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Iodine Monochloride and Iodine Complexes of Certain Mono- and Polyoxygenated Ethers and Ether Aromatic Donors

L. J. Andrews* and R. M. Keefer

Department of Chemistry, University of California, Davis, California 95616

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Equilibrium constants for the formation of 1:1 complexes of iodine monochloride and iodine with a series of ether donors in which there is more than one coordination site have been evaluated. Both polyoxygenated donors and ethers that also contain aromatic rings have been used. Polyoxygenated substances in which the oxygens are in close proximity are relatively weak donors. For other polyoxygenated donors the ratios of the equilibrium constants to the number of donor molecule oxygen atoms are similar. Ethers containing aromatic rings to which oxygens are not directly attached form both n- and π-donor type complexes as evidenced by the UV-visible spectra of the complexes. The equilibrium constants for this type of complex are sufficiently large to suggest that the ether oxygen is the primary coordination site in the donor. Complexes formed when donor oxygens are directly attached to a benzene ring are relatively weak and presumably are predominantly of the π-donor type.

Over the past few decades reports have appeared from various laboratories concerning the stabilities of complexes of iodine and oxygen containing organic donors as influenced by the existence of more than one coordination site in the donor molecule. Perhaps the earliest of these dealt with the 1:1 1,4-dioxane–iodine complex formed in solutions in which the donor was in substantial excess of the halogen acceptor.[1] Interestingly enough, this complex is less stable than certain iodine complexes of cyclic ethers that contain only one oxygen atom per molecule.[2,3] This same ordering is apparent in the relative base strengths of these cyclic ethers and 1,4-dioxane in aqueous sulfuric acid.[4] More recently, attention has been given to the polyoxygenated crown ethers as strong donors in iodine complex formation.[5] Limited consideration has also been given to iodine complexes in which the donors have both ether oxygen and aromatic ring coordination sites, mostly in relation to the UV–vis spectra of the complexes.[6,7]

Because of its polar nature, iodine monochloride is a much stronger acceptor than iodine. As such, it responds more dramatically than iodine with respect to changes in stability of its donor–acceptor complexes with changes in donor strength.[8] Iodine monochloride, therefore, appears to be a potentially better acceptor than iodine for revealing the consequences, including the spectral consequences, of changing donor structure on halogen–ether complex stability. Accordingly, a spectrophotometric study of iodine monochloride complexes of a variety of mono- and polyoxygenated donors, including some that are also aromatic in character, has been conducted. Equilibrium constants for the formation of 1:1 complexes in carbon tetrachloride at 25.0 °C have been evaluated.[9] Because of complications stemming from the high chemical reactivity of the halogen (see the Experimental Section), a detailed spectral study has not always been possible. Though some of them have been investigated previously, the iodine complexes of these same donors have been similarly studied to provide an extended set of data (for ether–iodine and –iodine monochloride complexes) collected under a self-consistent set of experimental conditions.

Experimental Section

Materials. Most of the donor ethers and alcohols were of the best grade available from Aldrich Chemical Co. Tetrahydrofuran and 1,4-dioxane, as well as the carbon tetrachloride used as a solvent, were obtained from Fisher Scientific. Phenetole, benzyl methyl ether, and 1,1-dimethoxyethane were obtained from Eastman Kodak Co. The 1,4-dimethoxybenzene came from Matheson, Coleman, & Bell and the 12-crown-4 from Sigma Chemical Co. The liquids, including the carbon tetrachloride, were generally dried over molecular sieves before use. Baker and Adamson resublimed iodine was used directly. Iodine monochloride (Aldrich) was redistilled before use.

