2.5 g. of white powder, melting with decomposition at 225–230° and insoluble in the common organic solvents, was obtained. The infrared spectrum of this product was found to be nearly identical to that of the propylene–sulfur dioxide copolymer.

The copolymer in Nujol mull revealed bands at 745 (shoulder), 760, 790, 845, 1015, 1075, 1130 (strong), 1230 and 1305–1320 cm.$^{-1}$ (strong); the polysulfone produced by oxidation revealed bands at 745 (broad), 790, 845, 1010, 1075, 1130 (strong), 1230 and 1300–1320 cm.$^{-1}$ (strong).

A sample of the oxidized polymer was prepared for analysis by drying in an Abderhalden pistol at 100°.

Anal. Calcd. for $[C_3H_6SO_2]_x$: C, 33.95; H, 5.70. Found: C, 32.16; H, 5.98.

To 1.50 ml. of 1.15 *N* sodium hydroxide solution was added 0.35 g. of the oxidized polymer. Most of the material went into solution rapidly; the solution was filtered, acidified to congo red with 2 *N* hydrochloric acid, and allowed to stand for two days. Upon filtration, 0.11 g. of crystalline product was obtained, melting at 329° (crude) and identical in its infrared spectrum to the disulfone (XXV) obtained from the propylene–sulfur dioxide copolymer.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC CO.]

Molecular Compounds. I. Picryl Chloride–Hexamethylbenzene in Chloroform Solution

BY SIDNEY D. ROSS, MORTON BASSIN, MANUEL FINKELSTEIN AND WILLIAM A. LEACH

RECEIVED JANUARY 24, 1953

The equilibrium constant for complex formation in chloroform between picryl chloride and hexamethylbenzene has been determined by a spectroscopic method and a method based on determinations of reaction rates. The latter method gives a value for *K* which is more than ten times larger than the spectroscopic value of 0.073 ± 0.009 liter × mole^{-1}. The spectroscopic value is taken as a measure of the complexing due to the formation of a charge-transfer type intermolecular bond. The latter value measures, 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.

Picryl chloride and hexamethylbenzene react to form orange-yellow, orthorhombic crystals of a 1:1 molecular compound. This complex has been the subject of extensive investigations, all in the solid state. Powell and Huse[1] have studied the crystal structure by Patterson analyses and general space group considerations and have shown that the crystal consists of alternate layers of picryl chloride and hexamethylbenzene molecules almost parallel to (100) and equally spaced at 3.5Å., although there are observed local disorder structures. Nakamoto[2] has measured the dichroism of this complex and demonstrated that "for the first bands which are supposed to consist of absorptions principally due to π-electrons and the substituents of the benzene rings, the absorption with the electric vectors vibrating perpendicular to the ring plane are always bathochromic and hyperchromic to the absorptions with those vibrating parallel to it." From this it is concluded that the compound results from overlapping of the π-electron clouds in the perpendicular direction between benzene layers. These results support the quantum-mechanical theory of molecular compound formation recently presented by Mulliken,[3] who has extended the previous hypotheses of Weiss,[4] Woodward[5] and Brackmann[6] on molecular compound formation and presented them in a more general and more accurate form.

Our own interest is in the properties of molecular compounds in solution. In this paper we wish to report the results of measurements of the equilibrium constant of the picryl chloride–hexamethylbenzene compound in chloroform solution by a spectroscopic method and by a method involving reaction rate determinations.

Absorption Spectra Studies.—The formation of a molecular compound is in many cases accompanied by the appearance of strong color, and advantage may be taken of this phenomenon to determine the equilibrium constant for compound formation. The spectroscopic method has been used by Landauer and McConnell[7] to determine the equilibrium constants and absorption spectra of the aromatic amine–polynitrohydrocarbon complexes and by Keefer and Andrews[8] to study the interaction of iodine and bromine with organic halides.

