Table II illustrates the catalytic activity and synthesis characteristics of the cobalt–thoria–manganous oxide–kieselguhr catalyst on which adsorption measurements were carried out. The data refer to runs at atmospheric pressure and at the optimum temperature of 190° under which conditions the activity of the catalyst was nearly constant for two months.

The catalyst after being thoroughly carbided with carbon monoxide at 200° was found to have the same characteristics as previously reported for similar carburized catalysts,[4,5] yielding with synthesis gas an apparent contraction of only 7.3% at the temperature of 190°.

Discussion

Carbiding of the catalyst results in only a slight reduction of the surface area but reduces the volume of chemisorbed carbon monoxide to about a fourth of the value found prior to carbiding. This experiment also establishes that carbided cobalt is not appreciably "cleared" by heating at 300° for several hours in high vacuum.

The amount of carbon monoxide chemisorbed by the reduced catalyst after use in synthesis is 73% of the value obtained with the original reduced catalyst. Nearly three-fourths of the cobalt atoms on the surface could thus be "cleared" by evacuation alone at 200° and hence the inference can be drawn that during active synthesis the catalyst does *not* contain appreciable amounts of either bulk or even surface carbide. If either had been present, the surface could not have been cleared by evacuation alone. The temperature of evacuation in this step was kept low enough to avoid cracking the carbide, if it were formed at all, or the hydrocarbon product. The reason for stopping the synthesis run almost immediately after the induction period was to avoid excessive deposition of oil and wax on the catalyst which would be difficult to remove by evacuation.

The 40% decrease in the surface area of the reduced catalyst after its brief use in synthesis indicates the blocking up of a portion of the surface by tenaciously held products of the synthesis. It is interesting to note that on using the sample for synthesis the surface area decreases relatively more than the carbon monoxide chemisorption. This may be due to the presence of narrow pores which were too remote to be covered with cobalt during the impregnation of kieselguhr and which were later filled with oil during synthesis.

Craxford and Rideal put forward the view that during the induction period a steady accumulation of surface carbide took place, and when thereafter the initial methane formation gave place to synthesis of higher hydrocarbons the surface was almost entirely covered with carbide. The experiments reported in the present paper show that appreciable amounts of carbide are not formed under synthesis conditions either as an active intermediate or as a poison to hydrogenation-cracking. It is concluded therefore that carbon monoxide is held on the surface mostly in the chemisorbed state and is not appreciably converted into any "fixed" phase such as carbide or oxide on the surface during the steady state synthesis.

Acknowledgment.—The authors are deeply indebted to their Director, Dr. Sir J. C. Ghosh, for his interest in this investigation and guidance in the preparation of this paper.

KHARAGPUR, INDIA

[CONTRIBUTION FROM THE HUMBLE OIL AND REFINING COMPANY,* BAYTOWN, TEXAS, AND DEPARTMENTS OF PHYSICS AND CHEMISTRY, THE UNIVERSITY OF TEXAS,† AUSTIN, TEXAS]

Molecular Complexes Involving Iodine[1]

BY S. H. HASTINGS,* J. L. FRANKLIN,* J. C. SCHILLER* AND F. A. MATSEN†

RECEIVED JUNE 7, 1952

Absorption bands have been found in the ultraviolet spectra of solutions of iodine in a number of "inert" solvents such as saturated hydrocarbons and alkyl halides which are not found in the spectra of either iodine or the solvents alone. These bands are attributed to molecular complexes between iodine and the solvents such as have been previously reported for solutions of iodine in aromatic and olefinic hydrocarbons. It is shown that a relationship exists between the frequencies of the absorption bands of all the iodine complexes and the ionization potentials of the corresponding bases (solvents). This work has led to a simple extension of Mulliken's theory of molecular complexes to the prediction of the frequencies of the absorption bands of the complexes. It is shown that $h\nu = I_B - D + 2\beta^2/(I_B - D)$, where $h\nu$ is the absorption frequency of the iodine complex; I_B is the ionization potential of the base; $D = E_A + e^2/r - C_{AB}$; E_A is the electron affinity of the acid; e^2/r is a coulomb attraction term; C_{AB} is the sum of all other energy terms; and β is an approximately constant term arising out of the quantum mechanical treatment. A discussion is given of the observed frequency–ionization potential relationship in light of the equation.

