


TOPICS IN CURRENT CHEMISTRY

251

Volume Editor S. Kato

Chalcogenocarboxylic Acid Derivatives

 Springer

Chalcogenocarboxylic Acid Derivatives

Volume Editor: Shinzi Kato

With contributions by

S.-I. Fujiwara · A. Ishii · N. Kambe · N. Kano · S. Kato · T. Kawashima
T. Murai · J. Nakayama · O. Niyomura

The series *Topics in Current Chemistry* presents critical reviews of the present and future trends in modern chemical research. The scope of coverage includes all areas of chemical science including the interfaces with related disciplines such as biology, medicine and materials science. The goal of each thematic volume is to give the nonspecialist reader, whether at the university or in industry, a comprehensive overview of an area where new insights are emerging that are of interest to a larger scientific audience.

As a rule, contributions are specially commissioned. The editors and publishers will, however, always be pleased to receive suggestions and supplementary information. Papers are accepted for *Topics in Current Chemistry* in English.

In references *Topics in Current Chemistry* is abbreviated Top Curr Chem and is cited as a journal.

Visit the TCC content at springerlink.com

Library of Congress Control Number: 2004111708

ISSN 0340-1022

ISBN 3-540-23012-2 **Springer Berlin Heidelberg New York**

DOI 10.1007/b98140

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other ways, and storage in data banks. Duplication of this publication or parts thereof is only permitted under the provisions of the German Copyright Law of September 9, 1965, in its current version, and permission for use must always be obtained from Springer-Verlag. Violations are liable to prosecution under the German Copyright Law.

Springer is a part of Springer Science+Business Media

springeronline.com

© Springer-Verlag Berlin Heidelberg 2005

Printed in The Netherlands

The use of general descriptive names, registered names, trademarks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

Cover design: KünkelLopka, Heidelberg/design & production GmbH, Heidelberg

Typesetting: Fotosatz-Service Köhler GmbH, Würzburg

Printed on acid-free paper 02/3141/xv - 5 4 3 2 1 0

251

Topics in Current Chemistry

Editorial Board:

**A. de Meijere · K. N. Houk · H. Kessler · J.-M. Lehn · S.V. Ley
S. L. Schreiber · J. Thiem · B. M. Trost · F. Vögtle · H. Yamamoto**

