be taken to be minimum values, however, since it is not certain that phase mixing was adequate for the more rapid nitrogen-exchange process; the rates observed for nitrogen could be less than true exchange rate values, which would make the nitrogen to oxygen exchange rate ratios greater than observed by this method.)

The exchange of oxygen between H_2O and NO_2^- has been investigated previously.[13,14] It seems plausible that the H_2O–NO exchange may be a similar process with respect to the transfer of oxygen between H_2O and NO_2^-, but since there is no direct interaction between NO and H_2O, the ultimate transfer of aqueous-phase oxygen to NO must occur through interaction with a dissolved, nitrogen-containing species. Given the observed first-order dependence of the over-all process upon NO, the latter could be considered a catalyst to the H_2O–NO_2^- exchange if its mechanism is otherwise unchanged by the presence of NO, a point that awaits further investigation.

The interesting fact that NO–NO_2^- nitrogen exchange is more rapid than NO–H_2O oxygen exchange in a single system suggests that there may be a direct attack of NO on NO_2^-. If so, diatomic NO units would undergo continuous exchange with nitrite ions, and the rate of appearance of ^{18}O in the gas phase would be limited by the rate of its exchange in the solution between H_2O and NO_2^-. To test this idea, an experiment was carried out in which NO_2^- was labeled with ^{18}O before NO was admitted. This was accomplished by addition of a measured quantity of HCl to an outgassed solution of NO_2^- in $H_2{}^{18}O$ and allowing H_2O–NO_2^- exchange to take place in the resultant HNO_2 solution during a period of 17 hr. NO was then admitted to the solution containing $N^{18}OO^-$ and HNO_2, and kinetic data were obtained in the usual way, with the result shown in Figure 4. As seen, the nitrogen-exchange curve is normal, although there is an intercept, probably caused by release of NO by disproportionation of HNO_2 during the long preexchange period. The oxygen-exchange plot, however, is characterized by continuous curvature. Curvature in an exchange plot could be caused by a change in chemical composition, but since no curvature was observed in similar experiments conducted without prelabeling, it is not thought to have occurred here. Rather, the result is readily interpreted in terms of an NO–NO_2^- interaction in which the rate of appearance of ^{18}O in the gase phase is limited by the rate of oxygen exchange between H_2O and NO_2^- which is in turn considerably slower than the NO–NO_2^- exchange. Thus at the outset of the exchange with prelabeled $N^{18}OO^-$ the apparent O-exchange rate is rapid, but falls off as NO_2^- becomes increasingly depleted in ^{18}O at a rate greater than that at which it can be restored by H_2O–NO_2^- exchange. This accounts for the appearance of continuous curvature in the O-exchange plot and is in accordance with the hypothesis of a direct attack of NO on NO_2^-.

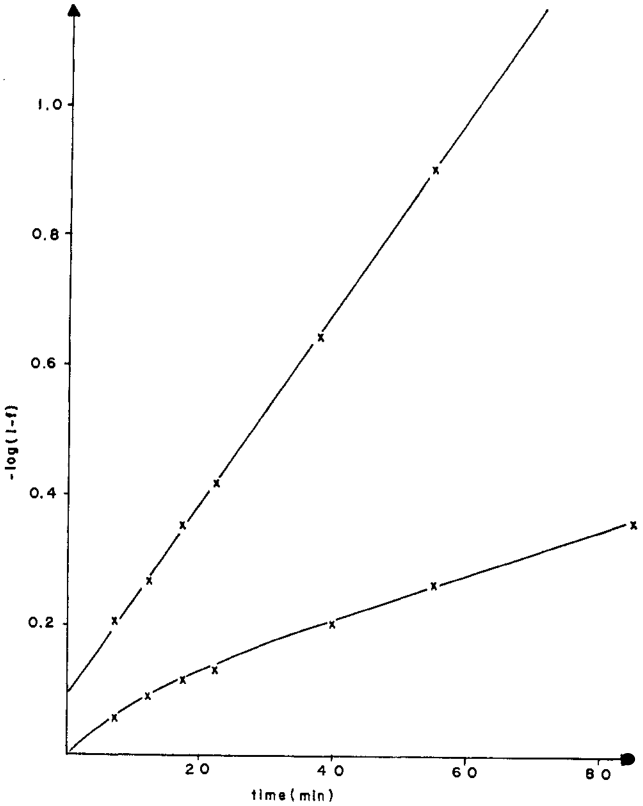


Figure 4. N exchange (upper curve) and O exchange (lower curve) in solution containing $N^{18}OO^-$. Conditions: $[HNO_2] = 0.00147$, $[NO_2^-] = 0.0226$, 25°.

