

Decomposition of Tetrakis(*N,N*-diethyldithiocarbamato)selenium(IV)

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The kinetics of the decomposition of tetrakis(*N,N*-diethyldithiocarbamato)selenium(IV) have been studied by proton magnetic resonance. The decomposition is first order in ethyl selenac and in water. Major decomposition products are *N,N,N',N'*-tetraethylthiuram disulfide and selenium, obtained through selenious acid and *N,N*-diethyldithiocarbamic acid intermediates. The impor-

tance of decomposition of the intermediate *N,N*-diethyldithiocarbamic acid to diethylamine and carbon disulfide is greater at high water concentrations and low pH values. The activation thermodynamic parameters for the ethyl selenac decomposition are $\Delta G^\ddagger = 19.9$ kcal/mol, $\Delta H^\ddagger = 17.5$ kcal/mol, $\Delta S^\ddagger = -8.2$ eu, and the Arrhenius activation energy, $E_a = 18.1$ kcal/mol.

Dithiocarbamate derivatives have been found to be useful in many applications since they were first patented for use as fungicides (Tisdale and Williams, 1934). The metallic dialkyldithiocarbamates have found extensive commercial acceptance as fungicides and as accelerators in compounding sulfurless or sulfur heat-resisting rubber. Knowledge of the rates of degradation and degradation products of these compounds is of environmental and biological significance in two major areas of concern, namely: the effects of "weathering" of the metallic dialkyldithiocarbamates when they are used as fungicides (for example, possible crop residues which may be ingested); and the possibility of residues of these compounds and the products of their decomposition as occupational hazards to persons involved in rubber compounding and formulations and as environmental hazards from the decay of rubber products in widespread use, such as tires.

Excellent reviews of the chemistry and mode of action of the dithiocarbamates and related compounds have been published (Ludwig and Thorn, 1960; Thorn and Ludwig, 1962; Owens, 1963; Halls, 1969). Studies of the decomposition of several dithiocarbamates have been carried out (Dröger and Gattow, 1968; Joris *et al.*, 1970; Vandebek *et al.*, 1970). The decomposition of diethyldithiocarbamic acid as a function of pH and ionic strength has been studied (Aspila *et al.*, 1970). Proton magnetic resonance spectroscopy has been used to investigate the stability of sodium diethyldithiocarbamate in aqueous solution (Dale and Fishbein, 1970). Solvent isotope effects on the decomposition of several *N,N*-dialkyldithiocarbamic acids have also been studied (Aspila *et al.*, 1971). In the work reported here, proton magnetic resonance techniques were used to follow the decomposition of tetrakis(*N,N*-diethyldithiocarbamato)selenium(IV), commonly known as ethyl selenac.

MATERIALS AND METHODS

Ethyl selenac of reagent quality was obtained from R. T. Vanderbilt Co., New York, N.Y. Recrystallized from ethanol, it melted at 110.5–113°C, and showed no significant impurity peaks in the ir or nmr spectra. Deuterated solvents were commercial spectral grade. Water was triply distilled and deionized. Organic solvents were dried with $1/16$ -in. pellets of Linde 3A molecular sieves. Nmr tubes and glassware were dried overnight in an oven at 110°C before use.

Proton magnetic resonance spectra were obtained with a Varian HA-100 spectrometer, operated in the frequency sweep mode with tetramethylsilane as an internal lock. The Varian temperature controller maintained the sample temperature while in the probe within $\pm 1^\circ\text{C}$. A YSI telethermometer, with a thermistor enclosed in a glass tube and positioned in the center of the receiver coil, was used to measure the probe temperature within $\pm 0.5^\circ\text{C}$. Outside the spectrometer, samples were kept in a stirred water bath using a Cole-Parmer 4812 magnetic stirrer with hot plate and liquid immersion probe which controlled the water temperature within $\pm 0.5^\circ\text{C}$.