Following these latter authors,[8] we define the equilibrium constant for complex formation as

$$K = \frac{(PH)}{(P)(H)} \qquad (1)$$

where (PH), (P) and (H) are the molar equilibrium concentrations of the molecular compound, picryl chloride and hexamethylbenzene, respectively, and assume that, at any wave length

$$d_{PH} = d - (P)\epsilon_P l - (H) \qquad \epsilon_H l = PH\epsilon_{PH} l \qquad (2)$$

where d is the measured optical density, d_{PH}, the optical density due to the molecular compound, l, the light path in cm. and ϵ_P, ϵ_H and ϵ_{PH} are the extinction coefficients of picryl chloride, hexamethylbenzene and the complex, respectively. Keefer and Andrews have used these two expressions in the form

$$\frac{A}{d_{PH}} = \frac{1}{K\epsilon_{PH}} \times B + \frac{1}{\epsilon_{PH}} \qquad (3)$$

where A and B represent, respectively, $(P)_0(H)_0/(P)_0 + (H)_0 - (PH)$ and $1/(P)_0 + (H)_0 - (PH)$ and where $(P)_0$ and $(H)_0$ represent molar concentrations

---

[1] H. M. Powell and G. Huse, *Nature*, **144**, 77 (1939); *J. Chem. Soc.*, 435 (1943).

[2] K. Nakamoto, THIS JOURNAL, **74**, 1739 (1952); see also R. Tsuchida, M. Kobayashi and K. Nakamoto, *Nature*, **167**, 726 (1951).

[3] R. S. Mulliken, THIS JOURNAL, **72**, 600 (1950); **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

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

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

[6] W. Brackmann, *Rec. trav. chim.*, **68**, 147 (1949).

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

[8] R. M. Keefer and L. J. Andrews, *ibid.*, **74**, 1891 (1952).

of picryl chloride and hexamethylbenzene both in the free and complexed state.[9]

In obtaining K from equation 3 we first determined ϵ_H and ϵ_P independently as shown in Fig. 1.

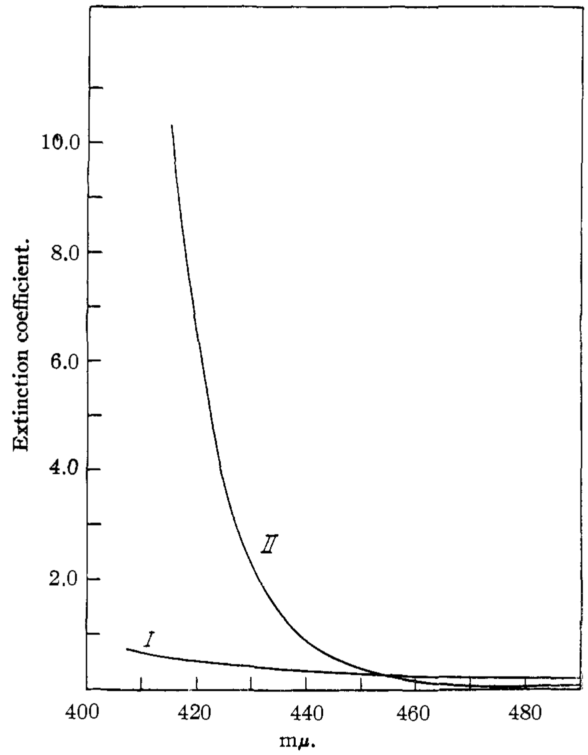

Fig. 1.—Spectra in chloroform at 23.8 ± 0.1°: I, hexamethylbenzene; II, picryl chloride.

We then determined d from 400–500 mμ for various combinations of $(H)_0$ and $(P)_0$, all measurements being made in chloroform solution at 23.8 ± 0.1°. The data are presented in Fig. 2. To check the validity of equation 3, A/d_{PH} and B were calculated, assuming that $(P) \cong (P)_0$, $(H) \cong (H)_0$ and $(P)_0 + (H)_0 >>> (PH)$, and plotted one against the other, and the required straight line was obtained. The method of least squares was used to define the best straight line through the experimental points, and from this line, values of K and ϵ_{PH} were determined.[10] The results are tabulated in Table I, and lead to a value for K of 0.073 ± 0.009 liter mole^{-1}.

