83° (faintly yellow needles). This material gave a black coloration with an aqueous ferric chloride solution.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.43; H, 6.70.

2,6-Dihydroxy-3,5-dimethylacetophenone.—The compound 2,4-dihydroxy-5-methylbenzaldehyde[15] (m. p. 146–147°, lit.[15] 146–145°) was prepared by formylation of 4-methylresorcinol[6] (yield, 85%), and the product was converted to the dimethyl ether, m. p. 117–118° (lit.[15] 116.5°) in a yield of 87%. This aldehyde was reduced through the use of the Huang modification of the Wolff-Kishner reaction[6] to give a 78% yield of 1,3-dimethoxy-4,6-dimethylbenzene, m. p. 75–76° (lit.[16] 76°). This substance was demethylated with 48% HBr to give a 92% yield of 4,6-dimethylresorcinol, m. p. 127–128° (lit.[16] 124.5–125°). The procedures used for the above transformations are strictly analogous to procedures recorded for similar reactions,[6] and are not duplicated here.

A mixture of 1 g. of 4,6-dimethylresorcinol, 0.75 g. of acetic anhydride and 1 ml. of a 45% solution of boron fluoride-etherate was allowed to stand at room temperature overnight. The yellow needles that separated were collected and boiled with a 50% methanol–50% water solution, cooled, and the needles that separated were recrystallized twice from methanol and water, wt. 200 mg., m. p. 139–140° (yellow needles). This material gave a black coloration with an aqueous ferric chloride solution.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.83; H, 6.92.

Fries Rearrangement of the Diacetate of 4,6-Dimethylresorcinol.—The diacetate of 4,6-dimethylresorcinol (m. p. 44°, lit.[16] 45°) was prepared from the free phenol by the method of Pfaff.[16] A mixture of 1.2 g. of this acetate and 2.4 g. of aluminum chloride was heated to 120° and the temperature was raised to 180° over a period of an hour. The material was then cooled, decomposed in boiling water, and the product was extracted with ether. The ether solution was extracted with a dilute alkaline solution, and this aqueous extract was washed with ether, acidified, and the product was extracted with ether; the ether solution was then washed with water, dried and evaporated to an oil. The oil was dissolved in a small amount of methanol, the solution was treated with charcoal, filtered and the product crystallized by the addition of water. The material that separated was recrystallized from methanol and water to give 210 mg. of faintly yellow needles of 2,4-diacetyl-6-methylresorcinol, m. p. 83–84°.

Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.40; H, 5.63.

Summary

1. The preparations of 2,6-dihydroxy-3,5-dimethylacetophenone, 2,6-dihydroxy-3,4-dimethylacetophenone and 2,4-diacetyl-6-methylresorcinol are described.

2. The ultraviolet absorption spectra of all possible mono- and di-nuclear methylated derivatives of 2,4-dihydroxyacetophenone and 2,6-dihydroxyacetophenone have been reported. An empirical correlation of the positions of the spectral bands of these compounds has been made.

LOS ANGELES, CALIFORNIA RECEIVED APRIL 23, 1949

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[15] Gattermann, *Ann.*, **357**, 340, 372 (1907).

[16] Pfaff, *Ber.*, **16**, 1138 (1883).

[CONTRIBUTION FROM THE PHYSICS DEPARTMENT, UNIVERSITY OF CHICAGO]

Structures of Complexes Formed by Halogen Molecules with Aromatic and with Oxygenated Solvents[1]

BY ROBERT S. MULLIKEN*

I. Introduction

It is a familiar fact that iodine forms violet-colored solutions in certain solvents, brown solutions in others. In some solvents, for example benzene and methylated benzenes, it forms solutions of intermediate color. The most usual, although not universally accepted, explanation of the brown solutions has been that the altered color results from formation of molecular complexes.

Recently Benesi and Hildebrand,[1a] using spectroscopic methods, have shown definitely that benzene and mesitylene form 1:1 complexes of considerable stability with iodine. For solutions of iodine in these substances as solvents, they find that 60 or 85%, respectively, of the dissolved iodine is present in the complexes. This work lends support to earlier strong but less conclusive evidence by Hildebrand[1b] and others for the presence of 1:1 complexes in solutions of iodine in alcohol and other "brown" solvents.

On the other hand, the close agreement in form and intensity between the spectrum of iodine in the vapor state and in "violet" solvents (aliphatic hydrocarbons, carbon tetrachloride, etc.) indicates that complexes are not formed in these.[2,3,4] Other evidence[1a] supports this.

In the present paper, the existence of specific 1:1 complexes will be *assumed as established* in all cases except for the "violet" solvents.[5] An at-

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* Harvard University National Research Council Fellow 1923–1925.

[1] This work was in part assisted by the ONR under Task Order IX of Contract N6ori-20 with the University of Chicago.

[1a] H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **70**, 2382 (1948); **71**, 2703 (1949).

[1b] Hildebrand and Glascock, THIS JOURNAL, **31**, 26 (1909).

[2] See refs. 1a, 3, 4 and additional references given in refs. 1a, 3.

[3] G. Kortüm and G. Friedheim, *Z. Naturforschung*, **2a**, 20 (1947): comparison of absorption spectra of iodine in vapor, in cyclohexane solution, and in ether solution, from visible to λ2330.

[4] E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, **32**, 540 (1936): comparative graph of extinction coefficient ε in visible for vapor, vapor plus foreign gas at 50 cm. pressure, and carbon tetrachloride solution; and useful brief survey. By using foreign gas, the usual errors due to band structure below the convergence point of the bands are overcome, and the resulting ε curve is perhaps the most reliable measure available for the vapor. In bromine,[9] foreign gas causes a considerable increase in ε, but internal evidence indicates that this effect is absent in iodine.

[5] Further work will of course be desirable in order to establish the correctness of this assumption as directly as possible for examples of the second and third of the types of complexes considered here.

tempt will then be made to diagnose the observed absorption spectra so as to explain the nature of the chemical binding in these complexes. To anticipate briefly, iodine complexes falling into three distinct spectroscopic and chemical types will be distinguished, namely complexes with (1) simple benzene derivatives; (2) ethers, alcohols and water; (3) ketones. It will also be shown, from their analogous spectroscopic behavior in solution, that bromine, and iodine bromide and chloride, probably form analogous complexes. The present conclusions are in general agreement with the views of Fairbrother, and of Benesi and Hildebrand who suggest that the complexes result from "an acid-base interaction in the electron-donor sense" in which iodine functions as the acid, or electron-acceptor. However, the present proposals are more specific as to both electronic and geometrical structure.

