

The ratio D/b is recorded to show the linear variation of colour density with addition of hydrocarbon required by equation (v).

TABLE I.

Benzene. $T = 20.8^\circ$.						Toluene. $T = 20.8^\circ$.					
b	1.666	2.332	3.332	3.918	4.664	6.664	0.14	0.28	0.39	0.49	0.59
D	0.085	0.114	0.159	0.198	0.229	0.344	0.128	0.243	0.343	0.443	0.542
D/b	0.051	0.049	0.048	0.051	0.049	0.52	0.91	0.87	0.88	0.90	0.92
<i>o</i> -Xylene. $T = 20.8^\circ$.						<i>m</i> -Xylene. $T = 20.8^\circ$.					
b	0.0395	0.0790	0.1185	0.1580	0.1975	0.2765	0.039	0.078	0.116	0.155	0.194
D	0.230	0.435	0.670	0.887	0.124	0.56	0.218	0.444	0.645	0.890	0.101
D/b	5.82	5.51	5.65	5.61	5.69	5.64	5.58	5.69	5.56	5.74	5.68
<i>p</i> -Xylene. $T_1 = 20.8^\circ$. $T_2 = 60.0^\circ$.											
b	0.019	0.048	0.077	0.116	0.193						
$D_{20.8^\circ}$	0.165	0.423	0.700	1.030	1.720						
$D_{60.0^\circ}$	—	0.361	0.574	0.872	—						
$D_{28.0^\circ}/b$	8.68	8.81	9.09	8.88	8.91						
$D_{60.0^\circ}/b$	—	7.52	7.46	7.52	—						
Phenol. $T = 21^\circ$.						Phenyl acetate. $T = 21^\circ$.					
b	0.0239	0.0478	0.0716	0.0955	0.0552	0.1380	0.2208	0.3312			
D	0.295	0.589	0.878	1.166	0.097	0.226	0.367	0.543			
D/b	12.34	12.32	12.26	12.21	1.767	1.64	1.66	1.64			
Diphenyl ether. $T = 20.0^\circ$. $T = 60.0^\circ$.											
b	0.0106	0.0212	0.0372	0.0532	0.1062						
$D_{20.0^\circ}$	0.159	0.306	0.553	0.798	1.601						
$D_{60.0^\circ}$	0.125	0.247	0.439	0.633	1.238						
$D_{20.0^\circ}/b$	15.00	14.43	14.86	15.00	15.06						
$D_{60.0^\circ}/b$	11.79	11.65	11.80	11.90	11.65						
Anisole. $T = 21.0^\circ$.						Phenetole. $T = 21.0^\circ$.					
b	0.0115	0.0231	0.0404	0.0577	0.0134	0.0269	0.0403	0.0537			
D	0.233	0.475	0.829	1.172	0.277	0.555	0.832	1.102			
D/b	20.26	20.56	20.52	20.31	20.68	20.63	20.64	20.52			
Naphthalene. $T_1 = 20.8^\circ$. $T_2 = 60.2^\circ$.						β -Methylnaphthalene. $T_1 = 20.8^\circ$. $T_2 = 62.0^\circ$.					
b	0.006	0.012	0.0201	0.0302	0.0053	0.0106	0.0159	0.0212			
$D_{20.8^\circ}$	0.211	0.414	0.680	1.037	0.213	0.418	0.632	0.838			
$D_{60.2^\circ}$	0.182	0.370	0.613	0.920	0.184	0.366	0.546	0.726			
$D_{20.8^\circ}/b$	35.2	34.5	34.0	34.6	40.19	39.44	39.75	39.53			
$D_{60.2^\circ}/b$	30.3	30.9	30.7	30.7	34.72	34.53	34.34	34.25			
2 : 4-Dimethylnaphthalene. $T_1 = 20.8^\circ$. $T_2 = 61.0^\circ$.						β -Naphthol. $T_1 = 20.8^\circ$. $T_2 = 62.3^\circ$.					
b	0.00493	0.00986	0.01479	0.01972	0.0051	0.0102	0.0153	0.0204			
$D_{20.8^\circ}$	0.247	0.484	0.723	0.968	0.260	0.524	0.780	1.045			
$D_{61.0^\circ}$	0.217	0.423	0.643	0.861	0.218	0.435	0.658	0.859			
$D_{20.8^\circ}/b$	50.11	49.09	48.88	49.09	50.98	51.37	50.98	51.22			
$D_{61.0^\circ}/b$	44.02	42.91	43.47	43.66	42.74	42.64	43.00	42.10			
α -Nitronaphthalene. $T_1 = 20.8^\circ$. $T_2 = 63.0^\circ$.						Anthracene. $T_1 = 21.0^\circ$. $T_2 = 54.0^\circ$.					
b	0.0648	0.1296	0.216	0.337	0.0129	0.0257	0.0386	0.0514			
$D_{20.8^\circ}$	0.187	0.382	0.650	0.968	0.330	0.659	0.990	1.337			
$D_{63.0^\circ}$	0.177	0.341	0.580	0.861	0.254	0.495	0.753	1.005			
$D_{20.8^\circ}/b$	2.89	2.74	3.01	2.84	25.58	25.64	25.64	26.01			
$D_{63.0^\circ}/b$	2.73	2.63	2.68	2.56	19.69	19.26	19.50	19.55			

