[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Effect of Ring Size on the Infrared Spectra of Cyclic Ethers. Characteristic Frequencies of Trimethylene Oxides and Tetrahydrofurans

BY GORDON M. BARROW AND SCOTT SEARLES

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The infrared spectra of several trimethylene oxides and tetrahydrofurans have been obtained. These rings are characterized by very strong bands at 10.2 to 10.3 and 9.1 to 9.3 μ respectively. The trimethylene oxides also show consistently strong bands at 8 microns. It is also shown that these strong infrared bands fit in regularly with similar bands of the 3- and 6-membered rings. It is shown that this series of infrared bands arises from an antisymmetric type vibration of the ether links and that corresponding vibrations of the cyclic hydrocarbons give rise to frequencies which form a similar series. The strong polarized Raman bands of these series are also added for comparison.

The infrared spectra of the cyclic ethers have not been studied sufficiently to allow the assignment of infrared bands for the general identification of these compounds. Although a number of ethylene oxides have been studied,[1] the trimethylene oxides have not been investigated in the infrared and the infrared spectra of only the unsubstituted tetrahydrofuran and tetrahydropyran are available.[1,2] It seemed of interest to measure the infrared spectra of several trimethylene oxides and tetrahydrofurans available in this Laboratory and to consider possible assignments of the bands observed.

A correlation of some of the Raman bands of 3-, 4-, 5- and 6-membered rings, including the ethers, has been discussed by Kohlrausch and Reitz[3] but no similar attempt has been made in the infrared. Another purpose of this work was to compare the effect of ring size on certain infrared active ring vibrations with that observed by Kohlrausch and Reitz in the Raman spectra.

Experimental

Materials.—The compounds used were fractionally distilled through a six inch Fenske column packed with glass helices. Only the middle cuts were used, physical constants for which were: trimethylene oxide, b.p. 47° (750 mm.), $n^{25}\text{D}$ 1.3893; 1-methyltrimethylene oxide, b.p. 60° (747 mm.), $n^{25}\text{D}$ 1.3890; 1,1-dimethyltrimethylene oxide, b.p. 70° (752 mm.), $n^{25}\text{D}$ 1.3878; 2,2-dimethyltrimethylene oxide, b.p. 76–78°; 1-phenyltrimethylene oxide, b.p. 81° (4 mm.), $n^{25}\text{D}$ 1.5321; tetrahydrofuran, b.p. 65° (750 mm.), $n^{25}\text{D}$ 1.4440; 1-methyltetrahydrofuran, b.p. 80° (755 mm.), $n^{21}\text{D}$ 1.4060; 2,5-dimethyltetrahydrofuran, b.p. 88° (750 mm.), $n^{23}\text{D}$ 1.4018. The synthesis of 1-methyltrimethylene and 1-phenyltrimethylene oxide will be described in a separate communication.

Discussion

The trimethylene oxides are immediately characterized by very strong bands at 10.2 to 10.3 μ. In view of the strength and constancy of these bands and correlation with other cyclic ethers they are considered to arise from a ring vibration, involving particularly the ether links. Some other bands in the spectra can be readily assigned. These include the CH_2, CH_3 bending vibration at 6.9 μ and the methyl deformation mode at 7.3 μ occurring in the methyl substituted compounds. The prominent band at about 8 μ, (8.3 μ for 1-phenyltrimethylene oxide) probably due to a methylene wagging motion, occurs fairly generally in compounds containing this group. However, the unusual strength of this band in the trimethylene oxides investigated suggests that it may be a useful band, together with that at 10.2, 10.3 μ, to characterize such compounds. It is interesting that the spectra of trimethyleneimine and trimethylene sulfide, both of which have recently been obtained in this Laboratory, as well as that of cyclobutane[4] show strong bands at 8 μ. The strong trimethylene oxide band at 11.1 μ shifts, or breaks up, in the substituted compounds and bands of somewhat longer wave length appear. In this region both ring and CH_2 rocking vibrations are expected. In tetrahydropyran a strong infrared band at 11.4 μ has been assigned by Burket and Badger[2] to a ring vibration and a weaker band at slightly longer wave length to a CH_2 rocking mode.

