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Synthesis and Characterization of Sodium Polytellurides in Liquid Ammonia Solution

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Solutions of sodium polytellurides in liquid ammonia have been studied by using UV–visible spectroscopy. The results of the investigation indicate that Na_2Te_2 and Na_2Te_3 are distinctive, spectroscopically identifiable species. During the sequential reaction of sodium and tellurium, a species postulated to be NaTe is observed spectroscopically as a precursor to Na_2Te. Na_2Te is either virtually insoluble in liquid ammonia or does not absorb in the spectral region 220–700 nm. The proposed species Na_2Te_4 was found to be a 1:1 molar mixture of Na_2Te_3 and insoluble excess tellurium, and no evidence for the formation of a higher polytelluride under the conditions of study was obtained. The short-lived precursor species exhibited a yellow color in the liquid ammonia solution and showed an absorption maximum at 428 nm. The spectra of the polytellurides consisted of several overlapping bands that were submitted to curve resolution procedures. Results were as follows: Na_2Te_2, blue solution (290.4, 329.3, 351.5, and 561.9 nm); Na_2Te_3, red solution (273.2, 303.0, 335.1, 374.6, and 513.5 nm).

Introduction

The reaction of sodium with tellurium in liquid ammonia was first reported in 1899 by Hugot,[1] who observed the initial reaction product to be a colorless, gelatinous precipitate, insoluble in liquid ammonia, which he identified as Na_2Te. Upon addition of additional tellurium, this material went into solution, and the final compound formed was assigned the stoichiometry Na_2Te_3. Studies reported in 1916 by Allison[2] and in 1917 by Power[3] observed the ratio of tellurium to sodium in liquid ammonia to vary as a function of concentration, reaching a maximum Te:Na of approximately 1.95. A more comprehensive investigation by Kraus and Chiu in 1922[4] established the identities of the species sequentially formed in liquid ammonia solution to be Na_2Te (yellow solution, white crystalline precipitate), Na_2Te_2, and Na_2Te_4 (deep red solution). These authors attributed the discrepancies between their results and those of the earlier investigators to the presence of impurities in their reagents—water in the case of Hugot,[1] which would have resulted in the coprecipitation of hydroxide and interpretation as gelatinous Na_2Te, and impure tellurium in the studies of Allison[2] and Power.[3] In 1931 Zintl, Goubeau, and Dullenkopf[5] also investigated the sequential reactions of tellurium with sodium in liquid ammonia and reported the compounds formed to be Na_2Te (white precipitate, yellow solution), Na_2Te_2 (violet solution), and Na_2Te_3 (red solution). These authors questioned the formation of Na_2Te_4. At a later date Kraus and Ridderhof[6] measured the heats of formation of Na_2Te, Na_2Te_2, and Na_2Te_4 in liquid ammonia; Klemm, Sodomann, and Langmesser[7] reported the synthesis of a number of alkali-metal chalcogenides, including Na_2Te; Zintl, Harder, and Dauth[8] reported the X-ray structure of Na_2Te prepared in liquid ammonia solution. Although the monotelluride had been shown to be a crystalline material,[8] Kraus and Chiu[4] observed the product remaining when the ammonia was evaporated from a solution of a complex telluride to be distinctly metallic in appearance, although no free tellurium was present. The materials were unstable upon exposure to air.

An interesting observation is that the compounds purportedly formed in liquid ammonia solution differ from those formed by thermal analysis methods. The latter were first reported in 1910 by Pellini and Guercigh,[9] who reported the formation of Na_2Te, Na_2Te_3, and Na_2Te_7. In 1929 Kraus and Glass[10] studied the specific resistance of a series of sodium–tellurium alloys and deduced the existance of Na_2Te_6 as the highest ratio tellurium species formed. These authors also reported the sodium–tellurium phase diagram[11] and observed the species Na_2Te, Na_2Te_2, and Na_2Te_6. This is in agreement with the reports of several other investigators.[12] The phase diagram Na_2Te–Te also shows the existance of the species NaTe and $NaTe_3$.[13] Therefore, the thermal analysis methods are reported to produce a higher ratio of tellurium to sodium than do the liquid ammonia preparative methods.

