lite IR4B anion exchange resin to remove the excess hydrogen bromide. The filtrate was distilled under vacuum to remove the water, and 139 g. (1.04 mole) of 2-(2-hydroxypropoxy)-1-propanol, b.p. 96–96.5° (4 mm.), 224° (760 mm.), were obtained. This is a 52% yield based on alcohol taken. The substance did not solidify at −40°. It possessed the following properties: sp. gr. 1.0229 (25/25), 0.9925 (60/4); $n^{25}$D 1.4391, $n^{60}$D 1.4283.

*Anal.* Calcd. for $C_6H_{14}O_3$: C, 53.71; H, 10.52. Found: C, 53.68; H, 10.45.

Its **bis-*p*-nitrobenzoate**, prepared in 85% yield, melted at 83–84°.

*Anal.* Calcd. for $C_{20}H_{20}N_2O_9$: N, 6.48. Found: N, 6.40.

III. **Preparation** of 1,1′-Oxydi-2-propanol.—The apparatus was the same as used in I above. Twenty moles (1520 g.) of propylene glycol and 16 g. of sodium metal were added to the flask under a nitrogen blanket and the mixture was heated to 105°. Twenty moles (1160 g.) of propylene oxide was added dropwise at 105–144° over a period of 3.5 hours. The mixture was distilled as in II above and 1092 g. (8.15 moles) of 1,1′-oxydi-2-propanol; b.p. 113–114° (10 mm.), 222.2° (760 mm.), yield 47.5%, was obtained. On recrystallizing from ether this material melted at 45–46.5°. It had the following properties: sp. gr. 0.9878 (60/4), $n^{60}$D 1.4284.

*Anal.* Calcd. for $C_6H_{14}O_3$: C, 53.71; H, 10.52. Found: C, 53.70; H, 10.50.

Its **bis-*p*-nitrobenzoate**, prepared in 96% yield, melted at 150–151°.

*Anal.* Calcd. for $C_{20}H_{20}N_2O_9$: N, 6.48. Found: N, 6.42.

Its **bis-triphenylmethyl** ether, prepared[6] in 75% yield, had m.p. 145–146°.

*Anal.* Calcd. for $C_{44}H_{42}O_3$: C, 85.40; H, 6.84. Found: C, 85.07; H, 6.84.

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## The Iodine Complexes of Polyalkylbenzenes[1]

BY M. TAMRES, D. R. VIRZI AND S. SEARLES

RECEIVED JANUARY 31, 1953

In recent papers, Mulliken has proposed structures for the benzene complexes with silver ion[2] and with iodine.[2,3] His structure for the Ar·Ag$^+$ complex with the silver ion in the region between and somewhat above two carbon atoms in the aromatic ring, makes plausible the observation that continued methyl substitution in the ring eventually leads to a decrease in stability of the complex. (The association constant of silver ion with mesitylene is smaller than that with the xylenes or with toluene,[4] a result which is opposite to the normal inductive effect.) This decrease in stability may occur when there are no longer available two adjacent unsubstituted carbon atoms to serve as a site for the silver ion.[2] The fact that the complex with durene is more stable than that with mesitylene[5] is still in accord with this hypothesis.

Mulliken considered several structural possibilities for the Ar·$I_2$ complex. These are as follows (where the roman numerals and the capital letters in parentheses designate the models in references 2 and 3, respectively): the iodine molecule located along an edge or corner of the benzene ring with the iodine axis either in the plane of the ring (II or T and L), or perpendicular to the plane of the ring (III or E), or inclined to the plane of the ring (O); the iodine axis coinciding with the sixfold symmetry axis of benzene with the two iodine atoms on the same side of the benzene plane (IV or A), or on opposite sides of the benzene plane (V); the iodine molecule located with its center on the sixfold axis of symmetry of the aromatic ring, with the iodine axis being parallel and slightly above the plane of the aromatic ring (I or R). Of these possibilities, the one favored most strongly by Mulliken on the basis of spectroscopic and electrostatic principles is model R (or I). With this model it would be difficult to imagine that the methyl groups in polymethylbenzenes could interact sterically with the iodine molecule, as they apparently do with the silver ion, and one would expect hexamethylbenzene to be a stronger base toward iodine than any of the other methylbenzenes.[6] The results published recently by Andrews and Keefer[5] on the interaction of of polyalkylbenzenes with iodine and with iodine monochloride show that this is actually the case. Working independently in this Laboratory we also found this to be true, and our results on the interaction of several polyalkylbenzenes with iodine offer interesting comparison with the data of Andrews and Keefer.

