[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF THE UNIVERSITY OF MICHIGAN AND OF KANSAS STATE COLLEGE]

Hydrogen Bonding Abilities of Cyclic Sulfoxides and Cyclic Ketones[1]

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The effect of ring size on the electron donor ability of an oxygen atom in saturated cyclic ketones (4- to 7-membered ring) and cyclic sulfoxides (4- to 6-membered ring) has been studied. The experimental criterion employed was the ability of these compounds to form hydrogen bonds with (1) chloroform, as determined by heats of mixing, and with (2) methanol-*d*, as determined by the shifts in O–D frequency. For the cyclic ketones, the variation of basicity with ring size is in the order 7- > 6- > 5- > 4-membered ring, while for the cyclic sulfoxides it is 6- ≥ 5- > 4-membered ring. These results contrast markedly with those observed for saturated cyclic ethers.

Introduction

It has been established through studies on hydrogen bonding with chloroform and methanol-*d*[2], through the determination of the stabilities of iodine complexes,[3] and through an investigation of proton magnetic resonance[4] that the basicity of cyclic ethers varies with ring size in the order 4- > 5- > 6- > 3-membered ring. However, hydrogen bonding studies with lactones[5] give a basicity order 6- > 5- > 4-membered ring. It was shown for the lactones that the carbonyl and not the alkoxyl oxygen was the one involved in forming hydrogen bonds. This suggested that ring size effects are markedly different depending upon whether the oxygen atom is inside or outside the ring. It was thought of interest to investigate further this effect on an oxygen atom attached to different size rings, and the results of hydrogen bonding studies on cyclic ketones and cyclic sulfoxides are presented in this paper.

Experimental

Apparatus and Methods.—The calorimetric technique used for the heat of mixing determinations was similar to that used previously[2,5] and which had been reported by Zellhoefer and Copely.[6] A modification in calorimeter construction consisted of sealing a platinum cup to a 34/28 female joint which could be attached to the male part. The calorimeter was supported and held rigid by an assembly consisting of three long screws which passed through a fitted brass plate on which the platinum cup was seated and which were attached to a brass ring around the neck of the male 34/28 joint.

Weighed quantities of ketone or sulfoxide were sealed in thin-walled ampoules. Because of the hygroscopic nature of the sulfoxides, the ampoules were filled inside a dry-box. The ampoule was placed in the calorimeter and an equimolecular quantity of chloroform or carbon tetrachloride was added. After temperature equilibrium was established, mixing was accomplished by crushing the ampoule and stirring the contents in the calorimeter.

At least two determinations were made of the heat of mixing with chloroform in this manner, with the exception of pentamethylene sulfoxide. This compound is a solid and the heats of mixing with chloroform were run on solutions of the sulfoxide in carbon tetrachloride at various concentrations. The average deviation of the mean of the results was about 6 calories per mole of solution. Only single determinations of the heats of mixing with carbon tetrachloride were made.

The spectroscopic method used for determining the hydrogen bonding abilities of the cyclic ketones and cyclic sulfoxides has been described previously.[2a,7] As in those studies, the reference system consisted of a 0.1 molar solution of methanol-*d* in carbon tetrachloride, and gave a monomeric OD band at 2689 cm.$^{-1}$. The centers of the hydrogen bonded OD bands in the 1.0 molar solutions of methanol-*d* in the ketones were determined after subtracting the absorption of the pure ketone in the same absorption cell, as has been described previously.[5,8] Reproducibility of the OD shifts was of the order of 2 cm.$^{-1}$ for the ketone solutions and about two to three times that for the sulfoxide solutions, the OD band in the latter solutions being much more broad. Measurements were made with a Perkin–Elmer model 12B spectrometer equipped with lithium fluoride optics, and some of the results were checked with a Perkin–Elmer model 21 spectrometer using a calcium fluoride prism. The latter instrument was equipped with sodium chloride optics for the studies on sulfoxide frequencies. A polystyrene film was used for standardization.

Materials.—The cyclobutanone used in this work was kindly provided by Dr. F. E. Blacet. The other ketones were the best cuts from fractional distillation of commercial products of good grade. The boiling points and refractive indices of these compounds checked closely with the literature values in all cases.