Although there is general agreement about the species formed by sodium and tellurium in the thermal methods, there is still disagreement as to the identity of the highest sodium polytelluride formed in liquid ammonia solution. Another curious observation is that a reportedly white crystalline solid should be observed to produce a yellow solution in liquid ammonia. The reported product stoichiometries are generally based upon the reactant stoichiometries, which is a questionable assumption in light of more recent work on the polyselenides.

A similar problem involving the sodium polyselenides in liquid ammonia was investigated by Sharp and Koehler[14] utilizing UV–visible spectrophotometric methods. These authors found that of the species previously reported to exist in liquid ammonia solution, some were indeed spectroscopically isolatable, some existed only in equilibrium with other species, and some were only mixtures. Therefore, their methodology was applied to the sodium–tellurium systems in liquid ammonia solution. The present study involved reaction of appropriate stoichiometric amounts of sodium and tellurium in liquid ammonia with isolation of the resultant products, elemental analysis of these products, ultraviolet–visible spectral investigation of liquid ammonia solutions of the products, and computer resolution of the resultant spectra.

Experimental Section

General Information. Since all materials synthesized were air-sensitive, all work was carried out by using vacuum line and drybox techniques. The drybox used was a Vacuum Atmospheres Model HE-43 Dri-Lab glovebox equipped with a Model HE-493 Dri-train accessory and maintained under a positive pressure of 99.99% argon with a Model HE-43 Pedatrol accessory. Sodium metal maintained a shiny surface and a constant weight for periods of time in excess of 1 h under these conditions. The vacuum line was all glass, and Dow-Corning high-vacuum grease was used on all joints. All weighings were done on a Cahn electrobalance in the drybox and were accurate to ±0.1 mg.

Chemicals. Anhydrous ammonia was purified by distillation over sodium metal on the vacuum line prior to use. Pure sodium metal (J. T. Baker) was purified by removal of all oxide surfaces under argon in the drybox and degassed under vacuum before use. Tellurium powder (99.95%) was obtained from Alfa Inorganics, degassed under vacuum prior to use, and stored in the drybox.

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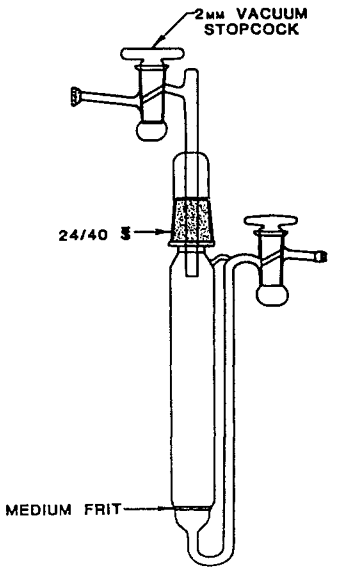

Figure 1. Fritted collection flask.

Preparation of Sodium Polytellurides. All sodium polytellurides were prepared by following the same basic procedure. Two reaction flasks of the type shown in Figure 1 were connected in series, and a third waste flask was connected to the second reaction flask to serve as a container for ammonia used in rinsing. The entire system was then rinsed with liquid ammonia. The reaction flask was then isolated and taken into the drybox, charged with stoichiometric amounts of sodium and tellurium (approximately 2 g total weight), and replaced on the vacuum line. After evacuation of the flask, 200–300 mL of ammonia was condensed into the reaction flask by immersing the flask in a dry ice–2-propanol bath. When the condensation of ammonia was completed, the bath was removed and the solution was allowed to boil. In order for the desired reaction to go to completion, the solution was allowed to boil to dryness over the period of several hours, the flask was evacuated again, and another 200–300 mL of liquid ammonia was condensed into the flask. This procedure was repeated until no unreacted tellurium was observed at the bottom of the reaction flask. The entire procedure usually involved three to five condensations over a period of 3–5 days. When the reaction was judged to be complete, the product was again dissolved in liquid ammonia and vacuum filtered into the second flask by opening the stopcock on the side arm of the reaction flask and simultaneously evacuating the second flask.