Determination of Equilibrium Constants. As in previous investigations,[1a,10] a series of carbon tetrachloride solutions of varying concentrations of the halogen, iodine or iodine monochloride, and the donor were prepared at 25.0 °C. The donor concentrations of these solutions usually ranged from 0.10 to 1.3 M. With very weak donors, somewhat more concentrated solutions were used; with very strong donors, somewhat less concentrated ones were used. The iodine monochloride concentrations of the ether donor solutions were of the order of 5.0×10^{-4}–5.0×10^{-3} M. The iodine concentrations of such solutions ranged from 10^{-3} to 10^{-4} M. With toluene as the donor, somewhat lower halogen concentrations were employed. The absorbances of these solutions at various wavelengths in the region from 300 to 560 nm were measured at 25.0 °C against blanks of corresponding donor concentration with 1-cm absorption cells. A Beckman DU-2 spectrophotometer, upgraded with a solid-state power supply (Update Instrument Co.), was used to make these measurements.

The absorbances of iodine-containing solutions of certain of the donors, such as the crown ethers,[11] were unusually high in the region from about 400 to 320 nm, presumably because reaction had occurred to produce traces of triiodide ion. In such cases the spectral measurements were confined to the visible region. A few of the donors, as for example phenetole, consumed iodine monochloride slowly during the time required to make spectral measurements. In those instances, the absorbances were measured repeatedly at a few selected wavelengths as a function of time. The absorbances needed to calculate equilibrium constants were

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[1] (a) Ketelaar, J. A. A.; van de Stolpe, C.; Gersmann, H. R. *Recl. Trav. Chim. Pays-Bas* **1951**, *70*, 499. (b) Ketelaar, J. A. A.; van de Stolpe, C.; Goudsmit, A.; Dzcubas, W. *Ibid.* **1952**, *71*, 1104.

[2] Brandon, M.; Tamres, M.; Searles, S., Jr. *J. Am. Chem. Soc.* **1960**, *82*, 2129.

[3] Garito, A. F.; Wayland, B. B. *J. Phys. Chem.* **1967**, *71*, 4062.

[4] Arnett, E. M.; Wu, C. Y. *J. Am. Chem. Soc.* **1962**, *84* 1684.

[5] Hopkins, H. P., Jr.; Jahagirder, D. V.; Windler, F. J., III *J. Phys. Chem.* **1978**, *82*, 1254.

[6] de Maine, P. A. D. *J. Chem. Phys.* **1957**, *26*, 1189.

[7] Wayland, B. B.; Drago, R. S. *J. Am. Chem. Soc.* **1964**, *86*, 5240.

[8] Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* **1952**, *74*, 4500.

[9] Results of equilibrium studies of a few ether–iodine monochloride complexes have been reported previously; see: (a) Popov, A. I.; Castellani-Bisi, C.; Person, W. B. *J. Phys. Chem.* **1960**, *64*, 691. (b) Santini, S.; Orriso, S. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 3153.

[10] Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc.* **1953**, *75*, 3561.

[11] It has been observed frequently that ethers and alcohols react with iodine to form traces of triiodide ion that obscure the ultraviolet region of the spectrum; see, for example: Reference 5. (a) Awtrey, A. D.; Connick, R. E. *J. Am. Chem. Soc.* **1951**, *73*, 1842. (b) Ham, J. S. *J. Chem. Phys.* **1952**, *20*, 1170.

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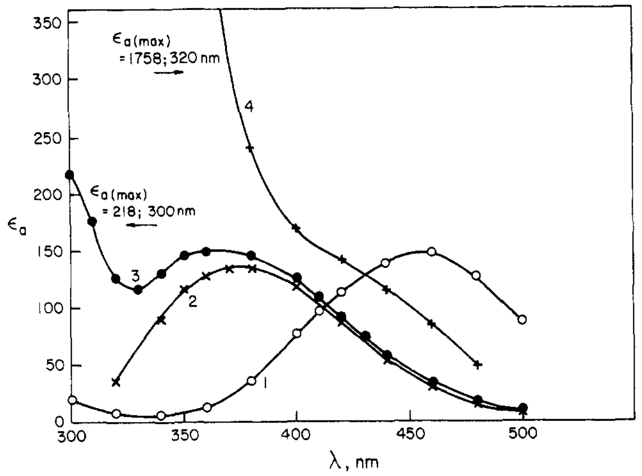

Figure 1. Spectrum of iodine monochloride in carbon tetrachloride solutions of various donors. Curves: 1, CCl_4; 2, 1.32 M di-*n*-butyl ether; 3, 1.33 M benzyl methyl ether; 4, 1.25 M diphenyl ether.

obtained by extrapolation to zero time (the time of mixing of the donor and halogen solutions).