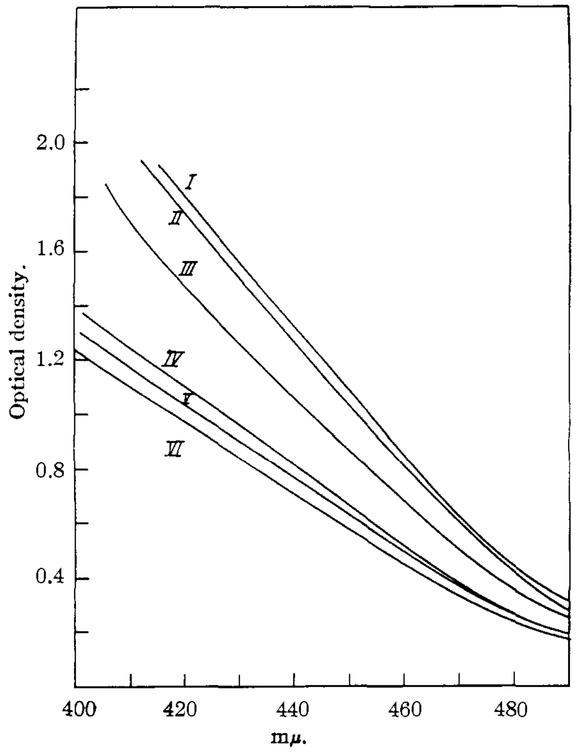

Fig. 2.—Spectra of solutions of hexamethylbenzene and picryl chloride in chloroform at 23.8 ± 0.1°: I, $(H)_0$ 1.249 M; $(P)_0$ 2.5816 × 10^{-2} M; II, $(H)_0$ 0.7756 M; $(P)_0$ 4.022 × 10^{-3} M; III, $(H)_0$ 0.2486 M; $(P)_0$ 1.005 × 10^{-2} M; IV, $(H)_0$ 0.9899 M; $(P)_0$ 2.003 × 10^{-3} M; V, $(H)_0$ 1.5015 M; $(P)_0$ 1.3085 × 10^{-3} M; VI, $(H)_0$ 0.4959 M; $(P)_0$ 3.330 × $10^{-3}M$.

Reaction Rate Studies.—Assume that we have two compounds, A and B, in solution in equilibrium with a molecular compound, AB

$$A + B \rightleftarrows AB$$

and that we add to the system a compound, C, capable of reacting with B to give a product, D. If, now, we measure

$$B + C \longrightarrow D$$

the rate of formation of D, in the absence of A and in the presence of varying concentrations of A, we can deduce from these measurements the equilibrium constant for molecular compound formation provided that the rates of formation and dissociation of AB are both very rapid with respect to the rate of reaction to form D and provided that the rate of reaction of AB with C is negligible with respect to the rate of reaction of B with C. That the equilibrium between A, B and AB is usually very rapid and reversible is clearly indicated by the work of Hammick and Yule,[11] who found that the usual donor, acceptor, molecular compound systems were completely and rapidly reversible even at very low temperature. The validity of the as-

Table I

Equilibrium Constant and Extinction Coefficient for the Picryl Chloride-Hexamethylbenzene Compound in Chloroform at 23.8 ± 0.1°

Wave length, mμ	K, l. moles^{-1}	ϵ_{PH}
420	0.064	8863
425	.066	8118
435	.080	5821
445	.072	5263
455	.079	3834
465	.077	2986

---

[9] It may also be shown that $K = (\epsilon_{PH} - \epsilon_P - \epsilon_H)(d - \epsilon_P(P)_0 - \epsilon_H(H)_0)/(\epsilon_{PH}(P)_0 - \epsilon_H(P)_0 - d + \epsilon_H(H)_0)(\epsilon_{PH}(H)_0 - \epsilon_P(H)_0 - d + \epsilon_P(P)_0)$ where all symbols are as defined above. This permits an estimation of K from determinations of d at two sets of values of $(P)_0$ and $(H)_0$.

