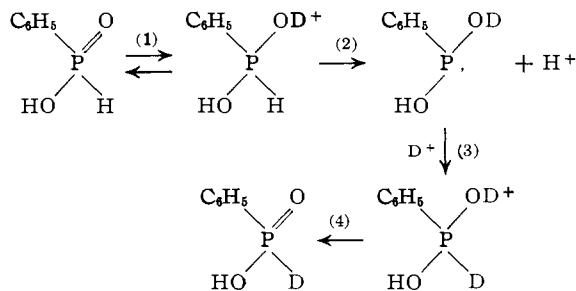


since, if the hydroxyl groups of intermediate IV are equivalent, a path is available for oxygen exchange between substrate and solvent. The mechanism of hydrogen exchange are assumed to be the same as those presented for the dialkyl phosphonates.⁶⁻⁸ The acid-catalyzed exchange may be formulated as



The first step (1) involves a fast pre-equilibrium protonation, followed by the rate-determining step (2), the fission of the P-H bond to give the tricovalent tautomer, which subsequently picks up deuterium from the sol-

vent, step (3), and loses a proton from one of the hydroxyl groups, step (4). The hydroxide ion catalysis of exchange presumably proceeds by direct proton abstraction. There is no physical evidence for the tricovalent tautomer of phenylphosphonous acid. The

normal form $\begin{array}{c} \text{C}_6\text{H}_5 \\ \diagup \\ \text{P} \\ \diagdown \\ \text{H} \quad \text{OH} \end{array}$ is probably stabilized by conjugation of the phenyl and phosphoryl groups.²⁰ The tautomer $\begin{array}{c} \text{C}_6\text{H}_5 \\ \diagup \\ \text{P} \\ \diagdown \\ \text{OH} \end{array}$ will lose this stabilizing energy, but a partial compensation may be expected due to the conjugation of the phenyl group and the lone pair of the phosphorus atom, such as Jaffé²¹ has found in triphenylphosphine.

(20) M. I. Kabachnik, T. A. Mastryukova, and T. A. Melentiyeva, *Tetrahedron*, **17**, 239 (1962).

(21) H. H. Jaffé and L. D. Freedman, *J. Am. Chem. Soc.*, **74**, 1069 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MISSISSIPPI, UNIVERSITY, MISS.]

Solvent Effects on Charge-Transfer Complexes. I. The *s*-Trinitrobenzene-Naphthalene Complex in Carbon Tetrachloride, *n*-Heptane, *n*-Hexane, Cyclohexane, Chloroform, or Carbon Disulfide^{1a}

BY C. C. THOMPSON, JR., AND P. A. D. DE MAINE^{1b}

RECEIVED MAY 13, 1963

Formation constants and absorptivities for the 1:1 *s*-trinitrobenzene-naphthalene complex in six *inert solvents* (CCl₄, *n*-hexane, cyclohexane, *n*-heptane, CHCl₃, or CS₂) were calculated with spectrophotometric data collected at fifteen wave lengths between 3300 and 4000 Å. at 20 and 45°. All data were processed with an IBM 620-60 K computer using programs with the self-judgment principle, fail-safe procedure, error-analysis, and instructions for correcting concentrations for density-volume-temperature changes incorporated. Absorptivities (*a_c*) for the complex at the absorption maxima (near 3600 Å.) at 20° vary from 1294 (±22) for *n*-heptane to 1540 (±13) for *n*-hexane. As the temperature is increased from 20 to 45°, the absorptivities decrease by approximately 10% except in CHCl₃ systems where those between 3650 and 4000 Å. are unchanged. The formation constant (*K*) is independent of wave length at each temperature in all solvents except *n*-heptane where at 20° *K*, in moles/l. units, is 9.58 (±0.17) for wave lengths between 3300 and 3700 Å., and then gradually increases to 14.61 (±0.17) at 4000 Å. At 45°, *K* in *n*-heptane is 6.12 (±0.09) at wave lengths up to 3850 Å., then it increases to 8.27 (±0.09) at 4000 Å. Average values for *K* at 20° vary from 1.82 (±0.08) in CHCl₃ to 9.58 (±0.17) in *n*-heptane. However, the heat of complex formation appears to be independent of the inert solvent with a median value near -3.0 kcal. per mole except for cyclohexane where the value is -4.16 (±0.63) kcal. Recent developments in theories of complex formation are examined. Variations of *K* with wave length and of *a_c* with temperature are attributed to simultaneous higher order reactions.

Introduction

In the new computer method² preselected limits of experimental error are used in tests of data compatibility with a number of alternate equations or theories. The method yields precise information for each parameter, thereby completely removing ambiguities in reported results.

For the reaction, $A + B \xrightleftharpoons{K} C$, the Benesi-Hildebrand,^{3a} Ketelaar,^{3b} and Scott⁴ noniterative spectrophotometric methods can be used to calculate the equilibrium constant, *K*, and *a_C*, the absorptivity for C, only if [A] ≫ [B], *a_A* and *a_B* are known, and *a_A*, *a_B*, and *a_C* are independent of concentration. Recent computer work in our laboratories has shown that *a_A* and *a_B* are seldom completely independent of concentration and the use of constant values for *a_A* and *a_B*

(1) (a) Taken from the Ph.D. thesis of C. C. T., University of Mississippi, 1964. (b) Department of Chemistry, University of Illinois, Urbana, Ill.

