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(III) as shown by infrared spectroscopy, m.p. and mixture m.p. with an authentic sample. (Found: C 29.60; H 4.40; N 28.28. Calc. for C\textsubscript{5}H\textsubscript{8}N\textsubscript{2}S\textsubscript{2}: C 29.79; H 4.38; N 26.06.)

Pyrolysis of 4,4-diethylthiosemicarbazide. A flask containing 3 g of 4,4-diethylthiosemicarbazide was heated at 0.2 mm Hg in an oil bath at 110°C. As soon as the compound had melted, an evolution of gas was observed. After heating for 5 min more the melt solidified. Heating was then interrupted and the flask cooled. Boiling ethanol was added and the insoluble crystals filtered off and washed with ethanol. Yield 0.8 g, m.p. 183—184°C. (Found: C 32.61; H 6.88; N 30.63; S 27.96. Calc. for C\textsubscript{5}H\textsubscript{10}N\textsubscript{2}S\textsubscript{2}: C 32.55; H 6.84; N 31.64; S 28.96. The infrared spectrum indicated this to be 1- (or 2-) diethylthiocarbamoylthiocarbonyldiazide. The last alternative would account for the resistance of this compound to undergoing further changes analogously to II.

Pyrolysis of 4,4-dipropylthiosemicarbazide. The same procedure as described for the above thiosemicarbazide yielded 0.4 g of colourless crystals, m.p. 166—167°C, from 2 g of starting material. (Found: C 38.60; H 7.55; N 27.66; S 25.23. Calc. for C\textsubscript{5}H\textsubscript{14}N\textsubscript{2}S\textsubscript{2}: C 38.52; H 7.69; N 28.08; S 25.70. The infrared spectrum similarly suggested this to be 2-dipropylthiocarbamoylthiocarbonyldiazide.

3,6-Bis(dimethylamino)-1,2,4,5-tetrazine. This tetrazine was prepared according to the procedure given by Lin, Lieber and Horwitz for the preparation of 3,6-diazoanil-1,2,4,5-tetrazine. 4,4-Dimethylthiosemicarbazide (I) (15 g) and methyl iodide (17 g) were dissolved in ethanol (150 ml). On addition of 60 ml of 2 N sodium hydroxide, the solution turned red and methanethiol was formed. After standing for one week at room temperature the smell of methanethiol had almost disappeared, and the solution was evaporated to dryness in vacuo.

The residue was extracted with two 100-ml portions of hot benzene (dried over sodium), and the combined extracts were evaporated to dryness. The residue (a red oil) was purified by column chromatography on alumina. Yield 0.5 g of red crystals, m.p. 121—123°C. (Found: C 42.90; H 7.37. Calc. for C\textsubscript{5}H\textsubscript{12}N\textsubscript{2}: C 42.84; H 7.19.) The ultraviolet spectrum showed an absorption at 493 m\textmu \mu, log \epsilon_{max} 3.044. An essentially identical preparation has been reported recently.

Acknowledgment. The authors wish to thank Professor K. A. Jensen for very helpful discussions and advice in some crucial experiments of this investigation.


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A Note on the Computation of Rate Constants by Steepest Decent and Related Methods

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In kinetic investigations of chemical reactions, the following problem often arises. The differential equation system thought to represent the reaction in question, can be integrated to an analytical function, but this is too complex to allow direct graphical evaluation of the rate constants from experimental data.

One frequently occurring example is the function

$$a_1 = a_0 + a_1e^{-k_1t} + a_2e^{-k_2t} + \ldots + a_ne^{-k_nt}$$

(1)

which arises from some first order reaction schemes. Wiberg has published two computer programs for the evaluation of the parameters \(a_i\), \(k_i\), and \(k_i\), from experimental data given as a series of \((a_i, t_i)\) pairs. The first program \((P1)\) varies one parameter at a time until no further decrease in \(U = \sum |\delta_t|\) can be observed, and the second program \((P2)\) is based on the method of steepest descent.

In connection with a kinetic investigation both these methods have been tested on data represented by eqn. 1, and found

Table 1.