II. Spectra and Structure of Halogens in Vapor and Inert Solvents

Before considering solvent complexes, it will be useful to review critically, and clarify somewhat, existing knowledge of the structure of the halogens and their spectra in vapor and in inert solvents. The theory of the normal and lower excited electronic states has been extensively discussed, in particular by the writer.[6] It has been shown that each of the heavier halogens must possess a remarkably large number of excited electronic states in the energy range up to 6 ev., corresponding to numerous absorption transitions extending from infrared throughout the ordinary ultraviolet. However, most of these transitions are forbidden in the homopolar halogens by rigorous selection rules, while most of the remainder are predicted to be weak. In this way, the relative simplicity of the observed spectra can be understood. But it should be emphasized that the theory is completely definite and reliable[7] as to the existence and general nature of the numerous predicted excited levels. The importance of these levels in the present connection is the possibility that some of them may give rise to absorption transitions of appreciable intensity under suitable environmental conditions, even when the same transitions are absent or too weak to be noticed in pure vapor at low pressure.

A brief survey of the electronic structures involved will be useful here and in the later discussion of the natures of the various halogen complexes. In terms of MO's (molecular orbitals), the electron configuration for the outermost electrons in the ground state of any homopolar halogen, and the over-all state type, are

$$\ldots\sigma_{\mathrm{g}}np)^2\ \pi_{\mathrm{u}}np)^4\ \pi_{\mathrm{g}}np)^4,\ {}^1\Sigma_{\mathrm{g}}^+ \tag{1}$$

Here $\sigma_{\mathrm{g}}np$ is a bonding MO related to the $np\sigma$ bonding valence orbital of the halogen atom (n = 3, 4, 5 for Cl, Br, I, respectively), while $\pi_{\mathrm{u}}np$ and $\pi_{\mathrm{g}}np$ are, respectively, bonding and antibonding π MO's. The pair of bonding electrons in the $\sigma_{\mathrm{g}}np$ MO forms the bond, while the eight π electrons, which correspond in valence-bond theory to four unshared pairs of π electrons on each atom, taken together produce little effect on the bond strength (probably a slight weakening).

The *lowest excited* group of electronic states or substates in all the homopolar halogens is

$$\ldots\sigma_{\mathrm{g}}np)^2\ \pi_{\mathrm{u}}np)^4\ \pi_{\mathrm{g}}np)^3\ \sigma_{\mathrm{u}}np,\ {}^3\Pi_{2\mathrm{u}},\ {}^3\Pi_{1\mathrm{u}},\ {}^3\Pi_{0^-\mathrm{u}},\ {}^3\Pi_{0^+\mathrm{u}},\ {}^1\Pi_{\mathrm{u}} \tag{2}$$

Because of the presence of the strongly antibonding $\sigma_{\mathrm{u}}np$ MO here, these states are in part weakly bound, in part have repulsive potential energy curves. Transitions to three of these states are responsible for the well-known moderately intense visible (and infrared in bromine and iodine, or near-ultraviolet in chlorine and fluorine) absorption bands and continua.

In iodine, by far the strongest transition in the long wave length part of the spectrum is to the ${}^3\Pi_{0^+\mathrm{u}}$ member of the group of states in (2). This is a highly characteristic but highly anomalous type of transition, since it runs counter to ordinary selection rules. It is nevertheless satisfactorily explainable by quantum theory, essentially in terms of strong intraatomic spin-orbit coupling which is present especially in iodine.[6]

The numerous additional predicted low-energy states mentioned previously are obtained by various distributions of the ten outer electrons among the four MO's which are present in (2). From the observed visible bands (transition (1) → (2)), the approximate energy difference between the MO's $\pi_{\mathrm{g}}np$ and $\sigma_{\mathrm{u}}np$ is known, and that between $\sigma_{\mathrm{g}}np$ and $\sigma_{\mathrm{u}}np$ can be obtained from ultraviolet spectra near λ2000; that between $\pi_{\mathrm{u}}np$ and $\pi_{\mathrm{g}}np$ can be estimated. With these data, the mean positions of the electronic states associated with each of the electron configurations given below in (3) can be estimated. The order in (3) is that of increasing estimated mean energy, for iodine. For iodine, the predicted states nearly all lie within 6 ev. of the ground level; for the other halogens, the predicted spread is somewhat greater.

$$\begin{array}{l}
\sigma_{\mathrm{g}}np)^2\ \pi_{\mathrm{u}}np)^3\ \pi_{\mathrm{g}}np)^4\ \sigma_{\mathrm{u}}np;\ (\mathrm{g},\ 5)\\
\sigma_{\mathrm{g}}np)^2\ \pi_{\mathrm{u}}np)^4\ \pi_{\mathrm{g}}np)^2\ \sigma_{\mathrm{u}}np)^2;\ (\mathrm{g},\ 4)\\
\sigma_{\mathrm{g}}np)^2\ \pi_{\mathrm{u}}np)^3\ \pi_{\mathrm{g}}np)^3\ \sigma_{\mathrm{u}}np)^2;\ (\mathrm{u},\ 10)\\
\sigma_{\mathrm{g}}np)^2\ \pi_{\mathrm{u}}np)^2\ \pi_{\mathrm{g}}np)^4\ \sigma_{\mathrm{u}}np)^2;\ (\mathrm{g},\ 4)\\
\sigma_{\mathrm{g}}np)\ \pi_{\mathrm{u}}np)^4\ \pi_{\mathrm{g}}np)^4\ \sigma_{\mathrm{u}}np);\ (\mathrm{u},\ 3)
\end{array} \tag{3}$$

For each configuration, the even (g) or odd (u) character of the states is indicated in parentheses, likewise the number of different electronic states or substates associated with the configuration. In (1), the one state is *g;* in (2), the states are all *u*. In view of the rigorous selection rule $g \longleftrightarrow u$ for homopolar molecules, absorption from the ground state can occur only to *u* states, except in the presence of external perturbations which destroy the symmetry. Transitions to many of the other states are also forbidden for isolated molecules; and in addition, many of the remaining *allowed* transitions are predicted to be weak. Most of the electronic states in (3) are unstable, that is, correspond to repulsion curves, but this in itself does not make them less active spectroscopically; it means merely that they would give continuous instead of discrete absorption spectra.

Recently Kortüm and Friedheim have re-examined the iodine vapor absorption down to about λ2300. The visible bands obey Beer's law, as does the beginning of an absorption in the farther ultra-

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(6) R. S. Mulliken, especially *Phys. Rev.*, **46**, 549 (1934), *e. g.*, Table III; **57**, 500 (1940); also *J. Chem. Phys.*, **8**, 234, 382 (1940). For recent experimental work and interpretation and a valuable survey, see also P. Venkateswarlu and R. K. Asundi, *Indian J. Phys.*, **21**, 101 (1947), and forthcoming paper by P. Venkateswarlu.

(7) The theory is of course not strictly quantitative as yet, but it is probably safe to say that actual electronic levels lie within 1 or 2 ev. of the predicted positions in nearly all cases predicted to lie in the range 0–6 ev. The quantitative aspects of the predictions are based largely on empirical data—see paragraph containing Eq. (3).

violet whose intensity is still rising at the limit of absorption of these authors.

