Synthesis and characterization of potassium polytellurides in liquid ammonia solution

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(Received February 1, 1990; revised May 29, 1990)

Abstract

Elemental potassium and tellurium have been combined in liquid ammonia to form materials with elemental analyses consistent with potassium polytellurides. Solutions of these materials in liquid ammonia have been studied using UV–Vis spectroscopy. The results of this investigation indicate that K_2Te_2 and K_2Te_3 are distinctive, spectroscopically identifiable species. During the reaction sequence, a yellow solution color is observed prior to the formation of K_2Te. This transient species has a broad absorption band with a maximum at 367 nm, a shoulder at 390 nm, a small shoulder at 425 nm, and is postulated to be the intermediate KTe. K_2Te is a yellowish-white solid for which no absorption is noted in the spectral region 220–700 nm. The spectra of the polytellurides consisted of several overlapping bands that were submitted to curve resolution procedures. Results were as follows: K_2Te_2, blue solution (282.8, 306.8, 329.4, 358.0 and 562.1 nm) and K_2Te_3, red solution (285.7, 324.8, 370.4 and 516.0 nm). No evidence for the formation of a polytelluride greater than the tri-species was observed under the conditions of this investigation.

Introduction

The reaction of elemental potassium with tellurium in liquid ammonia to form potassium polytellurides is well documented, but the air-sensitive nature of these materials has limited investigation of their properties. The recent discovery of the utility of these substances in the synthesis of tellurium containing organometallic compounds [1–3] indicates that the polytellurides of potassium warrant further characterization.

Potassium telluride, K_2Te, was first reported by Zintl and coworkers [4] in 1934 and characterized by X-ray diffraction. Klemm and coworkers [5] reported the synthesis of a series of potassium polytellurides by direct combination of the elements in liquid ammonia. The compounds reported by these investigators included K_2Te, K_2Te_2 and K_2Te_3. A species of stoichiometry, K_2Te_4, was also prepared, but was not considered a compound because of the observation of the presence of free tellurium in the sample. Samples were sealed into glass tubes and studied by magnetic susceptibility techniques. No unpaired electrons were noted. The identities of the compounds were based upon elemental composition. However, elemental analysis as an identification technique does not make allowance for stoichiometric mixtures or solution equilibria [6].

UV–Vis spectroscopic techniques have been used by Sharp and Koehler [6] to characterize the sodium polyselenides in liquid ammonia solution and, more recently, in this laboratory [7] to characterize the sodium polytellurides. Therefore, this methodology was applied to the potassium–tellurium systems in liquid ammonia solution. The present study involved reaction of appropriate stoichiometric amounts of potassium and tellurium in liquid ammonia with isolation of the resultant products, elemental analysis of these products, UV–Vis spectrophotometric investigation of solutions of the products in liquid ammonia, and computer resolution of the resultant spectra.

Experimental

General information

All work was done using vacuum line and drybox techniques as previously described [7].

Chemicals

Pure potassium metal (J.T. Baker) was purified by removal of all oxide surfaces under argon in the

0020-1693/90/$3.50

drybox and degassed under vacuum prior to use. Tellurium powder (99.95%) was obtained from Alfa Inorganics, stored under argon in the drybox, and degassed under vacuum prior to use. Anhydrous ammonia was purified by distillation over sodium metal on the vacuum line before use.

Preparation of potassium polytellurides

All potassium polytellurides were prepared by direct combination of the elements in liquid ammonia solution using the procedures previously described for the synthesis of the sodium polytellurides [7]. The initial step in the reaction sequence, formation of the monotelluride, progressed more rapidly with potassium and tellurium than with sodium, probably due to the greater tendency of the K_2Te particles to remain suspended in solution rather than precipitate and protectively coat the unreacted tellurium as did Na_2Te. However, to ensure completion of the reaction sequence to higher polytellurides it was still necessary to allow the reaction mixture to boil to dryness and be redissolved in liquid ammonia several times prior to collection of the final product.

Potassium telluride, K_2Te, was prepared in the identical manner, except that, since it is not soluble in liquid ammonia, it was not filtered but was obtained directly from the initial reaction flask.