When the transfer was complete, the ammonia was allowed to boil off, leaving a solid material on the walls and frit of the second flask. The flask was then evacuated for several hours to assure complete removal of absorbed ammonia and taken into the drybox. The solid materials had a uniform, grayish color, similar to that described by Kraus and Chiu.[4] Ground samples exhibited a dull, gray appearance. These materials were stored in the drybox for subsequent analysis.

Elemental Analyses. Sodium polytelluride samples were weighed on the Cahn microbalance in the drybox, removed from the drybox, and taken into solution in a mixture of nitric acid, sulfuric acid, and water. The mixture was boiled until all particles had gone into solution and all oxides of nitrogen had been expelled. The samples were then assayed by the spectrophotometric method of Johnson and Kwan[15] using tellurium standards prepared in the identical manner. All spectrophotometric measurements were made on a Perkin-Elmer Model 320 UV–visible spectrophotometer. Results were as follows: Na_2Te_2 (exptl 84.93% Te, calcd 84.73% Te), Na_2Te_3 (exptl 89.20% Te, calcd 89.26% Te), and Na_2Te_4 (exptl 92.02% Te, calcd 91.74% Te). Na_2Te was obtained from Pfaltz and Bauer and analyzed by this same procedure. The results were 73.58% Te obtained experimentally, which may be compared to a calculated value of 73.51% Te. Therefore, the elemental composition of the species in solution is consistent with the proposed stoichiometries.

UV–Visible Spectroscopy. All spectra were obtained on a Perkin-Elmer Model 320 UV–visible spectrophotometer interfaced to a Perkin-Elmer Model 3600 data station. Spectral data were stored in the data station over a range of 220–700 nm at 1-nm intervals. The optical cell used was the quartz flow cell sealed into a Dewar assembly described by Sharp and Koehler.[14] The path length of the cell was 0.021 cm.

Solution concentrations were determined by condensing a measured volume of liquid ammonia into the optical Dewar and adding weighed amounts of the polytellurides into the ammonia in small buckets using the all-glass winch assembly also described by Sharp and Koehler.[14] All weighing and loading of the polytelluride materials were done in the drybox. This procedure gave concentrations accurate to within 0.5%.

Temperature measurements were monitored by using a thermistor with a Yellow Springs Model 42SL digital thermometer. Temperature was also monitored by observation of the vapor pressure of the ammonia above the solution. Temperature control by judicious addition of dry ice to a dry ice–2-propanol bath in the optical Dewar proved to be adequate for the periods of time necessary for obtaining spectra, and a temperature variation of less than 1 °C was observed during a spectral determination. Variations of peak intensities and locations with temperature were observed to be negligible.

Prior to addition of the polytellurides to the liquid ammonia, a baseline spectrum of liquid ammonia was recorded. Then a glass bucket of compound was lowered into the ammonia, and the solution was agitated by raising and lowering the bucket rapidly. Additional agitation was provided by pulling solution through the flow cell by utilizing varying pressure in a reaction flask connected in series with the optical cell. Spectra were monitored until a constant maximum absorbance was obtained.

Data Treatment. Overlapping spectral bands were resolved on an IBM Model 4341 computer by using the nonlinear, damped least-squares program described by Sharp[16] and modified by Dr. Ivan F. Taylor of the Texas Christian University Computer Center for this investigation.

Results and Discussion

Liquid Ammonia Spectrum. The spectrum of liquid ammonia has an intense band around 220 nm.[16] An overlap of this ammonia band with the charge-transfer band of the iodide ion has been reported by Burrow and Lagowski.[17] This overlap was observed to increase with increasing concentration of iodide ion, suggesting a perturbation of the ammonia band to lower energy with increasing solute concentration. Similar effects have been reported for the amide ion[18] and for the polyselenides.[14]

Because of this overlap of the ammonia wing with the polytellurides, the curve-fitting procedure incorporated parameters describing the ammonia band. The location of this band was observed to shift to longer wavelengths with increasing polytelluride concentration in the same manner as that reported for the polyselenides.