Topics in Current Chemistry

Recently Published and Forthcoming Volumes

Anion Sensing

Volume Editor: Stibor, I.
Vol. 255, 2005

Organic Solid State Reactions

Volume Editor: Toda, F.
Vol. 254, 2005

DNA Binders and Related Subjects

Volume Editors: Waring, M.J., Chaires, J.B.
Vol. 253, 2005

Contrast Agents III

Volume Editor: Krause, W.
Vol. 252, 2005

Chalcogenocarboxylic Acid Derivatives

Volume Editor: Kato, S.
Vol. 251, 2005

New Aspects in Phosphorus Chemistry V

Volume Editor: Majoral, J.-P.
Vol. 250, 2005

Templates in Chemistry II

Volume Editors: Schalley, C.A., Vögtle, F.,
Dötz, K.H.
Vol. 249, 2005

Templates in Chemistry I

Volume Editors: Schalley, C.A., Vögtle, F.,
Dötz, K.H.
Vol. 248, 2004

Collagen

Volume Editors: Brinckmann, J.,
Notbohm, H., Müller, P.K.
Vol. 247, 2005

New Techniques in Solid-State NMR

Volume Editor: Klinowski, J.
Vol. 246, 2005

Functional Molecular Nanostructures

Volume Editor: Schlüter, A.D.
Vol. 245, 2005

Natural Product Synthesis II

Volume Editor: Mulzer, J.
Vol. 244, 2005

Natural Product Synthesis I

Volume Editor: Mulzer, J.
Vol. 243, 2005

Immobilized Catalysts

Volume Editor: Kirschning, A.
Vol. 242, 2004

Transition Metal and Rare Earth Compounds III

Volume Editor: Yersin, H.
Vol. 241, 2004

The Chemistry of Pheromones and Other Semiochemicals II

Volume Editor: Schulz, S.
Vol. 240, 2005

The Chemistry of Pheromones and Other Semiochemicals I

Volume Editor: Schulz, S.
Vol. 239, 2004

Orotidine Monophosphate Decarboxylase

Volume Editors: Lee, J.K., Tantillo, D.J.
Vol. 238, 2004

Long-Range Charge Transfer in DNA II

Volume Editor: Schuster, G.B.
Vol. 237, 2004

Long-Range Charge Transfer in DNA I

Volume Editor: Schuster, G.B.
Vol. 236, 2004

Spin Crossover in Transition Metal Compounds III

Volume Editors: Gülich, P., Goodwin, H.A.
Vol. 235, 2004

Spin Crossover in Transition Metal Compounds II

Volume Editors: Gülich, P., Goodwin, H.A.
Vol. 234, 2004

Spin Crossover in Transition Metal Compounds I

Volume Editors: Gülich, P., Goodwin, H.A.
Vol. 233, 2004

Volume Editors

Prof. Dr. Shinzi Kato
Department of Applied Chemistry
School of Engineering
Chubu University
Kasugai
Aichi, 487-8501, Japan
kshinzi@nifty.com

Editorial Board

Prof. Dr. Armin de Meijere
Institut für Organische Chemie
der Georg-August-Universität
Tammannstraße 2
37077 Göttingen, Germany
ameijer1@uni-goettingen.de

Prof. Dr. Horst Kessler
Institut für Organische Chemie
TU München
Lichtenbergstraße 4
85747 Garching, Germany
kessler@ch.tum.de

Prof. Steven V. Ley
University Chemical Laboratory
Lensfield Road
Cambridge CB2 1EW, Great Britain
svl1000@cus.cam.ac.uk

Prof. Dr. Joachim Thiem
Institut für Organische Chemie
Universität Hamburg
Martin-Luther-King-Platz 6
20146 Hamburg, Germany
thiem@chemie.uni-hamburg.de

Prof. Dr. Fritz Vögtle
Kekulé-Institut für Organische Chemie
und Biochemie der Universität Bonn
Gerhard-Domagk-Straße 1
53121 Bonn, Germany
voegtle@uni-bonn.de

Prof. Kendall N. Houk
Department of Chemistry and Biochemistry
University of California
405 Hilgard Avenue
Los Angeles, CA 90024-1589, USA
houk@chem.ucla.edu

Prof. Jean-Marie Lehn
ISIS
8, allée Gaspard Monge
BP 70028
67083 Strasbourg Cedex, France
lehn@isis.u-strasbg.fr

Prof. Stuart L. Schreiber
Chemical Laboratories
Harvard University
12 Oxford Street
Cambridge, MA 02138-2902, USA
sls@slsiris.harvard.edu

Prof. Barry M. Trost
Department of Chemistry
Stanford University
Stanford, CA 94305-5080, USA
bmtrost@leland.stanford.edu

Prof. Hisashi Yamamoto
Arthur Holly Compton Distinguished
Professor
Department of Chemistry
The University of Chicago
5735 South Ellis Avenue
Chicago, IL 60637
773-702-5059, USA
yamamoto@uchicago.edu

Topics in Current Chemistry Also Available Electronically

For all customers who have a standing order to Topics in Current Chemistry, we offer the electronic version via SpringerLink free of charge. Please contact your librarian who can receive a password for free access to the full articles by registration at:

springerlink.com

If you do not have a subscription, you can still view the tables of contents of the volumes and the abstract of each article by going to the SpringerLink Homepage, clicking on "Browse by Online Libraries", then "Chemical Sciences", and finally choose Topics in Current Chemistry.

You will find information about the

- Editorial Board
- Aims and Scope
- Instructions for Authors
- Sample Contribution

at springeronline.com using the search function.

Preface

Chalcogenocarboxylic acid derivatives are a large class of compounds including more than one chalcogenocarboxyl group in which one or two oxygen atoms of the carboxyl group are replaced by sulfur, selenium or tellurium atoms. There are 15 kinds of compounds of chalcogenocarboxylic acid (Table 1). As the hydrogen atom of hydrochalcogenoxide (EH) group in RCOEH (E=S, Se, Te) can also be replaced by all of the element in the periodic Table and in addition, Group 2 to 16 elements can formally bind with more than two chalcogenocarboxyl groups, the number of the types increases to over 10000, even limited to the case where R=methyl group. The chemistry of metal chalcogenocarboxylates has not been explored extensively as that of carboxylates and dithiocarbamates. This volume presents a comprehensive overview of the syntheses and their limitations, structures and reactions of chalcogenocarboxylic acid derivatives, by emphasizing the developments in organic and inorganic chalcogen chemistry over the last 5 to 20 years.