The tetrahydrofuran spectra follow a similar pattern to that found for the trimethylene oxides. The principal characteristic of the 5-membered rings is a strong band occurring at 9.1 to 9.3 μ. The CH_2, CH_3 band again occurs at 6.85 and the CH_3 band comes in at 7.2 in the methyl substituted compounds. Beside this band a CH_2 vibration now shows up at 7.4 μ. The strong 8-μ band of the trimethylene oxides is markedly absent in these 5-membered rings and possibly has shifted to the rather broad band of medium intensity at 8.4 or 8.5 μ. The strong 11-μ band of tetrahydrofuran breaks up in the substituted compounds giving rise to several bands not readily assignable.

It is interesting to compare the prominent features of the infrared and Raman spectra of the 3-, 4-, 5- and 6-membered ring hydrocarbons and ethers. Kohlrausch and Reitz[3] have calculated the frequencies of the skeletal vibrations on the basis of a simple force field and have compared some of the Raman data with the expected frequencies. The totally symmetric ring breathing vibrations give rise to strong polarized Raman lines for both series of compounds, that for the hydrocarbons being somewhat better defined. The frequencies tend to lower values for the larger rings (Fig. 3) as was calculated by Kohlrausch and Reitz on the basis of one value for the bond force constant for all members of the series. The trend, therefore, is primarily a reduced mass effect and to detect changes in bond force constants along the series would require a rather detailed calculation of the

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[1] O. D. Shreve, M. R. Heether, H. B. Knight and D. Swern, *Anal. Chem.*, **23**, 277 (1951).

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

[3] K. W. F. Kohlrausch and A. W. Reitz, *Z. physik. Chem.*, **45B**, 249 (1940).

[4] A.P.I. Research Project 44, Carnegie Institute of Technology Catalog of Infrared Spectral Data, No. 1158, contributed by the University of California, Berkeley.

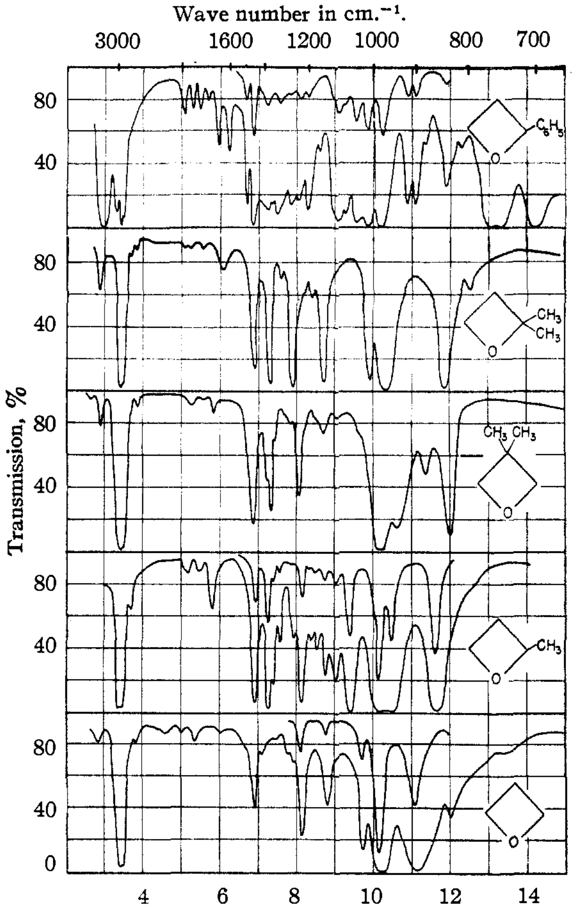

Fig. 1.—Infrared spectra of liquid trimethylene oxides in 0.03 mm. cell and as 10% solutions in CCl_4 in 0.03 mm. cell.

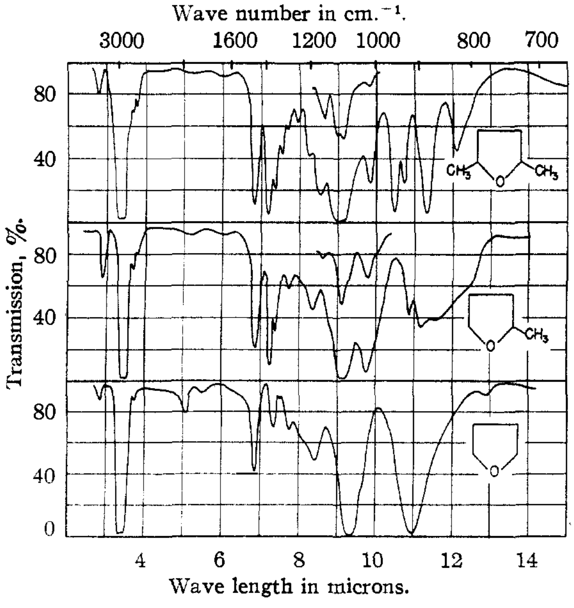

Fig. 2.—Infrared spectra of liquid tetrahydrofurans in 0.03 mm. cell and as 10% solutions in 0.03 mm. cell.

