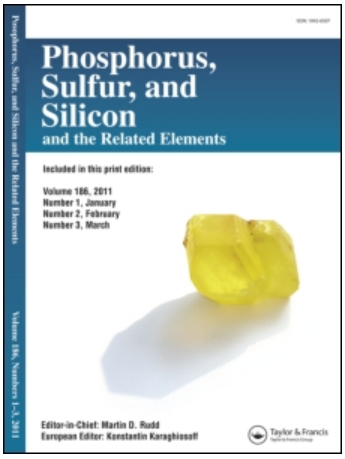


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Kinetics and Mechanism of the Nucleophilic Substitution of Tellurium(II) Dialkanethiolates, $Te(SR^1)_2$ with Thiols, HSR^2

Holger Fleischer[a]
[a] Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg Universität Mainz, Mainz, Germany

To cite this Article Fleischer, Holger(2005) 'Kinetics and Mechanism of the Nucleophilic Substitution of Tellurium(II) Dialkanethiolates, $Te(SR^1)_2$ with Thiols, HSR^2', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 3, 815 — 825
To link to this Article: DOI: 10.1080/10426500590907507
URL: http://dx.doi.org/10.1080/10426500590907507

Phosphorus, Sulfur, and Silicon, 180:815–825, 2005

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500590906337

Kinetics and Mechanism of the Nucleophilic Substitution of Tellurium(II) Dialkanethiolates, $Te(SR^1)_2$ with Thiols, HSR^2

Holger Fleischer
Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg Universität Mainz, Mainz, Germany

The equilibrium reaction between tellurium(II) dithiolates and thiols, $Te(SR^1)_2 + 2\,HSR^2 \rightleftharpoons Te(SR^2)_2 + 2\,HSR^1$ was studied by means of ^1H- and ^{125}Te NMR spectroscopy and ab initio *quantum chemical methods. It was found that the reaction is catalyzed by Brønsted acids and bases, the catalytic activity corresponding to the strength of the respective acid or base. Investigation of the initial step of the reaction, $Te(SR^1)_2 + HSR^2 \rightleftharpoons Te(SR^1)(SR^2) + HSR^1$, showed it to proceed according to first order kinetics for $Te(SR^1)_2$, HSR^2 and for the catalyst.* Ab initio *geometry optimizations and frequency calculations suggest $[Te(SR^1)(HSR^1)(HSR^2)]^+$ and $[Te(SR^1)_2(SR^2)]^-$ to be stable intermediates and not transition states in the acid and base catalyzed reactions, respectively. The reaction hence proceeds via an additional elimination rather than an S_N2 mechanism. The catalytic activity displayed by acids and bases can be applied to reduce the temperature in synthesis of thermally labile tellurium(II) dithiolates.*

Keywords Ab initio; tellurium; ^{125}Te NMR; thiolate

INTRODUCTION

Nucleophilic substitution is a fundamental reaction and played a central role in the development of modern physical organic chemistry. Interest in extending this strategy to heteroatoms is growing.[1] There are indications that the mechanism is different between first- and second-row atoms. For example, a classic S_N2 mechanism is evident for nucleophilic substitution at carbon,[2] nitrogen,[3–5] and oxygen,[6,7] but an addition-elimination pathway occurs for reactions at phosphorus[8,9] and is implied for reactions at silicon.[10]

In the present work, kinetics and mechanism of the exchange reaction of tellurium(II) dithiolates, $Te(SR^1)_2$, with thiols, HSR^2, according

Received January 20, 2004; accepted October 12, 2004.

Address correspondence to Holger Fleischer, Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg Universität Mainz, Duesbergweg 10-14, Mainz D-55099, Germany. E-mail: fleische@mail.zdv.uni-mainz.de

to (1) (R^1, R^2 = alkyl, alkenyl)

$$Te(SR^1)_2 + 2\ HSR^2 \rightleftharpoons Te(SR^2)_2 + 2\ HSR^1 \quad (1)$$

was studied by means of NMR-spectroscopy and *ab initio* methods. Eq. (1) was recently found to be a straightforward approach towards novel tellurium(II) dithiolates, e.g. $Te(SC_6H_4(o\text{-}NH_2))_2$.[11] This route proved to be an efficient alternative to the already known method of reductive elimination according to (Eqs. (2) and (3)):[12,13]

