Ligands which form good covalent bonds to mercury such as NH_3 or CN^- cause disproportionation of the hypothetical Hg^IL_2 into $Hg^{II}L_2$ complexes and elementary mercury. Thus, our hypothesis is that a tendency to form a strong covalent Hg–X complex weakens the Hg–Hg bond and leads to disproportionation. In order to get good mercurous complexes, therefore, one should use strong "ionic" ligands, such as $P_2O_7^{-4}$, $C_2O_4^{--}$, etc., which complex by virtue of their charge and chelating characteristics. With these ligands, the contribution of covalent bond formation to the binding is small, as indicated by their relatively strong binding for the alkaline earth and group IIIb tripositive ions. These are in fact the complexing agents which do form mercurous complexes which are stable to disproportionation.[26]

The structure of the mercurous pyrophosphate and other mercurous complexes which were studied here is an interesting problem in structural chemistry. The three structures A, B and C already shown are all conceivable. The evidence that OH^- binds all Hg_2L^{-q+2} ligands equally tends to indicate that the chelate L is attached to only one mercury as in structures A and B.

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PASADENA, CALIFORNIA

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[26] Several interesting facts may be mentioned incidentally. R. Rosen and E. E. Reid report the existence of the compound $HO–CH_2–CH_2–S–Hg–Hg–S–CH_2–CH_2–OH$, a yellow solid, soluble in hot alcohol and melting at 108° (THIS JOURNAL, **44**, 635 (1922)). It is not known whether this substance is stable to disproportionation. There are the curious facts that the substances $Hg_2(CO_2CX_3)_2$(X = Cl or F) exist and are soluble in benzene (N. Davidson and L. E. Sutton, *J. Chem. Soc.*, 565 (1942)). See also J. Sand, *Ber.*, **34**, 2913 (1901); K. A. Hofmanu and J. Sand, *Ber.*, **33**, 2700 (1900).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN, AND KANSAS STATE UNIVERSITY, MANHATTAN, KANSAS]

The Iodine Complexes of Some Saturated Cyclic Ethers.[1,2] I. The Visible Region

BY SISTER MARY BRANDON, O.P.,[3] MILTON TAMRES AND SCOTT SEARLES, JR.

RECEIVED MAY 1, 1959

The thermodynamic constants in *n*-heptane for the iodine complexes of a series of cyclic ethers—namely, trimethylene oxide, tetrahydrofuran, 2-methyltetrahydrofuran, tetrahydropyran and propylene oxide—were obtained by a study of the temperature dependence of the absorption spectra in the visible region. The thermodynamic results show that the order of electron donor ability of the cyclic ethers is 4- > 5- > 6- > 3-membered ring. These results are in agreement with those reported previously from studies on hydrogen bonding and nuclear magnetic resonance and offer strong support for the proposal that the redistribution of electrons with change in ring size has a pronounced effect on the properties of cyclic compounds.

Introduction

The work of Benesi and Hildebrand[4] on the spectroscopic study of iodine in various solvents established the formation of 1:1 complexes of iodine with several electron donor species. Since that report there has been a rapid growth in the number of publications on molecular complex formation,[5] particularly with regard to use of the spectroscopic method. This growth has been prompted not only by the theoretical import of Mulliken's charge transfer theory[6] but also by the general consideration of acid–base theory which seems to offer the best interpretation for the formation of these complexes.[4,7]

Although it is known that side reactions often occur when iodine is dissolved in oxygenated solvents, it has been shown that the spectroscopic technique is applicable to the determination of the thermodynamic characteristics of 1:1 complexes formed by iodine with a large number of oxygen containing compounds,[8] notably with ethers. Among the ethers for which spectral characteristics and equilibrium constants, and in some cases enthalpy and entropy data, have been reported for the formation of 1:1 complexes with iodine are *n*-butyl ether,[9] 1,4-dioxane,[10] ethyl ether,[11] methyl butyl ether[12] and isopropyl ether.[10c] These data indicate that the interaction is rather moderate, the enthalpy of interaction being of the order of magnitude of that shown in formation of stronger hydrogen bonds. Consequently, it is reasonable to assume that the interaction will produce no major alteration in the character of the lone pair electrons on the oxygen and that this interaction

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 130th Meeting of the American Chemical Society, Atlantic City, New Jersey, Sept., 1956.

[2] Taken in part from the Ph.D. thesis of Sister Mary Brandon Hudson, University of Michigan, June, 1957.

[3] Department of Chemistry, Rosary College, River Forest, Illinois.

[4] (a) H. Benesi and J. H. Hildebrand, THIS JOURNAL, **70**, 2832 (1948); (b) **71**, 2703 (1949).

[5] A review of this subject is given by L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954).

[6] R. S. Mulliken, THIS JOURNAL, **74**, 811 (1952).

[7] R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

[8] P. A. D. de Maine, *J. Chem. Phys.*, **26**, 1199 (1957), summarizes literature data.

[9] L. J. Andrews and R. M. Keefer, THIS JOURNAL, **75**, 3561 (1953).

