valence electrons, respectively. The carbon monoxide species on copper oxide (2173, 2127 and 2000 cm.$^{-1}$) were placed at intervals separated by one electron, as were the carbon monoxide species on cobalt (2179, 2160 and 2091 cm.$^{-1}$). The excellent fit of the data to the smooth curve shown in Fig. 1 supports the hypothesis that the vibration frequency of a carbon monoxide unit is a function of the number of valence electrons associated with the unit. Thus it has been possible to assign a specific adsorbed species to each of the infrared absorption bands observed in this investigation.

The experimental results of Eischens and Pliskin[8] on the chemisorption of carbon monoxide on iron and iron oxide may be examined with respect to Fig. 1. These investigators found infrared absorption peaks at 4.95 (2020 cm.$^{-1}$) and 4.70 microns (2128 cm.$^{-1}$). According to the curve of Fig. 1 the numbers of electrons corresponding to these two species of CO on iron are 11.23 ± 0.05 and 10.23 ± 0.05, respectively. The agreement shown here gives added support to the graph of Fig. 1 as representing a fundamental property of the CO unit.

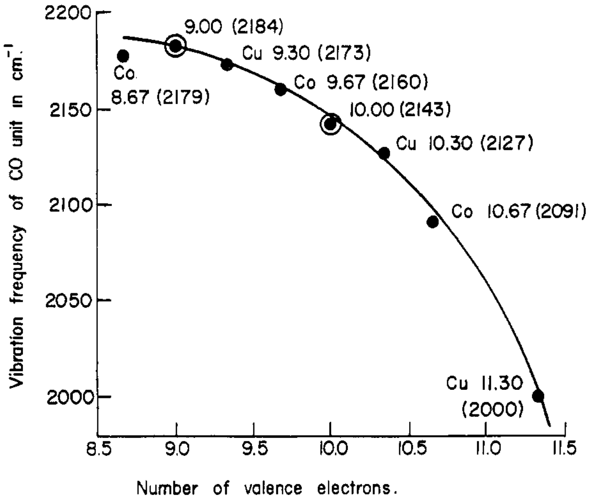

Fig. 1.—Vibration frequency of CO units *vs.* number of electrons associated with the CO unit: ◉, data from Herzberg; ●, data from this study.

Conclusions

This investigation was concerned with the chemisorption of carbon monoxide on metals and metal compounds. The adsorbents used were copper oxide, nickel and cobalt. An infrared technique was used to obtain the spectra of chemisorbed carbon monoxide on these solids. The interpretation of the data became possible through the use of the basic concepts of the Wolkenstein hypothesis on the mechanism of chemisorption.

1. The observations made in this investigation serve to support and extend the Wolkenstein hypothesis by conclusively demonstrating the existence of multiple forms of a single adsorbate on a single adsorbent. As proposed by Wolkenstein, the numbers of electrons associated with each adsorbed species have been shown to differ by one electron between successive forms of the adsorbate. But whereas Wolkenstein considered only integral numbers of valence electrons for the chemisorbed species, the vibration frequencies for chemisorbed CO observed in this investigation correspond to non-integral numbers of valence electrons.

2. A fundamental characteristic of the carbon monoxide unit has been discovered: namely, that the vibration frequency of the carbon monoxide unit, as electrons are added or removed from it, changes by a predictable amount. This relationship has been represented graphically. The existence of chemisorbed carbon monoxide units ranging from $(CO)^{+0.70}$ to $(CO)^{-1.30}$ has been experimentally observed; the stretching vibration frequencies of these forms range from 2173 to 2000 cm.$^{-1}$.