$$TeO_2 + 4\ HSR \rightarrow Te(SR)_2 + RSSR + 2\ H_2O \quad (2)$$

$$Te(O^iPr)_4 + 4\ HSR \rightarrow Te(SR)_2 + RSSR + 4\ HO^iPr \quad (3)$$

In both reactions, only half of the thiol is converted to the tellurium(II) dithiolate, while the other half is used to form the disulfide. Formation of the latter is a disadvantage, if the tellurium(II) dithiolate and the disulfide are difficult to separate from each other or if the thiol is rather valuable. In that respect, $Te(SMe)_2$ and $Te(S^tBu)_2$ are suitable reactants for preparative reactions according to Eq. (1). The thiols, HSMe and HS^tBu, generated from those tellurium(II) dithiolates, are very volatile compounds and the equilibrium according to Eq. (1) can be shifted to the right side by distilling the thiols from reaction mixture.

Equations (1)–(3) are not only of synthetic use, but also have physiological importance. Te^{IV} compounds react with the cysteine residue in glutathione peroxidase by reductive elimination which leads to a deactivation of the latter. It was reported that reactivation could be achieved by addition of cysteine,[14] and it is highly probable that the re-activation is based on an exchange reaction analogous to Eq. (1).

In the present work, kinetics of Eq. (1) and appropriate mechanisms are presented and compared to analogous reactions at two-valent sulfur atoms.[15,16]

RESULTS AND DISCUSSION

Chemical Equilibria

For a variety of combinations of $Te(SR^1)_2$ and HSR^2, dissolved in C_6D_6, the equilibrium according to Eq. (1), was investigated by means of ^1H- and ^{125}Te NMR spectra. Table I gives the equilibrium constants for several equilibria according to (1), with

$$K(1) = \frac{c[Te(SR^2)_2] \cdot c[HSR^1]^2}{c[Te(SR^1)_2] \cdot c[HSR^2]^2}$$

TABLE I Data for Equilibrium According to Eq. (1) for Several Combinations of Tellurium(II) Dithiolates, Te(SR^1)$_2$ and Thiols, HSR^2,[a]

R^1	R^2	c_0[Te(SR^1)$_2$][a]	c_0(HSR^2)[a]	K(1)	ΔG^{298}
Me	^{t}Bu	0.41	0.88	2.1	−1.8
Me	Et	0.59	0.91	1.8	−1.5
Me	Allyl	0.35	0.37	2.0	−1.7
Me	Ph	0.18	0.24	2.0	−1.7
^{t}Bu	Et	0.22	0.62	1.0	0

[a]Substochiometric amounts of NMI or pyridine were used to catalyze the exchange reactions.

[b]Initial concentrations, c_0 are molalities, given in mol kg^{-1}.

An attempt to study equilibrium and kinetics of the reaction of Te(SMe)$_2$ with HSC$_6$F$_5$ failed, since the tellurium(II) dithiolates rapidly were decomposed to elemental tellurium and disulfides.

The data suggests a slight shift of the equilibrium towards the right side, if R^2 = Me is replaced by R^2 = Allyl, Et, ^{t}Bu, or Ph. Uncertainties of the equilibrium concentrations, due to errors in their determination from NMR intensities, are rather large. It can nevertheless be stated that none of the investigated ligands shifts the equilibrium entirely to one side. From a purely statistical distribution of SR^1 and SR^2 to Te^{II} and H, an equilibrium constant $K(1) = 1.0$ would result. The experimentally obtained constants are close to these values, and it is hence inferred that for equilibrium Eq. (1) $\Delta H^{298} \approx 0$.

Kinetic and Catalysis of Ligand Exchange

Equation (1) has to proceed in two steps

$$\mathrm{Te(SR^1)_2 + HSR^2 \rightleftharpoons Te(SR^1)(SR^2)_2 + HSR^1} \quad (1a)$$

$$\mathrm{Te(SR^1)(SR^2)_2 + HSR^2 \rightleftharpoons Te(SR^2)_2 + HSR^1}. \quad (1b)$$

Compared to the ligand exchange between Te(OR^1)$_4$ and HOR^2,[17,18] reactions according to Eqs. (1a) and (1b) proceed very slowly. It took about two weeks for a solution of Te(S^{i}Pr)$_2$ and HS^{t}Bu in CDCl$_3$ to reach the equilibrium state.[13] It was observed that Eq. (1a) proceeds quicker than Eq. (1b) for the exchange of Te(SMe)$_2$ and HS^{t}Bu, a fact attributed to the steric requirement of the *tert*-butyl group.

