[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

Molecular Addition Compounds of Dinitrogen Tetroxide with Several Aliphatic and Alicyclic Ethers[1]

BY BERNARD RUBIN,[2] HARRY H. SISLER AND HAROLD SHECHTER

The results of thermal, magnetic and spectroscopic studies on the systems N_2O_4–$(C_2H_5)_2O$, N_2O_4–C_4H_8O, N_2O_4–$C_5H_{10}O$, N_2O_4–$O(CH_2CH_2)_2O$ and N_2O_4–$(ClCH_2CH_2)_2O$ have served to prove the existence of the compounds $N_2O_4 \cdot 2(C_2H_5)_2O$ (m.p. −74.8°), $N_2O_4 \cdot 2C_5H_{10}O$ (m.p. −56.8°), $N_2O_4 \cdot C_4H_8O$ (m.p. −20.5°), $N_2O_4 \cdot 2C_4H_8O$ (?) (incongruent melting) and $N_2O_4 \cdot O(CH_2CH_2)_2O$ (m.p. 45.2°) and the presence of N_2O_4 units and absence of NO_2, NO_2^+, NO_2^-, NO^+ and NO_3^- in appreciable amounts in their structures. These results are discussed in terms of possible structures of these complexes and as to their implications toward the reactions of dinitrogen tetroxide with olefins in basic and non-basic solvents.

During recent years, interest in dinitrogen tetroxide has increased because of (a) its ready availability, (b) its properties as a solvent for carrying out various chemical reactions,[3] (c) its use as a reagent for preparing various organic oxy-nitrogen compounds[4] and (d) questions concerning its molecular structure.[5] It has been found[4b,4c] that in many of the reactions of dinitrogen tetroxide with olefins, the type of products formed depends upon the nature of the solvent in which the reaction is conducted. In certain solvents of the ether–ester type; *e.g.*, ethyl ether, dioxane, ethyl acetate, etc., the oxidizing action of dinitrogen tetroxide on olefins is moderated and excellent yields of *vicinal* dinitroalkanes, nitronitrites and nitronitrates are obtained.[4c] In reactions of dinitrogen tetroxide in dioxane, a solid addition compound having the formula $C_4H_8O_2 \cdot N_2O_4$ is formed; it has therefore been suggested that the specific reactions of dinitrogen tetroxide with olefins may result from the formation of addition compounds between dinitrogen tetroxide and the basic solvents. Because of the interest in this Laboratory in molecular addition compounds of various Lewis acid–base systems as well as in the structure and properties of nitrogen compounds, binary systems of dinitrogen tetroxide and various ethers were investigated in the liquid and solid states. The methods used for these studies involved thermal, magnetic and spectroscopic analysis.

I. Thermal Analysis

Materials.—Dioxane was purified by the method of Fieser[6] and was fractionally distilled; b.p. 101.5° (743.6 mm.); f.p. 10.5°. Diethyl ether (Merck and Co., Inc., absolute) was dried over sodium for 24 hours and fractionally distilled; b.p. 34.4° (745.6 mm.); f.p. α-form, −116.0°; f.p. β-form, −123.3°. Tetrahydrofuran (E. I. du Pont de Nemours Co.) was dried over sodium hydroxide pellets for 2 days and then fractionally distilled under nitrogen, b.p. 66.0–66.5° (746.8 mm.); f.p. −108.5°. Tetrahydropyran (E. I. du Pont de Nemours Co.), b.p. 86.5–87.0° (746.8 mm.), f.p. −44.2°, and β,β'-dichlorodiethyl ether, b.p. 176.5–177.0° (743 mm.) and f.p. −50°, was purified similarly to tetrahydrofuran. Final rectification of the purified ethers was effected under nitrogen at a reflux ratio of 20 to 30:1 in a 5-foot column packed with glass helices. The ethers were stored under nitrogen and over sodium and iron wire in dark bottles. Periodic checks were made to ensure the absence of peroxides in the ethers. All the physical constants recorded above agree closely with accepted values from the literature except the freezing point of tetrahydropyran which is 5° higher than that reported previously.[7,8,9] It is believed that this probably represents a previously unknown higher melting form of the ether; the other physical constants and properties of the substance attest to its identity.

Dinitrogen tetroxide (Matheson Co.) was purified by a method similar to that of Giauque and Kemp[10] in an all-glass apparatus. The dinitrogen tetroxide was obtained as a white, crystalline solid which melts to an orange-red liquid at −11.5°, lit. −11.5°.[10]

Procedure.—The freezing points of the various mixtures of ethers and N_2O_4 were determined in an all-glass cell equipped with two ground-glass inlets (14/35 S.T.). Known amounts of ethers were admitted, with minimum exposure to the air, through a Lunge pipet ground to fit one of the cell inlets; the remaining inlet was attached to a drying tube filled with phosphoric anhydride and sand.

To introduce known weights of N_2O_4 to samples of ethers, a cylindrical glass transfer cell equipped with ground glass joints and a stopcock was used. Purified N_2O_4 was stored in the transfer cell until it was ready for use. The transfer cell was connected to the freezing point cell by a glass bridge (7-mm. tubing) equipped with ground-glass ends and a stopcock at the center. The length of the bridge was minimized so that only small volumes of air would be admitted with the N_2O_4.