Acknowledgment.—The authors wish to express their appreciation to the Standard Oil Company (Ohio) for the grant of an Educational Assignment to R. A. Gardner and for the use of certain laboratory facilities of the Chemical and Physical Research Division during this study.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, RENSSELAER POLYTECHNIC INSTITUTE, TROY, NEW YORK]

Charge-transfer Spectra of Iodine Atom–Aromatic Hydrocarbon Complexes[1]

BY R. L. STRONG, S. J. RAND AND J. A. BRITT[2]

RECEIVED MARCH 18, 1960

Iodine atoms, produced by the flash photolysis of molecular iodine in various aromatic solvents, form charge-transfer complexes that absorb light in the visible region. The charge-transfer absorption spectra have been measured at room temperature for complexes between iodine atoms and benzene, toluene, *o*-xylene, *p*-xylene and mesitylene. Absorption maxima are at 495, 515, 570 520 and 590 mμ, respectively. Decreases in charge-transfer transition frequencies with decreasing ionization potentials of the donor molecules are the same as those for complexes involving I_2, Br_2, and ICl as acceptor species. The I atom–*p*-xylene band is at a lower wave length than expected and is quite broad and may be the resultant of charge-transfer transitions from two slightly different donor orbitals of the *p*-xylene molecule.

In a previous paper,[3] the formation of a transient intermediate in the flash photolysis of iodine in benzene was reported. This intermediate, which was proposed to be a complex between an iodine atom and a benzene molecule comparable to similar

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[1] From the thesis by S. J. Rand, submitted in partial fulfillment of the requirements for the Ph.D. degree to the Graduate School, Rensselaer Polytechnic Institute (1960). Available from University Microfilms, Ann Arbor, Michigan.

[2] Participant in the National Science Foundation Research Participation for Teacher Training Program conducted at Rensselaer Polytechnic Institute during the summer of 1959.

[3] S. J. Rand and R. L. Strong, THIS JOURNAL, **82**, 5 (1960).

complexes involving molecular iodine,[4] was detected by its strong charge-transfer absorption spectrum[5] in the visible region. Disappearance of the complex was second order, and values of k/ϵ_0, where k is the second order rate constant and ϵ_0 is the molar extinction coefficient, were calculated at 420 and 490 mμ. Since k is independent of the analyzing wave length, this provides a method of obtaining relative extinction coefficients, or the absorption spectrum.

The possible role of atom charge-transfer complexes in the gas-phase recombination of halogen atoms in the presence of benzene and methylated benzenes as third bodies also has been presented by Porter,[6] who has independently detected the spectrum in the liquid phase of the iodine atom–benzene complex spectrographically by flash photolysis.[7]

This paper presents the results of the spectral study in the visible region of iodine atoms complexed with benzene, toluene, *ortho*- and *para*-xylene and mesitylene.

Experimental

Flash Apparatus.—The flash photolysis equipment, type of reaction cell and method of spectrophotometric analysis used in this work have been described elsewhere.[3] All cells were filled in air but were tightly stoppered with a ground-glass cap to prevent evaporation of the solution. Each was completely wrapped with a Wratten K2 (yellow) gelatin filter with a low-wave length cut off at approximately 470 mμ.

In order to analyze at different wave lengths in the visible region, several interchangeable Bausch and Lomb second order interference filters were used, combined with the appropriate auxiliary filter to eliminate extra pass bands. Characteristics of the 9 filters used, as determined with a Beckman Model DU Spectrophotometer, are given in Table I.

TABLE I

CHARACTERISTICS OF INTERFERENCE FILTERS

λ_{max} (mμ)	Auxiliary filter	Peak transmittance (%)	Half band width (mμ)
410	[a]	31.6	10
422	[b]	41.8	11
460	[b]	49.0	9
489	[b]	42.4	7
527	[b]	49.2	9
558	[c]	47.3	8
605	[c]	38.0	7
646	[c]	41.2	11
687	[c]	36.2	13

[a] Third order pass band from 605 mμ filter. The higher (second order) band was eliminated with a Kodak No. 35 gelatin Wratten filter. [b] Corning 3850-051 filter. [c] Kodak K2 gelatin Wratten filter.