[10] (a) J. A. A. Ketelaar, C. van de Stolpe and H. R. Gersmann, *Rec. trav. chim.*, **70**, 499 (1951); (b) J. A. A. Ketelaar, C. van de Stolpe, A. Goudsmit and W. Dzcubas, *ibid.*, **71**, 1104 (1952); (c) C. van de Stolpe, Ph.D. thesis, Amsterdam, 1953.

[11] (a) J. Ham, *J. Chem. Phys.*, **20**, 1170 (1952); (b) P. A. D. de Maine, *ibid.*, **26**, 1192 (1957).

[12] G. Kortum and M. Kortum-Sieler, *Z. Naturforsch.*, **5a**, 544 (1950).

TABLE I

PHYSICAL CONSTANTS FOR REAGENTS

Compound	Density (g./ml., 20°) Obsd.	Density (g./ml., 20°) Lit.	n^{20}_D Obsd.	n^{20}_D Lit.	B.p. Obsd.[a] ± 0.2	B.p. Lit.	Ref.
Trimethylene oxide	0.8902[b]	0.8930[b]	1.3941	1.3897[b]	47.0	47.8	[c]
Tetrahydrofuran	.8863	.888	1.4070	1.4040[b]	65.2	65.4	[d]
Tetrahydropyran	.8848	.8814	1.4207	1.420	87.7	88.0	[e]
2-Methyltetrahydrofuran	.8524	.853	1.4049	1.405	79.8	80.0	[f]
Propylene oxide	.8283	.8311	1.3662	1.3664	34.2	34.5	[g]
Ethyl ether	.7073[b]	.70788[b]	1.3527	1.3527	34.1	34.48	[g]
n-Heptane	.6792[b]	.6795[b]	1.3877	1.38765	98.2	98.427	[g]

[a] Not corrected for atmospheric pressure (approximately 740 mm.). [b] At 25°. [c] Ref. 18. [d] du Pont Electrochemicals Dept., Bulletin No. A 2185-5m-6-51, Wilmington, Del. [e] du Pont Electrochemicals Dept., Elchem. 596, Bulletin No. 19, Wilmington, Del. [f] du Pont Electrochemicals Dept., Elchem. 1151, Bulletin No. 29, Wilmington, Del. [g] A. Weissberger, editor, "Technique of Organic Chemistry," Vol. VIII, "Organic Solvents," 2nd ed., Interscience Publishers, Inc., New York, N. Y., 1955.

could serve as an "electron density probe."[13]

Previous reports on hydrogen bonding studies[14] and on nuclear magnetic resonance measurements[15] for saturated cyclic ethers showed that the electron donor ability of the oxygen atom is dependent upon the size of the ring, the basicities being in the order 4->5->6->3-membered ring. The spectroscopic investigation of the iodine complexes with the saturated cyclic ethers was undertaken because the method seems particularly well suited to provide a more detailed evaluation of the effect of ring size on basicity. Not only is it possible to obtain thermodynamic data in the visible region but the data can be checked in the ultraviolet region and the latter spectral characteristics can be interpreted in terms of the basic properties of the ethers.

Also, it is well known that, as a result of steric requirements, the order of base strength can be altered by a different choice of reference acid. It was felt that selection of a more bulky acid would serve as an independent check on the order of basicity observed in the hydrogen bonding studies,[14] and at the same time it would permit testing experimentally the applicability of the theory based on strain factors which was proposed by Brown and Gerstein[16] to explain the variation in basicity with ring size observed for the interaction of cyclic imines with boron trimethyl.

Experimental

Apparatus.—Preliminary studies to determine optimum conditions were made at room temperature on a Cary recording spectrophotometer, Model 11. The studies on the temperature dependence of the equilibrium constant were made with a Beckman quartz spectrophotometer, Model DU, which was equipped with Beckman No. 2180 double thermospacers through which water was circulated from a constant-temperature bath. The desired bath temperatures were controlled by the use of preset mercury thermoregulators which were placed together with a thermometer in a small Thiele-type tube in the circulating water system, thus permitting the measurement of the temperature of the water as it left the cell compartment. The temperatures were constant to within ±0.1° during the readings of the absorbancies. A 200 watt electric light bulb served as the heater for the bath. Dry air was passed through the cell housing to prevent fogging at low temperatures.

The standard copper sulfate and the standard potassium dichromate solutions as well as the tables of spectral absorbancy recommended by the National Bureau of Standards[17] were used to check the photometric scale of the Beckman instrument.

Compartmentalized bottles, consisting of a glass cylinder fused to the base of a glass stoppered bottle, were used. These could easily accommodate 25 ml. of solution. Aliquots from an iodine-*n*-heptane stock solution were pipetted into the inner cylinders and aliquots from an ether-*n*-heptane stock solution were pipetted into the outer portions of the compartmentalized bottles. This made it possible to bring the system to temperature equilibrium before the components were mixed and to keep the time between mixing the solutions and scanning the spectrum at a minimum. A rubber bulb with three ball valves (Propipette No. R 1725 from Schaar and Co.) facilitated the pipetting of the volatile liquids.

