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Ligand-Exchange Reactions in Organotellurides by ^{125}Te NMR Spectroscopy

Rein U. Kirss*,† and Duncan W. Brown*

Advanced Technology Materials, 7 Commerce Drive, Danbury, Connecticut 06810

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^{125}Te NMR spectra for a series of symmetric and unsymmetric tellurides containing allyl and 2-methylallyl groups are reported. The effect of allyl substitution on the chemical shift was found to be additive, consistent with earlier observations for alkyl substitution. Alkyl and allyl ligand exchange was observed in solutions of two symmetrical tellurides ($R_2Te + R'_2Te \rightarrow 2RTeR'$ for R, R′ = allyl, 2-methylallyl, isopropyl, and *tert*-butyl). The relative rates of these reactions were found to be in the order R = allyl, R′ = 2-methylallyl > *tert*-butyl, isopropyl > *tert*-butyl, 2-methylallyl ∼ *tert*-butyl, allyl > isopropyl, 2-methylallyl ∼ isopropyl, allyl. Equilibrium constants for the forward reaction were determined for each combination of symmetrical tellurides and for the reverse reaction in the case of ^{t}BuTeR (R = allyl, 2-methylallyl) over the temperature range 25–80 °C. ΔGs for the reactions were calculated to be in the range −0.89 kcal/mol for R = allyl, R′ = 2-methylallyl to −2.1 kcal/mol for R = *tert*-butyl, R′ = allyl. The formation of symmetrical ditellurides (^{t}BuTeTe^{t}Bu and ^{i}PrTeTe^{i}Pr) was observed after prolonged heating in reactions of ^{t}BuTeR and ^{i}PrTeR, respectively (R = allyl, 2-methylallyl). Spectroscopic evidence for the formation of unsymmetrical ditellurides ^{t}BuTeTeR (R = allyl, 2-methylallyl) was observed.

Introduction

Ligand exchange (reaction 1) is a common reaction pathway for main-group organometallic compounds.[1] A

$$R_2M + R'_2M \rightarrow 2RMR' \qquad (1)$$

convenient synthesis of mixed alkylaluminum compounds utilizes reaction 1.[2] Similar reactions are known for the heavier group III (Ga, In),[3] group IV (Ge, Sn, Pb),[4] and group V (As, Sb, Bi)[5] alkyls. In general, the exchange becomes more facile when proceeding down a group in the periodic chart. Analogous alkyl-exchange reactions are expected for alkyl selenides and tellurides, although relatively few studies have been reported for these elements.[6]

Our interest in alkyl-exchange reactions derived from our earlier work on the decomposition mechanisms of symmetrical and unsymmetrical organotellurides.[7] During gas-phase pyrolytic decomposition of unsymmetrical tellurides, RTeR′ (for R = methyl, R′ = allyl, 2-methylallyl, *tert*-butyl and R = *tert*-butyl, R′ = allyl, 2-methylallyl), the symmetrical tellurides RTeR and R′TeR′ were detected. Prior to our work, it was proposed that the initial step in the decomposition of unsymmetrical tellurides was symmetrization to form the two symmetrical tellurides (reaction 2).[9] Evidence for this process was based largely

$$2RTeR' \rightarrow RTeR + R'TeR' \qquad (2)$$

on differential scanning calorimetry studies. Ligand redistribution reactions have also been observed in the synthesis of unsymmetrical organotellurium compounds as a function of solvent.[10] During our study, Mullin et al. reported on a ligand exchange in reactions between alkyl tellurides, RTeR (R = ^{t}Bu, ^{i}Pr, allyl, Et, Me, ^{s}Bu, ^{i}Bu), and alkyl ditellurides, R′TeTeR′ (R′ = Me, ^{i}Pr).[11]

Our results indicated that ligand exchange reactions in the gas phase occurred at relatively low temperatures (∼90 °C) without significant decomposition to tellurium metal. While it is risky to extrapolate results obtained in solution to the gas phase, we decided to measure the equilibrium constants for reaction 2 in solution in order to assess the importance of reaction 2 in the thermal decomposition mechanisms of organotellurides.

