molecule. Data to be reported in a succeeding paper on the viscosity of 1,4-dioxane–dinitrogen tetroxide mixtures and on molecular weights of dinitrogen tetroxide in 1,4-dioxane confirm these conclusions. Further, it should be noted that the cyclic character of the 1,4-dioxane molecule undoubtedly presents less possibility of steric interference in coördinating with the N_2O_4 molecule than does the extended chain molecule of the diethyl ether of ethylene glycol.

The very close resemblance between the phase diagram for the system 1,3-dioxane–N_2O_4 and that reported previously[1] for the system 1,4-dioxane–N_2O_4 cannot escape notice. When plotted on the same scale the maxima in the freezing point curves can be superimposed. It thus appears that 1,3-dioxane, like 1,4-dioxane, forms an unusually stable complex with dinitrogen tetroxide. A superficial consideration of this might lead one to consider this fact as arguing against the bicyclic structure for the $N_2O_4 \cdot$1,4-dioxane compound. However, calculation of the oxygen to oxygen distances in the "boat" forms of the two dioxanes show that the two distances are the same within 0.1 Å. (2.4 Å. in 1,3-dioxane and 2.5 Å. in 1,4-dioxane). It thus appears that either of the two dioxanes could form the bicyclic structure. Trioxane likewise presents the possibility of entering into this same structure. Unfortunately, the disparity in the freezing points of dinitrogen tetroxide and trioxane so modifies the character of the trioxane–N_2O_4 phase diagram that the maximum in the freezing point curve is "hidden." However, it appears likely that the compound is a 1:1 addition product. Further, the slope of the curve approaching the incongruent melting point is steeper than in the case of the aliphatic ethers and is about the same as for the corresponding portion of the 1,4-dioxane curve.

The failure of perfluorotetrahydrofuran to form compounds with dinitrogen tetroxide serves further to confirm our concept that additions of ether molecules to dinitrogen tetroxide are Lewis acid–base reactions. The introduction of eight fluorine atoms so decreases the electron density around the oxygen atom that the ether is no longer sufficiently basic to react with dinitrogen tetroxide.

The character of the freezing point curve for the system α-methyltetrahydrofuran–dinitrogen tetroxide indicates that the compound $N_2O_4 \cdot 2C_4H_7(CH_3)O$ is quite stable at its melting point. It thus appears that any steric interference resulting from one α-methyl group is at least balanced by the increase in electron density about the oxygen atom produced by the methyl group.

Columbus, Ohio

[Contribution from the McPherson Chemical Laboratories of The Ohio State University]

Molecular Addition Compounds of Dinitrogen Tetroxide. IV.[1] Cryoscopic and Viscosimetric Studies in the 1,4-Dioxane–Dinitrogen Tetroxide System

By Harry W. Ling and Harry H. Sisler

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Viscosimetric measurements on mixtures of dinitrogen tetroxide and 1,4-dioxane in the range of 0 to 50 mole per cent. dinitrogen tetroxide have served to indicate the absence of indefinitely extended chains of alternate dinitrogen tetroxide and dioxane molecules. This conclusion is supported by the fact that cryoscopic measurements on dilute solutions of dinitrogen tetroxide in dioxane indicate only one dinitrogen tetroxide unit per solute molecule.

In the first paper in this series,[2] two alternative structures for the unusually stable complex $N_2O_4 \cdot$1,4-$O(CH_2CH_2)_2O$ were proposed: (a) one in which indefinitely extended chains composed of alternate dioxane and dinitrogen tetroxide molecules were postulated, and (b) the other in which it was postulated that the two oxygen atoms of the dioxane molecule were coördinated, respectively, with the two nitrogen atoms of the dinitrogen tetroxide molecule to yield a bicyclic configuration. In the first case, the relatively high melting point of the compound was explained as resulting from its high molecular weight and, in the second case, by analogy with a number of other compounds having bicyclic structures which also have unusually high melting points, *e.g.*, camphor.

