and inverting

$$\frac{1}{k'} = \frac{1}{k''} + \frac{K_D}{[H^+]k''}$$

is obtained. Hardwick and Robertson[6] have obtained an equilibrium constant of 5.2 for the dissociation reaction in 2 *M* perchloric acid at 25°. Using their value with our data, satisfactory slope and intercept are obtained for a $1/k'$ *versus* $1/[H^+]$ plot.

The most probable first product in the reaction is probably the free radical ion, Cl_2^-. This ion apparently has sufficiently lower free energy than the Cl atom that it may be formed, and Cl atoms may not be formed. This reaction may be

$$CeCl^{+3} + Cl^- \longrightarrow Ce^{+3} + Cl_2^-$$

or a complex of the form $CeCl_2^{+2}$ may be formed before formation of the products. The ion Cl_2^- and similar ions have been found as intermediates in previous work.[7]

(6) T. Hardwick and Robertson, *Canadian J. Chem.*, **29**, 818 (1951).

(7) H. Taube and W. Bray, THIS JOURNAL, **62**, 3357 (1940); H. Taube, *ibid.*, **69**, 1418 (1947); *ibid.*, **70**, 3928 (1948).

AMES, IOWA

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

Molecular Addition Compounds of Dinitrogen Tetroxide. III.[1,2] Binary Systems with a Series of Aliphatic and Alicyclic Mono-, Di- and Tribasic Ethers

BY JEAN GUTHRIE WHANGER[3] AND HARRY H. SISLER

RECEIVED JUNE 8, 1953

The binary systems formed by dinitrogen tetroxide with the following ethers have been studied by the freezing point method: *n*-propyl ether, *n*-butyl ether, isopropyl ether, *t*-butyl ether, ethylene glycol diethyl ether, 1,3-dioxane, trioxane, perfluorotetrahydrofuran and *α*-methyltetrahydrofuran. Compounds of the type $N_2O_4{\cdot}2B$ are formed with *α*-methyltetrahydropyran and ethylene glycol diethyl ether, and probably with *n*-propyl ether, isopropyl ether, *n*-butyl ether though in these cases incongruent melting points obscure the maxima in the freezing point curves. Compounds of the type $N_2O_4{\cdot}B$ were obtained with 1,3-dioxane, ethylene glycol diethyl ether and probably with trioxane. No compounds of dinitrogen tetroxide, with *t*-butyl ether and perfluorotetrahydrofuran were indicated by these studies. Theoretical implications of these results are briefly discussed.

Introduction

In a recent publication[1] from this Laboratory, one of the authors and his co-workers showed that dinitrogen tetroxide combines with several aliphatic and alicyclic ethers to form molecular addition compounds of the type $N_2O_4{\cdot}2B$ where B is one molecule of the ether. In a few instances, compounds of the formula $N_2O_4{\cdot}B$ are obtained. Magnetic and spectroscopic studies reported at that time indicated that these compounds are true addition compounds of the N_2O_4 molecule and do not contain NO_2 radicals or NO^+, NO_3^-, NO_2^+ or NO_2^- ions.

In an effort to obtain information concerning the various parameters which limit the field of application of this reaction and perhaps thereby to establish certain implications concerning the structures of these dinitrogen tetroxide–ether addition compounds, the binary systems of dinitrogen tetroxide with the following additional ethers were studied: *n*-propyl ether, isopropyl ether, *n*-butyl ether, *t*-butyl ether, 1,3-dioxane, trioxane, ethylene glycol diethyl ether, perfluorotetrahydrofuran and *α*-methyltetrahydrofuran. 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 gratefully acknowledged.

Experimental

Preparation of Materials.—The preparation and purification of dinitrogen tetroxide has been discussed in the previous publication in this series.[1] The ethers were all prepared or purified and stored according to accepted procedures. Physical constants for the purified samples used are listed in Table I along with comparable data from the literature for comparison. It should be noted that tendency to glass formation prevented our obtaining good freezing points for *α*-methyltetrahydrofuran and perfluorotetrahydrofuran.

TABLE I

PHYSICAL CONSTANTS OF ETHERS

Ethers	Boiling points, °C. Exptl.	Boiling points, °C. Lit.	Freezing points, °C. Exptl.	Freezing points, °C. Lit.
n-Propyl[a]	89.5 (751 mm.)		−122	−122.5
Isopropyl[a]	68.3 (754 mm.)		−85	−85.89
n-Butyl[a]			−95	−95.37
Ethylene glycol–diethyl[a]			−73	−74
Tertiary butyl[b]			−60	−60
1,3-Dioxane			−42.7	−42
Trioxane[c]			63 to 64	63 to 64
α-Methyltetrahydrofuran[d]	80	80	Forms glass	
Perfluorotetrahydrofuran[e]			Forms glass	

[a] Eastman Kodak Company. [b] Furnished by the American Petroleum Institute at The Ohio State University. [c] Heyden Chemical Corporation. [d] Furnished by Christopher E. Wilson, Ohio State University. [e] Furnished by Minnesota Mining and Manufacturing Company.

