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Equilibrium among potassium polytellurides in N,N-dimethylformamide solution

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HIGHLIGHTS

- Potassium polytellurides form when the elements directly combine in DMF solution.
- $Te^{2-} + Te_3^{2-} \rightleftharpoons 2Te_2^{2-}$ occurs in DMF solution.
- Equilibria do not occur in liquid ammonia solution, because Te^{2-} is not soluble.
- Potassium tetratelluride is formed in DMF solution.

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ABSTRACT

Reactions between elemental potassium and tellurium in N,N-dimethylformamide (DMF) are monitored using UV–visible spectroscopy and compared with those in liquid ammonia solution. In liquid ammonia, the elements react together, via a step-wise sequence, to form polytellurides, each of which is characterized by a distinctive color, the highest being potassium tritelluride. However, when the elements are combined in DMF, these distinctive color changes are not observed – the solution develops an initial plum color, which gradually darkens to purple as the reaction progresses. UV–visible and Raman spectroscopic studies indicate that equilibrium exists among the mono-, di-, and tritelluride in DMF. This equilibrium is not seen in liquid ammonia solution due to the insolubility of potassium monotelluride in that solvent. Spectral data also indicate that potassium tetratelluride is formed in DMF solution.

1. Introduction

The reaction of elemental tellurium with alkali metals in liquid ammonia to form polytellurides has been known since the early 1900s, although the air-sensitivity of the products recovered from these solutions rendered them of limited interest [1]. This situation changed dramatically with the discovery that polytellurides could be used as versatile synthetic reagents to form a wide variety of exciting organometallic materials. Work in this area has been well summarized in a series of review articles which appeared in the 1990s [2–6], and since 2000 [7–9]. A major factor in this dynamic growth was the discovery that these materials were stable and soluble in polar solvents, such as N,N-dimethylformamide (DMF) [10]. However, although a vast number and variety of compounds have been synthesized utilizing polytellurides and characterized by X-ray crystallography and other techniques, the reaction mechanisms are not known and the actual identity of the polytelluride species in solution is often not known with certainty, although they are generally considered to be equilibrium mixtures [11].

1.1. Alkali metal polytellurides in liquid ammonia

One classic procedure for alkali metal polytelluride synthesis is direct reaction of the elements in liquid ammonia solution. This results in initial formation of an alkali metal cation and a solvated electron, which is characterized by a deep blue color. The solvated electron then reduces tellurium in a step-wise manner to form the polytelluride of appropriate stoichiometry. The anions formed can be differentiated by their distinctive colors as follows:

(1) $2\ M \rightarrow 2\ M^+ + 2e^-$ (solvated electron, blue, forms rapidly)
(2) $Te + 2e^- \rightarrow Te^{2-}$ (white precipitate)
(3) $Te^{2-} + Te \rightarrow Te_2^{2-}$ (blue/violet solution)
(4) $Te_2^{2-} + Te \rightarrow Te_3^{2-}$ (red solution)

These anions have been characterized in liquid ammonia and ethylenediamine solution by ^{123}Te and ^{125}Te NMR [12]. However, since the solutions are so intensely colored, UV–visible spectroscopy

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is also an excellent tool for monitoring the reaction process. This technique has been successfully applied to sodium polyselenides [13] and ammonium polysulfides [14] in liquid ammonia solution. In this laboratory, it has also been used to investigate polytellurides of sodium [15], potassium [16], and rubidium (unpublished results) in liquid ammonia solution.

1.2. Alkali metal polytellurides in DMF

Alkali metal polytellurides synthesized in liquid ammonia solution have been successfully utilized as reactants in DMF solution for many interesting syntheses – including some in which product materials containing tetratelluride bidantate ligands have been formed [17–19]. However, although the polytellurides of sodium and potassium are well-defined entities in liquid ammonia solution, when these materials were synthesized in liquid ammonia and transferred to DMF solution, a color change was observed. Rather than the characteristic compound colors observed in liquid ammonia, a deep permanganate purple solution was noted, which was independent of alkali metal/tellurium stoichiometry and alkali metal identity. Therefore, a study of potassium polytelluride anions in DMF solution was initiated in this laboratory.

Although liquid ammonia and N,N-dimethylformamide have very different chemical characteristics, since the former is a protic polar solvent and the latter an aprotic polar solvent, one physical property which is very similar is their dielectric constants; 26.6 versus 26.7 for DMF and liquid ammonia, respectively [20]. In DMF neither element is soluble nor is the solvated electron of the liquid ammonia reaction formed; thus no reaction is expected from the direct combination of these two elements. However, direct combination in DMF does result in formation of deep purple solutions, which appear to be identical to those formed when alkali metal polytellurides synthesized in liquid ammonia are transferred to DMF solution [17].

