

## Brief Communications

### Resonance capture of electrons by molecules of dialkyl trisulfides

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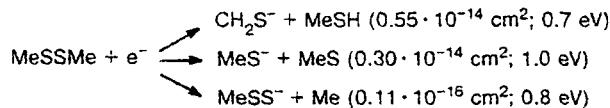
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Using negative ion mass spectrometry in the mode of resonance electron capture, it was found that the energy of dissociation of the S–S bond in dialkyl trisulfides is 0.6 eV smaller than that in their disulfide analogs and is equal to  $1.9 \pm 0.1$  eV.

**Key words:** dialkyl trisulfides, negative ions, bond dissociation energy.

Previously<sup>1,2</sup> we have studied the mass spectra of negative ions (NI) derived from disulfides under the conditions of resonance capture of electrons (RCE) and have shown that NI are formed from a dimethyl disulfide molecule according to Scheme 1 (the effective cross-sections of the formation and the energies of the resonance maxima are given in parentheses).

Scheme 1



In this work, we studied the RCE by molecules of dimethyl, ethyl methyl, and diethyl trisulfides prepared by a procedure described previously.<sup>3</sup> All of the compounds studied were found to contain the corresponding

disulfides, whose proportions, according to positive ion mass spectrometry were as high as 85–90%.

#### Results and Discussion

The most intense peaks in the RCE mass spectra of  $\text{R}_2\text{S}_3$  molecules correspond to  $\text{RS}^-$  ions, whose maximum yield is observed at an energy of 0.4 eV in the case of  $\text{MeS}^-$  or 0.3 eV in the case of  $\text{EtS}^-$ .

The resonance maximum of  $\text{MeS}^-$  ions at 1.0 eV and that of  $\text{EtS}^-$  at 0.9 eV are due to their formation from the corresponding disulfides present in the trisulfides studied.

The formation of  $\text{CH}_2\text{S}^-$  and  $\text{C}_2\text{H}_4\text{S}^-$  ions is not typical of trisulfides, but in the mass spectra of disulfides, these ions are the most intense. The peaks due to  $\text{CH}_2\text{S}^-$  and  $\text{C}_2\text{H}_4\text{S}^-$  ions observed in the RCE spectra of trisulfides at 0.7 eV and 0.6 eV, respectively, are due to the fact that they are formed from disulfides.

**Table 1.** Energies of formation ( $AP$ ), resonance maxima ( $E_{\max}$ ), and cross-sections of formation of negative ions ( $\sigma$ ) from molecules of disulfides and trisulfides

Compound	Ion	$AP/\text{eV}$	$E_{\max}/\text{eV}$	$\sigma \cdot 10^{-14}/\text{cm}^2$
MeS <sub>2</sub> Me	MeS <sup>-</sup>	0.6	1.0	0.3
	MeSS <sup>-</sup>	0.36	0.8	$0.11 \cdot 10^{-2}$
MeS <sub>3</sub> Me	MeS <sup>-</sup>	0.0	0.4	1.7
	MeSS <sup>-</sup>	0.0	0.4	$0.6 \cdot 10^{-2}$
EtS <sub>2</sub> Et	EtS <sup>-</sup>	0.6	0.9	0.17
EtS <sub>3</sub> Et	EtS <sup>-</sup>	0.0	0.3	1.2
MeS <sub>2</sub> Et	MeS <sup>-</sup>	0.6	1.0	0.28
	EtS <sup>-</sup>	0.6	0.9	0.16
	MeSS <sup>-</sup>	0.35	0.8	$0.1 \cdot 10^{-2}$
MeS <sub>3</sub> Et	MeS <sup>-</sup>	0.0	0.4	1.5
	EtS <sup>-</sup>	0.0	0.3	1.2
	MeSS <sup>-</sup>	0.0	0.4	$0.55 \cdot 10^{-2}$

The RCE spectra of dimethyl and ethyl methyl trisulfides also exhibit low-intensity peaks for MeS<sub>2</sub><sup>-</sup> ions with a resonance maximum at 0.4 eV. No EtSS<sup>-</sup> ions were detected in this region of energy.

