

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

Molecular Addition Compounds of Dinitrogen Tetroxide. VI. Binary Systems with Trimethylene Oxide, 2,5-Dimethyl Tetrahydrofuran and 1,3-Dioxolane

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RECEIVED OCTOBER 5, 1955

The binary systems of dinitrogen tetroxide with the ethers trimethylene oxide, 2,5-dimethyltetrahydrofuran and 1,3-dioxolane, respectively, have been studied by the cryoscopic method. Trimethylene oxide give the compounds $N_2O_4 \cdot C_3H_6O$ and $N_2O_4 \cdot 2C_3H_6O$. 2,5-Dimethyltetrahydrofuran gives only the compound $N_2O_4 \cdot 2(CH_3)_2C_4H_8O$. 1,3-Dioxolane gives the compound $3N_2O_4 \cdot 2C_3H_6O_2$. In the latter system there is some indication of what might be a 1:1 or 1:2 compound.

During the past few years we have been investigating the ability of dinitrogen tetroxide to form molecular addition compounds with a variety of ethers and tertiary amines.¹ The present paper reports the results of the latest in this series of studies, *viz.*, the investigation by cryoscopic methods of the binary systems N_2O_4 -trimethylene oxide, N_2O_4 -2,5-dimethyltetrahydrofuran and N_2O_4 -1,3-dioxolane.

Experimental

Preparation of Materials.—The purification and handling of dinitrogen tetroxide has been described in previous communications in this series.¹

Trimethylene oxide was prepared by the method of Noller² from γ -chloropropyl acetate which was in turn prepared from 1-chloro-3-propanol by the method of Allen and Spangler.³ The crude trimethylene oxide was dried over KOH pellets, over freshly fused KOH, distilled, allowed to stand for 24 hours over sodium wire and again distilled, and the middle fraction boiling at 47.5–47.8° collected (literature value 47.5–47.9°). The value for n_D^{25} for the product was 1.3892 in good agreement with the literature value 1.3895 ± 0.0002 .⁴

The 2,5-dimethyltetrahydrofuran was prepared from 2,5-hexanediol, by the method of Reynolds and Kenyon,⁵ using pyridine as solvent and benzene sulfonyl chloride as cyclizing agent. The product was dried over sodium and fractionated. The boiling point of the purified product was 90.5–91.5° (literature value⁶ 90.5–91.0°). An excessive tendency toward supercooling made it impossible to check the purity of this material by freezing point.

1,3-Dioxolane was obtained from Carbide and Carbon Chemicals Company. It was dried over potassium and then over sodium, and was fractionated, the fraction boiling at 74.0–74.8° being collected (literature value 74–75°). Its freezing point was –95.3° in good agreement with the literature value –95°.⁷

Procedure.—The freezing point-composition diagrams for the binary systems were determined by methods previously described.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, all glass cell equipped for continuous magnetic stirring. In all three of these systems there was a tendency toward slow oxidation-reduction reactions. This effect was minimized by not warming the mixtures any higher than necessary and by frequently taking fresh samples. In some instances, however, this factor, or an excessive tendency to supercool, made the obtaining of accurate data impossible.

Results

The Trimethylene Oxide System.—The data for this system are recorded graphically by curve A in Fig. 1. This curve shows two well-defined

maxima indicating the formation of two compounds having ether to dinitrogen tetroxide mole ratios of 1:1 and 2:1, both with congruent melting points of approximately –53°. Three eutectics appear, at –99.8° and 94 mole % ether, at –58.5° and 57 mole % ether, and at –55.4° and 43 mole %. At 80.5° and 86.5 mole % ether there is a break in the curve which could indicate either a third and incongruently melting compound or else polymorphism of the 2:1 compound. In order to distinguish between these two possibilities the cooling curve for the mixture containing 73.2 mole % ether was examined more closely. If the break in question were due to an incongruently melting compound, the eutectic halt at –99.8° would not appear on the cooling curve. If, however, the break were due to polymorphism of the 2:1 compound this eutectic halt would appear. The cooling curve for the 73.2 mole % mixture does show a typical eutectic halt in the neighborhood –100° so we have concluded that the 2:1 compound exists in two crystalline forms.