[10] The simplifying assumptions, indicated above, are in this case warranted since K is small. Where K is larger, it becomes necessary to use this first value of K to determine (P), (H) and (PH), to revise the values of A/d_{PH} and B accordingly and to repeat the above process to obtain a corrected value for K.

[11] D. L. Hammick and R. B. M. Yule, *J. Chem. Soc.*, 1539 (1940).

sumption with respect to the rate of reaction of AB with C is subject to test by the constancy of the deduced *K*'s.

We have measured the rate of reaction of triethylamine with picryl chloride in chloroform solution at 24.4 ± 0.1°. The product is the expected picryl triethylammonium chloride and the reaction is bimolecular. The average rate constant from four determinations at varying initial amine and chloride concentrations is 0.149 l. moles^{-1} hours^{-1}, and the maximum deviation of an individual run from the average is 6%. The results are summarized in Table II.

TABLE II

RATE OF REACTION OF PICRYL CHLORIDE WITH TRIETHYLAMINE IN THE PRESENCE AND ABSENCE OF HEXAMETHYLBENZENE IN CHLOROFORM AT 24.4 ± 0.1°

Picryl chloride, moles/l.	Triethylamine, moles/l.	Hexamethylbenzene, moles/l.	*k*, l. moles^{-1} hr.$^{-1}$
0.0504	0.1981	0	0.155
.0969	.2081	0	.140
.0483	.2040	0	.152
.0529	.4030	0	.149
.0500	.2516	1.00	.079
.0500	.2508	0.750	.093
.0500	.2517	0.502	.109
.0502	.2496	0.253	.126

Based on our spectroscopic determination of the equilibrium constant for formation of the picryl chloride–hexamethylbenzene complex, we anticipated that the addition of hexamethylbenzene to the above system would have a small and barely detectable effect on the second-order rate constant. All of our determinations were made with approximately 0.05 *M* picryl chloride and 0.25 *M* triethylamine and the hexamethylbenzene concentration was varied from 0.25 to 1.0 *M*. Again the individual runs gave satisfactory second-order plots. However, the added hexamethylbenzene had an unexpectedly large effect on the reaction rate, dropping the rate constant by almost 50% at a concentration of 1.0 *M*. The results are summarized in Table II, and Fig. 3 shows the rate constant for the triethylamine–picryl chloride reaction as a function of the concentration of added hexamethylbenzene.

The rate of reaction between a tertiary amine and a halide is particularly sensitive to changes in the medium.[12] To some extent the rate changes parallel the changes in the dielectric content of the medium, with a decrease in the effective dielectric constant resulting in a lowering of the rate constant.[13] At equivalent volumes hexadecane might be expected to be at least as effective as hexamethylbenzene in lowering the effective dielectric constant of the chloroform medium, since both compounds have nearly zero dipole moment. We have, therefore, studied the reaction between picryl chloride and triethylamine in chloroform at 24.4 ± 0.1° in the presence of added hexadecane. Once again, the individual runs gave satisfactory second-order plots, and the added hexadecane had a very definite effect on the rate. The results are given in Table III and the effect of added hexadecane on the picryl chloride–triethylamine reaction is shown in Fig. 3.