Introduction

A considerable amount of interest has been shown in the fact that iodine in solution in various solvents exhibits different colors. Originally these solvents were divided into two classes, those which caused a violet color (inert) and those which caused a brown color (active). The original assumption that solvates were formed only in the case of the so-called "brown" solvents had to be modified later when a number of workers showed that the visible absorption band of iodine shifted gradually to the blue in a series of solvents.[2]

A number of significant developments in the study of iodine solutions have occurred in the last few years. Benesi and Hildebrand[2] have found a new absorption band in the ultraviolet spectra of

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(1) Presented at the Symposium on Molecular Structure and Molecular Spectroscopy, Ohio State University, June 9–13, 1952.

(2) H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **71**, 2703 (1949).

solutions of iodine in aromatic hydrocarbons. The overlapping of this band into the visible causes a greater change in the color of the iodine solution than does the observed small shift of the visible iodine band to the blue. Benesi and Hildebrand showed that the band was due to a 1:1 complex between the aromatics and iodine and proposed an acid–base type of interaction. They reported that no analogous band was found in the 270–400 mμ range for solutions of iodine in solvents such as carbon tetrachloride, carbon disulfide, *n*-heptane, ethyl ether, acetone and 1,1-dichloroethane.

More recently Mulliken[3] has presented theoretical treatments of the interaction of electron acceptors and donors to form molecular complexes and has achieved satisfactory agreement between the calculated and observed oscillator strengths of the iodine–benzene complex absorption band at 297 mμ based on the assumption that this is an intermolecular charge-transfer spectrum. It is interesting to note that complexes between iodine and olefins predicted by Mulliken have been observed by Andrews and Keefer[4] and also by Freed and Sancier.[5]

Both Benesi and Hildebrand and Mulliken point out that no absorption bands for complexes of iodine and saturated aliphatic hydrocarbons have been reported and it was assumed that these "violet" solvents are truly inert. However, work in our laboratories has definitely established the presence of weak absorption bands in the ultraviolet spectra of solutions of iodine in such "inert" solvents as cyclohexane, paraffin hydrocarbons and alkyl halides. Detection of these bands in saturated aliphatic hydrocarbons is difficult because of their proximity to the intense absorption due to iodine near 190 mμ, and detection in alkyl halides is difficult because the complex absorption bands lie very near the ultraviolet absorption bands of the halides themselves.[6]

Experimental

The spectra reported here were obtained on a Cary recording ultraviolet spectrophotometer employing rock salt cells of 0.102 and 1.03 mm. thickness in the sample beam. Cells of approximately the same thickness were filled with the solvent under study and placed in the reference beam. Appropriate corrections were applied for differences in cell absorbance.

Phillips Petroleum Company "Pure" grade saturated hydrocarbons (99 mole per cent. minimum purity) were employed after percolation over silica gel to remove strongly ultraviolet-absorbing impurities.

Eastman Kodak Company "White Label" alkyl halides were employed without further purification.

Spectra of olefin–iodine mixtures were obtained by blending NBS certified olefins in spectroscopically-pure isoöctane (99.5^+ per cent. 2,2,4-trimethylpentane percolated over silica gel).

Figure 1 shows the ultraviolet absorption of iodine in some saturated hydrocarbons. It is quite apparent that there is an absorbing species in the cyclohexane (and possibly in the *n*-heptane and 2,3-dimethylbutane) which is not present in appreciable concentrations in the *n*-hexane. These absorbing species are believed to be iodine complexes similar to those formed with aromatic hydrocarbons. Since the hydrocarbons employed do not absorb in this region it is obvious that the absorption shown in Fig. 1 is due to iodine in the complexed and uncomplexed states. To obtain the absorption spectra of the iodine–cyclohexane and iodine–2,3-dimethylbutane complexes the spectra shown in Fig. 1 must be corrected for absorption due to uncomplexed iodine. It may well be supposed that the strong absorption band in iodine at about 190 mμ is not greatly affected by complex formation; *i.e.*, the appearance of the charge transfer spectrum is not accompanied by a simultaneous disappearance of the molecular iodine spectrum. Furthermore, as is shown below, the amount of iodine tied up in the complexes with saturated hydrocarbon is small so that the difference between the absorption of iodine in a truly inert or noncomplexing solvent and in a complexing solvent should yield the absorption spectrum of the complex being studied. With the finding that even saturated hydrocarbons form complexes the determination of the absorption of uncomplexed iodine becomes quite difficult. However, the data in Fig. 1 indicate that *n*-hexane must approach the truly inert solvent and hence the difference between the iodine–cyclohexane and the iodine–*n*-hexane spectra should represent fairly closely the absorption spectrum of the iodine–cyclohexane complex. This is shown in Fig. 2. The half-band width of this curve of 5000 cm.$^{-1}$ compares favorably with values of 5800 cm.$^{-1}$ in toluene and 2,3-dimethylbutene-2. Similarly, the difference between the iodine–2,3-dimethylbutane and iodine–*n*-hexane spectra approximates the absorption spectrum of the iodine–2,3-dimethylbutane complex as shown in Fig. 2.