The reaction sequence in DMF is also visually different from that in liquid ammonia. Instead of the dramatic sequence of differently colored solutions observed in liquid ammonia, alkali metal and tellurium in DMF do not appear to react at all initially. After about 30 min, at room temperature, a faint pink color does appear, which gradually deepens to a final dark purple as the reaction progresses over a period of several hours.

2. Experimental

2.1. Chemicals

All chemicals were reagent grade from Aldrich Chemical Company and were used without further purification.

2.2. Procedures

To elucidate the reaction sequence, the progress of the reaction between potassium and tellurium was followed using UV–visible spectroscopy for a series of varying alkali metal/tellurium ratios in the millimolar concentration range. All mass determinations were performed on an analytical balance to the nearest 0.1 mg under ultrapure argon in a Vacuum Atmospheres Dry Box. DMF was transferred under ultrapure argon using standard Schlenk techniques for air-sensitive materials. Reactions were run at room temperature, under an argon atmosphere, and solution temperatures were monitored with a mercury thermometer and were $22(\pm1)\,^\circ$C. Samples were withdrawn at timed intervals with a glass syringe, transferred into a fused silica cuvet, and capped. The sample was then immediately scanned using a Perkin-Elmer Model 320 UV–visible spectrophotometer with a Model 3600 data station. The data obtained were then hand entered into Microsoft© Excel spreadsheets and imported into PeakFit® for peak resolution analysis.

All reactions in liquid ammonia were carried out on an all-glass vacuum line. The liquid ammonia was initially condensed over sodium to remove any impurities and then distilled by temperature differential into a reaction flask on the vacuum line.

Solutions with K:Te ratios of 2:1, 2:2, 2:3, and 2:4 of approximately 0.01 M were prepared in DMF and sealed in glass NMR tubes with a torch on a vacuum line, as was a sample of pure DMF to be used as a background.

A solution of K_2Te_3 in liquid ammonia was prepared and sealed in an NMR tube on the vacuum line, as was a sample of liquid ammonia to be used as a background.

Raman spectra were obtained on a Nicolet Magna 550 FT-IR/Raman with a resolution of 4 cm^{-1} and were analyzed using Thermo-Nicolet OMNIC 6.2 software.

3. Results

3.1. UV–visible spectra

When potassium and tellurium were placed in DMF, no color was evident for approximately 30 min. Then a pale pink/amber color was observed, which progressed to a plum color, then deepened to a dark permanganate color as higher polytellurides were formed. No unreacted potassium was observed in the solutions after approximately 5 h, but solution color continued to darken for some time – especially with higher potassium/tellurium ratios.

As shown in Fig. 1, the actual reaction sequence in DMF becomes more evident when spectra are obtained during the reaction sequence. This figure shows spectra for a K:Te reaction ratio of 2:4 at 30 min intervals for the initial 4 h of reaction.

At 30 min, no color is evident. However, two overlapping absorption peaks are noted – one at about 290 nm and one at about 330 nm. These are attributed to the formation of a monotelluride species, which one would expect to be colorless, and would be consistent with the reaction sequence in liquid ammonia.

At 60 min the solution is pale pink/amber, the peaks previously observed have increased in intensity, and a peak has appeared at about 400 nm. This is attributed to the formation of a ditelluride.

At 90 min the solution is darker and beginning to acquire a purple tint, the previously mentioned peaks have increased in intensity, and a peak at 530 nm has appeared.

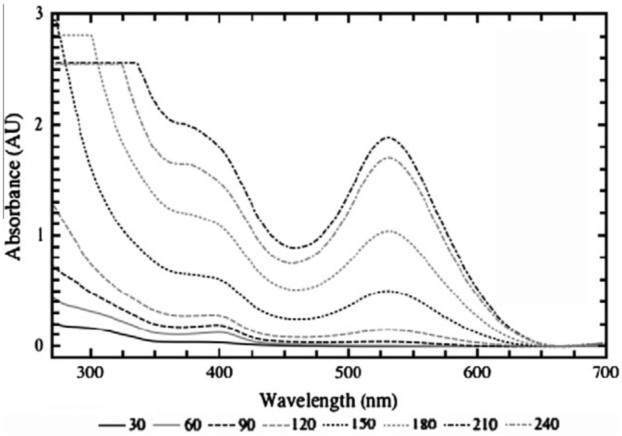

Fig. 1. Reaction of tellurium with potassium in DMF: reaction mixture absorbance spectra taken every 30 min over 4 h. The 240 min spectrum was off scale at 530 nm, so the spectrum shown is diluted 1:1 with DMF.

