# **317.** Complex Formation between Polynitro-compounds and Aromatic Hydrocarbons. Part III. Systems containing Tetranitromethane.

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WHEN a considerable variety of substances, having in common the property of anionoid reactivity, are mixed with tetranitromethane, which is colourless when pure, the production of coloured solutions shows that interaction of some kind takes place (Werner, Ber., 1909, 42, 4324; Ostromisslensky, J. pr. Chem., 1911, 84, 489; Clarke, Macbeth, and Stuart, P., 1913, 29, 161; Harper and Macbeth, J., 1915, 107, 87, 1824). The colours produced are generally yellow (maximum absorption at about 4500 A.) but not uncommonly reddishorange (anthracene). They are, in fact, very similar to the colorations produced when aromatic polynitro-compounds such as trinitrobenzene are mixed in solution with aromatic or unsaturated hydrocarbons or with bases such as aniline. As is well known, definite crystalline complexes can usually be obtained from the polynitro-aromatic systems; the existence of such solids containing tetranitromethane has not yet been definitely established. The latter fact suggests that in the tetranitromethane systems the complex molecules responsible for the colour are much less stable than those derived from polynitro-aromatic compounds and are never present in liquid phases in sufficient concentration for saturation to be reached.

We have obtained some information as to the relative stability of the coloured complexes present in solutions containing tetranitromethane by adding to a standard solution of the nitro-compound in carbon tetrachloride increasing amounts of various hydrocarbons, the total volume of solution, V, being kept constant. Assuming that the colour density of the solutions is proportional to the number of coloured molecules present, we have followed the production of the latter with the addition of hydrocarbon by means of a spectrophotometer. Whether the coloured molecule is a dipole aggregate or a true chemical compound, we assume that there is an equilibrium between complex molecules and their components to which the law of mass action can be applied. Then, if a gram-molecules of tetranitromethane and b gram-molecules of a hydrocarbon are mixed in a volume V of carbon tetrachloride, c gram-molecules of complex (1:1) being produced, we have :

$$c/(a-c)(b-c) = K/V$$
 . . . . . . (i)

and

$$(\partial c/\partial b)_{a, V} = (a - c)/(a + b - 2c + V/K)$$
 . . . . (ii)

If c is small compared with a, K will also be small and V/K large compared with a + b - 2c. We thus have

Now the colour density D, on the assumption that Lambert's law holds, is connected with c by

$$D = \varepsilon \cdot d \cdot c/V \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (iv)$$

( $\varepsilon$  = extinction coefficient, d = length of absorption tube) and hence in (iii),

$$(\partial D/\partial b)_{a, V} = (a/V^2)(K/\varepsilon d)$$
 . . . . . . (v)

Under these conditions, the variation of colour density D with addition of hydrocarbon should therefore be linear and, as will be seen from the data recorded in the experimental part, in all cases except one of the tetranitromethane systems investigated straight line plots of D against b are obtained.

From equation (v) it follows that ratios of the slopes  $(\partial D/\partial b)_{a, V}$  should give the relative stabilities (K) of the coloured complexes, provided the extinction coefficient  $\varepsilon$  is independent or approximately independent of the nature of the added hydrocarbon. The pure complexes cannot be obtained and hence no direct determination of the extinction coefficient can be made. In order, therefore, to form some idea of the variation of  $\varepsilon$  with the nature of the hydrocarbon added to tetranitromethane, we have determined the slopes  $(\partial D/\partial b)_{a, V}$ 

for a series of hydrocarbons which form, with picric acid in chloroform solution, complexes whose relative stabilities are known from the experiments of Dimroth and Bamberger (Annalen, 1924, 438, 67) and Moore, Shepherd, and Goodall (J., 1931, 1447). Our tetranitromethane colour density slopes, which are proportional to  $K \cdot \varepsilon$ , give the same sequence (with one exception, discussed below) as the equilibrium constants for the picrates and we take this as implying that the extinction coefficient does not vary greatly with the nature of the added hydrocarbon.