Four matched silica cells (ranging in length from 0.996 to 1.000 ± 0.001 cm.) were used. The cells were equipped with ground glass stoppers to minimize evaporation.

Materials.—Propylene oxide was obtained from the Eastman Kodak Co. (best quality) and trimethylene oxide was prepared and purified as previously described.[18] Each was fractionally distilled from sodium metal through a 20 cm. Vigreux column immediately before use.

Tetrahydrofuran, 2-methyltetrahydrofuran and tetrahydropyran were generously donated by the du Pont Company. Immediately before use they were freed of peroxides by treatment with ferrous sulfate and sodium bisulfate, then solid potassium hydroxide, followed by drying and fractional distillation from sodium metal. Special difficulty was encountered in the purification of tetrahydropyran. The ultraviolet spectrum contained several absorption maxima in the 249–268 mμ region, identical to the absorption bands of benzene.[19] The intensity corresponded to 0.02% benzene impurity. Fractional distillation through a three-foot column packed with glass helices removed most of the impurity and the less than 0.01% remaining was not considered sufficient to affect the results of the iodine–tetrahydropyran interaction.[20] Similar difficulty in purifying tetrahydropyran has been reported by Pickett and co-workers,[21] who also were unable to remove the last trace of benzene.

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(13) In much the same way as hydrogen bonding; M. Tamres, S. Searles, E. M. Leighly and D. W. Mohrman, THIS JOURNAL, **76**, 3983 (1954).

(14) (a) S. Searles and M. Tamres, *ibid.*, **73**, 3704 (1951); (b) S. Searles, M. Tamres and E. R. Lippincott, *ibid.*, **75**, 2775 (1953).

(15) H. S. Gutowsky, R. L. Rutledge, M. Tamres and S. Searles, *ibid.*, **76**, 4242 (1954).

(16) H. C. Brown and M. Gerstein, *ibid.*, **72**, 2926 (1950).

(17) Spectrophotometry, National Bureau of Standards Circular 484, U. S. Government Printing Office, Washington 25, D. C., 1949.

(18) S. Searles, THIS JOURNAL, **73**, 124 (1951).

(19) A. E. Gillam, E. S. Stern and E. R. H. Jones, "Electronic Absorption Spectroscopy," Edward Arnold Publishers Ltd., London, 1954, p. 117.

(20) Even greater difficulty was encountered in the more recent samples of 2-methyltetrahydrofuran from the du Pont Company. The ultraviolet spectrum indicated a benzene impurity of approximately 5.1%. A gas phase fractometry analysis showed the presence of 5.4% impurity in the 2-methyltetrahydrofuran. Various separation techniques reduced the impurity to about 2.2%. Finally, an older supply of 2-methyltetrahydrofuran from du Pont was located which showed a clear ultraviolet transmission to 230 mμ, showing the absence of any benzene impurity.

(21) L. W. Pickett, N. J. Hoeflick and Tien-Chuan Lu, THIS JOURNAL, **73**, 4866 (1951).

Ethyl ether (Mallinckrodt Analytical Reagent Grade) was dried over calcium hydride and fractionally distilled immediately before use. *n*-Heptane (Phillips' Pure Grade) was dried and fractionally distilled in the same way, after prior purification by the method described by Potts.[22]

The purity of all these reagents was checked by determining density, refractive index, boiling point, ultraviolet spectrum and infrared spectrum, and good agreement was observed with literature data. These data, except for the spectra,[23] are summarized[24] in Table I.

The iodine (Mallinckrodt Analytical Reagent Grade) was purified by sublimation from C. P. potassium iodide and was stored in a glass-stoppered weighing bottle in a desiccator.

Procedure for Making the Solutions.—A standard stock solution of about 1.25×10^{-2} mole/l. of iodine in *n*-heptane was prepared by weight. Aliquots of the iodine solution (to make the concentration approximately 1.5×10^{-3} mole/l. for the visible region) and samples of the ether (mole fraction 0.02–0.09) and *n*-heptane were weighed directly into glass-stoppered flasks.

Because the solutions contained such a low mole fraction of the ether, the correction for the iodine concentration at the various temperatures was made on the assumption that the change in volume of the solutions with temperature could be measured in terms of the density change of pure *n*-heptane. The density data for *n*-heptane were taken from Timmermans.[25]

n-Heptane was chosen as the solvent because it is available in a relatively pure state, is not very volatile and shows high transmission in the visible (as well as ultraviolet) region.

Method of Calculation.—It was shown by Benesi and Hildebrand[4] that the equilibrium constant for the reaction

$$\text{Ether} + I_2 \rightleftarrows \text{Complex}$$

could be evaluated by using the equation[26]

$$\frac{1}{a_i} = \frac{1}{a_c K_x} \times \frac{1}{N_e} + \frac{1}{a_c} \qquad (1)$$

where N_e is the mole fraction of ether, K_x is the equilibrium constant when mole fraction units are used for the ether, a_c is the molar absorbancy index of the complex and a_i is an apparent molar absorbancy index which is calculated on the basis of the concentration of total iodine, C_i, from the experimentally observed absorbancy by using the relation $A = a_i b C_i$.