The equilibrium constant of the complex, $K$, and the molar extinction coefficient of the complex, $\epsilon_c$, were determined from the equation first derived by Benesi and Hildebrand.[7]

$$\frac{(I_2)l}{d_c} = \frac{1}{K\epsilon_c} \times \frac{1}{N_a} + \frac{1}{\epsilon_c}$$

The notation for this equation is similar to that which has been employed by Andrews and Keefer.[8] Plots of $(I_2)/d_c$ *versus* $1/N_a$ (based on at least four points for each aromatic compound) gave straight lines. Since $\epsilon_c$ and $K$ are sensitively dependent upon the line drawn through the experimental points, the equation for the line was determined by the method of least squares and the values of $\epsilon_c$ and

TABLE I

WAVE LENGTHS OF MAXIMUM ABSORPTION, MOLAR EXTINCTION COEFFICIENTS AND EQUILIBRIUM CONSTANTS OF IODINE–AROMATIC COMPLEXES IN CARBON TETRACHLORIDE AT ROOM TEMPERATURE

| Aromatic cpd. | $\lambda_{max}$, mμ | $\epsilon_c$ × $10^{-3}$ | $K$ |
|---|---|---|---|
| Benzene | 295 | 14.7 | 1.60[a] |
| Mesitylene | 332 | 10.2 | 5.96[a] |
| Isodurene | 339 | 8.70 | 6.87 |
| Pentamethylbenzene | 355 | 7.77 | 9.72 |
| Hexamethylbenzene | 371 | 6.69 | 15.2 |
| Hexaethylbenzene | 375 | 4.57 | 4.58 |

[a] H. A. Benesi and J. H. Hildebrand (ref. 7) report for benzene $\lambda_{max}$ 297 mμ, $\epsilon_c$ 15.4 × $10^3$, $K$ 1.72; and for mesitylene $\lambda_{max}$ 333 mμ, $\epsilon_c$ 9.3 × $10^3$, $K$ 7.2.

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[1] From the B.S. honor's thesis of Donald Robert Virzi submitted to the chemistry department, University of Illinois, June, 1952.

(2) R. S. Mulliken, THIS JOURNAL, **74**, 811 (1952).

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

(4) L. J. Andrews and R. M. Keefer, *ibid.*, **71**, 3644 (1949); **72**, 5034 (1950).

(5) L. J. Andrews and R. M. Keefer, *ibid.*, **74**, 4500 (1952).

(6) In a private discussion, Professor Mulliken agreed with this prediction.

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

(8) L. J. Andrews and R. M. Keefer, *ibid.*, **72**, 4677, 5170 (1950); *ibid.* **73**, 462 (1951).

$K$ were then calculated. These data, together with the wave length of maximum absorption of the complex, are given in Table I.

In this work as in that of Benesi and Hildebrand,[7] $K = (Ar{\cdot}I_2)/N_a(I_2)$ is a dimensionless quantity, where $N_a$ is the mole fraction of the aromatic compound in carbon tetrachloride and $(Ar{\cdot}I_2)$ and $(I_2)$ are the molar concentrations of the complex and free iodine, respectively. The equilibrium constant, $K_c$, of Andrews and Keefer[5] is in units of reciprocal moles per liter, *i.e.*, $K_c = (Ar{\cdot}I_2)/(Ar)(I_2)$ where (Ar) is the molar concentration of the aromatic compound in carbon tetrachloride. The relative values of the equilibrium constants for the two sets of data are in fair agreement[9]; this being true also for the $\lambda_{max}$ and $\epsilon_c$ data.

Of the polymethylbenzenes which they investigated, Andrews and Keefer found that the interaction with iodine could be correlated qualitatively with the data of McCaulay and Lien[10] who reported on the interaction of the aromatics with HF–$BF_3$. Our result for isodurene, which was not determined by Andrews and Keefer, is in agreement with this observation.