To effect transfer of a given weight of N_2O_4, the transfer cell was weighed at room temperature and then connected to the transfer bridge. After the freezing point cell had been cooled with a Dry Ice–acetone mixture, the stopcocks on the bridge and the transfer cell were opened simultaneously. The N_2O_4 distilled freely into the freezing point cell. When the desired quantity of N_2O_4 (0.2–0.9 g.) had been condensed, the stopcock on the transfer bridge was closed. The transfer cell was cooled with liquid air until all of the N_2O_4 vapor beyond the bridge stopcock had been condensed into the transfer cell. The stopcock on the transfer cell was then closed, and the cell was removed from the bridge. The weight of N_2O_3 condensed was determined by the difference in weights of the transfer cell before and after distillation.

To stir the samples, a glass stirrer, equipped with an enclosed iron slug and actuated by an intermittent magnetic field produced by an air-cooled solenoid placed around the neck of the freezing point cell was used.

Temperatures were measured with a recording potentiometer (Leeds and Northrup Micromax) using a copper-constantan thermocouple immersed in the well of the freezing point cell. The heat-transfer medium in the well was 2,3-dimethylpentane. The apparatus was calibrated at

---

[1] Presented in part before the American Chemical Society, Division of Physical and Inorganic Chemistry at Cleveland, Ohio, April, 1951.

[2] Taken in part from a thesis submitted in partial fulfillment of the requirements for the Ph.D. degree by B. Rubin, March, 1951. For a detailed description of the apparatus used in this investigation, this thesis should be consulted.

(3) C. C. Addison and R. Thompson, *J. Chem. Soc.*, S211 (1949).

(4) (a) V. L. Riebsomer, *Chem. Revs.*, **36**, 157 (1945); (b) J. A. Crowder, U. S. Patent 2,402,315, June 18, 1946; *C. A.*, **40**, 6092 (1946); (c) N. Levy and C. W. Scaife, *J. Chem. Soc.*, 1093 (1946); N. Levy, C. W. Scaife and A. E. Wilder-Smith, *ibid.*, 52 (1948).

(5) C. K. Ingold and E. H. Ingold, *Nature*, **159**, 743 (1947).

(6) L. F. Fieser "Experiments in Organic Chemistry," D. C. Heath and Company, Boston, Mass., Part II, 1941, p. 368.

(7) Ninth Annual Report of American Petroleum Institute Research Project No. 45, The Ohio State University, Columbus, Ohio.

(8) H. H. Sisler, H. H. Batey, B. Pfahler and R. Mattair, THIS JOURNAL, **70**, 3821 (1948).

(9) Dr. G. L. Eichhorn, working in this Laboratory, has recently obtained both melting points on the same sample of tetrahydropyran.

(10) W. F. Giauque and J. D. Kemp, *J. Chem. Phys.*, **6**, 40 (1938).