NaTe and Na_2Te Spectra. When mixtures of elemental sodium and tellurium were placed in liquid ammonia, the initial color observed was the intense blue generally attributed to the presence of the solvated electron. As the tellurium began to react, a yellowish color formed in the solution and the solution took on a greenish hue. This greenish color rapidly progressed to a mustard yellow as the solution was allowed to boil, and a white solid began to precipitate. The yellow phase persisted for only a few seconds and was often observed only as a flash, which was followed by a greenish solution, which in turn progressed rapidly to a dark blue solution. This sequence of color changes has been reported previously[4,5] and has been attributed to the formation of Na_2Te (white precipitate, yellow solution). The duration of the yellow solution was much longer when pieces of solid tellurium were used instead of powdered tellurium. The yellow persisted while white Na_2Te began to precipitate from solution, coating the remaining tellurium pieces and greatly slowing the reaction. This was probably the reason that the yellow solution color was attributed to Na_2Te. However, when commercial Na_2Te was placed in liquid ammonia and the ammonia was allowed to boil, no color was observed. In fact, the material appeared virtually insoluble.

To further investigate the relationship between the appearance of the yellow color and Na_2Te, a weighed amount of Na_2Te was placed in a glass bucket and lowered into liquid ammonia in the optical Dewar. Although the bucket was constantly agitated and the ammonia was even allowed to boil, no significant spectral features were noted over a period of several hours in the spectral range 700–220 nm. Some of the solute was dislodged from the bucket, producing spectral noise due to the presence of particulate matter in the optical cell.

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Table I. Band Parameters for Na_2Te_2

$10^3 \times$ concn, M	position, nm	abs	w, nm
0.49	291.6	0.049	30.0
	330.1	0.052	27.9
	351.6	0.017	114.8
	571.5	0.020	119.8
2.04	288.9	0.286	33.9
	327.1	0.162	34.6
	350.8	0.070	88.8
	562.5	0.059	104.6
3.43	288.8	0.305	34.2
	328.7	0.194	34.8
	352.2	0.117	134.8
	551.7	0.080	107.2
5.36	292.4	0.601	39.1
	331.2	0.307	34.2
	351.4	0.193	101.9
	562.0	0.145	92.0

The failure to detect any spectral features attributed to the telluride ion in liquid ammonia solution is in marked contrast to the behavior of Na_2S and Na_2Se in liquid ammonia. Na_2S has an absorption peak at 270.0 nm,[19] and Na_2Se has a peak at 290.0 nm that exhibits the energy–temperature dependence typical of charge-transfer–solvent transitions.[14] However, the observations are consistent with those of Bamberger et al.,[20] who observed that the Te^{2-} species either did not absorb in the 200–2000-nm range or was too insoluble to detect in molten $LiF-BeF_2$.

In an attempt to follow spectrophotometrically the synthesis of Na_2Te, stoichiometric amounts of sodium and tellurium were placed in glass buckets and lowered into liquid ammonia in the optical Dewar. The reaction was followed for several hours; however, the spectrum became too noisy to interpret after approximately 2 h due to the precipitation of Na_2Te. Again, no significant spectral features were noted in the 250–350-nm range. However, as the blue color of the solvated electron phased into a greenish color, a broad absorption peak was observed at approximately 428 nm, which was attributed to the formation of the yellow solution phase.

In an attempt to determine the stoichiometry of the "yellow phase", a solution resulting from a 2:1 mol ratio mixture of sodium and tellurium was filtered on the vacuum line as it passed through the yellowish color change. However, due to the short lifetime of this phase, the resultant filtrate was greenish and did not yield enough residue for elemental analysis. An elemental analysis of the material remaining in the reaction flask showed a tellurium percentage of 72.02, which may be compared to 73.51% Te for Na_2Te. Since this was a decrease from the starting percentage of tellurium, the "yellow phase" must contain a higher ratio of tellurium to sodium than does Na_2Te. The species NaTe has the same stoichiometry as Na_2Te_2 (84.73% Te) and would account for this observation. Therefore, the yellow color may indicate the presence of the transitory Te^- ion.

The Te^- ion has been proposed by Manning[21] from polarization experiments at a tellurium electrode. Te^- is also identified as the dominant ion present in molten LiCl–KCl by Toth and Hitch.[22] In the molten salt the Te^- ion is characterized by an intense band at 478–497 nm.