With the hope of obtaining information which would assist in resolving this question, viscosity and molecular weight determinations were carried out on 1,4-dioxane–dinitrogen tetroxide solutions.

The assistance of the Ordnance Corps, U. S. Army, through a contract with The Ohio State University Research Foundation in carrying out this research is greatfully acknowledged.

Experimental

Preparation of Materials.—The 1,4-dioxane and dinitrogen tetroxide were purified by methods described in a previous publication in this series.[2]

Method for Determining Viscosities.—The viscosity measurements were carried out with the modified Ostwald–Cannon–Fenske viscosity pipet illustrated in Fig. 1. The relationship

$$\eta_1/\eta_2 = d_1t_1/d_2t_2$$

was used, where η refers to the coefficient of viscosity, d refers to the density and t refers to the time required for a given volume of liquid to flow through a given capillary section. The subscript "1" refers to a reference liquid, in this case doubly distilled water, and the subscript "2" to the sample being measured.

A typical measurement on a dinitrogen tetroxide–1,4-dioxane mixture was carried out as follows: The apparatus was thoroughly cleaned and dried. 1,4-Dioxane was added to weighed vessel A through the stopcock g from a weight buret and vessel A weighed again. The viscosity pipet C and the dinitrogen tetroxide transfer cell were fitted into

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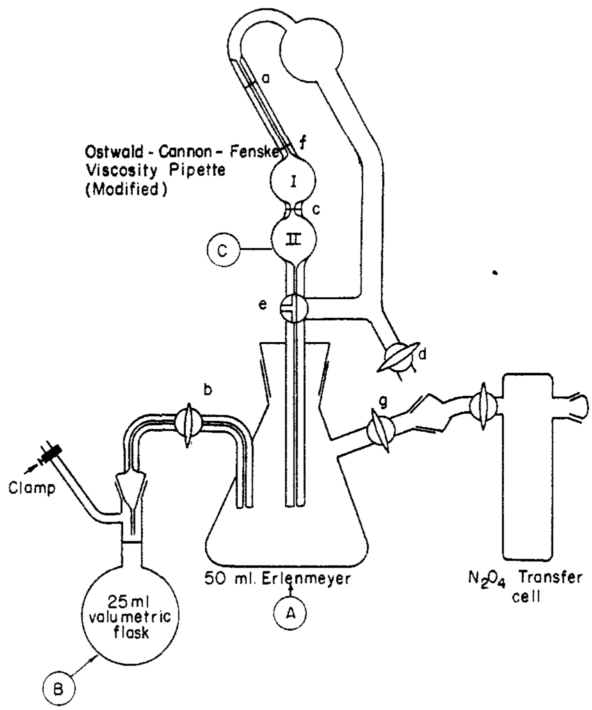
1) The preceding paper in this series: J. Whanger and H. Sisler, This Journal, **75**, 5188 (1953).

(2) B. Rubin, H. Sisler and H. Shechter, *ibid.*, **74**, 877 (1952.)



Composite viscosity cell (not drawn to scale)

Fig. 1.—Apparatus for viscosity determinations.

place and the required amount of dinitrogen tetroxide distilled into vessel A, the vessel being cooled in a Dry Ice–acetone-bath. The weight of dinitrogen tetroxide was determined by the change in weight of the transfer cell. The dry flask B was then attached to the left side arm and the system placed in a thermostat at 48.02 ± 0.04°, a temperature slightly above the melting point of $N_2O_4 \cdot O(CH_2CH_2)_2O$. After thermal equilibrium was attained, stopcock b was opened and some of the mixture forced over into the flask B which had been previously calibrated and weighed. The flask B was then removed and weighed. From this weight the density of the liquid mixture was calculated. With stopcocks b and d closed, stopcock e was opened as shown in the figure and the viscosity pipet filled to mark a by nitrogen pressure through stopcock g. The stopcock e was immediately closed.