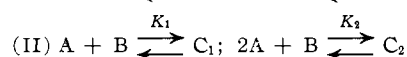
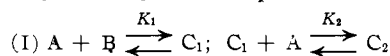
(2) P. A. D. de Maine and R. D. Seawright, "Digital Computer Programs for Physical Chemistry, Vol. I, The Macmillan Co., New York, N. Y., 1963.

(3) (a) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949); (b) J. A. A. Ketelaar, C. van de Stolpe, A. Goudsmit, and W. Dzubas, *Rec. trav. chim.*, **71**, 1104 (1952).

(4) R. L. Scott, *ibid.*, **75**, 787 (1956).

can result in erroneous conclusions. In the iterative method used in this work (see Data Processing Method) the restrictions on relative concentrations and the required concentration independence of *a_A* and *a_B* are removed.

For three systems researchers⁵⁻⁷ have reported that the values for *K* calculated for 1:1 complex formation vary with wave length. Such variations in *K* and non-linear Benesi-Hildebrand or Ketelaar plots have been attributed to the neglect of unsuspected higher order reactions. Recently⁸ there have been devised mathematically exact iterative methods for calculating *K*₁, *K*₂, *a_A*, *a_B*, *a_{C1}*, and *a_{C2}* for the equation sets



In these methods there are no restrictions on concentra-

(5) P. A. D. de Maine, M. M. de Maine, and C. Froese, *J. Mol. Spectry.*, **8**, 373 (1962).

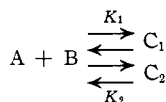
(6) P. A. D. de Maine and P. Carapellucci, *ibid.*, **7**, 83 (1961).

(7) H. J. G. Hayman, *J. Chem. Phys.*, **37**, 2290 (1962).

(8) P. A. D. de Maine, *J. Mississippi Acad. Sci.*, in press.

tions or absorptivities. Jurinski⁹ has solved these equation sets for K_1 , K_2 , a_{C_1} , and a_{C_2} with noniterative methods by imposing the restrictions: $[A] \gg [B]$, a_A and a_B are known, and a_A , a_B , and a_C are concentration independent. He has shown that both consecutive (equation set I) and simultaneous (equation set II) higher order reactions can explain variations in K with wave length and that the method used by Hayman⁷ is unsound because of the neglect of second and higher degree terms in the binomial expansions used.

For the two simultaneous isomeric charge-transfer reactions



with restrictions: $[A] \gg [B]$, a_A and a_B known, and a_A , a_B , a_{C_1} , and a_{C_2} concentration independent, the formation constant (K_Q) and absorptivity (a_Q) calculated with the assumption that only one complex is formed are related to K_1 , K_2 , a_{C_1} , and a_{C_2} thus¹⁰

$$K_Q = K_1 + K_2 \quad (1)$$

$$a_Q = (K_1 a_{C_1} + K_2 a_{C_2}) / K_Q \quad (2)$$

In systems of this type K_Q will be independent of wave length, and a_Q may increase, decrease, or remain constant as the temperature is increased. In contact charge-transfer theories,¹¹⁻¹³ reviewed by McGlynn,¹⁴ eq. 1 and 2 are modified

$$K_Q = K_1 + K_2 + K_3 + \dots \approx K_1 + K_2 \quad (3)$$

$$a_Q = (K_1 a_{C_1} + K_2 a_{C_2} + K_3 a_{C_3} + \dots) / K_Q \quad (4)$$

Here $K_3 \ll K_1$, K_3 being the formation constant for the collision (or contact charge-transfer) complex with absorptivity a_{C_3} . In eq. 3 and 4 K_1 and K_2 will decrease and K_3 will increase as the temperature is increased. Thus a_Q can increase, decrease, or remain constant.

In 1949, Benesi and Hildebrand^{3a} reported the formation constant, K , for the 1:1 benzene- I_2 complex as 1.15 in *n*-heptane and 1.72 in CCl_4 . Similar results were reported for the mesitylene-iodine complex.^{3a} More recently, Foster¹⁵ concluded that K 's for the 1:1 complexes between hexamethylbenzene and each of the three trinitrobenzenes or 1,2,3,5-tetranitrobenzene are vastly different in $CHCl_3$, CCl_4 , and cyclohexane. For the *s*-trinitrobenzene-hexamethylbenzene complex values for K were 0.76 (± 0.05), 5.7 (± 0.3), and 13.5 (± 0.4) in concentration (moles/liter) units for the three solvents. Ross and Labes¹⁶ data for the 1:1 complexes of *s*-trinitrobenzene with naphthalene or aniline in $CHCl_3$ -ethanol and *p*-dioxane-water are not to be compared because they failed to consider significant specific interactions with the strong donor solvents (ethanol, dioxane, and water). Similar studies reported by Kosower¹⁷ and Brownstein¹⁸ suffer from the same fault. Isenberg and Baird¹⁹ have investigated solvent effects for the chloranil-aromatic amine complexes and have concluded that there occurs the reaction: donor + acceptor (chloranil) \rightleftharpoons DA \rightleftharpoons D⁺ + A⁻, with stabilization by ion-solvent interactions. Browning²⁰ has studied the effect of solvent on the in-

tensity of charge-transfer bands. de Maine²¹ concluded from a survey of the literature that formation constants for iodine complexes with ethanol, ethyl acetate, or *p*-dioxane and the ethanol-sulfur dioxide complex are unaffected by changing the solvent. On the other hand, formation constants for the diethyl ether-iodine and naphthalene-iodine complexes²² are very sensitive to the *inert* solvent used. However, the heat of formation of the naphthalene-iodine complex appears to be unchanged in the five inert solvents studied.²² The heat of formation of the I_2 - I_2 complex varies with the inert solvent²³ in accord with classical ideas.