Equation 1 is valid for the condition that the ether concentration is much greater than that of iodine and that the complex is the only species which contributes to the absorbancy. For the case where the absorption due to free iodine cannot be neglected and where ether-solvent is used as the blank, Ketelaar and co-workers[10] derived the equation

$$\frac{1}{(a_i - a_f)} = \frac{1}{(a_c - a_f)K_x} \times \frac{1}{N_e} + \frac{1}{(a_c - a_f)} \qquad (2)$$

where the additional terms a_f and a_e refer to the molar absorbancy index of free iodine and of ether, respectively.

For the condition where the ether absorption can be neglected and where the reference solution is an iodine-solvent solution of the same concentration as the sample, the equation which applies is

$$\frac{1}{a_i} = \frac{1}{(a_c - a_f)K_x} \times \frac{1}{N_e} + \frac{1}{(a_c - a_f)} \qquad (3)$$

This equation, which was used in the present study, is similar to that of Ketelaar and co-workers except for the first term. The linear plot of $\frac{1}{a_i}$ *vs.* $\frac{1}{N_e}$ permits evaluation of the intercept and slope, from which the molar absorbancy index and equilibrium constant of the complex can be obtained. The molar absorbancy index of free iodine, a_f, is determined separately for the spectral region of interest from the absorbancy of a solution of iodine in *n*-heptane of known concentration.[27] Use of an iodine–*n*-heptane blank has the advantage that several solutions may be run against a single blank by varying the ether concentration but keeping the same iodine concentration in all the solutions.

Results and Discussion

Typical results of individual determinations in the visible region are presented in Table II.[28] They were obtained by using equation 3. Duplicate determinations were made in most cases for each ether–iodine complex and these were found to be in good agreement.

TABLE II

SPECTROSCOPIC DATA FOR THE VISIBLE REGION OF ETHER–IODINE COMPLEXES[a]

Ether	Solvent	λ_{max}, mμ	a_c	K_x	t^0
Trimethylene oxide[b]	n-C_7H_{16}	452	800	60.9	2.5
				43.9	11.5
				26.1[c]	25.0
2-Methyltetrahydrofuran[b]	n-C_7H_{16}	454	850	56.8	1.0
				37.7	10.0
				27.1	20.0
				20.2[c]	25.0
Tetrahydrofuran[b,d]	n-C_7H_{16}	455	950	30.2	6.0
				14.3	28.6
				12.4	34.8
				17.2[c]	25.0
Tetrahydropyran[b]	n-C_7H_{16}	456	930	31.6	5.5
				22.4	15.5
				16.9	25.5
				11.6	40.0
				17.0[c]	25.0
Propylene oxide[b]	n-C_7H_{16}	460	970	11.9	1.0
				9.5	9.0
				8.7	15.0
				6.4[c]	25.0
Ethyl ether[b,d]	n-C_7H_{16}	462	950	9.9	4.0
				8.6	10.0
				6.6	17.4
				5.9[c]	25.0
Ethyl ether[e]	n-C_7H_{16}	466	960	4.9	21.5
Ethyl ether[g]	CCl_4	468	873	8.7	25
1,4-Dioxane[h]	CCl_4	450	930	8.9	21.5
1,4-Dioxane[i]	CCl_4	452	965	10.6	17
1,4-Dioxane[i]	n-C_6H_{14}	452	993	9.5	25

[a] For comparison to other ether–iodine complexes see ref. 8. [b] This research. [c] Calculated value. [d] Results in the ultraviolet region were slightly higher. [e] Ref. 11a. [g] Ref. 11b. The reported result of $K_x = 8.7$ at 25° was obtained by extrapolating from data at lower temperatures using the experimental value of -4.30 kcal./mole for ΔH^0. [h] This research. Data were obtained at 21.5 ± 0.5° on the Cary recording spectrophotometer, Model 11. [i] Ref. 10b and 10c. Average from visible and ultraviolet data for K_x values at 25° are 9.1 and 9.3 in CCl_4 and *n*-hexane solution, respectively.

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(22) W. F. Potts, *J. Chem. Phys.*, **20**, 809 (1949).

(23) The infrared spectra of propylene oxide, tetrahydrofuran and tetrahydropyran are given by O. D. Shreve, R. Heether, H. B. Knight and D. Swern, *Anal. Chem.*, **23**, 277 (1951); those of trimethylene oxide, tetrahydrofuran and 2-methyltetrahydrofuran are given by G. M. Barrow and S. Searles, THIS JOURNAL, **75**, 1175 (1953).

(24) The data in Table I may be used to calculate the molar refractions of the cyclic ethers. An "optical exaltation" of about 0.2 unit is obtained for propylene oxide; the values for the molar refractions of the other cyclic ethers are closer to "additivity" [S. Glasstone, "Textbook of Physical Chemistry," 2nd Ed., 1946, pp. 528-531].