Takayuki Kawashima and Naokazu Kano wrote Chapter 3, Juzo Nakayama and Akio Ishii Chapters 4 and 5, Nobuaki Kambe and Shin-ichi Fujiwara contributed Chapter 6, and Toshiaki Murai submitted Chapter 7 and Osamu Niyomura and I presented Chapters 1 and 2.

Finally I thanks Professors Hisashi Yamamoto of Chicago University and Tamejiro Hiyama of Kyoto University for suggesting we write this book and the encouragement they gave us.

Nagoya, November 2004

Shinzi Kato

Contents of Volume 231

Elemental Sulfur and Sulfur-Rich Compounds II

Volume Editor: R. Steudel

ISBN 3-540-40378-7

Quantum-Chemical Calculations of Sulfur-Rich Compounds

M. W. Wong

Molecular Spectra of Sulfur Molecules and Solid Sulfur Allotropes

B. Eckert · R. Steudel

Inorganic Polysulfanes H_2S_n with $n > 1$

R. Steudel

Inorganic Polysulfides S_n^{2-} and Radical Anions S^{n-}

R. Steudel

Polysulfido Complexes of Main Group and Transition Metals

N. Takeda · N. Tokitoh · R. Okazaki

Sulfur-Rich Oxides S_nO and S_nO_2

R. Steudel

Contents

Chalcogenocarboxylic Acids O. Niyomura · S. Kato	1
Group 1–17 Element (Except Carbon) Derivatives of Thio-, Seleno- and Telluro-Carboxylic Acids S. Kato · O. Niyomura	13
Thio-, Seleno-, and Telluro-Carboxylic Acid Esters S.-i. Fujiwara · N. Kambe	87
Dithiocarboxylic Acid Salts of Group 1–17 Elements (Except for Carbon) N. Kano · T. Kawashima	141
Carbodithioic Acid Esters A. Ishii · J. Nakayama	181
Carboselenothioic and Carbodiselenoic Acid Derivatives and Related Compounds A. Ishii · J. Nakayama	227
Thio-, Seleno-, and Telluro-Amides T. Murai	247
Author Index Volume 251	273
Subject Index	275

Chalcogenocarboxylic Acids

Osamu Niyomura¹ · Shinzi Kato² (✉)

¹ Division of Chemistry, Center for Natural Sciences, College of Liberal Arts and Sciences, Kitasato University, Kitasato, Sagamihara, Kanagawa 228–8555, Japan
niyomura@clas.kitasato-u.ac.jp

² Department of Applied Chemistry, School of Engineering, Chubu University, Matsumoto-Cho, Kasugai, Aichi, 487–8501, Japan
kshinzi@nifty.com

1 Introduction	2
2 Syntheses	3
2.1 Monochalcogenocarboxylic Acids	3
2.2 Dichalcogenocarboxylic Acids	3
3 Structures and Physical Properties	4
3.1 Spectroscopic Studies	4
3.2 X-ray Structural Analyses	6
3.3 Theoretical Studies	7
4 Reactions	8
4.1 Thiocarboxylic Acids	8
4.2 Dithiocarboxylic Acids	10
4.3 Seleno- and Tellurocarboxylic Acids	10
References	11