The rates of reaction of Eqs. (1a) and (1b) are tremendously enhanced by Brønsted acids and bases. The change of HSMe concentration with time was monitored for the reaction of Te(SMe)$_2$ with HS^{t}Bu in benzene

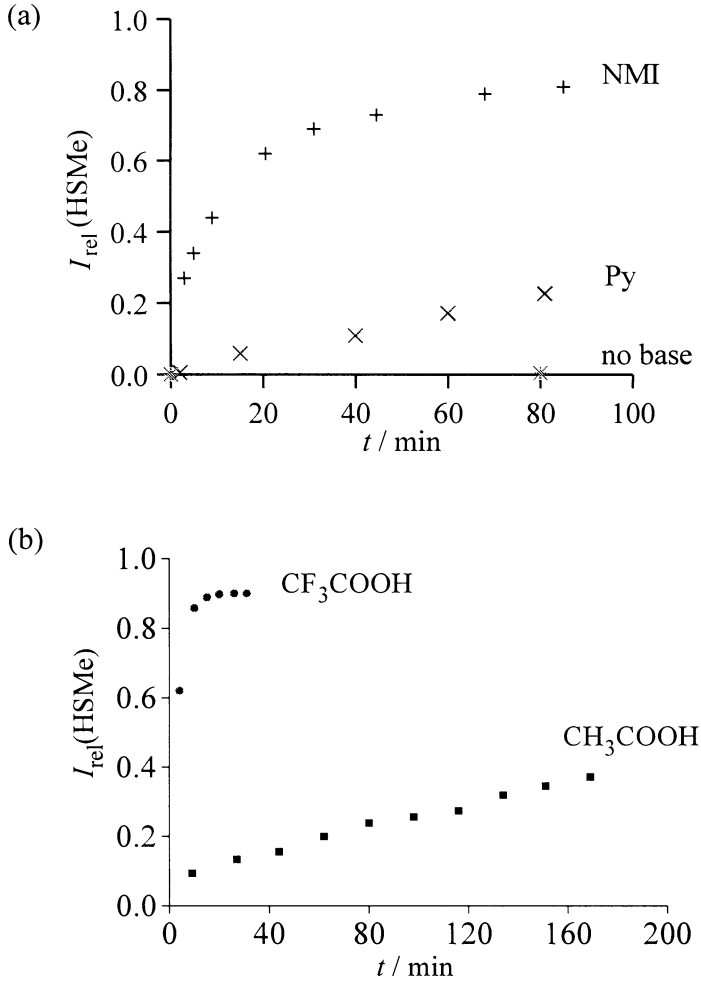


FIGURE 1 Catalytic activity of Brønsted acids and bases regarding equilibrium (1). (a): (+) 0.25 equivalents of NMI, (×) 0.25 equivalents of pyridine, (✳) no base. (b) (●) 0.5 equivalents of CF_3COOH, (■) 8 equivalents of CH_3COOH. All equivalents relative to $Te(SMe)_2$.

solutions that contained acids and bases of different strengths. Results are depicted in Figure 1.

Regarding the pK_a and pK_b values of the Brønsted acids and bases, respectively ($pK_a(HOAc) = 4.75$,[19] $pK_a(CF_3COOH) = 0.23$,[20] $pK_b(py) = 8.87$,[21] $pK_b(NMI) = 6.88$,[22] all in aqueous solution at 25°C), their catalytic activity with respect to Eq. (1) corresponds to their acid and base

strength. Dimethylsulfoxide, which is a good Lewis base (donor number DN = 30 according to *Gutmann*,[23] cf. pyridin, DN = 33), but a week Brønsted base, does not act as a catalyst for this reaction. By plotting the initial reaction rates against the initial concentrations of the respective reactant and keeping initial concentrations of the other reactants constant, the reaction orders of the single species were obtained. For the pyridine catalyzed exchange reaction of $Te(SMe)_2$ with HS^tBu, orders were $Te(SMe)_2$: 0.86, HS^tBu: 1.05, and pyridine: 0.94. According to these data, first order kinetics for each of the reactants is assumed, and hence Eq. (1a) is a second order reaction.

