222. *Interaction between Polynitro-compounds and Aromatic Hydrocarbons and Bases. Part X. Picric Acid and Alkylated Benzene Derivatives in Chloroform Solution.*

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Using the method of Moore, Shepherd, and Goodall (*J.*, 1931, 1447), we have compared the stabilities of the products of interaction of picric acid in chloroform solution with a series of monoalkylated derivatives of benzene (*n*-alkylation from toluene to *n*-amylbenzene, branched-chain alkylation to *iso*propyl, *sec.*-butyl and *tert.*-butyl). The analytical requirements necessary to achieve an accuracy of 2—4% in the equilibrium constants involved an accurate determination of the partition of picric acid between water and chloroform. The results obtained from the equilibrium (" stability ") constants show an alternating effect of increasing *n*-alkyl chain length; this is related to a " packing effect." The branching of the chain shows a progressive and presumably steric effect.

In the present communication we record the results of a study of the interaction of picric acid in chloroform solution with benzene and a number of its alkyl derivatives. We have compared the stabilities of the products of interaction as nuclear methylation is increased from toluene to durene and as the methyl group in toluene is extended by *n*-alkylation to *n*-amylbenzene and by branched-chain alkylation to *iso*propyl-, *sec.*-butyl-, and *tert.*-butyl-benzene.

We have made the basis of our comparative stabilities the equilibrium constant $K = C_{\text{complex}}/(C_{\text{hydrocarbon}} \times C_{\text{picric acid}})$ and this we have determined by the method of Moore, Shepherd, and Goodall (*J.*, 1931, 1447) which depends on the change in the distribution ratio of picric acid between a solvent (chloroform) and water when an aromatic substance, immiscible in water, is added to the solvent.

Interaction between picric acid and the added substance in the chloroform layer will withdraw picric acid from the aqueous layer and lead to an enhanced concentration in the chloroform; at the same time, replacement of chloroform molecularly by the added substance will lower the amount of picric acid in chloroform by a solubility depression effect (Rothmund, *Z. physikal. Chem.*, 1910, **69**, 523; Moore, Shepherd, and Goodall, *loc. cit.*). The overall effect measured, from which the stability constant K is to be derived, is thus a difference between two small quantities, one of which we require to know in order to calculate a stability constant; the other, the solubility-depression effect, we obtain by determining the effect on the picric acid distribution by the addition of substances such as hexane, which would not be expected to interact with picric acid, to the chloroform layer.

We will now obtain a relation between the various parameters involved. Consider a distribution of picric acid between water and chloroform, in the latter of which the concentration (in g.-mols./l.) is P. Let the addition of an aromatic substance, soluble only in the chloroform, depress the concentration of picric acid to y by the amount $(P - y)$. At the same time let the concentration in the chloroform be increased to y_1 by the amount $(y_1 - P)$ owing to interaction between the aromatic substance and picric acid. On the assumption that the two opposite effects are arithmetically additive, then Y, the experimentally found picric acid concentration in the chloroform, is

$$Y = P + (y_1 - P) - (P - y)$$

whence

$$Y = y + y_1 - P \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(i)}$$

Now let us define a solubility-depression constant as

$$k = (P - y)/yZ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

where Z is the number of g.-mols. of aromatic substance in a litre of the chloroform layer and where the concentration of picric acid is initially P; k is thus the lowering of solubility due to " salting out " per unit concentrations of picric acid and added substance.