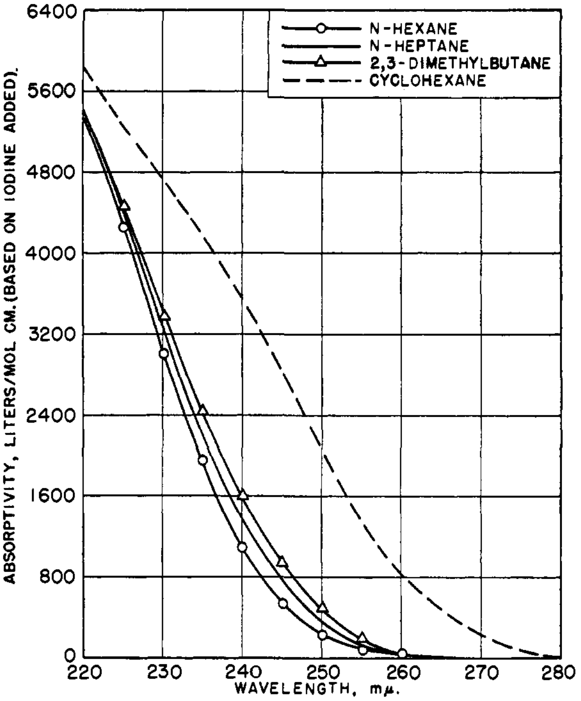

Fig. 1.—Ultraviolet absorption of iodine in saturated hydrocarbons.

To evaluate the extinction coefficient of the complex and the equilibrium constant of the complex formation reaction

$$I_2 + A \longrightarrow I_2{\cdot}A$$

one makes use of the technique described by Benesi and Hildebrand. A plot of $1/[A]$ *versus* $[I_2]/\log I_0/I$ gives $1/\epsilon_c$ as the intercept and $1/K\epsilon_c$ as the slope as shown by the relationship

$$l[I_2]/\log I_0/I = (1/K\epsilon_c)(1/[A]) + 1/\epsilon_c$$

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[3] R. S. Mulliken, THIS JOURNAL, **74**, 811 (1952); **72**, 600 (1950).

[4] L. J. Andrews and R. M. Keefer, *ibid.*, **74**, 458 (1952).

[5] S. Freed and K. M. Sancier, *ibid.*, **74**, 1273 (1952).

[6] A recent article by Keefer and Andrews (*ibid.*, **74**, 189 (1952)) also reports on the interaction of iodine with organic halides. However, although they detected absorption apparently due to the iodine–ethyl iodide complex they were unable to go to low enough wave lengths to establish the absorption maximum, because of the ethyl iodide absorption. We have shown below that use of a thin (0.10 mm.) sample cell permits measurement of the position of the complex absorption band with some degree of certainty.

where

l = cell length in centimeters
$[I_2]$ = concentration of iodine in moles/liter
$\log I_0/I$ = absorbance due to complex
K = equilibrium constant
ϵ_c = extinction coefficient of complex
$[A]$ = concentration of other partner in complex formation in moles/liter

We choose to employ moles/liter for [A] instead of mole fraction as given by Benesi and Hildebrand since light absorption in the liquid state (in which A is concerned) is related to the former and not to the latter. Andrews and Keefer[7] also employed this unit of concentration although for a different reason.

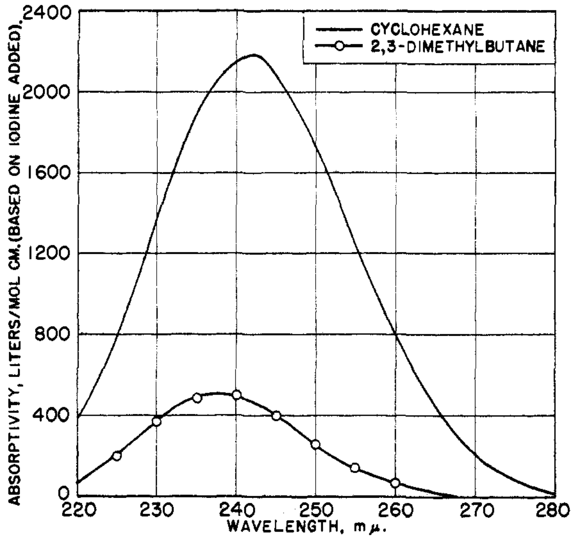

Fig. 2.—Iodine complex absorption bands of saturated hydrocarbons.