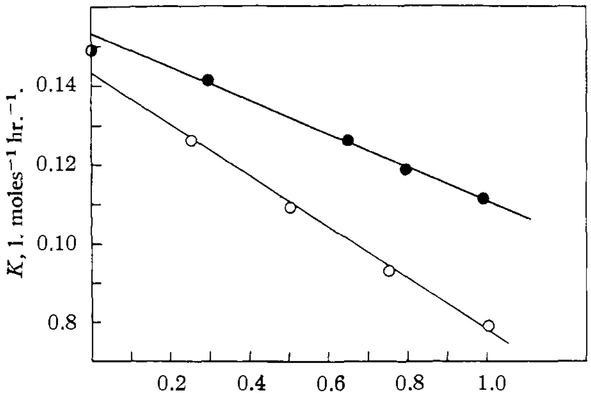

Fig. 3.—The effect of added hexamethylbenzene and hexadecane on the rate of reaction of picryl chloride and triethylamine in chloroform at 24.4 ± 0.1°: ○, hexamethylbenzene; ●, hexadecane.

TABLE III

RATE OF REACTION OF PICRYL CHLORIDE WITH TRIETHYLAMINE IN THE PRESENCE OF HEXADECANE IN CHLOROFORM AT 24.4 ± 0.1°

Picryl chloride, moles/l.	Triethylamine, moles/l.	Hexadecane, moles/l.	*k*, l. moles^{-1} hr.$^{-1}$
0.0500	0.2528	0.987	0.111
.0502	.2578	.790	.119
.0500	.2604	.648	.126
.0500	.2565	.296	.141

More important than these dielectric constant effects are effects attributable to solvation of either the transition state or the reaction products. In this respect hexadecane does not represent an adequate approximation of hexamethylbenzene, which has available π-electrons which may be operative in solvation. To test this possibility, we studied the effect of added hexamethylbenzene and hexadecane on the rate of reaction of *n*-butyl bromide and triethylamine in chloroform at 40.5 ± 0.1°. For this particular reaction, no complications due to complex formation are to be anticipated, and our results permit an estimate of the relative effects in chloroform of both hexamethylbenzene and hexadecane on the rate of a Menschutkin reaction. These results are summarized in Table IV and shown graphically in Fig. 4.

The average rate constant for the four runs in the absence of hexamethylbenzene and hexadecane is 0.0116 l. moles^{-1} hours^{-1}, and the maximum deviation of any individual run from this average is less than 5%. It is also apparent from the data of Table IV and Fig. 4 that hexadecane and hexamethylbenzene do not exert comparable effects on the reaction rate. The former lowers the rate constant by 42% when present in a concentration of 1.0 *M*, whereas the latter slightly accelerates the rate, the rate constant being increased 16% in the presence of 1.0 *M* hexamethylbenzene.

Not all Menschutkin reactions are equally sensitive to medium effects. From the data of Table III it is clear that the triethylamine–picryl chloride reaction in chloroform is much less sensitive to added

---

[12] N. Menschutkin, *Z. physik. Chem.*, **6**, 41 (1890).

[13] K. J. Laidler and H. Eyring, *Ann. N. Y. Acad. Sci.*, **39**, 303 (1940).

Table IV

The Effect of Added Hexamethylbenzene and Hexadecane on the Rate of Reaction of n-Butyl Bromide and Triethylamine in Chloroform at 40.5 ± 0.1°

n-Butyl bromide, moles/l.	Triethylamine, moles/l.	Hexamethylbenzene, moles/l.	Hexadecane, moles/l.	k, l. moles^{-1} hr.$^{-1}$
0.5598	0.0806	0	0	0.0113
.9066	.07116	0	0	.0114
.1787	.3561	0	0	.0121
.4549	.0715	0	0	.0116
.4552	.07204	0.250	0	.0126
.4549	.07165	0.500	0	.0130
.4550	.0718	1.00	0	.0135
.4562	.07204	0	0.250	.0116
.4562	.07204	0	0.500	.00983
.4562	.07203	0	1.00	.00695