Mulliken²⁴ has emphasized the importance of dipole-dipole, van der Waals, and other nonspecific interactions between solute and solvent molecules in his charge-transfer theory. His views clearly imply that the formation constant and heat of formation of the complex must both depend on the solvent used. Moreover for systems studied over wide variations of solution composition, Benesi-Hildebrand, Ketelaar, or Scott plots must be nonlinear since K is dependent on average solution properties, and the spectrophotometric analysis will yield inconsistent results (*i.e.*, K depends on wave length, etc.). While isolated studies^{22,23} have disproved each of these views, no definite attempt has been made to study quantitatively the effect of environment on all parameters which describe a charge-transfer complex.

Coulson²⁵ has discussed the effect of medium on molecular energy levels and concludes that a nonspecific explanation for the frequency shift in vibrational spectra is inadequate. This implies that all solvent-shift theories which assign a major role to nonspecific solute-solvent interactions are inadequate.

In the Dewar-Lepley²⁶ molecular orbital theory of charge transfer in π -complexes the back coordination can nearly equal the charge transfer. Thus the authors conclude that complex formation can occur without any net transfer of charge. This means that even for strong complexes the solvation energy may be small.

In this series of papers, computer-processed data for various charge-transfer complexes dissolved in several different inert solvents will be discussed. The *s*-trinitrobenzene-naphthalene complex is considered in this paper.

Experimental

Reagent grade CS_2 , supplied by Baker and Adamson, and Fisher certified spectroanalyzed CCl_4 , *n*-heptane, *n*-hexane, and cyclohexane were purged with oxygen-free dry nitrogen (dew point less than -40°) immediately before use. Fisher spectrograde chloroform was purified by a sulfuric acid-potassium hydroxide method,²⁷ then was distilled from fresh anhydrous calcium chloride and purged with dry oxygen-free nitrogen immediately before use. Eastman Kodak *s*-trinitrobenzene and naphthalene were recrystallized from Fisher spectrograde methanol. Melting points of the purified materials were 121-122 $^\circ$ and 80-80.5 $^\circ$, respectively. In separate experiments it was shown that further purification of the solid materials was unnecessary.

Solutions containing one (*s*-trinitrobenzene or naphthalene) or two solutes dissolved in each of the six *inert* solvents were prepared using the techniques described elsewhere.²⁸ Experimental details of the systems studied are given in Table I. For each mixed solute system, six solutions of the set of eighteen were prepared from separate portions of freshly prepared materials.

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(25) C. A. Coulson, *Proc. Roy. Soc. (London)*, **A255**, 69 (1960).

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 (14) S. P. McGlynn, *Chem. Rev.*, **58**, 1113 (1958).
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 (17) E. M. Kosower, *ibid.*, **80**, 3253 (1958).
 (18) S. Brownstein, *Can. J. Chem.*, **38**, 1590 (1960).
 (19) I. Isenberg and S. L. Baird, Jr., *J. Am. Chem. Soc.*, **84**, 3803 (1962).

TABLE I

CONCENTRATIONS (IN MOLES/LITER) FOR THE SYSTEMS STUDIED AT 20 AND 45°

G is the number of solutions in the indicated concentration range for which spectral measurements were made at 50 Å. intervals in the indicated spectral region at both temperatures; TNB = *s*-trinitrobenzene.

Solvent	Concn. for separate systems			G	Concn. for mixed systems			G
	Naphthalene	TNB × 10 ⁴			Naphthalene	TNB × 10 ⁴		
CCl ₄	0.011–0.32	3.8–19.0		9	0.012–0.15	5.6		18
<i>n</i> -Heptane	.041–.21	1.6–8.2		9	.011–.13	4.9		18
<i>n</i> -Hexane	.020–.10	1.7–8.6		9	.010–.13	4.8		18
<i>c</i> -Hexane	.016–.075	1.7–8.7		9	.011–.13	5.1		18
CS ₂	.010–.10	3.2–15.8		9	.010–.12	4.9		18
CHCl ₃	.04–.18	4.4–21.9		9	.019–.22	5.9		18
Region of spectra, Å.	3000–4000	2650–4000			3300–4000			

The absorption spectra of all solutions were measured at 20 and 45° with one of two line-operated Beckman DU spectrophotometers and four matched 1-cm. glass-stoppered quartz cells with the pure solvent as reference. Measurements were reproducible to better than 0.003 absorbance unit. Except with chloroform below 3500 Å., where the absorbance slowly increases with time, no measurable changes in absorption spectra were observed even after 24 hr.