There are several differences between the two sets of data, however, which should be mentioned. In this work it is found that the equilibrium constant for the hexaethylbenzene complex with iodine is larger than that for the benzene complex, whereas Andrews and Keefer report the opposite to be more likely correct. Furthermore, our extinction coefficient ($4.57 \times 10^3$) for the hexaethylbenzene complex is the smallest of any of the complexes studied here, whereas the value of Andrews and Keefer ($16.7 \times 10^3$) was the largest of the complexes investigated by them.

Also it appears that, for the data of Table I at least, an increase in $K$ as methyl groups are introduced in the benzene nucleus is accompanied by a corresponding decrease in $\epsilon_c$. The product of $\epsilon_c$ and $\sqrt[3]{K}$ seems to be constant,[11] except possibly for mesitylene where the result is slightly high. This is borne out in Fig. 1 in which there is plotted $\epsilon_c$ *versus* $1/\sqrt[3]{K}$.

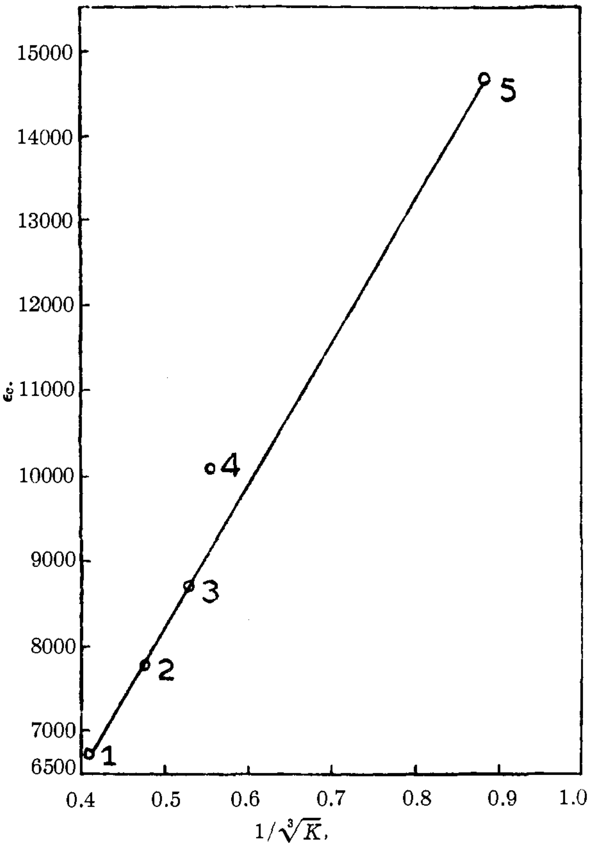

Fig. 1.—Relation between molar extinction coefficients and equilibrium constants for several aromatic–iodine complexes: 1, hexamethylbenzene; 2, pentamethylbenzene; 3, isodurene; 4, mesitylene; 5, benzene.

It was reported by Benesi and Hildebrand that increasing methyl substitution in benzene shifts the visible absorption peak of iodine dissolved in aromatic hydrocarbons toward shorter wave lengths. From the results in Table II, this effect does not seem apparent at first. The lack of shift toward shorter wave lengths for the polyalkylbenzenes may be due to the dilution of the system with carbon tetrachloride. This would cause a shift in absorption toward longer wave lengths, that is, toward the absorption in pure carbon tetrachloride. Also it may be that some overlap in the absorption curves of the free iodine and of the complex occurs since the absorption maxima of the two are not far apart. Dilution with carbon tetrachloride favors a larger free iodine to complex ratio, which may account for the shift to longer wave lengths. For the pentamethyl-, hexamethyl- and hexaethylbenzene data in Table II, the per cent. of free iodine is approximately 57, 69 and 83%, respectively.

TABLE II

VISIBLE ABSORPTION DATA

| Solvent | Mole fraction in carbon tetrachloride | $(I_2) \times 10^4$, moles/l. | $d_0$ | $\epsilon_{max}$[a] | $\lambda_{max}$ mμ |
|---|---|---|---|---|---|
| Carbon tetrachloride | 1.0000 | 23.22 | 2.10 | 904 | 517 |
| Benzene[b] | 1.0000 | 6.91 | 1.45 | 1050 | 500 |
| Mesitylene[b] | 1.0000 | 9.20 | 2.21 | 1200 | 490 |
| Isodurene | 0.3476 | 2.13 | 0.21 | 987 | 495 |
| | .2165 | 4.66 | 0.47 | 1001 | 500 |
| | .1554 | 5.18 | 0.50 | 964 | 505 |
| | .0748 | 7.77 | 0.73 | 942 | 503 |
| Pentamethylbenzene | .0770 | 3.80 | 0.33 | 870 | 503 |
| Hexamethylbenzene | .0290 | 19.12 | 1.94 | 1023 | 506 |
| Hexaethylbenzene | .0438 | 19.34 | 1.86 | 964 | 510 |

[a] Calculated by use of the Beer–Lambert equation assuming all the iodine to be free. [b] Data from Benesi and Hildebrand (ref. 7).

