ample, that, in chloroform, picric acid complexes with m-dinitrobenzene 100 times as much as it complexes with benzene. They found, further, that although color appeared in solutions of picric acid with benzene, the solutions of picric acid with nitro compounds gave little color, although the equilibrium constants found were comparatively large. These results are contrary to expectations if complexing is due solely to Mulliken's charge-transfer intermolecular bonding. The partition method, like our rate constant method, is not a discriminating method for determining the equilibrium constant. It measures all these interactions which affect the solubilities of the two components in the two solvents. We have repeated the Moore, Shepherd and Goodall measurements of the equilibrium constants for the naphthalene–picric acid complex and the m-dinitrobenzene–picric acid complex in chloroform using the spectroscopic method rather than the partition method.[17] In the former case we get a value for K which is only 50% of that reported by Moore, Shepherd and Goodall. In the latter case, we find no evidence of complexing by the spectroscopic method. The naphthalene–picric acid case is thus comparable to the picryl chloride–hexamethylbenzene case. The partition measurements indicate an interaction between m-dinitrobenzene and picric acid, but our spectroscopic measurements indicate that this interaction is not of the charge-transfer type.

Dewar[18] has made his major objection to the

(17) These results will be reported in detail in paper II of this series.

(18) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 184.

Weiss[4] theory on the ground that it cannot account for complexing between picric acid and the nitrobenzenes and has explained complex formation as due to dispersion forces. If the picric acid–nitrobenzene complex were of the same type as the donor-acceptor complexes discussed by Weiss and Mulliken, Dewar's objection would apply with equal force to Mulliken's revision and extension of the Weiss theory. However, our results indicate that interactions of more than one kind are involved. When the equilibrium constant is measured by the reaction rate method, the constant obtained reflects all of the interactions which can affect the reaction rates. Clearly there are interactions in addition to charge-transfer complexing, since in the case which we have studied, the equilibrium constant obtained by this method is more than ten times larger than the value obtained by the spectroscopic method. Similarly, when the partition method is used, the equilibrium constant reflects all the interactions which affect the solubilities of the two components in the two phases, and these may include interactions other than charge-transfer complexing. The point to be stressed is that only the spectroscopic method uniquely measures the complexing of the charge-transfer type. As a result, only those equilibrium constants determined by the spectroscopic method are self-consistent and adequately encompassed by the Mulliken theory.

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NORTH ADAMS, MASS.

Molecular Compounds. II. Picric Acid–Naphthalene, Picric Acid–m-Dinitrobenzene and Picric Acid–1,3,5-Trinitrobenzene in Chloroform

By SIDNEY D. ROSS AND IRVING KUNTZ

Spectroscopic measurements of chloroform solutions of m-dinitrobenzene and picric acid and 1,3,5-trinitrobenzene and picric acid offer no evidence for complex formation. The equilibrium constant for complex formation between naphthalene and picric acid in chloroform has been measured at 19.5, 25.0 and 35.0° by the spectroscopic method. These results are compared with previous measurements made by a partition method, and the large differences in the results obtained by the two methods are discussed.

In the first paper of this series,[1] we reported measurements of the equilibrium constant for complex formation between picryl chloride and hexamethylbenzene in chloroform by a spectroscopic method and by a method based on determinations of reaction rates. The latter method gave a value for K more than ten times larger than the spectroscopic value, which was taken as a measure of complexing of the charge-transfer type.[2] The larger value was considered to measure, in addition to this type of complexing, the sum of all those interactions which can, in any manner, affect the rate of the reaction between picryl chloride and triethylamine.

(1) S. D. Ross, M. Bassin, M. Finkelstein and W. A. Leach, THIS JOURNAL, 76, 69 (1954).

(2) R. S. Mulliken, ibid., 72, 600 (1950); 74, 811 (1952); J. Phys. Chem., 56, 801 (1952).