Experimental Section

Synthesis of Tellurium Compounds. The dialkyltellurium compounds used in this study were prepared by literature methods.[7,12–14] All of the compounds studied were dense, volatile, yellow, orange, or red colored, extremely pungent, air- and light-sensitive liquids, which were purified by distillation under reduced pressure.

Table I. ^{125}Te Chemical Shifts for Symmetrical and Unsymmetrical Tellurides

	R′				
R	methyl	allyl	2-methyl-allyl	isopropyl	*tert*-butyl
methyl	0				
allyl	162 182^{a}	377 391^{a}			
2-methylallyl	169	369	358		
isopropyl	342	532 550^{a}	523	342	
tert-butyl	497	704 717^{a}	690	866	999

^{a} See ref 14.

NMR Studies. The NMR samples were prepared as benzene-d_6 solutions in 5-mm-o.d. NMR tubes and were flame sealed under vacuum. Concentrated samples (∼50% by volume) were used to reduce data collection times. ^{125}Te NMR spectra were recorded at room temperature on a WP 200SY NMR spectrometer equipped with a VSP200 broad-band probe. The spectra were referenced to $^{t}Bu_2Te$ at 999 ppm downfield of Me_2Te (0 ppm). Chemical shifts for the symmetrical and unsymmetrical tellurides are listed in Table I. The tubes were stored in the dark unless otherwise indicated. The samples were heated in an oil bath and spectra recorded at regular intervals. The samples were deter-

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† Current address: Department of Chemistry, Northeastern University, Boston, MA 02115.

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Table II. Equilibrium Constants and Free Energies of Ligand Exchange in Organotellurides

reaction		K_{eq} at T, K			
R	R′	323	343	353	ΔG, kcal/mol
allyl	2-methylallyl	3.95	3.54	3.48	−0.89
^{t}Bu	^{i}Pr		13.0	12.9	−1.7
^{t}Bu	2-methylallyl			20.5	−2.1
^{t}Bu	allyl			20.9	−2.1
^{i}Pr	2-methylallyl			5.3	−1.2
^{i}Pr	allyl			5.5	−1.2

mined to have equilibrated when the product ratios remained constant over several half-lives.

Results and Discussion

NMR Spectra. The chemical shifts for symmetrical and unsymmetrical allyltellurium compounds are listed in Table I. Allyl ligands can be considered to be vinyl-substituted methyl groups and led to an average downfield shift of 180 ± 16 ppm[10,15] for the ^{125}Te resonance upon introduction of an allyl group, similar to the effect of methyl substitution.[16] The effects of successive methyl substitution at the α and β carbons of alkyl tellurides have been found to be additive. Downfield shifts of 189, 162, and 160 ppm were observed upon conversion of methyl to ethyl, ethyl to isopropyl, and isopropyl to *tert*-butyl groups, respectively.[16] On the basis of these values, calculation of the chemical shifts for the compounds in Table I demonstrated that similar additivity rules could be used to predict the chemical shift of allyl tellurides relative to dimethyl telluride at 0 ppm. For example, the chemical shift for *tert*-butyl allyl telluride was calculated as 189 (Me to allyl) + 189 (Me to Et) + 162 (Et to ^{i}Pr) + 160 (^{i}Pr to ^{t}Bu) = 700. The observed value is 704 ppm. The effect of a methyl group at the β carbon of an allyl group (generating a 2-methylallyl group) was markedly less than the effect of substitution of a methyl group at the β carbon of an alkyl group (e.g., *n*-propyl to isobutyl). Both groups caused an upfield shift in the ^{125}Te resonance with an average change of 50 ± 1 ppm for ^{n}Pr to ^{i}Bu and 9 ± 3 ppm for allyl to 2-methylallyl. Substitution of methyl groups on more remote carbons in an allyl group also had a small downfield effect on the chemical shift (e.g., $(Me_2C{=}CHCH_2)_2Te$, 400 ppm versus $(CH_2{=}CHCH_2)_2Te$, 377 ppm).