Iodine monochloride stock solutions were prepared fresh and standardized each day and discarded at the end of the day. On prolonged standing, such solutions diminished in halogen concentration (as determined by titration with standard sodium thiosulfate) and also underwent changes in absorption spectrum.

Results and Discussion

The frequently applied graphical procedure[1a] based on eq 1 was used in evaluating equilibrium constants for formation of the 1:1 ether–halogen complexes from the data collected as described in the Experimental Section.

$$\frac{1}{\epsilon_a - \epsilon_{X_2}} = \left(\frac{1}{\epsilon_c - \epsilon_{X_2}}\right)\left(\frac{1}{K_c C}\right) + \frac{1}{\epsilon_c - \epsilon_{X_2}} \qquad (1)$$

In this equation, $\epsilon_a = A/l[X_2]_t$ where A is the absorbance of the solution in question, l is the light path length in centimeters, $[X_2]_t$ is the total halogen concentration (free and complexed), ϵ_{X_2} and ϵ_c are the absorptivities of free and complexed halogen, respectively, and C is the molar concentration of the donor. The equilibrium constants K_c (eq 2) for the various complexes that have been investigated were calculated from the slopes and intercepts of the straight lines obtained by plotting $1/(\epsilon_a - \epsilon_{X_2})$ values at a particular wavelength vs. the corresponding $1/C$ values.

$$K_c = [R_2O{\cdot}X_2]/[R_2O][X_2] \qquad (2)$$

Table I provides a summary of K_c values, listed as K_{ICl} and K_{I_2}, for the various complexes that have been studied. The wavelengths at which data were collected to evaluate the constants and the corresponding ϵ_c values are also listed. Equilibrium constants for the toluene–halogen complexes are included in the table for comparison with the constants for ethers containing aromatic rings. Also included are values of K^s_{ICl} and $K^s_{I_2}$ wheres $K^s_{X_2} = K_{X_2}$/the number of oxygen atoms in the donor molecule.

Nonaromatic Ethers as Donors. The visible absorption peak for iodine in carbon tetrachloride appears at about 520 nm, while that for iodine monochloride lies at about 460 nm (see Figures 1 and 2). When a mono- or polyoxygenated ether (an n-donor) is also present in these halogen solutions, the visible peaks are shifted to lower wavelengths, increasingly so as the ether concentration is increased (see Figure 1 for the di-*n*-butyl ether–ICl complex and Figure 2 for the 1,4-dioxane–I_2 complex). As donor strength increases, the shift becomes greater. For example, as evidenced by K_{ICl} and K_{I_2} values, 1,4-dioxane is a substantially stronger donor than 1,3,5-trioxane,[12] and the absorption peaks of iodine monochloride in 1.3 M solutions of 1,4-dioxane and 1,3,5-trioxane in carbon tetrachloride lie at 370 and 395 nm, respectively. A relationship between halogen visible peak shift and donor strength has been observed previously for certain iodine monochloride complexes.[9b] Though the halogen peaks are shifted to lower wavelengths, the absorptivities, ϵ_c, at the complex absorption maxima are closely similar to the absorptivities of the free halogens at their absorption maxima. That is, the absorption intensity of the halogen is not much altered when it coordinates with one of these n-donors.

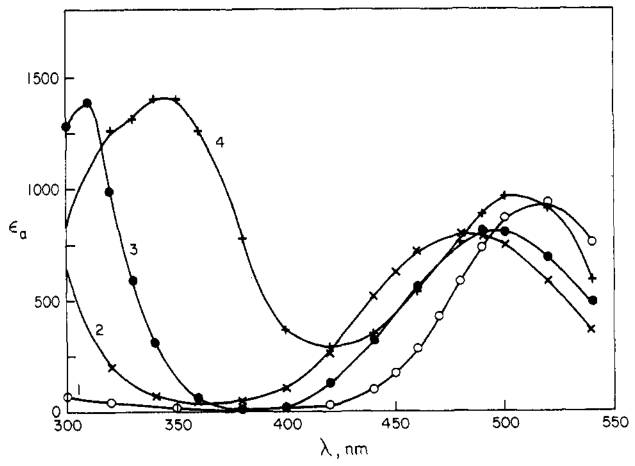

Figure 2. Spectrum of iodine in carbon tetrachloride solutions of various donors. Curves: 1, CCl_4; 2, 1.32 M 1,4-dioxane; 3, 1.33 M benzyl methyl ether; 4, 1.25 M anisole.