Although our results clearly indicated the presence of these additional interactions in solution, they did not permit an exact specification of their nature. It is our present purpose to report spectroscopic studies of complexing between naphthalene and picric acid, between m-dinitrobenzene and picric acid and between 1,3,5-trinitrobenzene and picric acid, all in chloroform. It is our contention that these results offer a possible insight into the nature of the interactions, in addition to charge-transfer complexing, which we observed in the picryl chloride–hexamethylbenzene case.

Moore, Shepherd and Goodall[3] have studied complexing between picric acid and aromatic hydrocar-

(3) T. S. Moore, F. Shepherd and E. Goodall, J. Chem. Soc., 1447 (1931).

bons and nitrated aromatic hydrocarbons in chloroform at 18° by a partition method. As might be expected they observed extensive complexing with naphthalene ($K = 2.17$ l. moles^{-1}) but, surprisingly, they also found extensive complexing between picric acid and m-dinitrobenzene ($K = 1.03$ l. moles^{-1}). This latter result is contrary to expectations if this complexing is due to the type of molecular interaction considered by Mulliken,[2] Weiss,[4] Woodward[5] or Brackmann,[6] since both picric acid and m-dinitrobenzene are strong electron acceptors, and the two together offer little possibility for a strong donor–acceptor interaction.

Results

The absorption spectra of four chloroform solutions containing picric acid and m-dinitrobenzene were examined from 320 to 460 mμ at 25°. The picric acid concentrations varied from 9×10^{-2} to 3×10^{-4} M and the m-dinitrobenzene concentrations ranged from 1×10^{-2} to 3×10^{-4} M. In all cases the observed optical density was, within experimental error, equivalent to the sum of the absorptions of the individual components. Table I presents some typical results of these experiments.

TABLE I

ABSORPTION OF SOLUTIONS OF PICRIC ACID AND m-DINITROBENZENE IN CHLOROFORM AT 25°

Picric acid, mole/l.	m-Dinitrobenzene, mole/l.	Wave length, mμ	Optical density	$(P)\epsilon_P l +$ $(D)\epsilon_D l$
0.08307	0.01077	410	1.45	1.45
		424	0.329	0.331
		430	.184	.185
		444	.057	.058
		454	.029	.033
.008307	.001077	390	1.34	1.33
		410	0.171	0.166
.08725	.02692	434	.142	.143
		454	.036	.035
		460	.027	.026
.0003160	.0002874	320	1.16	1.18
		330	1.42	1.44
		340	1.45	1.47
		350	1.17	1.18
		364	0.568	0.565
		384	.114	.112

Similar results were obtained with picric acid and 1,3,5-trinitrobenzene. In this case the picric acid concentrations varied from 10^{-1} to 10^{-4} M, and the trinitrobenzene concentrations ranged from 9×10^{-3} to 10^{-4} M. These results are given in Table II.

In the case of picric acid and naphthalene in chloroform the absorption in the range 450–500 mμ for the mixtures was clearly greater than the sum of the absorptions of the two individual components. The equilibrium constant for formation of the complex and extinction coefficient of the complex, ϵ_c, were determined at 19.5, 25 and 35° by methods previously described.[1] These results are summarized in Table III.

(4) J. Weiss, *J. Chem. Soc.*, 245 (1942).

(5) R. B. Woodward, THIS JOURNAL, **64**, 3058 (1942).

(6) W. Brackmann, *Rev. trav. chim.*, **68**, 147 (1949).

TABLE II

ABSORPTION OF SOLUTIONS OF PICRIC ACID AND 1,3,5-TRINITROBENZENE IN CHLOROFORM AT 25°

Picric acid, mole/l.	1,3,5-Trinitrobenzene, mole/l.	Wave length, mμ	Optical density	$(P)\epsilon_P l +$ $(T)\epsilon_T l$
0.1096	0.004692	430	0.217	0.220
		440	.088	.089
		460	.022	.022
		470	.013	.013
.07039	.009385	420	.422	.419
		430	.154	.155
.0001587	.0001520	320	.602	.602
		330	.739	.737
		360	.375	.379
		370	.193	.195
		380	.085	.088
		390	.040	.043