(The data for the system α -nitronaphthalene-tetranitromethane have been corrected for the absorption due to the nitronaphthalene.)

Mesitylene. $T = 20.8^\circ$.								
b	0.0043	0.0086	0.0172	0.0258	0.0344	0.0428	0.0600	0.0856
D	0.090	0.198	0.415	0.592	0.740	0.860	1.08	1.20
D/b	20.93	23.02	24.12	22.94	21.51	20.09	18.06	17.5

SUMMARY AND DISCUSSION OF RESULTS.

As has been pointed out above, the magnitudes of the colour density–hydrocarbon slopes are proportional to the constants for the equilibrium between components and complex in solution, provided the extinction coefficients for the different solutions can be taken as approximately the same. In Table II these slopes, in arbitrary units, are compared with the equilibrium constants found by Moore, Shepherd, and Goodall (*loc. cit.*) in chloroform solution for the picric acid complexes of the same hydrocarbons.

TABLE II.

	Benzene.	Toluene.	α -Nitro-naphthalene.	<i>o</i> -, <i>m</i> -, <i>p</i> -Xylenes.	Mesitylene.	Naphthalene.	β -Methylnaphthalene.
$\partial D/\partial b_{a,v} \dots$	0.05	0.895	2.88	5.64, 5.65, 8.73	21.0 *	34.6	39.73
$K_{Pic.} \dots\dots\dots$	0.09	0.12	[1.02]	0.15	0.18	2.17	3.44

* From initial slope.

It is seen that, with one exception (α -nitronaphthalene), the order of stability of the picric acid complexes is the same as that given by the colour density slopes for the tetranitromethane complexes. The partition method used by Moore, Shepherd, and Goodall gives equilibrium constants that cover the total interaction of nitro-compound and hydrocarbon due to association between permanent dipoles and between induced dipoles as well as chemical interaction, if any. According to the view adopted by Moore, Shepherd, and Goodall, chemical interaction is alone responsible for the production of colour and hence our comparative stabilities, which depend solely on colour densities, should refer to chemical equilibria only. The different positions occupied by α -nitronaphthalene in the two series in Table II then become readily explicable, for it is the only highly polar compound among the aromatic substances whose interactions with the two polynitro-compounds are compared. Moore, Shepherd, and Goodall's constant takes account of dipole association as well as chemical interaction and hence has a higher relative value than that given by our comparative method, which refers to chemical interaction alone.