The viscosity pipet was removed, inverted and placed in the thermostat. After temperature equilibrium was attained the liquid in the pipet was forced up into bulb II by nitrogen pressure through stopcock d. The stopcock e was then turned so as to make the inner chamber of the viscometer a complete circuit isolated from the environment. The time required for the liquid meniscus to pass from c to f was then carefully measured. From the known or measured values of η_1, d_2, t_2, d_1, and t_1 the value of η_2 was calculated. Measurements were limited to the range of 0 to 50 mole per cent. N_2O_4 because of the high vapor pressures developed by mixtures rich in dinitrogen tetroxide.

Method for Cryoscopic Measurements.—In order to calculate the number of N_2O_4 units per solute molecule in solutions of dinitrogen tetroxide in 1,4-dioxane, the relationship

$$X = K_f m / (-\Delta T_f)$$

was used, where X is the number of N_2O_4 units per molecule, K_f is the cryoscopic constant for 1,4-dioxane, ΔT_f is the change in the freezing point of 1,4-dioxane produced by a molality (moles/1000 g. of solvent) of dinitrogen tetroxide equal to m.

A G-2 Mueller bridge equipped with a platinum resistance thermometer was used for measuring the temperature. A freezing point cell in which the sample was constantly stirred and yet protected from moisture in the air was used. The resistance thermometer used was protected by a perforated glass shield to which it was attached through a teflon plug which was machined to fit snugly into a ground glass joint at the top of the cell. These unions were sealed with De Khotinsky cement. Continuous stirring was obtained by a glass stirrer actuated by an intermittent magnetic field produced in a solenoid placed around the neck of the cell. A small iron slug was hermetically sealed within the stirrer. A typical measurement was carried out as follows: The clean and dry apparatus was assembled and protected from the atmosphere by a drying tube containing phosphorus (V) oxide and sand. A weight buret containing 1,4-dioxane was attached at another opening and dioxane allowed to enter the cell, the difference in weight of the buret being noted. The freezing point of the dioxane was then determined. A dinitrogen tetroxide transfer cell[2] was then connected to the cell through a glass bridge containing a stopcock. The stopcock was opened and a small amount of dinitrogen tetoxide distilled into the cell, after which the stopcock was closed. The transfer cell was then chilled in liquid nitrogen before removal from the connecting bridge in order to condense all the gas which might otherwise remain in the bridge and, hence, be lost to the air. The weights of the transfer cell before and after adding dinitrogen tetroxide to the freezing point cell were noted. The new freezing point of the mixture was then determined. The freezing points were determined by plotting cooling curves. Since supercooling was commonly encountered the extrapolation method of Rossini and co-workers[3] was employed to determine the true freezing points. Each freezing point was checked by running the cooling curve twice.

Though values for the cryoscopic constant for dioxane are available in the literature, it was decided to check this value in our own equipment. Four solutes, *viz.*, benzene, *o*-oxylene, toluene and *t*-butylbenzene, were used and sixteen separate determinations were made using solutions in the same concentration range as for our freezing point determinations in the dinitrogen tetroxide solutions. The average value of K_f obtained was 4.68°C./mole which is in excellent agreement with values 4.7[4] and 4.63[5] from the literature.

Results and Conclusions

The results of a series of representative viscosity determinations are summarized in Table I.

TABLE I

VISCOSITIES OF N_2O_4–1,4-DIOXANE SOLUTIONS

Mole fraction N_2O_4	Density, g./ml.	Viscosity, centipoise	Mole fraction N_2O_4	Density, g./ml.	Viscosity, centipoise
0.0000	1.0031	0.7964	0.2473	1.0916	0.8149
.0247	1.0162	.8002	.2961	1.1150	.8127
.0886	1.0405	.8165	.3853	1.1368	.8162
.1073	1.0340	.8235	.3855	1.1440	.7993
.1326	1.0462	.8088	.4232	1.1612	....
.1879	1.0764	.8305	.4983	1.1880	.7782
.2163	1.0766	.8098			

It is quite apparent that the above viscosity data, which vary only slightly with mole fraction, preclude the existence of indefinitely extended chains of alternate N_2O_4 and dioxane molecules, for such aggregates should greatly increase the viscosity of the solution as the stoichiometric composition (50 mole per cent.) is approached.