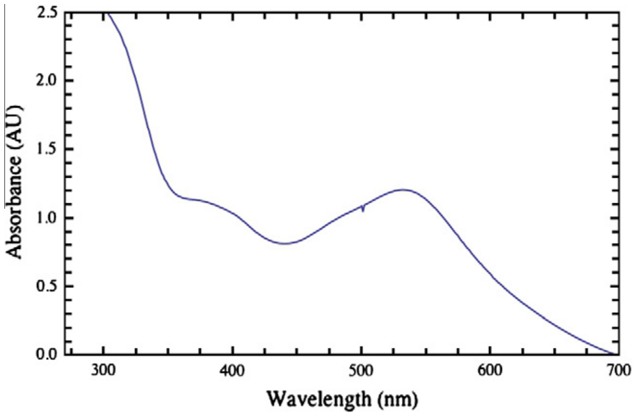

Fig. 2. Reaction of tellurium with potassium in DMF after 2 days.

At 120 min the solution is a pale plum color and all of the previously observed peaks have increased in intensity. The 400 nm peak is more intense than the 530 nm peak, but the relative intensity of the 530 nm peak is slightly greater. It should be noted that unreacted potassium and tellurium are still visible in the reaction flask.

At 180 min, the color of the solution resembles dilute potassium permanganate, all peak intensities are increased, and relative peak intensities are not greatly changed. However, by 240 min the solution required dilution by approximately 50% to obtain a spectrum due to the color intensity, and the observed intensity at 530 nm is greater than that at 400 nm.

An identical mixture was prepared and allowed to react for 2 days before samples were withdrawn for analysis. The solution color was a deep cranberry red color. The intensity was too great for the spectrophotometer to read (A > 3.0), so the solution was diluted in the cuvet approximately 1:1 with DMF to obtain the spectrum, which is shown in Fig. 2. The highest telluride absorbance peak appeared at ~550 nm, and the next highest peak was at ~400 nm. This is consistent with the previous spectrum reported for the 240 min reaction mixture. Attempts to obtain spectra at longer reaction times were unsuccessful due to sample decomposition.

3.2. Resolved spectra

All spectra consisted of a series of overlapping peaks and were resolved using PeakFit®. Optimal resolution was obtained with a 5 peak fit. Major peaks were located at about 293–315 nm (variable because several spectra went off scale close to this peak), 376 nm, 403 nm, and 530 nm. Fig. 3 shows a plot of peak intensities versus time.

The peak at about 293 nm appears first, and is attributed to the formation of a monotelluride. The peaks at 403 nm and 373 nm both increase continuously with time and are assigned to the ditelluride and tritelluride respectively. The peak at 530 nm is the last to appear and steadily increases, with its intensity passing that of both the 403 nm and 376 nm peaks, and is, therefore, assigned to a tetratelluride.

3.3. Raman spectra

The Raman spectrum of K_2Te_3 in liquid ammonia shows a prominent peak at about 163 cm^{-1}. All of the polytelluride spectra in DMF solution also show a similar peak at about 160–163 cm^{-1} (Spectrosc. Lett., accepted), but this peak is absent in the Raman spectrum of the 2:1 ratio of K:Te (monotelluride).

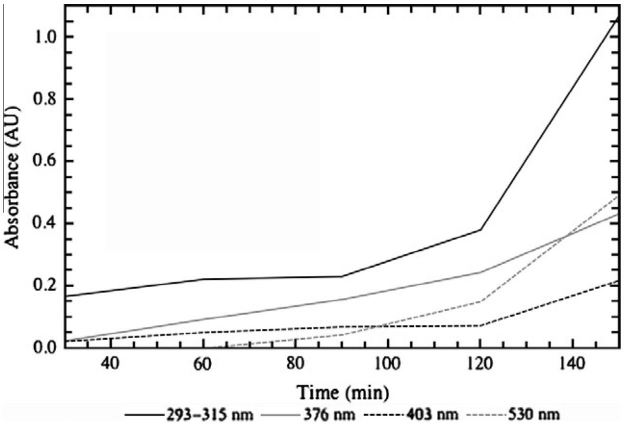

Fig. 3. 30 min interval spectral peak intensities: K:Te molar reactant ratio 2:4.