It has been demonstrated previously[3] that the equilibrium constants for formation of the iodine complexes of 1,1-dimethoxyethane and 1,3-dioxane are less than those for 1,2-dimethoxyethane and 1,4-dioxane. This has been explained in terms of "simple inductive arguments". The results of the present investigation clearly reflect the complex destabilizing effect of moving oxygen atoms in polyoxygenated donors close together. Both for iodine and iodine monochloride complexes, equilibrium constants change with changes in donor in the order 1,3,5-trioxane < trimethyl orthoformate < 1,1-dimethoxyethane < 1,2-dimethoxyethane ~ 1,4-dioxane < diethylene glycol dimethyl ether. The changes are much more marked for the iodine monochloride than for the iodine complexes. The values of K^s_{ICl} and also of $K^s_{I_2}$ change with donor in the order 1,3,5-trioxane < trimethyl orthoformate < 1,1-dimethoxyethane < 1,2-dimethoxyethane ~ 1,4-dioxane ~ diethylene glycol dimethyl ether ~ di-*n*-butyl ether (see Table I).

In trioxane, each oxygen atom is opposing another oxygen atom in the polarization of the C–O bonds (O←C→O). The oxygens as donors are, therefore, weaker than in compounds in which two or more oxygens are separated by more than one carbon atom. In trimethyl orthoformate, three oxygen atoms are competing in polarizing bonds to a common carbon, which results in a loss of donor strength. Each oxygen is, however, also attached to a methyl group, which apparently offsets in part the oxygen proximity effect. In 1,1-dimethoxyethane, two oxygens are bound to a common carbon and each is also bound to a methyl group. As a donor it is still significantly

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[12] The fact that the specific conductance of iodine–trioxane solutions in dichloromethane reaches a maximum when the mole ratio of solutes is 1:1 has been cited as evidence that they form a complex; see: Atreyi, M.; Kumar, S. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 471.

Table I. Equilibrium Constants and Molar Absorptivities for the ICl and I_2 Complexes of Ethers and Toluene in Carbon Tetrachloride at 25 °C

