

Addition Compounds of Tertiary Phosphines and Carbon Diselenide

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We have found that carbon diselenide and trialkylphosphines form compounds analogous to the adducts of carbon disulfide and trialkylphosphines, discussed in the preceding paper.

Trimethylphosphine forms a red compound, $\text{Me}_3\text{P}^+\text{CSe}_2^-$. The corresponding triethyl- and tripropylphosphine compounds are green, but turn red on melting. The compounds are less stable than the carbon disulfide compounds, but analyses and infra-red spectra show them to be analogous to these compounds.

The infra-red spectra of these selenium compounds are very similar to the spectra of the corresponding sulfur compounds, the main difference being that the strong band near 1050 cm^{-1} , which we have assigned to the dithiocarboxylate ion, is missing. This fact lends strong support to our assignment.

Instead of the dithiocarboxylate band, a band due to the $-\text{CSe}_2^-$ grouping would be expected. The triethyl- and tripropylphosphine compounds (II and III) both have a strong band near 900 cm^{-1} which is absent in the spectra of the corresponding sulfur compounds and therefore probably is due to the diselenocarboxylate grouping. The spectrum of the trimethylphosphine compound (I) shows no new bands in comparison with the corresponding sulfur compound, but the spectrum of this has three strong bands near 900 cm^{-1} which appear to be somewhat broader in the spectrum of the selenium compound. It is therefore reasonable to ascribe the absence of a specific CSe_2^- band to coupling of this vibration with other vibrations in the same range.

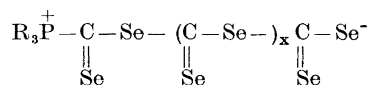
I. $(\text{CH}_3)_3\text{P}^+\text{CSe}_2^-$:	680 w, 745 w, 780 vw, 865 sh, 880 m, 955 s, 975 s, 1290 m, 1415 m, 2920 w, 2980 w.
II. $(\text{C}_2\text{H}_5)_3\text{P}^+\text{CSe}_2^-$:	718 w, 732 s, 762 vs, 842 s, 893 vs, 925 w, 1010 m, 1040 s, 1250 m, 1375 w, 1400 s, 1452 s, 2890 m, 2940 m, 2970 m.
III. $(n\text{-C}_3\text{H}_7)_3\text{P}^+\text{CSe}_2^-$:	715 m, 847 m, 900 vs, 930 m, 1048 sh, 1075 s, 1222 w, 1295 vw, 1332 w, 1370 w, 1390 m, 1450 s, 2930 m, 2965 m.

The selenium compounds react with methyl iodide as do the sulfur compounds, but the reaction products were semi-solid and were apparently rapidly transformed into other compounds. It has not been possible to isolate crystalline, well-defined compounds. The reaction with methyl iodide is very rapid: When methyl iodide is added to a chloroform solution of $\text{Et}_3\text{P}\cdot\text{CSe}_2$ the infra-red band at 893 cm^{-1} disappears immediately. This fact also supports the assignment of this band to the CSe_2^- grouping.

The infra-red spectra (*cf.* the preceding paper) exhibit the following bands (cm^{-1}):

The spectra further contained a weak band at $1145\text{--}1150\text{ cm}^{-1}$. Work with the carbon disulfide compounds has shown that this band, however, is due to phosphineoxide, which is easily formed on exposure of the compounds to air.

The propylphosphine compound (III) is rapidly transformed into a brown-red semi-solid mass. From this we succeeded in isolating a dark red, crystalline substance, the composition of which approximately corresponded to a compound of one mole of tripropylphosphine with four moles of carbon diselenide. The formation of this compound is tentatively ascribed to the ready polymerisation of carbon diselenide which may give rise to compounds of the type:



The infra-red spectrum of this compound is similar to that of the green tripropylphosphine compound, except that the medium strong band at 930 cm^{-1} has been shifted to 955 cm^{-1} ; it is noteworthy that the strong band at 900 cm^{-1} is still found.