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Assuming that $h_1$ and $h_2$ are the best rate constants defining the absolute minimum of $U = \sum \delta^2$, eqn. 1 can be rewritten as

$$a_t = a_0 + a_1 e^{-k_1 t} e^{-h_1 h_2 t} + a_2 e^{-k_2 t} e^{-h_1 t} + \delta$$

(2)

where $k_1$ and $k_2$ are approximate trial values of $h_1$ and $h_2$, respectively. This can again be rewritten as

$$a_t = a_0 + a_1 e^{-k_1 t} [1 - (h_1 - k_1)] + a_2 e^{-k_2 t} [1 - (h_1 - k_2)] + \delta$$

(3)

using truncated Taylor series for the exponential terms containing $h_1$ and $h_2$. Eqn. 3 is now linear ($k_1$ and $k_2$ are the known trial values), and an ordinary regression analysis gives new approximations to $h_1$ and $h_2$ if the terms $(h_1 - k_1)$ and $(h_2 - k_2)$ in eqn. 3 are taken as corrections to $k_1$ and $k_2$, respectively. These new $k$-values are now used in a new regression analysis, giving new corrections etc. The process converges rapidly, provided that the starting values of $k_1$ and $k_2$ are reasonably close to the final values $h_1$ and $h_2$.

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Organic Selenium Compounds

III. Dimethyl Selenoxide Complexes of Transition Elements

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Metal complexes of dimethyl sulfoxide (DMSO) have been studied extensively.1,2,3 The present investigation was initiated to compare the tendency of dimethyl selenoxide (DMSO) to form metal complexes to that of DMSO.

DMSO complexes of iron, cobalt, nickel, copper, palladium, cadmium, and mercury could easily be prepared from the metal chlorides and dimethyl selenoxide. The complexes are soluble in water and insoluble in nonpolar solvents. In most cases the isolated complexes had a composition corresponding to the formula $\text{MC}_{2} \cdot 2\text{DMSO}$, however, from $\text{FeCl}_{3}$ and $\text{PdCl}_{2}$ the $\text{FeCl}_{4}^{-}$ and $\text{PdCl}_{4}^{2-}$ complexes were obtained. The $\text{NiCl}_{4}^{2-}$ and $\text{NiBr}_{4}^{2-}$ complexes were only obtained with 1 mole of DMSO and the $\text{HgCl}_{4}^{2-}$ complex with 1 mole of DMSO. The composition $\text{MC}_{2} \cdot 2\text{DMSO}$ would be in accord with the formation of tetrahedral (Cd, Co) or square-planar (Cu, Ni) complexes, but the structure may be more complicated (e.g. with $\text{MC}_{4}^{2-}$ ions), as is indicated by the composition of the nickel complexes.

In the DMSO complexes the $\nu(\text{S}=\text{O})$ stretching frequency of the free ligand (1055 cm$^{-1}$) in most cases decreases on coordination, indicating that the ligand is oxygen-bonded. However, in DMSO complexes of $\text{Pd}^{2+}$, $\text{Pt}^{2+}$, $\text{Th}^{4+}$, $\text{Zr}^{4+}$, and $\text{UO}_{2}^{2+}$ $\nu(\text{S}=\text{O})$ increases and this has been explained by assuming that the ligand is sulfur-bonded in these cases. In dialkyl selenoxides the $\nu(\text{Se}=\text{O})$ linkage has a more polar character than the $\nu(\text{S}=\text{O})$ linkage in DMSO, and it therefore seems less probable that coordination should occur to selenium. Actually, it was found that the $\nu(\text{Se}=\text{O})$ stretching frequency was lowered for all complexes studied here.

Paetzold and Vordank,4 in a paper which appeared during the present investigation, have studied complexes of diphenyl selenoxide with some transition elements and similarly found a lowering of $\nu(\text{Se}=\text{O})$ for all the complexes studied (Pd or Pt complexes were, however, not prepared).

The infrared spectrum of DMSO was determined in KBr, chloroform, acetonitrile, and dioxan (it was only slightly soluble in carbon tetrachloride or carbon disulfide). The absorption maxima due to $\nu(\text{CH})$ stretching, deformation and rocking (in KBr: 3010 vv, 2920 vv, 1425 m, 1275 m, 960 m, 906 m) coincide essentially with the corresponding bands of DMSO in solution (the gas spectrum*) is, of course, more fully resolved. The $\nu(\text{Se}=\text{O})$ band appears as an extremely strong band at 800 cm$^{-1}$ in the solid spectra and at 820 cm$^{-1}$ in the solution spectra. In acetonitrile and dioxan, DMSO also exhibits a strong band at 760 cm$^{-1}$, which may be due to complex formation with the solvent. A weak band at 585 cm$^{-1}$ is assigned to antisymmetric C-Se stretching (corresponding to the C-S band of DMSO at 690 cm$^{-1}$). The symmetric stretch was not observed.

The infrared spectra of most of the DMSO complexes in the NaCl region differ insignificantly from the spectrum of DMSO, except for the $\nu(\text{Se}=\text{O})$ stretching.