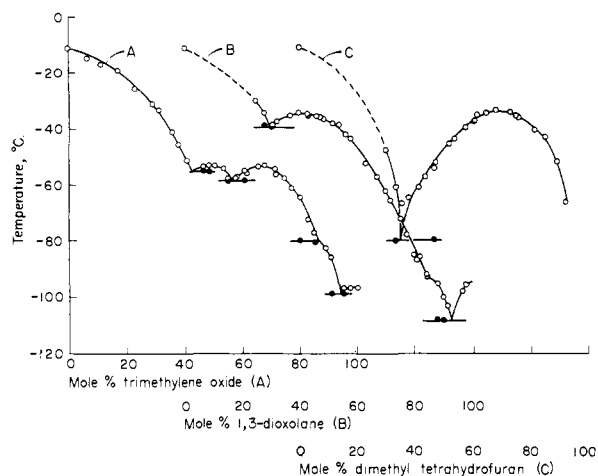


Fig. 1.

In this system there was evidence of some oxidation-reduction as the mixtures become more concentrated in dinitrogen tetroxide. Also, a considerable degree of supercooling was encountered in the ether-rich mixtures.

The 2,5-Dimethyltetrahydrofuran System.—The data for this system are recorded graphically in curve C, Fig. 1. These data show clearly the formation of a compound having a 2:1 mole ratio of ether to dinitrogen tetroxide, which melts congruently at –34°. A eutectic appears in this system at –80° and 36 mole % of ether. Another

- (1) H. H. Sisler, *et al.*, THIS JOURNAL, **74**, 877 (1952); **75**, 4175 (1953); **75**, 5188 (1953); **75**, 5191 (1953); **76**, 4668 (1954).
- (2) C. R. Noller, *Organic Syntheses*, **29**, 92 (1949).
- (3) C. F. H. Allen and F. W. Spangler, *ibid.*, **29**, 33 (1949).
- (4) J. S. Allen and H. Hibbert, THIS JOURNAL, **56**, 1398 (1934).
- (5) D. D. Reynolds and W. O. Kenyon, *ibid.*, **72**, 1593 (1950).
- (6) E. V. Whitehead, *et al.*, *ibid.*, **73**, 3632 (1951).
- (7) W. Baker and F. Field, *J. Chem. Soc.*, 86 (1932).

eutectic probably occurs at about 97 mole % of ether, but, because of severe supercooling, the freezing point curve in the region of 97 to 100 mole % of ether was not determined. All mixtures of dinitrogen tetroxide and 2,5-dimethyltetrahydrofuran showed a blue color which deepened gradually toward N_2O_4 -rich end of the system, indicating an increasing tendency toward oxidation-reduction as the concentration of the oxide increases. One mixture containing 75 mole % N_2O_4 exploded rather violently during the warm up period preceding the taking of the cooling curve. The region of 70 to 100 mole % N_2O_4 , therefore, was not further investigated.

The 1,3-Dioxolane System.—The data for this system (curve B, Fig. 1) show that a stable compound is formed having a 2:3 mole ratio of dioxolane to dinitrogen tetroxide, with a congruent melting point of about -34.7° . Since this is unlike any compound previously reported in systems of this type, the system was rechecked very carefully and the results confirmed. Another break, probably due to a compound having an incongruent melting point occurs at about -90° and 82 mole % dioxolane. No meritectic halts or breaks indicating existence of a metastable phase could be detected on the cooling curves of mixtures on the dinitrogen tetroxide side of this break, but a careful study of the freezing points in this region shows definitely that the break in the freezing point curve is real. Eutectics occur at -108.4° and 92 mole % dioxolane and -39.2° and 30% dioxolane.

When as much as 20 mole % of dinitrogen tetroxide had been added to the dioxolane, a pale blue color appeared, and this color became gradually deeper as the concentration of dinitrogen tetroxide increased. Because of this it was decided not to attempt investigation of the region from 75 to 100 mole % dinitrogen tetroxide.

