Chromatography-mass spectrometry studies of transarylation and disproportionation reactions of diaryl telluroxides

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Electrospray ionization chromatography-mass spectrometry was used to study transarylation and disproportionation reactions of di(4-methoxyphenyl) and di(4-dimethylaminophenyl) telluroxides in refluxing toluene. The reaction mixture compositions were established based on the mass spectrometry data and relative retention times. General schemes for fragmentation of the reaction mixture components were suggested.

Key words: chromatography-mass spectrometry, electrospray ionization, tandem mass spectrometry, diaryl telluroxide, diaryl telluride, triaryltelluronium ion, aryloxytriaryltellurane, disproportionation, transarylation.

Chromatography-mass spectrometry is widely used in different areas of science and technique,¹ in particular, in the study of mechanisms of organic reactions and identification of synthesized products. For labile compounds, it is important to use "mild" ionization, allowing transition of such molecules into the gas phase without decomposition. Electrospray ionization mass spectrometry (ESI-MS) is one of the variants of "mild" ionization. Tandem mass spectrometry (ESI-MS/MS) is used to increase the reliability of identification. An important supplementation to mass spectrometric identification is chromatographic identification based on the use of chromatographic retention time values.^{2,3} These methods were used earlier for the studies of mechanisms of different organic reactions, including those involving organotellurium compounds.^{4–6}

A number of works were devoted to the reactions of inorganic and organic derivatives of di- and tetracoordinated tellurium as reagents and catalysts. Reaction pathways of tellurium tetrachloride and aryltellurium trichloride with alkynes were investigated.^{5,7} Using ESI-MS/MS, it was found out that during bromination of different organic compounds in the presence of diaryl ditellurides in catalytic amounts the diaryl ditellurides underwent oxidation by hydrogen peroxide with the formation of the corresponding aryltelluronium acids, which acted as the catalysts.⁸

Mass spectrometry and chromatography-mass spectrometry studies of diaryl telluroxides and other organotellurium compounds allowed one to identify specific features of analysis of individual diaryl telluroxides and their model mixtures under conditions of liquid^{9,10} and gas chromatography^{11,12} with mass spectrometric detection. The results of the gas chromatography studies of diaryl telluroxides with mass spectrometric detection allowed one to draw a conclusion that heating a mixture of symmetric diaryl telluroxides led to the formation of unsymmetric compounds of this class and disproportionation of the starting compounds is possible. Earlier, ^{13,14} chromatography-mass spectrometry study of the reactions of formation of unsymmetric diaryl telluroxides has been carried out upon heating a mixture of symmetric diaryl telluroxides for 2 h at 100 °C in a sealed quartz tube. However, some side products were not identified.

Experimental

Diaryl telluroxides were synthesized at the Department of Analytical and Expert Chemistry of the S. P. Korolev Samara National Research University according to the known procedures.¹⁵

Preparation of reaction mixtures. The reaction mixtures were obtained by the disproportionation and transarylation reactions of di(4-methoxyphenyl)- and di(4-dimethylaminophenyl) tellur-oxide (Table 1) upon reflux of the starting reagents (0.1 mmol) in toluene for 4 h using a reflux condenser.

Chromatography-mass spectrometry study of the reaction mixture compositions. Chromatographic separation of components of reaction mixtures was carried out on an Agilent Technologies 1260 Infinity liquid chromatograph with a Bruker Maxis Impact mass spectrometric detector, a ZORBAX SB-C18 column (2.1×150 mm, 3.5μ m), electrospray ionization (ESI). The column thermostat temperature was 45 °C. A four-component mixture of solvents water—methanol—acetonitrile (50:40:10) with addition of 0.05% of trifluoroacetic acid (TFAA) (phase A) and pure aceto-

Published in Russian in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 4, pp. 0636–0642, April, 2017.

1066-5285/17/6604-0636 © 2017 Springer Science+Business Media, Inc.

Reaction mixture	Starting reagent	Reaction
1	Di(4-methoxyphenyl)	Dispropor-
	telluroxide	tionation
2	Di(4-dimethylaminophenyl)	Dispropor-
	telluroxide	tionation
3	Di(4-methoxyphenyl) telluriumoxide	Transarylation
	Di(4-dimethylaminophenyl) telluroxide	Dispropor- tionation

Table 1. Starting reagents for the preparation of reaction mixtures

nitrile with addition of 0.05% of TFAA (phase B) were used as mobile phases. The following gradient of eluents was used: first three minutes phase A, from 4th to 10th min phase B, from 11th to 15th min phase A. These conditions of chromatographic separation were found to be the most acceptable for the analysis of studied reaction mixtures after variation of parameters.