Equilibrium Studies. Mixtures of symmetrical tellurides were heated in benzene solution and observed to undergo a slow exchange to equilibrium mixtures of the starting compounds and the corresponding unsymmetrical tellurides. Visual examination of the solutions did not indicate decomposition to tellurium metal during the course of these experiments. After months of continuous heating at 80 °C, significant decomposition to tellurium metal was observed in the mixture containing diallyl and bis(2-methylallyl) telluride. Precipitates of grey tellurium metal were not observed in any of the remaining tubes. Slow exchange of symmetrical ditellurides and between ditellurides and monotellurides have been reported,[11,17] but there were no reports of facile ligand exchange of monotellurides. Of the six possible two-component mixtures, independent synthesis of the asymmetrical products was possible for the two cases ^{t}BuTe(allyl) and ^{t}BuTe(2-methylallyl). The achievement of equilibrium for these compounds could be determined from both directions in reaction 2. The reactions under consideration are listed in Table II along with the equilibrium constants determined at various temperatures and values for ΔG for the reaction.[18] In each case the formation of the unsymmetrical telluride was favored over that of the two symmetrical tellurides.

Table III. ^{125}Te Chemical Shifts for Symmetrical and Unsymmetrical Ditellurides

	R′			
R	allyl	2-methylallyl	isopropyl	*tert*-butyl
allyl	270	*a*	*a*	556
2-methylallyl	*a*	263	*a*	568
isopropyl	*a*	*a*	313	490[a,b]
tert-butyl	209	192	325[a,b]	497

[a] Not detected in the reaction mixtures. [b] From ref 15.

In the absence of light the equilibration of the symmetrical tellurides was slow. Ratios of products to reactants as function of time at constant temperature were determined by integration of the respective ^{125}Te resonances. Spectra were recorded every 1–2 days for a period of 60 days until identical mixtures were obtained for at least three consecutive measurements. The time required to reach equilibrium ranged from days to months. Relative rates for the reactions in Table II were found to be R = allyl, R′ = 2-methylallyl > *tert*-butyl, isopropyl > *tert*-butyl, 2-methylallyl ~ *tert*-butyl, allyl > isopropyl, 2-methylallyl ~ isopropyl, allyl. The thermodynamic parameters in Table II indicated that formation of the unsymmetrical tellurides from a mixture of symmetrical tellurides was thermodynamically favorable. In two cases, the reverse reaction was also studied. The equilibration of the unsymmetrical compounds ^{t}BuTeR (R = allyl, 2-methylallyl) with the corresponding symmetrical tellurides was much slower, requiring up to 2 months, consistent with the thermodynamic data in Table II (higher activation energy for an uphill reverse reaction).

The presence of light greatly accelerated the ligand-exchange process but did not affect the position of the equilibrium. At room temperature in the dark, the equilibration of diallyl, bis(2-methylallyl), and allyl (2-methylallyl) telluride required more than 30 days, while equilibration was complete after 1 day in room light. In the presence of a H$^\bullet$ source, 1,4-cyclohexadiene,[19] and room light, the same reaction required 6 days.

Prolonged heating of the mixtures caused a color change from yellow to orange and finally to red. With the exception of the diallyl/bis(2-methylallyl) telluride mixture, new resonances of weak intensity were observed in the ^{125}Te NMR spectra, corresponding to symmetrical and unsymmetrical ditellurides. The chemical shifts of the ditellurides are listed in Table III. In mixtures containing ^{t}BuTeR or ^{t}BuTe^{t}Bu and RTeR, (R = allyl, 2-methylallyl), di-*tert*-butyl ditelluride was identified by comparison of the chemical shift with literature data and with an authentic sample.[15] The two additional resonances were assigned as the nonequivalent tellurium atoms in unsymmetrical ditellurides, ^{t}BuTeTeR.

During the thermolysis of ^{t}Bu$_2$Te, alone, in benzene-d_6 at 80 °C, a 4% increase in the concentration of ^{t}BuTeTe^{t}Bu was observed after 25 days. The data indicated a

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(15) The chemical shift of tellurium compounds has been found to be highly concentration dependent. When the ^{125}Te resonance of a ~50% solution of ^{t}Bu$_2$Te in C_6D_6 was set at 999.0 ppm,[16] neat ^{t}Bu$_2$Te (4 drops of C_6D_6 as a lock) was observed to have a chemical shift of 1008 ppm, while a ~10% solution showed a chemical shift of 992 ppm.