Materials.—Benzene and iodine were purified as before.[3] Toluene (Fisher certified reagent) and *o*-xylene, *p*-xylene and mesitylene (all Eastman grade organic chemicals) were further purified by shaking each solvent with three portions of concentrated sulfuric acid, followed by a rinse with distilled water, three washings with 10% sodium hydroxide and three additional rinses with distilled water. The wet organic liquid was flash distilled over P_2O_5, followed by refluxing and a slow distillation also over P_2O_5, only the middle half being retained.

Results

For all five systems of iodine in benzene, toluene, *o*-xylene, *p*-xylene and mesitylene, a transient increase in absorbency in the visible region has been observed upon dissociation of the iodine by flash photolysis, indicating the formation of a charge-transfer complex between an iodine atom and an aromatic molecule. Assuming validity of Beer's law for the complex, for the small changes observed (2% maximum) the increase in light absorbed is directly proportional to the concentration of the complex. Disappearance of the complex as a function of time was followed over at least a fivefold change in concentration. For all solvents good second order kinetics plots were obtained consistent with the recombination mechanism

$$2\text{Aro}\cdot\text{I} \xrightarrow{k} \text{Aro}\cdot\text{I}_2(+\text{Aro}) \qquad (1)$$

$$\frac{-d[\text{Aro}\cdot\text{I}]}{dt} = 2k[\text{Aro}\cdot\text{I}]^2 \qquad (2)$$

In this equation, Aro represents an aromatic molecule and $\text{Aro}\cdot\text{I}_2$ the molecular iodine–aromatic complex.

As pointed out in reference 3, it is impossible to calculate the combination rate constant k without knowledge of the absolute value of the concentration of the complex, or the primary quantum yield of dissociation of I_2 in the solvent and the stability of the complex. The ratio ϵ_0/k can be calculated from the integrated form of equation 2, however, since the product of the molar extinction coefficient of the complex, ϵ_0, and the complex concentration are known as a function of time from the oscillographic measurements of transmittancy, (I/I_0), in a cell of length d

$$\epsilon_0[\text{Aro}\cdot\text{I}] = (1/d)\log(I_0/I) \qquad (3)$$

Values of these relative extinction coefficients at room temperature for the five solvents are tabulated in Table II. Each value represents the average from at least 12 oscillograms of the same cell. Standard deviations ranged from ±8% in regions of relatively high absorbency to ±20% at the ends of the spectral curves (*i.e.*, benzene at 605 mμ) where the deflections approached the order of magnitude of the shot noise from the photomultiplier tube. The molar extinction curves in Fig. 1 are averages for each solvent and represent the smoothest possible interpolations assuming no irregularities between experimental points.

The attendant increase in the concentration of molecular iodine—which also absorbs to some extent at most of the wave lengths used—with decreasing complex concentration could conceivably contribute to the total change in transmittancy. It was shown[3] for the iodine–benzene system that this contribution is a maximum of only about 3% of the total change, by assuming that (a) every I_2 molecule that absorbs a photon eventually dissociates (*i.e.*, $\phi = 1$), and (b) all iodine atoms are either complexed with an aromatic molecule or are in the molecular form. The complete rate expression for the production of the complex, assumed to be proportional to the light absorbed I_a, and simultaneous disappearance by

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

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

[6] G. Porter and J. A. Smith, *Nature*, **184**, 446 (1959).

[7] G. Porter, private communication.