The dimethyl sulfoxide was the gift of the Stepan Chemical Co., Chicago, Ill. The remaining sulfoxides were prepared by oxidation of the corresponding sulfide in cold acetone solution with 30% hydrogen peroxide, as described by Tarbell and Weaver.[9] The boiling points and refractive indices of the sulfoxides also agreed with literature values where such data were available. Thiacyclohexane-1-oxide was obtained in 60–75% yield as a waxy white solid, m.p. 60–61.5°, b.p. 90° (1 mm.), $n^{35}D$ 1.5080 (after standing in air a few minutes). The compound is extremely hygroscopic. *Anal.* Calcd. for $C_5H_{10}SO$: C, 50.8; H, 8.5. Found: C, 50.0; H, 8.7. Bateman, Cunneen and Ford[10] reported the following properties for this compound: b.p. 127–128° (15 mm.) and 60–62° (0.001 mm.), $n^{35}D$ 1.5080. Thiacyclobutane-1-oxide was obtained first as the generous gift of Drs. F. G. Bordwell and B. M. Pitt and also was prepared by hydrogen peroxide oxidation of thiacyclobutane in 60% yield, b.p. 102° (25 mm.), $n^{21}D$ 1.5075. *Anal.* Calcd. for C_3H_6SO: C, 39.97; H, 6.71; S, 35.57. Found: C, 39.91; H, 6.85; S, 35.45.

Methanol-*d* (b.p. 65° at 750 mm.) was prepared by the method of Redlich and Pordes.[11] Carbon tetrachloride and chloroform were purified in the manner described by Fieser.[12]

Results and Discussion

The data for the hydrogen bonding abilities of the cyclic ketones as well as some acyclic ones are given in Table I. These results are in fair agree-

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 131st Meeting of the American Chemical Society, Miami, Fla., April, 1957.

[2] (a) S. Searles and M. Tamres, THIS JOURNAL, **73**, 3704 (1951); (b) S. Searles, M. Tamres and E. R. Lippincott, *ibid.*, **75**, 2775 (1953).

[3] (a) Sister M. Brandon, M. Tamres and S. Searles, Abstracts, 130th Meeting of American Chemical Society, September, 1956, p. 53R; (b) Sister Mary Brandon Hudson, Ph.D. thesis, University of Michigan, June, 1957.

[4] H. S. Gutowsky, R. L. Rutledge, M. Tamres and S. Searles, THIS JOURNAL, **76**, 4212 (1951).

[5] S. Searles, M. Tamres and G. M. Barrow, *ibid.*, **75**, 71 (1953).

[6] G. F. Zellhoefer and M. J. Copley, *ibid.*, **60**, 1343 (1938).

[7] W. Gordy, *J. Chem. Phys.*, **7**, 93 (1939).

[8] M. Tamres, S. Searles, E. M. Leighly and D. W. Mohrman, THIS JOURNAL, **76**, 3983 (1954).

[9] D. S. Tarbell and C. Weaver, *ibid.*, **63**, 2939 (1941).

[10] L. Bateman, J. I. Cunneen and J. Ford, *J. Chem. Soc.*, 1539 (1957); reported that their compound had a 98.4% SO content, but the analytical method was not given.

[11] O. Redlich and F. Pordes, *Monatsh.*, **67**, 203 (1936).

[12] L. F. Fieser, "Experiments in Organic Chemistry," second ed., D. C. Heath, Boston, Mass., 1941, p. 365.

TABLE I

HYDROGEN BONDING OF KETONES

	Heat of mixing at 25° with 50 mole % $CHCl_3$, cal./mole	Heat of mixing at 25° with 50 mole % CCl_4, cal./mole	OD band of 1 *M* CH_3OD, cm.$^{-1}$	OD shift, cm.$^{-1}$	C=O frequency, cm.$^{-1}$	C=O shift, cm.$^{-1}$[g]
Cyclobutanone	. .	. .	2615	74	1775[d]	. .
Cyclopentanone	566	93	2598	91	1740[d]	5
Cyclohexanone	618[a]	146	2590	99[c]	1710[d]	10
Cycloheptanone	706	175	2576	113	1704[e]	9
Diethyl ketone	560	42	2611	78	1723[f]	. .
Acetone	420[b]	−75	2608	81[c]	1722[f]	6
Methyl ethyl ketone				77[e]	1718[e]	
Diisobutyl ketone				90[c]		