The reaction mixtures were injected into chromatograph without dilution (in toluene) in the amount of 1 μ L.

Mass spectrometry detection of the reaction mixture components was carried out in the positive ion mode in the range m/z = 50-3000 at a capillary and a counter electrode voltage of 3500 and 500 V, respectively. The flow rate was 4.5 L min⁻¹, the temperature of nitrogen was 250 °C. The registration rate was four spectra per 1 s. The structure of products formed in disproportionation and transarylation was studied using MS/MS-spectrometry by scanning a certain m/z range and the choice of a required ion-precursor, subsequent dissociation of the ionprecursor upon collision with nitrogen molecules in the collision cell and TOF-analysis of masses of resulting ions. The ion transmission band value of chosen ions $\Delta m/z = 11$. The energy of collisions was 10 eV. The experimental m/z values were compared with the m/z values calculated using the IsoPro 3.0 software.

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Results and Discussion

Chromatography-mass spectrometry studies of starting compounds. To confirm the absence of impurities which can interfere with the determination of the reaction mixture compositions, we carried out chromatography-mass spectrometry examination of the starting compounds. The retention times of di(4-methoxyphenyl) and di(4-dimethylaminophenyl) telluroxide were found to be 1.2 and 1.8 min, respectively. Therefore, this parameter can be used for the identification of these compounds.

Under the ESI mass spectrometry conditions, di(4methoxyphenyl) and di(4-dimethylaminophenyl) telluroxides form protonated molecules, which have the maximum signal intensities (Fig. 1). Apart from that, the mass spectra of these compounds exhibit ions, the structure of which corresponds to diaryl tellurides $[M - O]^+$, diaryls $[Ar + Ar]^+$, dimers $[2 M + H]^+$, associates with the components of mobile phases $[M + H + MeOH - H_2O]^+$, $[M + H + CF_3COOH - H_2O]^+$, $[2 M + H + CF_3COOH - - H_2O]^+$. The obtained *m/z* values of ions agree with the calculated values. Under ESI conditions, the diaryl telluroxide ions are formed following the same scheme (Scheme 1), which can serve as an additional indication of identification in the determination of other representatives of organotellurium compounds under consideration.

Chromatography-mass spectrometry study of disproportionation reaction. Earlier,^{13,14} when studying the influence of high temperatures on binary mixtures of diaryl tellur-



Fig. 1. Mass spectra of di(4-methoxyphenyl) (a) and di(4-dimethylaminophenyl) telluroxide (b).

[M - O] $[Ar + Ar]^+$ -C OMe ÓМе R $[M + H + MeOH - H_2O]^+$ -MeOH +H+CF₃COOH Ĉ $[M + H]^{+}$ +M $[\mathsf{M} + \mathsf{H} + \mathsf{CF}_3\mathsf{COOH} - \mathsf{H}_2\mathsf{O}]^+$ +MR O +CF₃COOH OH ·H,0 $[2 M + H]^+$ $[2 M + H + CF_3COOH - H_2O]^+$ R R

Scheme 1

oxides we detected formation of products, the structure of which was not established. We suggested that diaryl telluroxides treated with heat underwent disproportionation. To confirm a possibility of this process, we carried out chromatography-mass spectrometry studies of the reaction mixtures (Fig. 2) obtained by heating individual diaryl telluroxides.

From the recorded chromatographic patterns, it follows that the reaction mixture **1** contains two components, while the reaction mixture **2** is composed of four components. Based on the retention time values (t_R) and mass spectra, we identified the starting di(4-methoxyphenyl) telluroxide $(t_R = 1.3 \text{ min})$ and di(4-dimethylaminophenyl) telluroxide ($t_{\rm R} = 2.1$ min). The structures of other components of the reaction mixtures under study were inferred from the mass spectrometry data (Table 2).

We found that fragment ions are practically absent in the mass spectra of the second peak in the chromatographic pattern of the reaction mixture **1** and of the forth peak in the chromatographic pattern of the reaction mixture **2**, the structure of the most abundant ions supposedly corresponds to triaryltelluronium ions $[Ar_3Te]^+$.