It is certain, on the basis of results reported here, that N and O exchanges proceed *via* distinct mechanisms in this interesting system. Further investigation is in progress, in an effort to eludicate differences between the two exchange mechanisms in detail.

Acknowledgments.—The author is grateful to Dr. E. Roth and the Commissariat a l'Energie Atomique for their kind hospitality and support, to Dr. E. Saito for the hospitality of his laboratory and for assistance in experimental design, to G. Ducheylard for mass spectrometry, and to the above and to Dr. I. Dostrovsky for helpful discussions.

---

[13] M. Anbar and H. Taube, *J. Am. Chem. Soc.*, **76**, 6234 (1954).

[14] C. A. Bunton, D. R. Llewellyn, and G. Stedman, *J. Chem. Soc.*, 568 (1959).

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
UNIVERSITY OF MISSOURI—KANSAS CITY,
KANSAS CITY, MISSOURI 64110

Tellurium Tetrakis(tetramethylenedithiocarbamate)

BY JAMES WU, PETER F. LOTT, AND HENRY A. DROLL

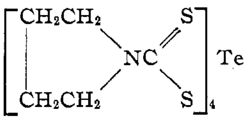
Received July 7, 1969

In the course of a study of the determination of tellurium by means of atomic absorption spectroscopy[1] we observed that a yellow microcrystalline substance was precipitated from mixtures of aqueous solutions of

---

[1] J. Wu, H. A. Droll, and P. F. Lott, *At. Absorption Newsletter*, **7**, 90 (1968).

tellurium in dilute sulfuric acid and ammonium tetramethylenedithiocarbamate (1-pyrrolidinecarbodithioic acid, ammonium salt, also called ammonium pyrrolidinedithiocarbamate and hereafter referred to as APDC). Analytical and spectroscopic data subsequently obtained suggest that the yellow substance is tellurium tetrakis(tetramethylenedithiocarbamate)



We wish to report the results of the analytical and spectroscopic investigation.

Experimental Section

Preparation of Tellurium Tetrakis(tetramethylenedithiocarbamate).—Potassium tellurite, purified (Fisher), was used without further purification. APDC (Camag, Inc., Milwaukee, Wis.) was recrystallized from ethanol. The addition of 0.02 *M* aqueous K_2TeO_3 solution to an excess of 0.1 *M* aqueous APDC gave a yellow precipitate which was collected on a porcelain filter, washed several times with ethanol, and dried at 70–75°. The yield was 99% based on the original amount of tellurium. The dried product on heating changed to an orange color near 130° before it melted at 136° (uncor).

Anal. Calcd for $C_{20}H_{32}N_4S_8Te$: C, 33.71; H, 4.53; N, 7.86; S, 35.99. Found: C, 33.26; H, 4.61; N, 7.58; S, 35.00. Analysis was performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Determination of Composition.—The absorption spectrum (Figure 1) of an acetone solution containing APDC and an excess of K_2TeO_3 was recorded with a Bausch and Lomb Model 505 spectrophotometer. A continuous variations study[2] was made of acetone solutions of K_2TeO_3 and APDC at two different wavelengths in the flat portion of the absorption spectrum. The results are shown in Figure 2. It was found that acetone solutions of the reactants began to fade on standing after about 15–20 min. Consequently, absorbance measurements were made on freshly prepared solutions in the series.

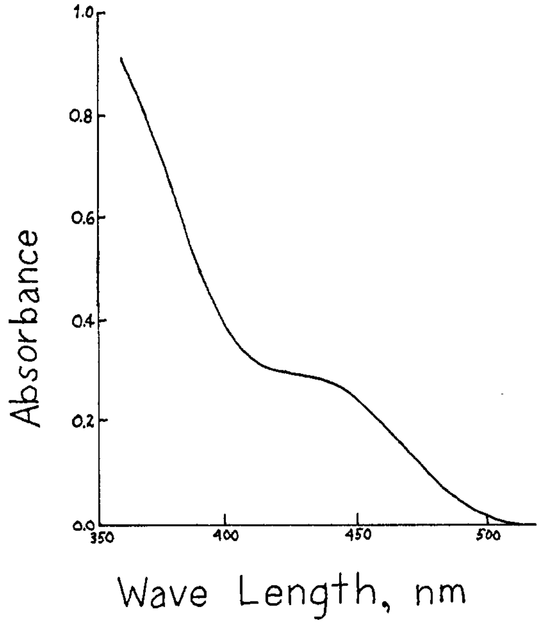


Figure 1.—Absorption spectrum of an acetone solution 3.14 × 10^{-3} *M* in ammonium tetramethylenedithiocarbamate (APDC) and 4.70 × 10^{-3} *M* in K_2TeO_3. Separate solutions of reactants are transparent.