[a] Through an error in transcription, this was reported previously as 576 cal./mole (ref. 5). [b] C. S. Marvel, M. J. Copley and E. Ginsberg, THIS JOURNAL, **62**, 3109 (1940), report a value of 495 cal./mole at 3° for a solution of mole fraction 0.458 with respect to acetone. [c] W. Gordy and S. C. Stanford, *J. Chem. Phys.*, **8**, 170 (1940), report the following OD shifts: cyclohexanone, 117; acetone, 97; methyl ethyl ketone, 77; diisobutyl ketone, 84. Acetone and cyclohexanone were previously reported as giving OD shifts of 78 and 98, respectively (ref. 5). [d] Foil A. Miller, Chapter 2 "Organic Chemistry," Vol. III, H. Gilman, editor, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 153. [e] W. M. Schubert and W. A. Sweeney, THIS JOURNAL, **77**, 4172 (1955). [f] This research; 0.05 ml. of ketone in 1.0 ml. of carbon tetrachloride run *versus* pure carbon tetrachloride, 0.1-mm. cell, CaF_2 optics. [g] Determined qualitatively by comparing the spectrum of approximately 0.03 ml. of ketone dissolved in 2 ml. of carbon tetrachloride with the spectrum of approximately 0.03 ml. of ketone dissolved in 2 ml. of chloroform, 0.1-mm. cell, NaCl optics.

TABLE II

HYDROGEN BONDING OF SULFOXIDES

	Heat of mixing at 25° with 50 mole % $CHCl_3$, cal./mole	Heat of mixing at 25° with 50 mole % CCl_4, cal./mole	OD band of 1 *M* CH_3OD in sulfoxide, cm.$^{-1}$	OD shift, cm.$^{-1}$	S → O frequency cm.$^{-1}$	
					In CCl_4[b]	In $CHCl_3$[c]
Trimethylene sulfoxide	813	135	2561	128	1192	1073
Tetramethylene sulfoxide	1001	231	2528	161	1035	1020
Pentamethylene sulfoxide[a]	. .	. .	2533	155	1053	1031[d]
35.93 mole % in CCl_4	744					
17.55 mole % in CCl_4	598					
Diethyl sulfoxide	1082	234	2522	167	1066	1054
35.94 mole % in CCl_4	723					
17.55 mole % in CCl_4	610					
Dimethyl sulfoxide	657	−46	2530	158	1069	1054

[a] This compound is a solid at room temperature. [b] Spectra were taken on solutions of approximately 0.03 ml. of sulfoxide in 2.0 ml. of carbon tetrachloride run *versus* pure carbon tetrachloride, 0.1-mm. cell, NaCl optics. [c] Spectra were taken on solutions of approximately 0.03 ml. of sulfoxide in 2.0 ml. of chloroform run *versus* pure chloroform, 0.1-mm. cell, NaCl optics. [d] Overlaps with another band.

ment with literature values reported previously where such data are available. Similar data for the sulfoxides are given in Table II.

Barnard, Fabian and Koch[13] already have noted the unusual ability of sulfoxides to enter into hydrogen bonding and, as may be seen from the tables, they are much stronger hydrogen bonding agents than are the ketones. This strong interaction is apparent in *o*-hydroxy sulfoxides,[14] and it has been reported that the ultraviolet spectrum of sulfoxides is subject to considerable solvent effects especially when using a solvent containing a hydroxyl group.[15] Still stronger acidic solvents, such as sulfuric acid, can result in the transfer of a proton[16] to the sulfoxide to form the species R_2SOH^+.