Dimroth and Bamberger's experiments (*loc. cit.*) on the picric acid complexes of the following hydrocarbons place them in the following order of stability; our relative values for the equilibrium constants are shown below the respective hydrocarbons:

Benzene.	Anthracene.	Naphthalene.	β -Methylnaphthalene.	[2 : 4-Dimethylnaphthalene.]	[\beta-Naphthol.]
0.05	25.72	34.6	39.7	49.3	54.1

From these results we conclude that our assumption that the extinction coefficients for the various tetranitromethane–hydrocarbon systems are approximately the same is substantially valid.

In Table III are collected the relative values for the equilibrium constants K found for the interaction between tetranitromethane in carbon tetrachloride and a series of benzene derivatives, C_6H_5R .

TABLE III.

R	H	CH ₃	O-CO-CH ₃	OH	O-C ₆ H ₅	O-CH ₃	O-C ₂ H ₅
K	0.05	0.90	1.68	12.28	15.87	20.41	20.62

The order of the substituents is that required on the Robinson–Ingold principles for increasing reactivity towards additive reagents except in the case of phenol, which would be expected to follow diphenyl ether. It must be remembered, however, that phenol is associated in solution, which means that the $(\partial D/\partial b)_{a,v}$ slope quoted for phenol is certainly too small.

TABLE IV.

Substance.	<i>p</i> -Xylene.	Diphenyl ether.	Naphthalene.	β -Methylnaphthalene.
H (kg.-cals.)	0.72	1.55	0.60	0.71
Substance.	2 : 4-Dimethylnaphthalene.	β -Naphthol.	α -Nitronaphthalene.	Anthracene.
H (kg.-cals.)	0.58	0.86	1.69	1.59

The heats of interaction of tetranitromethane with the various substances that were examined at two different temperatures are summarised in Table IV.

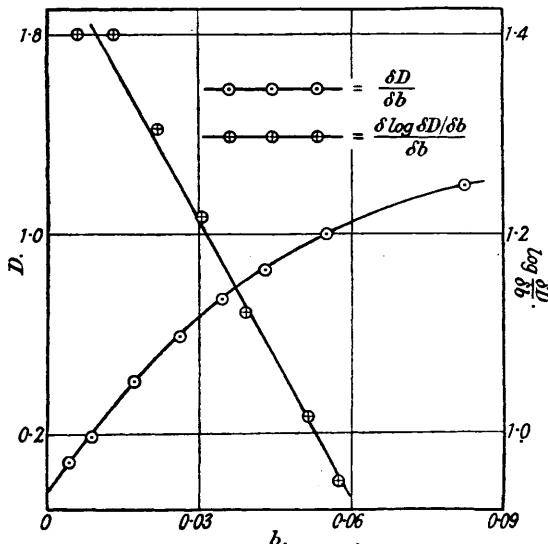
The non-linear variation of colour density with addition of mesitylene to tetranitromethane in carbon tetrachloride is shown in the figure. The necessary data for the application of equation (vii) were obtained from the curve and are given in Table V.

TABLE V.

b	0.0065	0.0129	0.0215	0.0301	0.0386	0.0514
$\log (\partial D / \partial b)$	1.400	1.402	1.314	1.236	1.125	1.107

These values are also plotted in the figure (crossed circles) and are seen to lie satisfactorily about a straight line.

The slope of $\log (\partial D / \partial b)$ against b is 7.4. Converting into Napierian logarithms and



introducing into equation (vii) with $V = 0.004$ litre, the actual volume of solution to which the colour densities refer, we obtain the value 0.068 for the true equilibrium constant. This value may be compared with Moore, Shepherd, and Goodall's constant K (corr.) for the system mesitylene-picric acid in chloroform, which is more of a dissociating solvent than carbon tetrachloride. Approximate values for the true equilibrium constants for the other tetranitromethane systems can be derived from the absolute value for mesitylene and the relative values derived from the colour density slopes. Thus for benzene K will be of the order 10^{-4} , which implies that in a molar solution of the constituents in carbon tetrachloride the concentration of coloured molecules will be about 10^{-4} g.-mol. per litre.

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