Na_2Te_2 Spectrum. Combination of a 1:1 molar ratio of sodium and tellurium in liquid ammonia resulted in a solution of an intense violet-blue color. This is in agreement with the observations of Zintl and co-workers.[5] Spectra of the product material were obtained at four concentrations, and the computer-resolved spectral parameters are given in Table I. A resolved sample spectrum is shown in Figure 2, and Beer's law plots for the four resolved peaks are shown in Figure 3. The marked deviation from linearity of the Beer's law plot at 290.4 nm is due to the difficulty in resolving the shortest wavelength absorption peak from the overlap of the much more intense liquid ammonia band. Na_2Te_2 is concluded to be a spectroscopically distinct species in liquid ammonia solution.

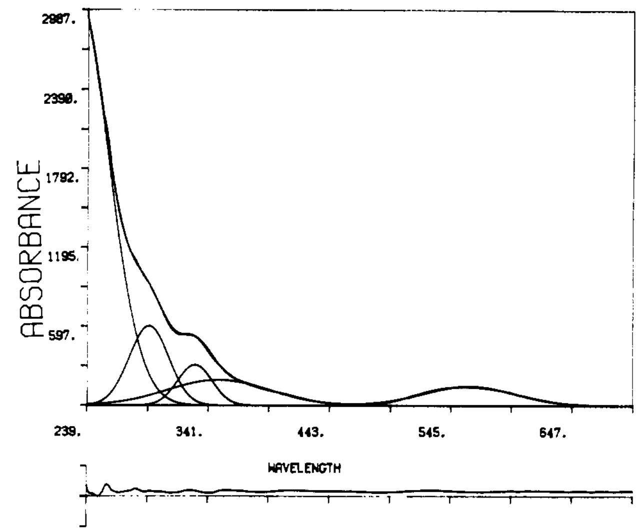

Figure 2. Computer-resolved UV–vis sample spectrum for 5.36×10^{-3} M Na_2Te_2.

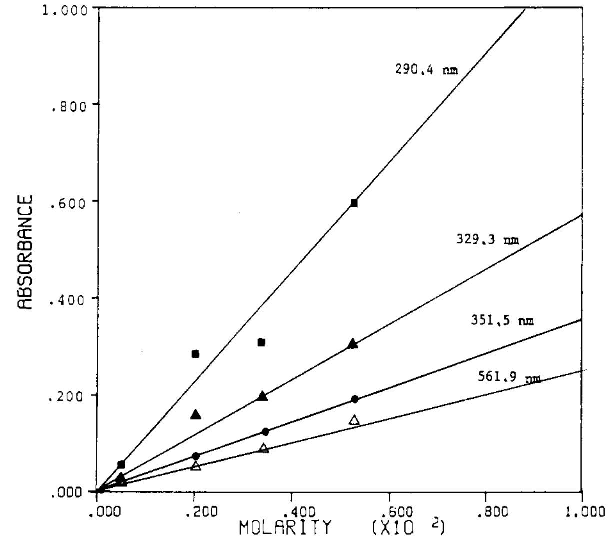

Figure 3. Concentration vs. absorbance for Na_2Te_2.

The homologous polyselenide Na_2Se_2 was observed by Sharp and Koehler[14] to exist in liquid ammonia solution only in an equilibrium with Na_2Se and Na_2Se_3. This was evidenced by the continual presence of Na_2Se precipitate in solutions of Na_2Se_2 and was confirmed by spectral analysis. Na_2Se_2 absorption peaks were determined by spectral subtraction to occur at 256.0, 320.0, 475.0, and 560.0 nm. However, no evidence of this equilibrium behavior was observed for Na_2Te_2.

The liquid ammonia spectrum of Na_2S_2 is reported to consist of bands at 256.0 and 282.0 nm.[19] The low-energy band located between 500 and 600 nm in the diselenide and ditelluride spectra is not observed in the disulfide spectrum. Sharp and Koehler[14] noted that this band occurs in the spectra of all of the polyselenides and none of the polysulfides and attributed it to transitions arising from the polyselenide ions.