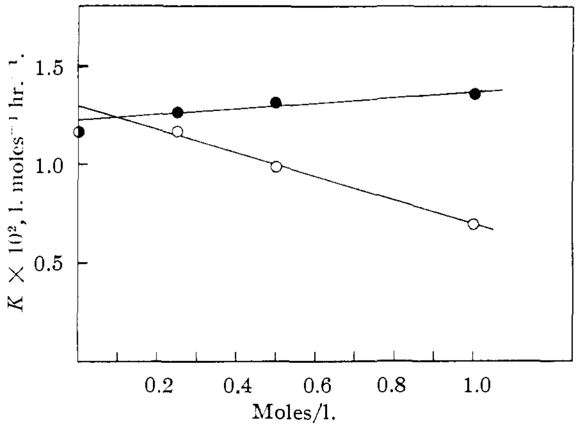

Fig. 4.—The effect of added hexamethylbenzene and hexadecane on the rate of reaction of n-butyl bromide and triethylamine in chloroform at 40.5 ± 0.1°: ○, hexadecane; ●, hexamethylbenzene.

hexadecane than is the triethylamine–n-butyl bromide reaction. The addition of 1.0 M hexadecane lowers the rate constant by only 28% in this case. Although it cannot be asserted with certainty, it is probable that the picryl chloride-triethylamine reaction is also less sensitive to the effect of added hexamethylbenzene insofar as a purely medium effect is concerned. In the absence of complex formation, we would, therefore, expect the added hexamethylbenzene to increase the reaction rate slightly. From the available data there is certainly no basis for attributing the very large decrease in rate which we in fact observe to a purely medium effect.

On the contrary, the probability is that the observed decrease in rate reflects some interaction between hexamethylbenzene and a reactant. If we assume that the hexamethylbenzene complexes with picryl chloride and temporarily withdraws it from reaction with triethylamine, we can estimate K, the equilibrium constant for picryl chloride–hexamethylbenzene compound formation, from our data. Focusing our attention on the zero time condition and using our previous symbolism, our experimental rate constants, for runs with added hexamethylbenzene are calculated from the expression

$$\frac{dD}{dt} = k(\mathrm{P})_0(\mathrm{T})_0 \qquad (4)$$

where D is the concentration of quaternary ammonium salt formed, $(\mathrm{T})_0$ is the initial triethylamine concentration and $(\mathrm{P})_0$ represents the initial concentration of picryl chloride in both the free and complexed state. But only picryl chloride in the free state is effective for forming D. If, now instead of $(\mathrm{P})_0$ in the above expression, we substitute the concentration of free picryl chloride, (P), this will result in a new rate constant, k', independent of the amount of added hexamethylbenzene and equal to the rate constant obtained in the absence of added hexamethylbenzene. Again at zero time

$$\frac{dD}{dt} = k'(\mathrm{P})(\mathrm{T})_0 = k'(\mathrm{T})_0(\mathrm{P})_0(1 - Z) \qquad (5)$$

where Z is the fraction of $(\mathrm{P})_0$ which is complexed. By equating 4 and 5 we obtain 6

$$Z = (k' - k)/k' \qquad (6)$$

from which we can calculate Z, using our experimentally determined values of k and k'. Knowing Z, we can calculate K from the expression

$$K = \frac{Z}{(1 - Z)((\mathrm{H})_0 - Z(\mathrm{P})_0)} \qquad (7)$$

The estimated K's obtained using expression 7 are tabulated in Table V. The average value is 0.82 l. moles^{-1}, and the maximum deviation from this average is 0.13 l. moles^{-1} or less than 16%. If we make the very optimistic assumptions that there is no uncertainty in the value of k' and that there is only a 5% uncertainty in the value of each k, the resultant uncertainties in the values of the calculated K's are those given in the last column of Table V. The constancy of our calculated K's is thus more than can be legitimately expected and supports the hypothesis that we are measuring an interaction governed by a true equilibrium expression.