	ICl complexes				I_2 complexes			
donor	λ, nm	K_{ICl}	$10^{-2}\epsilon_c$	$K^s{}_{ICl}$	λ, nm	K_{I_2}	$10^{-2}\epsilon_c$	$K^s{}_{I_2}$
toluene[a]	320	0.85	25		330	0.17	86	
	310	0.80	49		320	0.16	127	
	300	0.85	57		310	0.18	138	
					300	0.19	126	
	K_{av}	0.83 ± 0.02			K_{av}	0.18 ± 0.01		
Nonaromatic Donors								
1,3,5-trioxane	480	2.6	0.20		540	0.39	2.1	
	460	2.3	0.40		520	0.30	3.7	
	380	2.4	1.3					
	360	2.3	0.98					
	K_{av}	2.4 ± 0.1		0.8	K_{av}	0.35 ± 0.05		0.12
trimethyl orthoformate	480	11.5	0.10		540	0.53	0.70	
	460	11.5	0.29		520	0.49	2.6	
					460	0.49	10.0	
	K_{av}	11.5		3.8	K_{av}	0.50 ± 0.02		0.17
1,1-dimethoxyethane	480	15.4	0.08		560	0.66	0.19	
	460	15.9	0.22		540	0.60	0.60	
	360	14.5	1.34		520	0.57	2.0	
					460	0.69	9.8	
	K_{av}	15.3 ± 0.5		7.7	K_{av}	0.63[b] ± 0.05		0.32
di-*n*-butyl ether	480	14.5	0.13		560	0.42	0.45	
	460	14.2	0.25		540	0.46	1.5	
	380	12.0	1.44		520	0.44	3.4	
	360	12.5	1.35					
	K_{av}	13.3 ± 1.1		13.3	K_{av}	0.44[c] ± 0.01		0.44
1,4-dioxane	480	28	0.13		540	0.99	0.79	
	460	26	0.25		520	1.10	3.4	
	360	28	1.6		460	0.84	11.0	
					450	0.97	10.0	
	K_{av}	27.3[d] ± 0.9		13.7	K_{av}	0.98[b] ± 0.07		0.49
1,2-dimethoxyethane	480	30	0.12		560	1.02	0.41	
	460	32	0.28		540	0.95	0.74	
	380	28	1.38		520	0.82	2.2	
	360	26	1.30		460	1.01	10	
	K_{av}	29 ± 2		14.5	K_{av}	0.95[b] ± 0.07		0.48
diethylene glycol dimethyl ether	380	44	1.38		540	1.23	0.60	
	360	45	1.21		520	1.08	2.3	
					460	1.36	10.6	
					440	1.08	8.7	
	K_{av}	44.5 ± 0.5		14.8	K_{av}	1.18 ± 0.11		0.39
15-crown-5	480	110	0.12		560	2.33	0.37	
	460	106	0.25		540	2.26	0.60	
	360	101	1.61		520	1.95	2.15	
	K_{av}	106 ± 3		21.2	K_{av}	2.18[e] ± 0.16		0.44
12-crown-4[f]					560	2.8	0.82	
					540	2.4	1.4	
					520	1.8	2.3	
					K_{av}	2.3[e] ± 0.4		0.58
18-crown-6	480	121	0.10		560	2.9	small	
	460	121	0.23		540	3.0	0.09	
	360	134	1.76		520	2.4	0.54	
	340	124	1.59					
	K_{av}	125 ± 5		20.8	K_{av}	2.8[e] ± 0.2		0.47
tetrahydrofuran	480	74	0.10		560	1.6	0.56	
	460	74	0.19		540	1.5	1.10	
	360	69	1.63		520	1.4	2.4	
					460	1.2	11.0	
					440	1.1	9.9	
	K_{av}	72.3[g] ± 2.2		72.3	K_{av}	1.4[h] ± 0.2		1.4
Ethers Donors—Also Aromatic[i]								
1,3-dimethoxybenzene[j]					380	0.29	72	
					360	0.28	94	
					K_{av}	0.285 ± 0.005		0.14
diphenyl ether	340	0.88	25		360	0.41	32	
	330	0.88	31		340	0.21	48	
	320	1.00	31		310	0.28	51	
	K_{av}	0.92 ± 0.05		0.92	K_{av}	0.30 ± 0.07		0.30
1,4-benzodioxane	380	2.1	7.3		360	0.34	44	
	360	2.5	12		340	0.27	59	
	340	2.6	18		330	0.31	56	
	320	2.5	22		320	0.41	44	
	K_{av}	2.4 ± 0.2		1.2	K_{av}	0.33 ± 0.04		0.17

Table I (Continued)