In addition, they report an extremely weak absorption, with maximum at $\lambda 2670$, which does *not* obey Beer's law: its extinction coefficient ϵ increases with pressure; another group of investigators find the same absorption in saturated vapor. Kortüm and Friedheim attribute this to loosely-bound I_4 molecules (see following paragraph with respect to the same or a similar transition in solution). Bands with similar behavior are known in oxygen gas and liquid, and attributed to loosely-bound O_4. An equally satisfactory explanation would be that the bands are due to I_2–I_2 collisions. On either explanation, it is highly probable that the observed transition is one of those mentioned above which, while forbidden or extremely weak for isolated iodine molecules, becomes allowed under the perturbing action of intermolecular forces.

The same authors have investigated iodine absorption in cyclohexane, a "violet" solvent. Here the visible bands appear with a slight increase in intensity and a slight shift of wave length toward the red.[8] The Beer's law ultraviolet absorption whose intensity is still rising at the limit of observation ($\lambda 2300$) appears as before, but with 100 times the extinction coefficient it shows in the vapor; there it is weak but not forbidden, here it is strong.[9] Finally there is a rather weak absorption with maximum near $\lambda 3100$, whose ϵ increases with concentration; this is evidently similar to and perhaps identical with the pressure-sensitive vapor absorption with peak at $\lambda 2670$. The same absorption was also observed earlier by Gróh and Papp[2] and attributed to I_6 molecules.

Similar effects occur for bromine, but sensitivity to pressure and to inert solvents is much increased. For the *visible* absorption (*cf.* (2)), foreign gases[10] cause increases in intensity up to 30% (as compared with practically none for iodine[4]), inert solvents (carbon tetrachloride, chloroform, cyclohexane) cause increases of 30–60%[4,11,12,13] and in liquid bromine an increase of about 135% is observed.[14] In the *ultraviolet*, two or three transitions which are very weak or absent in the pure vapor at low pressure are brought out with appreciable intensities by inert foreign gases; probable maxima occur at about $\lambda 3130$, 2700 and 2270.[10] The last of these is also observed very weakly in bromine vapor ($\epsilon_{\max.} \approx 5$),[15] and with high intensity ($\epsilon \approx 1000$) in liquid bromine.[14] In the inert solvents mentioned above, an absorption maximum two or three times as strong as that in the visible is observed in the range $\lambda 2500$–2750.[12] This may be the same as the $\lambda 2700$ maximum observed under the influence of foreign gases.[16] Most of the maxima brought out by foreign gases or inert solvents apparently obey Beer's law, but there are indications of additional weak bands[15,12] which, like the iodine maximum near $\lambda 2670$,[3] do *not*, and so may be probably attributed to loosely-bound Br_4 molecules or to Br_2–Br_2 collisions.

Summarizing, the foregoing discussion shows that both allowed and forbidden or nearly forbidden vapor transitions in the halogens are enhanced in intensity or made allowed, sometimes rather strongly, by the action of inert gases and of inert liquid solvents, especially in the case of bromine. In addition, at least one normally forbidden transition is made weakly allowed by dimerization or halogen–halogen collisions. In the former type of transitions, Beer's law appears to be obeyed for any one particular environment; in the latter, not.

III. Spectra and Structure of Halogen Complexes with Aromatic Solvents

In aromatic solvents, the visible iodine absorption is somewhat shifted toward higher frequencies. The absorption intensities are also slightly enhanced, but scarcely more than in inert solvents (see Table I).

TABLE I

IODINE VISIBLE ABSORPTION[a]

Inert solvents			Aromatic solvents		
	$\lambda_{\max}$	$\epsilon_{\max}$		$\lambda_{\max}$	$\epsilon_{\max}$
Vapor plus foreign gas[4]	5200	820	Benzotrifluoride	5120	870
n-Heptane	5200	910	Nitrobenzene[b]	5000	
Cyclohexane[3]	5270	1070	Benzene	5000	1040
CCl_4[11]	5200	980	Toluene	4970	1020
CCl_4	5170	930	*o*-Xylene	4970	1060
CS_2	5180	1120	*p*-Xylene	4950	1080
CH_3CHCl_2	5030	870	Mesitylene	4900	1185

[a] The values of λ and ϵ are for the position of maximum absorption at room temperature. A better measure of absorption intensity would be the value of $\int \epsilon(\nu) d\nu$ integrated over the whole absorption band, or the corresponding f value. The data are from ref. 1a except as indicated by other reference numbers. [b] From a review by J. Kleinberg and A. W. Davidson, *Chem. Revs.*, **42**, 601(1948).

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(8) Other authors[1,11] find similar results in *n*-heptane, carbon tetrachloride, carbon disulfide, dichloroethane, etc. The degree to which the intensity is increased varies somewhat, however. In most cases the wave-length shift is very small, or in one case toward shorter wave lengths (see Table I).

(9) Possibly this is due to a wave-length shift of the long wave length tail of a very strong vapor absorption which occurs at shorter wave lengths, rather than to a solvent intensification effect.

(10) N. S. Bayliss and A. L. G. Rees, *Trans. Faraday Soc.*, **35**, 792 (1939): bromine vapor plus foreign gases.

(11) A. E. Gillam and R. A. Morton, *Proc. Roy. Soc. (London)*, **124A**, 604 (1929): halogens in solution.

(12) R. G. Aickin, N. S. Bayliss and A. L. G. Rees, *ibid.*, **169A**, 234 (1938): bromine in solution.

(13) N. S. Bayliss, A. R. H. Cole and B. G. Green, *Australian J. Sci. Res.*, **1A**, 472 (1948): visible bromine bands in solution. See especially the oscillator strengths (f values) in Table I.

(14) D. Porret, *Proc. Roy. Soc. (London)*, **162A**, 414 (1937): liquid bromine. The spectra of solid bromine, iodine, and chlorine at very low temperatures have been studied by A. Nikitina and A. Prikhotko, *Acta Physicochimica U. R. S. S.*, **11**, 633 (1939).

(15) R. G. Aickin and N. S. Bayliss, *Trans. Faraday Soc.*, **34**, 1371 (1938): bromine vapor.

(16) It is of course possible that different transitions are favored by different environmental conditions; also, in view of the numerous theoretically demonstrated excited levels, that any given observed maximum may be composite.

TABLE II

ULTRAVIOLET ABSORPTION OF HALOGEN–AROMATIC COMPLEXES

	Iodine complexes[a,b]				Bromine complexes[c]		
	λ_{max}	ϵ_{max}	f		λ_{max}	ϵ_{max}	f
Benzotrifluoride	$<\lambda 2800$			Chlorobenzene	2960	$<$Benzene	
Benzene	2970	9770		Benzene	2930	6800	0.18
	2980	9200	0.23[a]	Toluene	2975	$>$Benzene	
Toluene	3060	8400					
o-Xylene	3190	8400					
p-Xylene	3150	7400					
Mesitylene	3330	8300					

[a] Ref. 1a, except ref. 17 for the second set of benzene figures. [b] It is to be noted that the ϵ data are per mole of iodine, not of complex.[1] When allowance is made for the partial dissociation of the complex, the ϵ_{max} values for the complex become 16,000 in benzene, 10,000 in mesitylene, and f becomes 0.38 for the benzene–iodine complex. [c] Refs. 12, 17.