TABLE III

EQUILIBRIUM CONSTANTS AND EXTINCTION COEFFICIENTS FOR THE PICRIC ACID–NAPHTHALENE COMPLEX IN CHLOROFORM

Temp., °C.	Wave length, mμ	K, l. mole^{-1}	ϵ_c
19.5	470	1.08	142
	476	1.07	104
	480	1.09	83
	486	1.08	60
	Av.	1.08	
25.0	470	0.98	143
	480	0.97	86
	490	1.01	47
	Av.	0.99	
35.0	470	0.97	133
	480	.97	76
	490	.92	44
	Av.	.95	

Experimental

Materials.—Picric acid, Eastman Kodak Co. White Label, was crystallized from chloroform; yellow needles and plates; m.p. 120.3–121.5°. m-Dinitrobenzene, Eastman Kodak Co. White Label, was crystallized from ethanol; straw-colored needles; m.p. 89–90°. 1,3,5-Trinitrobenzene, Eastman Kodak Co. White Label, was crystallized from chloroform; almost colorless needles, m.p. 121°. Naphthalene was recrystallized several times from methanol; colorless plates, m.p. 80–81°.

The chloroform, which was used as the solvent in the spectroscopic studies, was Baker and Adamson, Reagent ACS, Code 1564, Lot H287 and was used as supplied. This material, which is spectroscopically satisfactory and contains approximately 0.75% ethanol as preservative, proved stable whereas chloroform, purified in the usual manner, shows a tendency for the oxidative formation of small amounts of phosgene.

Spectroscopic Studies.—The absorption measurements were made with a Beckman Model DU quartz spectrophotometer, in which the cell compartment was maintained at constant temperature with a series of Beckman thermospacers. The constant temperature circulating bath kept its temperature constant to within ±0.2°. Solutions were prepared where possible by weighing the components directly into small volumetric flasks and filling to the mark with solvent maintained at the appropriate temperature, or by dilution (pipet) of stock solutions. One-cm. silica cells were used throughout. In the measurements of the picric acid–naphthalene complex the ranges of naphthalene concentrations employed were at 19.5°, 10^{-1} to 2.8 M; at 25° 10^{-1} to 2.4 M; at 35°, 8×10^{-2} to 2.9 M. The range of picric acid concentrations used were at 19.5°, 2.5×10^{-3} to

$5.5 \times 10^{-2} M$; at $25°$, 3×10^{-3} to $7 \times 10^{-2} M$; at $35°$, 3×10^{-3} to $7 \times 10^{-2} M$.

The equilibrium constants and extinction coefficients were calculated by methods previously described.[1,7] Naphthalene showed negligible absorption in the region of measurement. For picric acid in the same region, Beer's law was obeyed over only narrow concentration ranges. A number of determinations of the extinction coefficients of picric acid were made at various concentrations, and in calculating the optical density due to the complex, d_c, that extinction coefficient for picric acid determined at the nearest comparable concentration was employed.

Discussion

Using a partition method Moore, Shepherd and Goodall[3] found extensive complexing in chloroform at $18°$ between picric acid and nitrobenzene ($K = 0.56$ l. mole^{-1}), m-dinitrobenzene (K 1.03 l. mole^{-1}), 2,4-dinitrotoluene ($K = 0.67$ l. mole^{-1}) and 2,4,6-trinitrotoluene ($K = 1.02$ l. mole^{-1}). These solutions, however, are not strongly colored. We have studied the absorption spectra of solutions of m-dinitrobenzene and picric acid in chloroform and, as anticipated, we have found no evidence for complex formation in either the ultraviolet or visible spectra. Similar results were obtained with picric acid and 1,3,5-trinitrobenzene, and it is highly probable that comparable results would be obtained with picric acid and any of the other nitrated hydrocarbons studied by Moore, Shepherd and Goodall.

