[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

Complexes of Naphthalene with Iodine and Bromine. On the Origin of the Spectra of Complexes between Halogens and Aromatics

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Molecular complexes of naphthalene with iodine and with bromine have been found. Comparison of their absorption spectra with those of the corresponding benzene complexes suggests very strongly that the aromatic part of an aromatic-halogen complex has the greater influence in determining its spectrum. A perturbation calculation based on Mulliken's proposal that such complex spectra are just shifted aromatic spectra serves to correlate the observed intensities and wave engths of the complex spectra.

A number of examples[2] of molecular complexes between halogens and aromatic compounds have been reported recently. Naphthalene also is now found to form complexes with iodine and bromine. The ultraviolet absorption spectra of these complexes have been used to demonstrate their existence, as in the previous investigations; furthermore, comparison of the naphthalene complex spectra with those reported for complexes of benzene and of benzene derivatives offers a test for explanations[3] of the nature of the absorption and the structure of the complexes.

Experimental

Purity of Materials.—Naphthalene: Resublimed naphthalene was distilled and recrystallized three times from itself. Iodine: Reagent grade resublimed iodine was used without further purification. Bromine: Reagent grade bromine was distilled from phosphorus pentoxide. Carbon tetrachloride: Reagent grade carbon tetrachloride was dried over calcium chloride, and then distilled.

Apparatus.—Absorption curves were determined by means of a Cary Recording Quartz Spectrophotometer, Model 11, manufactured by Applied Physics Corporation of Pasadena. Matched 2-cm. quartz cells were used. The cells were thermostated at 25.0° by a copper block cell holder through which water from a large reservoir was circulated.

Solutions were prepared by weighing out an appropriate amount of naphthalene, adding iodine or bromine by volume from a standard solution in carbon tetrachloride, and diluting with carbon tetrachloride to the desired volume in a volumetric flask. The volume of carbon tetrachloride required was noted.

Results

In Table I are listed the experimental values of optical density at frequency of maximum absorption as a function of the concentration of naphthalene. Figures 1 and 2 show typical spectra for mixtures of naphthalene with bromine or iodine, together with the spectra of the unmixed materials for comparison. All spectra shown are for solutions in carbon tetrachloride.

TABLE I

OPTICAL DENSITIES DUE TO COMPLEXES OF BROMINE OR IODINE WITH NAPHTHALENE IN CARBON TETRACHLORIDE SOLUTION

$C_{\text{naphthalene}}$ (moles/liter)	$C_{\text{iodine}} \times 10^4$ (moles/liter)	$C_{\text{bromine}} \times 10^4$ (moles/liter)	Density of complex at $\lambda_{\max}$ in 2-cm. cell
2.02		3.69	1.33
1.005		5.16	1.10
2.00		2.65	0.94
1.00		3.71	.78
0.692		5.30	.83
0.688		7.96	1.20
1.99	2.85		1.39
0.747	4.54		1.06
0.509	8.70		1.45

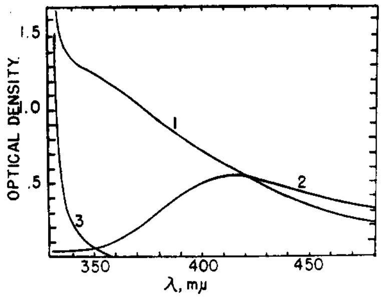

Fig. 1.—Absorption spectra of solutions in CCl_4: Curve 1, $C_{\text{naphthalene}} = 0.688$, $C_{\text{bromine}} = 0.793 \times 10^{-3}$ mole/liter; Curve 2, $C_{\text{naphthalene}} = 0$, $C_{\text{bromine}} = 1.325 \times 10^{-3}$ mole/liter; Curve 3, $C_{\text{naphthalene}} = 2.032$, $C_{\text{bromine}} = 0$ mole/liter.

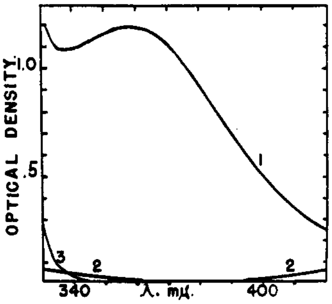

Fig. 2.—Spectra of solutions in CCl_4: Curve 1, $C_{\text{naphthalene}} = 0.4039$, $C_{\text{iodine}} = 1.745 \times 10^{-3}$ mole/liter; Curve 2, $C_{\text{naphthalene}} = 0$, $C_{\text{iodine}} = 1.745 \times 10^{-3}$ mole/liter; Curve 3, $C_{\text{naphthalene}} = 0.500$, $C_{\text{iodine}} = 0$ mole/liter.