Na_2Te_3 Spectrum. Combinations of sodium and tellurium in a 2:3 molar ratio in liquid ammonia resulted in the formation of a solution of an intense wine-red color. This is consistent with the report of Zintl et al.[5] Spectra of the solution product were obtained at three different concentrations, and the computer-resolved spectral parameters are given in Table II. A resolved

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Table II. Band Parameters for Na_2Te_3

10^3 × concn, M	position, nm	abs	*w*, nm
1.06	273.7	0.268	34.6
	305.9	0.053	20.5
	337.5	0.038	60.9
	374.6	0.096	110.0
	513.6	0.083	77.9
3.07	273.6	0.437	34.3
	305.5	0.083	20.6
	341.9	0.060	60.7
	373.3	0.150	115.2
	513.4	0.135	74.9
6.10	272.5	0.886	34.6
	303.9	0.139	19.4
	331.2	0.083	64.8
	377.5	0.272	109.3
	513.5	0.261	75.1

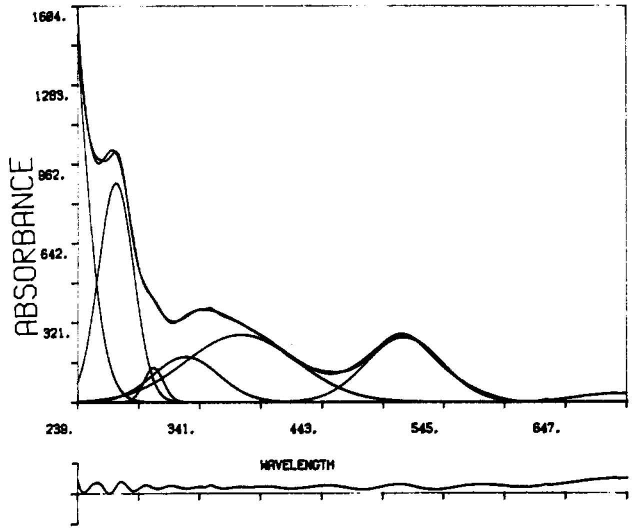

Figure 4. Computer-resolved UV–vis sample spectrum for 6.10×10^{-3} M Na_2Te_3.

sample spectrum is shown in Figure 4, and Beer's law plots of the resolved data are shown in Figure 5 for the five peak locations. As in the Beer's law plots of Na_2Te_2, deviation from linearity is observed for the peak at 273.3 nm, which is severely overlapped by the liquid ammonia band. Na_2Te_3 is concluded to be a spectroscopically distinctive species in liquid ammonia solution.

A comparison between Na_2Se_3 and Na_2Te_3 reveals that Na_2Se_3 is also a spectroscopically distinct species in liquid ammonia solution.[14] The bands observed for Na_2Se_3 occur at 278.0, 317.0, 386.0, and 592.5 nm. The spectra of Na_2Se_3 and Na_2Te_3 are quite similar in appearance, but the absorption peaks are shifted to higher energy for the telluride species. A common spectral feature is the presence of the previously noted low-energy band, which is absent in the polysulfide spectra. This peak is attributed to a transition arising from the tritelluride ion.

Although no crystal structure has been reported for sodium tritelluride, the structures of several tritelluride species have been reported. These include $(C_{18}H_{36}N_2O_6K)_2Te_3$,[23] K_3Te_3,[24] and Rb_2Te_3 and C_5Te_3.[25]

Na_2Te_4 Spectrum. The species Na_2Te_4 has been postulated to be the highest sodium polytelluride to exist in liquid ammonia solution.[4,6] Reaction of sodium and tellurium in a 1:2 molar ratio resulted in the formation of a deep blood red solution in liquid ammonia. However, great difficulty was experienced in forcing the reaction to go to completion. Spectra of the product material were obtained at three different concentrations, and computer-resolved spectral parameters are given in Table III. These spectra were essentially identical with those of Na_2Te_3, but Beer's law was not well followed for this material, which would indicate that the theoretical solution compositions were incorrect. Furthermore, undissolved material was observed to remain in the glass buckets in the optical Dewar. This would be consistent with the presence of elemental tellurium, which is insoluble in liquid ammonia under these conditions. Therefore, Na_2Te_4 is concluded to be a species that does not exist in liquid ammonia solution, and the solid material obtained was a 1:1 molar mixture of Na_2Te_3 and excess finely divided tellurium that passed the filtration steps.