In view of the slightness of the changes, and in view of the peculiar and characteristic nature of the visible iodine absorption (see discussion following (2)), there can be little doubt that the iodine molecule is present in its aromatic complexes without more than a small change in its electronic structure.[16a] This statement holds, moreover, not only for the ground state (1), but also for the excited states (2) of the *visible* absorption.

On the other hand, the iodine–aromatic complexes show a very strong ultraviolet absorption near λ3000 (see Table II)[1a,17] which is not found for iodine in inert solvents, nor for the aromatic molecules by themselves. Since the visible bands show so little change, and since inert solvents do not cause vapor-forbidden iodine transitions to appear with at all nearly so high an intensity as the new bands here under discussion, it seems very improbable that this can be attributed to the iodine part of the complex.[17] It must then be due to the aromatic part of the complex, or else to a transition to an excited state belonging somehow to the complex as a whole.

It may be recalled that benzene itself shows a *weak* ultraviolet absorption ($\epsilon_{max} \approx 100$ for benzene in heptane) with maximum about λ2600. As is well known, this corresponds to an electronic transition *forbidden* by electronic selection rules alone, but weakly allowed by vibrational-electronic interaction. As is also well known, the analogous transition becomes *moderately strongly* allowed in certain benzene analogs (*e. g.*, pyridine) and derivatives (*e. g.*, aniline, where $\epsilon_{max} \approx 1000$) in which the hexagonal symmetry present in benzene has been lost. In unsymmetrical methyl derivatives such as toluene and the xylenes, it becomes *weakly* allowed. In most substituted benzenes, the absorption peak is shifted somewhat toward longer wave lengths.

The foregoing facts suggest that the observed absorptions of the iodine–aromatic complexes near λ3000 are essentially the same as the forbidden λ2600 transition in benzene, but now made strongly allowed by the close presence of the iodine molecule in some orientation which destroys the hexagonal symmetry. The data in Table II on the ultraviolet absorption spectrum of bromine in benzene and its derivatives now likewise find a probable interpretation in terms of the existence of analogous bromine complexes with analogous spectra.

As Benesi and Hildebrand have shown,[1a] the iodine–mesitylene complex is a much tighter one than the iodine–benzene complex, a fact which can be correlated with the much greater shift of the wave length (though not of the intensity) of the absorption peak as compared with that of the aromatic molecule by itself. Benesi and Hildebrand have concluded that the entire series of changes from benzotrifluoride to mesitylene (*cf.* Table II, also the smaller changes in Table I) are correlated with increasing ability of the variously substituted benzenes to act as electron donors. This idea is in entire agreement with what is known of the relative ionization energies of the various molecules: 9.24 ev. for benzene, 8.92 ev. for toluene, and probably about 8.3 for the xylenes and 8.1 for mesitylene.[18] It also receives support from work of Fairbrother,[19] who finds that iodine in benzene shows an apparent dipole moment of 0.6 *D*, in *p*-xylene one of 0.9 *D;* and one of 1.3 *D* in the "brown" solvent dioxane. These and other data can be understood if in the wave functions of the aromatic complexes there are appreciable amounts of resonance structures of the type $Ar^+ \cdot I_2^-$, where Ar denotes the aromatic molecule.

It is of interest to inquire whether conclusions as to the geometrical configuration of the iodine–aromatic and probable bromine–aromatic complexes can be reached using electronic structure theory. Suggestive is the fact that van der Waals forces taken alone would probably favor the closest

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(16a) The data for aromatic solvents in Table I should of course represent averages for associated and unassociated iodine (mostly the latter in benzotrifluoride, mostly the former in mesitylene[1a]). But if the unassociated molecules absorb nearly like iodine in inert solvents, the conclusion just stated is easily seen to be unaffected.

(17) N. S. Bayliss, *Nature*, **163**, 764 (1949). However, Bayliss attributes the strong absorption of both bromine and iodine near λ3000 in benzene to a greatly shifted strong halogen transition which in the free halogens occurs below λ2000.

(18) *Cf.* W. C. Price, *Chem. Revs.*, **41**, 257 (1947).

(19) F. Fairbrother, *Nature*, **160**, 87 (1947); *J. Chem. Soc.*, 1051 (1948), where also are references to earlier work by others. Note that if the benzene complex is 40% dissociated,[1a] this would make the dipole moment 0.77 *D* for molecules of the benzene–iodine complex itself.

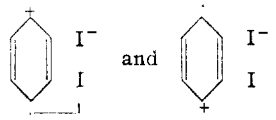
possible packing of the two molecules.[20] This would place the iodine molecule with its center on the six-fold symmetry axis of the benzene molecule and its axis parallel to the plane of the benzene ring, at a distance of about 3.4 Å. above the latter.[21] The additional polar forces involved in a structure of the type $Ar^+ \cdot I_2^-$ would also probably give maximum attraction for this same model.

The interatomic distance in I_2 (2.67 Å.) closely matches the distance (2.78 Å.) between opposite carbon atoms in the ring. On constructing the $Ar \cdot I_2$ model just proposed, using an "atom kit," it appears that there would be little if any preference for the iodine axis to lie across two opposite sides of the ring as compared with the alternative of being parallel to a line joining two opposite carbon atoms. Moreover, there would apparently be little if any steric hindrance in methylated benzenes if the iodine axis should be directly above a methyl group, at least provided the latter were allowed to orient itself suitably by rotating about the bond joining it to the ring.

The indicated model has the right symmetry so that the iodine molecule can break down the selection rules for the $\lambda 2600$ transition of benzene in qualitatively the same way that the methyl or amino groups do (mildly) in *p*-xylene or (more strongly) in *p*-phenylenediamine. Thus it might explain, at least qualitatively, the observed high intensities in Table II.

However, the observed intensities are so very high as to indicate a need for further consideration. A plausible quantum-mechanical explanation is the following. In iodine near $\lambda 1800$ or $\lambda 2000$ there occurs an extremely intense absorption, of the so-called N → V type, accompanying a transition from the $^1\Sigma_g^+$ ground state (see (1)) to a $^1\Sigma_u^+$ state belonging to the last of the electron configurations listed in (3).[6] The electric moment of this transition vibrates parallel to the line joining the iodine nuclei. Also in benzene near $\lambda 1800$ there occurs an extremely strong transition ($f = 0.8$)[22] of the N → V type, one of whose two electric moment components can vibrate parallel to that of the iodine N → V transition, if the geometrical model of the complex is that proposed above. Further, the upper electronic states of the $\lambda 1800$ and $\lambda 2600$ absorptions of benzene (also of a third transition near $\lambda 2000$) all belong, in terms of MO theory, to a single electron configuration.[23] Now even though the benzene-iodine complex in its ground state is but loosely bound, leaving the electronic structures of the two partners but little altered, nevertheless strong interaction, connected with a resonance between the N → V transitions of the two partners, may well occur between their respective excited states, provided the geometrical model is that assumed above. Further, the influence of this interaction may reasonably be expected to extend also to the other benzene excited states of the same electron configuration, including the upper state of the $\lambda 2600$ bands. In some such way the large wave-length shifts from $\lambda 2600$, and especially the high intensities, of the absorptions in Table II might well be accounted for.