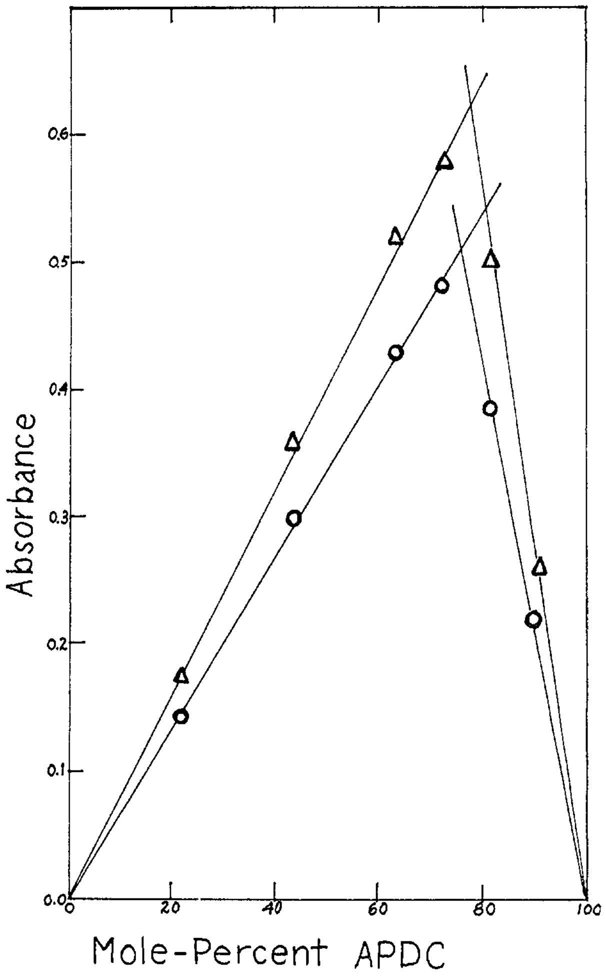


Figure 2.—Job plot for the interaction of ammonium tetramethylenedithiocarbamate (APDC) with K_2TeO_3 in acetone solutions. Wavelengths are 425 nm (Δ) and 445 nm (O). Total concentrations of reagents are equal to 6.96 × 10^{-3} *M*.

Infrared Spectra.—The infrared spectra were recorded with a Perkin-Elmer Model 621 spectrometer. The spectra of solid APDC and solid tellurium tetrakis(tetramethylenedithiocarbamate) were taken as KBr pellets.

Results and Discussion

The Job continuous-variations study of mixtures of acetone solutions of APDC and K_2TeO_3 (Figure 2) suggests a 4:1 mole ratio of reactants consistent with the equation $4(CH_2)_4NCS_2NH_4 + K_2TeO_3 \rightarrow ((CH_2)_4NCS_2)_4Te + 4NH_3 + 2KOH + H_2O$. This assumption is consistent with the elemental analysis of the yellow product.

In the infrared spectrum of the ammonium and tellurium tetramethylenedithiocarbamates, the characteristic bands are those that are attributable to the CN and the CS vibrations. For APDC we observed strong energy absorption in a broad band at 1350–1490 cm^{-1} with a shoulder at 1465 cm^{-1} (CN vibration) and a doublet at 992 and 980 cm^{-1} (CS vibration). The ammonium ion absorbs strongly at 1400 cm^{-1}, partly obscuring the CN absorption. Other investigators

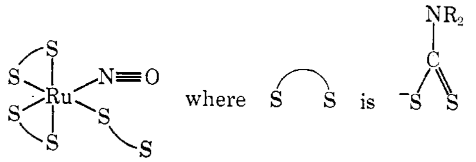
---

[2] P. Job, *Compt. Rend.* **180**, 928 (1925).

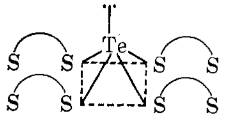
have observed CN and CS bands in the respective ranges of 1465–1490 and 960–985 cm^{-1} for sodium dialkyldithiocarbamates (*viz.*, dimethyl,[3,4] diethyl,[4] dipropyl,[4] and dibutyl[4]). Mann[5] observed a CN doublet at 1420 and 1482 cm^{-1} for sodium pentamethylenedithiocarbamate.

The CN vibration in tellurium tetrakis(tetramethylenedithiocarbamate) occurs as a strong band at 1440 cm^{-1} and as a broad band in the range 1452–1510 cm^{-1} with a peak at 1468 cm^{-1} followed by a succession of shoulders at 1475 and 1490 cm^{-1}. Moore and Rice[6] reported a very strong doublet at 1504 and 1515 cm^{-1} for dioxomolybdenum(VI) bis(tetramethylenedithiocarbamate).