	ICl complexes				I_2 complexes			
donor	λ, nm	K_{ICl}	$10^{-2}\epsilon_c$	K^s_{ICl}	λ, nm	K_{I_2}	$10^{-2}\epsilon_c$	$K^s_{I_2}$
phenetole	380	1.5	6.6		380	0.28	34	
	360	1.2	16.3		360	0.29	50	
	340	1.2	31.3		350	0.31	59	
					340	0.29	50	
					320	0.30	42	
	K_{av}	1.3 ± 0.1		1.3	K_{av}	0.29 ± 0.01		0.29
1,4-dimethoxybenzene	360	2.9	10		400	0.55	19	
	340	3.1	9.6		380	0.56	17	
					360	0.50	14	
	K_{av}	3.0 ± 0.1		1.5	K_{av}	0.54 ± 0.02		0.27
anisole	340	1.7	28		380	0.32	21	
	320	2.0	23		360	0.37	35	
					340	0.32	44	
	K_{av}	1.9 ± 0.2		1.9	K_{av}	0.34 ± 0.02		0.34
1,2-dimethoxybenzene	360	5.7	11		380	0.66	27	
	340	6.1	14		360	0.58	31	
					340	0.58	31	
	K_{av}	5.9 ± 0.2		3.0	K_{av}	0.61 ± 0.04		0.31
dibenzyl ether	480	7.9	0.23		480	0.51	12.1	
	460	7.9	0.43		460	0.45	10.6	
	380	7.8	1.8					
	370	6.9	1.8					
	K_{av}	7.6 ± 0.4		7.6	K_{av}	0.48 ± 0.03		0.48
benzyl methyl ether	480	10.9	0.12		560	0.52	0.17	
	460	10.7	0.27		460	0.52	8.4	
	380	11.5	1.6		320	0.50	25	
	K_{av}	11.0 ± 0.3		11.0	K_{av}	0.51 ± 0.01		0.51

[a] Values of K_{ICl} = 0.87 and K_{I_2} = 0.16 for toluene complexes (CCl_4, 25.0 °C) have been reported previously.[8] [b] Values of K_{I_2} = 0.636, 1.080, and 1.182 for 1,1-dimethoxyethane, 1,4-dioxane, and 1,2-dimethoxyethane (CCl_4, 25.0 °C) have been reported previously.[3] For earlier related work on the 1,4-dioxane–iodine complex, see: references 1a and 2. Thompson, H. *J. Chem. Soc.* **1955**, 471. [c] A value of K_{I_2} = 0.73 (cyclohexane solvent, 25.0 °C) has been reported.[10] [d] A value of K_{ICl} = 23.27 (CCl_4, presumably at 25.0 °C) has been reported previously.[9a] [e] Values of K_{I_2} (cyclohexane solvent, 25 °C) for 15-crown-5, 12-crown-4, and 18-crown-6 have been reported[5] as 4.78, 5.36, and 4.93, respectively. [f] The K_{ICl} value could not be determined; when carbon tetrachloride solutions of donor and acceptor were mixed, a fine solid suspension formed rapidly. [g] A value of K_{ICl} = 56.5 (CCl_4, 25.0 °C) has been reported previously.[9b] [h] An equilibrium constant, K_X = 17.2 (*n*-heptane solvent, 25.0 °C), has been reported previously;[2] K_X is the equilibrium constant when the donor concentration is expressed as a mole fraction rather than in mole/liter units. [i] When there are two nonequivalent coordination sites in a donor molecule, the ϵ_c values obtained through graphical application of eq 1 are a function of the individual equilibrium constants and extinction coefficients of the two isomeric complexes that contribute to the overall complex. [j] This compound consumed ICl so rapidly that K_{ICl} could not be determined.

weaker than 1,2-dimethoxyethane. It is noteworthy that when statistical corrections for the number of oxygen atoms are made, 1,2-dimethoxyethane, 1,4-dioxane, and diethylene glycol dimethyl ether each have a donor strength per oxygen atom comparable to that for di-*n*-butyl ether. This suggests that no significant donor-weakening effects result when two oxygen atoms in a donor are separated by two carbon atoms as contrasted to a one-carbon separation. As noted in the current and earlier[3] work with respect to the strength of the two compounds as donors, it has been observed that no significant change in base strength in aqueous sulfuric acid occurs through cyclization of 1,2-dimethoxyethane to 1,4-dioxane.[4]