Experimental data on a number of iodine–cyclohexane–*n*-heptane mixtures are shown in Table I and plotted in Fig. 3. The line drawn in Fig. 3 is the least squares line and the least squares solution of all the data gives a value of 19,000 l./mole cm. for ϵ_c and 0.0126 l./mole for K. These values

TABLE I

EQUILIBRIUM CONSTANT DATA FOR IODINE–CYCLOHEXANE COMPLEX

$[I_2]$, moles/l.	1/[Cyclohexane], l./mole	$y \times 10^4$, cm. moles/l.	K, l./mole
0.00197	0.108	4.92	0.0129
.00197	.108	5.00	.0127
.00394	.108	5.02	.0126
.00590	.108	4.96	.0128
.00789	.108	5.14	.0123
.00801	.108	5.09	.0125
.00079	.120	5.64	.0130
.00789	.144	6.45	.0128
.00800	.144	6.54	.0126
.00789	.216	9.50	.0127
.00800	.216	9.55	.0126
.00394	.216	9.85	.0122
.00551	.360	15.18	.0129
.00590	.431	18.26	.0128
.00789	.431	18.48	.0127
.00799	.431	18.84	.0124
.00630	.539	22.60	.0128
.00689	.862	35.60	.0129
.00798	.862	37.48	.0123
.00709	1.079	45.50	.0126
			Av. 0.01265

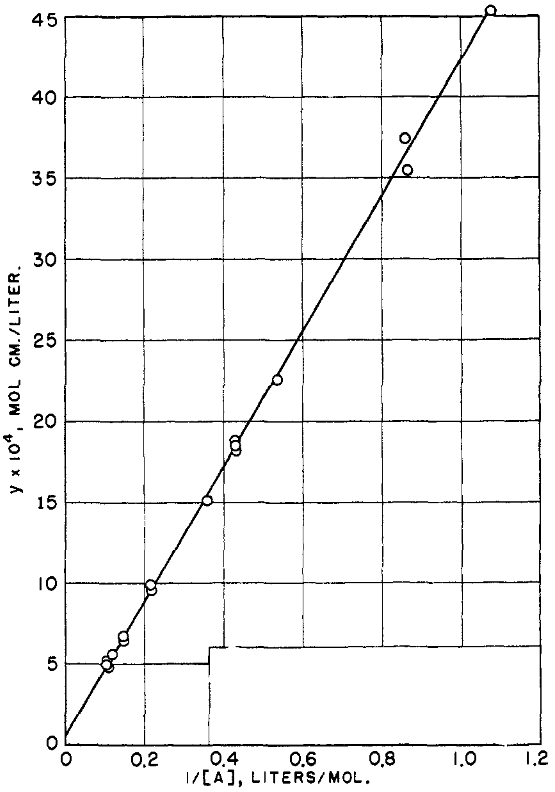

Fig. 3.—Equilibrium data for cyclohexane–iodine complex.

TABLE II

EQUILIBRIUM CONSTANT DATA FOR IODINE–2,3-DIMETHYLBUTANE COMPLEX

$[I_2]$, moles/l.	1/[2,3-Dimethylbutane], l./mole	$y \times 10^3$, cm. moles/l.	K, l./mole
0.00789	0.130	2.01	0.00346
.00789	.130	1.99	.00350
.00789	.162	2.48	.00347
.00789	.216	3.36	.00340
.00789	.260	4.29	.00320
.00789	.260	4.31	.00318
.00789	.325	4.84	.00354
.00789	.520	8.39	.00325
.00789	.520	8.48	.00321
.00789	.650	9.74	.00349
			Av. 0.00337

EQUILIBRIUM CONSTANT DATA FOR IODINE–1-BROMOBUTANE COMPLEX

$[I_2]$, moles/l.	1/[1-Bromobutane], l./mole	$y \times 10^4$, cm. moles/l.	K, l./mole
0.00394	0.107	0.581	0.288
.00079	.119	.515	.544
.00158	.134	.581	.372
.00394	.215	.696	.341
.00473	.268	.774	.332
.00551	.357	.869	.345
.00590	.429	.929	.363
.00630	.538	1.084	.349
.00669	.714	1.330	.337
.00689	.858	1.498	.342
.00709	1.073	1.790	.336
			Av. 0.359

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[7] L. J. Andrews and R. M. Keefer, THIS JOURNAL, **74**, 4500 (1952).

are to be compared with values of ϵ_c = 16,600 l./mole cm. and K = 0.15 l./mole for benzene.[7]

Similar data for the iodine–2,3-dimethylbutane–*n*-hexane system are given in Table II. The least squares solution gives ϵ_c = 19,200 and K = 0.0034.