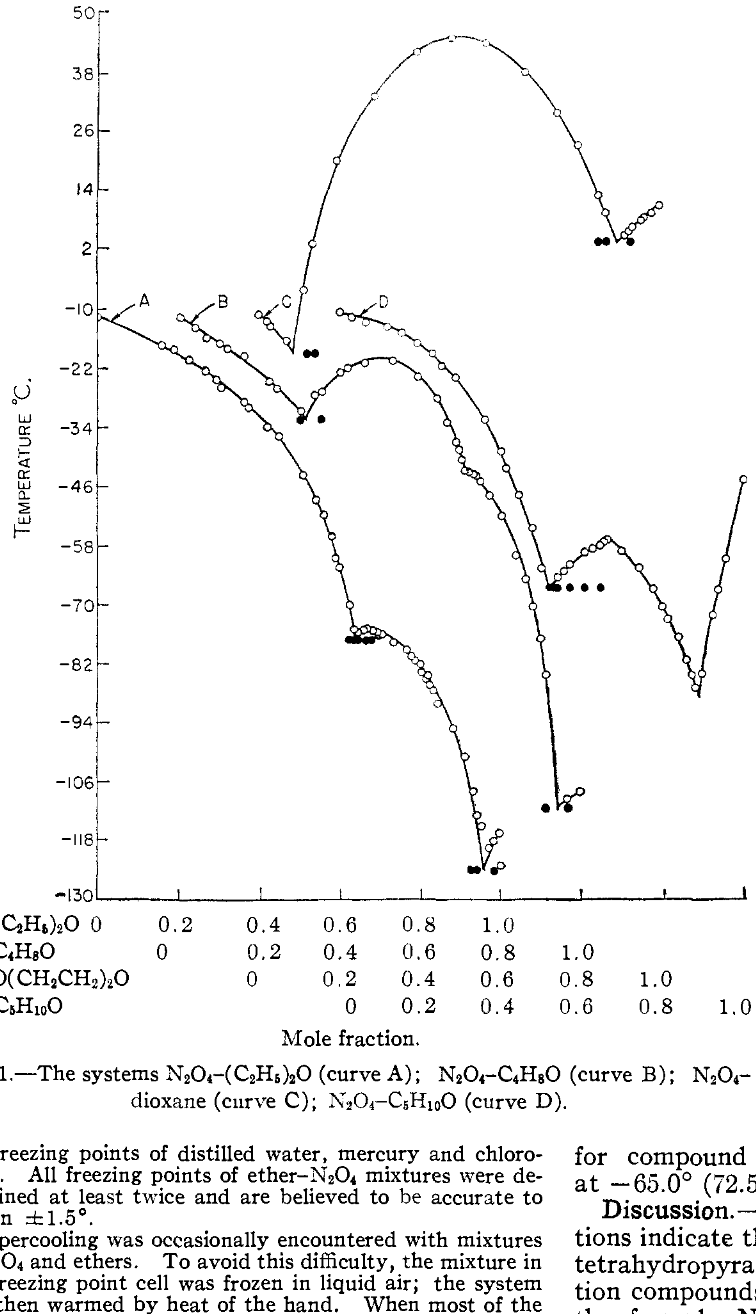


Fig. 1.—The systems N_2O_4–$(C_2H_5)_2O$ (curve A); N_2O_4–C_4H_8O (curve B); N_2O_4–dioxane (curve C); N_2O_4–$C_5H_{10}O$ (curve D).

the freezing points of distilled water, mercury and chloroform. All freezing points of ether–N_2O_4 mixtures were determined at least twice and are believed to be accurate to within ±1.5°.

Supercooling was occasionally encountered with mixtures of N_2O_4 and ethers. To avoid this difficulty, the mixture in the freezing point cell was frozen in liquid air; the system was then warmed by heat of the hand. When most of the solid had liquefied and the temperature was near the freezing point of the mixture, the cell was immersed in the cooled concentric Pyrex tubes. The few remaining crystals acted as nuclei for further crystallization and the freezing point of the mixture was then obtained.

Results of Thermal Studies.—In the system diethyl ether–dinitrogen tetroxide (Fig. 1-A), a compound of the composition $N_2O_4·2(C_2H_5)_2O$ is formed which melts congruently at −74.8°. Since the maximum in the freezing point curve is not very sharp, it is probable that the compound is dissociated considerably at its melting point. Eutectics occur at −75.6° (64 mole % $(C_2H_5)_2O$) and at −124.5° (96 mole % $(C_2H_5)_2O$).

The data obtained for the system tetrahydrofuran–dinitrogen tetroxide are illustrated in Fig. 1-B. There are two compounds formed in this system: one which has the composition $N_2O_4·C_4H_8O$ and melts congruently at −20.5°, and another which does not melt congruently but probably has the empirical formula $N_2O_4·2C_4H_8O$. Eutectics appear at −32.5° (32 mole % tetrahydrofuran) and at −111.0° (95 mole % tetrahydrofuran).

Data for the system tetrahydropyran–dinitrogen tetroxide are contained in Fig. 1-D. They indicate that a compound having the empirical formula $N_2O_4·2C_5H_{10}O$ and melting at −56.8° is formed. Eutectics occur at −65.5° (51 mole % ether) and −87.0° (88 mole % ether). It appears from the shape of the freezing point curve that $N_2O_4·2C_5H_{10}O$ is not highly dissociated at its melting point.

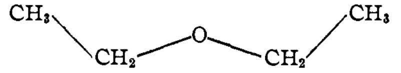
The freezing points for the system dioxane–dinitrogen tetroxide are represented graphically in Fig. 1-C. A compound of the formula $N_2O_4·O(CH_2CH_2)_2O$ is formed which melts at 45.2°. This compound is a colorless crystalline solid at room temperature but becomes dark brown as its temperature approaches its melting point. The discoloration is reversible, however, because the compound again becomes colorless when its temperature is lowered. It is stable at room temperature if kept in closed tubes. It has an appreciable vapor pressure of NO_2. Eutectics in this system occur at −19.0° (11 mole % dioxane) and at 4.0° (88 mole % dioxane).

The data for the system β,β'-dichlorodiethyl ether–dinitrogen tetroxide (Fig. 2) give no evidence for compound formation. There is a eutectic at −65.0° (72.5 mole % ether).

Discussion.—The results from these investigations indicate that diethyl ether, tetrahydrofuran, tetrahydropyran and dioxane form definite addition compounds with dinitrogen tetroxide having the formula $N_2O_4·2R_2O$ (in dioxane both ether units are in the same molecule, $N_2O_4·O(C_2H_4)_2O$). Tetrahydrofuran also forms a 1:1 addition compound, $N_2O_4·C_4H_8O$. The shapes of the freezing point curves indicate that the compounds exist to some extent even in the liquid state. If it is assumed that compound formation occurs by an acid–base reaction in which the oxygen of the ether is the basic center, it appears that the stability of the adducts of the monobasic ethers (tetrahydrofuran and tetrahydropyran > diethyl ether) is in accord with that predicted by modern concepts of steric strain.[11] The relatively flat curve obtained for the compound $N_2O_4·2(C_2H_5)_2O$, indicating considerable dissociation at its melting point, may be due to steric strains produced by the ethyl groups

[11] H. C. Brown and R. M. Adams, This Journal, **64**, 2557 (1942).

of the ether. Brown and Adams suggest that if diethyl ether has the configuration



then there is probably strain as a result of the position of the $-CH_3$ groups, and the addition of an acid is accompanied by a rearrangement of the diethyl ether molecule into a configuration of higher energy.