4. Discussion

We believe an initial reaction occurs between potassium and tellurium when physical contact is made between the elements in DMF, not unlike in a thermal technique. This results in formation of the Te^{2-} ion, which is colorless and absorbs at about 290 nm. This species is soluble in DMF and acts as a reducing agent toward the excess elemental tellurium present, forming polytelluride ions as shown in the following sequence:

(1) $Te + 2\,M \rightarrow 2\,M^{+} + Te^{2-}$
(2) $Te^{2-} + Te \rightarrow Te_2^{2-}$
(3) $Te_2^{2-} + Te \rightarrow Te_3^{2-}$
(4) $Te_3^{2-} + Te \rightarrow Te_4^{2-}$

The following equilibrium also occurs in DMF:

$$Te^{2-} + Te_3^{2-} \rightleftharpoons 2Te_2^{2-}$$

This equilibrium is analogous to that reported by Sharp and Koehler [13] for sodium polyselenides in liquid ammonia and Kolis [17] for alkali metal polytellurides in other solvents, but is not observed with polytellurides in liquid ammonia because of the insolubility of the Te^{-2} ion in that solvent [15,16]. The appearance of the 162 cm^{-1} peak observed in the Raman spectrum of K_2Te_3 in liquid ammonia solution and in all of the DMF solutions *except* the theoretical monotelluride supports this conclusion.

This equilibrium would be characterized by the equilibrium constant expression

$$K = \frac{[Te_2^{2-}]^2}{[Te^{2-}][Te_3^{2-}]}$$

Since Beer's Law states that *absorbance*$_x$ = $\varepsilon_x[X]$, or $A_x = \varepsilon_x[X]$, the above equilibrium constant can be rewritten as

$$K = \frac{A^2_{\text{ditelluride}}}{A_{\text{monotelluride}} \times A_{\text{tritelluride}}} \times \frac{\epsilon_{\text{monotelluride}} \times \epsilon_{\text{tritelluride}}}{\epsilon^2_{\text{ditelluride}}}$$

Although molar absorptivities cannot be measured in this experiment due to the existence of multiple species in solution, these values are considered constants, and hence the second component of the above equation is also a constant. Therefore, if the peak assignments are correct and the postulated equilibrium does exist, the first component of the above equation (K′) will also be a constant and can be written as follows.

$$K' = \frac{A^2_{\text{ditelluride}}}{A_{\text{monotelluride}} \times A_{\text{tritelluride}}}$$

Table 1
Resolved peak intensities and times with resultant values of K′.

Peak location Telluride	293 nm Mono-	376 nm Tri-	403 nm Di-	530 nm Tetra	K′
30 min	0.168	0.025	0.023		0.13
60 min	0.223	0.093	0.052		0.13
90 min	0.231	0.158	0.069	0.043	0.13
120 min	0.381	0.245	0.074	0.149	0.06
150 min	1.072	0.433	0.218	0.492	0.10
2 days	2.231	0.688	0.399	1.135	0.10

The absorbances of the peaks assigned to the mono-, di-, and tetratelluride species and the resultant values calculated for K′ when these are substituted into the above equation are shown in Table 1.

The calculated value for K′ remains constant for the initial portion of the reaction. However, when significant absorbance at 530 nm occurs, this value drops markedly, indicating that the new species being formed is affecting the equilibrium. The increasing absorbance at 530 nm is also accompanied by a marked increase in the 293 nm peak, attributed to the monotelluride, and would be expected to result in a lower value of K′. K′ stabilizes again after about 150 min at a slightly lower value.

The delayed appearance of this peak at 530 nm, whose increasing intensity does not markedly affect the relative values of the 376 nm and 403 peaks but is accompanied by a sharp increase in the relative intensity of the 293 nm peak, is indicative of the formation of a tetratelluride in DMF, whereas the highest polytelluride observed in liquid ammonia is tritelluride [15,16]. This is consistent with the hypothesis of Kolis that a tetratelluride species reacts with $M(CO)_6$ in DMF [17,21].

Therefore, it is concluded that DMF solutions which would be expected to contain a polytelluride species of predetermined stoichiometry, based upon relative reactant concentrations, actually contain a mixture of four species, and the relative amounts are controlled by both the ratio of tellurium to potassium and the reaction time.

5. Conclusions

Potassium polytelluride species in DMF solution do form by a sequential reaction process at room temperature when the elements are combined with stirring. They also undergo the following equilibrium.

$$Te^{2-} + Te_3^{2-} \rightleftharpoons 2Te_2^{2-}$$

The presence of this equilibrium results in a mixture of the mono-, di-, and tritelluride species. This process is not observed in liquid ammonia solution, because Te^{2-} is not soluble in liquid ammonia. Additionally, further reaction in DMF results in formation of a tetratelluride anion, which is not observed in liquid ammonia solutions.

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