Assuming therefore that the colour density slope  $(\partial D/\partial b)_{a, \mathbf{v}}$  is approximately proportional to the equilibrium constant K, we have investigated a series of systems containing tetranitromethane and benzene derivatives  $C_6H_5R$ , the anionoid reactivity of the nucleus varying with the nature of R. As will be seen below, the relative magnitude of the equilibrium constant increases with increasing reactivity.

In a number of cases the colour density slopes have been determined at two temperatures. From equation (v) we obtain, on the assumption that  $\varepsilon$  is independent of temperature and neglecting the expansion of the solvent,

$$\partial \ln(\partial D/\partial b)_{a, \mathbf{v}}/\partial T = \partial \ln K/\partial T = H/RT^2$$

from which we have calculated heats of interaction H.

Equation (v) was derived from (ii) for the condition that the amount c of complex produced is negligible in comparison with the amount a of tetranitromethane in solution. As the amount of c increases, the a of equation (v) must be replaced by a - c before it becomes necessary to take the difference a + b - 2c into account in comparison with V/K in the denominator in equation (ii). In other words, when on the addition of a hydrocarbon to a tetranitromethane solution the linear variation of colour density breaks down, we may expect equation (ii) to approximate to

$$(\partial c/\partial b)_{a, V} = (a - c)/(a + b - 2c + V/K) = (a - c) \cdot K/V$$
 . (vi)

from which we get

$$\partial (\partial c/\partial b)/\partial b = -K/V \cdot \partial c/\partial b$$

or

$$\partial \ln(\partial c/\partial b)/\partial b = -K/V$$

Introducing (iv), this leads to

$$\partial \ln(\partial D/\partial b)/\partial b = -K/V$$
 . . . . . . . . . (vii)

We have applied this equation to the data for the system mesitylene-tetranitromethane and obtained a value of approximately 0.07 for the equilibrium constant.

#### EXPERIMENTAL.

*Materials.*—Tetranitromethane, prepared by Chattaway's method (J., 1910, 97, 2099), was washed with dilute sodium carbonate solution, dried with anhydrous sodium sulphate, and fractionally distilled under diminished pressure (b. p.  $34-35^{\circ}/20$  mm.; m. p.  $12 \cdot 5^{\circ}$ ). The carbon tetrachloride used as solvent in all the experiments was free from sulphur and free chlorine and was distilled from phosphoric oxide immediately before use.

Measurement of Colour Density.—In all cases the following procedure was adopted : 1 c.c. of a solution of 8.25 g. of tetranitromethane in 25 c.c. of carbon tetrachloride (1 g.-mol. in 2.381 l.) was run, from a micro-burette, into the absorption tube of a Hilger–Nutting spectrophotometer. To the tetranitromethane solution was added, also from a micro-burette, the requisite volume of a solution in carbon tetrachloride of the second component of the system to be examined and the mixture was made up to 4 c.c. with carbon tetrachloride. The absorption tube was then screwed into a metal jacket through which a thermostatically controlled stream of water could be circulated. In all cases determinations of colour density were made at  $\lambda$  4300 A. Data are given below. Under b are the ratios of hydrocarbon to tetranitromethane molecules in the solutions examined. As in all cases the number of g.-mols. of tetranitromethane was the same, viz.,  $(1/2.381) \times 10^{-3}$ .

