Chemistry

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1960

SovietRxiv

Abstract

Full Text

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ON THE ATOMIC REFRACTION OF ANTIMONY

The atomic refraction of phosphorus for the sodium D line has been reliably determined by many investigators on the basis of the study of a large number of organophosphorus compounds ([1–6]). For arsenic it has been calculated from several alkyl and mixed alkyl-aryl organoarsenic compounds ([7]). The atomic refractions are completely unknown for both trivalent and pentavalent antimony.

Table 1

Constants of alkenyl compounds of antimony, mercury, and arsenic

Nos.	Compound	n_D^t	d_4^t	t°	MR	Difference in mol. refr.	Atomic refr. of metal
1	$\left(\begin{matrix}CH_3\\H\end{matrix}C=C\begin{matrix}H\\H\end{matrix}\right)_3Sb$	1,5511	1,2870	20	60,74	0,32	17,28
2	$\left(\begin{matrix}CH_3\\H\end{matrix}C=C\begin{matrix}H\\H\end{matrix}\right)_3As$	1,5390	1,3092	20	60,42	0,32	16,96
3	$\left(\begin{matrix}CH_3\\H\end{matrix}C=C\begin{matrix}H\\H\end{matrix}\right)_5Sb_2$	1,5490	1,1702	20	88,92	0,45	16,48
4	$\left(\begin{matrix}CH_3\\H\end{matrix}C=C\begin{matrix}H\\H\end{matrix}\right)_5As_2$	1,5310	1,1972	20	88,483	0,45	16,05
5	$\left(\begin{matrix}Cl\\H\end{matrix}C=C\begin{matrix}H\\H\end{matrix}\right)_3Sb$	1,6298	1,7617	50	61,85	0,83	17,54([9])
6	$\left(\begin{matrix}Cl\\H\end{matrix}C=C\begin{matrix}H\\H\end{matrix}\right)_3As$	1,6180	1,7580	50	61,02	0,83	16,71([9])
7	$\left(\begin{matrix}CH_3\\H\end{matrix}C=C\begin{matrix}H\\H\end{matrix}\right)_3HgCl_2$	1,5820	1,9056	20	70,02	–	14,63
8	$\left(\begin{matrix}CH_3\\H\end{matrix}C=C\begin{matrix}H\\H\end{matrix}\right)_3AsCl_2$	1,6270	1,8396	20	77,16	–	15,97

Nos.	Compound	n_D^t	d_4^t	t°	MR	Difference in mol. refr.	Atomic refr. of metal
9	$\left(\mathrm{CH_2{=}C(CH_3)}\right)_3\mathrm{Sb}$	1,5475	1,2879	20	60,38	–	16,92
10	$(\mathrm{CH_2{=}CH})_3\mathrm{Sb}$	1,5614	1,4341	20	45,84	–	16,23
11	$(\mathrm{CH_2{=}CH})_3\mathrm{Sb}$	1,5590	1,2986	20	63,91	–	14,57
12	$(\mathrm{CH_2{=}CH})_3\mathrm{SbBr_2}$	1,5848	2,1153	20	62,38	–	15,05
13	$\left(\mathrm{CH_3(H)C{=}C(H)}\right)_2\mathrm{Hg}$	1,5622	2,9120	20	41,40	0,19	12,43([10])
14	$\left(\mathrm{CH_3(H)C{=}C(H)}\right)_2\mathrm{Hg}$	1,5628	2,9297	20	41,21	0,19	12,24([10])
15	$\mathrm{ClHC{=}C(H)AsCl_2}$	1,6105	1,8877	20	38,10	0,71	11,43([11])
16	$\mathrm{ClAsCl_2C{=}CHH}$	1,5888	1,8682	20	37,39	0,71	10,72([11])
17	$\mathrm{ClHC{=}C(H)AsCl_2}$	1,6076	1,8793	25	37,61	0,22	10,94([12])
18	$\mathrm{ClAsCl_2C{=}CHH}$	1,5859	1,8598	25	37,39	0,22	10,72([12])

In studying the stereochemistry of organometallic compounds of the ethylene series, we synthesized a number of liquid stereoisomers of propenyl compounds of trivalent and pentavalent antimony* ([8]) and determined the atomic refractions of antimony from molecular refractions calculated by the Lorentz–Lorenz formula.

From the atomic refractions of antimony given in Table 1, it follows that they, like the atomic refractions of phosphorus, depend on the valence state of antimony and on the nature of the bonds.

Comparison of the molecular refractions of the corresponding pairs of cis- and trans-isomers–namely, tri-(propenyl)antimony (Nos. 1, 2), penta-(propenyl)antimony (Nos. 3, 4), tri-(β-chlorovinyl)antimony (Nos. 5, 6), dipropenylmercury (Nos. 13, 14), and β-chlorovinyldichloroarsine (Nos. 15, 16, 17, 18)–leads to the conclusion that the trans-isomers possess greater molecular refraction than their cis-isomers. This increased polarizability of trans-isomers (as compared with the cis-isomer) of alkenyl organoelement compounds is fully consistent with their increased reactivity in the sense of the greater ease of cleavage of the C–M bond, which we have noted repeatedly ([13–16]).

Institute of Organoelement Compounds
Academy of Sciences of the USSR

Received
20 IV 1960

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* The synthesis and isolation of the reaction products of organoantimony compounds were carried out in a dry stream of nitrogen.

Note: Figure translations are in progress. See original paper for figures.