It is known that triaryltelluronium ions exist as salts. However, their formation under the studied reaction conditions is impossible. According to the literature data,

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Fig. 2. Mass chromatograms of the reaction mixtures 1 (a) and 2 (b) for the main ions.

derivatives of tetracoordinated tellurium do not form stable molecular ions. The desorption chemical ionization mass spectrometry data for Te^{IV} alkoxy derivatives are considered in the work.¹⁶ One of the compounds, namely, ethoxytriphenyltellurane, is characterized by the absence in the mass spectrum of a molecular ion. The fragmentation of its protonated molecular ion is accompanied by elimination of a protonated alkoxy group with the formation of the Ph₃Te⁺ ion.

Thus, it was suggested that the heating of diaryl telluroxides under study led to the formation of (4-methoxyphenoxy)tri(4-methoxyphenyl)tellurane and (4-dimethylaminophenoxy)tri(4-dimethylaminophenyl)tellurane, the structures of which are shown in the text below.

To confirm the structures of disproportionation products, we studied the principal directions of fragmentation of triaryltelluronium ions under the ESI-MS/MS conditions. It was found that in the MS/MS spectra, the peaks of the most abundant ions correspond to diaryls. The ions

Table 2. Retention times and main ions in the mass spectra of the reaction mixture components

		,	
Reac-	$t_{\rm R}$	m/z	Structure of ion
tion	/min	of main	corresponding to the most
mixtur	e	ion	abundant peak
1	1.3	361.0109	$[(p-MeOC_{6}H_{4})_{2}TeO + H]^{+}$
	3.6	451.0616	$[(p-MeOC_6H_4)_3Te]^+$
2	0.8	122.0976	$[Me_2NPh + H]^+$
	2.1	387.0742	$[(p-Me_2NC_6H_4)_2TeO + H]^+$
	4.8	371.0791	$[(p-\text{MeOC}_6\text{H}_4)_2\text{Te} + \text{H}]^+$
	5.1	490.1513 [($(p-\text{MeOC}_6\text{H}_4)\text{Te}(p-\text{Me}_2\text{NC}_6\text{H}_4) + \text{H}]^+$



R = -OMe, -NMe₂

with the structure of diaryl tellurides and aryl tellurides give peaks with low intensities. The molecular formulas of ions were found by the comparison of the experimental m/z values with the calculated data. The principal directions of fragmentation of triaryltelluronium ions are given in Scheme 2.

The results of the MS/MS spectroscopy study are confirmed by the literature data. Under the desorption chemical ionization conditions, ethoxytriphenyltellurane is characterized by the formation of the Ph_2Te^+ and $PhTe^+$ ions.¹⁶ The studies¹⁷ of tellurium tetrachloride by ESI mass spectrometry showed that the most abundant peak corresponds to the structure of $TeCl_3^+$. The MS/MS spectrum obtained for this ion contained the peaks of the $[TeCl_2]^+$ and $[TeCl]^+$ ions formed by sequential elimination of a chlorine atom.

The reaction mixture 2 is distinguished by the presence of a larger number of disproportionation products. The retention time of the first component corresponds to N,N-dimethylaniline. The mass spectrum does not exhi-





bit peaks of tellurium-containing ions, while the main peak corresponds to the structure of the protonated molecule $[(C_8H_{11}N) + H]^+$ with m/z 122.0976.

The mass-chromatographic pattern also contains a component with the retention time of 4.8 min. The structure of the corresponding compound was inferred from the mass spectrum and the MS/MS spectrum.

The most abundant ion in the mass spectrum (Fig. 3) corresponds to the protonated molecule of di(4-dimethylaminophenyl) telluride [M + H] with m/z 371.0789. Apart from that, the mass spectrum exhibits peaks for the following ions: $[(C_8H_{10}N)_2 + H - Me]^+$ with m/z 226.1507, [M + H - M] with m/z 356.0550, and $[M + (C_8 H_{10} N)Te]^+$ with m/z 618.0555. The presence of a signal for the ion with m/z 490 in the mass spectrum is related to the insufficient efficiency of chromatographic separation of two components of the reaction mixture. This signal belongs to the mass spectrum of (4-dimethylaminophenoxy)tri(4dimethylaminophenyl)tellurane. Under the tandem mass spectrometry conditions, di(4-dimethylaminophenyl) telluride practically does not form fragment ions. The most abundant peak in the MS/MS spectrum corresponds to the $[(C_8H_{10}N)_2 + H - Me]^+$ ion.

Based on the chromatography-mass spectrometry studies of the reaction mixtures obtained by reflux of each of the diaryl telluroxides in toluene, it was found that di(4methoxyphenyl) and di(4-dimethylaminophenyl) telluroxides undergo disproportionation.