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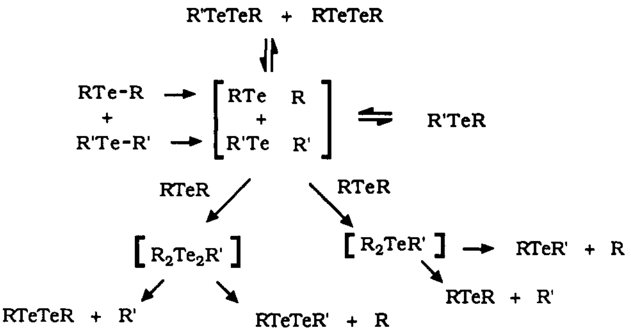
Scheme I. Possible Pathways for Ligand Exchange in Organotellurides



10-fold acceleration in the rate of ditelluride formation in the presence of diallyl or bis(2-methylallyl) telluride. In the presence of RTeR, the concentration of ^{t}BuTeTe^{t}Bu increased by 23% and 16% over 11 days at 80 °C for R = allyl and 2-methylallyl, respectively. In each case, only di-*tert*-butyl ditelluride was observed along with smaller amounts of the unsymmetrical ditelluride. Thermolysis of benzene-d_6 solutions of R_2Te (R = allyl, 2-methylallyl) at 80 °C led to a color change from yellow-orange to red, accompanied by the precipitation of tellurium metal. Weak resonances were observed in the ^{125}Te NMR at 270 and 263 ppm for R = allyl and 2-methylallyl, respectively. By comparison with the chemical shifts of the unsymmetrical ditellurides ^{t}BuTeTeR, these resonances were assigned to the corresponding symmetrical ditellurides RTeTeR. While a distinct color change from orange to red was also observed in the mixtures of diallyl and bis(2-methylallyl) telluride, the low concentration and stability of any ditellurides prevented their detection by ^{125}Te NMR. The presumed thermal and/or photochemical instability of diallyl and bis(2-methylallyl) ditelluride prevented independent syntheses of these compounds.

The formation of diisopropyl ditelluride in mixtures containing ^{i}PrTe^{i}Pr and RTeR (R = allyl, 2-methylallyl) was also confirmed by comparison of the chemical shift with literature data and an authentic sample. Unsymmetrical ditellurides were not observed in these mixtures.

In a recent paper, the effect of structure on the growth temperature of tellurium alloys from alkyl tellurides was discussed.[20] Increased delocalization of the free radical electronic charge by substituents on the alkyl chain (i.e., stability of the alkyl radical produced by bond homolysis) correlated with the observed decrease in growth temperature for the series diethyltellurium, diisopropyltellurium, di-*tert*-butyltellurium, and diallyltellurium. The preferential formation of di-*tert*-butyl ditelluride or ^{i}PrTeTe^{i}Pr over ^{t}BuTeTeR, ^{i}PrTeTeR, and RTeTeR (R = allyl, 2-methylallyl) can be rationalized with the same argument. Since allyl and 2-methylallyl radicals are more stable than either ^{t}Bu or ^{i}Pr radicals,[21] the strength of the Te–R bond was expected to be weaker, leading to the observed product distribution. Similar arguments predicted the formation of diisopropyl ditelluride over di-*tert*-butyl ditelluride in a ^{t}BuTe^{t}Bu/^{i}PrTe^{i}Pr mixture. Empirically, only the latter was observed at 80 °C in benzene solution.

The thermolysis of two additional unsymmetrical tellurides, MeTe(2-methylallyl) and PhTe(allyl), was briefly investigated. Heating a solution of methylallyltellurium in benzene at 60 °C in the dark was reported to cause it to equilibrate to a 1:1:1 mixture after 10 min.[10] In our experiments, disproportionation to symmetrical tellurides was not observed. Dimethyl ditelluride and diphenyl ditelluride respectively were formed upon heating benzene solutions of MeTe(2-methylallyl) and PhTe(allyl), suggesting a significant stability for RTe$^{\bullet}$ radicals derived from bond homolysis.

