 1964 m, 1950 s, 1937 s (CCl_4)	2065 m, 2052 s, 1976 m, 1962 s, 1949 s
$[Tc(PTFA)(CO)_3(Et_2NH)]$	2040, 1939, 1916 (CCl_4)	2048, 1956, 1934

PTFA = $CF_3COCHCOCMe_3^-$

Mass spectra of technetium carbonyl halides

$[TcX(CO)_5]^+$ ---→ $[Tc(CO)_5]^+$

$[TcX(CO)_5]^+$ ↓–CO $[TcX(CO)_4]^+$ ↓–CO … ↓–CO $[TcX]^+$ ↓–X Tc^+ (major pathway)

$[Tc(CO)_5]^+$ ↓–CO $[Tc(CO)_4]^+$ ↓–CO … ↓–CO Tc^+ (minor pathway)

$[Tc_4X_4(CO)_{12}]^+$ ↓–CO $[Tc_4X_4(CO)_{11}]^+$ ↓–CO … ↓–CO $[Tc_4X_4]^+$ ↓ Further fragmentation

Mass spectra of technetium carbonyl complexes with organic ligands

$[TcBr(CO)_3(en)]^+$
↓–CO
$[TcBr(CO)_2(en)]^+$
↓–CO
$[TcBr(CO)(en)]^+$
↓–CO
$[TcBr(en)]^+$
↓
$[TcBr(en) - H_2]^+$
↓
$[TcBr(en) - 2H_2]^+$
↓
$[TcBr]^+$

$[TcL(CO)_3(Et_2NH)]^+$ ------------------------→ $[TcL(CO)_3]^+$
↓–CO
$[TcL(CO)_2(Et_2NH)]^+$ → $[TcL(CO)_2NEt]^+$
↓–CO
$[TcL(CO)(Et_2NH)]^+$
↓–CO
$[TcL(Et_2NH)]^+$

$[TcL(CO)_2NEt]^+$
↓–CO
$[TcL(CO)NEt]^+$
↓–CO
$[TcLNEt]^+$

$[TcL(CO)_3]^+$
↓–CO
$[TcL(CO)_2]^+$
↓–CO
$[TcL(CO)]^+$
↓–CO
$[TcL]^+$

L = $CF_3CHCOCHCMe_3$, $CF_3CHCOCHCH_3$

Volatility of technetium carbonyls

- Readily volatile (<100°C/vacuum, noticeable volatility at room temperature: $Tc_2(CO)_{10}$, $TcX(CO)_5$, $TcY(CO)_4$, $TcCp(CO)_3$, [Tc(β-diketonate)$(CO)_3(Et_2NH)$] (X = Hlg, CF_3COO, H; Y = $CF_3COCHCOCF_3$, Et_2NCS_2, $MeOCS_2$)
- Moderately volatile (100–150°C/vacuum): $[TcHlg(CO)_4]_2$, [Tc(β-diketonate)$(CO)_3]_2$, $Tc_3H_3(CO)_{12}$
- Difficultly volatile (≥200°C/vacuum): $[TcX(CO)_3]_4$ (X = Hlg, OH); $[TcBr(CO)_3(en)]$

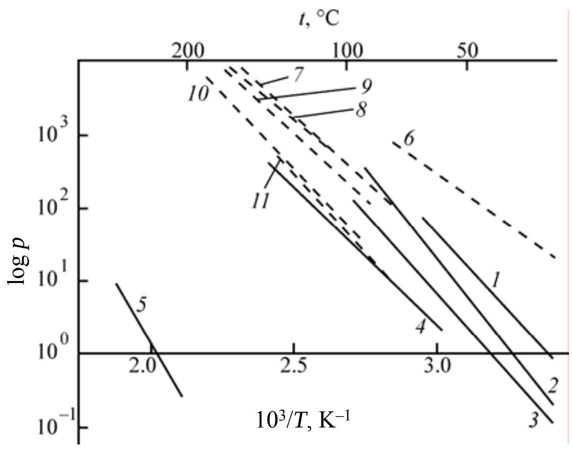
Thermal stability of technetium carbonyls at vaporization

- **Highly stable (sublime without decomposition in vacuum and in inert gas flow at atmospheric pressure)**
- *Moderately stable (sublime without decomposition only in vacuum)*
- Low-stable (partially decompose during vacuum sublimation)

Examples

Stability	Volatility		
	High	Moderate	Low
High	**$Tc_2(CO)_{10}$, $TcCp(CO)_3$, [Tc(β-diketonate)$(CO)_3(Et_2NH)$]**	**[Tc(β-diketonate)$(CO)_3]_2$**	
Moderate	*$TcI(CO)_5$*		*$[TcHlg(CO)_3]_4$, $[TcBr(CO)_3(en)]$*
Low	$TcCl(CO)_5$	$[TcHlg(CO)_4]_2$	$[Tc(OH)(CO)_3]_4$