Because of the multiplicity of coordination sites that they offer, 12-crown-4, 15-crown-5, and 18-crown-6 are the strongest of the donors for which K_{ICl} and K_{I_2} values have been obtained in the current study. The values of $K^s_{I_2}$ for 15-crown-5 and 18-crown-6 are comparable to those for di-*n*-butyl ether, 1,2-dimethoxyethane, and 1,4-dioxane; that for 12-crown-4 is somewhat higher. The values of K^s_{ICl} for 15-crown-5 and 18-crown-6 are very close to each other (~21) but somewhat higher than those for di-*n*-butyl ether, 1,2-dimethoxyethane, and 1,4-dioxane. It is clear that when statistical corrections for the number of coordination sites are made, the donor strengths of the crown ethers are not so unusual. As has been recognized previously,[2,9b] tetrahydrofuran is a very powerful donor with respect to iodine complex formation, considering that it has only one oxygen atom per molecule. In terms of its K^s_{ICl} and $K^s_{I_2}$ values, 72.4 for the iodine monochloride complex and 1.4 for the iodine complex, it is by far the strongest donor used in this research. A reasonable explanation[4,9b] for this unusual donor strength centers on the fact that the unshared electrons on oxygen are virtually eclipsed by the adjacent C–H bonds. This maximizes the repulsion between the unshared electrons and the electrons in the bonds to the hydrogen atoms in question.

Ether Donors That Are Also Aromatic. Donors of this kind are potentially capable of forming complexes by sharing lone pairs on oxygen atoms (n-donor behavior) or π electrons of aromatic rings (π-donor behavior) with acceptor molecules.[7] When two such isomeric complexes form simultaneously, equilibrium constants for the overall donor–acceptor interaction, which have been evaluated from spectrophotometric data as in the present study, are the sum of the formation constants for the individual complexes.[6,7] The results summarized in Table I and Figures 1 and 2 indicate that the relative amounts of the two types of complexes formed from phenolic ethers are significantly different from those formed when donor oxygen is not subject to electron delocalization to an aromatic ring also present in the molecule.

The results of a ^{13}C NMR study of the thioanisole–iodine complex show that the sulfur atom is the principal donor site.[13] In studying the phenol adduct of anisole, Wayland and Drago observed that the oxygen atom of that donor is subject to more electron delocalization to the ring than is the sulfur atom of thioanisole; it has been estimated that 20–25% of the anisole–phenol interaction product is π

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(13) Niedzielski, R. J.; Drago, R. S.; Middaugh, R. L. *J. Am. Chem. Soc.* **1964**, *86*, 694.

complex.[7] They reasoned that in anisole the n-bonding ability of the oxygen is decreased (as compared with that of a nonaromatic ether) and the π-bonding ability is increased (as compared with that of benzene) and estimated that the anisole–iodine complex should be an approximately equal mixture of π- and n-donor complexes.

The K_{ICl} and $K_{\mathrm{I_2}}$ values listed in Table I for the anisole complexes are of the order of twice those for toluene and significantly less than those for di-*n*-butyl ether. A substantial ultraviolet absorption peak characteristic of the π complex is apparent in the spectrum of the iodine complex (curve 4, Figure 2).[14] This peak is shifted considerably toward the visible from the corresponding peak for the toluene–iodine complex ($\lambda_{\max}$ ca. 310 nm), no doubt in reflection of the delocalization of unshared electrons on oxygen to the anisole ring. The visible peak in the complex spectrum is shifted downward somewhat from that of the pure iodine peak, which suggest that some n-donor complex is present. The spectrum of iodine monochloride in 0.63 M anisole looks very much like that for diphenyl ether (curve 4, Figure 1). The visible iodine monochloride peak is somewhat shifted toward the ultraviolet and swallowed in the much more intense ultraviolet peak. The latter reaches a maximum in the 320–340-nm region as compared with less than 300 nm for the toluene complex.

The $K_{\mathrm{I_2}}$ values for diphenyl ether, anisole, and phenetole are closely similar. The K_{ICl} values, which spread noticeably, fall in the order diphenyl ether < phenetole < anisole, and the value for diphenyl ether is not much larger than that for toluene. In diphenyl ether, the oxygen atoms have, through electron delocalization, to a very large degree relinquished their roles as coordination centers to the rings to which they are attached. The donor strength of those rings are not, however, much enhanced.