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(9) The ratio of (Ar) to $N_a$ for each aromatic compound is a variable which depends upon the composition. The limiting ratio of (Ar) to $N_a$ as $N_a \rightarrow 0$ is 1000 $\rho/M$ where $\rho$ and $M$ are the density and molecular weight, respectively, of carbon tetrachloride. If this constant of 10.3 is employed to convert $K$ into $K_c$ the following results are obtained which may be compared with those of Andrews and Keefer given in parentheses: benzene 0.15 (0.15); mesitylene 0.58 (0.82); pentamethylbenzene 0.94 (0.88); hexamethylbenzene 1.47 (1.35); and hexaethylbenzene 0.44 (0.13).

(10) D. A. McCaulay and A. P. Lien, THIS JOURNAL, **73**, 2013 (1951).

(11) Note Added to Proof.—The recent literature survey by H. McConnell, J. S. Ham and J. R. Platt (*J. Chem. Phys.*, **21**, 66 (1953)) revealed no strong correlation between the molar extinction coefficients and the equilibrium constants of the complexes.

It is of interest to note that increasing methyl substitution in benzene affects $\lambda_{max}$ of the complex as well, but in this case the shift is toward longer wave lengths. If this shift were to be employed as a qualitative criterion for the change in basicity of the electron donor molecule[12] then the low result for the equilibrium constant of the hexaethylbenzene–iodine complex could be attributed to fewer, though comparatively strongly bound, associated molecules as a consequence of unfavorable steric requirements. Consideration of molecular models, as pointed out by Andrews and Keefer,[5] indicates that an ethyl group can fold back and overlap a small area above the aromatic ring. .

The investigation of steric factors in the formation of iodine complexes with polymethylbenzenes cannot be considered as confirming uniquely the Mulliken model R for the $Ar \cdot I_2$ complex. Although structures in which the iodine molecule is at a corner or edge of the benzene ring (as in models L, E and O) now appear highly improbable, structures other than R in which the iodine molecule is centrally located with respect to the benzene ring (as in model A) still remain. Comparing the possibilities R and A for the hexaethylbenzene–iodine complex, the one which would be predicted the more likely to result in steric interaction between the iodine molecule and the ethyl groups is structure R. But the fact that a steric effect is observed experimentally does not necessarily eliminate model A, although it is a point in support of the Mulliken proposal.

### Experimental

**Materials.**—Carbon tetrachloride and the liquid hydrocarbons were purified by the distillation procedure previously described.[13] Carbon tetrachloride, $n^{20}D$ 1.4609, was purified as specified by Fieser.[14] The method of Benesi and Hildebrand,[7] except for the mercury treatment, was used to purify benzene and mesitylene, $n^{20}D$ of 1.5008 and 1.4965, respectively. Isodurene (prepared by the Organic Manufacturing Laboratory at the University of Illinois) was dried over calcium chloride and distilled, $n^{20}D$ 1.5095.

Pentamethylbenzene, hexamethylbenzene and hexaethylbenzene were made available to us by Dr. A. P. Lien. Several months of standing in capped vials did not affect the purity. Prior to use the uncorrected melting points were 52–53°, 164 and 127°, respectively.

Reagent grade iodine from the General Chemicals Company was sublimed and stored over phosphorus pentoxide in a desiccator.

**Procedure.**—The procedure for obtaining absorption spectra data was the same as that described by Benesi and Hildebrand.[7] The instrument employed was a Cary Recording Quartz Spectrophotometer with a matched pair of 1-cm. glass-stoppered quartz cells.