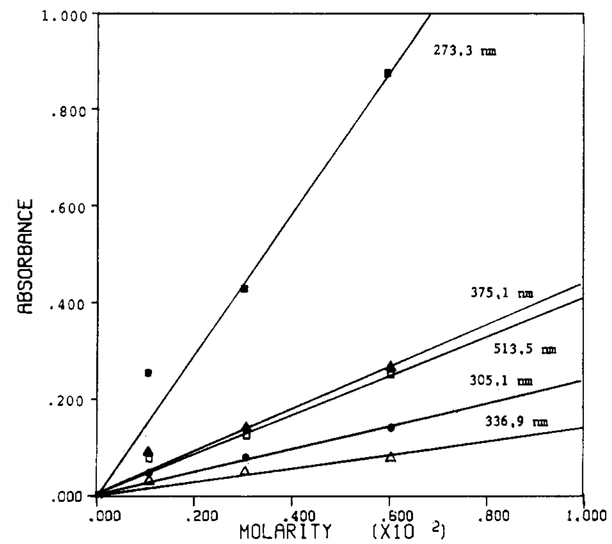

Figure 5. Concentration vs. absorbance for Na_2Te_3.

Table III. Band Parameters for Na_2Te_4

10^3 × concn, M	position, nm	abs	*w*, nm
0.99	272.3	0.285	33.47
	303.9	0.056	21.49
	336.7	0.038	51.74
	369.6	0.090	115.50
	512.5	0.083	72.89
2.58	274.8	0.544	28.61
	302.4	0.124	19.32
	336.4	0.176	98.30
	375.0	0.197	140.34
	515.2	0.228	74.50
5.31	272.4	1.262	32.58
	302.7	0.259	21.68
	332.3	0.276	65.99
	379.2	0.387	108.74
	512.9	0.374	74.99

In contrast, Na_2S_4 and Na_2Se_4 are spectroscopically identifiable species in liquid ammonia with peaks observed at 323.0 and 400.0 nm[19] and at 256.0, 304.0, 344.0, 416.0, and 515.5 nm,[14] respectively.

Higher Polytellurides. Higher polytellurides have been obtained under conditions different from those employed in this laboratory. These include the tetratelluride as $(Ph_4P)_2Te_4{\cdot}2CH_3OH$[26] and the pentatelluride as $(Bu_4N)_3Te_5$.[27] However, although attempts were made to react sodium and tellurium in mol ratios as great as 2:6, much unreacted tellurium remained; solution colors did not change from the red color of Na_2Te_3, and elemental analyses did not indicate the presence of any higher polytellurides.

Conclusion

Isolation, analysis, and spectroscopic investigation indicate that Na_2Te_2 and Na_2Te_3 are stable in liquid ammonia solution. An intermediate species, which may be NaTe, is formed during the

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reaction of elemental sodium and tellurium, and its presence is responsible for the yellow solution that precedes the precipitation of Na_2Te. Na_2Te is either insoluble in liquid ammonia or does not absorb in the spectral region 220–700 nm. No polytelluride higher than Na_2Te_3 is formed under the conditions of this investigation.

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Oxidation of 2-Propanol over Cobalt–Y Zeolites

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Cobalt–dinitrosyl complexes in zeolite Y may be oxidized with O_2, albeit rather slowly, to the corresponding nitro and nitrito complexes. In the absence of weakly adsorbed NO, the rate of oxidation is strongly inhibited by the presence of other ligands such as acetone. As an alternative, the nitro and nitrito complexes may be formed directly by reacting the Co–Y zeolite with NO_2. Both the nitro and nitrito complexes react with 2-propanol to form acetone and the dinitrosyl complexes. In a flow reactor at 70 °C this reaction occurs with high selectivity to acetone, but the turnover number is ca. 2.5, which suggests that the reaction is stoichiometric rather than catalytic. Thus, the potential utilization of cobalt–dinitrosyl complexes in zeolites for the catalytic activation of O_2 is limited by the rate at which the dinitrosyl complexes can be oxidized.