Procedure.—The freezing point–composition diagrams for the binary systems composed of dinitrogen tetroxide with each of the various ethers were determined by methods described in the previous publication in this series.[1] Briefly the freezing points of synthetic mixtures were determined by cooling curves measured by a Micromax self-recording potentiometer with a copper–constantan thermocouple, using a completely enclosed cell equipped for continuous magnetic stirring. In those instances where a slow oxidation–reduction reaction between dinitrogen tetroxide and the ether occurs (*t*-butyl ether and *α*-methyltetrahydrofuran) the effects of this reaction were minimized by not warming the mixtures any higher than necessary and by frequently taking fresh samples. However, in these instances, somewhat less than usual accuracy must be ascribed to the results.

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(1) The first paper in this series: B. Rubin, H. Sisler and H. Shechter, THIS JOURNAL, **74**, 877 (1952).

(2) The second paper in this series: D. Davenport, H. Burkhardt and H. Sisler, THIS JOURNAL, **75**, 4175 (1953).

(3) Taken in part from the dissertation submitted by J. G. W. in partial fulfillment of the requirements for the Ph.D. degree at The Ohio State University.

Results

The *n*-Propyl Ether System.—With *n*-propyl ether, dinitrogen tetroxide forms a compound which melts incongruently at −77.5°. Though the form of the freezing point curve (Fig. 1, curve B) does not establish the composition with certainty, it is believed that the compound is $N_2O_4{\cdot}2(n\text{-}C_3H_7)_2O$. It is interesting to note that evidence for the existence of a second form of solid *n*-propyl ether, not heretofore recorded, melting at about −114°, was found. Eutectics for each of the two forms with the compound were found at −114 and −126°, respectively. Both eutectic compositions contain more than 95 mole per cent. ether.

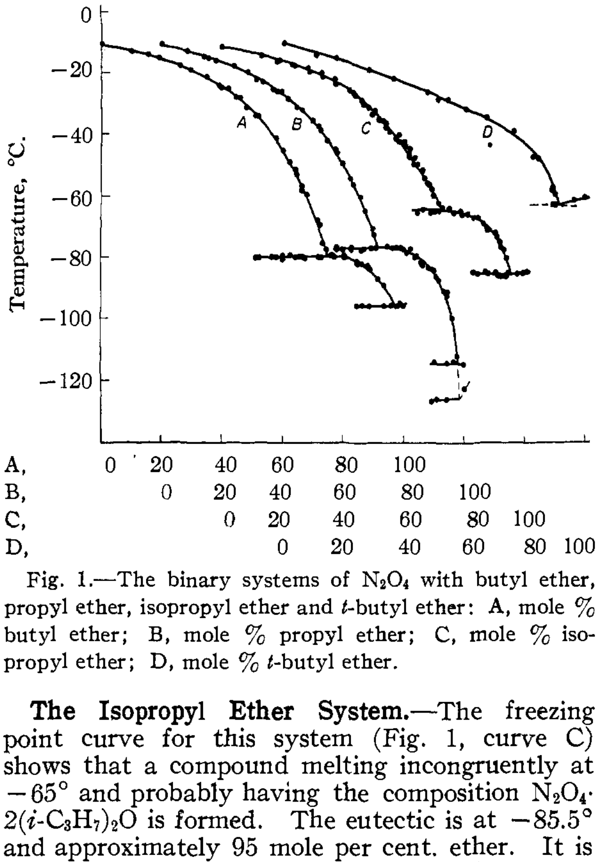

Fig. 1.—The binary systems of N_2O_4 with butyl ether, propyl ether, isopropyl ether and *t*-butyl ether: A, mole % butyl ether; B, mole % propyl ether; C, mole % isopropyl ether; D, mole % *t*-butyl ether.

The Isopropyl Ether System.—The freezing point curve for this system (Fig. 1, curve C) shows that a compound melting incongruently at −65° and probably having the composition $N_2O_4{\cdot}2(i\text{-}C_3H_7)_2O$ is formed. The eutectic is at −85.5° and approximately 95 mole per cent. ether. It is worth noting that synthetic mixtures in this system containing less than 35 mole per cent. ether always became somewhat colored even at their freezing points. It is believed that the ether tends to slowly undergo oxidation in the presence of dinitrogen tetroxide at higher temperatures. In one instance a vigorous (though not explosive) reaction occurred to yield a solution with a strong odor of acetic acid and from which, on standing, needle-like crystals melting at 128–133° were deposited.