It is of interest to inquire further into the forces which bring about the halogen-aromatic complexes. Van der Waals forces can help, but are not sufficient, since equally large or larger van der Waals forces must be present between the halogens and some of the inert "violet" solvent molecules, as Professor Hildebrand has pointed out to the writer. *Small admixtures* of $Ar^+ \cdot I_2^-$ resonance structures, as mentioned above, give a reasonable explanation of the observed stabilities in view of, (1), the relatively low ionization energies of unsaturated as compared with saturated organic molecules[18,24]; (2), the considerable electron affinity which the iodine molecule must possess[25]; and, (3), the possibility of weak covalent binding between Ar^+ and I or I_2^-. What is here meant by $Ar^+ \cdot I_2^-$ is mainly a mixture of the two resonance structures[25a]



with two similar structures having the opposite iodine negative, plus lesser amounts of other pairs of similar structures with different locations of the + charge and of the unpaired Ar electron. The $I^- I \longleftrightarrow I I^-$ part of this resonance corresponds to a Pauling 3-electron bond in an I_2^- ion, so that the above four structures can also be thought of in terms of resonance between *two* structures

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(20) See especially J. H. de Boer, *Trans. Faraday Soc.*, **32**, 10 (1936); J. H. de Boer and G. Heller, *Physica*, **4**, 1045 (1937). The stronger polarizability of benzene *in* than perpendicular to the plane of the ring, and of iodine *along* than perpendicular to its axis would *per se* favor an end-on arrangement of the iodine against the edge of the benzene ring, with its axis in the plane of the latter. But the closer approach afforded by the arrangement described in the text would very probably give greater stability in view of the inverse sixth-power forces involved. See also F. London, *J. Phys. Chem.*, **46**, 305 (1942).

(21) This is based on a van der Waals radius of 1.8 Å. for the iodine atoms[33] and 1.70 Å. (half the interplanar distance in graphite) for the benzene carbon atoms. A slight shortening, due to the $Ar^+ \cdot I_2^-$ attractive forces is then assumed.

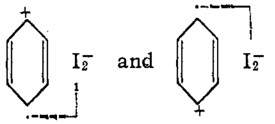
(22) J. R. Platt and H. B. Klevens, *Chem. Revs.*, **41**, 301 (1947).

(23) G. Nordheim, H. Sponer and E. Teller, *J. Chem. Phys.*, **8**, 455 (1940).

(24) The same reasoning suggests that olefins, especially methylated and conjugated olefins, which have relatively low ionization energies,[18] may form similar complexes. It is of interest that Fairbrother[19] reports that iodine dissolved in cyclohexene and diisobutylene respectively shows dipole moments of 1.1 and 1.9 *D*. *Cf.* also Ref. 25a.

(25) The electron affinity E_m of the iodine molecule is given by $E_m = E_a - D_m + D_m^-$, where E_a is the electron affinity of the iodine atom, and D_m and D_m^- are the energies of dissociation of iodine and of I_2^-, respectively. The value of D_m^- (3-electron bond) can fairly safely be estimated as half of D_m. Using the known figures E_a = 3.14 and D_m = 1.54 electron-volts, one obtains E_m = 2.37 ev. However, since the I–I distance in the complex is believed to be nearly that for unassociated iodine rather than that appropriate to I_2^-, the energy of the resonance structure $Ar^+ \cdot I_2^-$ in the actual complex must be somewhat higher. A rough estimate of the form of the potential curve for I_2^-, assuming R = 3.5 Å. and ω = 110 cm.$^{-1}$ for equilibrium, gives, for R = 2.67 Å. as in iodine, E_m = 1.8 ev. See also H. S. W. Massey, "Negative Ions," Cambridge University Press, 1938.

(25a) The proposed electronic structures are of the same general type as those suggested by Pauling for the complexes of Ag^+ with olefins, etc. (S. Winstein and H. J. Lucas, THIS JOURNAL, **60**, 836 (1938).) Electronic structures for $Bz \cdot I_2$ more or less similar to those below have been proposed by Dewar (*J. Chem. Soc.*, 406 (1946)) and by Fairbrother.[19] See also Williams, *Phys. Z.*, **29**, 174 (1929).



Thus far only one particularly plausible geometrical model, which may be called model I, has been considered. Other models which may be worth looking at briefly are: (II), with all atoms coplanar, the iodine molecule resting end-on against one side or corner of the benzene ring; (III), with the iodine resting waist-on against one side of the benzene plane, its axis perpendicular to the latter; (IV), with the iodine standing upright on the benzene plane, its axis coincident with the sixfold symmetry axis of benzene; (V), a filled-doughnut model similar to (IV) except that the two iodine atoms are on opposite sides of the benzene plane (suggested by Professor J. R. Platt). Other models involving oblique angles seem too improbable to need consideration.

Models II and III are of the same symmetry (C_{2v}) as I, so that both are effective in destroying the hexagonal symmetry of isolated benzene, thus making λ2600 of benzene into an allowed transition, as required. Models IV and V preserve the symmetry of benzene, IV partially (symmetry C_{6v}), and V completely (symmetry D_{6h}), so that in both cases the λ2600 transition of benzene remains forbidden. These models are then probably ruled out on that account. Model V also seems unlikely for other reasons.

Model II involves weaker electrostatic attractions than I in most of the $Ar^+ \cdot I_2^-$ resonance structures. In addition, it can be shown[26] that for model II an excited state of I_2^- would be necessary in order to meet symmetry requirements—a type of consideration customarily, but not always safely, ignored in discussions of resonance structures. Thus it appears fairly sure that model II must be ruled out as compared with I, where electrostatic and probably van der Waals attractions are more favorable, and where the ground state of I^- *does* meet the symmetry requirements.

For model III, the normal state of I_2^- again meets the symmetry requirements, but the electrostatic situation, although more favorable than for model II, is less favorable than for model I. Further, even though the forbiddenness of the λ2600 transition is removed in this model, nevertheless resonance between the N → V transitions of benzene and iodine is not possible because their electric moments are now perpendicular to each other; hence our proposed explanation of the strikingly high intensity of the λ3000 absorption would not be valid for model III.

Thus the original model I appears to be definitely the most probable geometrical arrangement for halogen–benzene complexes. The same reasoning and conclusions hold for iodine–mesitylene complexes, and similar reasoning and conclusions for complexes with other substituted benzenes.[26a] The indicated model is obviously of possible interest in connection with the mechanism of halogen substitution in the benzene ring.