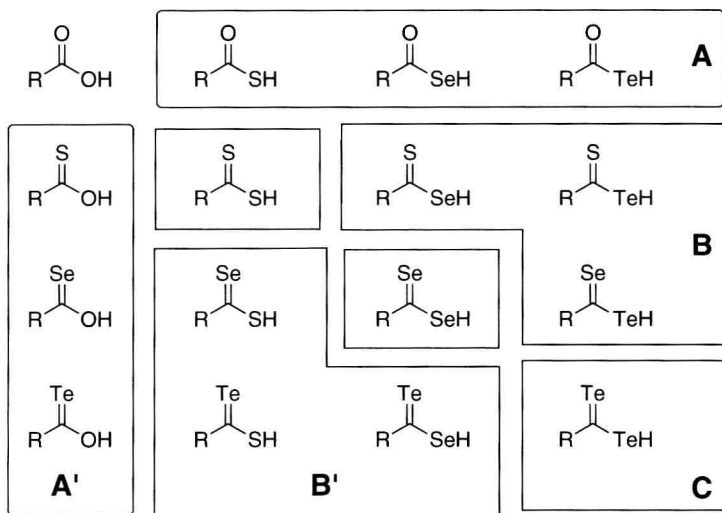
Abstract Although thio- and dithio-carboxylic acids have been extensively studied for some time now, research into other chalcogenocarboxylic acids – containing selenium and tellurium – has only blossomed over the last decade. Monochalcogenocarboxylic acids exist as fast tautomeric equilibrium mixtures of chalcogenol and chalcogenoxo forms. The chalcogenol form is the predominant species in solid state and nonpolar solvents. In contrast, in polar solvents at low temperature, the acids predominantly exist in the chalcogenoxo form. Syntheses of heavier dichalcogenocarboxylic acids have only been attempted very recently. This chapter presents the results from recent studies of chalcogenocarboxylic acids, their syntheses, structures and reactions.

Keywords Chalcogenocarboxylic acids · Chalcogenol form · Chalcogenoxo form · Carboxylic acids · Chalcogens

1 Introduction

Carboxylic acids are one of the most fundamental and important groups of compounds in organic chemistry. *Chalcogenocarboxylic acids*, RCEE'H (E, E'=O, S, Se, Te), are derived from carboxylic acids by replacing one or both oxygen atoms of the carboxyl group with S, Se or Te.

As shown in Scheme 1, there are 15 kinds of chalcogenocarboxylic acid. There are six monochalcogenocarboxylic acids, that have oxygen and chalcogen atoms (A), as well as their tautomers (A'). There are also dichalcogenocarboxylic acids (B and C), while the dichalcogenocarboxylic acids with two different chalcogen atoms (of which there are three kinds, B) also possess tautomers (B').



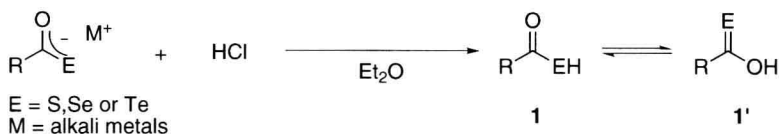
Scheme 1

Historically, the first chalcogenocarboxylic acid discovered was thiocarboxylic acid – thioacetic acid – reported by Kekulé in 1854 [1]. Since then, chalcogenocarboxylic acids, and particularly numerous thio- and dithiocarboxylic acid esters, have been synthesized and summarized in several review articles [2–9]. In contrast, until very recently, little has been known about the chemistry of the congeners containing heavier chalcogen atoms, such as selenium and tellurium, probably due to their instability and the handling difficulties associated with them. In this chapter, the chemistry of chalcogenocarboxylic acids, their syntheses, structures, spectral features and reactions are reviewed.

2 Syntheses

2.1 Monochalcogenocarboxylic Acids

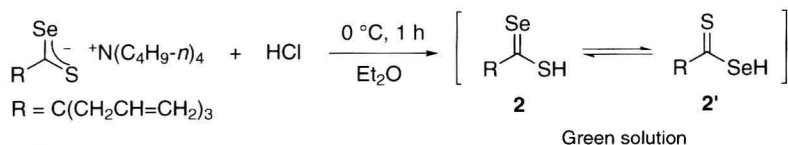
As mentioned above, the first isolation of a monochalcogenocarboxylic acid – thioacetic acid – was reported in the middle of the 1850s, having been synthesized from the reaction of thioacetic acid with P_4S_{10} [1]. This method cannot be applied to the synthesis of other thiocarboxylic acids, due to very low yields, although reactions in the presence of a catalytic amount of Ph_3SbO have been found to give good yields of aromatic thioacids [10]. Acidolysis of thiocarboxylic acid alkali and alkaline earth metal or ammonium salts with hydrogen chloride has proved to be the most convenient method to prepare the thiocarboxylic acids **1** and **1'** ($E=S$) (Scheme 2) [5, 6, 11, 12]. The first example of selenocarboxylic acid was confirmed spectroscopically in 1972 by Jensen et al., who synthesized selenobenzoic acid by reacting benzoyl chloride with H_2Se in the presence of pyridine, followed by sulfuric acid [13]. Isolations of a series of selenocarboxylic acids **1** and **1'** ($E=Se$) were gained through HCl-acidolysis of the corresponding sodium [14] or potassium salts (Scheme 2) [15]. Formation of the tellurocarboxylic acids **1** and **1'** ($E=Te$) (purple for the aliphatic compounds and blue for the aromatic compounds in THF solution) by similar HCl acidolysis of the corresponding cesium (or other alkali metals) tellurocarboxylates has also been observed spectroscopically (Scheme 2) and by conversion into the acyl carbamoyl telluride [16]. However, these are too air-sensitive to isolate.