The sharper maximum obtained for $N_2O_4 \cdot 2C_5H_{10}O$ indicates relatively greater stability of this compound at its melting point. This increased stability is probably due to the increased basic strength of the ether. The rigidity of the 6-membered ether ring greatly reduces the possibility of steric interference and is believed to be responsible for the high basicity of the cyclic ether.

Since the shape of the maximum for the compound $N_2O_4 \cdot 2C_4H_8O$ is obscured because of its incongruent melting point, little can be said about its stability. However, the occurrence of a 1:1 compound as well as a 2:1 compound is striking. A possible explanation for this phenomenon is that F-strain[12] in 5-membered rings is considerably smaller than in 6-membered rings or straight-chain ethers; the 1:1 compound may thus be stabilized and occur as a maximum in the phase diagram.

Similarly the low basicity of β,β'-dichlorodiethyl ether, as evidenced by failure to form an addition compound with N_2O_4, may be related to (a) steric interference of the β-halogens to approach of the acceptor atom and (b) the inductive effect of the halogen atoms, resulting in reduction of electron density of the ether oxygen.

Upon establishing that N_2O_4 forms addition compounds with various ethers, questions were raised concerning the structures of these adducts. Since the compounds $N_2O_4 \cdot 2R_2O$ may also be expressed by the formula $NO_2 \cdot R_2O$, and since dinitrogen tetroxide usually exists in equilibrium with nitrogen dioxide, the possibility exists that the addition compounds are composed of nitrogen dioxide radicals in combination with the ether. Since the NO_2 radical contains an odd number of electrons, its presence in these addition compounds should cause them to be paramagnetic. Therefore, studies of the magnetic susceptibilities of these compounds were undertaken.

II. Magnetic Measurements

Procedure.—The method used to determine magnetic susceptibilities was essentially that given by Gouy.[13] A typical Gouy balance was used in conjunction with a cryostat designed to fit between the pole pieces and to accommodate the glass cylinder containing the sample. The dewar cryostat was maintained at constant temperature by circulating refrigerated alcohol through copper coils imbedded in a lead block seated in the top half of the cryostat. Conduction of heat was effected by a copper cylinder which ran the length of the inner wall of the dewar flask. Windows in the copper cylinder permitted visual observation of the sample.

The field strength of the magnets was calibrated as a function of the potential across the magnet windings by using triply-distilled water that had been freshly boiled. A known volume of water was placed in a cylinder whose cross-sectional area was known and then suspended from a balance between the pole pieces. Known potentials, corresponding to the peak voltages generated by a rotating coil were read from the potentiometer; the change in weight of sample for each potential was determined using the equation

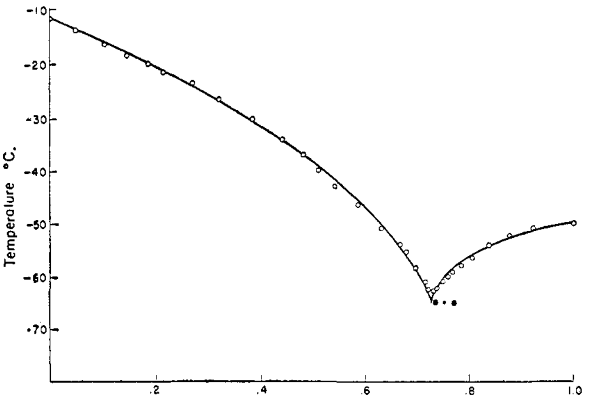


Fig. 2.—The system dinitrogen tetroxide-dichlorodiethyl ether.

$$g\Delta w = {}^1/_2(K_1 - K_2)H_1^2A$$

in which g is the gravitational constant, K_1 and K_2 are the volume susceptibilities of sample and surrounding atmosphere, H_1 is the field strength, and A is the cross-sectional area of the sample. For the constants $g = 980$, $K_1 = 0.0294 \times 10^{-6}$, and $K_2 = -0.720 \times 10^{-6}$, and with a cylinder of known dimensions, it was possible to determine the field strength, H_1, for every potential set on the potentiometer. In subsequent investigations it was only necessary to know the potentiometer value to determine the field strength. Corrections were made for the magnetic susceptibility of the glass by subtracting the change in weight due to the cell from the change in weight of the cell containing water.

The samples investigated were contained in a cylindrical Pyrex tube, approximately 15 cm. long and 0.4059 cm.² in cross-section, and equipped with a ground-glass inlet. The sample tube was closed with a ground-glass joint and held in position by rubber bands.

