(III) as shown by infrared spectroscopy, m.p. and mixture m.p. with an authentic sample.[2] (Found: C 29.60; H 4.40; N 26.28. Calc. for $C_4H_7N_3S_2$: 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 $C_6H_{15}N_5S_2$: C 32.55; H 6.84; N 31.64; S 28.96). The infrared spectrum indicated this to be 1- (or 2-) diethylthiocarbamoylthiocarbohydrazide. 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 7.65; N 27.56; S 25.23. Calc. for $C_8H_{19}N_5S_2$: C 38.52; H 7.69; N 28.08; S 25.70). The infrared spectrum similarly suggested this to be 2-dipropylthiocarbamoylthiocarbohydrazide.

3,6-Bis(dimethylamino)-1,2,4,5-tetrazine. This tetrazine was prepared according to the procedure given by Lin, Lieber and Horwitz [7] for the preparation of 3,6-diamino-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 aluminia. Yield 0.5 g of red crystals, m.p. 121—123°C. (Found: C 42.90; H 7.37. Calc. for $C_6H_{12}N_6$: C 42.84; H 7.19). The ultraviolet spectrum showed an absorption at 493 mμ, log ε_{max} 3.044. An essentially identical preparation [8] has been reported recently.

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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

$$\alpha_t = \alpha_0 + \alpha_1 e^{-k_1 t} + \alpha_2 e^{-k_2 t} + \delta_t \qquad (1)$$

which arises from some first order reaction schemes.[1] Wiberg [2,3] has published two computer programs for the evaluation of the parameters α_0, α_1, α_2, k_1, and k_2 from experimental data given as a series of (α_t, t) 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 decent.

In connection with a kinetic investigation [4] both these methods have been tested on data represented by eqn. 1, and found

Table 1.

	α_0	α_1	α_2	k_1	k_2
Parameters from Ref. 3	0.9023	−2.034	1.959	−0.671	−0.323
Parameters from Gauss analysis	0.8898	−1.558	1.503	−0.739	−0.279

α_t	t	δ_t from Ref. 3	δ_t Gauss anal.	α_t	t	δ_t from Ref. 3	δ_t Gauss anal.
1.028	0.3	0.0103	0.0040	1.382	2.8	−0.0028	0.0001
1.075	0.4	0.0058	0.0000	1.371	3.0	−0.0032	−0.0006
1.118	0.5	0.0026	−0.0026	1.360	3.2	−0.0018	0.0004
1.158	0.6	0.0012	−0.0034	1.345	3.4	−0.0030	−0.0013
1.230	0.8	0.0034	0.0002	1.335	3.5	−0.0057	−0.0043
1.283	1.0	0.0017	−0.0002	1.299	4.0	−0.0027	−0.0028
1.325	1.2	0.0019	0.0012	1.262	4.5	0.0010	−0.0007
1.350	1.4	−0.0041	−0.0036	1.222	5.0	0.0010	−0.0022
1.365	1.5	−0.0011	−0.0001	1.190	5.5	0.0069	0.0024
1.376	1.6	0.0000	0.0015	1.158	6.0	0.0099	0.0043
1.389	1.8	−0.0011	0.0010	1.097	7.0	0.0090	0.0023
1.398	2.0	0.0001	0.0027	1.044	8.0	0.0033	−0.0033
1.398	2.2	−0.0024	0.0006				
1.397	2.4	−0.0015	0.0016	$\sum \delta_t^2$		0.00051	0.00014
1.395	2.5	−0.0012	0.0019	$\sigma(\delta)$		0.0047	0.0025
1.391	2.6	−0.0021	0.0010				

to be inaccurate. The reason for this inaccuracy is that both methods converge more slowly the closer the procedure approaches the minimum of U, thus giving a false convergence. Rosenbrock [5] has discussed this problem in some detail. The best method to handle the above problem of parameter estimation seems to be that of Gauss, first applied to eqn. 1 by Moore and Zeigler [6,7] in connection with investigations of radio active decay. The Gauss method was used in the above mentioned kinetic investigation and was found to be very reliable. The accuracy of the Gauss method was tested by a parallel analysis with Sillén's pitmapping method,[8] which gave identical results, but was much more time-consuming.

As an example of the inaccuracy of the methods used by Wiberg, a series of data from Ref. 3, p. 183 has been recalculated by the Gauss method. As can be seen in Table 1, the resulting parameters are quite different from those obtained by P1 or P2. The standard deviation of δ is improved by almost 50 %, showing that P1 and P2 stop well before the absolute minimum of U.

Appendix. A short description of the Gauss method as applied on eqn. 1.

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

$$\alpha_t = \alpha_0 + \alpha_1 e^{-k_1 t} e^{-(h_1 - k_1)t} + \alpha_2 e^{-k_2 t} e^{-(h_2 - k_2)t} + \delta_t \qquad (2)$$

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

$$\alpha_t = \alpha_0 + \alpha_1 e^{-k_1 t} [1 - (h_1 - k_1)t] + \alpha_2 e^{-k_2 t} [1 - (h_2 - k_2)t] + \delta_t' \qquad (3)$$

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.[1-7] The present investigation was initiated to compare the tendency of dimethyl selenoxide (DMSeO) to form metal complexes to that of DMSO.

DMSeO 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 $MCl_2 \cdot 2DMSeO$, however, from $FeCl_2$ and $PdCl_2$ the $FeCl_3$ and $PdCl_4$ complexes were ob-

tained. The $NiCl_2$ and $NiBr_2$ complexes were only obtained with $1\frac{1}{2}$ moles of DMSeO and the $HgCl_2$ complex with 1 mole of DMSeO. The composition $MCl_2 \cdot 2DMSeO$ 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 $MCl_4{}^{2-}$ ions), as is indicated by the composition of the nickel complexes.

In the DMSO complexes the $S=O$ 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 Pd,[3] Pt,[3] Th,[6] Zr,[6] and $UO_2{}^7$ $\nu(S=O)$ increases and this has been explained by assuming that the ligand is sulfur-bonded in these cases. In dialkyl selenoxides the $Se=O$ linkage has a more polar character than the $S=O$ linkage in DMSO, and it therefore seems less probable that coordination should occur to selenium. Actually, it was found that the $Se=O$ stretching frequency was lowered for all complexes studied here.

Paetzold and Vordank,[8] 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 $\nu(Se=O)$ for all the complexes studied (Pd or Pt complexes were, however, not prepared).

The infrared spectrum of DMSeO was determined in KBr, chloroform, acetonitrile, and dioxan (it was only slightly soluble in carbon tetrachloride or carbon disulfide). The absorption maxima due to CH_3 stretching, deformation and rocking (in KBr: 3010 vw, 2920 vw, 1425 m, 1275 m, 960 m, 906 m) coincide essentially with the corresponding bands of DMSO in solution (the gas spectrum [9] is, of course, more fully resolved). The $Se=O$ 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, DMSeO 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 DMSeO complexes in the NaCl region differ insignificantly from the spectrum of DMSeO, except for the $Se=O$ stretching