The two spectrophotometers, equipped with phototubes and temperature control accessories, and the quartz cells were calibrated as recommended by the National Bureau of Standards²⁹ with standard KOH–K₂CrO₄ solutions. Calibration data for both instruments are given in Table II. Between 3000 and 4000 Å. the standard K₂CrO₄–KOH solutions have a sharp absorption band which cannot be measured accurately because for very small changes in the wave length scale the absorbance can change by as much as 0.005 unit. Outside this region ΔD (Table II) for both instruments is near the experimental error (0.003 unit). Thus the measured absorbances were not corrected. After careful consideration of the reproducibility and ΔD at each wave length for many solutions, an experimental error of less than 1% for each individual absorbance measurement used in calculations for this paper is claimed.

TABLE II

CALIBRATION DATA FOR THE TWO LINE-OPERATED BECKMAN DU SPECTROPHOTOMETERS AND THE FOUR MATCHED 1-CM. QUARTZ CELLS

ΔD is the mean deviation in absorbance between N.B.S. and measured values, while M.D. is the maximum deviation in ΔD . Both ΔD and M.D. are in absorbance units.

Spectral region, Å.	ΔD	M.D.	Spectral region, Å.	ΔD	M.D.
2350–2500	–0.003	±0.002	2350–2500	–0.002	±0.001
2500–3000	–.004	±.002	2500–3000	–.003	±.002
3000–3500	–.007	±.004	3000–3500	–.003	±.001
3500–4000	–.009	±.005	3500–4000	+ .003	±.002
4000–5000	–.005	±.003	4000–5000	–.004	±.003

First Beckman DU (serial number 173949) Second Beckman DU (serial number 22636)

Data Processing Method.—All data discussed in this paper were processed by the new computer method. The following computations were made: (a) Concentrations of *s*-trinitrobenzene and naphthalene at 20 and 45° in the single and mixed solutions were calculated from quantities measured at room temperature (r.t.) and the densities of the inert solvents at r.t., 20, and 45°. In correcting for volume–temperature changes, additivity of all components at each temperature was assumed.

(b) Spectral data for the single solute systems, taken at a fixed wave length and temperature, were fitted to the equation $a_A = a_0A + a_1[A]$ where a_A is the molar absorptivity of the species A, a_0A and a_1 are constants for each wave length and temperature, and $[A]$ is the molar concentration of A.

(c) The equations

$$C_C = (KC_A + KC_B + 1 - \sqrt{K^2(C_A - C_B)^2 + 2KC_A + 2KC_B + 1})/2K \quad (5)$$

$$A_C = a_C C_C = A_0 - a_A(C_A - C_C) - a_B(C_B - C_C) \quad (6)$$

$$C_A C_B / A_C = 1/Ka_C + (C_A + C_B - C_C)/a_C \quad (7)$$

(29) U. S. Department of Commerce, National Bureau of Standards, Letter Circular LC-1017, Jan., 1955.

(30) "International Critical Tables," Vol. 3, McGraw-Hill Book Co., Inc., New York, N. Y., 1926.

which describe the reversible 1:1 reaction: $A + B \xrightleftharpoons{K} C$, were solved by an iterative method for the formation constant (K) and the complex absorptivity (a_C) with spectral data taken at a fixed wave length and temperature. In deriving eq. 5, 6, and 7 it is assumed only that the concentrations of A, B, and C at equilibrium, $(C_A - C_C)$, $(C_B - C_C)$, and C_C , may be used in calculating K . The molar absorptivities of *s*-trinitrobenzene (a_A) and naphthalene (a_B) were calculated in step (b).

In the computer method the error zones² for eq. 7 are computed from the preselected limits of experimental error. Data points lying outside the error zone are discarded, and the maximum permitted errors for each value of the two parameters (K and a_C) are calculated. Thus the preselected limits of error, exactly defined by the instrument reliability factors, determine both the number of data points retained in the analysis and the maximum permitted errors in the parameters. The maximum permitted error is the maximum possible error in the value given for the designated parameter.

An adequate knowledge of the computer method is necessary only if the results are to be objectively challenged. If the values for the parameters and their associated maximum permitted errors are accepted, the remainder of this section can be quite safely omitted.

All data were processed on an IBM-1620 computer with 60K storage and card input–output by the new method.^{2,31} Programs used were 5 (call word EAAAA), 31 (EBAAA), 301 (AAAAS), 309 (IAAAS), and 310 (JAAAS). The programs contain the self-judgment principle³² and the reject-restore, automatic transposition, and normalization mechanisms. Programs 31, 309, and 310 have the fail-safe procedure. The input commands which activate the semiautomatic reject-restore mechanism in programs 31, 301, 309, and 310 were selected after processing input information for these programs by the autoplotted system.³¹ Autoplotted programs 501 (call word AEEEE), 502 (BEEEE), and 503 (CEEEE) were used.

The concentrations in moles/liter of *s*-trinitrobenzene and/or naphthalene in the single solute and mixed solute solutions were computed at each temperature (20 and 45°) with program 5 (call word EAAAA), with the assumption that the components are additive at each temperature. In this program concentrations are automatically corrected for temperature–density–volume changes. Input (II) and output (JJ) commands selected were: single solute systems: II = 3; JJ = 3; mixed solute systems: II = 11; JJ = 13

Program 309 (call word IAAAS) was used to show that the spectral data for the trinitrobenzene–solvent system are compatible with the following equation at each wave length and temperature

$$a_A = a_0A + a_1[A] \quad (8)$$

a_A is the molar absorptivity of TNB with molar concentration, $[A]$; a_0A and a_1 are constants. The instrument reliability factors used were: RLM1 = 0.003, WL1 = 0.020, WU1 = 1.200, DEVF1 = DEVF2 = 0.01. As program 309 is a special one-dimensional self-judgment program the values entered for RLM2, WL2, and WU2 are not significant. Input commands selected were K = 1, L = 1, M = 0, and J = 3. Although the absorptivities for naphthalene solutions are small in the 3300 to 4000 Å. region, the values are compatible with eq. 8.