Based on the kinetic data, mechanisms for the acid and base catalyzed exchange reactions can be developed. Since the ^3J(H,H)-coupling $HSCH_3$, formed in (1) for $R^1 = Me$, can be observed even in the presence of pyridine of NMI, fast deprotonation of the thiol and protonation of a thiolate anion can be excluded. If such an acid base reaction would operate, the ^3J(H,H)-coupling could not be observed due to exchange decoupling. The equilibrium constant for the acid base reaction of HSMe ($pK_s = 10.5$[24]) with NMI in aqueous solution is estimated as $4{\cdot}10^{-5}$. In benzene, the solvent in which exchange reactions were investigated, should be even smaller since SMe^- and $[NMIH]^+$ ions are less stabilized. It is thus inferred that the thiol coordinates to the tellurium(II) dithiolate before it interacts with the base. The acidity of the thiol is increased by complexation of the tellurium(II) dithiolate, similar to the enhanced acidity of H_2O that coordinates to metal ions like Zn^{2+}. This hypothesis is corroborated by *ab initio* calculations (see further down). The proposed mechanisms for the base and acid catalyzed thiolate exchange reactions are depicted in Scheme 1. The base catalyzed mechanism consists of the following steps (B = Brønsted base), Eq. (4a)–(4f):

$$Te(SR^1)_2 + HSR^2 \rightleftharpoons [Te(SR^1)_2(HSR^2)] \tag{4a}$$

$$[Te(SR^1)_2(HSR^2)] + B \rightleftharpoons [Te(SR^1)_2(B \cdot\cdot HSR^2)] \tag{4b}$$

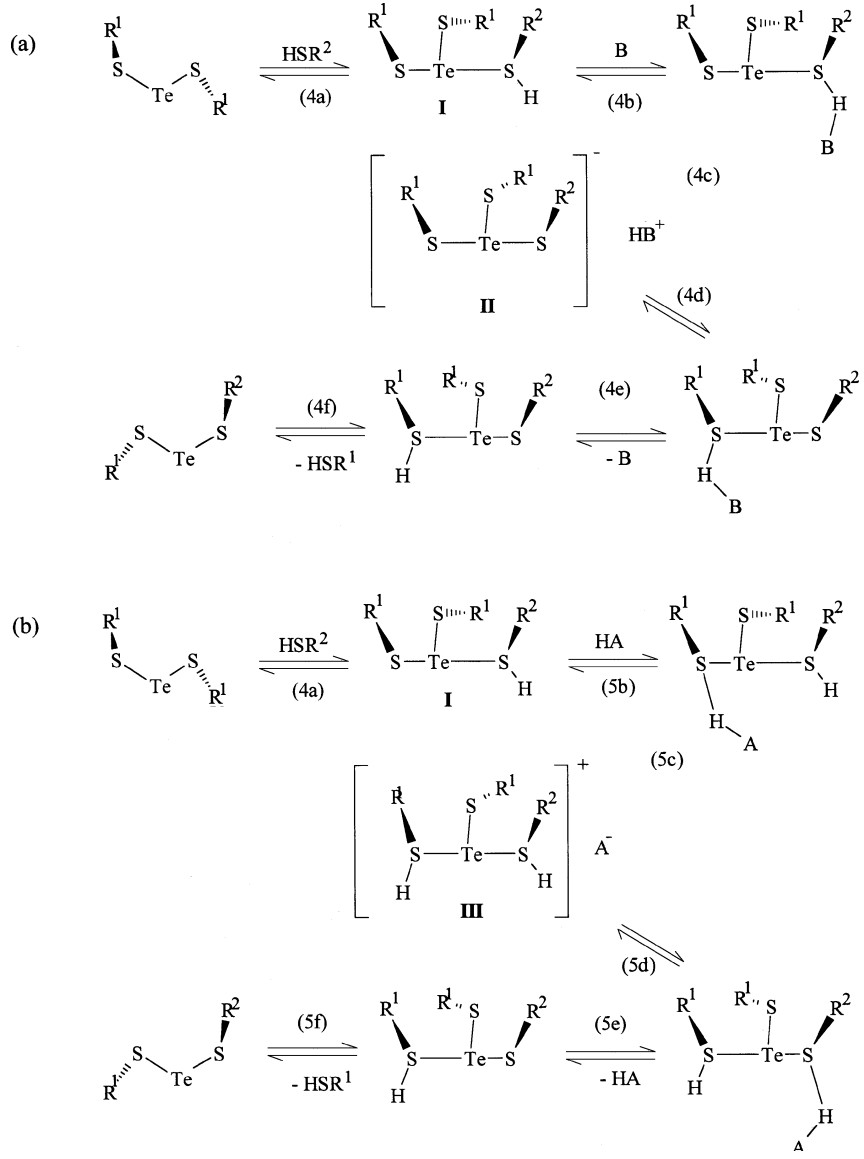
$$[Te(SR^1)_2(B \cdot\cdot HSR^2)] \rightleftharpoons [BH]^+ + [Te(SR^1)_2(SR^2)]^- \tag{4c}$$