Chromatography-mass spectrometry study of transarylation reaction. The examination of the main ions in the mass-chromatographic patterns of the reaction mixture **3** (Fig. 4) revealed the presence of ten components. Despite the insufficient efficiency of separation of the reaction mixture components under the applied chromatographic conditions, the identification is possible based on the mass spectrometry data.

The retention time values and the mass spectrometry and MS/MS data showed the presence in the reaction mixture **3** of the starting diaryl telluroxides and the products of their disproportionation. The structures of other components of the reaction mixture were inferred from mass and MS/MS spectra (Table 3).

4-Dimethylaminophenyl 4-methoxyphenyl telluroxide (Fig. 5) formed by transarylation was identified using a mass spectrum of the third peak.

In the mass spectrum of 4-dimethylaminophenyl 4-methoxyphenyl telluroxide (see Fig. 5), the most abundant signal corresponds to the protonated molecule $[M + H]^+$ with the m/z equal to 374.0376. This mass spectrum contains the following ion peaks: [M + H + MeOH - $- H_2O]^+$, m/z 388.0540; $[M + H + CF_3COOH - H_2O]^+$, m/z 470.0226; $[2 M + H]^+$, m/z 745.0656; [2 M + H + $+ CF_3COOH - H_2O]^+$, m/z 841.0522; $[(C_7H_7O) +$ $+ (C_8H_{10}N)]^+$, m/z 227.1330. The ion m/z values agree with the calculation results. The principal directions of the ion formation under the HPLC/MS-ESI conditions correspond to the general Scheme 1.

The main ions in the mass spectra of the seventh and the eighth peaks are the nonsymmetric triaryltelluronium ions $Ar'_2Ar''Te^+ (Ar' = p-MeO(C_6H_4), Ar'' = p-Me_2N(C_6H_4))$



Fig. 3. Mass spectrum of di(4-dimethylaminophenyl) telluride.



Fig. 4. Mass chromatogram of the reaction mixture 3 for the main ions.



Fig. 5. Mass spectrum of 4-dimethylaminophenyl 4-methoxyphenyl telluroxide.

m/z 464; Ar' = p-Me₂N(C₆H₄), Ar" = p-MeO(C₆H₄), m/z 477). The fragmentation of the indicated ions registered in the MS/MS spectra occurs according to the general fragmentation scheme (see Scheme 2), that additionally confirms their structure.

Table 3. Composition of the reaction mixture obtained in the transarylation reaction

t _R /min	Structure of ion corresponding to the most abundant signal	<i>m/z</i> of main ions
0.7	N,N-Dimethylaniline	122.0979
1.3	Di(4-methoxyphenyl) telluroxide	361.0077
1.5	4-Dimethylaminophenyl	374.0376
	4-methoxyphenyl telluroxide	
2.0	Di(4-dimethylaminophenyl) telluroxide	387.0695
3.5	(4-Methoxyphenoxy)tri-	451.0574
	(4-methoxyphenyl)tellurane	
4.3	Di(4-dimethylaminophenyl) telluride	371.0770
4.8	(4-Dimethylaminophenoxy)di-	464.0903
	(4-methoxyphenyl)-	
	(4-dimethylaminophenyl)tellurane	
5.0	(4-Methoxyphenoxy)di-	477.1221
	(4-dimethylaminophenyl)-	
	(4-methoxyphenyl)tellurane	
5.1	(4-Dimethylaminophenoxy)tri-	490.1509
	(4-dimethylaminophenyl)tellurane	
5.1	4-Dimethylaminophenyl	358.0442
	4-methoxyphenyl telluride	

Thus, it can be suggested that these components are nonsymmetric aryloxytriaryltelluranes: 4-dimethylaminophenyl(4-dimethylaminophenoxy)di(4-methoxyphenyl)tellurane and di(4-dimethylaminophenyl)(4-methoxyphenyl)(4-methoxyphenoxy)tellurane. The presence of these compounds in the reaction mixture **3** results from the disproportionation of nonsymmetric diaryl telluroxide formed by transarylation.

The mass spectrum of the tenth peak (Fig. 6) exhibits two peaks of the tellurium-containing ions with m/z 358 and 490. Both signals are characterized by considerable intensity. This fact indicates the presence of two different components, which are eluted simultaneously under the conditions used.