Association constants and extinction coefficients of the complexes at the frequency of maximum absorption were obtained by the method of Benesi and Hildebrand.[2a] For a 1:1 complex, a plot of $c_{\text{H}}l/d$ against $1/c_{\text{A}}$ should give a straight line of intercept $1/\epsilon$ and slope $1/\epsilon K$. c_{H} and c_{A} are the stoichiometric molar concentrations of halogen and aromatic, respectively, l is the length of the cell, and d is the observed optical density due to the complex after subtraction of any density due to the unassociated components. ϵ is the molar extinction coefficient of the complex, and K is the association constant in concentration units, $c_{\text{C}}/(c_{\text{H}} - c_{\text{C}})(c_{\text{A}} - c_{\text{C}})$, where c_{C} is the actual molar concentration of complex formed in the solution. Figure 3 exhibits the plots for the complexes of naphthalene with iodine and

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[2] (a) H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **71**, 2703 (1949); (b) R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 4677 (1950); (c) R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 5170 (1950).

[3] R. S. Mulliken, *ibid.*, **72**, 600 (1950).

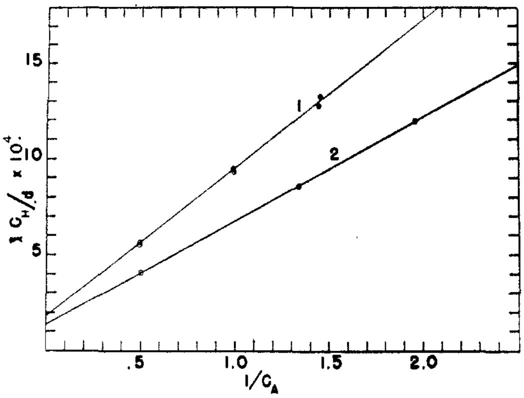

Fig. 3.—Plot of lC_H/d against $1/C_A$: Curve 1, for naphthalene–bromine; Curve 2, for naphthalene–iodine.

bromine. The results are presented in Table II, where K is given first as determined from the plot, in molar concentration units, and is then converted to the mole fraction basis for more direct comparison with previous results. The mole fraction constants shown were obtained by multiplying the concentration constants by the number of moles of carbon tetrachloride in a liter of the pure solvent. The results differ only insignificantly from those obtained when the correct conversion factor, the total number of moles in a liter of the actual solution, is employed.

TABLE II

EQUILIBRIUM CONSTANTS, MOLAR EXTINCTION COEFFICIENTS, AND WAVE LENGTHS OF MAXIMUM ABSORPTION FOR COMPLEXES OF BROMINE AND IODINE WITH NAPHTHALENE

	K (mole fraction)	K (concentration)	ϵ	λ_{max}, mμ
Iodine	2.66	0.257	7250	360
Bromine	2.38	0.229	5660	346

Plots of the extinction coefficient against wave number for the complexes are shown in Fig. 4, together with similar plots for the benzene complexes.

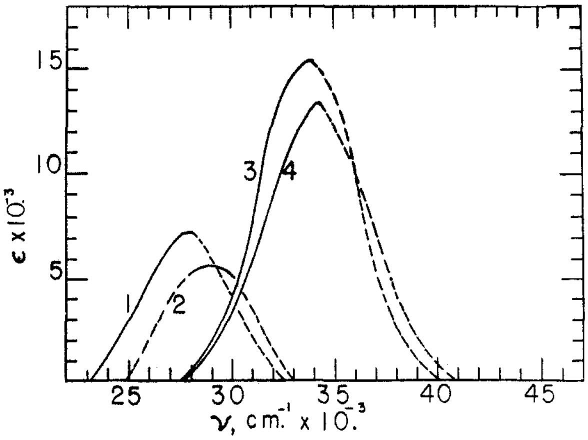

Fig. 4.—Characteristic absorption spectra of aromatic–halogen complexes: Curve 1, iodine–naphthalene; Curve 2, bromine–naphthalene; Curve 3, iodine–benzene; Curve 4, bromine–benzene.