The absorption spectra studies indicate that the interactions observed, in the above cases, by the partition method do not result from the formation of a charge-transfer intermolecular bond, since the characteristic charge-transfer spectrum is not observed. Yet the partition method experiments clearly indicate interaction, and the values of the equilibrium constants obtained are well beyond the limits of possible experimental error. It must, therefore, be concluded that, in these experiments, an interaction of a different type is involved.

Three types of interaction could account for the observed results. These are intermolecular hydrogen bonding, associations resulting from either permanent or induced dipoles and interactions resulting from dispersion forces.[8] Of these possibilities the first is the least probable, since intramolecular hydrogen bonding should be favored over intermolecular hydrogen bonding in the case of picric acid. For our purposes it is significant that all three of the above interactions could result in the observed equilibrium constants when the measurements are made by the partition method and yet fail to show any evidence of interaction when the measurements are made by the spectroscopic method. As has been pointed out already,[1] the spectroscopic method selectively measures only that complexing which results from the formation of a charge-transfer intermolecular bond. Clearly in the above cases, an interaction of another type is involved.

Briegleb[9] and, more recently, Dewar[10] have taken the position that all molecular compound formation

is attributable to dispersion forces, but this view is untenable where the complexing is measurable by the spectroscopic method. The case of naphthalene and picric acid in chloroform is of interest in this connection. The partition method gives a value of 2.17 l. mole^{-1} for the equilibrium constant at $18°$, whereas, using the spectroscopic method, we obtain the very much lower values given in Table III. From an Arrhenius plot of log K vs. $1/T$ and using the method of least squares, we can estimate ΔH^0 for the picric acid–naphthalene complex, and using the expressions, $\Delta F^0 = -RT \ln K$ and $\Delta F^0 = \Delta H^0 - T \Delta S^0$, we obtain the thermodynamic values given in Table IV.[11] In column 3 of Table IV we have listed those values of K which would exactly fit the least squares straight line.

TABLE IV

PICRIC ACID–NAPTHALENE COMPLEX IN CHLOROFORM

Temp., °C.	K(exptl.) l. mole^{-1}	K (calcd.)^a l. mole^{-1}	ΔH^0, kcal.	ΔF^0, cal.	ΔS^0, e.u.
19.5	1.08	1.06	-1.4	-44.7	-4.6
25.0	0.99	1.01	-1.4	$+ 6.0$	-4.7
35.0	0.95	0.94	-1.4	$+31.4$	-4.6

^{a} This is the required value for K for the point to exactly fit the least squares line of log K vs. $1/T$.

In this instance the spectroscopic equilibrium constant is only one-half the value of the equilibrium constant obtained by the partition method. If one attaches equal credence to both measurements—and there is no a priori reason for not doing so—it must be concluded that the partition method measures at least one other type of interaction in addition to charge-transfer complexing. Intramolecular hydrogen bonding may be eliminated from consideration in this case. Dispersion forces are always present, and since picric acid has an appreciable dipole moment, dipolar attractions must be considered. Either or both of these latter two forces could be the agency responsible for the additional complexing observed by the partition method. The available data do not permit a clear choice.

The more fundamental question is whether a single pair of molecules can give rise to two or more different species of complexes in solution. Both these results and our results on the picryl chloride–hexamethylbenzene complex demand the existence of more than one type of complex in solution. Perhaps there are several configurations for the pair of molecules in solution which have similar probabilities. If one configuration is favorable to formation of a charge-transfer complex and unfavorable to both dispersion and dipolar association, and if a second configuration is favorable to a dipolar or dispersion interaction but unfavorable to the formation of a charge-transfer complex, which requires a more definite geometrical arrangement, then two different species of complex might result.

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(10) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 184.

(11) For thermodynamic studies of the picric acid–naphthalene complex see J. N. Brönsted. Z. physik. Chem., 78, 284 (1912); F. S. Brown, J. Chem. Soc., 345 (1925); R. P. Bell and J. A. Fendley, Trans. Faraday Soc., 45, 121 (1949).