Elemental analysis

Samples of standard tellurium and the potassium–tellurium compound to be analyzed were weighed on the Cahn electrobalance in the drybox, removed from the drybox and dissolved in a nitric acid solution. After all particles had dissolved, the solutions were diluted to a known volume and analyzed for tellurium by atomic absorption on a Varian model 1275 atomic absorption spectrophotometer. *Anal.* Calc. for K_2Te: Te, 62.00. Found: Te, 62.09%. Calc. for K_2Te_2: Te, 76.54. Found: Te, 76.67%. Calc. for K_2Te_3: Te, 83.04. Found: Te, 83.41%.

UV–Vis spectroscopy

All spectra were obtained on a Perkin-Elmer model 320 UV–Vis spectrophotometer interfaced to a Perkin-Elmer model 3600 data station using procedures previously described for sodium polytelluride spectra [7]. Absorbance measurements were made over the range 220–700 nm. The spectrum of liquid ammonia has an intense band around 220 nm, and absorbance readings were too large for measurement below this wavelength.

Data treatment

Overlapping spectral bands were resolved on an IBM model 4341 computer using the non-linear, damped least-squares program described by Sharp and Koehler [6] and modified by Dr Ivan F. Taylor of the Texas Christian University Computer Center for this investigation.

The ammonia band at 220 nm has been observed to overlap with the charge-transfer band of the iodide ion [8] and the amide ion [9], as well as the polyselenides [6] and the polytellurides [7]. This overlap has been reported to increase with increasing ionic concentration, suggesting a perturbation of the ammonia band to lower energy with increasing solute concentration in each of the above cases. Because of this overlap of the ammonia wing with the spectra of the polytellurides, the curve-fitting program incorporated parameters describing the ammonia band.

The absorbances of the most concentrated solution of K_2Te_3 were too high to be measured below approximately 270 nm, so that data set omitted the ammonia parameters and treated the 285 nm band of the tritelluride in the same manner as the ammonia wing.

Results and discussion

KTe spectrum

When ammonia is condensed onto a mixture of elemental potassium and tellurium, the initial solution color observed is the intense blue generally attributed to the presence of the solvated electron. As the reaction between potassium and tellurium commences, a bright yellow color is observed at the site of the reaction, which rapidly diffuses into the solution, which begins to turn green. This color change continues rapidly until the solution passes through a yellow color phase and into the cloudy, creamy colored suspension of K_2Te. This yellow color has been noted during the reaction of sodium and tellurium [10, 11] and had been attributed to the formation of the Te^{2-} ion. However, sodium telluride does not give a yellow solution in liquid ammonia [7].

The reaction was observed spectroscopically by preparing a solution of approximately 2 mM potassium in liquid ammonia and lowering a glass bucket containing tellurium into the solution. This solution was then monitored spectroscopically for several hours. A band of approximately 100 nm bandwidth was observed to form with a maximum at approximately 367 nm, a broad shoulder at about 390 nm, and a small shoulder at 425 nm. No peaks were noted in the range 250–325 nm, which is a region in which both K_2Te_2 and K_2Te_3 absorb intensely. The appearance of this band corresponded with a gradual solution color change to an olive green.

The tendency of K_2Te to remain suspended in solution rather than precipitate immediately as did Na_2Te allowed better spectra of the reaction process to be obtained. The corresponding greenish solution formed during the sodium–tellurium reaction sequence exhibited a broad band with an absorption peak at approximately 428 nm [7], which was attributed to the presence of tellurium in a − 1 oxidation state.

The Te^- ion has been proposed by Manning and Manantov [12] from polarization experiments at a tellurium electrode. Te^- is also identified by Toth and Hitch [13] as the dominant ion present in molten LiCl–KCl, where it is characterized by an intense absorption band at 478–497 nm.

K_2Te

Potassium telluride was synthesized by the direct reaction of elemental potassium and tellurium in liquid ammonia, as previously described. The reaction product formed a creamy suspension, which dried to a pale, yellowish solid upon evaporation of the liquid ammonia. This material rapidly darkened to a dark brown, followed by a dark grey color, upon exposure to air.

An amount of K_2Te corresponding to approximately a 2 mM solution was placed in liquid ammonia in the optical Dewar, and the mixture was agitated for approximately 2 h. No spectral features were observed in the range 220–700 nm during this period. However, when air was allowed into the mixture at the conclusion of the experiment, the characteristic red color of the oxidation product was quickly noted. Therefore, K_2Te is either virtually insoluble in liquid ammonia or else does not absorb in the 220–700 nm spectral range.