Introduction

The utilization of transition-metal complexes to activate molecular oxygen for the catalytic oxidation of organic substrates via a nonradical mechanism has been the subject of intense investigation over the past two decades. Tovrog, Diamond, Mares, and co-workers,[1–6] as well as Andrews and co-workers,[7–9] have found that certain metal–nitro complexes are effective as intermediates in a variety of oxidation reactions, including oxygen atom transfer to alkenes. Solar et al.[10] have recently reviewed the literature in this field. Catalytic cycles generally involve the oxidation of a bent mononitrosyl ligand to a nitrogen-bound nitro complex, which is capable of oxidizing the organic substrate, and in the process the nitrosyl ligand is re-formed. The oxygen-bound nitro and nitrito ligands were not nearly so effective in the systems that have been studied. (Here we adopt the convention of referring to the oxygen-bound bidentate complex as a chelating nitro complex.[11])

Previous work in our laboratory has demonstrated that cobalt–dinitrosyl complexes may be formed in zeolite Y, and these complexes are intermediates in the catalytic reduction of nitric oxide by ammonia.[12–14] The cobalt(II) apparently was coordinated to two or three oxygen atoms of the zeolite framework, in addition to the nitrosyl ligands. The nitrosyl ligands were oxidized with O_2 at 25 °C, albeit the reaction was rather slow with a half-life on the order of several hours. Following oxidation, a new infrared band at 1520 cm^{-1} suggested that a nitrito complex was formed.[12]

Table I. N–O Stretching Bands of Cobalt–Dinitrosyl Complexes in Zeolite Y

complex[a]	ν_s, cm^{-1}	ν_a, cm^{-1}	R_s/R_a[b]	ϕ, deg[c]
$[Co(NO)_2]^{2+}$	1902	1818	0.48	111
$[(H_2O)Co(NO)_2]^{2+}$	1895	1814	0.23	129
$[(mixed)Co(NO)_2]^{2+}$	1886	1798	0.25	127
$[(C_3H_6O)Co(NO)_2]^{2+}$	1894	1803	0.34	120
$[(C_3H_6O)_nCo(NO)_2]^{2+}$	1890	1795	0.31	122
$[(2\text{-}PrOD)Co(NO)_2]^{2+}$	1895	1797	0.40	115
$[(2\text{-}PrOD)_nCo(NO)_2]^{2+}$	1891	1796	0.31	122
$[(NH_3)Co(NO)_2]^{2+}$	1878	1798	0.57	106
$[(NH_3)_nCo(NO)_2]^{2+}$	1872	1789	0.31	122

[a] The exact number of ligands, other than NO, is unknown. It is assumed that after extensive evacuation one ligand remains and after brief evacuation *n* ligands remain. [b] Intensity ratio of symmetric asymmetric bands. [c] ON–Co–NO bond angle.

The present study was carried out to determine whether these cobalt–dinitrosyl complexes in zeolite Y could be used as a starting point for the catalytic oxidation of 2-propanol to acetone, in a manner analogous to the use of cobalt–mononitrosyl complexes as homogeneous oxidation catalysts. It will turn out (see below) that the similarities between the two systems are not extensive, and in the zeolite a catalytic cycle is impeded by the slow reoxidation of a modified dinitrosyl complex. Moreover, the organic substrate appears to be oxidized in the zeolite by nitrito ligands, as well as by nitrogen-bound nitro ligands.

Experimental Section

The Co–Y zeolites were obtained by aqueous-ion exchange of a Na–Y zeolite supplied by Linde Co. (Lot No. Y-52 3365-94). Most of the results were obtained on a Co–Y zeolite that contained 14 Co(II) ions per unit cell; however, another sample that contained 2.8 ions per unit cell was also used to determine turnover numbers (TON). The zeolites were dehydrated by heating slowly to 400 °C, either under vacuum for spectroscopic studies or in flowing He for catalytic studies.

The CP grade NO obtained from Matheson contained NO_2, which was formed by the disproportionation of NO. The NO_2 was removed for spectroscopic studies by repeated distillation from a vessel at 138 K (cooled by pentane slush) to one at 77 K. For catalytic studies the NO

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