$$[BH]^+ + [Te(SR^1)_2(SR^2)]^- \rightleftharpoons [Te(SR^1)(SR^2)(B \cdot\cdot HSR^1)] \tag{4d}$$

$$[Te(SR^1)(SR^2)(B \cdot\cdot HSR^1)] \rightleftharpoons [Te(SR^1)(SR^2)(HSR^1)] + B \tag{4e}$$

$$[Te(SR^1)(SR^2)(HSR^1)] \rightleftharpoons Te(SR^1)(SR^2) + HSR^1. \tag{4f}$$

In experimental studies on the exchange reaction of disulfides, RSSR, with thiols, HSR ($R = CH_2CH_2NH_2$), in aqueous solution it was found that the thiolate ion, RS^- acts as nucleophile.[15]



SCHEME 1 Proposed mechanisms for the nucleophilic substitution reaction of $Te(SR^1)_2$ with HSR^2 catalyzed by (a) a Brønsted base, B and (b) a Brønsted acid, HA.

It is assumed that the acid-catalyzed mechanism also starts with Eq. (4a) and ends with Eq. (4f), but Eqs. (4b) to (4e) are replaced by Eqs. (5b) to (5e) (HA = Brønsted acid):

$$[\mathrm{Te(SR^1)_2(HSR^2)}] + \mathrm{HA} \rightleftharpoons [\mathrm{Te(SR^1)(AH \cdot\cdot SR^1)(HSR^2)}]^+ \quad (5b)$$

$$[\mathrm{Te(SR^1)(AH \cdot\cdot SR^1)(HSR^2)}] \rightleftharpoons [\mathrm{Te(SR^1)(HSR^2)(HSR^1)}]^+ + \mathrm{A}^- \quad (5c)$$

$$[\mathrm{Te(SR^1)(HSR^2)(HSR^1)}]^+ + \mathrm{A}^- \rightleftharpoons [\mathrm{Te(SR^1)(HSR^1)(AH \cdot\cdot SR^2)}] \quad (5d)$$

$$[\mathrm{Te(SR^1)(HSR^1)(AH \cdot\cdot SR^2)}] \rightleftharpoons [\mathrm{Te(SR^1)(HSR^1)(SR^2)}] + \mathrm{HA}. \quad (5e)$$

Ab Initio-Studies

The mechanisms of the acid and base catalyzed identity reaction with $R^1 = R^2 = Me$ were investigated by *ab initio* geometry optimizations and thermochemical calculations. Since in this case Eqs. (4d)–(4f), (5d), and (5e) are exactly the reverse reactions of (4c), (4b), (4a), (5c), and (5b), respectively. The latter had not to be considered. Thermochemical data are given in Table II, MP2/LANL2DZP optimized structures of reaction intermediates [Te(SMe)$_2$(HSMe)] (**I**), [Te(SMe)$_3$]$^-$ (**II**), and Te[(SMe)(HSMe)$_2$]$^+$ (**III**) are depicted in Figure 2. All three structures represent true minima on the potential energy surface, at the HF level as well as at the MP2 level, i.e. reactions proceed *via* an additional elimination mechanism instead of an S_N2 mechanism. This contrasts to recent investigations on the substitution reaction (Eq. (6))

$$\mathrm{R^1S^-} + \mathrm{R^2SSR^3} \rightarrow \mathrm{R^1S^-} + \mathrm{R^2SSR^3}$$