Vapor pressure of Tc carbonyl compounds



(1) $TcCp(CO)_3$,
(2) $TcI(CO)_5$,
(3) $Tc_2(CO)_{10}$,
(4) [Tc(PTFA)$(CO)_3(Et_2NH)$],
(5) $[TcCl(CO)_3]_4$,
(6) $MnCp(CO)_3$,
(7, 8) $Mn_2(CO)_{10}$,
(9) $MnRe(CO)_{10}$,
(10, 11) $Re_2(CO)_{10}$ (*dashed lines*: published data)

PTFA = $CF_3COCHCOCMe_3$

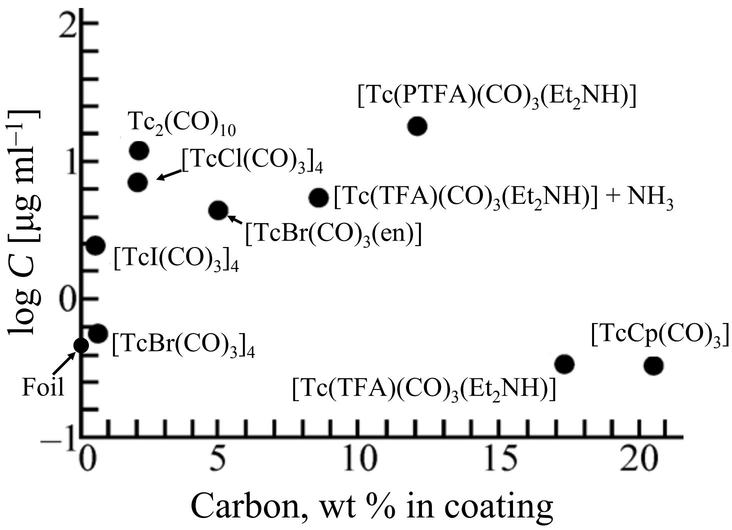
Thermal stability of technetium carbonyls: three aspects

- Resistance to decarbonylation:
  higher carbonyls like $TcHlg(CO)_5$, Tc(bidentate anion)$(CO)_4$, $[TcHlg(CO)_4]_2$
- Resistance to loss of neutral ligand L:
  $[TcHlg(CO)_3L]_2$, $[TcHlg(CO)_3L_2]$ (monodentate L);
  [Tc(β-diketonate)$(CO)_3$(EtOH)] (except β-diketonate = $CF_3COCHCOCF_3$)
- Resistance to deep decomposition:
  $[TcHlg(CO)_3]_4$, $[TcBr(CO)_3(en)]$, [Tc(β-diketonate)$(CO)_3(Et_2NH)$], $TcCp(CO)_3$, **$Tc_2(CO)_{10}$**

Temperatures required for deposition of technetium coatings

$Tc_2(CO)_{10}$	260–300°C
$[TcX(CO)_3]_4$ (X = Cl, Br, I)	330–350°C
$[TcBr(CO)_3(en)]$	370–380°C
$[TcL(CO)_3(Et_2NH)]$	370–400°C
$[TcCp(CO)_3]$	500°C (breakthrough still observed)

L = $CF_3COCHCOR$, R = CMe_3, CH_3

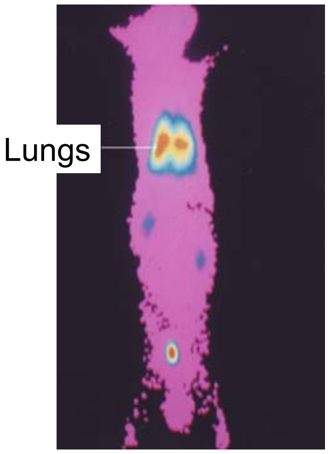


Coatings annealed in a vacuum at 900–940°C, kept in simulated seawater for ~3000 h. Precursors are indicated. (*C*) Accumulated Tc concentration in solution.

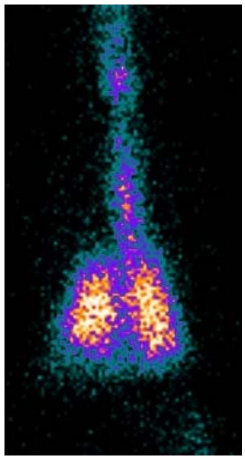
Mini-Autoclave for Generation of $^{99m}TcI(CO)_5$ (with CO source)

$K^{99m}TcO_4$ (eluate) + CO + HI → $^{99m}TcI(CO)_5$
(transferred through the gas phase during relief of CO)

Accumulation of $^{99m}TcI(CO)_5$ in Lungs of Rabbits



Intravenous injection



Inhalation

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- To all the attendants for attention