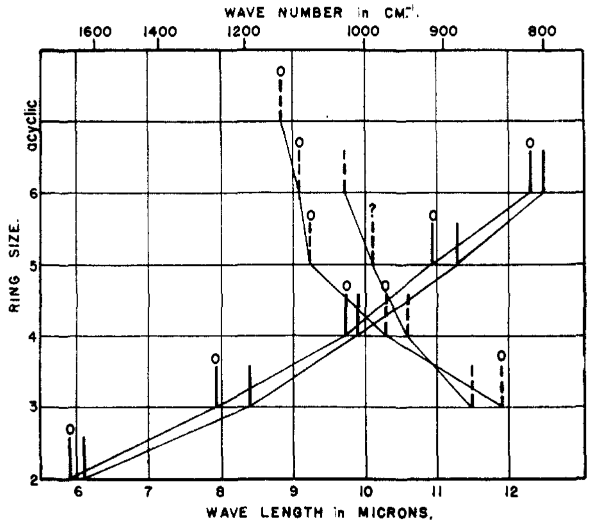

Fig. 3.—Symmetric stretching vibration frequencies of cyclic ethers, ⫯, and cyclic hydrocarbon, | ; and antisymmetric stretching vibration frequencies of cyclic ethers, ⫯, and cyclic hydrocarbons, ¦, for ring sizes of 2 to 6 atoms and for open chain ethers.

principal and interaction force constants of these compounds. The correlation of Raman frequencies can be extended to the ethylene and carbonyl groups considered as 2-membered rings as is shown in Fig. 3.

The infrared spectra of the hydrocarbons, as is to be expected, show no prominent bands which can be unambiguously assigned to ring stretching modes. The cyclic ethers do, however, show such bands which are easily identifiable, as has been shown for the 4- and 5-membered rings. For the 3-membered ring we identify this band as that occurring consistently at 11.9 μ in the spectra of the ethylene oxide derivatives. The spectrum of ethylene oxide itself is rather more complicated and the corresponding band apparently appears at about 11.7 μ. It should be remarked, however, that a 10.9-μ band appears fairly strongly in most of the ethylene oxide compounds and this band would fit in better with our correlation. The spectra of tetrahydropyran derivatives are not available but from that of the compound itself it appears that the strong band at 9.1 μ is the analog for the 6-membered ring. Likewise, the consistent strong band of the open chain ethers at 8.6 to 9.1 μ is undoubtedly a similar mode of vibration.

Considerable evidence exists that this series of strong infrared bands arises from an essentially antisymmetric stretching motion of the ether links. The antisymmetric, B_1, skeletal stretching mode of dimethyl ether has been assigned to a 9-μ band by Crawford and Joyce[5] and the position of this band remains fairly well fixed throughout all the open chain ethers. For ethylene oxide a band at 11.9 μ has been assigned to the B_1 ring deformation.[6] For a 4-membered ring a simple valence force field calculation shows that the antisymmetric vibration we are dealing with should have the same frequency as the totally symmetric mode and the observed infrared band, 10.2–10.3 μ, is sufficiently close to the Raman band at 9.75 μ. This trend in frequency with ring size (Fig. 3)

(5) B. L. Crawford and L. Joyce, *J. Chem. Phys.*, **7**, 307 (1939).

(6) H. W. Thompson and W. T. Cave, *Trans. Faraday Soc.*, **47**, 946 (1951).

indicates that the $9.1\text{-}\mu$ band of tetrahydropyran is of type A'' and is to be associated with the A_{1u} band of cyclohexane and the A_u band of *p*-dioxane. Although this is not the assignment accepted by Burket and Badger[2] it is not in serious disagreement with their work.

Although it is not expected that a vibration of this type will necessarily give rise to prominent infrared bands in the hydrocarbon series, we can attempt to choose from previous assignments for these molecules those vibrations which correspond to analogs of the antisymmetric stretching vibrations of the ethers. For cyclopropane this is the degenerate ring deformation at $11.5\ \mu$. For cyclobutane Wilson[7] has assigned $10.6\ \mu$ to the B_{1g} vibration. The A_{1u} band of cyclohexane has been given the value $9.7\ \mu$ by Beckett, Pitzer and Spitzer.[8] Assignments for cyclopentane are less definite. The most satisfactory correlation is provided by choosing the mean of the two bands at 9.7 and $10.5\ \mu$ interpreted by Miller and Inskeep[9] as arising from the splitting of the E_2' ring deformation due to lack of complete planarity of the ring.