Table V

Rate Constants for the Picryl Chloride–Triethylamine Reaction in the Presence of Hexamethylbenzene and Equilibrium Constants for Formation of the Picryl Chloride–Hexamethylbenzene Complex in Chloroform at 24.4 ± 0.1°

(Picryl chloride)$_0$, moles/l.	(Hexamethyl benzene)$_0$, moles/l.	(Triethylamine)$_0$, moles/l.	k, l. moles^{-1} hr.$^{-1}$	K, l. moles^{-1}	Uncertainty in K, %
0.0502	0.253	0.2496	0.126	0.75	32
.0500	.502	.2508	.109	.76	19
.0500	.750	.2517	.093	.82	16
.0500	1.00	.2496	.079	.95	15

There is a further uncertainty in the value of K, obtained in this manner, resulting from the fact that we have not corrected our k's for that portion of the change in rate, due to added hexamethylbenzene, which is due to a medium effect. Unfortunately it is not clear how such a correction is to be made since any compound which would adequately approximate the medium effect resulting from hexamethylbenzene would probably be equally effective in complexing picryl chloride. Based on our studies of the n-butyl bromide-triethylamine reaction, the medium effect on rate runs counter to the effect due to complexing. If this were the case, it would mean that the values for the equilibrium constant given in Table V are somewhat low. However, it is not completely certain that the medium effect due to added hexamethylbenzene would accelerate the rate of the picryl chloride–triethylamine reaction. In fact it is conceivable although improbable that in this case hexamethylbenzene would have either no effect or a slight retarding effect on the reaction rate. There is, therefore, a real area of uncertainty attached to the value of K obtained from the rate studies. However, it is highly probable that this uncertainty is very small with respect to the discrepancy in the value of K as obtained from the spectroscopic measurements and the value of K obtained from the rate studies.

Experimental

Reagents.—Picryl chloride was crystallized from ethanol until the m.p. was constant at 83–84°. Hexamethylbenzene was crystallized from ethanol and melted at 164–165°. Triethylamine was fractionally distilled, and a middle cut of b.p. 88–89.5° was used. *n*-Butyl bromide was fractionally distilled and a middle cut of b.p. 101–102° was used. The *n*-hexadecane was distilled at 0.1 mm., and a fraction of b.p. 106–109° was used. C.P. chloroform was used, and this was distilled before use.

The Absorption Spectrum Measurements.—A Beckman Model D.U. spectrophotometer was used throughout. Stoppered absorption cells were used, and the cell housing was maintained at constant temperature by means of two Beckman thermospacers, through which water from a constant temperature bath was circulated. The solutions for measurement were made up by weighing specific quantities of the requisite reagents directly into a volumetric flask and making it up to volume with chloroform at 23.8 ± 0.1°.

The Reaction Rate Measurements.—Reaction was initiated by rapidly mixing determinate chloroform solutions of picryl chloride and triethylamine, both at 24.4 ± 0.1°. When a third component such as hexamethylbenzene was used, the picryl chloride and the triethylamine solutions were made up with chloroform which already contained the requisite amount of the third component. At various time intervals, 10-ml. aliquots were withdrawn from the reaction mixture and run into a mixture of 25 ml. of 4.5 N nitric acid and 25 ml. of benzene. The mixture was shaken vigorously, the benzene layer was extracted with water, and the aqueous extracts were combined. An excess of 0.1003 N silver nitrate solution was added. The silver chloride was filtered by gravity, and the filtrate was back-titrated with 0.0500 N potassium thiocyanate solution using saturated ferric alum as indicator. The rate constants were calculated using the slope of the best straight line through the experimental points, plotted in the usual second-order fashion. Individual runs were carried to at least 60% reaction and, in most cases, to more than 80% of completion.

The *n*-butyl bromide–triethylamine rate measurements were carried out exactly as above except that in this case the determinate solutions were made up at 40.5 ± 0.1°.