The spectral data for the mixed solute systems at each wave length for each temperature were tested for compatibility with

the 1:1 reaction model, *s*-trinitrobenzene + naphthalene \xrightleftharpoons{K} complex, with program 310 (call word JAAAS) and molar absorptivities calculated with program 309 (call word IAAAS). Instrument reliability factors used in this special one-dimensional self-judgment program² were: RLM1 = 0.003, WAC1 = 0.500, WL1 = 0.060, WU1 = 1.200, DEVF1 = DEVF2 = 0.01 (except for CS₂ solution, where DEVF1 = DEVF2 = 0.02). Input commands selected for program 310 were: K = 1, L = 60, M = 1, J = 3.

The mean formation constant and the associated mean maximum permitted error were calculated with program 301 for each system at each temperature, from values obtained at each wave length with program 310. Next the mean molar absorptivities and the associated mean maximum permitted errors for the complex were calculated with programs 31 (call word EBAAA) and 301 (call word AAAAS). These calculations were made with the input information for program 310 and the centering procedure described elsewhere.³¹

Input information for program 310 for the *s*-trinitrobenzene–naphthalene–*n*-heptane system was also tested for compatibility

(31) P. A. D. de Maine and R. D. Seawright, "Digital Computer Programs for Physical Chemistry," Vol. II, The Macmillan Co., New York, N. Y., 1964.

(32) P. A. D. de Maine and R. D. Seawright, *Ind. Eng. Chem.*, **55**, No. 4, 29 (1963).

with Jurinski's⁹ equations, using programs 36 (call word IBAAA) and 303 (CAAAS).³¹

Results

The new data for naphthalene-inert solvent solutions are in agreement with earlier work.²² Detailed computer analyses of data for the *s*-trinitrobenzene-inert solvent solutions are discussed elsewhere.³³ Typical absorbance curves between 3200 and 4000 Å. for naphthalene and *s*-trinitrobenzene dissolved separately and together in inert solvents are shown in Fig. 1.

The spectral data were compatible with the 1:1 equilibrium reaction $s\text{-TNB} + \text{naphthalene} \xrightleftharpoons{K} \text{C}$ at all wave lengths and for each temperature studied. Usually only one or two random data points were discarded. For only sixteen of the 165 sets of data processed were as many as three or four random points rejected out of a maximum eighteen data points. With *n*-heptane as solvent at 20° the formation constant (K in moles/liter units) is independent of wave length between 3300 and 3700 (9.58 ± 0.17) then increases gradually to 14.61 (± 0.17) at 4000 Å. At 45°, the wave length-invariant K extends to 3850 Å. (6.12 ± 0.09) and then gradually increases to 8.27 (± 0.09) at 4000 Å. With all other inert solvents K is wave length-invariant at each temperature. Time effects in chloroform below 3550 Å. and the high absorbance by carbon disulfide below 3800 Å. have prevented extension of the spectral study to 3300 Å. in these solvents. Mean formation constants and the associated mean maximum permitted errors calculated from K for the wave length-invariant spectral region are given in Table III. Also given are heats of complex formation (ΔH) and the associated maximum permitted error, calculated from the formation constants at 20 and 45° with van't Hoff's equation.

TABLE III

MEAN FORMATION CONSTANTS (K , IN MOLES/LITER), THE MEAN MAXIMUM (PERMITTED) ERROR (DEV K), THE HEAT OF FORMATION (ΔH , KCAL./MOLE), AND ITS MAXIMUM (PERMITTED) ERROR (DEV ΔH) FOR THE 1:1 NAPHTHALENE-*s*-TRINITROBENZENE COMPLEX IN THE SOLVENT INDICATED

G_1 is the number of formation constants averaged to get K , and G is the number of wave lengths for which data were considered; D.E. is the dielectric constant of the pure solvent at 20° ("Handbook of Chemistry," 9th Ed., Handbook Publishers, Inc., Sandusky, O., 1956).

Solvent	Temp., °C.	K	DEV K	G_1/G	ΔH	DEV ΔH	D.E.
CCl ₄	20	5.16	0.07	11/14	-3.02	0.44	2.238
	45	3.43	.15	13/14			
<i>n</i> -Hexane	20	7.82	.13	10/13	-2.69	.47	1.890
	45	5.44	.25	10/13			
<i>c</i> -Hexane	20	9.15	.17	11/13	-4.16	.63	2.023
	45	5.22	.34	10/13			
<i>n</i> -Heptane	20	9.58	.17	8/9	-3.31	.25	1.924
	45	6.12	.09	11/12			
CHCl ₃	20	1.82	.08	8/10	-2.38	.90	4.806
	45	1.32	.10	7/10			
CS ₂	20	3.25	.27	4/6	-2.12	1.26	2.641
	45	2.44	.21	3/5			

Mean molar absorptivities and the associated mean maximum permitted errors for the *s*-trinitrobenzene-naphthalene complex, calculated from data as described in the preceding section, are given in Table IV.