The regularities in the series of strong infrared bands of the cyclic ethers and the assigned antisymmetric vibrations of the corresponding hydrocarbons are shown, together with the Raman frequencies in Fig. 3. Although the trends are not so parallel as in the case of the totally symmetric vibrations, it seems clear that in both the ether and hydrocarbon series we are dealing with a similar type of vibration, *i.e.*, one in which we can picture the ring as undergoing a deformation consisting approximately of stretching and compression of alternate bonds.

The trend of the infrared bands of the cyclic ethers leading to that for the open chain ethers suggests also that the B_1 skeletal stretching mode for propane should, in view of the cyclic hydrocarbon series, be assigned a value of about $9.5\ \mu$ unless a rather large interaction exists in this molecule. Such interactions have been suggested by McMurry and Thornton[10] but assignment of this vibration to a band at $9.5\ \mu$ has been made by Gates[11] while values of about $10.8\ \mu$ have been suggested by Wu and Barker[12] and by Pitzer.[13]

As with the Raman bands it appears that the trend of frequencies of the infrared bands to greater frequencies with increasing ring size is a reduced mass effect rather than an immediate consequence of bond strain in the smaller rings. We will present shortly a more detailed account of the spectra of trimethylene oxide and trimethyleneimine and we hope then to be able to determine reasonably reliable force constants for these molecules.

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EVANSTON, ILLINOIS

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[7] T. P. Wilson, *J. Chem. Phys.*, **11**, 369 (1943).

[8] C. W. Beckett, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2488 (1947).

[9] F. A. Miller and R. G. Inskeep, *J. Chem. Phys.*, **18**, 1519 (1950).

[10] H. L. McMurry and V. Thornton, *ibid.*, **19**, 1014 (1951).

[11] D. M. Gates, *ibid.*, **17**, 393 (1949).

[12] V. L. Wu and E. F. Barker, *ibid.*, **9**, 487 (1941).

[13] K. S. Pitzer, *ibid.*, **12**, 310 (1944).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Some Factors Which Influence the Iodine Affinity of Amylose as Shown by Potentiometric Titration[1]

BY EUGENE F. PASCHALL AND JOSEPH F. FOSTER

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The effects of certain experimental variables on the iodine titration behavior of several amylose preparations are investigated. Results obtained clearly do not represent an equilibrium state but reflect the previous history of the amylose preparations. Of particular importance are the time of aging of the alkaline solution prior to neutralization, and the time of aging and *p*H of the solution following neutralization. The affinity of amylose for iodine is enhanced by pretreatment with iodine. An attempt is made to interpret the results in terms of the state of aggregation of the amylose molecules.

The potentiometric titration method for study of the iodine-binding properties of starch and its fractions as introduced by Bates, *et al.*,[2] has proved of outstanding value for the estimation of amylose content. It has been shown that there is some correlation between binding affinity of amylose preparations and molecular weight.[2,3] Furthermore, since the reaction appears to be an all-or-none phenomenon,[3,4] amylose molecules tending to saturate successively with iodine, the intriguing possibility exists that if the titration could be carried out under equilibrium conditions it should be possible to determine molecular weight distributions by this technique. As a preliminary step in this direction a study has been made of some factors which influence the titration behavior of amylose. It is shown that equilibrium does not prevail under the condition customarily employed and that secondary effects are sufficient to mask completely relatively minor differences resulting from variation in molecular weight distribution.

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[1] Journal Paper No. J-2143 of the Iowa Agricultural Experiment Station, Ames, Iowa, Project 817. Supported in part by a grant from the Corn Industries Research Foundation. Taken from a thesis presented by E. F. Paschall in partial fulfillment of the requirements for the degree Doctor of Philosophy, Iowa State College, 1951.

[2] F. L. Bates, D. French and R. E. Rundle, THIS JOURNAL, **65**, 142 (1943).

[3] J. F. Foster, Ph.D. Thesis, Iowa State College, 1943.

[4] R. E. Rundle, J. F. Foster and R. R. Baldwin, THIS JOURNAL, **66**, 2116 (1944).