Samples were made up initially by adding a known weight of solvent, approximately 0.40 ml in volume, prewarmed in the water bath, to a weighed quantity of ethyl selenac ranging from 4.06 to 42.9 mg. The time of reaction was measured from the point of mixing of the solid ethyl selenac with the solvent. Concentrations of ethyl selenac and its decomposition products were determined as a function of time from the nmr spectra in the following way. Since the methylene quartet signals of reactant and product overlapped to some extent ($\tau = 6.11$ and $\tau = 6.01$ for ethyl selenac and major product, respectively, in acetone- d_6 at 27°C), the height of a single component of each quartet was measured. These heights were compared to the height of the peak due to partially nondeuterated solvent impurity in the deuterated solvent (*e.g.*, $\text{CHD}_2\text{COCD}_3$ in CD_3COCD_3). The concentration of this impurity remained constant with time, so its peak height served as an intensity standard.

After the decomposition had proceeded more than half-way in each case, the sample tubes were opened and the identity of the contents was confirmed by thin-layer chromatography and chemical tests.

RESULTS

The decomposition of ethyl selenac was followed by the methods outlined above in several solvents, including dimethyl sulfoxide- d_6 , tetrahydrofuran- d_5 , toluene- d_8 , acetone- d_6 and CDCl_3 . Considerable confusion obtained when results in these solvents were first compared, since there appeared to be no correlation with solvent, concentration, or temperature. A varying small percentage of water in the solvents was finally found to be responsible for the erratic results. When the solvents were carefully dried with molecular sieves, the results were consistent (except in dimethyl sulfoxide, which could not be dried sufficiently) and gave a linear dependence of the logarithm of the ethyl selenac concentration on time, indicating a first-order dependence on

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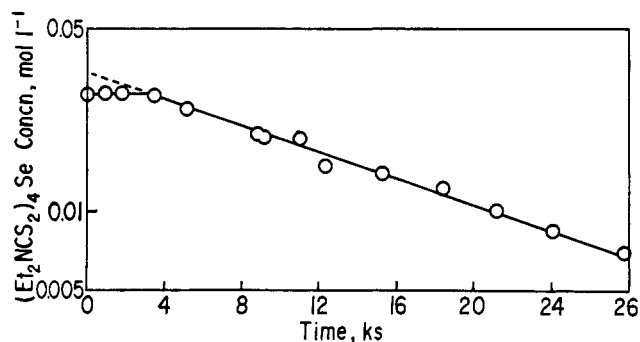


Figure 1. Semilogarithmic plot of the concentration of $(\text{Et}_2\text{NCS}_2)_4\text{Se}$ vs. time at 39.5°C in acetone- d_6 with $6.17 \times 10^{-4} M$ water

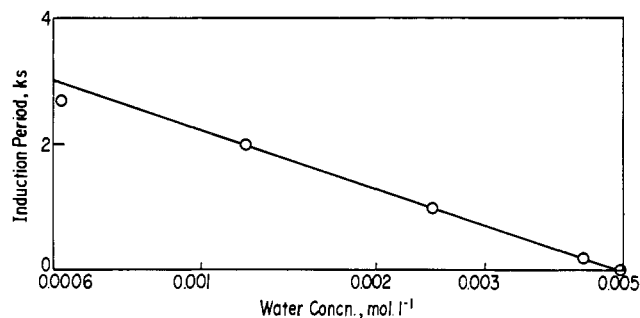


Figure 2. The induction period for $(\text{Et}_2\text{NCS}_2)_4\text{Se}$ decomposition as a function of water concentration at 28.0°C . The initial $(\text{Et}_2\text{NCS}_2)_4\text{Se}$ concentration in each case is $2.85 \times 10^{-2} M$, in acetone- d_6

ethyl selenac. A typical curve for the decomposition is shown in Figure 1. There is an initial induction period, during which the ethyl selenac concentration does not change. The length of this induction period depends on the water concentration, as shown in Figure 2.