(25) J. Timmermans, "Physico-chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., New York, N. Y., 1950, p. 60.

(26) The terminology and symbols recommended in the Letter Circular LC 857 of the National Bureau of Standards for use in ultraviolet, visible and infrared absorptiometry will be employed. Results in the literature will be expressed in this terminology regardless of how they appeared originally. The Bouguer–Beer laws are expressed as: $A = abC = -\log (I/I_0)$, where A = absorbancy of the sample, a = molar absorbancy index (l. mole^{-1} cm.$^{-1}$), b = length of absorbing path (cm.), C = concentration (mole l.$^{-1}$).

(27) Numerical data for the molar absorbancy index of iodine in *n*-heptane and in carbon tetrachloride for the region 700–350 mμ are given by P. A. de Maine (ref. 11b).

(28) Detailed experimental data for the spectroscopic analyses may be found in ref. 2.

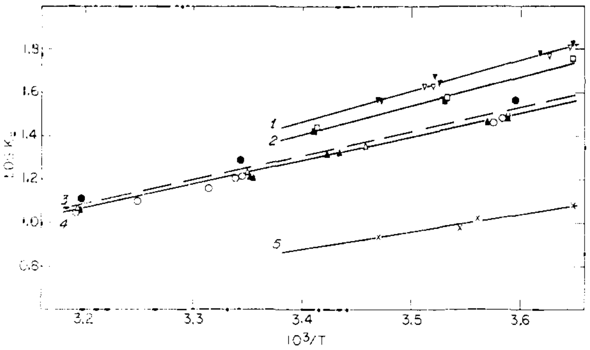

Fig. 1.—Log K_x *vs.* $1/T$ for the iodine–cyclic ether complexes: (1) trimethylene oxide (▽ *visible,* ▼ ultraviolet); (2) 2-methyltetrahydrofuran (□ *visible,* ■ ultraviolet); (3) tetrahydrofuran (○ *visible;* ● ultraviolet); (4) tetrahydropyran (△ *visible,* ▲ ultraviolet); (5) propylene oxide (× *visible*).

It will be noted in Table II that the experimental data for the iodine–trimethylene oxide complex do not go above 11.5°. Attempts were made to go to higher temperature but it was found that a rapid reaction occurred, as was evidenced by a changing absorbancy and an observable bleaching of the color of the solution. At or near 10° the absorbancy of this complex in the visible region remained constant for the length of time required to make the determination.

The equilibrium constants at 25° were calculated from the experimental data and are included in Table II to permit more direct comparison of the stabilities of the ether–iodine complexes. Molar absorbancy indices were assumed to be independent of temperature in each determination and the values recorded in Table II represent the average results over the temperature range investigated. The λ_{max} results were taken from the observed spectral curves. No correction was made for the contribution of other species[29] since, for the experimental conditions of this research, such correction is very small.

The plot of log K_x *versus* $1/T$, shown in Fig. 1, includes the points obtained in the ultraviolet region (to be presented in Part II of this study) to illustrate the generally good agreement resulting from the use of equation 3. The poorest agreement, but still within the limits of experimental error of the method, was obtained for the tetrahydrofuran–iodine system. For this case, higher ether concentrations were used than in the studies of the other complexes and this was found to lead to greater error, an observation which has been noted by others.[11b] The dashed line for the tetrahydrofuran–iodine complex represents an average result for both spectral regions.

The plot of both the visible and ultraviolet regions in Fig. 1 is intended to emphasize also that the set of thermodynamic values for the formation of iodine–ether complexes, summarized in Table III, represents the result of the complete study. The method of least squares was used to determine the best straight line through the combined data in order to evaluate $\Delta H°$.

TABLE III

THERMODYNAMIC VALUES FOR THE IODINE–ETHER COMPLEXES

Ether	Solvent	$-\Delta H^0$ $\pm$ 0.2 kcal./mole	$-\Delta F^0_{298}$ $\pm$ 0.02 kcal./mole	$-\Delta S^0$ $\pm$ 0.8 e.u.
Trimethylene oxide[a]	n-C_7H_{16}	6.4	1.93	15.0
2-Methyltetrahydrofuran[a]	n-C_7H_{16}	6.2	1.84	14.6
Tetrahydrofuran[a]	n-C_7H_{16}	5.3	1.70[b]	11.6
Tetrahydropyran[a]	n-C_7H_{16}	4.9	1.66	10.7
Propylene oxide[a]	n-C_7H_{16}	3.8	1.10	9.0
Ethyl ether[a]	n-C_7H_{16}	4.2	1.12	10.3
Ethyl ether[c]	CCl_4	4.30	1.31	9.86
Dioxane[d]	n-C_6H_{14}	3.5	1.3	7.3
Dioxane[d]	CCl_4	3.3	1.4	6.7

[a] This research. [b] Error limits ±0.05. [c] Ref. 11b. [d] Ref. 10.