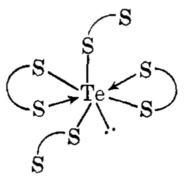
Domenicano, *et al.*,[7] observed for $Ru(NO)(S_2CNR_2)_3$, where R = CH_3 or C_2H_5, the CN vibration in the 1460–1470-cm^{-1} region, which is near the literature values for the sodium salts of dialkyldithiocarbamic acids (*vide supra*). However, the literature values[3-6] for the CN band for transition metal dialkyldithiocarbamates are in the 1490–1550-cm^{-1} region. They[7] concluded on the basis of the ir study and a priorly obtained X-ray result that one of the dialkyldithiocarbamates is unidentate and the other two are bidentate, *i.e.*



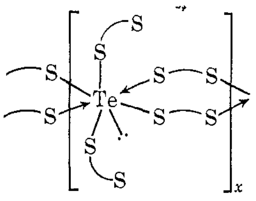
Our observation of relatively low-energy CN bands, *viz.*, 1468, 1475 (sh), and 1490 (sh) cm^{-1}, for tellurium tetrakis(tetramethylenedithiocarbamate) similarly suggests unidentate ligands. Plausible structures may be a square pyramid (A), a distorted octahedron (B), or a polymeric distorted octahedron (C). Molecular weight determinations would be helpful were it not for the rather low solubility of the complex in the usual solvents. It is interesting that Chatt, *et al.*,[3] also observed low-energy CN vibrations for $((C_2H_5)_2NCS_2)_3M$ at 1490 (M = P), 1492 (M = As), and 1488 (M = Bi) cm^{-1}. These compounds were considered by them to possess possibly a distorted octahedral or a pyramidal stereochemistry. It is conceivable to us that such structures would contain a stereochemically active lone-electron pair on the phosphorus, arsenic, and bismuth atoms and unidentate ligands for the pyramidal stereochemistry and the appropriate combination of bridging and unidentate ligands for the distorted octahedral stereochemistry.



A



B



C

The CS vibration in tellurium tetrakis(tetramethylenedithiocarbamate) appears as a weak band at 1000 cm^{-1}. This is an increase of 8 and 20 cm^{-1} from the respective 992 and 980 cm^{-1} doublet which appears in the spectrum of APDC. Similar increases have been observed by Moore and Larson[4] for dialkyldithiocarbamates of Mo(VI), Mo(V), and Mo(II).

---

(3) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Suomen Kemistilehti*, **B29**, 75 (1956).

(4) F. W. Moore and M. L. Larson, *Inorg. Chem.*, **6**, 998 (1967).

(5) J. Mann, *Trans. Inst. Rubber Ind.*, **27**, 232 (1951).

(6) F. W. Moore and R. E. Rice, *Inorg. Chem*, **7**, 2510 (1968).

(7) A. Domenicano, A. Vaciago, L. Zambonelli, P. L. Loader, and L. M. Venanzi, *Chem. Comm.*, 476 (1966).

Correspondence

The Linear Correlation of ΔH and ΔS of Complexation

Sir:

For a number of years there have been some very strong implications made[1,2] that a linear correlation of ΔH and ΔS for a series of analogous metal complexes is corroborative evidence for a common structure throughout the series. We wish to point out the incorrect reasoning of this interpretation, although the correct logic should have been obvious at a much earlier time, in order to prevent any later misguidance in the interpretation of these approximately linear relationships. It is not possible to interpret the free energy changes in metal complex equilibria as being diagnostic of the type of ion association without at the same time considering the accompanying enthalpy ΔH and entropy ΔS of complexation. In dismissing this idea we shall show that the linear correlation is no more informative than the free energy[3] in this regard.

From the Gibbs free energy (GFE) equation, a linear correlation of ΔH and ΔS for a series of n related reactions (for example the lanthanide ions with a common ligand) is an obvious result if the ΔG values for the reactions are zero or constant and the slope of the line is, by definition, $T°K/1000$, *i.e.*, $\Delta H_n = \Delta G_n + 0.298\Delta S_n$, for a temperature of 25°. In the real situation however there very often is variation in ΔG_n within the series. For the series of n related reactions, therefore,

---

(1) J. F. Duncan and D. L. Kepert in "The Structure of Electrolytic Solutions," W. J. Hamer, Ed., John Wiley & Sons, Inc., New York, N. Y., 1959, pp 380–400.

(2) R. E. Mesmer and C. F. Baes, Jr., *J. Phys. Chem.*, **72**, 4721 (1968).

(3) G. H. Nancollas, "Interactions in Electrolyte Solutions," Elsevier Publishing Co., New York, N. Y., 1966, p 94 ff.