Discussion

The equilibrium constant for complex formation between picryl chloride and hexamethylbenzene in chloroform solution has been measured by a spectroscopic method and a method involving reaction rate determinations. The latter method gave a value for the equilibrium constant which, in spite of uncertainties, is probably larger by a factor of more than ten than the spectroscopic K of 0.073 ± 0.009 l. moles^{-1}. It is our contention that both values are meaningful, and it is pertinent, at this point, to inquire what specifically was measured in each instance.

The spectroscopic method uniquely measures those complexes whose formation is accompanied by a change of absorption in the region of measurement. Mulliken[3] has pointed out that donor–acceptor interaction, resulting in a charge-transfer type intermolecular bond, adequately accounts for the formation of complexes of this type. The specific interaction may be represented as

$$\mathrm{P} + \mathrm{H} \rightleftarrows (\mathrm{P}, \mathrm{H}) \longleftrightarrow (\mathrm{P}\cdot^{-} - \cdot\mathrm{H}^{+}) \qquad (8)$$

the intermolecular binding in the complex being due to the resonance indicated above, although the contribution of the ionic structure is undoubtedly small. This is the type of interaction responsible for the highly colored solid complexes. These have intermolecular bond distances and crystal structures consistent with Mulliken's theory.

The reaction rate method, on the other hand, measures the sum of all those interactions which can, in any manner, affect the rate of the reaction of picryl chloride with triethylamine. These interactions include electrostatic attractions between electric dipoles, induced dipoles, London "dispersion forces,"[14] etc., as well as the formation of charge-transfer intermolecular bonds. It is not necessary that all of these interactions be reflected in the existence of an isolable solid complex. It is, in fact, certain that many of these interactions occur only in solution. A dipolar orientation and association in solution involving picryl chloride would affect its rate of reaction with triethylamine but would not necessarily lead to formation of a solid product. Moreover, this type of interaction would not necessarily result in any measurable absorption different from that resulting from the sum of the absorptions of the two components.

Brown and Brady,[15] in their study of the solubility of hydrogen chloride in aromatic hydrocarbons, have presented convincing evidence for the existence of two types of complexes. The first, which occurs in the absence of aluminum chloride results in a colorless solution. Brown attributes the formation of this complex to weak interaction between the electrophilic hydrogen chloride and the π-electrons of the aromatic ring. This he prefers to call a "π-complex" and would restrict this term to those complexes in which the π-electron cloud is not seriously distorted. In the presence of aluminum chloride, colored solutions are obtained. Brown attributes formation of this colored complex to actual protonation of the aromatic ring and has termed it a "σ-complex." The colored complex which we have measured spectroscopically is probably more closely related to Brown's "π-complex" than to his "σ-complex" but is better described in Mulliken's[3] terminology as a $b\pi_a$-$x\pi_a$ complex, resulting from intermolecular charge-transfer bonding. The additional complexing which is indicated by our rate studies cannot be adequately described by either of the types of complexes indicated by Brown.

More interesting, with respect to our findings, are the results of Moore, Shepherd and Goodall,[16] who measured the stability of compounds of picric acid with hydrocarbons and of nitro compounds with amines by a partition method. They found, for ex-

---

(14) R. Eisenchitz and F. London, *Z. Physik*, **60**, 491 (1930); F. London, *ibid.*, **63**, 245 (1930); F. London, *Z. physik. Chem.*, **B11**, 1222 (1930).

(15) H. C. Brown and J. D. Brady, THIS JOURNAL, **74**, 3570 (1952).

(16) T. S. Moore, F. Shepherd and E. Goodall, *J. Chem. Soc.*, 1497 (1931).

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 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.

Acknowledgment.—It is a pleasure to acknowledge helpful and stimulating discussion with Prof. Paul D. Bartlett of Harvard University and Dr. Fielding Brown of these laboratories.

NORTH ADAMS, MASS.

---

[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.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC COMPANY]

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

RECEIVED AUGUST 17, 1953

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.

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-

---

[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).

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