Keefer and Andrews showed that, for the alkylbenzene complexes with iodine[30a] and with iodine monochloride[30b] in carbon tetrachloride, increasing alkyl substitution produced a systematic change in all three thermodynamic properties, $\Delta H°$, $\Delta F°$ and $\Delta S°$. A linear relation was obtained by plotting any one property against one of the other two, except for hexaethylbenzene and *sym*-tributylbenzene, where steric factors predominate. These authors have suggested that the increase in bond strength of the complex as measured by $\Delta H°$ may result in a greater rigidity of the complex as reflected in the $\Delta S°$ term. In the cyclic ethers these factors are related to the availability of the lone pair electrons on the oxygen and, hence, to the base strength of the molecule (in the Lewis sense). The variation in $\Delta H°$ with $\Delta S°$ for the ether–iodine complexes is linear[31] within the limits of experimental error, including the data for the 2-methyltetrahydrofuran–iodine complex. This suggests, in view of the results obtained by Keefer and Andrews,[30] that no pronounced steric effect results from the presence of the methyl group.

It may be seen in Table III that the $\Delta F°$ values at 25° for tetrahydrofuran and tetrahydropyran are rather close together but the difference between these and the three- and four-membered ring ethers is quite clear. Thus, the over-all thermodynamic data indicate that the strength of complex formation between iodine and the saturated cyclic ethers is in the order 4- > 5- > 6- > 3-membered ring. This offers strong confirmation for the order of basicity reported previously in studies on hydrogen-bonding[14] and on nuclear magnetic resonance.[15] The results of this work are compared in Fig. 2 with those on nuclear magnetic resonance. The correlation with the heat of mixing experiments is shown in Fig. 3. It is apparent that the same trend is shown: a maximum value for the four-membered ring and a minimum for the three-

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[29] The actual position and shape of the curve is dependent on the composition of the reference solution, *i.e.*, whether iodine–n-heptane or ether–n-heptane is used as the blank. Any small correction in λ_{max} would have only a very slight effect on the molar absorbancy index since the spectral band is rather broad. The correction should have no effect on the equilibrium constant because equation 3 is applicable at any wave length.

[30] (a) R. M. Keefer and L. J. Andrews, THIS JOURNAL, **77**, 2164 (1955); (b) N. Ogimachi, L. J. Andrews and R. M. Keefer, *ibid.*, **77**, 4202 (1955).

[31] See Fig. 1 in Part II of this study.

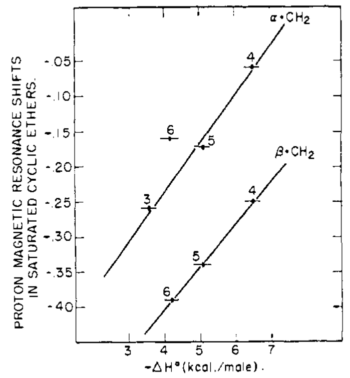

Fig. 2.—Heat of formation of the iodine–cyclic ether complexes *vs.* proton resonance shifts of the α- and β-methylene hydrogens in the cyclic ethers.

membered ring ether. A similar graph would result if the data for the heat of formation of the iodine complexes with cyclic ethers were compared with the shift in vibrational frequency of the OD band of methanol-*d* in the presence of the same cyclic ethers, since the latter data correlate with the heats of mixing of these ethers with chloroform.[14a]

The "F strain" and "I strain" concepts proposed by Brown and Gerstein[16] to correlate basicity with ring size of the addition compounds of the cyclic imines with boron trimethyl do not seem to be applicable to the iodine–ether complexes. If "I strain" alone were operative, the order of basicity that would be predicted is 6- > 5- > 4- > 3-membered ring. That "F strain" is not a predominant factor in the formation of the iodine–ether complexes is demonstrated by the fact that the 2-methyltetrahydrofuran is a stronger base than the unsubstituted tetrahydrofuran. This was pointed out also by Sisler and Perkins,[32] who made a cryoscopic study of the molecular addition compounds of dinitrogen tetroxide with trimethylene oxide, tetrahydrofuran, 2-methyltetrahydrofuran, 2,5-dimethyltetrahydrofuran, tetrahydropyran and dioxolane. They observed the same order of basicity for the ethers as is reported in this work. Since both of the substituted tetrahydrofurans were shown to be stronger bases than tetrahydrofuran itself, the investigators concluded that the methyl groups offer little steric hindrance, or else the steric effect is offset by the increase in electron density on the oxygen atom due to the inductive effect of the methyl groups.

Since "F strain" and "I strain" do not appear to be operative, it seems reasonable to assume that the availability of the lone pair electrons on the oxygen in the cyclic ethers differs with the size of the ring. The change in angular requirements in forming different-sized rings must result in a rehybridization of the orbitals, which in turn affects the electron distribution on the oxygen atom.