Conclusions and Mechanistic Implications

Ligand-exchange reactions between organotellurium compounds bearing branched alkyl and allyl ligands were facile, with the formation of unsymmetrical compounds being thermodynamically favored by 1–3 kcal/mol. The ligand-exchange reactions were accompanied by the formation of symmetrical and unsymmetrical ditellurides. Two possible pathways can be considered to account for these observations (Scheme I). Simple bond homolysis and recombination could lead to the formation of both the unsymmetrical tellurides and the ditellurides. Alternatively, the reaction may be a chain reaction catalyzed by the small amounts of radicals that were intercepted by a molecule of RTeR to yield [$R_2TeR'^{\bullet}$]. This radical could fall apart to either R_2Te or RTeR′ and regenerate either R$^{\bullet}$ or R′$^{\bullet}$. Ditelluride formation could be explained by interception of RTeR by a [R′Te$^{\bullet}$] radical, generating [$R_2Te_2R'^{\bullet}$], which could cleave to form both symmetrical and unsymmetrical ditellurides. We have previously demonstrated that the lifetimes of RTe$^{\bullet}$ (relative to dissociation to R$^{\bullet}$ and Te) were sufficient for coupling reactions to occur.[7] Precedent for the reactions depicted in Scheme I could be found in the chemistry of alkyl- and arylselenium compounds.[6] Diselenides were formed upon pyrolysis of symmetrical and unsymmetrical selenides. For unsymmetrical derivatives PhSeR, only diphenyl diselenide was observed.[22,23] Unsymmetrical selenides, RSeR′, were observed upon reaction of RSeR compounds (R = Me, Et) with carbon-centered radicals R′$^{\bullet}$ = Me, Ph, and C_6F_5.[24] Similarly, reactions of diselenides with carbon-centered radicals are reported to yield unsymmetrical selenides and alkylselenium radicals.[6] A triorganoselenuranyl radical intermediate, $R_2SeR'^{\bullet}$, has been proposed for the reaction of alkyl selenides with $Me_3SiO^{\bullet}$ ^{t}BuO$^{\bullet}$, and $CF_3S^{\bullet}$.[25] Work is in progress to measure the kinetics of the ligand-exchange reaction and to further probe the mechanism of the reaction.

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Registry No. ^{125}Te, 14390-73-9; $H_2C{=}CHCH_2TeCH_2C(CH_3){=}CH_2$, 135189-86-5; *t*-BuTePr-*i*, 83817-34-9; *t*-$BuTeCH_2C(CH_3){=}CH_2$, 135189-87-6; *t*-$BuTeCH_2CH{=}CH_2$, 118635-94-2; *i*-$PrTeCH_2C(CH_3){=}CH_2$, 135189-88-7; *i*-$PrTeCH_2CH{=}CH_2$, 125444-15-7; MeTeMe, 593-80-6; $H_2C{=}CHCH_2TeMe$, 114438-52-7; $H_2C{=}C(CH_3)CH_2TeMe$, 135107-01-6; *i*-PrTeMe, 83817-21-4; *t*-BuTeMe, 83817-28-1; $H_2C{=}CHCH_2TeCH_2CH{=}CH_2$, 113402-46-3; $H_2C{=}C(CH_3)CH_2TeCH_2C(CH_3){=}CH_2$, 135106-99-9; *i*-PrTePr-*i*, 51112-72-2; *t*-BuTeBu-*t*, 83817-35-0; $H_2C{=}CHCH_2TeTeCH_2CH{=}CH_2$, 135224-92-9; *t*-$BuTeTeCH_2CH{=}CH_2$, 135189-89-8; $H_2C{=}C(CH_3)CH_2TeTeCH_2C(CH_3){=}CH_2$, 135189-90-1; *i*-PrTeTePr-*i*, 51112-73-3; $H_2C{=}C(CH_3)CH_2TeTeBu$-*t*, 135189-91-2; *t*-BuTeTeBu-*t*, 79971-44-1.

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