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A Spectroscopic Study of the Benzene–*s*-Trinitrobenzene Molecular Complex[1]

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The existence of a 1:1 molecular complex containing benzene and *s*-trinitrobenzene has been established. The equilibrium constant for the formation of this complex in *n*-heptane solvent is 4.09 ± 0.22. The absorption spectrum of the complex has been obtained throughout the 210–410 mμ range. The molecular complex shows four electronic transitions in this wave length range.

I. Introduction

In a previous spectroscopic investigation it was shown that several polynitrobenzenes form colored molecular complexes with aniline.[3] This result originally suggested that benzene and *s*-trinitrobenzene might form spectroscopically detectable molecular complexes. The present investigation was subsequently undertaken for the purposes of (a) extending the results of the previous investigation[3] of molecular complexes containing two aromatic molecules and (b) obtaining the spectrum of a molecular complex which might reasonably be expected to exhibit several electronic transitions in an easily accessible wave length region. Purpose (b) is designed to assist the solution of the general theoretical problem of correlating the electronic states of molecular complexes with the electronic states of the individual (separated) molecules which form the complexes.

Part II of the present paper describes the various experimental procedures used to obtain the spectra of *s*-trinitrobenzene (*s*N)–benzene (B) solutions throughout the 210–410 mμ range. Part III describes the mathematical procedure used to interpret the observed spectra in terms of the equilibrium constant and absorption spectrum of the *s*NB complex. The analysis in part III is similar to one used previously[3]; part III is therefore somewhat condensed. In part IV the spectrum of the *s*NB complex is briefly discussed.

II. Experimental

Materials.—Phillips 99% grade *n*-heptane was treated successively with concentrated sulfuric acid, aqueous potassium carbonate, water, Drierite, sodium; and finally distilled. The product showed 100% transparency at 210 mμ in a one-cm. light path cell relative to water. Reagent grade benzene was used without further purification and the *s*-trinitrobenzene came from a sample described previously.[3]

Absorption Spectra.—The ultraviolet absorption spectra were determined with a model DU Beckman spectrophotometer. Optical densities were reproducible to 2%. Light paths of approximately 10.0, 1.0, 0.03 and 0.01 cm. were employed; the 0.03- and 0.01-cm. light paths were obtained with one-cm. quartz cells and calibrated quartz spacers.

In general the optical densities ($D = \log_{10}(I_0/I)$) of the solutions studied can be expressed by the equation

$$D = l\{\epsilon_B\,(B) + \epsilon_0(sN) + \epsilon_1(sNB) + \epsilon_2(sNB_2)\}, \quad (1)$$

where (B), (*s*N), (*s*NB), and (*s*NB$_2$) are the molar concentrations of benzene, free *s*-trinitrobenzene, the *s*NB and *s*NB$_2$ complexes, respectively. The ε's are the appropriate molar extinction coefficients and *l* is the optical light path.

Our spectroscopic data are expressed in terms of a formal extinction coefficient, $\bar{\epsilon}$, and the quantity *Q*

$$\bar{\epsilon} = [D - l\epsilon_B\,(B)]/(sN)_0 l \quad (2)$$

$$Q = [B]/(\bar{\epsilon} - \epsilon_0) \quad (3)$$

In (2), $(sN)_0$ is the formal concentration of $sN[(sN)_0 = (sN) + (sNB) + (sNB_2)]$. In (3), [B] is the mole fraction of benzene. In our experiments, $(sN)_0 = 10^{-2}$–10^{-4} formal; [B] = 0.01–1.0.

The relative values of the various terms appearing in (1) differ greatly for different regions in the 210–410 mμ range. This fact necessitated different experimental procedures in these regions; these various procedures together with estimated experimental errors are summarized below under the appropriate wave length headings.