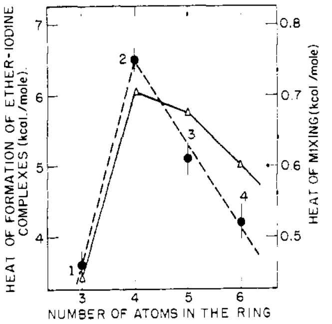

Fig 3.—Heats of mixing of chloroform with cyclic ethers as a function of ring size and heats of formation of iodine–cyclic ether complexes as a function of ring size. Solid line: heat of mixing at 25° of chloroform with 50 mole % of (1) propylene oxide, (2) trimethylene oxide, (3) tetrahydrofuran, (4) tetrahydropyran. Broken line: heat of formation of the complexes of iodine with the same ethers in *n*-heptane.

The Absorption Band in the Visible Region.—When an ether is added to a solution of iodine in *n*-heptane, the iodine absorption band in the visible region is broadened and is shifted toward the ultraviolet (blue shift). This effect is indicative of a polarization of the iodine molecule.[33] The apparent dipole moment of iodine in a number of solvents which produce a blue shift in the iodine color has been reported.[34−39] and the data are given in Table IV. It has been pointed out that the correlation of dipole moment with color is not exact because part of the observed moment must be attributed to electronic shifts within the donor molecule itself.[34b] However, it seems reasonable that the shift in color as measured by the wave length of maximum absorption of the complex, λ_{max}, might parallel the apparent dipole moment, μ, for a related series of electron donors.

That the shift in λ_{max} may be indicative of the basicity of the solvent[4,40] seems to be borne out in the data for the heats of association, a point discussed also by Kubota.[41] There is a qualitative relation between λ_{max} and $\Delta H°$ (Table IV) for the various classes of electron donors, with the possible exception of the alcohols.[42] Here, the exact nature

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(32) H. H. Sisler and P. E. Perkins, THIS JOURNAL, **78**, 1135 (1956).

(33) The halogen vibrational frequency, normally inactive in the infrared, not only appears when the halogen is dissolved in basic solvents but there is also a shift to longer wave lengths. This has been shown using benzene as a solvent for chlorine [L. D'Or and J. Collin, *J. Chem. Phys.*, **23**, 397 (1955)], for bromine [L. D'Or, R. Alewaeters and J. Collin, *Rec. trav. chim.*, **75**, 862 (1956); W. B. Person, R. E. Erickson and R. E. Buckles, *J. Chem. Phys.*, **27**, 1211 (1957)], and for iodine [E. K. Plyler and R. S. Mulliken, THIS JOURNAL, **81**, 823 (1959)]. Furthermore, it has been shown that the shift in the infrared spectrum of iodine monochloride is related to the base strength of the solvent [W. B. Person, R. E. Humphrey, W. A. Deskin and A. I. Popov, *ibid.*, **80**, 2049 (1959)]. These observations are consistent with the concept of a polarization of the halogen molecule, although recently it has been questioned that they rule out a symmetric orientation of the halogen with respect to the benzene [E. E. Ferguson and F. A. Matsen, *J. Chem. Phys.*, **29**, 105 (1958)].

(34) (a) F. Fairbrother, *Nature*, **160**, 87 (1947); (b) *J. Chem. Soc.*, 1051 (1948).

(35) Ya. K. Syrkin and K. M. Amisimova, *Doklady Akad. Nauk S.S.S.R.*, **59**, 1457 (1948).

(36) G. Kortüm and H. Walz, *Z. Elektrochem.*, **57**, 73 (1953).

(37) K. Higasi, *J. Sci. Research Inst.* (*Tokyo*), **24**, 57 (1934).

(38) G. W. Nederbragt and J. Pelle, *Mol. Phys.*, **1**, 97 (1958).

(39) H. Tsubomura and S. Nagakura, *J. Chem. Phys.*, **27**, 835 (1957).

(40) M. Tamres, D. R. Virzi and S. Searles, THIS JOURNAL, **75**, 4358 (1953).

(41) T. Kubota, *J. Chem. Soc. Japan*, **78**, 196 (1957).

(42) Y. Anako, *Sci. Repts.*, *Tohoku Univ.*, *First Ser.*, **40**, 147 (1956), reports data for the ethyl alcohol–iodine complex which are appreciably different from those of de Maine,[11c] even allowing for the use of different solvents.

of the complexes is uncertain due to the tendency of alcohol to undergo self-association. The low ΔH° probably reflects the requirement of supplying energy to break hydrogen bonds in order to form an iodine complex. There is evidence that the relation between $\lambda_{\max}$ and ΔH° also is offset by steric factors.[30]