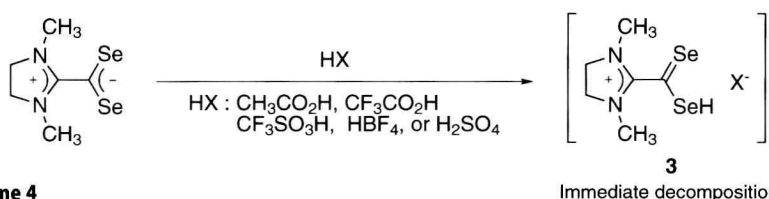
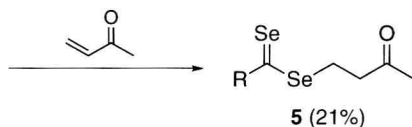
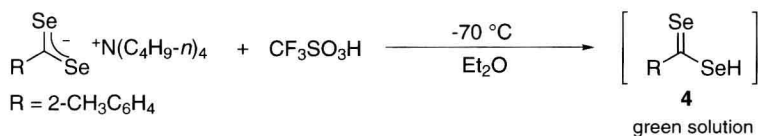
Scheme 2

2.2 Dichalcogenocarboxylic Acids

Dithiocarboxylic acids can be readily obtained by HCl-acidolysis of the corresponding magnesium halide, prepared by the reaction of a Grignard reagent with carbon disulfide [17] or ammonium salts [18]. Aromatic dithiocarboxylic acids cannot, in general, be distilled. The formation of green to blue selenothiocarboxylic acid **2** or **2'** $[(CH_2=CHCH_2)_3CCSSeH]$ in ether by treating the corresponding tetraalkyl ammonium salts with hydrogen chloride has been observed spectroscopically (Scheme 3) [19]. Nakayama et al. have found that treating diselenocarboxylic acid inner salts with acids such as CH_3CO_2H ,

**Scheme 3**

$\text{CF}_3\text{CO}_2\text{H}$, $\text{CF}_3\text{SO}_3\text{H}$, HBF_4 , and H_2SO_4 (Scheme 4) results in the formation of diselenocarboxylic acid **3** [20]. The formation of 2-methylbenzenecarbondiselenoic acid **4** (green in ether) by acidolysis of the corresponding tetramethyl ammonium salt with $\text{CF}_3\text{SO}_3\text{H}$ has also been reported [21]. The compound **4** reacts with methyl vinyl ketone to give γ -oxabutyl diselenoester **5** (Scheme 5) [21].

**Scheme 4****Scheme 5**

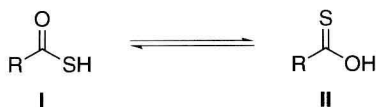
There is no reported example of a tellurium-containing dichalcogenocarboxylic acid (a tellurothio-, selenotelluro- or ditelluro-carboxylic acid) thus far.

3 Structures and Physical Properties

3.1 Spectroscopic Studies

The structures of thio- and dithiocarboxylic acids have been studied extensively using IR, UV/Vis and NMR spectra, and molecular orbital calculations for many decades now [3, 7–9]. Thiocarboxylic acids are considered to exist as fast tautomeric equilibrium mixtures of thiol (I) and thioxo (II) forms

(Scheme 6). Similarly, for seleno- and tellurocarboxylic acids, selenol and selenoxo, and tellurol and telluroxo forms may co-exist, respectively. Previous studies concerning the tautomerism of thiocarboxylic acids indicate that the thiol form (I) with the *s-cis* (*syn*) conformation is the predominant species.