After the induction period, the rate also depends on the water concentration, but since the water concentration does not change significantly throughout the experiment, the decomposition appears first order overall, that is, pseudo-first-order conditions prevail. The rate expression can be written as:

$$-\frac{d[(\text{Et}_2\text{NCS}_2)_4\text{Se}]}{dt} = k[(\text{Et}_2\text{NCS}_2)_4\text{Se}][\text{H}_2\text{O}]^n$$

At a given water concentration, this appears to be

$$-\frac{d[(\text{Et}_2\text{NCS}_2)_4\text{Se}]}{dt} = k'[(\text{Et}_2\text{NCS}_2)_4\text{Se}]$$

where $k' = k[\text{H}_2\text{O}]^n$. k' is obtained from the slope of the plot of $\log [(\text{Et}_2\text{NCS}_2)_4\text{Se}]$ vs. time. If the ethyl selenac concentration is the same, for two concentrations of water $[\text{H}_2\text{O}]_a$ and $[\text{H}_2\text{O}]_b$ at the same temperature,

$$\frac{k'_a}{k'_b} = \left(\frac{[\text{H}_2\text{O}]_a}{[\text{H}_2\text{O}]_b} \right)^n$$

and a plot of $\ln k'_a/k'_b$ vs. $\ln [\text{H}_2\text{O}]_a/[\text{H}_2\text{O}]_b$ should be linear, with slope equal to n . Such a plot is shown in Figure 3. The slope is 1.01.

The identification of the products was straightforward. The major product, N,N,N',N' -tetraethylthiuram disulfide, had an nmr spectrum identical, including lineshape behavior, to that reported (Wilson, 1971) in a study of hindered rotation

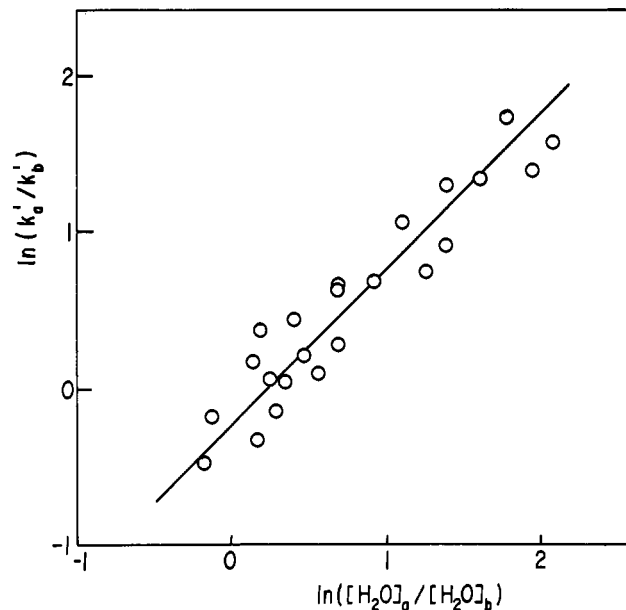


Figure 3. The logarithm of the ratio of apparent first-order rate constants vs. the logarithm of the ratio of water concentrations, for decomposition of initially $2.82 \times 10^{-2} M$ $(\text{Et}_2\text{NCS}_2)_4\text{Se}$ in acetone- d_6 at 39.5°C . Water concentrations ranged from $6.74 \times 10^{-3} M$ to $1.4 \times 10^{-1} M$

in this compound. The precipitate of gray selenium melted at 220°C , which compares well with a literature value of 217°C . A small amount of amorphous (red) selenium formed underwent a transition to the gray form at exactly the right temperature (80°C) and melted at 220°C also. Thin-layer chromatography confirmed the major product as N,N,N',N' -tetraethylthiuram disulfide (TETD).

Tlc also showed the presence of a small amount of diethylamine in most samples. The diethylamine was present to the extent of 10% or more of total products only in those samples in which the water concentration was greater than about twelve times the initial ethyl selenac concentration. Its production was followed by nmr and shown to parallel the decomposition of the ethyl selenac and to be first order. A strong odor of carbon disulfide came from these samples when opened.