The samples of N_2O_4–ethers were made up so that their volumes were approximately the same as that of the water samples. After they had been mixed and suspended in the thermostated dewar, the magnetic field was applied. Weighings were made at various field strengths.

To determine the change in susceptibilities of the sample as a function of temperature, the circulating pump for the cooling liquid was stopped and the temperature was allowed to rise slowly. Usually, 3–4 hours was necessary to cover the ranges of temperature in these investigations.

Results.—Plots of the change in weight $(-\Delta w)$ of $N_2O_4 \cdot O(CH_2CH_2)O$ at 21.1° and $N_2O_4 \cdot C_4H_8O$ at $-25.3°$ against the square of the field strength resulted in straight lines with a positive slope in the first quadrant that indicates typical dimagnetism. Plots of Δw against temperature at constant field strength indicate that samples having the composition $N_2O_4 \cdot C_4H_8O$ become paramagnetic at $-6.8°$; similarly, samples corresponding to $N_2O_4 \cdot 2C_5H_{10}O$ and $N_2O_4 \cdot 2(C_2H_5)_2O$ become paramagnetic at $-4.4°$ and $-7.1°$, respectively (Fig. 3).

Discussion.—The results from the magnetic studies reveal that $N_2O_4 \cdot 2(C_2H_5)_2O$, $N_2O_4 \cdot C_4H_8O$ and $N_2O_4 \cdot 2C_5H_{10}O$ do not contain any "unpaired structures" derived from NO_2 even at temperatures well above their freezing points. Since the adducts of diethyl ether, tetrahydrofuran and tetrahydropyran become paramagnetic at approximately the

---

[12] H. C. Brown, M. D. Taylor and M. Gerstein, THIS JOURNAL, **66**, 435 (1944).

[13] L. G. Gouy, *Compt. rend.*, **109**, 935 (1889).

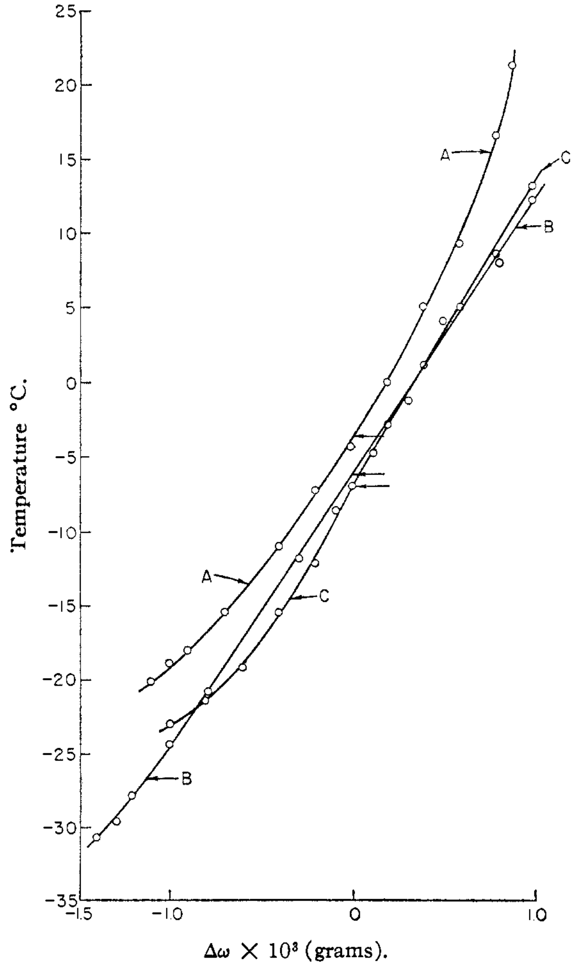


Fig. 3.—Change in magnetic susceptibility with temperature: curve A, $N_2O_4{\cdot}2C_5H_{10}O$; curve B, $N_2O_4{\cdot}C_4H_8O$; curve C, $N_2O_4{\cdot}(C_2H_5)_2O$.

temperature at which dinitrogen tetroxide becomes paramagnetic (−2.4°), it is presumed that the addition compounds dissociate into ether and N_2O_4 and at higher temperatures the N_2O_4 is dissociated into NO_2. Similar interpretation may be made for $N_2O_4{\cdot}O(CH_2CH_2)O$, a solid (m.p. 45.2°) which is still diamagnetic at room temperature. This substance, therefore, contains no NO_2 radicals. The fact that the compound becomes dark brown in color a few degrees below its melting point indicates that dissociation into N_2O_4 and further into NO_2 probably occurs in this system also.

III. Spectroscopic Studies

The thermal analyses and the magnetic measurements previously described established the empirical formulas for the compounds derived from dinitrogen tetroxide and various ethers and that these compounds do not contain singular NO_2 structures. Since N_2O_4 may dissociate into the diamagnetic ions NO_2^+ and NO_2^- and NO^+ and NO_3^-, it is possible that these species may be present in the adducts of dinitrogen tetroxide and various ethers. Since the characteristic Raman and infrared frequencies are known for NO^+, NO_2^+, NO_2^- and NO_3^- and for NO_2 and N_2O_4, a study was made of the Raman spectra of $N_2O_4{\cdot}2(C_2H_5)_2O$ and $N_2O_4{\cdot}2C_5H_{10}O$ at temperatures slightly above their respective melting points, and of the infrared spectrum of solid $N_2O_4{\cdot}O(CH_2CH_2)_2O$.