The *n*-Butyl Ether System.—Data for the *n*-butyl ether–dinitrogen tetroxide system (Fig. 1, curve A) show that a compound melting incongruently at −79.5° and probably having the composition $N_2O_4{\cdot}2(n\text{-}C_4H_9)_2O$ is formed. A eutectic was found at −95.5° and approximately 95 mole per cent. ether.

The *t*-Butyl Ether System.—Whereas a slow oxidation–reduction reaction takes place between this ether and dinitrogen tetroxide, it was possible to obtain freezing points on the mixtures by not warming them any higher than necessary and by taking all points on a given sample within a short period of time. Because of some oxidation–reduction, all mixtures containing more than 10 mole per cent. dinitrogen tetroxide had some green color in them. Except at the dinitrogen tetroxide-rich end, only the freezing points of samples with no more than a very small amount of color were used. As a result of the higher freezing points of the mixtures in the dinitrogen tetroxide-rich end and the greater concentration of dinitrogen tetroxide, the oxidation–reduction reaction was somewhat faster, and thus the freezing points are not as good in this region.

Although the freezing points (Fig. 1, curve D) over the entire range are probably not as accurate as those obtained on previous systems, it was possible to show that no addition compound is formed between *t*-butyl ether and dinitrogen tetroxide. A eutectic occurs at −62° and 91 mole per cent. ether.

The 1,3-Dioxane System.—The data for this system (Fig. 2, curve A) indicate that 1,3-dioxane forms a 1:1 addition compound with dinitrogen tetroxide. This compound is a white solid melting at 2.0°. Eutectics were found at −26° and 22 mole per cent. of ether and at −45.5° and about 91 mole per cent. ether.

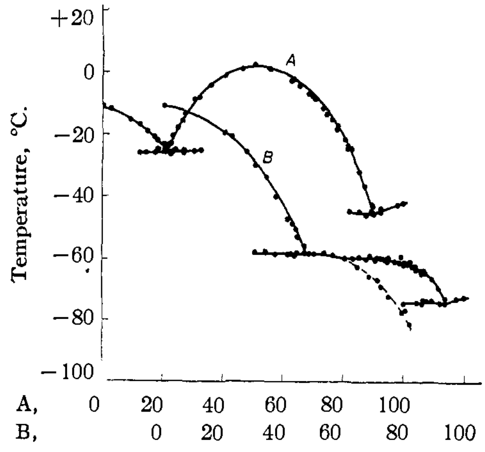

Fig. 2.—The binary systems of N_2O_4 with 1,3-dioxane and with ethylene glycol diethyl ether: A, mole % 1,3-dioxane; B, mole % ethylene glycol diethyl ether.

The Ethylene Glycol–Diethyl Ether System.—Study of this system was rendered difficult because of the very strong tendency for mixtures in this system to supercool. These data (Fig. 2, curve B) may be provisionally interpreted as indicating the formation of very unstable compounds of the formulas $N_2O_4{\cdot}2C_2H_5OCH_2CH_2OC_2H_5$ (m.p. approx. −59 to −60°) and $N_2O_4{\cdot}C_2H_5OCH_2CH_2OC_2H_5$ (m.p. approx. −58 to −59°). The maxima in these curves are so broad and the intersection of the curve for the second of the above phases with the curve for dinitrogen tetroxide is so close to the 50 mole per cent. mark that this interpretation is open to reasonable doubt. It is quite apparent, however, that compounds formed in this system, regardless of their composition, are of very limited stability.

The Perfluorotetrahydrofuran System.—The data for this system (Fig. 3, curve B) indicate no compound formation. Because of the tendency for mixtures containing high mole percentages of the ether to form glasses the eutectic in this region was not located.

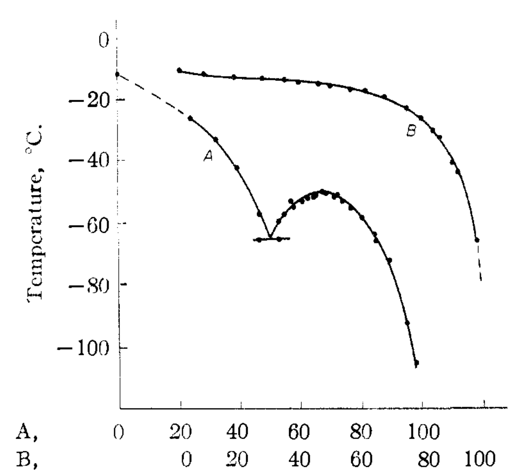

Fig. 3.—The binary systems of N_2O_4 with α-methyltetrahydrofuran and perfluorotetrahydrofuran: A, mole % α-methyltetrahydrofuran; B, mole % perfluorotetrahydrofuran.