TABLE II

ABSORPTION IN THE VISIBLE REGION OF IODINE ATOM–AROMATIC HYDROCARBON COMPLEXES AT ROOM TEMPERATURE

Solvent	$[I_2]_0 \times 10^5$ (m./l.)[a]	$\epsilon_c/k \times 10^7$ (sec./cm.) at wave length (mμ) 410	422	460	489	527	558	605	646	687
Benzene	2.86	1.5	1.9	2.8	3.2	2.6	1.3	0.5		
Benzene	2.08	1.4	1.6	2.3	3.0	2.1	1.2	0.5		
Toluene	4.48		1.2	2.1	2.5	2.7	2.4	1.4		
Toluene	3.21		1.4	2.0	2.6	2.8	2.5	1.6		
o-Xylene	2.11			1.5	2.2	3.2	3.8	3.3	2.4	
o-Xylene	2.90			1.8	2.7	3.5	4.2	3.8	3.0	
p-Xylene	2.21			2.1	2.5	2.6	2.5	2.3	2.0	
p-Xylene	2.08			2.3	2.7	2.8	2.7	2.4	2.2	
p-Xylene	3.46			1.8	2.3	2.5	2.3	1.8	1.8	
Mesitylene	2.38					3.6	4.8	5.6	4.3	3.2
Mesitylene	2.12					3.3	4.4	5.0	4.2	3.1

[a] Calculated using extinction coefficients at λ_{max} in the visible region from reference 4.

combination

$$\frac{d[\text{Aro}\cdot\text{I}]}{dt} = 2\phi I_a - 2k[\text{Aro}\cdot\text{I}]^2 \qquad (4)$$

was solved using the Runge–Kutta method with the aid of an IBM-650 digital computer. This method of computer solution, following the same assumptions, has been applied to the iodine–benzene (air-filled) and the iodine-methylated benzene systems reported here. Although the two experimentally determined quantities—ϵ_c/k and $\epsilon_c[\text{Aro}\cdot\text{I}]$ at 300 μsec. following initiation of the flash—are wave length-dependent, the quantity $k[\text{Aro}\cdot\text{I}]$ should be the same for each complex at all wave lengths. Within the limits of experimental error this was indeed found to be true, so that a computer solution was obtained only for an average value of $k[\text{Aro}\cdot\text{I}]$ for each solvent. Values of k and ϵ_c (at the wave length of maximum absorption by the complex, λ_{max}), *for an assumed* $\phi = 1$, are given in Table III.

TABLE III

COMPUTED VALUES OF THE COMBINATION RATE CONSTANT AND MOLAR EXTINCTION COEFFICIENT AT WAVE LENGTH OF MAXIMUM ABSORPTION BY THE COMPLEX FOR UNIT PRIMARY QUANTUM YIELD

Solvent	$k \times 10^{-9}$ (l. mole^{-1} sec.$^{-1}$)	ϵ_c at λ_{max} (l. mole^{-1} cm.$^{-1}$)	$(\epsilon_c + {}^1/_2\epsilon_{I_2})$ at λ_{max}
Benzene	3.0	930	1430
Toluene	2.04	570	1040
o-Xylene	0.89	365	490
p-Xylene	1.25	325	780
Mesitylene	1.27	695	740

The results for k are much closer to the rate constant for the recombination of "free" iodine atoms in carbon tetrachloride[8] (in which, however, ϕ is only 0.13) and therefore are more reasonable than the previously reported values. However, the computed ϵ_c values are considerably lower than would be expected from charge-transfer theory[5] and observed for comparable I_2 complexes.[4]

If these computed values are presumed correct, then the observed molar extinction coefficient, ϵ_c, is actually a resultant of the true molar extinction coefficient of the complex, ϵ_t, and the molar extinction coefficient of I_2, ϵ_{I_2}. Assuming all I atoms are either complexed with aromatic molecules or in the molecular form, $\epsilon_t = \epsilon_c + {}^1/_2\epsilon_{I_2}$. This sum is tabulated in the last column of Table III.