Procedure.—A high speed Raman spectrograph was used in conjunction with a low temperature cryostat which could be placed directly in the radiation path without altering the optics. Monochromatic radiation of 4358 Å. from two mercury lamps was used for excitation. For purposes of comparison, the Raman spectrum of tetrahydropyran was determined. It was not convenient to obtain the Raman spectra of $N_2O_4{\cdot}C_4H_8O$ or $N_2O_4{\cdot}O(CH_2CH_2)_2O$ because their melting points are too high for the cryostatic arrangement in our instrument.

The infrared spectrum of crystalline $N_2O_4{\cdot}O(CH_2CH_2)_2O$ was obtained in a sodium chloride cell with a Baird recording spectrophotometer (Model B). The infrared spectrum of pure dioxane was determined for comparison.

Results and Discussion.—The chief lines in the Raman spectrum of $N_2O_4{\cdot}2(C_2H_5)_2O$ at −72° (2.8° above its melting point) and their assignments are contained in Table I. These assignments were made by comparison with published data on the spectra of diethyl ether,[14] N_2O_4,[15] NO_3^-,[16] NO_2^+,[16] NO^+[16] and NO_2^-.[17]

TABLE I

RAMAN SPECTRA OF $N_2O_4{\cdot}2(C_2H_5)_2O$ AT −72°

w, cm.$^{-1}$	Relative intensity	Assignments
2980	Medium	$(C_2H_5)_2O$
2935	Medium	$(C_2H_5)_2O$
1714	Medium	N_2O_4
1458	Medium	$(C_2H_5)_2O$
1446	Medium	$(C_2H_5)_2O$
1380	Strong	N_2O_4
1340	Weak	N_2O_4
1274	Weak	$(C_2H_5)_2O$
1214	Weak	?
1168	Weak	$(C_2H_5)_2O$
1150	Weak	$(C_2H_5)_2O$
1103	Weak	?
1045	Weak	$(C_2H_5)_2O$
932	Very weak	$(C_2H_5)_2O$
916	Weak	$(C_2H_5)_2O$
845	Medium	$(C_2H_5)_2O$
833	Medium	$(C_2H_5)_2O$
812	Strong	N_2O_4
500	Very weak	N_2O_4 or $(C_2H_5)_2O$
441	Medium	$(C_2H_5)_2O$
276	Strong	N_2O_4
220	Weak	?

Raman spectra lines for $N_2O_4{\cdot}2C_5H_{10}O$ at −55° (1.8° above its melting point) and at −72° (supercooled state) and for $C_5H_{10}O$ at 21° are listed in Table II, along with assignments. The data obtained indicate that all of the lines in the spectra of $N_2O_4{\cdot}2(C_2H_5O)$ and $N_2O_4{\cdot}2C_5H_{10}O$, with the exception of three of four weak lines, correspond to characteristic N_2O_4 or ether frequencies; there is no evidence for the presence of ionic species derived from dinitrogen tetroxide. It is believed that the new weak lines result primarily from

---

(14) F. F. Cleveland, M. J. Murray, H. H. Haney and J. Shackelford, *J. Chem. Phys.*, **8**, 153 (1940).

(15) G. B. B. M. Sutherland, *Proc. Roy. Soc. (London)*, **141**, 535 (1933).

(16) D. R. Goddard, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2559 (1950).

(17) A. Langseth and E. Walles, *Z. physik. Chem.*, **B27**, 209 (1935).

bonding of the ether with N_2O_4 and that the structures of the adducts involve ether and undissociated dinitrogen tetroxide.