Experimental. The compounds I and II were prepared by addition of an equivalent amount of the phosphine to a well cooled and stirred solution of carbon diselenide in ether. The trimethylphosphine compound (I) separated as a red-brown precipitate, which was filtered and washed with ether. In the course of about one

hour the compound became sticky and the colour became a more intense red. M.p. 78–79°C (decomp.). (Found: C 20.45; H 3.60. Calc. for $C_4H_9PSe_2$: C 19.53; H 3.69).

The triethylphosphine compound (II) was obtained in a similar way as a green, crystalline powder, which melted at 72–75°C to a red liquid. It is soluble in most organic solvents with a green colour (it is more soluble than the corresponding carbon disulfide compound). (Found: C 29.90; H 5.37. Calc. for $C_7H_{15}PSe_2$: C 29.18; H 5.25).

On addition of tripropylphosphine to carbon diselenide in ether a green solution was first formed, but the colour soon became brown and on addition of pentane a semi-solid brown-red precipitate separated. On standing for about a week in a refrigerator the precipitate became crystalline and after stirring with a little chloroform and filtering it was isolated as a dark red crystalline powder. On heating it began to darken at 120°C and melted with decomposition at 130–132°C. (Found: C 19.2; H 2.69. Calc. for $(C_3H_7)_3P \cdot 4CSe_2$: C 18.6; H 2.50).

On adding tripropylphosphine to a solution of carbon diselenide in pentane we succeeded in isolating a green crystalline compound with the composition $(C_3H_7)_3P \cdot CSe_2$ (III). (Found: C 36.35; H 6.38. Calc.: C 36.38; H 6.41). It rapidly became red and sticky and no definite melting point could be determined. In some experiments this transformation took place before the precipitate could be filtered.

Carbon diselenide was prepared from methylene chloride and selenium¹. We thank stud.scient. J. Borchsenius Carlsen for assistance in preparing the carbon diselenide.

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Infra-red Spectra of Dithiocarboxylates and Diselenocarboxylates

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Additional evidence for the localization of the infra-red bands due to the dithio- and diselenocarboxylate ions, $-CS_2^-$ and $-CSe_2^-$ (*cf.* the preceding papers) has been found by comparison of the infra-red spectra of potassium ethylxanthate (potassium *O*-ethylthiocarbonate, $C_2H_5O-CS-SK$) and the corresponding diselenoxanthate¹ (potassium *O*-ethyldiselenocarbonate, $C_2H_5O-CSe-SeK$). The infra-red spectra of these two compounds are practically identical, apart from a strong band at 1055 cm^{-1} , found only in the spectrum of the sulfur compound, and a strong band at 942 cm^{-1} , found only in the spectrum of the selenium compound. It seems therefore rather convincing that these two bands should be ascribed to the groups $-CS_2^-$ and $-CSe_2^-$, respectively.

A comparison of the infra-red spectra of the carboxymethyl esters of ethylxanthogenic acid ($C_2H_5-CS-SCH_2COOH$) and the corresponding selenium compound ($C_2H_5O-CSe-SeCH_2COOH$) similarly served to localize the bands due to the groupings $-S-SR$ and $-Se-SeR$, respectively. Here again a strong band at 1050 cm^{-1} is only found in the spectrum of the sulfur compound, and a strong band at 950 cm^{-1} is only found in the spectrum of the selenium compound. Otherwise the spectra are almost identical.

Finally, the infra-red spectrum of zinc *N,N*-dimethyldiselenocarbamate², $[(CH_3)_2N-CSe-Se]_2Zn$ has a strong band at 878 cm^{-1} corresponding to a strong band at 981 cm^{-1} in the spectrum of zinc *N,N*-dimethyl dithiocarbamate.

Apart from diselenoxanthates and diselenocarbamates, diselenocarboxylates have hitherto been unknown. We have made several attempts to prepare esters of diseleno- or thioseleno-acids by the same methods which were used to prepare esters of dithio-acids³, but in most cases without success. It was, however, found that zinc salts of diseleno-acids are formed from dialkyl- or diarylzincs and carbon diselenide. Whereas, *e.g.*, diethylzinc is almost