From (ii) we get

$$y = P/(1 + kZ) = P(1 - kZ + \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad)$$

Substituting this value for y in (i), we get

$$y_1 - P = Y - y = Y - P + PkZ \text{ (neglecting powers of } kZ) \quad . \quad . \quad . \quad \text{(iii)}$$

The stability constant K (see above) $= \frac{y_1 - P}{P[Z - (y_1 - P)]}$

whence, since $(y_1 - P)$ is small

$$y_1 - P = KPZ \quad \text{(iv)}$$

and

$$K = \frac{y_1 - P}{PZ(1 - KP)} \quad \text{(v)}$$

Introducing the value of $y_1 - P$ from (iii) we have

$$K(1 - KP) = \frac{Y - P}{PZ} + k \quad \text{(vi)}$$

where $Y - P$ is the observed or overall change in picric acid concentration in the chloroform layer for the addition to it of Z g.-mols. of aromatic substance. If interaction and " salting out " are small, *i.e.*, if Z is taken as not differing significantly from the concentration of free hydrocarbon in solution, then KP is small compared with unity and we have

$$K = K_1 + k \quad \text{(vii)}$$

where $K_1 = (Y - P)/PZ$ and has the form of an " apparent " stability constant. This is the parameter that is measured directly. To obtain K, the " true " stability constant,* we must ascertain k, the solubility-depression constant; this we have done, as explained above, by finding K_1 in circumstances (addition of aliphatic hydrocarbon) where K in (vi) is zero or at any rate neglibible compared with K_1 and k. As will be seen below, k increases with molecular volume and is closely proportional to it.

This suggests that the solubility-depression effect may be mainly a molecular volume effect. If this is so, it is easy to show that $k = k_1V/1000$, where V is molecular volume of hydrocarbon in 10^3 c.c. of solvent and k_1 is a proportionality factor. We find the value $k_1 = 3{\cdot}8$ for the three non-aromatic substances examined (see below) and have used this value in equation (vi) in computing the stability constant K.

Experimental.

In addition to P, Y, and Z, as defined above, we define X as the concentration in g.-mols./l. of picric acid in the aqueous solution in equilibrium with chloroform solution.

Analytical Methods and Apparatus.—The stability constant K depends upon $Y - P$, which is obtained from the difference between two analyses of aqueous layers in equilibrium with the chloroform solution to which Y and P refer. The fundamental requirement of any analytical method is therefore an accurate determination of the particular ratios of picric acid between chloroform and water over the significant ranges of concentration. Such determinations were made by Moore, Shepherd, and Goodall (*loc. cit.*), who claimed an accuracy of 1 : 400, and if no error was introduced in reading off P from their graph from a measurement of X, their maximum error in $Y - P$ would be the sum of the errors in Y and X, and since $Y - P$ is very small, they could only measure the smaller stability constants with an accuracy of 1 : 5, though the accuracy of the larger ones reached 5%. As, however, we were concerned with changes in stabilities produced by progressive structural changes in aromatic substances, we required to raise the accuracy as high as possible.

In order to be able to derive all our stability constants K with an accuracy of 2—4%, it is necessary to be able to determine picric acid in the aqueous and chloroform layers correctly to 1 : 1000. The analytical method employed was based on highly purified picric acid as standard, analyses being made by thiosulphate titration of iodine liberated from potassium iodide and iodate. It was readily found possible to reach end-points with an accuracy of better than 1 : 1000. The real difficulties lay in measuring the titration solutions and the solution to be titrated to an equal degree of accuracy. These were overcome by taking stringent precautions to eliminate loss of chloroform by evaporation by the use of a specially designed weight-pipette that delivered through a very fine point under pressure, and by the use of a mercury-sealed apparatus in which chloroform and aqueous solution could be brought to equilibrium, removed, and added without exposure to the air. The equilibrium apparatus was kept in a thermostat at 18° ± 0·01°.

Materials.—Picric acid. This was crystallised three times and had m. p. 122·5° (corr.). With this specimen as standard, " AnalaR " potassium iodide and iodate were 99·63% and 99·83% pure, respectively.

Chloroform. " Pure chloroform for anæsthesia " was repurified by Lowry's method (Weissberger and Proskauer, " Organic Solvents "). It was stored in black bottles and tested with a solution of starch, potassium iodide, and iodate before use. No coloration was ever observed.