The Trioxane System.—The data for the dinitrogen tetroxide–trioxane system (Fig. 4) show that a compound melting incongruently at −11° and probably having the composition $N_2O_4 \cdot C_3H_6O_3$ is obtained. A eutectic occurs at −29° and 26 mole per cent. trioxane. Difficulties were encountered in the region 70 to 100 mole per cent. trioxane because of the high vapor pressures of the mixtures at their melting points. In this region considerable pressures of nitrogen dioxide above the condensed phase could be observed and there was considerable tendency of trioxane to sublime to the upper portions of the cell.

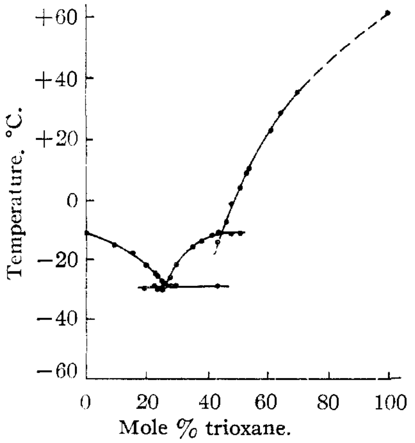

Fig. 4.—The system trioxane–dinitrogen tetroxide.

The α-Methyltetrahydrofuran System.—Oxidation–reduction slowly occurs in this system and reduces the accuracy of the freezing point determinations. This error was minimized by not heating the mixtures any higher than absolutely necessary and by taking freezing points promptly after mixing the two components. The region of 0 to 20 mole per cent. ether was not investigated, however, for a vigorous reaction occurred in the 20 mole per cent. mixture when it was warmed to −20°. The results (Fig. 3, curve A) show the formation of the stable compound $N_2O_4 \cdot 2C_4H_7(CH_3)O$ melting at −50.5°. A eutectic occurs at −65.5° and 50 mole per cent. ether. A second eutectic (between 98 and 100 mole per cent. ether) was not determined because of glass formation in the system.

Discussion and Conclusions

A comparison of the freezing point curves for the binary systems dinitrogen tetroxide–*n*-propyl ether, dinitrogen tetroxide–isopropyl ether, and dinitrogen tetroxide–*n*-butyl ether with the curves for the ethyl ether system[1] indicates that increasing the bulk of the hydrocarbon radicals attached to the ether oxygens decreases the stability of the addition compounds with dinitrogen tetroxide. This postulate of steric interference with compound formation is given further confirmation by the fact that *t*-butyl ether with its even more bulky alkyl groups forms no addition compound with dinitrogen tetroxide, whatsoever. This is in spite of the fact that, in terms of electron density, the oxygen atom in *t*-butyl ether should be the most basic of the series studied. In view of the fact that a nitrogen atom attached to two oxygen atoms and one other nitrogen atom as in the N_2O_4 molecule (the N–N bond is somewhat attenuated, to be sure)[4] should be somewhat "crowded" with respect to acting as an electron acceptor, the steric effects postulated in explaining our results are certainly not unreasonable. Furthermore, the appearance of these effects supports the theory that the dinitrogen tetroxide–ether addition compounds are formed through coördination of the basic oxygens of the ethers with the nitrogen atoms of the N_2O_4 molecule acting either separately or together as a single positive center.

In the preceding paper in this series[1] two alternative structures for the exceptionally stable $N_2O_4 \cdot$1,4-$O(CH_2CH_2)_2O$ compound were suggested. One postulated an indefinitely extended chain-like structure resulting from the bifunctional character of the 1,4-dioxane molecule. The other postulated a bicyclic structure in which one dioxane oxygen was coördinated with one nitrogen of the N_2O_4 molecule and the other dioxane oxygen with the other nitrogen atom. The fact that the compounds formed by the bifunctional molecule ethylene glycol–diethyl ether with dinitrogen tetroxide are much less stable (as indicated by the characteristics of their cooling curves) than those formed by 1,4-dioxane would seem to favor the latter of the above two postulated structures. For, though the ethylene glycol–diethyl ether could enter into either of the two types of structures, its failure to form compounds of high stability indicates that the high stability of this 1,4-dioxane complex is not simply the result of the bifunctionality of the dioxane

(4) J. Broadley and J. Robertson, *Nature*, **164**, 915 (1949).

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

Received June 8, 1953

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.)