The ion with the m/z 358.0442 corresponds to the protonated molecule of 4-dimethylaminophenyl 4-methoxyphenyl telluride. Apart from that, this mass spectrum exhibits the signals of the ions the structure of which is identical to those formed by the fragmentation of di(4dimethylaminophenyl) telluride: $[(C_8H_{10}N)(C_7H_7O) + H - Me]^+$ with m/z 213.1165 and [M + H - Me] with m/z 343.0222. An additional confirmation of the structure of nonsymmetric diaryl telluride is the presence in the MS/MS spectrum of the most abundant peak of the ion $[(C_8H_{10}N)(C_7H_7O) + H - Me]^+$.

In conclusion, we carried out chromatography-mass spectrometry studies of disproportionation reactions of di(4-methoxyphenyl) and di(4-dimethylaminophenyl) telluroxides. It was found that the disproportionation leads



Fig. 6. Mass spectrum of 4-dimethylaminophenyl 4-methoxyphenyl telluride.

to the formation of aryloxytriaryltelluranes. The disproportionation of di(4-dimethylaminophenyl) telluroxide is characterized by the formation of not only aryloxytriaryltellurane, but also of diaryl telluride.

The study of transarylation reaction of diaryl telluroxides showed the presence of nonsymmetric diaryl telluroxide in the reaction mixture. According to the mass spectrometry and MS/MS data, in this case a parallel disproportionation reaction of the starting reagents and a transarylation of the reaction product with the formation of symmetric and nonsymmetric aryloxytriaryltelluranes occur. The disproportionation of nonsymmetric diaryl telluroxide proceeds similarly to disproportionation of di(4dimethylaminophenyl) telluroxide, since a corresponding diaryl telluride was found in the reaction mixture.

Based on the analysis of the results of mass spectrometry and MS/MS studies, a general scheme for the formation of ions of diaryl telluroxides under the HPLC/ MS-ESI conditions was suggested, as well as a scheme of the fragmentation of aryloxytriaryltelluranes under tandem mass spectrometry conditions.

References

- 1. A. K. Buryak, T. M. Serduk, Russ. Chem. Rev., 2013, 82, 369.
- L. D. Belyakova, A. K. Buryak, O. G. Larionov, Protection of Metals and Phys. Chem. Surfaces, 2013, 49, 605.
- 3. A. K. Buryak, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1990, 39, 1812.
- 4. M. N. Eberlin, Eur. J. Mass Spectrom., 2007, 13, 19.

- 5. L. S. Santos, Eur. J. Org. Chem., 2008, 235.
- H. Wang, Y. Li, R. Zhang, K. Jin, D. Zhao, C. Duan, J. Org. Chem., 2012, 77, 4849.
- L. S. Santos, R. L. O. R. Cunha, J. V. Comasseto, M. N. Eberlin, *Rapid Commun. Mass Spectrom.*, 2007, 21, 1479.
- E. E. Alberto, L. M. Muller, M. R. Detty, *Organometallics*, 2014, 33, 5571.
- V. P. Gar´kin, T. A. Rodina, N. V. Solovova, A. K. Buryak, Russ. J. Phys. Chem., 2008, 82, 881.
- A. A. Sorokin, V. P. Gar´kin, N. A. Red´kin, A. K. Buryak, Russ. J. Appl. Chem., 2010, 83, 2163.
- 11. N. A. Red'kin, V. P. Gar'kin, A. V. Ul'yanov, A. K. Buryak, Sorbtsionnye i khromatograficheskie protsessy [Sorption and Chromatographic Processes], 2007, 37 (in Russian).
- N. A. Red'kin, V. P. Gar'kin, A. V. Ul'yanov, A. K. Buryak, Sorbtsionnye i khromatograficheskie protsessy [Sorption and Chromatographic Processes], 2007, 244 (in Russian).
- T. A. Rodina, Ph. D. (Chem.), A. N. Frumkin Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences, Moscow, 2009, 191 pp. (in Russian).
- 14. N. A. Red'kin, Ph. D. (Chem.), Samara State Univ., Samara, 2008, 150 pp. (in Russian).
- I. D. Sadekov, A. A. Maksimenko, V. I. Minkin, *Khimiya* tellurorganicheskikh soedinenii [Chemistry of Organotellurium Compounds], Rostov Univ. Publ., Rostov-on-Don, 1983, 327 pp. (in Russian).
- 16. M. Cojocaru, I. Elyashiv, M. Albeck, J. Mass Spectrom., 1997, 31, 705.
- L. S. Santos, R. L. O. R. Cunha, J. V. Comasseto, M. N. Eberlin, *Rapid Commun. Mass Spectrom.*, 2007, 21, 1479.

Received September 29, 2016; in revised form November 8, 2016