An attempt was made to determine the nature of the 2:3 compound formed in this system by making a mixture of the reactants in a 2:3 mole ratio, allowing the compound to decompose at room temperature and studying the residue. It was found that the decomposition proceeds very violently. After the brown vapors had stopped coming off, a pale yellow liquid remained which had a noticeably higher viscosity than the dioxolane itself.

Discussion and Conclusions

A comparison can be made of the behavior of the trimethylene oxide-dinitrogen tetroxide system with that of the tetrahydrofuran-dinitrogen tetroxide and tetrahydropyran-dinitrogen tetroxide systems. Previous communications¹ have shown that tetrahydrofuran forms two compounds with dinitrogen tetroxide having 1:1 and 2:1 mole ratios of ether to dinitrogen tetroxide. However, tetrahydropyran forms only a 2:1 compound with dinitrogen tetroxide. The fact that the steric effects of the α -methylene groups in the five-membered ring are considerably smaller than in the six-membered ring was offered as a possible explanation for this, since this effect would cause the basicity of the tetrahydrofuran to be higher than that of the tetrahydropyran. It was postulated that this higher basicity might stabilize the 1:1 compound.

This line of reasoning can be extended to the trimethylene oxide-dinitrogen tetroxide system. It would be expected that the small, compact ring of this ether would offer even less steric hindrance to compound formation and hence be more basic than either the corresponding five- or six-membered rings. This would be in line with formation of a 1:1 compound of almost equal stability to the 2:1 compound in this system. This increase in basicity in going from a six- to a four-membered ring is in agreement with the conclusions reached by Searles and Tamres⁸ following their study of hydrogen bonding in these ethers. These workers showed that the hydrogen bonding in these cyclic ethers increases in the following order: trimethylene oxide > tetrahydrofuran > tetrahydropyran.

Comparing the α -methyltetrahydrofuran-dinitrogen tetroxide system¹ and the 2,5-dimethyltetrahydrofuran system, it is seen that their behavior is very similar, both forming stable compounds having 2:1 ether to dinitrogen tetroxide mole ratios. Both these ethers are strong bases compared to the unsubstituted ether because of the increased electron density on the oxygen atoms due to the electron donor effect of the methyl groups. Though the result was somewhat unexpected, it appears that the methyl groups on the carbons in these ethers offer little steric hindrance, or else the steric effect they do have is offset by the increase in electron density produced on the oxygen atoms.

The compound in the 1,3-dioxolane-dinitrogen tetroxide system having a 2:3 mole ratio of ether to N_2O_4 is quite unlike any other compounds reported previously¹ in this series. However, Gresham⁹ has shown that 1,3-dioxolane undergoes acid-catalyzed polymerization to products of the type $(-CH_2-O-CH_2-CH_2-O-)_x$ whose exact structure is not known. It may thus be that the formation of the 2:3 phase in this system has involved some ring-fission. However, this point remains to be clarified. The viscous residue remaining after decomposition of the 2:3 phase is suggestive in this regard.

The break on the phase diagram of this system at -90° and 82 mole % dioxolane is probably due to the formation of a compound having an incongruent melting point. Because of the similar oxygen-to-oxygen distances in all three compounds, the behavior here might be comparable to that of 1,4- and 1,3-dioxane. If such a comparison is valid, it would be expected that this incongruently melting compound would have a 1:1 mole ratio of reactants. However, as far as the data are concerned it could equally well be a 2:1 compound. In the region of this break the temperature and concentration of dinitrogen tetroxide may both be too low to produce ring fission, but as both these variables are increased, the breaking of the ring may proceed at the expense of the incongruently melting compound. Since such a polymerization would not be reversible, this would explain the fact that no points indicating a meritectic could be picked up on the N_2O_4 -rich side of the break.

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(8) S. Searles and M. Tamres, *THIS JOURNAL*, **73**, 3704 (1951).

(9) W. F. Gresham, U. S. Patent 2,394,910 (1946).