Detection of the iodine-complex band of alkyl halides is difficult because of the high absorption shown by these compounds in the ultraviolet region. As a consequence of Beer's law it is necessary to dilute the alkyl halides considerably in order to come into the optimum absorbance range. Furthermore, the iodine concentration must be maintained fairly low since it also exhibits some absorption in this region. By employing 0.1-mm. cells instead of the usual 1-cm. cells it was possible to increase the iodine and alkyl halide concentrations 100-fold thus bringing the iodine–alkyl halide complexes into a measurable absorbance range. Rock salt cells (ordinarily employed in infrared studies) were found to serve quite well in this application. Absorption spectra of (1) iodine in *n*-heptane, (2) 1-bromobutane in *n*-heptane and (3) iodine plus 1-bromobutane in *n*-heptane are shown in Fig. 4. The fourth curve in this figure is the sum of curves 1 and 2 (the same concentrations of iodine and 1-bromobutane were employed in each mixture). Here again the difference between the absorption of iodine in the mixed solvents and the sum of the absorptions in the individual solvents should represent fairly closely the absorption of the complex. This is shown in Fig. 5.

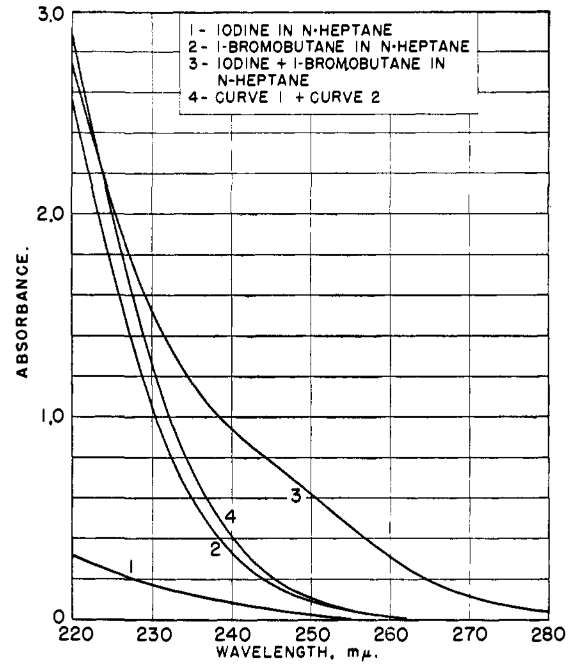

Fig. 4.—Ultraviolet absorption of iodine in 1-bromobutane.

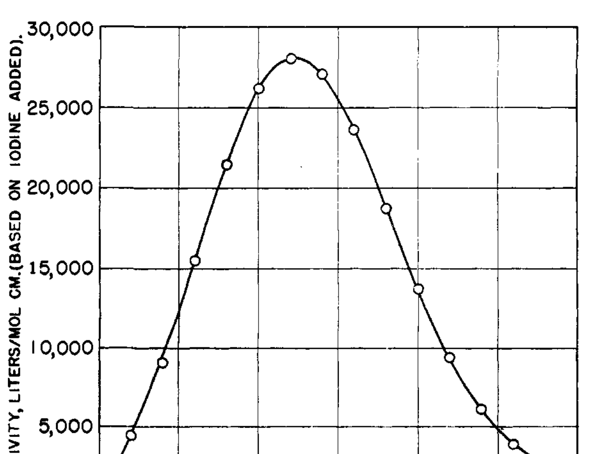

Fig. 5.—Iodine complex absorption band of 1-bromobutane.

Equilibrium data for the 1-bromobutane–iodine complex are given in Table II and Fig. 6. The value obtained for ϵ_c is 23,400 l./mole cm. and the value of K is 0.339 l./mole (from slope). It will be observed from these data that alkyl halides form complexes with iodine of considerable stability.