A standard iodine stock solution was prepared at room temperature by dissolving a known weight of iodine (0.3105 g.) in 100 ml. of carbon tetrachloride. More dilute solutions were prepared, as required, by taking a known aliquot of the stock solution and diluting with carbon tetrachloride in a calibrated 25-ml. volumetric flask. The concentrations of the iodine solutions were checked spectrophotometrically from time to time.

A solution of each aromatic compound was prepared by dissolving a known weight of the compound in a known weight of carbon tetrachloride. The use of solutions was necessary for the solid aromatic compounds, but solutions of the liquid aromatics in carbon tetrachloride were made also in order to study the same range of concentrations. Aliquots were taken by means of calibrated pipets and each aliquot was weighed. To each was added a known weight of iodine solution, delivered through a calibrated pipet, and the absorption measurement was then made immediately. From these data, the mole fraction of the aromatic compound and the molar concentration of iodine could be calculated. The ranges of mole fractions of the aromatic compounds in the mixtures thus prepared were: benzene 0.901–0.0239; mesitylene 0.366–0.0317; isodurene 0.216–0.0748; pentamethylbenzene 0.0770–0.0254; hexamethylbenzene 0.0594–0.0196; hexaethylbenzene 0.0805–0.0253.

**Acknowledgment.**—We are indebted to Dr. A. P. Lien of the Standard Oil Company of Indiana for the pentamethylbenzene, hexamethylbenzene and hexaethylbenzene which he generously provided.

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[12] The data of this investigation and that of Andrews and Keefer suggest that this may apply to closely related derivatives of a parent compound. It does not appear to apply to unrelated compounds. Note Added to Proof.—McConnell, Ham and Platt[11] have shown that there is an inverse linear relationship between the ionization potential, $I_p$, of the electron donor molecule and the wave length of maximum absorption, $\lambda_{max}$, of its complex with iodine. The ionization potential increases in the order: mesitylene < *o*- or *m*- xylene < toluene < benzene. This is the same order for decreasing stability of the complex. Since the magnitude of the equilibrium complex, $K$, is regarded as an indication of basic strength (barring steric factors) as well as a measure of stability, there is some justification for relating $K$ with $\lambda_{max}$. A plot of $\epsilon_c$ *versus* $\lambda_{max}$ for benzene and its methyl derivatives (data of Table I) gives a smooth curve except for mesitylene which, as was noted previously, does not lie on the $\epsilon_c$ *versus* $1/\sqrt[3]{K}$ graph of Fig. 1.

There is some doubt at present that the $K$ and $\lambda_{max}$ values for the iodine complexes of all electron donor molecules can be related by a single expression. Diethyl ether, which lies on the linear $I_p$ *versus* $\lambda_{max}$ plot, has an ionization potential which is considerably greater than that for benzene. If taken to mean that the equilibrium constant for the diethyl ether–iodine complex is less than that for the benzene–iodine complex, this would constitute an unusual reversal of expected basic characteristics. There is a need for additional data for the $K$ values of iodine with other electron donors. But until such data are forthcoming, it seems best to restrict the use of $\lambda_{max}$ as a qualitative measure of basicity to closely related compounds.

[13] M. Tamres, THIS JOURNAL, **74**, 3375 (1952).

[14] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1935, p. 309.

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## The Reaction of Trifluoroacetone with Acetylene

BY PAUL TARRANT, D. A. WARNER AND R. E. TAYLOR

RECEIVED MARCH 30, 1953

It has been claimed[1] that trifluoroacetone reacts with ethynylmagnesium bromide to give a product which was dehydrated with oxalic acid to 3-trifluoromethylbutyn-1-ene-3. The acetylenic compound was then treated with hydrogen to yield 3-trifluoromethylbutadiene-1,3. No physical constants nor analyses were given for the intermediate compounds.

As part of the program in this Laboratory on the preparation of fluoroölefins for the Arctic rubber program for the Office of Quartermaster General, it seemed desirable to repeat the experiments described in the patent to obtain trifluoromethylbutadiene. Although a number of runs were carried out with trifluoroacetone and the Grignard reagent prepared from ethylmagnesium bromide, no product which could be dehydrated with either magnesium sulfate or oxalic acid was obtained. However, there was obtained some 3-trifluoromethyl-1-butyne-3-ol and a larger amount of 2,5-

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[1] H. M. Hill and E. B. Towne, U. S. Patent 2,490,753 (Dec. 6, 1949).