TABLE II Free Standard Enthalpies, ΔG^{298}, of Eqs. (4a), (4b), (4c), (5b), and (5c) ($R^1 = R^2 = Me$, Values are Given in kJ·mol^{-1}). Different Bases, B, and Different Acids, HA, Were Used (See Footnotes.)

Equation	ΔG^{298}	ΔG^{298}
(4a)	+20	
(4b)[a]	+14 (5b)[c]	+36
(4b)[b]	+14 (5b)[d]	+23
(4c)[a]	+476 (5c)[c]	+563
(4c)[b]	+460 (5c)[d]	+457

[a] B = pyridine.
[b] B = imidazole (imidazol ($pK_b = 6.97$) was used as model compound for N-methylimidazol.
[c] HA = CH_3COOH,
[d] HA = CF_3COOH.

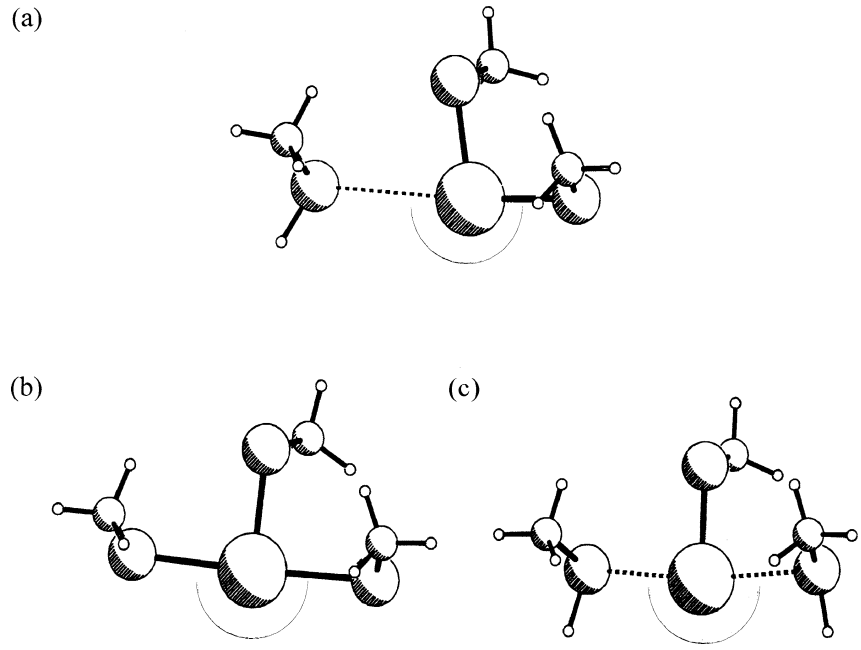


FIGURE 2 *Ab-initio*-optimized molecular structures of $[Te(SMe)_2(HSMe)]$ (a), $[Te(SMe)(HSMe)_2]^+$ (b), and $[Te(SMe)_3]^-$ (c). Internuclear distances in pm, bond angles in °.

where an S_N2 mechanism was found at the HF level and an additional elimination mechanism at all levels including electron correlation.[16]

Formation of $[Te(SMe)_2(HSMe)]$ from $Te(SMe)_2$ and HSMe was calculated to be an endergonic process, i.e., the adduct only is formed to a small fraction. Deprotonation Eq. (4c) and protonation Eq. (5c) lead to charge separation and hence strongly are endergonic processes (see Table II) for isolated molecules and molecular ions. Equations (4c) and (5c), respectively, are decisive for the rates of base and acid catalyzed ligand exchange reactions, as can be seen from the data given in Table II. The thermochemical data was calculated for gas phase reactions but reflects nevertheless the experimentally observed trends. Especially Eq. (4c) proceeds less endergonic for imidazole than for pyridine and Eq. (5c) proceeds less endergonic for trifluoro acetic acid than for acetic acid. If a linear-free enthalpy relation is assumed between the free enthalpy of activation of Eqs. (4c) and (5c) (kinetic data), respectively, and the associated free enthalpy of reaction (thermodynamic data), the higher reaction rates with the stronger acids and bases can be rationalized from the data given in Table II. Formation of a hydrogen