Scheme 6

In 1996, spectroscopic observations were reported that indicated that the thioxo form of thiocarboxylic acid predominates in polar solvents at low temperature [16]. Since then, several theoretical studies of tautomerism in chalcogenocarboxylic acids have been reported. Spectroscopic experiments have shown that monochalcogenocarboxylic acids (RCOSH, RCOSeH, RCOTeH) exist in chalcogenol forms in nonpolar solvents and the solid state [14, 16]. The IR spectra (neat or Nujol) of selenocarboxylic acids show Se–H and C=O stretching frequencies at 2290–2324 and 1680–1720 cm^{-1} . In the ^1H and ^{13}C NMR spectra (in CDCl_3 solution), signals due to SeH and C=O are observed at $\delta=2.3$ –4.7 and $\delta=190$ –207, respectively. In contrast, in polar solvents such as tetrahydrofuran (THF) and acetone methanol, tautomeric equilibria between chalcogenol and chalcogenoxo forms have been observed, and the chalcogenoxo forms are the predominant species at low temperatures (below $-90\text{ }^\circ\text{C}$) [14, 16]. In the IR spectra of 4-methoxybenzenecarboxylic acid in THF at room temperature, the intensities of C=O stretching frequencies at 1682 cm^{-1} were observed to be less than those seen in the solid state. The resonance from $^{13}\text{C}=\text{Se}$ is observed at $\delta=222.2$, and the peak from Se^1H occurs at $\delta=15.3$, indicating the likely existence of hydrogen bonding with the oxygen atom of THF (Table 1). In

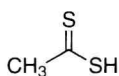
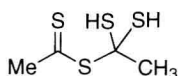
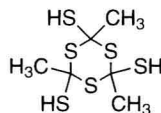
Table 1 NMR spectra for monochalcogenocarboxylic acids

E=S, Se, Te R=4- $\text{CH}_3\text{OC}_6\text{H}_4$					
		chalcogenol form		chalcogenoxo form	
E=S	NMR (^1H)	SH	4.48 ^a	OH	14.52 ^c
	(^{13}C)	C=O	188.5 ^a	C=S	212.3 ^c
E=Se	NMR (^1H)	SeH	2.59 ^a	OH	15.3 ^c
	(^{13}C)	C=O	189.6 ^a	C=Se	222.2 ^c
	(^{77}Se)		427.5 ^a		753.9 ^c
E=Te	NMR (^1H)	TeH	–	OH	16.02 ^c
	(^{13}C)	C=O	–	C=Te	222.2 ^c
	(^{125}Te)		535 ^b		952 ^c

^a In CDCl_3 at rt; ^b in toluene- d_8 at $-90\text{ }^\circ\text{C}$; ^c in THF- d_4 at $-90\text{ }^\circ\text{C}$.

the UV/Vis spectra of 4-methoxybenzene-substituted chalcogenoxo acids, the absorption maxima attributed to the $n-\pi^*$ transitions of the C=S, C=Se and C=Te groups were observed at 413, 502 and 652 nm, respectively.

It has been reported that dithiocarboxylic acids exist as monomers in dilute solution and as hydrogen-bonded dimers in concentrated solution. NMR spectra for neat dithioacetic acid **6** revealed that reversible covalent associations exist, resulting in dimer **7** and cyclic trimer **8** [22]. At 19.5 °C, the ratios of these species are 61% monomer, 38% **7** and ~1% **8**.

**6****7****8**

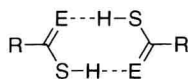
The acidities of thio- and dithiocarboxylic acids have been discussed in an earlier review [3]. For example, the pK_a values of PhCOOH, PhCOSH and PhCSSH are 4.20, 2.48 and 1.92, respectively. The acidities of some chalcogenocarboxylic acids have been estimated through theoretical studies. The gas-phase acidities (ΔH) of formic acid and its sulfur congeners are 342.1 for HC(O)OH, 332.2 for HC(O)SH, 328.8 for HC(S)OH and 325.8 kcal/mol for HC(S)SH. Therefore, the acidity appears to increase roughly in proportion to the number of sulfur atoms present [23]. For selenocarboxylic acids, gas-phase acidities are 340.4 for HC(O)OH, 327.6 for HC(O)SeH, and 321.9 kcal/mol for HC(Se)OH, indicating that selenocarboxylic acids are more acidic than their parent carboxylic acids [24]. It was also predicted that selenocarboxylic acids may be more acidic than their corresponding thioic acids [14].