Discussion

The new data for *s*-trinitrobenzene plus naphthalene dissolved in carbon tetrachloride, *n*-hexane, cyclohexane, or carbon disulfide are entirely consistent with the

(33) C. C. Thompson, Jr., Ph.D. Dissertation, University of Mississippi, 1964.

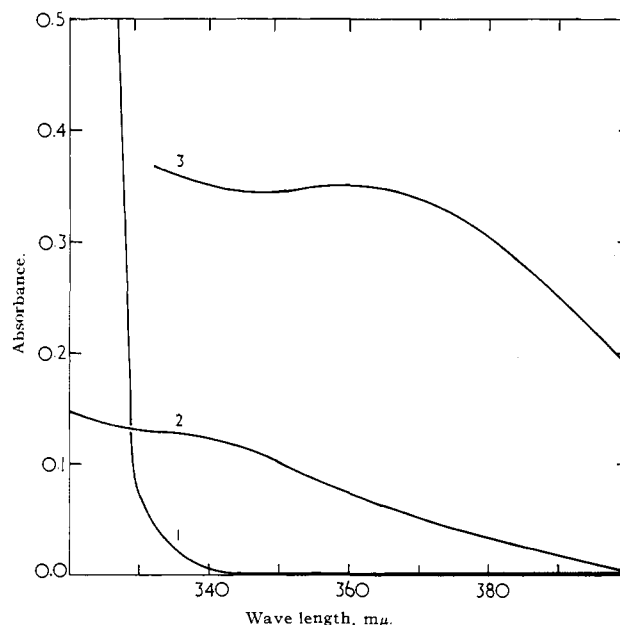
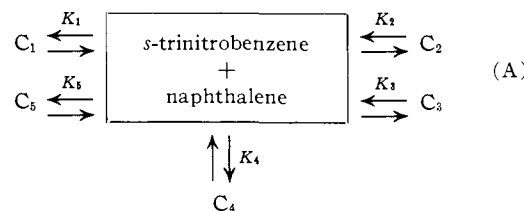


Fig. 1.—Absorbance curves for solutions of (1) naphthalene (2) *s*-trinitrobenzene, and (3) naphthalene-*s*-trinitrobenzene in CCl₄ at 20°. Naphthalene concentration (in 1 and 3) is 0.11 M and *s*-trinitrobenzene concentration (in 2 and 3) is $5.7 \times 10^{-4} M$.

following model of N simultaneous isomeric 1:1 reversible reactions.



[The restrictions imposed in deriving equations similar in form to eq. 3 and 4 (see Introduction) are: (a) the molar absorptivities of all complexes are independent of the solution composition; (b) activity coefficients for all species are unity; (c) C_1 and C_2 are the LN and TN charge-transfer complexes,¹⁰ and C_3 , C_4 , and C_5 are contact charge-transfer complexes.] Thus the wave length invariance of the formation constant (K) (Table III), calculated with the assumption that only one 1:1 reaction occurs, is predicted by eq. 3, while the decrease in the calculated molar absorptivities (a_C) at the elevated temperatures (Table IV) is predicted³⁴ by eq. 4.

With *n*-heptane as solvent the wave length invariance of K between 3300 and 3700 Å. (Table III) and the decrease in a_C at the higher temperature at all wave lengths studied (Table IV) are consistent with the above model (A). However, the gradual increase in K at the longer wave lengths is not predicted by eq. 4. The observed increase cannot be attributed to neglect of unsuspected interactions between solvent and naphthalene or *s*-trinitrobenzene or complex (C_1 , C_2 , C_3 , . . .) molecules, or between the naphthalene or *s*-trinitrobenzene molecules themselves. Moreover, if there exist M_N and M_T isomeric forms of naphthalene or *s*-trinitrobenzene in solution, with $M_N \times M_T$ simultaneous sets of reactions of type A, the mathematical form of eq. 3 and 4 is retained. Thus the increase in K at longer wave lengths (>3700 Å. at 20°, >3850 Å. at 45°) cannot be attributed to neglect of unsuspected isomeric forms of either component.

(34) V. Ramakrishnan and P. A. D. de Maine, *J. Mol. Spectry.*, submitted.

TABLE IV

CONSTANTS FOR THE NAPHTHALENE-*s*-TRINITROBENZENE COMPLEX IN THE INDICATED SOLVENT AT EACH TEMPERATURE AND WAVE LENGTH

There are listed vertically the mean molar absorptivity, the associated mean maximum (permitted) error, and the ratio, G_1/G_2 ; G_1 is the number of data values from which the mean molar absorptivity was calculated, and G_2 is the number of measured data values. Also given are the absorption maximum (λ_{max}), the mean formation constant (K), and its mean maximum (permitted) error (DEVK).