Note added in proof.—An attractive alternative to the explanation above for the strong $Ar \cdot I_2$ absorption near λ3000 is that this is an ***intermolecular charge-transfer spectrum***,[26b] essentially $Ar \cdot I_2 \rightarrow Ar^+I_2^-$. If the $Ar \cdot I_2$ wave function contains a small amount of $Ar^+I_2^-$ resonance structures, as discussed above, it follows that there must exist low excited states whose wave functions are ***principally*** $Ar^+I_2^-$ but contain small amounts of $Ar \cdot I_2$. Transition to the lowest of these would correspond essentially to the jump of an electron from the most easily ionized molecular orbital of the aromatic molecule to a previously unoccupied iodine molecular orbital. The oscillator strength of the transition can be shown[26b] to be given for Model I by

$$f = 1.085 \times 10^{11}\nu Q^2; \quad Q^2 \cong 2S^2z^2, \qquad (4)$$

where S is the overlap integral between the two molecular orbitals, and z is the distance at which their overlap is a maximum, measured from the center of Ar toward that of I_2. If we assume z = 1.7 Å., then to match the observed f of 0.23 for benzene (*cf.* Table II), S = 0.33 is required. Unfortunately, this S value appears improbably high (an upper limit for reasonable estimates appears to be about 0.1–0.2).

Nevertheless, the foregoing explanation may be worth considering, especially since it seems qualitatively well suited to explain the color phenomena which are characteristic of so many organic molecular complexes.[26c]

If the foregoing explanation should be correct, the spectroscopic arguments given above for and against the various models of $Ar \cdot I_2$ must of course be modified. For model I in the new explanation, the electric moment of the λ3000 absorption would vibrate along the line joining the Ar and I_2 centers.

IV. Spectra and Structure of Halogen Complexes with Solvents of Type RR′O

Iodine forms brown solutions in ether, alcohols,

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(26) The $Bz \cdot I_2$ wave function (Bz = benzene) is symmetrical with respect to all symmetry operations *of the model*, for any of the models. According to quantum mechanics, resonance is possible only between wave functions having identical symmetry properties. But for model II, the wave function of $Bz^+ \cdot I_2^-$ formed using ground-state I_2^- is antisymmetric to the plane of the molecule, because the orbital of the π electron removed from Bz is antisymmetric, while that of the σ electron added to iodine is symmetric, to this plane. Hence ground-state $Bz^+ \cdot I_2^-$ in model II cannot resonate. The desired resonance can be obtained only if the I_2^- is excited to a state having one less π electron and one more σ electron.

(26a) For a discussion of other benzene complexes, see G. Briegleb, "Zwischenmolekulare Kräfte und Molekülstruktur," F. Enke, Stuttgart, 1937. Of interest here are complexes like that formed by benzene with nitrobenzene, where according to Briegleb the two rings lie one above the other with their planes parallel,—a model which is similar to our benzene-iodine model I, and may very likely be explained at least partially in a similar way (*cf.* especially J. Weiss, *J. Chem. Soc.*, 245 (1942), who, however, suggests nearly 100% ionic structures, which surely cannot be correct). (According to Briegleb, the dipole moment of the nitro group polarizes the benzene in the plane of the ring, where the polarizability is especially high, and thus stabilizes the complex.) In complexes like those of benzene with BX_3 and AlX_3 (X = halogen), where the large dipole moments indicate a pyramidal structure for the BX_3 or AlX_3, a partial $Ar^+\text{-}MX_3^-$ structure with dative bond between the Ar and an M electron (*cf.* Dewar's π complexes) seems likely. Andrews and Keefer have very recently proposed a similar interpretation for Ar·Ag complexes (THIS JOURNAL, **71**, 3644 (1949); see also Ref. 25a).

(26b) On *interatomic* charge-transfer spectra, see R. S. Mulliken, *J. Chem. Phys.*, **7**, 20 (1939); R. S. Mulliken and C. A. Rieke, Reports on Progress in Physics, The Physical Society, London, **8**, 231 (1941); E. Rabinowitch, *Rev. Mod. Phys.*, **14**, 112 (1942). Eq. (4) is obtained by treating the Ar and I_2 molecular orbitals as if they were *atomic* orbitals in the *atomic* orbital method for interatomic charge-transfer spectra.

(26c) See for example W. Brackmann, *Rec. trav. chim. pays-bas*, **68**, 147 (1949). Neither Brackmann nor Weiss[26a] gives, in the writer's opinion, a satisfactory explanation of color phenomena in molecular complexes.

water, dioxane, pyridine and certain other similar solvents.[26d] For some of these the spectroscopic evidence is conflicting, probably because of chemical reactions, or in some cases, it may be surmised, because of benzene impurity whose iodine complex gives rise to strong absorption near λ3000. Allowing for these possibilities, the evidence[1a,3,4,27] seems to be consistent with the existence of a class of complexes between iodine and molecules of the type ROR′ (R,R′ = hydrogen or alkyl or other group), with a characteristic absorption having its maximum between λ4500 or 4600 and 4800.[27a] This is of about the same intensity as, but is at considerably shorter wave length than, the iodine λ5200 absorption in inert solvents.

The most reliable data seem to be those for iodine in ethyl ether.[1a,3] Here the visible absorption has its maximum at λ4620[1a] or λ4650,[3] with peak intensity $\epsilon_{\max} = 880$[1a] or 870.[3] The total absorption in the band is somewhat greater than for the visible band in violet solvents, since the absorption region is broader. The most probable explanation appears to be that (1) a 1:1 complex is formed[1b]; (2) the absorption near λ4600 corresponds to essentially the same electronic transition, occurring in the iodine part of the complex, as the visible absorption of iodine alone or of iodine in aromatic complexes; but (3) the complex is a tighter one, involving a greater change in the structure of the molecule, than in the aromatic complexes.

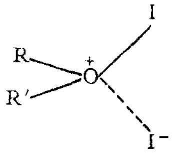
As for each other type of complex, we should carefully consider whether the change in electronic structure may be mainly in the ground state, or mainly in the excited electronic state, or more or less equally in both. Usually this question can be answered fairly well when a correct explanation of the spectrum is obtained, since this involves an identification of the nature of the electronic structure in both electronic states, for an atomic arrangement which is that of the ground state.[28]

In addition to the visible absorption, there is for the ether complex a stronger ultraviolet absorption ($\epsilon_{\max} = 2450$) with peak at λ2480.[3] Kortüm and Friedheim[3] also report indications of the non-Beer's-law absorption near λ3100 which they find in cyclohexane solution and attribute to I_4.

