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### Autopolycondensation of 1-Halo-2-Propanethiones. New Organic Metals and Photoconductors

M. G. Voronkov; L. G. Shagun; O. N. Dabizha; G. F. Myachina; G. I. Sarapulova; T. I. Vakulskaya

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## Autopolycondensation of 1-Halo-2-Propanethiones. New Organic Metals and Photoconductors

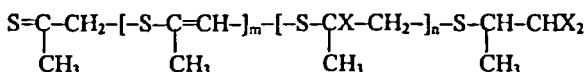
M.G. VORONKOV, L.G. SHAGUN, O.N. DABIZHA,  
 G.F. MYACHINA, G.I. SARAPULOVA and T.I. VAKULSKAYA

*Irkutsk Institute of Chemistry, Siberian Division RAS, Irkutsk 664033, Russia*

The reviously unknown 1-halo-2-propanethiones

$\text{CH}_3\text{-C}(\text{C}=\text{S})\text{-CH}_2\text{X}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ) were prepared by the reaction of the corresponding propanones with hydrogen sulfide in the presence of hydrogen chloride without solvent at  $-70^\circ\text{C}$  [1,2]. Iodo-2-propanethione ( $\text{X} = \text{I}$ ) was synthe-sized by exchange reaction of 1-bromo-2-propanethione with  $\text{NaI}$  in acetone at  $-70^\circ\text{C}$  [3].

At  $20^\circ\text{C}$  1-halo-2-propanethiones ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) undergo spontaneous polymerization to form linear polymers 1-3 with molecular mass of 1800, 1400 and 1200, respectively. Their structure is described by a general formula:



$\text{X}=\text{Cl}$ ,  $m=17$ ,  $n=4$  (1);  $\text{X}=\text{Br}$ ,  $m=14$ ,  $n=0$  (2);  $\text{X}=\text{I}$ ,  $m=11$ ,  $n=0$  (3).

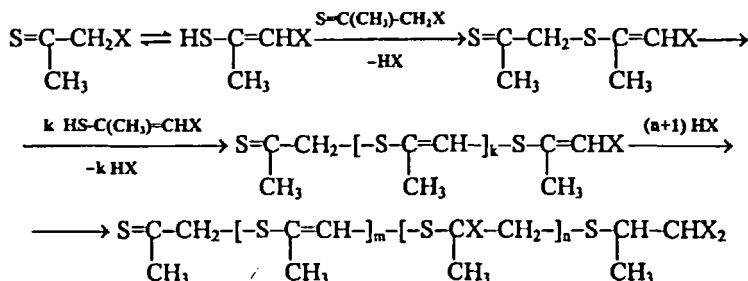
1-Fluoro-2-propanethione remains unchangeable even when heated to  $80^\circ\text{C}$  over 24 h.

The structure of polymers 1-3 was established using the methods of IR [ $\nu/\text{cm}^{-1}$ : 2960, 2870 ( $\text{CH}_3$ ), 2730, 2690 ( $\text{S}-\text{CH}_2$ ), 1640 ( $\text{C}=\text{C}$ ), 1220 ( $\text{C}=\text{S}$ ), 750 ( $\text{C}-\text{Cl}$ ), 720 ( $\text{C}-\text{Br}$ ), 600 ( $\text{C}-\text{I}$ )]. UV spectroscopy [ $\lambda$ , nm: 460-500 ( $n \rightarrow \pi^*$   $\text{C}=\text{S}$ ), 238-300 ( $n \rightarrow \pi^*$ ,  $n \rightarrow \sigma^*$   $\text{CH}_2=\text{CH}-\text{S}-$ )] and polarography. The electrochemical study of polymers 1-3 carried out on a mercury

dropping electrode in  $\text{CH}_3\text{CN}$  against 0.05 M  $\text{Bu}_4\text{NClO}_4$  background, has revealed the presence of (C=S) group (0.017v, 8.8  $\mu\text{A}\times\text{ml}/\text{mg}$ ).

As shown by ESR spectroscopy, polymers 1-3 are paramagnetic [ $g$ : 2.0062,  $H = 0.82$  mT,  $N = 0.93 \times 10^{17}$  spin/g. 1; 2.0069, 0.80,  $1.00 \times 10^{17}$  2. 2.0060, 1.42,  $1.60 \times 10^{17}$  3]. The signal parameters are typical of poly conjugated systems.

The following scheme describing the formation of polymers 1-3 is suggested:



The electroconduction (in air and vacuum,  $\sigma$  Cm/cm, 1:  $2.1 \times 10^{-14}$ ,  $1.0 \times 10^{-14}$ ; 2:  $6.5 \times 10^{-14}$ ,  $4.1 \times 10^{-14}$ ; 3:  $2.6 \times 10^{-8}$ ,  $1.2 \times 10^{-8}$ ), photoconduction ( $I_{\text{photo}} / I_{\text{dark}}$ , relative units,  $\lambda_{\text{max}}$ , nm, 1: 12, 460; 2: 11, 450) of polymers 1-3 and ESR data provide evidence for the presence of developed conjugation system and allow assignment of these polymers to organic semiconductors 1-2 and to organic metals 3.

## References

- [1] L.G. Shagun, V.A. Usov, M.G. Voronkov, T.L. Usova, L.N. Il'icheva, *J. Org.Chem.*, USSR, 1989, 25, 878.
- [2] L.G. Shagun, I.A. Dorofeev, B.A. Kozireva, T.L. Usova, M.G. Voronkov, *J. Org. Chem.*, USSR, 1995, 31, 792.