210–236 mμ.—Scattered light in the spectrophotometer was shown to be negligible from a study of the Beer's law behavior of *s*N in heptane solvent, and of benzene in heptane solvent. The spectrum of *s*N was also determined in water solvent (*cf.* Fig. 1) and is in good agreement with this spectrum as obtained by Kortüm.[4]

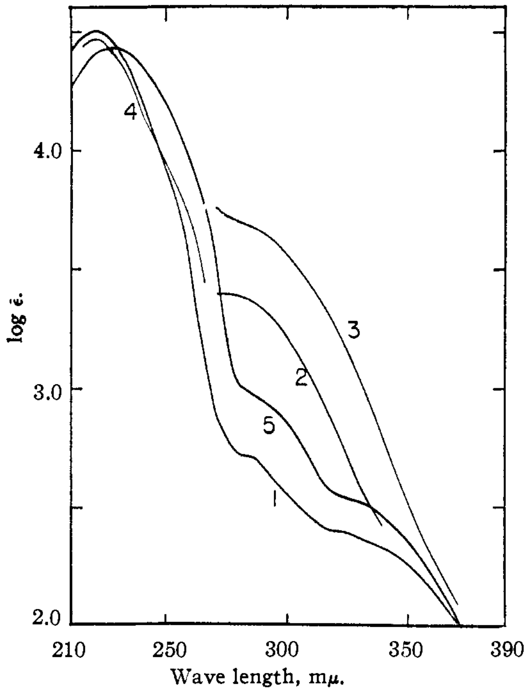

Fig. 1.—Formal extinction coefficients, $\bar{\epsilon}$, of *s*-trinitrobenzene in different solvents: 1, pure *n*-heptane; 2, *n*-heptane–benzene mixture, [B] = 0.219; 3, pure benzene; 4, *n*-heptane–benzene mixture, [B] = 0.148; 5, pure water. (Light absorption by uncomplexed benzene is not included in curves 2, 3 and 4; *cf.* Eq. (2).)

241–267 mμ.—Optical densities were measured only at wave lengths 241.0, 246.5, 252.5, 259.0 and 267.0 mμ.

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[3] J. Landauer and H. McConnell, THIS JOURNAL, **74**, 1221 (1952).

[4] G. Kortüm, *Z. physik. Chem.*, **B42**, 39 (1939).

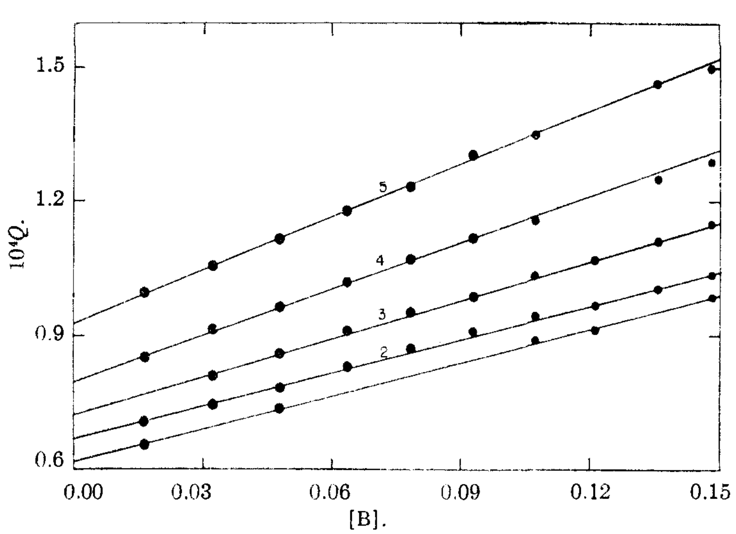

Fig. 2.—Typical plots used for the graphical determination of the equilibrium constant and extinction coefficients of the 1:1 complex. Wave lengths in mμ are 1, 280; 2, 285; 3, 290; 4, 295; 5, 300. A similar plot for 275 mμ lies between lines (1) and (2) in this figure.

These wave lengths are very close to the absorption minima or "windows" in the 240–270 mμ bands of benzene (*cf.* Fig. 4). Low optical slit widths of 0.3–0.4 mm. were maintained by replacing the usual 2,000-megohm resistor of the phototube circuit with a 10^4-megohm resistor. The light path was 0.0111 cm. The mole fractions of benzene used were in the range 0.00–0.15. The above conditions were necessary in our experiments to obtain measurable optical densities, to obtain values of $\bar{\epsilon}$ in (2) significantly different from zero and to ensure that the light absorption of benzene followed Beer's law. (At these wave lengths, the blank cell always contained pure heptane, and the light absorption of benzene was measured in the same cell used to determine the light absorption of *s*N in heptane–benzene mixtures.)