The strength of interaction should be apparent also in the effect on the C=O and S→O vibration frequencies. Barnard, *et al.*,[13] reported a shift of about 20 cm.$^{-1}$ in the S→O frequency for a number of sulfoxides in changing from carbon tetrachloride to chloroform as the solvent. This order of magnitude was observed for the sulfoxides listed in Table II. For comparable conditions, the shift for the ketones is only about half as great.[17]

Besides this difference in hydrogen bonding ability, the sulfoxides and ketones differ also with respect to the effect on basicity due to replacement of an alkyl group by an alkoxyl group. Audrieth and Steinman[18] have measured at 3° the heats of mixing of chloroform with diethyl carbonate and with diethyl sulfite over a range of concentrations. They obtained the following maxima in the heat of mixing curves: 523 cal./mole for 44.6 mole % chloroform with diethyl carbonate, and 505 cal./mole for 39.7 mole % chloroform with diethyl sulfite. Comparing these to the heats of mixing with chloroform for diethyl ketone and diethyl sulfoxide, it may be seen that the ketone and the carbonate data are about the same, but the sulfoxide is much better in forming hydrogen bonds than

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(13) D. Barnard, J. M. Fabian and H. P. Koch, *J. Chem. Soc.*, 2442 (1949).

(14) E. D. Amstutz, I. M. Hunsberger and J. J. Chessick, THIS JOURNAL, **73**, 1220 (1951).

(15) H. P. Koch, *J. Chem. Soc.*, 2892 (1950).

(16) H. H. Szmant and G. A. Brost, THIS JOURNAL, **73**, 4175 (1951).

(17) (a) Greater shifts in carbonyl frequency can be obtained by forming stronger hydrogen bonds, as with phenols; E. Gray, *Ann. Chim.*, **3**, 355 (1948). (b) Interactions other than hydrogen bond formation will also produce shifts, of course, as with iodine; J. Morcillo and J. Herranz, *Anales real soc. espan. fis. y quim. (Madrid)*, **50B**, 117 (1954).

(18) L. F. Audrieth and R. Steinman, THIS JOURNAL, **63**, 2115 (1941).

the sulfite. The difference in the effect of replacing ethyl by ethoxyl on carbonyl and on sulfoxyl may be due to the essentially single bond character of the sulfoxyl link,[13] which would make it more polarizable.

The heats of mixing of ketones and of sulfoxides with carbon tetrachloride are rather small, although this does not preclude the possibility of complex formation.[19] The much larger effects with chloroform can be attributed primarily to the formation of hydrogen bonds, and it has been shown for ethers[1] and for amines[8] that a plot of the spectroscopic OD shifts of methanol-*d vs.* the calorimetric heats of mixing with chloroform gives a linear relation. Generally, points which are far removed from the line are low on the heat of mixing side, and these points have been taken as being indicative of steric factors which arise due to the difference in bulkiness between the chloroform and methanol molecules. The spectroscopic *versus* calorimetric data for the ketones and sulfoxides are plotted in Fig. 1. Dimethyl sulfoxide is very far from the line and low on the calorimetric side. Less removed from the line but also low on the same side is acetone. For these molecules, steric interaction with chloroform or methanol is very unlikely and, in fact, substitution of ethyl groups for methyl produces a substantial increase in the heat of mixing with chloroform. A possible explanation is that in acetone and in dimethyl sulfoxide the molecules are associated. This would account for the low calorimetric data without affecting the spectroscopic results. It is interesting to note that of all the compounds studied only acetone and dimethyl sulfoxide gave negative heats of mixing with carbon tetrachloride.

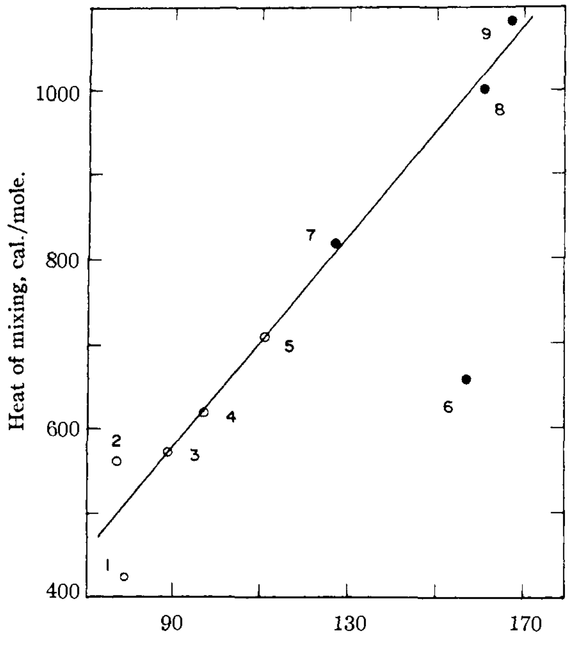

Fig. 1.—Heat of mixing at 25° of chloroform with ketones and with sulfoxides (50 mole %) *vs.* shift in vibrational frequency of OD bond of CH_3OD in ketones and in sulfoxides: (1) acetone, (2) diethyl ketone, (3) cyclopentanone, (4) cyclohexanone, (5) cycloheptanone, (6) dimethyl sulfoxide, (7) trimethylene sulfoxide, (8) tetramethylene sulfoxide, (9) diethyl sulfoxide.