TABLE II

RAMAN SPECTRA OF $N_2O_4 \cdot 2C_5H_{10}O$ AT −72 AND −55° AND OF $C_5H_{10}O$ AT 21°

$N_2O_4 \cdot 2C_5H_{10}O$ $\Delta\nu$ (cm.$^{-1}$)	Relative intensity	Assignments	$C_5H_{10}O$ $\Delta\nu$ (cm.$^{-1}$)	Relative intensity
Lines at −72°				
2950	Medium	$C_5H_{10}O$	3048	Very weak
2911	Weak	?	2966	Weak
2853	Medium	$C_5H_{10}O$	2938	Weak
2719	Weak	$C_5H_{10}O$	2849	Weak
1715	Medium	N_2O_4	2785	Very weak
1456	Medium	$C_5H_{10}O$	2757	Very weak
1437	Medium	$C_5H_{10}O$	2717	Strong
1385	Strong	N_2O_4 or $C_5H_{10}O$	2681	Very weak
1347	Medium	N_2O_4 or $C_5H_{10}O$	2648	Very weak
1302	Medium	$C_5H_{10}O$	1460	Medium
1275	Medium	$C_5H_{10}O$	1438	Medium
1256	Medium	$C_5H_{10}O$	1382	Medium
1197	Weak	$C_5H_{10}O$	1342	Weak
1171	Weak	$C_5H_{10}O$	1303	Very weak
1157	Weak	$C_5H_{10}O$	1278	Very weak
1048	Medium	$C_5H_{10}O$	1261	Medium
1032	Medium	$C_5H_{10}O$	1201	Medium
1012	Medium	$C_5H_{10}O$	1173	Medium
971	Very weak	?	1159	Very weak
875	Very weak	$C_5H_{10}O$	1053	Very weak
854	Very weak	$C_5H_{10}O$	1034	Strong
816	Very strong	N_2O_4	1014	Strong
761	Weak	$C_5H_{10}O$	875	Weak
716	Very weak	$C_5H_{10}O$	857	Very weak
684	Very weak	?	819	Weak
504	Medium	N_2O_4	763	Weak
458	Medium	$C_5H_{10}O$	718	Very strong
433	Medium	$C_5H_{10}O$	461	Very strong
403	Weak	$C_5H_{10}O$	434	Very strong
284	Very strong	N_2O_4	405	Very strong
229	Weak	?	257	Strong
Lines at −55° other than those due to $C_5H_{10}O$				
1714	Weak	N_2O_4		
1386	Medium	N_2O_4		
282	Strong	N_2O_4		

The infrared spectra of dioxane and of $N_2O_4 \cdot O(CH_2CH_2)_2O$ were determined at 25°. The wave numbers of the dioxane–N_2O_4 adduct which do not correspond to those of dioxane are listed in Table III. Our data for dioxane agree with those of Burket and Badger.[18] A comparison of our data with published results for N_2O_4,[19] NO_2^- [17] and NO_3^- [20] indicates: (a) three wave numbers which are characteristic of N_2O_4, (b) two lines (1678 and 1408) which do not correspond to any known wave numbers for N_2O_4, NO_2^- or NO_3^- and (c) one wave number 821 that might be attributed to NO_2^- or NO_3^- but probably belongs to neither. It is believed that these infrared spectra indicate the presence of N_2O_4 units and that the wave numbers 1678, 1408 and 821 result from bonds formed between dinitrogen tetroxide and dioxane.

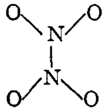
TABLE III

INFRARED FREQUENCIES FOR $N_2O_4 \cdot O(CH_2CH_2)_2O$

Wave numbers (cm.$^{-1}$) other than those of $O(CH_2CH_2)_2O$	Relative intensity	Assignments
1745	Medium	N_2O_4
1678	Medium	?
1408	Weak	?
935	Medium	N_2O_4
821	Weak	?
746	Strong	N_2O_4

IV. Conclusions

The recent X-ray studies by Broadley and Robertson[21] indicate the following planar configuration for dinitrogen tetroxide in the solid state.



The N–N bond distance is 1.64 ± 0.03 Å., considerably higher than the length of the typical N–N covalent linkage (1.47 Å).

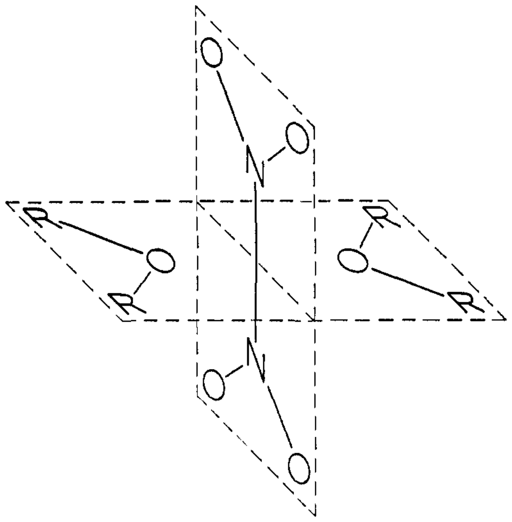


Fig. 4.

The "radius ratio effect" ordinarily limits the coördination number of nitrogen with respect to oxygen (or other similarly sized atoms) to three. Perhaps the somewhat longer than normal N–N distance would serve to minimize this limitation and allow for an increase in the coördination number of the nitrogen atoms so as to make possible the formation of a fourth covalent bond with the ether oxygen. We are inclined, however, to consider a structure in which the two nitrogen atoms (which have positive formal charges) together act as a center of attraction for the ether oxygen atoms as more likely. Thus, the

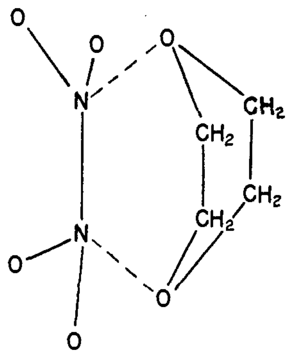


Fig. 5.

---

[18] S. C. Burket and R. M. Badger, THIS JOURNAL, **72**, 4397 (1950).

[19] G. B. B. M. Sutherland, *Proc. Roy. Soc.* (*London*), **141**, 342 (1933).