The dashed portions of the curves could not be determined with great accuracy because the absorption of the complex was obscured by the absorption of either the naphthalene or the halogen. Nevertheless, we believe that the area under the curve, $\int \epsilon d\nu$, is known to within 10–20%. The f-numbers were computed from the equation[4]

$$f = 2.3\,(nc^2m/N\pi e^2)\int \epsilon d\nu = 4.28 \times 10^{-9}\int \epsilon d\nu$$

where ν is frequency in cm.$^{-1}$, and the results are listed in Table III as the experimental f-numbers. The deviation of the index of refraction of the medium, n, from unity was ignored.

TABLE III

COMPARISON OF EXPERIMENTAL AND CALCULATED INTENSITIES

Complex	Experimental f-number	Calculated f-number	Experimental $Q \times 10^8$	Calculated $Q \times 10^8$
C_6H_6–I_2	0.38[a]	0.073	1.02	0.45
C_6H_6–Br_2	.35[b]	.048	0.98	.36
$C_{10}H_8$–I_2	.21[c]	.21	.84	.84
$C_{10}H_8$–Br_2	.11[c]	.17	.59	.74

[a] Ref. 3. [b] Calculated from data of Ref. 2b. [c] This research.

TABLE IV[a]

FREQUENCIES AND OSCILLATOR STRENGTHS FOR THE FIRST THREE TRANSITIONS IN BENZENE AND NAPHTHALENE

	1st band ν in cm.$^{-1}$ × 10^{-3}	f	2nd band ν in cm.$^{-1}$ × 10^{-3}	f	3rd band ν in cm.$^{-1}$ × 10^{-3}	f
Benzene	38.0	0.002	48.0	0.1	54.5	0.69
Naphthalene	32.0	.002	34.6	.18	45.4	1.70

[a] Ref. 5.

Discussion

Iodine forms a stronger complex with naphthalene than does bromine, which might have been anticipated from the properties of the corresponding benzene complexes, and the naphthalene complex association constants are larger than those for benzene. This circumstance is further evidence for the correctness of Benesi and Hildebrand's proposal that the complex formation is a Lewis acid–base interaction, since it may be inferred from naphthalene's lower ionization potential and generally greater reactivity toward positively charged reagents that it is a stronger Lewis base, or electron donor, than benzene.

Although the hypothesis of Lewis acid–base interaction is so useful in correlating the stabilities of these complexes, it is not very helpful in interpreting their spectra. This is not surprising, because the stability of a complex is a property of its electronic ground state, while the spectrum depends as much upon the upper electronic levels. Inspection of Fig. 4 shows that the absorptions of the benzene complexes of iodine and bromine are very similar, and markedly different from those of the two complexes with naphthalene, which again are very similar to each other. (The iodine monochloride complex of benzene, an account[2c] of which was published during the preparation of this paper, has a spectrum very similar to the other two benzene complexes.) Certainly the absorption bands depend much more strongly upon the aromatic member of the complex than upon the halogen. The visible portions of the complex spectra appear to be but little shifted from the halogens' own visible absorptions. This is particularly evident for io-

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(4) A. L. Sklar, *Rev. Modern Phys.*, **14**, 232 (1942), Eq. 5.

dine[2a] and bromine[2b] in pure benzene, where a large fraction of the halogen is complexed. It is very difficult to accept any interpretation of the new ultraviolet bands appearing in the complex which depends principally upon changes in the electronic structure of the halogen. Mulliken's proposal[3] that the complex absorption is due to a shifted level of the aromatic seems much more satisfactory.

The spectra of benzene and naphthalene exhibit similarities which have been discussed extensively by Klevens and Platt.[5] Going toward higher frequencies from the visible, there is first a very weak absorption, then a stronger one, and then, quite far in the ultraviolet, a very strong absorption. The naphthalene spectrum is several thousand cm.$^{-1}$ toward the visible from the benzene spectrum, which is reminiscent of the relations between the corresponding complex spectra. The relevant information is summarized in Table IV. Mulliken[3] has described the complex absorption as a transition to the lowest excited level of the aromatic (upper state of its first transition), shifted toward the visible by a perturbation which also mixes into the excited wave function of the complex enough of the wave function corresponding to the strongest aromatic transition to give the observed intensity, which is larger than that of the longest wave length aromatic transition, but considerably smaller than that of the most intense aromatic transition.

This interpretation can be given semi-quantitative support by comparing the observed relations between frequencies and intensities in the complexes with those to be expected from a simple theoretical treatment. We assume that the major part of the shift of absorption frequency from the aromatic to the complex is due to the *mixing of the upper level of the very strong ultraviolet absorption of the aromatic with the upper level of its lowest frequency absorption*. The experimentally observed shift can then be used to compute the coefficient of the mixed-in wave function in the final wave function, and so to estimate the intensity of the complex absorption from the shift.