The variation in carbonyl frequency with ring size has been observed by many investigators[20]; the frequency decreases from the 4- to the 7-membered ring, remains nearly constant through the 10-membered ring and increases slightly beyond that.[20e] The initial variation in the series, which implies a loosening of the C=O bond, parallels the observed increase in hydrogen bonding ability; the latter data suggest that the order of basicity is 7- > 6- > 5- > 4-membered ring.[21]

Pratt and Matsuda,[22] have determined the relative basicities of several ketones from kinetic studies of the rate of the acid-catalyzed self-etherification of benzhydrol. Their basicity order of cyclohexanone > cyclopentanone > diethyl ketone agrees with that found in this study. Also, it has been reported that derivatives of cyclopentanone are more acidic than those of cyclohexanone.[23]

It should be pointed out that in using hydrogen bonding as an "electron density probe"[8] the ground state of the molecule is not affected appreciably. Strong interactions, especially those involving passage through a transition state, are known to give an unusual enhancement in reactivity with cyclohexanone.[24] The rate of reaction of cyclohexanone with hydrogen cyanide is greater than that of either cyclopentanone or cycloheptanone,[25] and the cyclohexanone cyanohydrin is much less dissociated than those of other cyclic ketones.[20f,26]

As in the case of the cyclic ketones, the 4-membered ring sulfoxide exhibits the lowest basicity of the series investigated. The present techniques are not sufficiently sensitive to distinguish clearly the basic strength between the 5- and 6-membered rings. Because of the strong interaction of methanol-*d* with sulfoxides there is considerable broadening of the OD band. Consequently, a difference of only 6 cm.$^{-1}$ between the OD shift in tetramethylene sulfoxide and in pentamethylene sulfoxide cannot be considered

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[19] J. C. Pariand, *Bull. soc. chim. France*, 1239 (1950), reports from cryoscopic study the formation of a cyclohexanone:carbon tetrachloride complex of mole ratio 1:1 having a melting point of −39.6°.

[20] (a) E. J. Corey, THIS JOURNAL, **75**, 2301 (1953); (b) E. D. Bergmann and S. Pinckus, *J. chim. phys.*, **49**, 537 (1952); (c) F. J. Taboury, *J. Phys. Rad.*, **15**, 419 (1954); (d) W. M. Schubert and W. A. Sweeney, THIS JOURNAL, **77**, 4172 (1955), report that the ring size variation of the carbonyl frequency in the 5- to 8-membered rings as observed for cyclanones carries over to the benzocyclanones; (e) T. Burer and Hs. H. Gunthard, *Helv. Chim. Acta*, **39**, 356 (1956), give the frequency, half-width and integrated absorption intensity of the carbonyl bond for an extensive set of cyclanones; (f) V. Prelog, *J. Chem. Soc.*, 420 (1950), presents an excellent review of the properties of ring compounds.

[21] The fact that this correlation of carbonyl frequency and hydrogen bonding ability is observed for this series of cyclic ketones does not mean that the carbonyl frequency can serve generally as a measure of base strength.

[22] E. F. Pratt and K. Matsuda, THIS JOURNAL, **75**, 3739 (1953).

[23] (a) G. Schwarzenbach and E. Felder, *Helv. Chim. Acta*, **27**, 1701 (1944); (b) P. B. Russell, *Chemistry & Industry*, 326 (1956).

[24] See H. C. Brown, J. H. Brewster and H. Shechter, THIS JOURNAL, **76**, 467 (1954), for a general discussion with references.

[25] J. Jullien, M. Mousseron and P. Fouche, *Bull. soc. chim. France*, 408 (1956).

[26] V. Prelog and M. Kobelt, *Helv. Chim. Acta*, **32**, 1187 (1949).