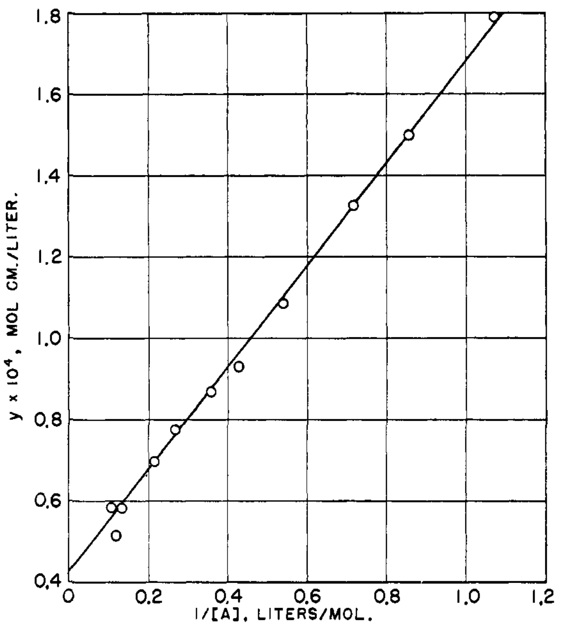

Fig. 6.—Equilibrium data for 1-bromobutane–iodine complex.

The absorption maxima of the iodine complexes of a number of hydrocarbons, alkyl halides and alcohols were obtained in a manner similar to that described above and these are shown in Table III. We have also included those literature values which are available for the absorption maxima of some other iodine complexes.

Theoretical

From the Mulliken theory[3] it appears that sufficient conditions for a compound to act as a Lewis base with respect to I_2 are that it possesses an ionizable electron in an exposed position and that the matrix element between the wave functions of the no-bond and the dative forms is not zero. It is to be expected that not only aromatics and olefins should complex with iodine but RSH, RNH_2, ROH, RI, RBr and RCl as well. Cyclopropane and cyclohexane also appear to possess the ability to complex.

Further it can be seen from the Mulliken theory that there should exist a simple relation between the frequency of absorption of the complex and the ionization energy of the base. The frequency of the absorption band is obtained directly from Mulliken's equations (5) and (10).

$$h\nu = W_E - W_N = W_1 - W_0 + \frac{(H_{01} - SW_1)^2 + (H_{01} - SW_0)^2}{W_1 - W_0}$$

It is convenient to write

$$W_1 - W_0 = I_B - E_A - (e^2/r) + C_{AB}$$

where I_B is the ionization energy of the base, E_A is the electron affinity of the acid, e^2/r is the coulomb energy of the excited state with a separation of charge equal to r, and C_{AB} is the difference between all additional energy quantities in the dative and in the no-bond forms. It will be assumed that for complexes with a common acid the greatest variation in the several quantities is in the ionization energy, I_B, of the base. Then one may write

$$h\nu = I_B - D + 2\beta^2/(I_B - D) \qquad (1)$$

where D and β are approximately constant quantities. In Fig. 7 is plotted the curve obtained from equation (1) for β and D equal to 1.3 and 6 electron volts, respectively. It is clear from the figure that expression (1) gives rather good agreement with experiment. Equation (1) goes to infinity for $I_B = D$, a consequence of the use of perturbation theory.

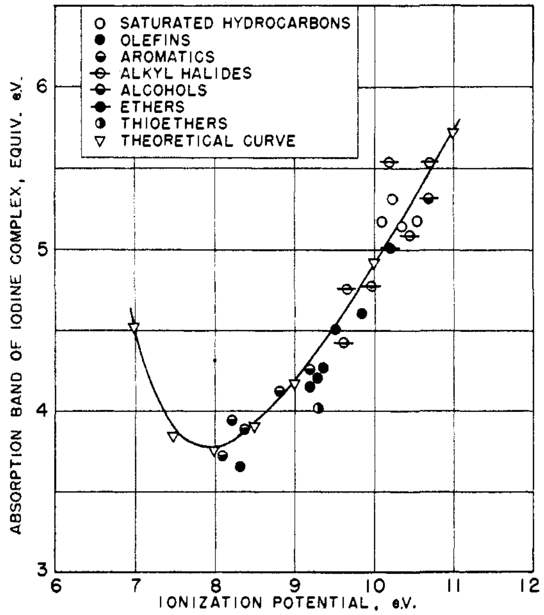

Fig. 7.—Ionization potential *vs.* equivalent energy of iodine complex absorption band.

Six e.v. is not an unreasonable value for D. This can be seen by taking Mulliken's value of 1.8 e.v. for the electron affinity of iodine, 3.4 Å. for the charge separation in the benzene–I_2 complex, and setting C_{AB} equal to zero, which yields D = 6.3 e.v. The value 1.3 for the resonance integral β is to be compared with the 2–3 e.v. used in the intramolecular π electron calculations where the interaction is stronger.