The largest experimental errors are thought to occur at these wave lengths. Although optical densities were reproducible to the usual 2% of *D*, the large errors arise from the fact that for the solutions employed the $l\epsilon_B$(B) term in (2) was often *ca.* 90% as large as *D*. Some of the $\bar{\epsilon}$'s calculated under these circumstances might be in error by ±25%. To a large extent our net errors at these wave lengths were reduced by taking data on a large number of solutions (thirteen) and by making repeated checks on the blank corrections for the absorption cells. Part III evaluates the errors in the calculated spectra which might arise from the errors discussed here. A further discussion of possible errors and of the characteristics of our spectrophotometer can be found in a previous paper dealing with a similar problem.[5]

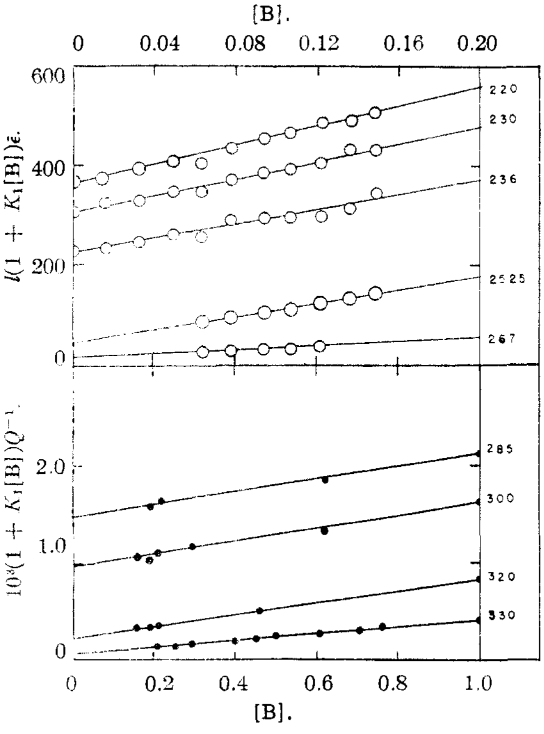

Fig. 3.—Upper: plots used for the graphical determination of the extinction coefficient of the 1:1 complex in the 215–270 mμ range. Wave lengths in mμ are indicated in right-hand margin. Lower: Plots used for the graphical determination of the extinction coefficient of the 1:1 complex in the 280–400 mμ range. Slopes of these lines give the quantity $K_2(\epsilon_2 - \epsilon_0)$ (*cf.* Eq. (5).)

277–410 mμ.—The largest errors in the data at these wave lengths are brought about by loss of significant figures in the subtraction of ϵ_0 from $\bar{\epsilon}$ in (3). Extreme care was taken in obtaining the data used for the *Q* values in Fig. 2; the errors in these *Q*'s are thought to be less than 5%. The errors in the *Q*'s and $\bar{\epsilon}$'s in Fig. 3 are larger, *ca.* 10%.

In general room temperature was 21.5 ± 2.5° except for the data in Fig. 2 where room temperature was 24.0 ± 0.05°.

III. Spectrum and Equilibrium Constant of the *s*-Trinitrobenzene–Benzene Complex

By analogy with equations developed previously, the quantity *Q* can be related to the spectra and equilibrium constants of 1:1 and 1:2 *s*-trinitrobenzene–benzene complexes by the equation[3]

$$Q = (1 + K_1[B] + K_2[B]^2)/\{(\epsilon_1 - \epsilon_0)K_1 + (\epsilon_2 - \epsilon_0)K_2[B]\} \quad (4)$$

In (4), K_1 is the equilibrium constant of the *s*NB complex, $K_1 = (s\text{NB})/(s\text{N})[\text{B}]$. The quantity K_2 is the equilibrium constant for the formation of the $s\text{NB}_2$ complex. All of the data obtained in this investigation showed the $K_2[B]^2$ term in (4) to be negligible relative to the $K_1[B]$ term.

In order to obtain K_1 and ϵ_1 for *s*NB, we first studied the dependence of *Q* on [B] for [B] = 0.01–0.15. These low [B] values were used to minimize possible contributions of $(\epsilon_2 - \epsilon_0)K_2[B]$ to *Q* and also to minimize possible variations of K_1 and ϵ_1 with benzene concentration. This study was carried out in the 270–300 mμ wave length range since *Q* is highly sensitive to small changes in [B] at these wave lengths. The linearity of the plots of *Q* *vs.* [B] shown in Fig. 2 is in accordance with (4) when all terms corresponding to 1:2 complexes are omitted and when K_1 and ϵ_1 are independent of [B]. The values of K_1 and $K_1(\epsilon_1 - \epsilon_0)$ obtained from these plots are given in Table I, and values of ϵ_1 are given in Fig. 4.