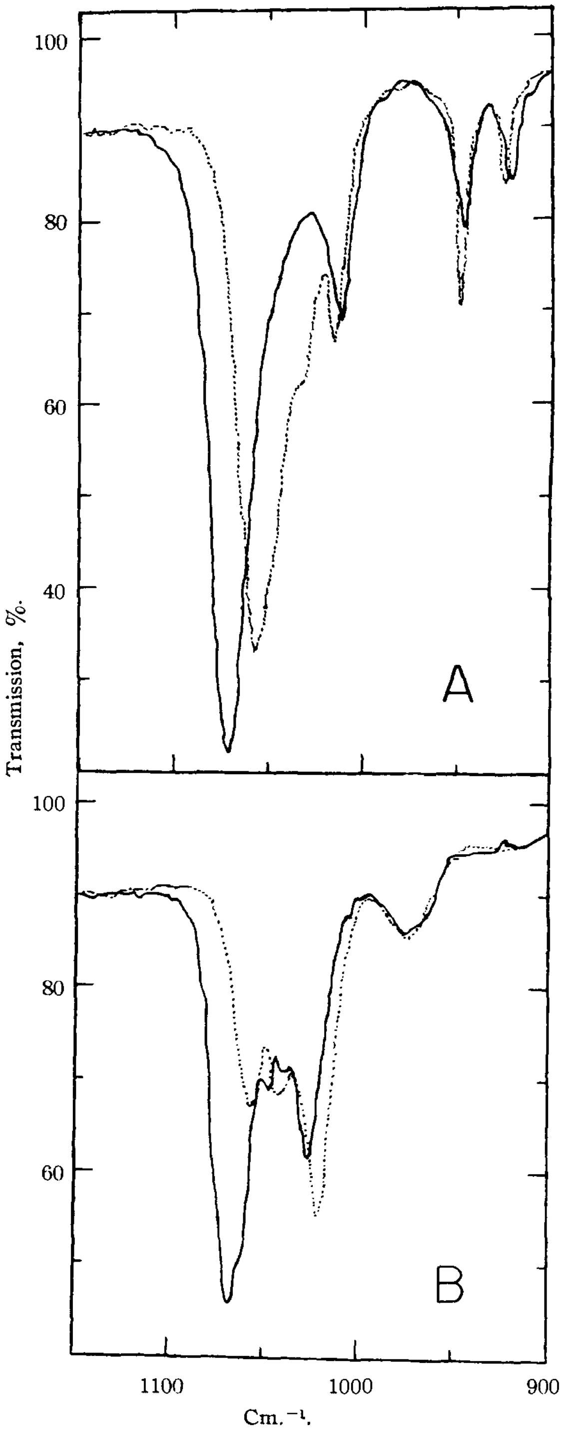

Fig. 2.—Sulfoxyl frequencies of cyclic sulfoxides in carbon tetrachloride (solid line) and in chloroform (dotted line); approximately 0.03 ml. of sulfoxide in 2.0 ml. of solvent, 0.1-mm. cell, NaCl optics: (A) dimethyl sulfoxide, (B) diethyl sulfoxide.

significant since this is within the limits of experimental error. Direct comparison of the heat of mixing with chloroform of the 5- and 6-membered ring sulfoxides is not possible because pentamethylene sulfoxide is a solid at room temperature, and its heat of fusion is not known. An estimate was attempted by dissolving various amounts of