This is in agreement with the reported behavior of Na_2Te [7], and is consistent with the observations of Bamberger *et al.* [14] who noted that the Te^{2-} species either did not absorb in the 200–2000 nm range or was too insoluble to detect in molten $LiF–BeF_2$. However, it is of interest to note that the S^{2-} species in liquid ammonia exhibits an absorption peak at 270.0 nm [15], and the Se^{2-} species absorbs at 290 nm [6].

K_2Te_2 spectrum

Combination of potassium and tellurium in a 1:1 molar ratio in liquid ammonia resulted in the formation of a solution of an intense violet–blue color. The dark grey solid material obtained from the solution was extremely air-sensitive, and spectra were obtained at four concentrations only with great difficulty. In one instance, when the characteristic red solution color of the tritelluride was noted, elemental potassium was added and reduction to the ditelluride was followed spectrophotometrically. A resolved sample spectrum is shown in Fig. 1. A five-band fit was required to give consistent results, and the computer resolved spectral parameters are given in Table 1. Beer's Law plots were satisfactory. The relatively smooth spectral overlaps made resolution difficult, as was evidenced by the range of peak locations and the quality of the Beer's Law plots for the peaks in the 300–400 nm region.

The overall spectral appearance is not dissimilar to that of Na_2Te_2 [7]. The longest wavelength peak occurs in essentially the same position, about 562 nm, in both species, and the remainder of the spectra

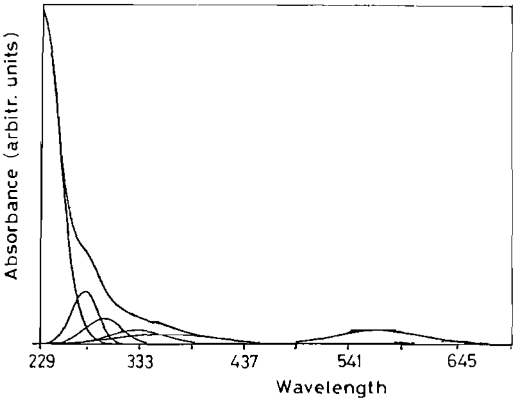

Fig. 1. Computer resolved spectrum of 1.14×10^{-3} M K_2Te_2 in liquid ammonia solution (wavelength in nm).

TABLE 1. Band parameters for K_2Te_2

$10^3 \times$ conc. (M)	Position (nm)	Absorption	*w* (nm)
1.14	279.4	0.955	29.7
	298.3	0.465	42.8
	332.1	0.255	65.8
	358.9	0.183	112.4
	564.8	0.292	99.1
1.48	282.7	1.072	25.8
	304.6	0.422	32.3
	334.9	0.436	73.9
	358.8	0.208	141.4
	560.4	0.357	91.5
4.50	283.3	3.741	33.9
	312.4	1.567	45.6
	326.3	1.383	44.7
	357.8	0.947	80.5
	562.1	0.982	97.6
4.87	281.8	3.871	30.4
	311.9	1.770	42.7
	324.1	1.328	56.8
	356.6	1.010	81.1
	561.1	1.199	91.2

consist of a series of overlapping peaks beginning at about 360 nm whose intensity increases with decreasing wavelength. However the apparent shoulders in the spectrum occur at about 290 and 330 nm for Na_2Te_2 and at about 280 and 340 nm for K_2Te_2, so the profile of the ultraviolet portion of the spectrum is slightly different for the two compounds. The similarity of the visible portion of the spectra would be expected, since the color observed for K_2Te_2 solutions is the same as that reported for solutions of Na_2Te_2 [7, 10].

The spectra of K_2Te_2 were distinctly different from those of K_2Te_3, and no cloudiness due to K_2Te was noted, so it is concluded that no equilibria such as that noted by Sharp and Koehler [6] for the Na_2Se_2 system are present and K_2Te_2 is a distinct, spectroscopically identifiable species in liquid ammonia solution. This conclusion is in agreement with that reached by Klemm *et al.* [5] based upon magnetic susceptibility data.

K_2Te_3 spectrum

Combination of potassium and tellurium in a 2:3 molar ratio in liquid ammonia resulted in the formation of a solution of an intense wine-red color. Spectra of the isolated product were obtained at three different concentrations, and a representative resolved spectrum is shown in Fig. 2. A four-band fit produced consistent results, and the resultant computer resolved spectral parameters are shown in Table 2. Beer's Law plots for these parameters were well behaved.