Benzene. Thrice frozen-out " AnalaR " benzene, b. p. 80·0°/765 mm., was the substance from which most of the alkylbenzenes were prepared.

Alkylbenzenes and aliphatic hydrocarbons. These were prepared by standard methods.

* It is realised that values for K cannot be absolute values unless interaction between picric acid and chloroform can be taken into account. It is not at present possible to do this.

We are indebted to Professor Sir Robert Robinson and Dr. L. E. Sutton for pure specimens of *tert.*-butylbenzene, *cyclo*hexane, and carbon tetrachloride.

Results.

Partition Ratio of Picric Acid between Chloroform and Water at 18°.—Specimen data for one determination are given, followed in Table I by the complete set of distribution ratios.

Expt. 1. Temp. 18°. Concentration of picric acid in chloroform layer (by direct weight-titration with thiosulphate of concentration 0·03704 g.-mol./1000 g.); three titrations gave :

Density of chloroform layer, g./ml.	1·4963	1·4963	1·4963
Wt. of $Na_2S_2O_3$ soltn./Wt. of $CHCl_3$ layer	1·0734	1·0739	1·0741

Average density, 1·4963 g./ml. Average ratio, 1·0738. Hence concentration of picric acid in chloroform layer = 1·0738 × 0·03704 × 1·4963 = 0·05952 g.-mol./l.

Concentration of picric acid in water layer : three titrations gave :

Density of water layer, g./ml.	1·0059	1·0062	1·0061
Wt. of $Na_2S_2O_3$ soltn./Wt. of H_2O layer	0·9294	0·9284	0·9294

Average density, 1·0061 g./ml. Average ratio, 0·9291. Hence concentration of picric acid in water layer = 0·9291 × 0·03704 × 1·0061 = 0·03463 g.-mol./l.

FIG. 1.

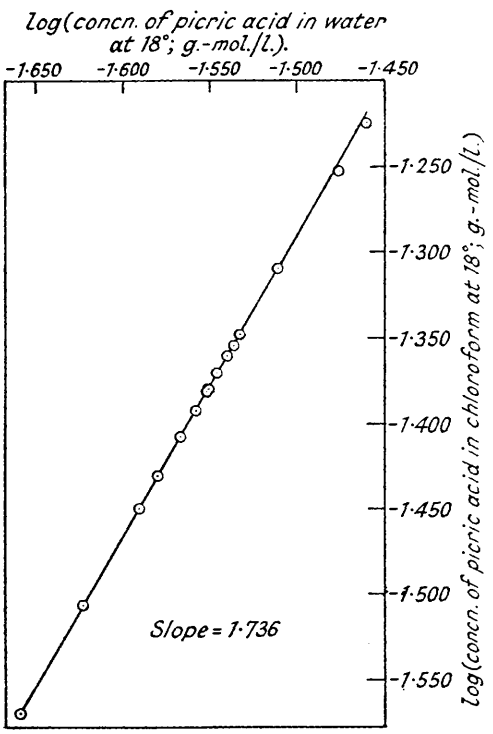


TABLE I.

Partition coefficient for picric acid between water and chloroform at 18°.

$10^5C_{CHCl_3}$, g.-mol./l.	$10^5C_{H_2O}$, g.-mol./l.
5952	3463
5593	3339
4912	3084
4493	2935
4421	2911
4366	2890
4262	2848
4176	2813
4165	2808
4055	2766
3918	2713
3719	2631
3562	2565
3125	2381
2695	2189

Fig. 1 shows a plot of the logarithms of the concentrations in Table I, giving a straight line of slope 1·736. Over the above concentration range the equation

$$\log C_{CHCl_3} = 1{\cdot}736 \log C_{H_2O} + 1{\cdot}3124$$

gives values within 0·5% of the experimental results.

Solubility-depression Constant.—Example. n-Hexane at 18° :

Concentration of thiosulphate = 0·03700 g.-mol./1000 g.