bridge between pyridine and [Te(SMe)$_2$(HSMe)] according to Eq. (4b) proceeds with $\Delta G^{298} = +14$ kJ·mol^{-1} and is thus thermodynamically favored compared to a hydrogen bridge between pyridine and HSMe (+17 kJ·mol^{-1}). This corroborates the suggestion that coordination to tellurium increases the acidity of HSR.

Parameters from *ab-initio*-optimized molecular structures show an increased Te1–S2 and a decreased Te1–S4 distance on protonation as well as deprotonation of [Te(SMe)$_2$(HSMe)] (see Figure 2). Both structural changes lead to a transition of the reactant towards the products. n_p(S4)-σ^*(Te1–S2) energy of interaction (NBO basis) was estimated as 26 kJ·mol^{-1} for [Te(SMe)$_2$(HSMe)], 619 kJ·mol^{-1} for [Te(SMe)$_3$]$^-$, and 15 kJ·mol^{-1} for [Te(SMe)(HSMe)$_2$]$^+$. In the latter case, an additional n_p(S4)-d(Te1) orbital interaction with 35 kJ·mol^{-1} strengthens the bond between the nucleophile and the Te atom. (According to *ab initio* calculations, [Te(SR)$_3$]$^-$ anions are stable towards dissociation to Te(SR)$_2$ and RS$^-$. Attempts to isolated those anions with suitable counter cations are currently undertaken in this lab). The Te1–S3 bond in [Te(SMe)$_2$(HSMe)] only is slightly influenced by protonation or deprotonation. It is a bit shorter in the cation and longer in the anion, compared to the neutral complex.

CONCLUSION

The ligand exchange at the Te atom in Te(SR^1)$_2$ by reaction with HSR$_2$ proceeds *via* an S$_N$2-mechanism. The reaction is catalyzed by Brønsted acids and bases. The former destabilize the Te—S bond to be cleaved while the latter increase the nucleophily of the attacking thiol. The catalytic activity of acids and bases allows the exchange of Eq. (1) to proceed at lower temperatures and hence enables thermally labile tellurium(II) dithiolates to be synthesized via this route.

EXPERIMENTAL PART

General Procedures

Te(SMe)$_2$[25] and Te(S^{t}Bu)$_2$[13] were prepared according to literature procedure, thiols and C$_6$D$_6$ were used as purchased. NMR: spectra were recorded on a Bruker DRX 400, $B_1(^1\text{H}) = 400.0$, $B_1(^{125}\text{Te}) = 126.387$ MHz. Standard: TMS (^{1}H) and Te(CH$_3$)$_2$ (^{125}Te).

Kinetic Measurements

The amounts of reactants and solvent (C$_6$D$_6$) used in a given experiment were weighted and the time of the experiment was started when

the compounds were mixed with each other. The starting employed concentrations varied between 0.01 and 0.5 mol L^{-1}. The concentrations of reactants and products during the course of the reaction were obtained from the initial concentrations and the intensities of the signals in the ^1H NMR spectra. The orders of Eq. (1a) with respect to HSR^2 and $Te(SR^1)_2$ were determined by using an excess of the other reactant, such that its concentration was kept nearly constant throughout the experiment (method of *pseudo first order kinetic*). Employing then different amounts of HSR^2 or $Te(SR^1)_2$, the orders of Eq. (1a) with respect to the compounds were determined from the ratio of the initial reaction rates (differential method).[26] In a similar manner, the orders of Eq. (1a) with respect to the catalytically active compounds acetic acid and pyridine were determined.

Theoretical Methods

Quantum chemical *ab initio* investigations were performed with the GAUSSIAN 94 program package.[27] Optimization of molecular geometries, calculation of vibrational frequencies and an analysis of the electronic structure in terms of natural orbitals[28] were performed at the MP2 level, with an effective core double zeta valence basis set,[29] augmented by appropriate polarization functions for Te, S (with exponents according to Höllwarth et al.),[30] and C (exponent 0.75).