Chemical tests for sulfite and sulfate (Wiig *et al.*, 1954) and for selenite and selenate (Rosenfeld and Beath, 1964) indicated that none of these were present in the samples when initially made up. After decomposition of ethyl selenac had proceeded more than halfway, the selenium precipitate was filtered off and the supernatant again tested for the presence of these anions. In about one-third of the samples, a positive test was obtained for the presence of selenite. The amount present appeared to be fairly small.

In a mixed tetrahydrofuran- d_8 - H_2O solvent, it was found that the pH remained constant throughout the experiment. When a sample was acidified to pH 3.67, the rate of decomposition of the ethyl selenac remained the same. However, the rate of formation of TETD decreased, indicating removal of an intermediate at low pH. Added base to bring the pH from 7 to 10 did not appear to affect the rates.

After decomposition has proceeded for about three half-lives, the relative concentrations of ethyl selenac and the N,N,N',N' -tetraethylthiuram disulfide product appear to level off, indicating an equilibrium has been reached. The equilibrium constant is 0.413 mol/l. at 33°C , assuming the equilibrium constant can be written as $(\text{Et}_2\text{NCS}_2)_4\text{Se} \rightleftharpoons \text{Se} +$

$2(\text{Et}_2\text{NCS}_2)_2$. Further decomposition of the ethyl selenac then occurs only as the TETD is removed by its own slow decomposition.

The activation energies, E_a , for the decomposition in several solvents were obtained from Arrhenius plots of $\ln k$ vs. $1/T$, where T is the absolute temperature according to $k = Ae^{-E_a/RT}$, where A is a frequency factor and R is the gas constant. Values of the parameters ΔH^\ddagger , ΔG^\ddagger , and ΔS^\ddagger , the activation enthalpy, free energy, and entropy, respectively, were obtained similarly using the Eyring equation

$$k = \frac{\kappa k_B T}{h} e^{-\Delta G^\ddagger/RT}$$

and $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$. k_B is the Boltzmann constant, κ a transmission coefficient, taken to be 1, and h is Planck's constant. Figure 4 shows a typical plot to obtain these parameters. The resultant values are given in Table I.

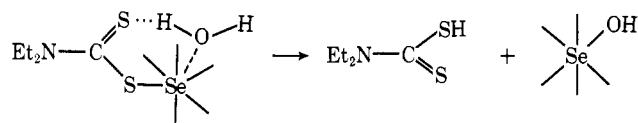
DISCUSSION

The overall rate equation for the decomposition of ethyl selenac has been shown to be of the form

$$\frac{-d[(\text{Et}_2\text{NCS}_2)_4\text{Se}]}{dt} = k[(\text{Et}_2\text{NCS}_2)_4\text{Se}][\text{H}_2\text{O}]$$

Samples in nonpolar solvents which had been very carefully dried showed little decomposition over long periods of time (several weeks) although they eventually did decompose. The data point to a reaction in which the water used in the initial stage is later regenerated. If every trace of moisture could be removed, the rate of decomposition of ethyl selenac samples would be essentially zero.

By analogy with bis(*N,N*-diethyldithiocarbamato)selenium(II), which has an asymmetric planar molecular structure with all four sulfurs bound to the selenium (Husebye and Helland-Madsen, 1970), and with tetrakis(*N,N*-diethyldithio carbamato)tin(IV), in which there is a six-coordinate tin atom in a distorted octahedron (Harreld and Schlemper, 1971), the tetrakis compound might be expected to have an asymmetric octahedral structure, in which six of the eight sulfurs are bound to the selenium. During the induction period, solvation of the ethyl selenac by water takes place. No change in the nmr spectrum occurs during this period. Water solvation is followed by the splitting off of diethyldithiocarbamic acid, in a stepwise process involving a quasi six-membered ring transition state, whose slowest step is rate-determining.



The large negative activation entropy for the reaction is consistent with the increase in order accompanying formation of the six-membered ring transition state.