For higher benzene mole fractions, [B] = 0.2–1.0, and for all wave lengths in the 270–410 mμ range, the observed dependence of *Q* on [B] shows that the $(\epsilon_2 - \epsilon_0)K_2[B]$ term must be included in (4). When this term is retained (and $K_2[B]^2$ is dropped), (4) may be rewritten to give

$$(1 + K_1[B])Q^{-1} = K_1(\epsilon_1 - \epsilon_0) + K_2(\epsilon_2 - \epsilon_0)[B] \quad (5)$$

Plots of $(1 + K_1[B])Q^{-1}$ *vs.* [B] are given in the lower half of Fig. 3. The ordinates were calculated by using the value of K_1 given in Table I, $K_1 = 4.09$. These plots were used to calculate ϵ_1 in the 300–410 mμ range, and also to obtain values of $K_2(\epsilon_2 - \epsilon_0)$ throughout the 270–400 mμ range. The values of ϵ_1 obtained from straight-line plots of *Q* *vs.* [B]([B] = 0.01–0.15) and from straight-line plots of $(1 + K_1[B])Q^{-1}$ *vs.* [B]([B] = 0.2–1.0) agreed with one another to within 7% in the 270–300 mμ range. Calculated values of $K_2(\epsilon_2 - \epsilon_0)$ obtained from plots such as those in the lower part of Fig. 3 are given in Table I.

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(5) J. S. Ham, J. R. Platt and H. McConnell, *J. Chem. Phys.*, **19**, 1301 (1951).

TABLE I

THERMODYNAMIC AND SPECTROSCOPIC DATA FOR *s*-TRINITROBENZENE–BENZENE COMPLEXES

Wave length, mμ	K_1	10^{-4} $(\epsilon_1 - \epsilon_0)K_1$	10^{-3} $(\epsilon_2 - \epsilon_0)K_2$
270	4.12	1.36	8.0
275	3.92	1.59	
280	4.07	1.63	7.4
285	3.70	1.49	
290	3.91	1.38	7.1
295	4.35	1.26	
300	4.57	1.08	6.8
310		0.59	6.2
320		.22	5.3
330		.06	4.0
340		.00	1.7
350		.00	0.12
360		.00	0.00

Best $K_1 = 4.09 \pm 0.22$

The variation of Q with [B] in the 210–267 mμ range is not sufficiently great to permit accurate and independent determinations of both K_1 and the ϵ_1's, as was done in the 270–300 mμ range. The most accurate ϵ_1 values at these wave lengths were obtained by (a) taking $K_1 = 4.09$, (b) employing experimental data for small [B]'s, [B] = 0.00–0.20, (c) dropping all terms in (4) corresponding to the 1:2 complex, and (d) plotting the experimental values of $l\bar{\epsilon}(1 + K_1[\mathrm{B}])$ *vs.* [B]. According to approximation (c) above, equations (1), (2), (3) and (4) can be combined to give

$$l\bar{\epsilon}(1 + K_1[\mathrm{B}]) = l(\epsilon_0 + \epsilon_1 K_1[\mathrm{B}]) \qquad (6)$$

Typical plots of the left-hand member of (6) for $l = 0.0111$ cm. are given in the upper half of Fig. 3. Values of ϵ_1 obtained from these plots are given in Fig. 4. It is estimated that the log ϵ_1's in Fig. 4 may be uncertain by as much as ±0.15 in the 241–267 mμ range; we believe our data to be sufficiently accurate to show definitely that an absorption maximum or inflection is characteristic of the *s*NB spectrum at 250 mμ.

IV. Discussion

The known properties of the *s*-trinitrobenzene–benzene (*s*NB) complex can be accounted for in terms of an *acid–base* interaction between the *s*N and benzene molecules. This interaction involves resonance between a no-bond structure (*s*N, B) and an ionic or charge-transfer structure ($s\mathrm{N}^-$–B^+). This proposal of intermolecular charge-transfer in the *s*NB complex is supported by the observations of LeFèvre and LeFèvre[6] who have found that *s*N has an apparent dipole of 0.7 *D* in benzene solvent. The geometrical structure of the *s*NB complex is thought to be similar to the structures of the polynitrobenzene–aniline complexes discussed previously.[4]

The absorption spectrum of the *s*NB complex shows distinct electronic transitions at 225 mμ, $\epsilon_{\max} = 22{,}000$; 280 mμ, $\epsilon_{\max} \approx 4{,}600$; 350 mμ, $\epsilon = 180$ (inflection). The existence of a fourth transition at 250 mμ is very likely (*cf.* part III). A fifth transition at *ca.* 400 mμ may be inferred from a previous discussion[7] of the *s*N spectrum and from the apparent similarity of the *s*N and *s*NB spectra at 400 mμ.