In reference 3 it was noted that the iodine–benzene cells filled in air had slightly lower k/ϵ_c values than comparable cells filled *in vacuo*, and the very large difference between the value of k computed earlier for the evacuated cell and the k computed in this work for the air-filled cell is due primarily to this relatively small difference in k/ϵ_c (although the I_a values were also somewhat different). This emphasizes again the considerable uncertainties present in the computer results because of the extreme sensitivity of the computer integration to errors in I_a and $k[\text{Aro}\cdot\text{I})$. In addition, the assumption of $\phi = 1$ is used solely to give a maximum contribution by changes in I_2 concentration to the observed transmittancy changes and would be expected to be less than 1 because of the "cage effect."[9] It also would be expected to be a function of solvent viscosity[10] and energy of absorbed light,[11] as well as the binding energies of the I_2 and I complexes. For these reasons we believe that the ϵ_c/k values, rather than ϵ_t, are more valid for comparison purposes.

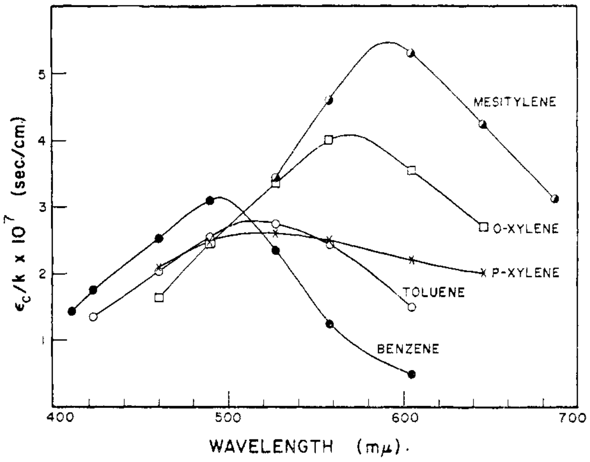

Fig. 1.—Visible absorption spectra of various I atom–aromatic systems: ●, benzene; ○, toluene; □, *o*-xylene; ×, *p*-xylene; ◑, mesitylene.

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TABLE IV

COMPARISON OF I ATOM–AROMATIC HYDROCARBON SPECTRA WITH COMPARABLE MOLECULAR HALOGEN COMPLEXES

Aromatic molecule	I_p (e.v.)[13]	I Complex λ_{max} (mμ)	I Complex ΔE (e.v.)[a]	I_2 Complex[14] λ_{max} (mμ)	I_2 Complex[14] ΔE (e.v.)[a]	ICl Complex[14] λ_{max} (mμ)	ICl Complex[14] ΔE (e.v.)[a]	Br_2 Complex[15] λ_{max} (mμ)	Br_2 Complex[15] ΔE (e.v.)[a]
Benzene	9.24	495		292		282		292	
Toluene	8.82	515	0.10	302	0.14	288	0.09	301	0.13
o-Xylene	8.56	570	.33	316	.32	298	.24	313	.29
p-Xylene	8.44	520	.12	304	.17	292	.16	306	.20
Mesitylene	8.39	590	.40	332	.52	307	.36	326	.44

[a] Shift in λ_{max} (in e.v.) relative to benzene.

At most wave lengths it was impossible to make measurements at times less than 300 μsec. because of interference by scattered light from the flash. At 422 mμ, however, where this interference filter and the K2 Wratten filter surrounding the reaction cell are mutually exclusive, it was possible to measure ϵ_c[Aro·I] as a function of time from 100 μsec. over a sixteenfold change in complex concentration for the benzene–iodine system, with no apparent deviation from a linear second order kinetic plot.