The binding energy is given by formula (1) to be $\beta^2/(I - D)$ which yields a value of 0.5 for the benzene–iodine complex. The actual binding energy should be less than this because the two molecules forming the complex have been pulled together against the no-bond state repulsive forces.[8] An experimental binding energy of 0.06 e.v. has been reported.[9] For the dioxane–iodine complex the calculated binding energy, neglecting repulsion, is 0.36 e.v. while the experimental value is 0.15 e.v.[10]

Table III

Ionization Potentials and Iodine Complex Absorption Maxima of Various Organic Compounds

Compound	Ionization potential, e.v.	Reference	Abs. max. iodine complex, mμ	Equiv. energy, e.v.	Reference
1-Chloropropane	10.7	*a*	224	5.53	This work
2-Chloropropane			224	5.53	This work
2-Methyl-2-chloropropane	10.2	*a*	224	5.53	This work
Propanol-1	10.7	*b*			
Propanol-2			233	5.31	This work
n-Octane	10.24	*c*	234	5.30	This work
2,3-Dimethylbutane	10.50	*d*	236	5.24	This work
Cyclohexane	10.39	*d*	242	5.10	This work
Bromoethane	10.45[r]	*c*			
1-Bromopropane			244	5.08	This work
2-Bromopropane			244	5.08	This work
1-Bromobutane			244	5.08	This work
1-Bromopentane			244	5.08	This work
1,1-Dimethyl-1-bromopropane			244	5.08	This work
Ethyl ether	10.2	*f*	248	5.00	*g*
Cyclopropane	10.1	*h*	240	5.16	*i*
Propene	9.84	*c*	270	4.59	*i*
cis-1,2-Dichloroethene	9.66	*j*	262	4.75	*k*
trans-Dichloroethene	9.96	*j*	262	4.75	*k*
Octene-1	9.52	*c*	275	4.50	This work
Iodoethane	9.64[r]	*e*	280	4.42	This work
2-Iodopropane			280	4.42	This work
Butene-2	9.3	*c*	296	4.19	*i*
2-Methylpropene	9.35	*c*			
2-Methylbutene-1			292	4.25	This work
Cyclohexene	9.2	*l*	295	4.20	This work
			302	4.10	*k*
Benzene	9.24	*m*	287	4.31	This work
			297	4.17	*n*
Toluene	8.82	*o*	298	4.16	This work
			306	4.05	*n*
o-Xylene	8.58	*p*	319	3.89	*n*
p-Xylene	8.48	*p*	315	3.93	*n*
1,3,5-Trimethylbenzene	8.1	*q*	333	3.72	*n*
2,3-Dimethylbutene-2	8.3	*l*	340	3.64	This work
Thioethers	9.3[r]	*b*	308	4.01	This work

[a] Stevenson and Hipple, This Journal, **64**, 2766 (1942). [b] Sugden and Price, *Trans. Faraday Soc.*, **44**, 108, 116 (1948). [c] Hoenig, *J. Chem. Phys.*, **16**, 105 (1948). [d] Unpublished data, F. H. Field, Humble Oil and Refining Company. [e] Price, *J. Chem. Phys.*, **4**, 539, 547 (1936). [f] Price, *Chem. Revs.*, **41**, 257 (1947). [g] Kortium and Friedheim, *F. Naturforschung*, **2a**, 20 (1947). [h] Field, *J. Chem. Phys.*, **18**, 1122 (1950). [i] Reference 5. [j] Walsh, *Trans. Faraday Soc.*, **41**, 35 (1945). [k] Reference 4. [l] Price and Tutte, *Proc. Roy. Soc.* (London), **A174**, 207 (1940). [m] Price and Wood, *J. Chem. Phys.*, **3**, 439 (1935). [n] Reference 2. [o] Price and Walsh, *Proc. Roy. Soc.* (London), **A191**, 22 (1947). [p] Price, Hammond, Teegan and Walsh, *Faraday Soc. Discussion*, **9**, 53 (1950). [q] Reference 3. [r] Average of limits given.

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(8) See reference 3, Fig. 1. This effect should have a smaller influence on the spectroscopic transition.

(9) T. M. Cromwell and R. L. Scott, This Journal, **72**, 3825 (1950).

(10) J. A. A. Ketelaar, C. van der Stolpe, A. Goudsmit and W. Dzcubas, *Rec. trav. chim.*, **71**, 1104 (1952); **70**, 499 (1951).

It is of interest to compare the intermolecular attraction due to complex formation with that due to dispersion forces as developed by London.[11] Here the excited state is taken to be the ionization of both molecules in the interacting pair. This excited state lies $I_a + (e^2/r) + E_a$ higher than the excited state in the Mulliken complex. For the I_2–benzene system, the dispersion force excited state lies some 19 e.v. above the ground state; while for the complex, the excited state lies 3 e.v. above the ground state. Consequently, could the dispersion transition be observed, it would lie at much shorter wave lengths than those observed for the complex. It is of interest to note that both types of interaction are inversely proportional to the ionization energy of the base.[12] The matrix element in the dispersion force formulation is fairly large since it is, in effect, the sum over a large number of matrix elements for individual excited states. Consequently there is detectable attraction even though the separation of the excited state (states) from the ground state is large.