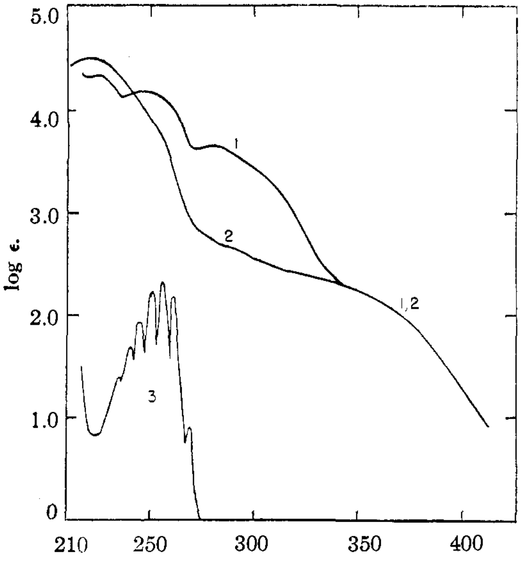

Fig. 4.—Absorption spectra: molar extinction coefficients of (1) the *s*-trinitrobenzene-benzene molecular complex; (2) *s*-trinitrobenzene in *n*-heptane; (3) benzene in *n*-heptane. Curves (1) and (2) are identical for wave lengths greater than 350 mμ.

As seen in Figs. 1 and 4, the *s*N molecule shows electronic transitions at 222 mμ, $\epsilon_{\max} = 32{,}000$; 280 mμ, $\epsilon = 550$ (inflection) and 350 mμ, $\epsilon \approx 180$ (inflection). Nearly hidden transitions are at 250 mμ, $\epsilon \approx 8{,}000$[8]; and 400 mμ, $\epsilon \approx 20$. The transition in *s*NB at 225 mμ, $\epsilon_{\max} = 22{,}000$, appears to result from a perturbation of the *s*N transition at 222 mμ, $\epsilon_{\max} = 32{,}000$. The transitions of *s*N at 350 and 400 mμ are remarkably unaffected by complex formation with benzene. The transition in *s*NB at 250 mμ, $\epsilon_{\max} = 15{,}000$, may result from a slight intensification (*ca.* × 2) and red-shift ($\sim 1{,}500$ cm.$^{-1}$) of the electronic transition which is nearly hidden in *s*N at 250 mμ, $\epsilon \approx 8{,}000$.[8]

We propose that the absorption by the *s*NB complex at 280 mμ is due to an intermolecular charge-transfer transition similar to those found in aniline–polynitrobenzene and other molecular complexes.[4,9] More extensive evidence supporting this interpretation of the 280 mμ transition of *s*NB will be given elsewhere in a paper dealing with regularities in the spectra of molecular complexes.[10]

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[6] LeFèvre and LeFèvre, *J. Chem. Soc.*, 1892 (1950).

[7] H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952).

[8] This transition is clearer in absorption in *m*-dinitrobenzene. In alkyl substituted s*N*, where the nitro groups are sterically hindered this transition is much weaker but more easily seen since the 225 mμ band undergoes a strong blue-shift. See P. Fielding and R. J. W. Le Fèvre, *J. Chem. Soc.*, 2812 (1950). The 250 mμ band of s*N* ($\epsilon = 8000$) is probably closely related to the 250 mμ band ($\epsilon_{\max} = 8000$) of nitrobenzene; the intensity of the latter transition is also highly sensitive to a twist of the nitro group. See W. G. Brown and H. Reagan, THIS JOURNAL, **69**, 1032 (1947).

[9] See R. S. Mulliken, *ibid.*, **74**, 811 (1952), and earlier papers given in this reference.

[10] H. McConnell, J. S. Ham and J. R. Platt, to be published, 1952 in *J. Chem. Phys.*