Concentration of hexane in chloroform layer, Z = 0·342 g.-mol./l.

Concentration of picric acid in chloroform layer = 0·02411 g.-mol/l.

Concentration of picric acid in water layer = 0·02250 g.-mol./l.

From graphical interpolation in Table I, the corresponding concentration, P, of picric acid in pure chloroform is 0·02832 g.-mol./l.

The solubility-depression constant $k = \dfrac{P - y}{yZ} = \dfrac{(0{\cdot}02832 - 0{\cdot}02411)}{0{\cdot}02411 \times 0{\cdot}342} = 0{\cdot}51.$

Values of k and k_1 (*i.e.*, 1000 k/v) for three hydrocarbons at 18° are given in the following table.

Hydrocarbon.	Spec. vol.	Mol. vol., V, ml.	k.	k_1.
Decalin	1·116	154	0·58	3·8
Hexane	1·512	130	0·51	3·9
*cyclo*Hexane	1·280	108	0·40	3·7

Stability Constants K (*from* K_1 *and* k).—*Example.* Benzene at 18°.
Concentration of thiosulphate = 0·03699 g.-mol./1000 g.
Concentration of benzene in chloroform layer, Z = 0·2197 g.-mol./l.
Concentration of picric acid in chloroform layer: three titrations gave:

Density of chloroform layer, g./ml.	1·4821	1·4817	1·4820
Wt. of $Na_2S_2O_3$ soltn./Wt. of $CHCl_3$ layer	0·4697	0·4701	0·4705

Average density, 1·4819 g./ml. Average ratio, 0·4701. Concentration of picric acid in chloroform layer, Y = 1·4819 × 0·4701 × 0·03699 = 0·02578 g.-mol./l.
Concentration of picric acid in water layer: three titrations gave:

Density of water layer, g./ml.	1·0044	1·0040	1·0039
Wt. of $Na_2S_2O_3$ soltn./Wt. of water layer	0·5688	0·5684	0·5692

Average density, 1·0041 g./ml. Average ratio, 0·5688. Hence concentration of picric acid in water layer

$$X = 1{\cdot}0041 \times 0{\cdot}5688 \times 0{\cdot}03699 = 0{\cdot}02113 \text{ g.-mol./l.}$$

From graphical interpolation of Table I, the corresponding concentration, P, of picric acid in pure chloroform is 0·02528 g.-mol./l., whence apparent stability constant,

$$K_1 = \frac{Y - P}{PZ} = \frac{0{\cdot}00050}{0{\cdot}02528 \times 0{\cdot}2197} = 0{\cdot}090$$

The solubility-depression constant, k, is calculated from the molecular volume at 18°:
Density at 18° = 0·881 g./ml., molecular volume, V = 78/0·881 = 88·7 ml./g.-mol., and k = 3·8 × 88·7/1000 = 0·337. Therefore the stability constant, $K = K_1 + k$ = 0·090 + 0·337 = 0·43.
The results are collected in Table II, where k = solubility depression constant, calculated from molecular volume as above; V = molecular volume; K_1 = "apparent" stability constant; K = "true" stability constant.

TABLE II.

Hydrocarbon.	k.	V.	K_1.	K.	K_1 (Moore *et al.*).
Benzene	0·34	88·7	+0·09	0·43	0·08
Toluene	0·40	106	+0·11	0·51	0·09
Ethylbenzene	0·46	122	−0·01	0·45	—
n-Propylbenzene	0·53	139	+0·07	0·60	—
*iso*Propylbenzene	0·53	139	−0·17	0·36	—
o-Xylene	0·45	118	+0·18	0·63	0·12
m-Xylene	0·47	122	+0·13	0·60	0·11
p-Xylene	0·47	123	+0·14	0·61	0·12
Mesitylene	0·53	139	+0·15	0·68	0·12
n-Butylbenzene	0·58	154	−0·23	0·35	—
sec.-Butylbenzene	0·59	155	−0·25	0·34	—
tert.-Butylbenzene	0·58	154	−0·27	0·31	—
n-Amylbenzene	0·65	171	−0·23	0·42	—
Durene	0·59	155	+0·42	1·01	—
Hexamethylbenzene	0·61	180	+1·12	1·73	—

DISCUSSION.