Discussion

The close correlation between the behavior observed with the iodine atom complexes and molecular halogen complexes involving the same methylated benzenes (Table IV) is strong confirmation of the charge-transfer nature of these atom-aromatic spectra. The shift of λ_{max} for each donor into the visible region is expected because of the much larger electron affinity (E_A) of the I atom (3.3 e.v.[12]) relative to that of I_2 (1.8 e.v.[5]). Similarly, for a given acceptor the frequency of the charge-transfer transition is a function of the ionization potential (I_p) of the donor molecule, the relation being approximately linear over a wide range of ionization potentials.[16–18] This linearity is not exact, however, and for only a few donor molecules a better comparison is the behavior of an acceptor with various donor molecules relative to that of other acceptors with the same donors.[19] Within the limits of error involved in determining λ_{max}, almost identical shifts in the charge-transfer bands with aromatic substitution, relative to the benzene complex peak, are observed for the I atom complexes and the complexes with I_2, ICl and Br_2 (ΔE columns in Table IV). This is logical if the binding energies are small relative to $I_p - E_A$ or of the same order of magnitude for the complexes. (Almost identical behavior is noted by Briegleb and Czekalla[18] for complexes involving nitrobenzene, chloranil and iodine, although the slopes of the $h\nu_{max}$ *vs.* I_p plots are approximately twice as great when a large number of different donors are considered, rather than just benzene and the methylated benzenes reported in this work.)

An apparent exception in this work to the generality that λ_{max} increases with decreasing I_p of the donor molecule is the behavior of the complex involving *p*-xylene, which however is the same for the molecular halogen complexes (Table IV). Orgel[20] has pointed out, however, that the twofold degeneracy of the e_{1g} orbital of benzene—the donor orbital—can be removed by proper ring substitution leading to two donor ionization potentials of slightly different energies. Maximum splitting should occur with *p*-substituted molecules.[20] Thus, the I atom–*p*-xylene spectrum is probably the resultant of two peaks, one near the I atom–benzene maximum and the other at a somewhat higher wave length. The very broad shape of the band (Fig. 1) supports this conclusion. Splitting presumably also occurs with toluene and *o*-xylene (although to a lesser extent than with *p*-xylene) but not with mesitylene; the shapes of the curves in Fig. 1 may indicate this, but the effect is slight. In the anisole–iodine system, two charge-transfer maxima are actually observed.[21]

It is difficult to arrive at any definite conclusions from the relative peak heights shown in Fig. 1, because of the several unknown factors contributing to ϵ_c and k, and the uncertainty in the extent of contribution to the observed spectra by changes in I_2 concentration. If one assumes that the combination of two complexes to give I_2 is diffusion-controlled, that the complex diameters are the same and further that the diffusion process can be represented by a sphere moving through a continuous viscous medium, then k should be inversely proportional to the coefficient of viscosity, η, at constant temperature.[22] In Table V are presented values of $(k/\epsilon_c)\eta$ at λ_{max} for the five solvents used.

While for benzene, toluene and *o*-xylene trends in k/ϵ_c are in the right direction and $\eta k/\epsilon_c$ values are reasonably close, the results for *p*-xylene (which, as pointed out above, also behave differently in other respects) and mesitylene are quite different and indicate the presence of effects other than those from viscosity alone. Other effects may, in fact, be even greater than indicated, for Rosman and Noyes[22] have shown that the effect on k of varying viscosity is less than predicted from simple hydrodynamic theory for the inert solvents hexane,

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TABLE V

COMPARISON OF SOLVENT VISCOSITIES AND RELATIVE RATE CONSTANTS AT WAVE LENGTH OF MAXIMUM ABSORPTION

Solvent	η (centipoise) at 20°	$k/\epsilon_c \times 10^{-6}$ at λ_{max} (cm. sec.$^{-1}$) (from Fig. 1)	$\eta k/\epsilon_c \times 10^{-4}$ (poise cm. sec.$^{-1}$)
Benzene	0.652	3.2	2.09
Toluene	.590	3.6	2.12
o-Xylene	.810	2.5	2.02
p-Xylene	.648	3.8	2.46
Mesitylene	.702[a]	1.8	1.26

[a] Measured in this Laboratory with an Ostwald viscometer calibrated with benzene.

carbon tetrachloride and hexachlorobutadiene-1,3.