Wave length, Å.	CCl ₄		<i>n</i> -Hexane		<i>c</i> -Hexane		<i>n</i> -Heptane		CHCl ₃		CS ₂	
	20°	45°	20°	45°	20°	45°	20°	45°	20°	45°	20°	45°
3300	1312	1176	1253	1225	1150	1069				
			16	13	10	16	22	14				
			16/18	14/18	16/18	14/18	17/18	14/18	Measured		Absorbance	
3350	1166	1100	1313	1187	1228	1213	1126	1075	absorbance		of solvent	
	17	18	11	18	10	13	17	16	increases		is too high	
	15/18	13/18	16/18	15/18	17/18	15/18	17/18	15/18	with time			
3400	1149	1087	1359	1221	1248	1238	1149	1103				
	11	21	12	20	9	17	15	13				
	16/18	14/18	16/18	15/18	17/18	15/18	17/18	15/18				
3450	1159	1100	1421	1279	1302	1295	1200	1151				
	20	22	15	20	9	16	14	18				
	16/18	14/18	17/18	15/18	17/18	15/18	17/18	16/18				
3500	1182	1126	1497	1333	1374	1347	1259	1196				
	12	20	14	24	11	18	15	15				
	16/18	14/18	17/18	16/18	16/18	16/18	17/18	16/18				
3550	1242	1156	1553	1339	1421	1382	1291	1211	1339	1506		
	16	20	12	20	9	17	18	17	24	11		
	17/18	15/18	17/18	16/18	16/18	16/18	17/18	16/18	8/14	7/14		
3600	1270	1177	1540	1335	1454	1396	1294	1195	1247	1356		
	13	21	13	18	18	14	22	16	51	12		
	17/18	15/18	17/18	16/18	18/18	17/18	18/18	17/18	8/14	7/14		
3650	1310	1205	1539	1329	1448	1391	1293	1184	1225	1263		
	14	28	14	19	19	13	19	20	24	13		
	17/18	16/18	17/18	17/18	18/18	17/18	17/18	17/18	9/14	9/14		
3700	1301	1185	1466	1262	1405	1338	1248	1138	1200	1208		
	15	17	19	19	12	17	28	13	20	14		
	17/18	16/18	18/18	17/18	18/18	17/18	18/18	17/18	9/14	9/14		
3750	1285	1141	1369	1153	1312	1257	1163	1047	1167	1217		
	29	24	22	16	12	20	24	13	26	29		
	18/18	17/18	18/18	17/18	18/18	17/18	18/18	17/18	10/14	10/14		
3800	1224	1065	1212	1027	1189	1110	1044	909	1144	1156	968	751
	27	27	16	14	12	16	29	17	18	12	15	34
	18/18	17/18	18/18	17/18	18/18	17/18	18/18	17/17	10/13	11/14	16/17	7/10
3850	1088	978	916	817	1082	1116	1044	874
	16	24					24	12	21	11	16	19
	18/18	17/17					18/18	17/17	10/12	11/14	16/16	9/9
3900	1030	889	943	771	932	892	788	699	1009	1018	991	893
	12	23	21	12	17	17	13	12	20	23	22	17
	17/17	16/16	17/17	16/16	18/18	16/16	17/17	16/16	10/12	12/13	16/16	8/8
3950	912	793	643	550	921	915	935	816
	13	17					12	11	10	14	18	22
	17/17	16/16					17/17	15/15	9/11	12/12	15/15	8/8
4000	794	670	548	430	598	531	470	413	832	836	844	804
	16	17	15	13	9	12	9	7	9	10	25	22
	17/17	15/15	16/16	12/12	17/17	14/14	16/16	13/13	8/10	11/11	14/14	6/6
λ_{max} , Å.	3650		3550-3650		3600-3650		3550-3650	
K	5.16	3.43	7.82	5.44	9.15	5.22	9.58	6.12	1.82	1.32	3.25	2.44
DEVK	0.07	0.15	0.13	0.25	0.17	0.34	0.17	0.09	0.08	0.10	0.27	0.21

Attempts to calculate K_1 and K_2 for the simultaneous 1:1 and 2:1 naphthalene-*s*-trinitrobenzene complexes in equation sets I and II (see Introduction) with data for *n*-heptane solutions at 20° by Jurinski's method⁹ were unsuccessful. We have shown that spectrophotometric equations are extremely sensitive to small errors in the molar absorptivities of the molecular components and that the molar absorptivities of *s*-trinitrobenzene in *n*-heptane are not exactly concentration independent.³³ Thus it is probable that the failure to calculate consistent values for K_1 and K_2 is due to our assumption in using Jurinski's method that both the naphthalene and *s*-trinitrobenzene obey Beer's law. When development of a more sophisticated computer

program is completed, another attempt will be made to calculate K_1 and K_2 .

The temperature invariance of a_C between 3650 and 4000 Å. in chloroform must mean that $C_3 = C_4 = C_5 = 0$, and either $K_1 = K_2$ or $a_{C_1} = a_{C_2}$ or either K_1 or K_2 is zero. Evidence of complex formation with chloroform^{35,36} suggests that either the LN or TN donor orbital in naphthalene is blocked by complex formation with the excess chloroform solvent. If this were the case, the low value for K (Table III) could be understood. The time effect observed at wave lengths below

(35) K. B. Whetsel and R. E. Kagarise, *Spectrochim. Acta*, **18**, 329 (1962).

(36) L. W. Reeves and W. G. Schneider, *Can. J. Chem.*, **35**, 251 (1957).

3550 Å. (Table IV) is reminiscent of earlier work with iodine-nitromethane³⁷ and suggests that the naphthalene-chloroform complex is thermodynamically unstable and reacts to form products which would complex with *s*-trinitrobenzene. The new complex(es) would absorb radiation shorter than 3550 Å. Time effects are not observed with naphthalene-chloroform or *s*-trinitrobenzene-chloroform solutions.