The X values obtained from a series of typical freezing point measurements are listed in Table II.

TABLE II

CRYOSCOPIC MEASUREMENTS ON N_2O_4–1,4-DIOXANE SOLUTIONS

Molality of N_2O_4	0.00352	0.0374	0.0410	0.0562	0.0946
ΔT_f, °C.	− .017	− .176	− .199	− .249	− .409
X (= $K_f m/(-\Delta T_f)$)	.998	.992	.965	1.058	1.084

The data show that in dilute solutions of dinitrogen

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(3) A. Glasgow, A. Streiff and F. Rossini, *J. Research Natl. Bur. Standards*, **35**, 355 (1945).

(4) A. Oxford, *Biochem. J.*, **28**, 1325 (1934).

(5) C. Kraus and R. Vingee, THIS JOURNAL, **56**, 511 (1934).

tetroxide in 1,4-dioxane there is no tendency toward polymerization. In the range up to 0.1 molal, X is equal to unity ±10%. The very slight upward trend at the two higher concentrations reflects the fact that as the concentration of dinitrogen tetroxide increases an appreciable partial pressure of dinitrogen tetroxide above the solution develops. This fact in addition to the general limitations of cryoscopy for molecular weight determinations limited our measurements to dilute solutions.

On the basis of the cryoscopic and viscosimetric data reported herein we may conclude that there is little basis for postulating a polymeric, chain-type structure for the compound $N_2O_4\cdot 1,4\text{-}O(CH_2CH_2)_2O$.

COLUMBUS, OHIO

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

Some Reactions of the Etherate of Aluminum Triethyl[1]

BY EVELYN BLUST BAKER AND HARRY H. SISLER

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The preparation of sodium aluminum tetraethyl and lithium aluminum tetraethyl by the reaction of the corresponding alkali metal alkyl with the etherate of aluminum triethyl has been carried out. The reactions of this etherate with pyridine to give the compound $Al(Et)_3\cdot C_5H_5N$, and with sulfur dioxide to give the aluminum salt of ethylsulfinic acid were studied. It was also found that the etherate of aluminum triethyl reacts with dinitrogen tetroxide to give a product which upon hydrolysis yields N,N-diethylhydroxylamine; with nitric oxide to give a product which is believed to hydrolyze to ethylnitrosohydroxylamine; and gives little, if any, reaction with carbon dioxide.

Though the compound aluminum triethyl has been known for almost a century, literature concerning its chemistry is rather sparse, presumably because of its extreme reactivity. The etherate of this compound, first prepared about thirty years ago,[2] is also very reactive but is less so than aluminum triethyl itself. We were interested, therefore, in observing some of the reactions of the etherate to see if it gives the same sort of reactions as would be expected for free aluminum triethyl.

Furthermore, no synthetic details for the compounds lithium aluminum tetraethyl and sodium aluminum tetraethyl have ever been published,[3] and in view of the current interest in alkyl derivatives of aluminum and boron it seemed desirable to us to investigate the synthesis of these compounds.

The present report includes the results of the investigation of the reactions of the etherate of aluminum triethyl with lithium ethyl, sodium ethyl, sulfur dioxide, dinitrogen tetroxide, nitric oxide, carbon dioxide and pyridine.

Experimental

General Precautions.—Since the alkali metal alkyls, the etherate of aluminum triethyl, and many of reaction products of these compounds react rapidly with water and air, these materials were prepared, purified, stored and sampled in a dry, inert atmosphere, usually nitrogen, except in the case of lithium ethyl where helium was used. The nitrogen and helium were purified and dried by passing successively through Fieser's solution, lead acetate solution, concd. sulfuric acid, Ascarite, Drierite and a phosphorus (V) oxide–sand mixture. Because of the reactivity of metal alkyls toward organic matter, all-glass equipment was used in these experiments, lubricated very sparingly with Silicone high-vacuum stopcock grease.