The observed colors of the K_2Te_3 solution are the same as those reported for Na_2Te_3 [7, 10], so a similarity in the visible portion of the spectrum is expected. Both the spectrum of K_2Te_3 and that of Na_2Te_3 show a broad absorption peak at approximately 515 nm and a series of overlapping peaks in the shorter wavelength region, beginning at about 370 nm. However, the peak profiles in the ultraviolet region of the spectra are quite different. K_2Te_3 exhibits a very marked peak at about 325 nm which is not evident in Na_2Te_3, while Na_2Te_3 has a large peak at about 273 nm and K_2Te_3 has a relatively small peak at about 285 nm. These spectral differences suggest the presence of ion pairing or some related phenomenon.

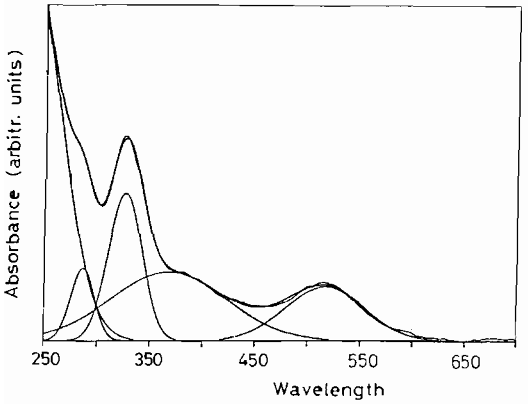

Fig. 2. Computer resolved spectrum of 1.57×10^{-3} M K_2Te_3 in liquid ammonia solution (wavelength in nm).

TABLE 2. Band parameters for K_2Te_3

$10^3 \times$ conc. (M)	Position (nm)	Absorption	*w* (nm)
1.57	285.9	1.467	26.2
	325.9	3.010	37.6
	367.5	1.389	130.7
	516.8	1.098	89.1
3.90	285.9	3.709	26.7
	325.0	7.947	36.6
	371.7	3.085	131.7
	516.2	2.533	81.0
6.35	285.4	–	–
	323.5	–	37.7
	372.0	4.845	122.6
	515.0	3.939	80.3

Like Na_2Te_3, K_2Te_3 is concluded to be a distinct, spectroscopically identifiable species in liquid ammonia solution. K_2Te_3 has been synthesized by direct combination of the elements using a tube procedure and characterized by X-ray crystallographic techniques [16]. This is also in agreement with the results of Klemm *et al.* [5] who characterized K_2Te_3 by magnetic susceptibility measurements.

Higher polytellurides

Potassium and tellurium were combined in a 1:3 molar ratio in liquid ammonia. A deep red solution color was observed, but when the solution was filtered, a large quantity of unreacted tellurium remained in the reaction flask. The material from this reaction was examined spectroscopically, and the characteristic spectrum of K_2Te_3 was observed. Therefore, it is concluded that no polytellurides higher than the tritelluride are formed under the conditions of this investigation. This is also in agreement with the results of Klemm *et al.* [5], whose magnetic susceptibility data indicated the presence of free tellurium in K_2Te_4, which caused them to question the existence of this species. This is also consistent with the sodium–tellurium system in liquid ammonia [7], in which Na_2Te_4 was found to be a mixture of Na_2Te_3 and excess tellurium. However, it should be noted that the compounds Rb_2Te_5 [17] and Cs_2Te_5 [18] have been prepared and characterized.

Conclusions

Isolation, elemental analysis and spectroscopic investigation indicate that K_2Te_2 and K_2Te_3 are stable species in liquid ammonia solution. An intermediate species postulated to be KTe is formed during the initial reaction of potassium and tellurium and is responsible for the yellow solution color which precedes the formation of K_2Te. K_2Te is either insoluble in liquid ammonia or does not absorb in the spectral range 220–700 nm. No polytelluride higher than K_2Te_3 is formed under the conditions of this investigation.

Acknowledgements

Portions of this data were collected as undergraduate research projects by Mr Greg Swindle, Mr Cody Yarborough, Mr Howard Westmoreland, Ms Sheila Schmidt, Mrs Lisa Broussard and Mrs. Jerri Howard. Dr Becky Krechel assisted with German translations.

We gratefully acknowledge the financial support of the Robert A. Welch Foundation and the Tarleton State University Organized Research Fund and thank Dr William Koehler of Texas Christian University for the use of computer facilities.

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