3.2

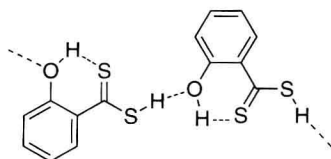
X-ray Structural Analyses

Little crystallographic information is available on chalcogenocarboxylic acids. Few (if any) thio- [25, 26] and dithiocarboxylic acids [25–28] are known, and no congeners containing selenium and tellurium have been found.

The substituted thiobenzoic acids **9** (R=2-HOC₆H₄) [25] and **10** (R=4-CH₃C₆H₄) [26] exist as cyclic dimers, with both molecules connected via inter-



- 9** E = O, R = 2-HOC₆H₄
10 E = O, R = 4-CH₃C₆H₄
11 E = S, R = 4-CH₃C₆H₄

**12**

(C=S: 1.651, C-S: 1.736 Å)

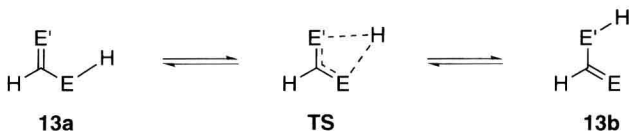
molecular hydrogen bonds ($S-H\cdots O=C$) in the crystal state, as in their parent benzoic acids [25, 29]. The bond distances of the thiocarboxylic acids indicate that the molecules exist in the thiol form in crystals. In the same way, in the solid state 4-methyldithiobenzoic acid **11** forms dimers through hydrogen bonds ($S-H\cdots S=C$) [26]. Intramolecular $C=S\cdots HO$ and intermolecular $S-H\cdots O(H)-C$ hydrogen bonds are observed in 2-hydroxydithiobenzoic acid **12** [25].

3.3

Theoretical Studies

Semiempirical and ab initio theory molecular orbital calculations have been carried out on chalcogenocarboxylic acids, especially simple thiocarboxylic acids [8]. Some model compounds have been investigated recently using higher basis sets and theory levels [23, 30–34]. Further calculations for heavier congeners containing selenium and tellurium have also been carried out [24, 30, 32, 35].

Jemmis et al. reported theoretical calculations for tautomeric rearrangements in mono- and dichalcogen congeners of formic acid $HC(E)E'H$ ($E, E' = O, S, Se, Te$) at the HF, MP2 and B3LYP levels (Scheme 7) [30]. The relative energies of the minima (**13a** and **13b**) and the transition states (TS) showed that the barrier to tautomerism reduced as the electronegativity of the chalcogens decreased. For monochalcogenocarboxylic acids ($HCOEH$), the relative energy values show a thermodynamic preference (~ 5 – 8 kcal/mol at the HF level) for the keto moiety (chalcogenol forms) more than the enol moiety (chalcogenoxo forms). The stabilization due to solvation (hydrogen bonding between $HCOEH$ and a polar solvent, such as THF and acetonitrile) is more for the chalcogenoxo forms than for the chalcogenol forms. But the greater stabilities of the chalcogenoxo forms are not sufficient to reverse the thermodynamic stability. For thio-, seleno- and telluroacetic acids, the chalcogenol forms are still preferred, in both the gas phase and the solvent model (self-consistent reaction field, SCRF method) studies.



Scheme 7

Hadad et al. found that $XC(=O)SH$ ($X = Me, NH_2, OH, F$) is preferred over $XC(=S)OH$ by 5–14 kcal/mol using ab initio calculations [23]. The C–O bond dissociation energy is greater than the C–S energy by ~ 30 kcal/mol and the C=O bond is significantly stronger than the C=S bond by about 40 kcal/mol. The C=O bond has more polar character ($C^{\delta+}-O^{\delta-}$) than the C=S bond, so that the bond order of the C=O bond is about 1.2 while the C=S bond order is ~ 2.0 . For selenocarboxylic acids, density functional theory (DFT) calculation results suggest that the *syn* selenol form is more stable than the other forms [24].