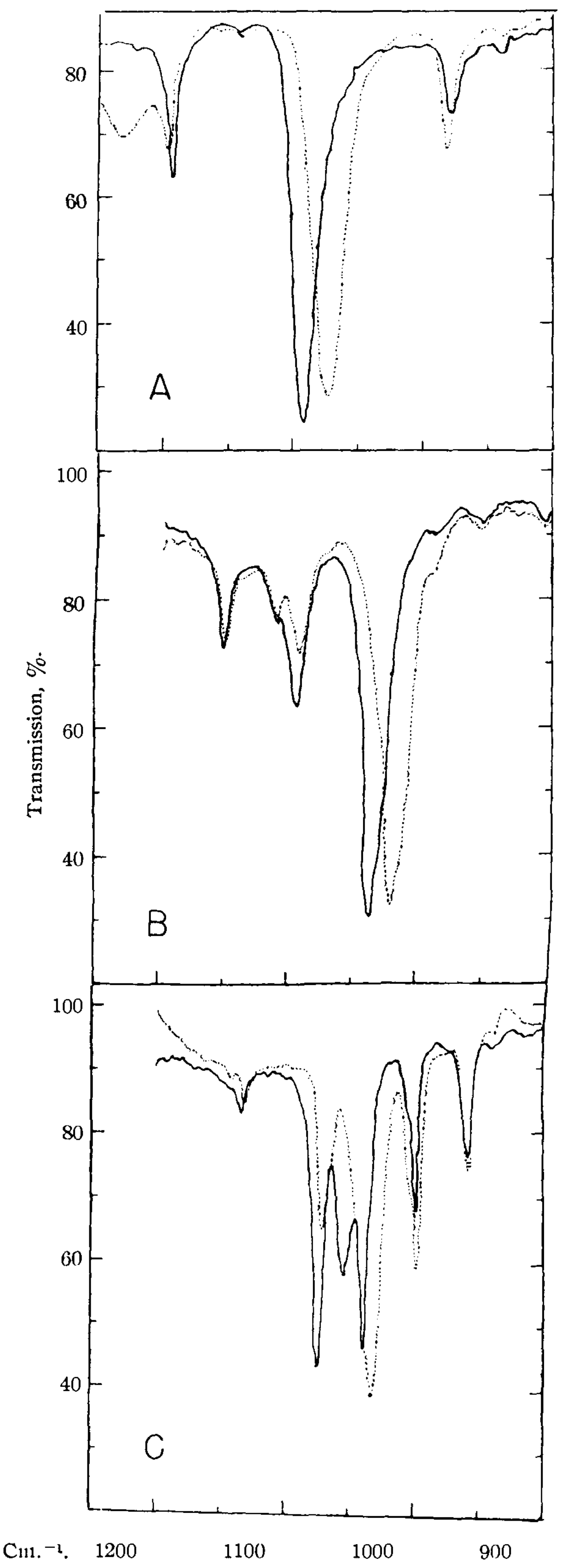

Fig. 3.—Sulfoxyl frequencies of cyclic sulfoxides in carbon tetrachloride (solid line) and in chloroform (dotted line); approximately 0.03 ml. of sulfoxide in 2.0 ml. of solvent, 0.1-mm. cell, NaCl optics: (A) trimethylene sulfoxide, (B) tetramethylene sulfoxide, (C) pentamethylene sulfoxide.

the solid in carbon tetrachloride and determining the heat of mixing of the solution with an equimolecular quantity of chloroform (with respect to sulfoxide). Determinations were made also for comparable solutions of diethyl sulfoxide in carbon tetrachloride. The similarity of results for these heats of mixing[27] suggests that pentamethylene sulfoxide is at least comparable in basicity to tetramethylene sulfoxide, and may perhaps be slightly more basic. Thus the order of base strength indicated is 6- $\geq$ 5- $>$ 4-membered ring.

The 4-membered ring cyclic ketone or cyclic sulfoxide is decidedly weaker in basicity than any of the other ring members investigated in their respective series. This order is in marked contrast to that obtained for the cyclic ethers,[2a,3,4] *e.g.*, trimethylene oxide being a better base than tetrahydrofuran or tetrahydropyran. But the order, especially for the cyclic ketones, is in agreement with that observed for the lactones,[5] in which study it was shown that the carbonyl oxygen and not the alkoxyl oxygen entered into the formation of hydrogen bonds.[28] Thus it appears that the variation of electron distribution about the oxygen atom depends upon whether the oxygen is a member of the ring or is outside the ring.