Preparation of the Etherate of Aluminum Triethyl.—This compound was prepared by the procedure of Kraus and Wendt[2] and of Hurd[4] in which anhydrous aluminum chloride is caused to react with ethylmagnesium bromide in ether solution and the product distilled under vacuum. A good yield of halide-free product having the composition $Al(C_2H_5)_3\cdot(C_2H_5)_2O$[5] was obtained.

Preparation and Properties of Sodium Aluminum Tetraethyl.—Sodium ethyl prepared[6,7] from 10 g. of sodium and 20 g. of mercury diethyl in 150 ml. of petroleum ether (65–100° fraction) was cooled in an ice-bath, and 41 ml. (a slight excess) of the etherate of aluminum triethyl was added dropwise with stirring. The funnel was rinsed with 50 ml. of petroleum ether and stirring continued for three hours. The solution was then filtered and the residue washed with 150 ml. of petroleum ether. The solvents were distilled off, using an oil-bath to heat the flask, and the bath temperature was kept at 110° for 10 min. after distillation had stopped. The contents were then heated under vacuum for 30 min. with the bath at 110°. This additional heating seemed necessary to remove the ethyl ether from the sodium aluminum tetraethyl. The mixture was then cooled, 150 ml. of benzene added, the mixture refluxed for one hour and filtered while hot. The benzene was then distilled off until approximately 100 ml. of the solution remained. As the solution was allowed to stand, crystals separated. Crystallization sometimes was slow, several days being required. The mixture was then cooled to 10° and filtered, washed twice with 15-ml. portions of benzene and twice with 15-ml. portions of petroleum ether and dried under vacuum. If the crystals were yellow they were recrystallized again from benzene. The yield after two recrystallizations was about 10 g., or 40% of theory.

Sodium aluminum tetraethyl is a white, crystalline solid which reacts violently with water, decomposing to oxide and hydroxide with gas evolution. It is highly soluble in diethyl ether, much less soluble in benzene, and still less soluble in petroleum ether. It melts, without sublimation, *in vacuo* at about 125°. Two preparations were analyzed for aluminum as the 8-hydroxyquinolate and for sodium as the sulfate. Calcd. for $NaAl(C_2H_5)_4$: Na, 13.84; Al, 16.23. Found: Na, 13.89, 14.02; Al, 16.11, 16.18.

Preparation and Properties of Lithium Aluminum Tetraethyl.—Lithium ethyl was prepared[8] in 350 ml. of petroleum ether (30–60° fraction) from 4.5 g. of lithium sand and 15 ml. of ether-free ethyl bromide. To this was added dropwise, with stirring, 41 ml. of the etherate of aluminum triethyl. The funnel was rinsed with 50 ml. of petroleum ether. Three hundred ml. of benzene was then added and

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(1) Taken from the Ph.D. dissertation of E. B. Baker, The Ohio State University, 1953.

(2) E. Krause and B. Wendt, *Ber.*, **56B**, 466 (1923).

(3) Grosse and Mavity reported at the 96th Meeting of the American Chemical Society, September, 1938, that they had prepared $LiAlEt_4$, $NaAlEt_4$ and $KAlEt_4$ by the reaction of $Al(Et)_3$ with either the alkali metal or the alkali metal alkyl, but gave few experimental details and the work has not yet been published.

(4) D. Hurd, *J. Org. Chem.*, **13**, 711 (1948).

(5) E. B. Baker and H. H. Sisler, THIS JOURNAL, **75**, 4828 (1953).

(6) F. Whitmore and H. Zook, *ibid.*, **64**, 1783 (1942).

(7) H. Gilman and R. Young, *J. Org. Chem.*, **1**, 315 (1936).

(8) T. Perrine and H. Rapoport, *Anal. Chem.*, **20**, 635 (1948).