Further loss of diethyldithiocarbamic acid occurs, with formation of selenious acid, so that the overall equation for the first and second steps is $(\text{Et}_2\text{NCS}_2)_4\text{Se} + 3\text{H}_2\text{O} \rightarrow \text{H}_2\text{SeO}_3 + 4\text{HS}_2\text{CNEt}_2$. The formation of selenious acid as an intermediate is confirmed by the presence of selenite ion in the reaction products. Selenious acid, an excellent oxidizing agent as evidenced by its reduction potential of +0.74 V for $\text{H}_2\text{SeO}_3 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{Se} + 3\text{H}_2\text{O}$ then oxidizes the dithiocarbamic acid in a rapid step to *N,N,N',N'*-tetraethyl-

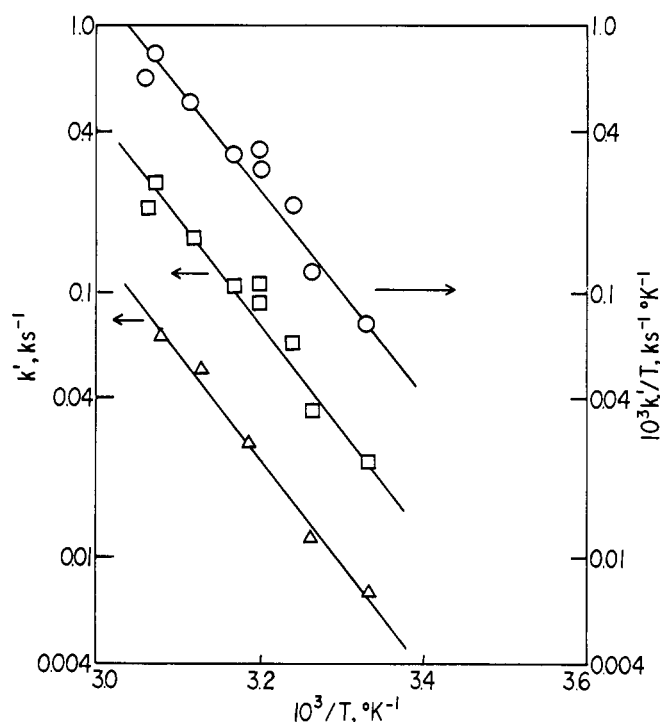


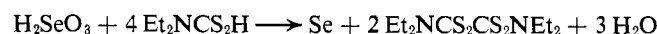
Figure 4. Arrhenius plots of the logarithm of the rate constant vs. the reciprocal of the absolute temperature for the decomposition of $(\text{Et}_2\text{NCS}_2)_4\text{Se}$ in acetone- d_6 dried with molecular sieves, Δ - Δ ; acetone- d_6 with $6.17 \times 10^{-4} M$ water, \square - \square ; and an Eyring plot for this decomposition in acetone- d_6 with $6.17 \times 10^{-4} M$ water, \circ - \circ

Table I. Thermodynamic Parameters for the Decomposition of Tetrakis(*N,N*-diethyldithiocarbamato)selenium(IV) at 25°C

	Solvent		
	acetone- d_6 + $10^{-3} M$ water	acetone- d_6 dried	toluene- d_8 dried
E_a , kcal mol $^{-1}$	18.1 ± 0.3	18.6 ± 0.3	19.1 ± 0.5
ΔH^\ddagger , kcal mol $^{-1}$	17.5 ± 0.3	18.0 ± 0.3	18.5 ± 0.5
ΔG^\ddagger , kcal mol $^{-1}$	19.9 ± 0.3
ΔS^\ddagger , eu	-8.2 ± 0.1

^a ΔG^\ddagger and ΔS^\ddagger were not calculated for the dried solvents due to uncertainty in the water concentration.

thiuram disulfide, with the production of elemental selenium and the regeneration of water.