[20] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945.

[21] J. S. Broadley and J. M. Robertson, *Nature*, **164**, 915 (1949).

compound $N_2O_4 \cdot 2R_2O$ can be pictured as having the structure shown in Fig. 4.

This concept is capable of explaining the relatively high melting point of the dioxane compound $N_2O_4 \cdot O(CH_2CH_2)_2O$, for the two oxygen atoms in a single dioxane molecule make possible an indefinitely extended aggregation.

If one is willing to accept the assumption that each of the nitrogen atoms in the N_2O_4 molecule is capable of accepting a pair of electrons from an ether oxygen, thus increasing the coördination number of the N-atom to four, a structure in which each oxygen atom from a given dioxane molecule is coördinated to one of the nitrogen atoms in the N_2O_4 molecule to form a bicyclic configuration (Fig. 5) may be considered.

The proof of these structures must, of course, await X-ray diffraction studies.

The results of this study are particularly interesting since they can be correlated with the recent studies of reactions of dinitrogen tetroxide with olefins in basic solvents. Since Levy, *et al.*,[4c] found that β,β'-dichlorodiethyl ether does not prevent oxidation as do other more basic ethers, the results of the present investigation that show that the dichloroether does not form an addition compound with dinitrogen tetroxide certainly lend support to the postulate that basic solvents moderate the oxidizing action of dinitrogen tetroxide through the formation of molecular addition compounds.

COLUMBUS, OHIO RECEIVED MAY 7, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Heat Capacities and Entropies of Melamine and Dicyandiamide

BY C. C. STEPHENSON AND D. J. BERETS

The heat capacities of melamine and dicyandiamide have been measured from 15 to 300°K. The calculated entropies at 298.16°K. are 35.63 cal./deg./mole and 30.90 cal./deg./mole, respectively.

The recent increased importance of organic compounds containing nitrogen has made it desirable to have adequate thermal data with which to carry out thermodynamic calculations on some of these compounds. Accordingly, the heat capacities of melamine, $C_3N_6H_6$, and dicyandiamide, $C_2N_4H_4$, have been measured from 15°K. to room temperature.

Experimental

Materials.—Both compounds were prepared and purified in the Stamford Research Laboratories of the American Cyanamid Company. The melamine was recrystallized from NaOH solution and analyzed to be 100.0% pure, containing 0.002% Na and 3.7 p.p.m. Fe. The dicyandiamide was recrystallized from hot water and was analyzed spectrographically to contain no more than 0.1% impurities. Both materials were dried under high vacuum for several days, but without heating. From the anomalies in the heat capacity curves at the melting point of ice, it was calculated that the melamine contained 0.05% by weight of water and the dicyandiamide, 0.34%. The final heat capacity values have been corrected for the contribution of this amount of water.

TABLE I

HEAT CAPACITIES AT EXPERIMENTAL TEMPERATURES

Melamine		Dicyandiamide	
T, °K.	C_p, cal./deg./mole	T, °K.	C_p, cal./deg./mole
15.62	0.63	14.40	0.54
17.04	0.77	15.59	0.64
18.43	0.94	16.89	0.75
19.87	1.17	18.33	0.92
23.03	1.65	20.18	1.16
26.15	2.16	26.61	2.14
29.31	2.72	30.33	2.84
32.76	3.35	33.72	3.46
36.42	4.01	37.31	4.11
40.25	4.71	41.22	4.83
44.44	5.46	45.40	5.58
49.09	6.30	49.81	6.35
54.14	7.17	54.82	7.16
59.44	8.04	60.11	7.97
63.64	8.69	64.26	8.60
69.29	9.58	69.19	9.22
74.88	10.36	74.18	9.86
80.46	11.11	79.26	10.41
86.00	11.81	84.43	10.94
91.61	12.52	89.67	11.47
97.40	13.22	95.03	11.98
103.45	13.94	100.62	12.50
109.65	14.68	106.42	13.00
116.09	15.43	112.52	13.54
122.48	16.18	118.67	14.06
126.63	16.64	124.83	14.57
131.75	17.23	131.29	15.10
137.20	17.83	137.74	15.60
142.92	18.50	144.18	16.15
148.89	19.19	150.62	16.69
155.15	19.97	157.12	17.25
161.73	20.77	163.74	17.80
168.48	21.55	170.81	18.39
175.45	22.40	178.13	18.99
182.78	23.25	185.53	19.57
190.24	24.17	192.97	20.19
197.81	25.06	200.49	20.78
205.46	25.98	208.12	21.37
213.15	26.88	215.43	21.99
220.55	27.76	223.12	22.57
228.30	28.68	230.86	23.19
236.09	29.63	238.72	23.81
243.90	30.56	246.37	24.38
251.74	31.47	254.17	24.99
259.16	32.39	262.12	25.64
267.04	33.50[a]	269.79	26.40[a]
275.24	34.78[a]	277.73	26.85[a]
283.58	35.32	285.97	27.50
291.73	36.30	294.63	28.14
299.95	37.31		

[a] Values are high due to melting of ice in sample.