Plots of the molar absorptivity (a_c) (Table IV) vs. wave length for each solvent at each temperature (not shown) displayed the typical broad bands with poorly defined maxima associated with isomeric charge-transfer systems.¹⁰ While the changes in band shape are small, there is no doubt that these molar absorptivity curves for the 1:1 *s*-trinitrobenzene-naphthalene complex are slightly different for each solvent and that they broaden at the higher temperature. On the other hand, the formation constant is markedly sensitive to the inert solvent used (Table III). The large maximum permitted Errors in calculated values of ΔH ($DEV\Delta H$) (Table III), obtained with spectral data accurate to 1%, emphasize the importance of an error analysis based on experimental limits of error. The size of $DEV\Delta H$ prevents analytical arguments based on ΔH . However, the marked variation in K -values is not reflected in the heats of formation (ΔH). The variations of K and a_c cannot be attributed to the dielectric constant (Table III), refractive index, or another electrical property of the solvent. Moreover the consistent results obtained in our analyses definitely eliminate any

(37) P. A. D. de Maine and W. C. Ahlers, *J. Chem. Soc.*, 211 (1960).

explanation which attributes the variations in K with solvent to the neglect of undefined nonspecific interactions in the solutions. Thus the new work does not support Mulliken's views of the role played by the solvent in charge transfer.²⁴ The Dewar-Lepley²⁶ theory of charge transfer in π -complexes is not contradicted by the new data.

While the size of terms like K_3a_c , in eq. 4 will not alter the preceding discussion, contact charge-transfer contributions (K_3a_c , K_4a_c , . . .) in the reaction scheme A are predicted to be negligible.^{11-14,38}

The variation in K and a_c in the first four solvents (Tables III and IV) and in CS_2 can be explained qualitatively if it is supposed that in *n*-hexane, *n*-heptane, and cyclohexane either the TN or LN complex is favored to a varying degree by the definitive geometry of the solvent. The lower values for K in CCl_4 could be attributed to the absence of structure in the solvent. Equations which support this view are given elsewhere.^{21,39} The low value for K in $CHCl_3$ has already been attributed to complex formation between naphthalene and the solvent.

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(38) S. F. Mason, *Quart. Rev. (London)*, **15**, 287 (1961).

(39) P. A. D. de Maine, *J. Mississippi Acad. Sci.*, in press.

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Equilibria in Solutions of Cyanuric Acid and its Chlorinated Derivatives¹

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In addition to OH^- , H^+ , ClO^- , and $HClO$, ten organic species are possible in aqueous solutions of cyanuric acid and its salts in the presence of $Cl(+1)$. These are found to be in labile equilibrium, so 11 independent equilibrium constants are necessary to describe the solution at a given arbitrary pH and over-all concentration of Cy (denoting the moiety $C_3N_3O_3$) and $Cl(+1)$. Four of these constants are reasonably well established (although only in the case of the dissociation of water is there complete agreement) and a fifth (the third dissociation constant for H_3Cy) has been estimated. The present paper describes titrimetric and spectrometric measurements that allow estimation of five of the six remaining equilibrium constants, and thus a description of the species present in compositions ranging from HCl_2Cy to Cy^{-3} . The concentration of Cl_3Cy in solution in the pH and concentration range studied is so small that only a crude lower limit can be set on the sixth constant, involving $Cl_3Cy + H_2O = HCl_2Cy + HClO$.

Introduction

Cyanuric acid is a tribasic acid in which the hydrogens may successively be replaced by positive (+1) chlorine. Trichlorocyanuric (or isocyanuric) acid and the salts of mono- and dichloro derivatives are articles of commerce. In aqueous solutions there is labile equilibrium among the various chlorinated derivatives. To avoid the problem, not germane to the present paper, of whether to write the various species as derivatives of *s*-triazine triol or the corresponding keto form (which may depend upon the pH²), the $C_3N_3O_3$ moiety will be denoted by Cy; *i.e.*, H_2Cy denotes the unchlorinated acid, Cl_2Cy^- the anion of the dichloro derivative, etc. In aqueous solutions containing hypochlorite, in addition to the inorganic species $HClO$, ClO^- , H^+ , and OH^- , ten organic species could conceivably be present. These are shown schematically in Fig. 1, which also serves to define most of the equilibrium constants.

For clarity the equations are not balanced, and thus do not show formation of $HClO$ or ClO^- , or changes in acidity. For setting up the K 's, the reactions are considered to proceed downward and to the right; the hydrolysis of positive chlorine is considered to be through H_2O with the production of $HClO$ in the first row to the left and through OH^- with the production of ClO^- in the remaining two.

The fourteen species that could be present require eleven independent constants to describe the system completely at a given pH and over-all concentration of positive chlorine and of cyanuric acid. Four of these, involving the dissociation constant of water, hypochlorous acid, and the first and second dissociation constants of cyanuric acid, are in the literature (although there is some disagreement concerning all except that of water) plus a crude estimate of a fifth (K_{12}) but, so far as the authors are aware, not even an estimate of any of the remaining six has appeared.

The present paper reports some titration and spectrometric studies which allow estimation of five more

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(2) Manuscript in preparation.