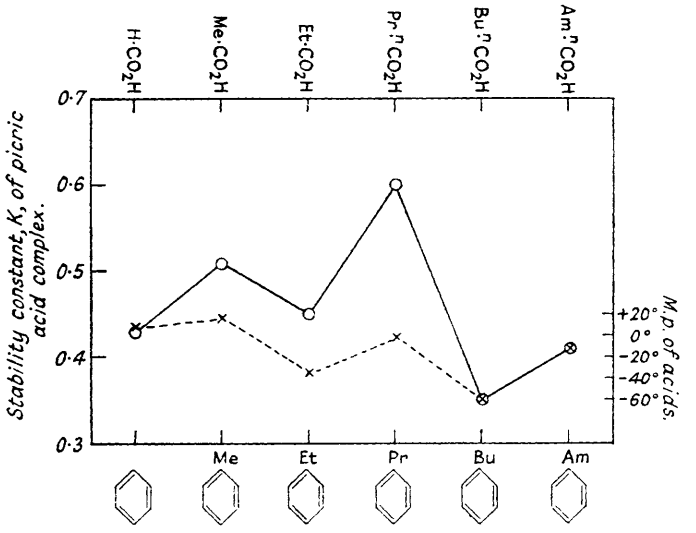
Interaction between polar and polarisable molecules has been discussed by Briegleb ("Zwischenmolekülare Kräfte und molekülar Struktur," Stuttgart, 1937). Using a semi-empirical calculation for the polarisabilities of certain aromatic hydrocarbons, he was able to show that for intermolecular distances of *ca.* 3·0 A., heats of interaction could be computed in satisfactory agreement with values obtained by other methods. Subsequent evidence from crystallographic studies (Huse and Powell, *J.*, 1943, 435) shows that in the case of the typical solid picrate of tri-iodoaniline, intermolecular distances are indeed of the order 3·0 A.

Briegleb's electrostatic interpretation of the type of molecular interaction that gives rise to the phenomena studied by us, by Moore, Shepherd, and Goodall, and by others (*locc. cit.*) and which in extreme cases leads to the setting up of stoicheiometrically controlled solid structures such as the "picrates" of aromatic hydrocarbons, is certainly incomplete. In the first place, interaction is seldom between inducing and induced dipoles only; electrostatic attraction between permanent dipoles must also be taken into account. In this connection it must be recognised that a molecule which has no overall dipole moment may nevertheless be capable of

localised induction by individual polar substituents which " cancel out " in the molecule as a whole. The same considerations will of course apply to electrostatic interaction between local permanent dipoles in each of two molecular species, which are each overall non-polar.

In studying the interaction of a given polarising molecule (in our case picric acid) with a series of polarisable aromatic hydrocarbons, it is clearly not possible to separate the two effects mentioned above. Nevertheless, the permanent polarity conferred upon a molecule by the

FIG. 2.



introduction of a methyl group is known to be small, and in considering the variation in our stability constants as we pass from toluene to hexamethylbenzene, we are probably justified in attributing increased interaction mainly to increasing polarisability in the hydrocarbon series. In fact, a close parallel can be shown between the stability constants and the molecular polarisabilities M (based on refractive indices for the D line of sodium; Landolt–Börnstein) for the series benzene, toluene, *m*-xylene, mesitylene, as follows :