Although Mulliken's charge-transfer theory predicts that the extinction coefficient should increase with decreasing donor ionization potential or increasing stability of the complex,[5] just the opposite behavior is observed in most cases.[23] A solution to this discrepancy has been proposed in terms of a contact charge-transfer spectrum (whereby the donor and acceptor species are close to each other but do not complex), either as a result of interaction between the charge-transfer state and the ground states of the donor and acceptor[24] or between the charge-transfer state and the donor-excited states.[25] In either case, if there is a mixture of complex and contact spectra, the contribution of the contact charge-transfer band would be expected to become less important with increasing complex stability. Therefore, one might expect the values of the extinction coefficient to pass through a minimum with increasing complex stability, as observed in this work (Fig. 1) where it is assumed (although not known) that the I atom complexes are more stable than comparable I_2 complexes and that increasing donor methylation increases the stability of the complex. Also, if the I atom–aromatic complex is highly symmetric with the atom centered over the benzene ring, there will be no contribution by the donor-excited states and the behavior should be as predicted by Mulliken for a complex spectrum. (As pointed out by Murrell,[25] this may be the case with complexes involving chloranil as the acceptor, for which the bands are also considerably less intense than those for comparable I_2 systems.)

Acknowledgments.—Valuable aid was obtained from Dr. J. W. Hollingsworth, Mr. W. G. McClintock and Mr. S. Tsao of the Computer Laboratory, Rensselaer Polytechnic Institute, in the computer work reported. We gratefully acknowledge support in part by National Science Foundation Grants NSF G-4181 and G-9988.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS, AND THE DEPARTMENT OF CHEMISTRY, FORDHAM UNIVERSITY, NEW YORK, NEW YORK]

The Determination of Double-bond Character in Cyclic Systems. V. Proton Chemical Shifts in Chelated Derivatives of Benzene, Naphthalene and Phenanthrene[1,2]

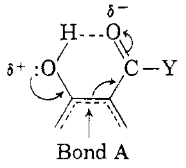
BY A. L. PORTE,[3] H. S. GUTOWSKY AND I. MOYER HUNSBERGER

RECEIVED FEBRUARY 15, 1960

The OH proton chemical shifts are measured for phenol, β-naphthol, 9-phenanthrol, and for chelated *o*-substituted derivatives of each containing an aldehyde, methyl ketone and methyl ester group. The large amounts ($\Delta\delta$) by which the shifts to lower applied fields are greater in the chelated derivatives than in the parent phenols are measures of the strengths of the intramolecular hydrogen bonds and are proportional to the bond multiplicity of the ring bonds between the carbon atoms holding the chelated substituents. The $\Delta\delta$ values are also proportional to $\Delta\nu(C{=}O)$ values determined earlier from infrared spectra of the same compounds. Mechanisms responsible for the proton chemical shifts are discussed.

Introduction

Previous papers[4,5] in this series have demonstrated that conjugated chelation of *ortho* carbonyl and hydroxyl groups in benzene, naphthalene and phenanthrene, lowers the C=O stretching frequency of the chelated compound (I) below that of the parent carbonyl compound (II) by an amount $\Delta\nu(C{=}O)$ which is proportional to the per cent. double-bond character (%DBC) of the ring bond (Bond A) between the carbon atoms holding the chelated substituents. Characteristic $\Delta\nu(C{=}O)$ values were obtained for the benzene bond, the 1,2- and 2,3-bonds of naphthalene, and the 9,10-bond of phenanthrene by examining the infrared spectra of the appropriate hydroxyaldehydes, hydroxyketones and hydroxyesters. For a given bond, the $\Delta\nu(C{=}O)$ values consistently increased in proceeding from the hydroxyaldehyde to the hydroxyketone to the hydroxyester, but



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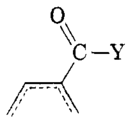

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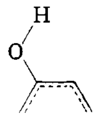

III

Y = —H, —CH_3, and —OCH_3

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[2] Acknowledgment is made to the donors of The Petroleum Research Fund, administered by The American Chemical Society, for partial support of this research. Support was also received from the National Science Foundation (Grant G-7640 to I.M.H.) and from the Office of Naval Research.

[3] Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois.

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