By using known cross-sections of the formation of MeS<sup>-</sup> and EtS<sup>-</sup> ions from molecules of disulfides ( $0.30 \cdot 10^{-14} \text{ cm}^2$  and  $0.17 \cdot 10^{-14} \text{ cm}^2$ , respectively<sup>1,2</sup>) and by comparing these values with the intensities of the peaks of positive molecular ions derived from di- and trisulfides, which characterize the proportions of the corresponding compounds in the mixtures, one can estimate the cross-sections of formation of ions: MeS<sup>-</sup> from MeSSSMe ( $1.7 \cdot 10^{-14} \text{ cm}^2$ ), MeS<sup>-</sup> from MeSSSEt ( $1.5 \cdot 10^{-14} \text{ cm}^2$ ), EtS<sup>-</sup> from EtSSSEt ( $1.4 \cdot 10^{-14} \text{ cm}^2$ ), EtS<sup>-</sup> from MeSSSEt ( $1.2 \cdot 10^{-14} \text{ cm}^2$ ), and MeSS<sup>-</sup> from MeSSSMe ( $0.6 \cdot 10^{-16} \text{ cm}^2$ ).

It follows from the data of Table 1 that the cross-sections for symmetrical and asymmetrical trisulfides differ only slightly from one another.

In addition, the curves for the effective yields of the RS<sup>-</sup> ions make it possible to estimate the relative energies of dissociation of S-S bonds in the molecules of trisulfides and of the corresponding disulfides. It is known<sup>4</sup> that  $AP(RS^-) = D(S-S) - EA(RS^-) + E^*$ , where  $AP$  is the energy of formation of the RS<sup>-</sup> ion,  $D(S-S)$  is the energy of dissociation of the S-S bond,  $EA$  is the electron affinity of RS<sup>-</sup> radical, and  $E^*$  is excess energy of the process. Since the  $EA(RS^-)$  values are identical, the difference between the  $AP(RS^-)$  values for the formation of this ion from di- and trisulfide molecules is equal to the difference between the dissociation energies of the S-S bonds in these compounds, if the excess energy of the process is neglected. It follows from Table 1 that the difference between the  $AP(RS^-)$

values for sulfides and trisulfides ( $0.6 - 0.0$  eV coincides with the difference between the energies of the resonance maxima for the MeS<sup>-</sup> ( $1.0 - 0.4$  eV) and EtS<sup>-</sup> ( $0.9 - 0.3$  eV) ions and is equal to 0.6 eV. Thus, the energy of dissociation of the S-S bond in molecules of dialkyl trisulfides is 0.6 eV (14 kcal mol<sup>-1</sup>) smaller than that for the corresponding dialkyl disulfides and amounts to 1.9 eV, if we neglect the excess energy of the formation of negative ions and use  $EA(RS^-) \approx 1.9$  eV.<sup>5</sup>

Note that the difference between the dissociation energies of di- and trisulfides (14 kcal mol<sup>-1</sup>) almost coincides with that in the case of di- and trioxides (15 kcal mol<sup>-1</sup>).<sup>6</sup>

## Experimental

A mixture of dialkyl disulfides (ethyl methyl disulfide, diethyl disulfide, and dimethyl disulfide) obtained from the setup for oxidative demercaptanization of hydrocarbon raw materials at the Ufa Petroleum Refinement Plant was used in this study. This mixture was a colorless liquid boiling at 110–160 °C with a density of  $1.0180 \text{ g cm}^{-3}$ . The material was converted into dialkyl polysulfides by a procedure described previously:<sup>3</sup> elemental sulfur was dissolved in dialkyl disulfides and then the reaction mixture was fractionated under reduced pressure in a flow of nitrogen.

NI mass spectra in the RCE mode were recorded on a MI 1201 mass spectrometer, transformed for detecting NI.<sup>4</sup> The scale of electron energies was calibrated against the resonance maxima of SF<sub>6</sub><sup>-</sup> from SF<sub>6</sub> (0.00 eV) and NH<sub>2</sub><sup>-</sup> from ammonia (5.65 eV). The cross-sections of formation of NI were estimated by admission of equal volumes of the sample studied and an internal standard (benzene) into the instrument.<sup>4</sup>

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