REFERENCES

[1] P. Beak, *Acc. Chem. Res.*, **25,** 215–222 (1992).
[2] S. Gronert, *J. Am. Chem. Soc.*, **113,** 6041–6048 (1991).
[3] P. Beak and J. Li, *J. Am. Chem. Soc.*, **113,** 2796 (1991).
[4] M. Bühl and H. F. Schaefer III, *J. Am. Chem. Soc.*, **115,** 9143–9147 (1993).
[5] M. N. Glukhovtsev, A. Pross, and L. Radom, *J. Am. Chem. Soc.*, **117,** 9012–9018 (1995).
[6] P. Beak and D. Loo, *J. Am. Chem. Soc.*, **108,** 3834 (1986).
[7] S. M. Bachrach, *J. Org. Chem.*, **55,** 1016–1019 (1990).
[8] J. Li and P. Beak, *J. Am. Chem. Soc.*, **114,** 9206–9207 (1992).
[9] S. M. Bachrach and D. C. Mulhearn, *J. Phys. Chem.*, **97,** 12229–12231 (1993).
[10] R. Damrauer, C. H. DePuy, and V. M. Bierbaum, *Organometallics*, **1,** 1553–1554 (1982).
[11] H. Fleischer and D. Schollmeyer, *Inorg. Chem.*, **41,** 4739–4747 (2002).
[12] W. Mazurek, A. G. Moritz, and M. J. O'Connor, *Inorg. Chim. Acta*, **113,** 143–146 (1986).
[13] H. Fleischer, S. Stauf, and D. Schollmeyer, *Inorg. Chem.*, **38,** 3725–3729 (1999).
[14] A. Albeck, H. Weitman, B. Sredni, and M. Albeck, *Inorg. Chem.*, **37,** 1704–1712 (1998).
[15] J. C. Pleasants, W. Guo, and D. L. Rabenstein, *J. Am. Chem. Soc.*, **111,** 6553–6558 (1989).

[16] S. M. Bachrach and D. C. Mulhearn, *J. Phys. Chem.*, **100,** 3535–3540 (1996).
[17] H. E. Gottlieb, S. Hoz, I. Elyashiv, and M. Albeck, *Inorg. Chem.*, **33,** 808–811 (1994).
[18] H. Fleischer, Y. Dienes, and D. Schollmeyer, *Eur. J. Inorg. Chem.*, 2073–2081 (2002).
[19] A. D. Headley, S. D. Starnes, L. Y. Wilson, and G. R. Famini, *J. Org. Chem.*, **59,** 8040–8046 (1994).
[20] L. A. Reinhardt, K. A. Sacksteder, and W. W. Cleland, *J. Am. Chem. Soc.*, **120,** 13366–13369 (1998).
[21] M. S. K. Niazi and J. Mollin, *Bull. Chem. Soc. Jpn.*, **60,** 2605–2610 (1987).
[22] C. S. Cassidy, L. A. Reinhardt, W. W. Cleland, and P. A. Frey, *J. Chem. Soc. Perkin Trans. 2*, **3,** 635–642 (1999).
[23] V. Gutmann, *Coord. Chem. Rev.*, **18,** 225–255 (1976).
[24] A. P. Munro, D. L. H. Williams, *J. Chem. Soc. Perkin Trans. 2*, **9,** 1794–1797 (2000).
[25] H. Fleischer, N. W. Mitzel, D. Schollmeyer, *Eur. J. Inorg. Chem.*, 815–821 (2003).
[26] K. J. Laidler, *Chemical Kinetics,* (2nd ed.), McGraw-Hill, New York, St. Louis.
[27] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, *Gaussian 94*, Revision E.1, Gaussian, Inc., Pittsburgh PA, 1995.
[28] A. E. Reed, L. A. Curtiss, and F. Weinhold, *Chem. Rev.*, **88,** 899–926 (1988).
[29] W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, **82,** 284–298 (1985).
[30] A. Höllwarth, M. Böhme, S. Dapprich, A. W. Ehlers, A. Gobbi, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp, and G. Frenking, *Chem. Phys. Lett.*, **208,** 237–240 (1993).