Several circumstances militate against this procedure giving very accurate results. We have assumed that the presence of the iodine molecule near the aromatic affects the spectrum by mixing the unperturbed aromatic wave function, resulting in the appearance of the first transition of the aromatic with an altered frequency and an intensity borrowed from higher and stronger transitions. We have limited the discussion to the mixing of the upper levels of the transitions at 38000 cm.$^{-1}$ and 54500 cm.$^{-1}$ in benzene and at 32000 cm.$^{-1}$ and 45400 cm.$^{-1}$ in naphthalene; an exact treatment would require that the contributions of all the other aromatic levels be taken into account as well. In particular, it might be expected that the upper level of the intermediate aromatic transition would either perturb the lowest excited level or be perturbed by a higher one. Although this possibility can certainly not be excluded, interaction between the first two excited levels is forbidden by symmetry for certain reasonable geometries of the complexes. Even if the complexes do not have exactly the symmetry necessary for this result, the interactions may well be small. As for perturbation of the intermediate level by the highest one, there is nothing to show that this does not occur, giving rise perhaps to a band still further in the ultraviolet than the complex absorption which has been observed. Another source of error is neglect of the first order energy correction of perturbation theory, equal to the perturbation averaged over the original aromatic wave functions before mixing. Evidence that this may be a small effect, at least in the ground state, is provided by Cromwell and Scott's[6] determination of the ΔH of formation of the benzene iodine complex as 500 cm.$^{-1}$. The first order correction to the ground state energy is probably not even as large as the ΔH (since very likely most of the stability of the complex arises from admixtures of the ionic type of wave function discussed by Mulliken[3]). There seems to be no reason to believe that this first order effect would be very much larger in the excited states. Even if these sources of error are operative, the formula based on our simple assumptions may still give order-of-magnitude agreement.

According to these assumptions, the square of the coefficient of the highest level in the final wave function of the complex is

$$a^2 = (E_1 - E_c)/((E_1 - E_c) - (E_c - E_3))$$

where E_1, E_c and E_3 are the energies of the first aromatic transition, the observed complex transition, and the third aromatic transition, respectively. The f-number is

$$f = a^2(E_c/E_3) \times f_3$$

where f_3 is the f-number of the third transition of the aromatic. A comparison of the f-numbers calculated in this way from the shift and those observed is shown in Table III. A somewhat gentler test is based on the calculated and observed transition moments, given by[7]

$$Q = 3.03 \times 10^{-4}(f/\nu_c)^{1/2}$$

where ν_c is the wave number of the complex transition. These are also listed in Table III.

In view of the uncertainties in the experimental and particularly in the theoretical values, the close agreement obtained for the naphthalene–iodine complex can only be fortuitous. The results for the benzene complexes are more in line with the probable accuracy of our treatment.

A qualitative prediction which can be made on the basis of these arguments is that the intensity will increase as the shift from the unperturbed aromatic frequency increases. This is borne out by the behavior of the complexes of any of the aromatic hydrocarbons so far investigated with different halogens; particularly, in the iodine,[2a] bromine[2b] and iodine monochloride[2c] complexes of benzene, the order of increasing shift is the order of increasing intensity, despite a different order of stability. Not enough data are available to test the theory in a case in which the halogen is kept the same and a series of substituted benzenes allowed to complex

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(5) H. B. Klevens and J. R. Platt, *J. Chem. Phys.*, **17**, 470 (1949).

(6) T. M. Cromwell and R. L. Scott, THIS JOURNAL, **72**, 3825 (1950).

(7) R. S. Mulliken, *J. Chem. Phys.*, **7**, 15 (1939).

with it. Still, the trend of absorption frequency for the complexes in such a series generally appears to follow the trend of the frequencies of the first absorptions of the substituted benzenes. However, the complexes of a given halobenzene with different halogens do not obey the rule. It has already been suggested[2b] on other grounds that there may be complexing by way of the halogen substituent in these cases as well as or instead of by the mechanism effective in hydrocarbons.

The crudity of the numerical treatment we have had to employ should not obscure the very striking qualitative evidence that the absorption of the complex is determined principally by the aromatic part. This experimental finding is most reasonably interpreted by ascribing the transition either to a shifted aromatic band, as we have done here, or to an electron transfer between aromatic and halogen. The latter alternative was deemed unlikely by Mulliken on the basis of the intensities. The shifted aromatic band remains as the most likely explanation; the appearance of such a band requires that the symmetry of the free molecule be disturbed. In this case, then, the benzene–halogen complexes could not have the structure favored by Keefer and Andrews,[2b] with the halogen molecule aligned along the hexagonal axis.