The excited state for the complex is stabilized against dissociation by the coulomb term. With a stable excited state, the electronic transition is usually well-defined and, transition probability permitting, so usually is the absorption spectrum.

NOTE ADDED IN PROOF.—McConnell, Hamm and Platt (*J. Chem. Phys.*, 21, 66 (1953)) have also reported on regularities in the spectra of molecular complexes. These authors discuss the effect of variation in the Lewis acid as well as the base.

Acknowledgments.—The authors wish to thank the management of the Humble Oil and Refining Company, in whose laboratories the present work was conducted, for permission to publish this material.

BAYTOWN, TEXAS
AUSTIN, TEXAS

[11] F. London, *Z. Physik*, **63**, 245 (1930).

[12] The inverse proportionality is obtained by assuming the approximate constancy of $\overline{r_A^2}$ and $\overline{r_B^2}$ in the expression

$$E = -\frac{2}{3}\frac{e^4\overline{r_A^2}\text{ and }\overline{r_B^2}}{(I_A + I_B)R^6}$$

H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 354.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

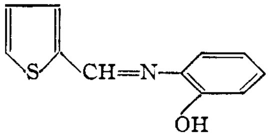
Metal Ion Catalysis in the Hydrolysis of Schiff Bases[1,2]

BY GUNTHER L. EICHHORN AND JOHN C. BAILAR, JR.

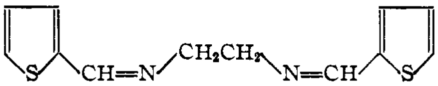
RECEIVED DECEMBER 29, 1952

The action of metallic ions in enhancing the rate of many organic and physiological reactions has frequently been attributed to the formation of complex intermediates. The present work represents a study of the cleavage of bis-thiophenal–ethylenediamine in the presence of metal ions. Spectrophotometric measurements have yielded evidence for the transitory existence of the intermediate, and have made possible a study of its rate of decomposition. It is believed that the formation of bonds between the positive ion and nitrogen brings about a labilization of the nitrogen to carbon double bonds, which are thereby rendered more susceptible to hydrolytic cleavage.

The capacity of the azo and azomethine groups to act as coördinating donors to metal ions has been demonstrated by the work of many investigators during the last quarter century. Generally the presence of an auxochrome, such as a hydroxyl, amino or carboxyl group, or a heterocyclic nitrogen (as in pyridine and pyrrole) is required to stabilize the complex through chelate formation. In order to determine whether or not a heterocyclic sulfur atom would perform the same function, the following Schiff bases were synthesized by the condensation of 2-thiophenaldehyde[3] with *o*-aminophenol (A) and ethylenediamine (B).



A



B

Although the participation of the sulfur atoms in these molecules during the coördination reactions would result in polycyclic chelation, a phenomenon usually associated with extraordinary stability, all attempts to isolate metal complexes of these compounds by the usual procedures were unsuccessful. However, an application of the method of continuous variation[4] to the system copper(II) sulfate–bis-thiophenal–ethylenediamine indicated the formation of 1:1 and 1:2 metal to base complexes. The striking resemblance of the absorption curves obtained in the continuous variation study to those reported by Jonassen and Dexter[5] suggested that the complexes in solution were those of ethylenediamine, rather than those of the Schiff base. This was corroborated by isolation of the ethylenediamine complexes from the solutions.

It had been observed during the preparation of the solutions for the continuous variation studies

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[1] Presented at the XIIth International Congress of Pure and Applied Chemistry, New York, September 10–13, 1951.

[2] Taken in part from the doctoral dissertation of G. L. Eichhorn, University of Illinois, 1950.

[3] The authors are indebted to Dr. Seymour Meisel and Dr. D. E. Badertscher, of the Socony–Vacuum Oil Co., Paulsboro, N. J., for furnishing the 2-thiophenaldehyde used in these studies, as well as for providing directions for its purification.

[4] P. Job, *Compt. rend.*, **180**, 928 (1925); *Ann. chim.*, [10] **9**, 115 (1928); W. C. Vosburgh and S. R. Cooper, THIS JOURNAL, **63**, 437 (1941).

[5] H. B. Jonassen and T. H. Dexter, *ibid.*, **71**, 1553 (1949).