The considerable shift and broadening of the iodine visible absorption in the $ROR'{\cdot}I_2$ complexes probably means that the valence structure of the iodine molecule in the complex has been very appreciably changed. If one asks what sort of a change this may be, the writer finds only one obvious answer, namely, a structure in which an electron of the "lone pair" of the oxygen atom is partially transferred to the iodine, in a manner to be described below. The ionization potential of this electron, which undoubtedly corresponds[29] to the observed minimum ionization potential of ROR′, at least for all ROR′ complexes in which R is a hydrogen atom or an alkyl group, varies considerably depending on R and R′. For example, it is 12.61 e. v. for water, 10.7 e. v. for ethyl alcohol, 10.2 e. v. for ether.[18] In analogy with the complexes formed by the substituted benzenes, one may then expect to find the stabilities of the complexes to increase markedly in this order. Fairbrother's finding[19] of an apparent dipole moment of 1.3 *D* for iodine dissolved in the double ether dioxane gives support to the type of structure just indicated.

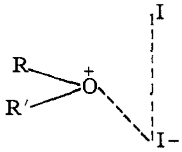
The existence of stable $RR'O{\cdot}I_2$ complexes can be understood if their wave functions, though mainly of van der Waals $RR'O{\cdot}I_2$ structure, attain very appreciable percentages of two resonance forms of the type

(I)



and of two other forms of the type

(II)



Type I resonance corresponds to one homopolar O–I bond plus one ionic O^+I^- bond, Type II to a three-electron I–I⁻ half-bond (I_2^- structure) plus one O^+I^- bond. The percentage of Type I structures in the wave function should depend in part on the strength of the O^+–I bond, and this in turn must depend on the O–I distance. For van der Waals contact, the O–I distance may be about 3.2 Å.[30] The actual distance may be estimated as somewhat less, say 3.0 Å. If the normal O–I bond length is 2.0 Å., and the O–I bond energy follows a Morse curve, the O^+–I bond energy at 3.0 Å. should be about one-third to one-fourth that for the normal bond length. Although this is not

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(26d) Presumably pyridine forms a complex more or less similar to that of benzene, or else one of an onium type. The pyridine complex $Py{\cdot}I_2$ is known also in crystalline form.

(27) J. Kleinberg and A. W. Davidson, *Chem. Revs.*, **42**, 601 (1948).

(27a) However, for iodine dissolved in ethyl alcohol glass at liquid hydrogen temperatures, the absorption maximum is reported to be shifted to about λ4000, with an increase in intensity (A. Prikhotko, *Acta Physicochimica U. R. S. S.*, **16**, 125 (1942)), perhaps due to a tightening of the complex, or possibly to a cage effect. Cage effects (N. S. Bayliss and A. L. G. Rees, *J. Chem. Phys.*, **8**, 377 (1940)) no doubt play some part in all solution spectra. However, such phenomena as the transition to a brown color when moderate amounts of a "brown" solvent are added to a "violet" iodine solution (*cf.*, *e. g.*, Ref. 1b) indicate that the color change here is primarily due to complex formation rather than cage effect. Further study will nevertheless be desirable.

(28) In interpreting any absorption spectrum it is important to keep always clearly in mind that the geometrical structure involved during the absorption process is that of the ground state. This is because according to the Franck–Condon principle, the peak of any molecular absorption region corresponds to the occurrence of an electronic transition with very little change in the configuration of the nuclei.

(29) R. S. Mulliken, *J. Chem. Phys.*, **3**, 506 (1935).

(30) *Cf.* A. L. G. Rees, *ibid.*, **16**, 995 (1948). However, Rees's values should probably not be accepted without reserve.

large, it may be enough to promote Type I resonance and help stabilize the complex to an appreciable extent.

The I–I axis probably lies *perpendicular* to the ROR′ plane in the manner shown, since the angles involved appear to give the best opportunity for O–I bonding by the available O^+ electron in the Type I resonance structures, and for $I–I^-$ bonding in the Type II structures. Coplanar arrangements of R′RO and iodine are unfavorable for reasons of symmetry, since, then (1), no O^+–I bond at all can be formed in the Type I structures; (2) in the Type II structures an excited state of I_2^- would be necessary, just as in $Ar^+ \cdot I_2^-$.[26] Other geometrical models for the complex also appear to be unfavorable.

If, assuming the above model, the resonance hybrid contains a total of say 10% (reckoned in terms of *squares* of coefficients in the wave function) of the four resonance structures indicated, the I–I bond would be slightly "sprung." An examination, if feasible, of the Raman and infrared spectra might throw further light on this.[30a] When one writes out the electron configuration in terms of molecular orbitals, one finds that the two molecular orbitals involved in the visible absorption, and the oxygen non-bonding orbital, are particularly strongly affected. This happens in such a way as might very well account for the observed shift of the λ5200 iodine band toward shorter wave lengths, although quantitative computations would be needed to say positively that the observed shift is what one would expect. The above type of structure would mean that the interaction of the two partners of the ether complex is fairly strong *both* in the ground state and in the λ4620-excited electronic state.

An attempt to interpret the first ultraviolet peak does not seem particularly promising as an easy source of further clear-cut evidence on the structure of the complex. However, further study of the ultraviolet spectra of various complexes of the type $R'RO \cdot I_2$ might give interesting results. Perhaps the λ2480 absorption of the ether complex is of the charge-transfer type (*cf.* Note at end of Section III).

The above-proposed structure for $R'RO \cdot I_2$ complexes seems to correspond to an attractive mechanism, as follows, for such rapidly reversible equilibria as that between I_2, HOI and HI in aqueous solution

$$I_2 + H_2O \rightleftarrows H_2O \cdot I_2 \rightleftarrows H_2\overset{+}{O}I + I^- \rightleftarrows HOI + HI$$

with analogous reactions for the other halogens.

Spectroscopic data relevant to oxonium complexes of other halogens than iodine are also available. For example, iodine chloride (vapor absorption maximum at λ4700) forms brown solutions in inert solvents (CCl_4, $CHCl_3$) with visible absorption maximum at λ4600 (ϵ_{max} about 150–160). But in oxygenated solvents (ether, ethyl acetate, acetic acid) it forms yellow solutions in which the first absorption maximum occurs at λ3500–3600, although without change of peak intensity.[31] Presumably we have here very stable complexes of the same structure as the iodine complexes, but in which the structure has gone rather far toward that of a normal valence compound of oxonium type. Iodine bromide shows a similar behavior (red solutions, $\lambda_{max} \approx 4900$, $\epsilon_{max} \approx 350–400$ in inert solvents, yellow solutions, $\lambda_{max} \approx 4000$, $\epsilon_{max} \approx 350–400$ in ethyl alcohol and the like).

The shift of the visible band in iodine chloride and iodine bromide solutions is so large that one might hesitate to identify it with confidence as belonging to the halogen molecule in the complex. However, in view of the fact that it is in both cases, just as in iodine, the first absorption of any considerable intensity, and that in all three cases its peak intensity is nearly independent of the type of solvent, the identification becomes rather convincing. Further, the steady shift of this band, in the case of iodine, in going from inert solvents to aromatic solvents to RR′O solvents, re-inforces this identification.