Hydrocarbon.	K.	M.	$\delta K/CH_3$.	$\delta M/CH_3$.
Benzene	0·43	26·18		
			0·08	4·88
Toluene	0·51	31·06		
			0·09	4·68
m-Xylene	0·60	35·74		
			0·08	4·87
Mesitylene	0·68	40·61		

o-Methylation, however, produces a larger increase in stability which is not proportional to the increase in polarisability or to the number of methyl groups, and which suggests that effects other than polarisability are operative :

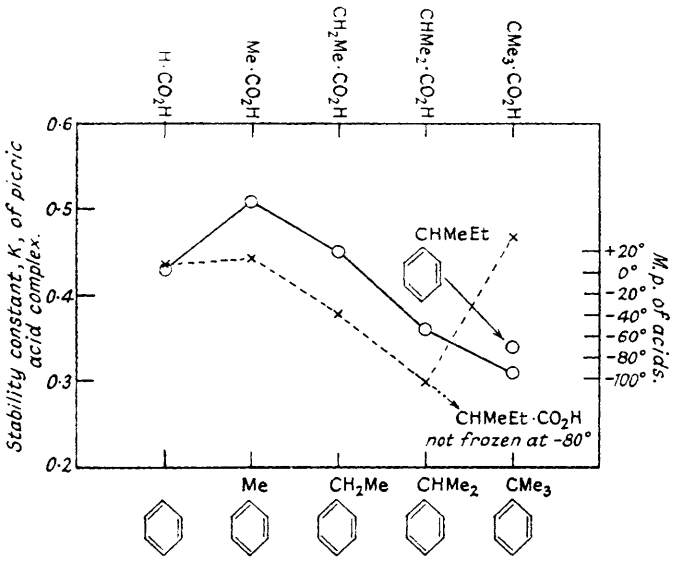
Hydrocarbon.	K.	M.	$\delta K/CH_3$.	$\delta M/CH_3$.
Benzene	0·43	26·18		
			0·10	4·78
o-Xylene	0·63	35·74		
			0·19	5·13
Durene	1·01	46·0		
			0·36	—
Hexamethylbenzene	1·73	—		

The following further points of interest emerge from the results collected in Table II : (i) the alternation in stability as the substituent *n*-alkyl chains lengthen, (ii) the effect of branching.

(i) Fig. 2 shows the variation of stability constants with increasing length of the *n*-alkyl substituent. The alternating effect is strongly reminiscent of the well-known alternation of the stabilities of the crystal structures of the normal fatty acids as indicated by their melting points, which are also shown in Fig. 2. The effect in the acid series is held (Piper, *J.*, 1929, 234) to be due to the fact that in the crystal lattices the alkyl groups are in the form of long, straight but zig-zag chains. This form of packing implies that the terminal groups should be on the same side for odd numbers of carbon atoms and on opposite sides for even numbers. The view is put forward (*loc. cit.*) that when the terminal groups are on the same side some form of

interaction renders the packing less stable than when they are on opposite sides. Now the energy of interaction in the liquid state between picric acid and aromatic hydrocarbons is small and comparable with latent heats of fusion of organic substances. It is therefore perhaps not unreasonable to expect that packing effects even in the liquid state might be detectable; we believe that such effects are revealed in our stability constants, which are measures of free-energy changes, for the *n*-alkylbenzenes and picric acid.

FIG. 3.



We also make the tentative suggestion that the marked drop in stability after *n*-propylbenzene may be related to the fact that beyond this point in the series the alkyl chain becomes longer than the benzene nucleus.

(ii) Fig. 3 shows how, after the initial increase in stability due to one methyl group, the stabilities of the picric complexes fall progressively through ethyl, *iso*propyl to *iso*butyl and *tert.*-butyl. The fall is nearly linear, though the slight alternations may be due to a secondary packing effect superimposed on the general steric effect due to the increasing bulk of the substituent. It will be noticed in Fig. 3 that the m. p.s of the corresponding fatty acids again follow the same trend as the stability constants, except in the case of trimethylacetic acid.

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