

unreactive towards carbon dioxide, it reacts slowly with carbon disulfide and very rapidly with carbon diselenide with formation of the zinc salts of dithiopropionic and diselenopropionic acid, respectively. Some representative diseleno-acids and their esters have been prepared in this way. Furthermore we have prepared some diselenocarboxylates from carbon diselenide and compounds with a reactive methylene group.

In the infra-red spectra of most dithiocarboxylates (salts and esters) a strong band is found near 1000–1100  $\text{cm}^{-1}$ . A comparison of these spectra with the spectra of the corresponding selenium compounds shows that this band must actually be due to the  $-\text{CS}_2^-$  or  $-\text{CSSR}$  groups. The corresponding band in the spectra of the selenium compounds is found near 900  $\text{cm}^{-1}$ .

The details of this investigation will be published in a forthcoming paper in this journal.

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## Infra-red Spectra of Thioamides Selenoamides

K. A. JENSEN

*Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, Copenhagen, Denmark*

In connexion with other studies of thioacids and their derivatives we have also studied the infra-red spectra of a great number (about 300) of these compounds. Although this study was made mainly for practical purposes, *i.e.* to obtain useful diagnostic information, it also led to information on the controversial problem of the origin of the absorption bands in the spectra of thioamides (including thioureas,

thiohydrazides and thiosemicarbazides). Thus, we have been able to locate various characteristic bands in the spectra of these compounds of which each behaves in a characteristic way when the compounds are deuterated, S-alkylated or transformed into metal complexes. Although it may be extremely difficult to decide from which molecular vibrations these bands originate, it is often easy to localize corresponding bands in various thioamide-compounds.

As a new method we have used the comparison of corresponding sulfur and selenium compounds. The pronounced chemical similarity between sulfur and selenium is also borne out in the infra-red spectra of such compounds. Whereas the infra-red spectra of corresponding oxygen and sulfur compounds are rather different, so that an identification of a specific vibration by comparison between the spectra of sulfur and oxygen compounds may be very uncertain, the spectra of analogous sulfur and selenium compounds are almost identical, except for the bands due to the sulfur- and selenium-containing groups. This method has been used to localize dithiocarboxylate and diselenocarboxylate bands (see the preceding papers) and also to determine the  $\text{P}=\text{S}$  and  $\text{P}=\text{Se}$  absorptions in phosphine sulfides and phosphine selenides and the corresponding bands in arsine sulfides and arsine selenides.

When this method was applied to the study of thioamides, thiosemicarbazides and thioureas it was found that the spectra of the corresponding selenoamides, seleno-semicarbazides and selenoureas were virtually identical with the spectra of the thio-compounds between 1000  $\text{cm}^{-1}$  and 3000  $\text{cm}^{-1}$ . Thus the absorption bands of corresponding thio- and seleno-compounds appear at the same place within a few  $\text{cm}^{-1}$  and in most cases with comparable intensity. Since a vibration which appears in the spectrum of a selenium compound can obviously not be due to  $\text{C}=\text{S}$  vibration the unavoidable conclusion seems to be that thioamides do not show a  $\text{C}=\text{S}$  vibration and that all assignments of infra-red bands to this vibration — in so far as the thioamides are concerned — have been erroneous. Perhaps this is a somewhat academic remark since it is now generally agreed that most strong bands in the infra-red spectra of these compounds contain contributions from several vibrations. Nevertheless, the proponents of the latter view also assume that the bands of thioamides contain contributions from a  $\text{C}=\text{S}$  vibra-

tion. The great similarity of the spectra of thioamides and selenoamides show that this can not be the case. Spectroscopically the thioamides behave as if they had the structure  $\bar{S}-C=\overset{+}{N}<$  and not the structure  $S=C-N<$ .

The strong band in the 1500–1600  $\text{cm}^{-1}$  range which has been called the "Amide II band of thioamides" or the "Thioureide band" is comparable with the "Amide I band" of amides and not with the "Amide II band", the difference being that the stretching of the  $>N-C=O$  grouping has predominantly  $C=O$  character whereas the vibration of the  $>N-C=S$  grouping has predominantly  $C=N$  character. Accordingly this band occurs in the spectra of both primary, secondary and tertiary thioamides. It has been asserted that this band is missing in the spectra of primary thioamides, but this is actually not the case; it may, however, be found at frequencies as low as 1400  $\text{cm}^{-1}$ .

The details of this investigation will be published in some forthcoming papers in this journal.

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## The Relative Yields of Fluorescence and Phosphorescence of Biacetyl in Fluid Solutions

KJELL SANDRÖS and MATS ALMGREN

*Institutionen för fysikalisk kemi, Chalmers Tekniska Högskola, Göteborg, Sweden*

In a previous paper<sup>1</sup> from this laboratory a calculation was presented indicating a quantum yield of 0.22% for the fluorescence of biacetyl in benzene solution at 20°C. This calculation was based on, *inter alia*, a value of 100  $\mu\text{sec}$  for the phosphorescence mean life of biacetyl in a 0.22 M solution. Other determinations of the phosphorescence lifetime in similar solutions have occasionally yielded considerably higher values. It has also been found that prolonged irradiation of a biacetyl solution may lead to a marked increase in the phosphorescence lifetime, presumably

owing to the removal of a quenching impurity in a photochemical reaction. In the experiments reported in the present communication, the phosphorescence mean life was determined both before and after the determination of the ratio between the quantum efficiencies of fluorescence and phosphorescence.

The experimental equipment was essentially the same as earlier<sup>1,2</sup>. The excitation light used was the more strongly absorbed Hg-lines at 405–408  $m\mu$  instead of the lines at 365–366  $m\mu$ , which enabled us to study more dilute solutions with less reabsorption of fluorescence. The measured ratio of fluorescence to phosphorescence was varied by adding varying amounts of isopropanol, which quenches the phosphorescence probably without measurably affecting the fluorescence. In all experiments the phosphorescence lifetime ( $\tau$ ) was found to be constant within limits of error before and after the determination of the ratio between the quantum efficiencies of fluorescence and phosphorescence ( $\Phi_F/\Phi_P$ ).

The results are summarized in Table 1. With increasing isopropanol concentration there is a small blue shift of the fluorescence spectrum and an increase in the value of the phosphorescence quenching constant for isopropanol. However, the gradual change of solvent seems to have a negligible effect on the value of  $\tau \times \Phi_F/\Phi_P$ . There is no trend in these values, although  $\tau$  varied by a factor of more than 20. The mean is 23.3  $\mu\text{sec}$ . This constant may be interpreted on the basis of the tentative transition diagram shown in Fig. 1. Upon excitation to a singlet excited state the molecule may either return to the ground state, emitting fluorescence ( $f$ ), or undergo intersystem crossing to a triplet state ( $x$ ). From this state the molecule may return to the ground state by emission of phos-

Table 1. Phosphorescence mean life and ratio of fluorescence to phosphorescence quantum yields of biacetyl in benzene and benzene-isopropanol solutions.

Conc. of biacetyl m M	Conc. of isopropanol M	$\tau$ $\mu\text{sec}$	$\Phi_F/\Phi_P$ $\times 10^2$	$\tau \times \Phi_F/\Phi_P$ $\mu\text{sec}$
13.5	—	826	2.66	22.0
15.8	—	653	3.31	21.6
12.4	2.89	124	21.0	26.0
10.8	4.04	67	30.5	20.4
12.9	6.05	39	68.5	26.7