Brief mention should be made here of a different well-known kind of complex formed by the halogens, namely, the $A^+X_3^-$ type. In their work on ICl, Gillam and Morton[31] concluded that ICl in HCl and Na^+Cl^- solutions respectively forms $HICl_2$ and $Na^+ICl_2^-$. The $AICl_2$ or ICl_2^- structure shows a characteristic absorption ($\lambda_{max} = 3420$, $\epsilon_{max} = 275$) which, probably by chance, is similar though not identical in position and intensity to that of the R′OR.ICl complexes. (The familiar I_3^- complex absorbs near λ3500.)

Presumably similar to the $RR'O \cdot I_2$ complexes are the very stable deeply colored $RR'S \cdot I_2$ and $RR'S \cdot Br_2$ complexes, several of which are known in crystalline form.[31a] The halogen is recoverable from these on heating.

V. Iodine–Acetone Complex

Although an absorption maximum at λ4600 has been reported for iodine in acetone,[31b] Benesi and Hildebrand did not find this.[1a] According to them, the first maximum occurs at λ3630, with an intensity very much higher ($\epsilon_{max} = 6100$) than for the first maximum of iodine in any of the solvents discussed hitherto.[32] [*Added in proof.*—

(30a) A rather similar case is that of the $Ag^+ \cdot$olefine complexes,[25a] where Raman studies (Taufen, Murray, and Cleveland, THIS JOURNAL, **63**, 3500 (1941)) have confirmed the predicted loosening of the C═C bond.

(31) ICl: A. E. Gillam and R. A. Morton, *Proc. Roy. Soc.* (*London*), **132A**, 152 (1931); IBr: A. E. Gillam, *Trans. Faraday Soc.*, **29**, 1132 (1933).

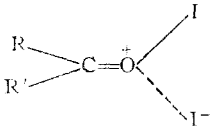
(31a) Fromm and Raizics, *Ann.*, **374**, 90 (1910).

(31b) F. H. Getman, THIS JOURNAL, **50**, 2883 (1928). According to Getman, acetone and acetophenone are brown solvents. Getman reports that acetone solutions of iodine lose their color on standing.

(32) Maxima at λ3630 (and at λ2820) have been reported by Walls and Ludlam for iodine in ethyl alcohol,[27] but Batley[3] reports no maximum except at λ4470 if reactions are avoided. Cennano[3] reports maxima at λ3600 and at λ2970 for iodine in $CHCl_3$, CH_3OH, and in acetone. The most likely explanation of the λ3600 and λ2970 maxima here is that they are due to small amounts of the *strongly-absorbing* I_3^- and benzene complexes, resp., present as impurities.

However, in further studies (private communication) they find that this is probably due to I_3^- formed in a rapid reaction. By using mixed acetone–CCl_4 solutions, they obtain evidence for a moderately shifted visible absorption, which perhaps after all may be in harmony with German's observations.[31b]]

It is of interest to consider briefly the probable structure of a 1:1 complex of iodine with acetone. An examination of possible resonance structures suggests that those which could cause complex formation are of a type $RR'CO^+ \cdot I_2^-$ very similar to those in the type $RR'O \cdot I_2$, except that the non-bonding oxygen orbital involved in the complex formation has its axis *in the RR'CO plane*, whereas in $RR'O^+ \cdot I_2^-$ the non-bonding oxygen orbital had its axis *perpendicular* to the RR'O plane



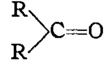
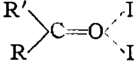
As compared with complexes of the RR'O type,[33] an additional stabilizing factor is present here. Namely, because of its planar structure, there must be a conjugation or hyperconjugation effect between some of the iodine non-bonding π orbitals (see (1)) and the orbitals occupied by the π bonding electrons in the C=O double bond. This effect could be represented by resonance structures, but in a rather cumbersome way; it is more easily seen using MO's (molecular orbitals). This might give a very appreciable further stabilization if the O–I bond distance is sufficiently short.

[*Added in proof.*—The reported complexes formed[1b] with iodine by the brown solvents ethyl acetate and acetic acid might be of either or both of the RR'O and RR'C=O types.]

Acknowledgments.—The writer is indebted to Professor J. H. Hildebrand and to Chicago colleagues for helpful discussion and criticism.

VI. Summary

The absorption spectra of solutions of iodine in aromatic and oxygenated solvents are interpreted on the assumption that they are spectra of 1:1 complexes of iodine with solvent molecules. (The correctness of this assumption at least for certain aromatic complexes has been shown by Benesi and Hildebrand.) The extent to which the λ5200 absorption region, highly characteristic of the iodine molecule in vapor and in inert solvents, is shifted toward the ultraviolet and altered in shape or intensity, is used as the principal basis for a division of these complexes into three classes. By valence-theoretical considerations a unique probable geometrical and electronic structure is obtained for each class.

The probable structures are as follows. In general agreement with considerations advanced by Benesi and Hildebrand, and others, the electronic wave functions of all three classes are believed to contain resonance components of the general type $A^+I_2^-$ or A^+I^-I. In the $Ar \cdot I_2$ complexes (Ar = benzene or methylated benzene), the iodine molecule lies above the plane of the benzene ring with its axis parallel to the latter. In the $R'RO \cdot I_2$ complexes the iodine molecule stands against the oxygen atom, with its axis perpendicular to the R'RO plane. The probable acetone–iodine complex is similar except that the iodine axis is coplanar with the  skeleton. The polar forces, which are present in all three cases, are aided in the first class by partial C–I bonding and in the second and third classes by partial O^+–I bonding, and further in  by conjugation between the C=O and the I–I π electrons. The indicated structures are suggestive as to reaction mechanisms for the halogens.

The ultraviolet spectra, especially of the aromatic complexes, are discussed. The very intense absorption of the aromatic complexes near λ3000 is attributed to a transition in the aromatic part of the complex. It is suggested that this transition, although nearly forbidden in the aromatic molecule, is made strongly allowed by strong interaction between excited states of the two partners in the complex. As an alternative, it is suggested that this absorption, as also the color of other organic molecular complexes, may be due to an *intermolecular charge transfer process* during light absorption.

Bromine in benzene and toluene solutions shows spectra which indicate that it forms complexes of the same kind as described above for iodine. Iodine chloride and bromide solution spectra in R'RO solvents also indicate the formation of complexes similar to those formed by iodine, but tighter.

Brief comments are made on some other organic molecular complexes.

The nature of the spectra of iodine and bromine in vapor and inert solvents is reviewed and it is hoped somewhat clarified.

CHICAGO, ILLINOIS RECEIVED NOVEMBER 11, 1949

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[33] The minimum ionization energies of ethyl ether (10.2 e. v.) and acetone (10.1 e. v.) are apparently about equal,[18] and since these probably correspond in both cases to removal of a non-bonding oxygen electron (see R. S. Mulliken, *J. Chem. Phys.*, **3**, 506 (1935), on RR'O; **3**, 564 (1935) on RR'CO), this indicates that this process is about equally easy in both cases.