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Chemical Methods for Estimating the Distribution of C^{14} in Biosynthetic Glucuronic Acid[1]

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In order to determine the location and specific activity of C^{14} in biosynthetic glucuronic acid derived from radioactive precursors, several chemical degradations have been developed which yield a series of fragments sufficient to permit the measurement or calculation of C^{14} in all of the carbon atoms of glucuronic acid. The pyranose structure assigned to conjugated glucuronides has been confirmed.

Although the phenomenon of detoxification by glucuronic acid has engaged the attention of biochemists for nearly a century, the origin of this compound in the animal organism has remained obscure. Numerous hypotheses have been suggested to account for its origin, but none has been definitive.[3-8] With the advent of tracer techniques it has become clear that it is now possible to investigate the biosynthesis of glucuronic acid from precursors labeled with C^{14}.

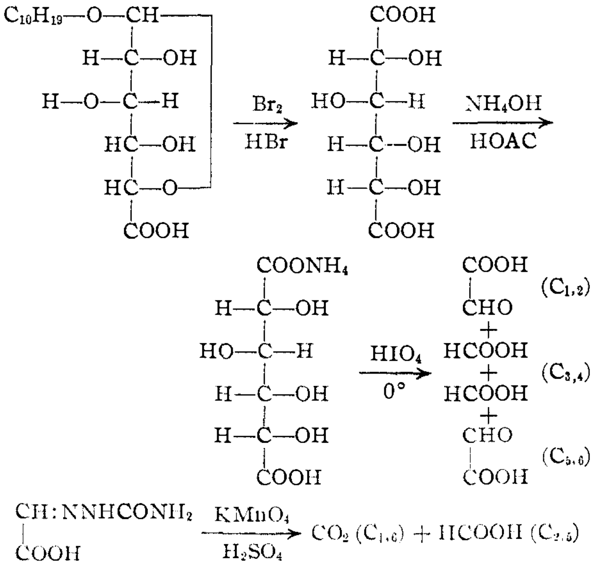

Fig. 1.

As a preliminary to this study, it was necessary to develop chemical degradations designed to locate the position and amount of C^{14} in the individual carbon atoms of radioactive glucuronic acid. The present paper describes several chemical degradations which yield five fragments: $C_{1,6}$, $C_{2,5}$, $C_{3,4}$, $C_{1,2}$ and $C_{4,5,6}$. Recent tracer studies on the biosynthesis of glucuronic acid[9] have utilized only the classical decarboxylation reaction, yielding C_6. From the C^{14} content of the abovementioned fragments including C_6, it is possible to calculate the specific activity of all six carbon atoms of glucuronic acid.

Procedure 1 (See Fig. 1).—Menthyl glucuronide, isolated from rabbit urine, was oxidatively hydrolyzed to saccharic acid which was subsequently cleaved by periodic acid to formic acid and glyoxylic acid. Sprinson and Chargaff[10] reported that tartaric acid can be oxidized at low temperature with the utilization of 1 mole of HIO_4. Since no CO_2 was evolved under these conditions, the tartaric acid was presumably cleaved to 2 molecules of glyoxylic acid. An analogous reaction has been found with saccharic acid. By measuring the utilization of HIO_4 at 0°, it was observed that exactly 3 moles of HIO_4

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(2) Presented by Frank Eisenberg, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Pennsylvania. Predoctoral fellow of the National Institutes of Health, United States Public Health Service, 1949–1950.

(3) O. Schmiedeberg and H. Meyer, *Z. physiol. Chem.*, **3**, 422 (1879).

(4) E. Fischer and O. Piloty, *Ber.*, **24**, 521 (1891).

(5) H. Thierfelder, *Z. physiol. Chem.*, **10**, 163 (1886).

(6) F. Schmid, *Compt. rend. soc. biol.*, **123**, 223 (1936).

(7) A. J. Quick, *J. Biol. Chem.*, **70**, 59, 397 (1926).

(8) W. L. Lipschitz and E. Bueding, *ibid.*, **129**, 333 (1939).

(9) E. H. Mosbach and C. G. King, *ibid.*, **185**, 491 (1950).

(10) D. B. Sprinson and E. Chargaff, *ibid.*, **164**, 433 (1946).