In their studies, Barnard, Fabian and Koch[13] reported the $S \rightarrow O$ frequencies for several aliphatic and aromatic sulfoxides. All frequencies fell within the range 1047–1061 cm.$^{-1}$, and the authors remarked on the relative constancy of the bond in spite of widely differing substituents on the sulfur atom.[29] For the study reported in this paper, the frequencies for dimethyl- and diethyl sulfoxide are about in this same region (see Fig. 2), but the cyclic sulfoxides are well outside this range. The $S \rightarrow O$ frequency at 1092 cm.$^{-1}$ in trimethylene sulfoxide is higher than that of any other compound studied. In this respect it is like cyclobutanone which has a $C{=}O$ frequency at 1775 cm.$^{-1}$, the highest of the ring series. The spectra of tetramethylene sulfoxide and especially of pentamethylene sulfoxide are more complex, several bands for the latter compound are in the region where the $S \rightarrow O$ frequency is expected. By determining the effect on the spectrum when first carbon tetrachloride and then chloroform were used as solvents, it was possible to choose that band due to $S \rightarrow O$ vibration (see Fig. 3). Thus the trend in the smaller ring compounds of decreasing $C{=}O$ frequency with increasing ring size apparently is not carried over into the cyclic sulfoxides.

Acknowledgment.—This research was supported in part by a grant from the Petroleum Research Fund Administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

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[27] The ampoule which could be accommodated inside the calorimeter was of limited size and generally contained no more than 10 cc. of sample. In the determinations involving solutions containing 17.55 and 35.93 moles % of pentamethylene sulfoxide in carbon tetrachloride, the total moles of the sulfoxide were 0.01474 and 0.02415, respectively. Determinations using these smaller quantities are subject to larger experimental error, and a difference of 20 cal./mole between results for diethyl sulfoxide and pentamethylene sulfoxide cannot be considered significant.

[28] R. L. Adelman and I. M. Klein, *J. Polymer Sci.*, **31**, **77** (1958), present data which indicate that perhaps alkoxyl oxygen rather than carbonyl oxygen is involved in solvent action on polyvinyl chloride. This point is discussed and references to other work on esters and lactones are given. Pratt and Matsuda, ref. 22, support the contention than the carbonyl oxygen in esters contributes more to the basicity.

[29] (a) C. C. Price and R. G. Gillis, THIS JOURNAL, **75**, 4750 (1953), show that the S–O bond frequency in methyl vinyl sulfoxide is at a shorter wave length than it is in methyl propyl sulfoxide; (b) C. W. N. Cumper and S. Walker, *Trans. Faraday Soc.*, **52**, 193 (1956), report that the change in dipole moment (in the direction of the S–O bond) when the sulfide is converted to the sulfoxide is greater in aromatic than in aliphatic compounds. The analysis involves certain assumptions in the calculation of bond moments, and the authors point out that this conclusion is based on limited results.

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Sulfur–Oxygen Scission *versus* Carbon–Oxygen Scission in Reactions of 2,4-Dinitrophenyl *p*-Toluenesulfonate and Related Esters with Nucleophilic Reagents[1]

BY J. F. BUNNETT[2] AND J. Y. BASSETT, JR.[3]

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A number of mono- and dinitrophenyl esters of *p*-toluenesulfonic and mesitylenesulfonic acids have been found to undergo both sulfur–oxygen and carbon–oxygen scission in reactions with nucleophilic reagents. With 2,4-dinitrophenyl *p*-toluenesulfonate, the fraction of C–O scission varies according to the reagent used from 100% with sodium thiophenoxide to but 12% with sodium methoxide. The relative rates of C–O and S–O scission are not related to over-all nucleophilic reactivity as represented by *n* of the Swain and Scott treatment, but rather to reagent polarizability. London forces appear to facilitate attack on the dinitrophenyl carbon by reagents of higher polarizability. Methyl groups introduced *ortho* to the sulfonate sulfur atom have relatively little effect on the proportion of C–O to S–O scission. They appear to provide little or no steric hindrance to nucleophilic attack on sulfonate sulfur.

Esters of sulfonic acids are in general easily cleaved by nucleophilic reagents. It has long been known that either the sulfur–oxygen bond or the carbon–oxygen bond can be cleaved depending on the structure of the ester. Thus *alkyl* esters of sulfonic acids undergo C–O bond scission with formation of alkyl derivatives of the nucleophilic reagents while *aryl* esters customarily are attacked at sulfur,

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[1] Research supported in part by the Office of Ordnance Research, U. S. Army. This work was presented in part at the American Chemical Society meeting in Miami, Florida, April, 1957.

[2] Department of Chemistry, Brown University, Providence, Rhode Island.

[3] R. J. Reynolds Fellow, 1956–1957. This manuscript is based on the Ph.D. thesis of J. Y. Bassett, Jr., October, 1957.