TABLE IV

SPECTROSCOPIC, DIPOLE MOMENT AND HEAT OF FORMATION DATA FOR IODINE COMPLEXES

Electron donor	$\lambda_{\max}$, mμ	μ, D	$-\Delta H^0$, kcal./mole
n-Heptane	520[a]		
Cyclohexane		0.0[b]	
Benzene	500[c]	0.6[b] 1.8[d]	1.3[c,e]
Toluene	497[c]		1.8[c]
p-Xylene	495[c]	0.9[b]	2.2[e]
Mesitylene	490[c]	1.1[f]	2.9[e]
1,4-Dioxane	452[g]	0.95[h]	3.5[i]
		1.3[b] 3.0[d]	
Ethyl ether	462[a]	0.7[j]	4.2[a]
Propylene oxide	460[a]		3.8[a]
Tetrahydropyran	456[a]		4.9[a]
Tetrahydrofuran	455[a]		5.3[a]
2-Methyltetrahydrofuran	455[a]		6.2[a]
Trimethylene oxide	452[a]		6.4[a]
Methanol	440[k]		1.9[k]
Ethanol	443[k]		2.1[k] 3.5[l]
Pyridine 1-oxide	438[m]		5.6[m]
2-Picoline 1-oxide	437[m]		6.0[m]
3-Picoline 1-oxide	435[m]		6.1[m]
4-Picoline 1-oxide	434[m]		6.2[m]
2,6-Lutidine 1-oxide	435[m]		5.6[m]
Pyridine	417[m]	4.5[e]	7.5[m]
	422[n]	4.17[o]	7.8[n]
Triethylamine	414[p]	11.3[q] (9.3)[r]	12.0[p]

[a] This research; n-heptane solvent. [b] Ref. 34. [c] Ref. 10c. [d] Ref. 36; cyclohexane solvent. [e] Ref. 30a; CCl_4 solvent. [f] Ref. 38. [g] Ref. 10b,c; in pure 1,4-dioxane at slightly above 17°. [h] Ref. 35; 1,4-dioxane solvent. [i] Ref. 10b,c; n-hexane solvent. [j] Ref. 37. [k] Ref. 11c; CCl_4 solvent. [l] Ref. 42; n-hexane solvent. [m] Ref. 41; CCl_4 solvent. [n] C. Reid and R. S. Mulliken, THIS JOURNAL, **76**, 3869 (1954); cyclohexane solvent. [o] Ref. 35; benzene solvent. [p] S. Nagakura, THIS JOURNAL, **80**, 520 (1958). [q] Ref. 39; 1,4-dioxane solvent. [r] V. M. Kazakova and Ya. K. Syrkin, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 673 (1958); lower limit; benzene solvent.

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ANN ARBOR, MICHIGAN
MANHATTAN, KANSAS

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN]

The Iodine Complexes of Some Saturated Cyclic Ethers.[1,2] II. The Ultraviolet Region

BY MILTON TAMRES AND SR. MARY BRANDON, O.P.[3]

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The thermodynamic data in n-heptane for the complexes formed by iodine with trimethylene oxide, tetrahydrofuran-2-methyltetrahydrofuran, tetrahydropyran, propylene oxide and ethyl ether were obtained by studying the temperature dependence of the absorption spectra in the ultraviolet region. These data check very well the results reported for the visible region. Application of the Mulliken charge transfer theory to the ultraviolet spectral characteristics of the complexes implies an order of basicity of 4- > 5- > 6- > 3-membered ring, in agreement with the thermodynamic results.

Introduction

In the preceding paper[4] results were reported for a spectroscopic study of a series of cyclic ether-iodine complexes in the visible region. Since these complexes also exhibit characteristic bands in the ultraviolet region, a study of the latter region serves as an independent check in determining the strength of interaction of these electron donors with iodine. In addition, the ultraviolet spectra are of significance in their own right because the data can be interpreted in terms of charge transfer theory.[5] In this paper, the theory is applied to correlate qualitatively the spectral characteristics with the relative basicities of the ethers.

Experimental

Apparatus.—The same apparatus was used as has been described for the study in the visible region[4] with the exception of adding a hydrogen lamp and power unit (Beckman Co., Model B).

Materials.—The purification of reagents has been given previously.[4]

Procedure for Making the Solutions.—The same range of concentrations of ether in n-heptane (0.02 to 0.09 in mole fraction units) was used in the ultraviolet region as in the visible.[4] However, the concentration of the iodine in solution, approximately 1.5×10^{-4} mole/l., is only about one-tenth that in the visible region. This dilution, which is possible because of the much larger molar absorbancy index of the complex in the ultraviolet region, is particularly advantageous whenever there is need to reduce kinetic effects which arise from the reaction of iodine with the electron donor.

Method of Calculation.—In each study of the ether-iodine complex, the reference solution was an iodine-n-heptane solution of the same concentration as the iodine in the ether solution. For this case, the equation which applies is

$$\frac{1}{a_\lambda} = \frac{1}{(a_c - a_t)K_x} \times \frac{1}{N_e} + \frac{1}{(a_c - a_t)} \qquad (1)$$

The terms have been defined previously.[4]

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 130th Meeting of the American Chemical Society, Atlantic City, New Jersey, Sept., 1956.

[2] Taken in part from the Ph.D. thesis of Sister Mary Brandon Hudson, University of Michigan, June, 1957.

[3] Department of Chemistry, Rosary College, River Forest, Illinois.

[4] Sr. M. Brandon, M. Tamres and S. Searles, Jr., THIS JOURNAL, **82**, 2129 (1960).

[5] R. S. Mulliken, *ibid.*, **74**, 811 (1952).