Dibenzyl ether and benzyl methyl ether are substantially stronger than those donors in which ether oxygen is attached directly to an aromatic ring. Their $K_{\mathrm{I_2}}$ values are comparable with those for 1,4-dioxane, 1,2-dimethoxyethane, and di-*n*-butyl ether. Their K_{ICl} values are severalfold larger than those for diphenyl ether, anisole, and phenetole. The visible peak of iodine is shifted quite obviously to a lower wavelength on complexing with benzyl methyl ether (Figure 1) as well as with dibenzyl ether, and ultraviolet peaks, less intense than that for the toluene–iodine complex, appear in the spectra of both ether complexes. The downward shift of the visible peak of iodine monochloride in a 1.3 M solution of benzyl methyl ether is strikingly similar to that observed for a 1.3 M solution of dioxane (Figure 2), as is that for a 1.3 M solution of dibenzyl ether. An ultraviolet peak, much less intense than that in toluene–iodine monochloride solutions, is also apparent in iodine monochloride–benzyl methyl ether and –dibenzyl ether solutions. Both the spectra and equilibrium constants of the benzyl methyl ether and dibenzyl ether complexes suggest strongly that in the coordination products the donor site is predominantly ether oxygen. The K_{ICl} value for benzyl methyl ether is 11, which is the sum of the equilibrium constants for formation of π-donor and n-donor complexes. If it is assumed that the constant for the π-donor complex is similar to that for the toluene–iodine monochloride complex ($\sim$0.8), it follows that the benzyl methyl ether complex is about 93% of the n-donor type. The same kind of calculation for the dibenzyl ether complex gives a figure of 89%. Similar calculations for the iodine complexes of benzyl methyl and dibenzyl ether give values of 65% and 62% n-donor complex, respectively.

The values of $K^{\mathrm{s}}_{\mathrm{I_2}}$ for 1,2- and 1,4-dimethoxybenzene are similar to those for anisole, while that for 1,3-dimethoxybenzene is, for reasons not apparent, considerably lower.[15] The value of $K^{\mathrm{s}}_{\mathrm{ICl}}$ for the 1,4-isomer falls between those of anisole (1.9) and phenetole (1.3), and that for the 1,2-isomer is somewhat larger than that for anisole. The 1,3-isomer proved to be so reactive with iodine monochloride that its complex equilibrium constant could not be evaluated. The spectra of the iodine complexes of the three dimethoxybenzenes resemble that of the anisole–iodine complex (Figure 2). The spectrum of the iodine monochloride complex of 1,2-dimethoxybenzene resembles that of the diphenyl ether–ICl complex (Figure 1).

1,4-Benzodioxane is a much weaker donor than 1,4-dioxane. The $K_{\mathrm{I_2}}$ value for the aromatic ether complex is about one-third that for 1,4-dioxane, and the corresponding ratio for the iodine monochloride complexes is about 1:11. The two equilibrium constants are similar to those for the anisole–halogen complexes. The spectrum of the iodine complex is similar to that shown in Figure 2 for anisole, and the spectrum of the iodine monochloride complex resembles that for diphenyl ether (Figure 2). As is the case for the other phenolic ether donors, the low donor strength of 1,4-benzodioxane must in large part reflect the relinquishment of donor function by the oxygen atoms to the aromatic ring. It may somehow also reflect the fact that in fusing with a benzene ring the chair conformation of 1,4-dioxane[16] is altered to half-chair.[17] The contention that the ring rather than the oxygens is to a very large degree the primary halogen coordination center is supported by the observation that in the crystalline 2:1 complex of 1,4-benzodioxane and silver perchlorate the silver is coordinated exclusively with the donor ring.[18]

The original intention was to include benzo-15-crown-5 and dibenzo-18-crown-6 in the group of donors used in this investigation. Unfortunately, they proved to be too insoluble in carbon tetrachloride to permit equilibrium study.

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[14] It has been observed previously[6] that in a solution of iodine and anisole in carbon tetrachloride two ultraviolet peaks appear. These have been attributed to two types of π complex with different coordination symmetry. In Figure 2, the two peaks are not well-defined, but they have been observed in this investigation in the spectra of solutions of lower anisole concentration.

[15] Statistical corrections of equilibrium constants for complexes of polyoxygenated donors may well be of limited significance when the oxygens are directly attached to aromatic rings and complete with each other in electron delocalization.

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