Although more than one water molecule is involved in the solvation and formation of $\text{Et}_2\text{NCS}_2\text{H}$, the overall reaction has a first-order dependence on water since the water concentration does not change over the course of the reaction. The formation of the breakdown products of diethyldithiocarbamic acid, diethylamine and carbon disulfide, confirms the diethyldithiocarbamic acid intermediate. The results in acidified media show that the pathway involving production of diethyldithiocarbamic acid and its decomposition to diethylamine and CS_2 is relatively more important at low pH values. Long-term experiments will of course lead to further breakdown of the tetraethylthiuram disulfide product into, among others, sulfur, H_2S , CS_2 , and tetraethylthiourea (Thorn and Ludwig, 1962), all of which have been found in

small amounts in samples which have stood for several days or more.

The metallic dialkyldithiocarbamates have been shown to exhibit inhibitory effects on certain enzyme systems (Thorn and Ludwig, 1962; Dailey *et al.*, 1969). In addition, the results of this study indicate that in any determination of the biological effects of ethyl selenac, the presence of thiuram disulfide, selenite, and diethyldithiocarbamate must be considered. Selenite ion is known to inhibit several enzyme systems (Rosenfeld and Beath, 1964). TETD, also known as Antabuse or Disulfiram, is not only a rubber accelerator, vulcanizer, seed disinfectant, and fungicide *per se*, but also has antialcoholic utility and exhibits a battery of *in vivo* effects. Among the known biological effects of TETD are: inhibition of acetaldehyde dehydrogenase (Graham, 1951); prolongation of hexobarbital sleeping time in rats (Maj and Przegalinski, 1967); inhibition of dopamine β -hydroxylase in rats (Goldstein *et al.*, 1964); increase in the toxicity of diphenylhydantoin in man (Olesen, 1966); and impairment of drug metabolism by rat liver microsomes (decrease in *N*-demethylase activity) (Stripp *et al.*, 1969). Additionally, diethyldithiocarbamate, an intermediate in the decomposition studied here and a metabolite of TETD, has been shown to have some inhibitory effect on dopamine β -hydroxylase (Musacchio *et al.*, 1964). Since in natural environmental conditions aqueous media are the rule, the pathway for production of diethyldithiocarbamate and its further degradation to diethylamine and CS₂ assumes perhaps even greater relevance than the production of TETD. Thus, to account for the known effects of ethyl selenac as well as to predict the effects of its breakdown in the environment, the presence of *N,N,N',N'*-tetraethylthiuram disulfide, *N,N*-diethyldithiocarbamate, selenite, and elemental selenium as well as their breakdown products must be considered.

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Rotenone Photodecomposition

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Irradiation of rotenone in oxygenated methanol solution with ultraviolet light yields the following crystalline products: *O*-demethylrotenone; 6 α ,12 α -rotenolone; rotenonone; and three acids (4,5-dimethoxysalicylic, rissic, and tubaic acids) which were methylated prior to their isolation. Rotenone photodecomposes on plant leaves exposed to sunlight and on glass surfaces irradiated with sunlight, ultraviolet light, or a sunlamp to yield at least 20 compounds, including *O*-demethylrotenone, 6',7'-

epoxyrotenone, 6 α ,12 α - and 6 α ,12 α -rotenolones, 6',7'-epoxy-6 α ,12 α -rotenolone, 6 α ,12 α -dehydrorotenone, and rotenonone. Methods of synthesis are described for the new *O*-demethyl- and 6',7'-epoxy derivatives of rotenone. In the determination of residues in or on crops treated with rotenone, it is important to determine the major toxic photodecomposition product, 6 α ,12 α -rotenolone, as well as rotenone.

Rotenone effectively controls many phytophagous insects but only for a short period of time after application because it decomposes in the presence of light and air. On the basis of work done several decades ago, it is known

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that rotenone photodecomposes in solution and as spray residues to yield rotenolones, 6 α ,12 α -dehydrorotenone, rotenonone, and a mixture of unidentified products (Cahn *et al.*, 1945; Jones and Haller, 1931; Subba Rao and Pollard, 1951). More recent studies on rotenone chemistry serve as a basis for a reexamination of the mechanisms and pathways of rotenone photodecomposition (Crombie, 1963).

This paper describes the products obtained when rotenone solutions in methanol and benzene are exposed to ultraviolet (uv) light, while oxygen is bubbled through the solutions, and