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

					Тав	le I.						
		Ber	zene.	T = 20	·8°.				Toluen	e. $T =$	20·8°.	
b	1.666	2.332	3.332	3.918	4.664	6.66	4	0.14	0.28	0.39	0.49	0.29
D $D/b$	0·085 0·051	0·114 0·049	0.129	0·198 0·051	0.229	0.34	4	0·128 0·91	0.243 0.87	0·343 0·88	0.443	0.542
2,0	0 001	0 0 10	0 0 10			0.01		0.01	000	0.00		0.02
		0-X	ylene.	T = 20	•8°.				<i>m</i> -Xyle	ne. $T$	$= 20.8^{\circ}$	•
b D	0.0395	0.0790	0.1185	0.1580	0.1975	0.276	35	0.039 0.218	0.078	0·116 0·645	0.155	0.194
D/b	5.82	5.21	5.65	5.61	5.69	5.64		5.28	5.69	5.26	5.74	5.68
			L 3	Zaulomo	T	an.00	т	60.00				
	Ь		p-2		$I_1 = 0.04$	20 <sup>.</sup> 8°.	$1_2 = 0.077$	: 00'0'. 0.1	16	0.103		
	$D_{20.8^{\circ}}$			0.013	0.42	3	0.700	1.0	030	1.720		
	D60.0°		•••••		0.36	1	0.574	0.8	872	 9.01		
	$D_{28\cdot0^{\circ}}$ $D_{60\cdot0^{\circ}}$	b  b			7.52		9.09 7.46	8-8 7-8	58 52	8.91		
	,	т	)h em el	т о	10			Dha		tata T	010	
h	0	.0930	0.0478	1 = 2 0.071	1. 6 0.	0055		0.0559	0.1380	1 $1$ $1$ $1$ $1$	$= 21^{\circ}$ .	.2219
$\stackrel{o}{D}$	0	·295	0.589	0.878	3 I·	166		0.092	0.226	0.36	67 C	543
D/b	12	·34 1	2.32	12.26	12.	21		1.767	1.64	1.66	5 1	•64
			Diph	enyl eth	er. T	= 20.0	о°. Т	$= 60.0^{\circ}$				
	b		(	0.0106	0.05	12	0.037	2 0.0	)532	0.1062		
	$D_{20 \cdot 0^{\circ}}$			0·159	0.30	6	0.553	0.2	798	1.601		
	$D_{60.0^{\circ}} = D_{20.0^{\circ}} / D_{2$	'b	1	5.00	14.43	•	14.86	15.0	)0 )0	15.06		
	$D_{60\cdot0^{\circ}}$	Ъ	1	1.79	11.65		11.80	11.6	<del>)0</del>	11.62		
		А	nisole.	T = 2	1•0°.			Р	henetol	e. <i>T</i> =	21.0°	
ь	0	).0115	0.0231	0.04	04 0	·0577		0.0134	0.026	9 0.0	403 (	0.0237
D	0	).233	0.475	0.82	9 1	·172		0.277	0.555	0.8	32	1.102
D/0	20	).26	20.90	20.95	20	-31		20.08	20.03	20.0	4 20	).22
<b>NT</b> 1/1		<b>T</b> 90	00 T	00.00	5		β-3	Methylna	aphthale	ene. $T_1$	= 20.8	° <b>.</b>
Naphtha	liene.	$T_1 = 20$ .	8°. 1 <sub>3</sub>	$= 60.2^{\circ}$		L		0.00	$I_{2} = 0$	52.0°.	0150	0.0919
D	0.000 0.211	0.012	0.02	01 00 00 00 00 00 00 00 00 00 00 00 00 0	302 37		••••••	0.01	13 0.4	418 0 <sup>-</sup>	632	0.838
D <sub>60</sub> ·2°	0.182	0.370	0.61	3 0.9	20	D	62·0° ·	0.18	34 0.3	366 <sup>0</sup>	546	0.726
$D_{20-8^{\circ}}/b \dots$	35.2	34·5 30·9	34·0 30·7	34.6			20-8°/D	40.19	) 39·4 2 34·5	14 39 <sup>.</sup> 13 34.	75 3	9·53 4·25
1060.20/0	000					2	52.2.10	01.12		0 01	01 0	1 20
2 : 4-Din	nethylna T	$- 61.0^{\circ}$	ne. $T_1$	$= 20.8^{\circ}$	•		R-Na	phthol	$T_{-} = $	20·8° 7	<b>-</b> - 62	•3°
h	0.0049	= 010. 3 0.0098	86 0.01	479 0.0	1972	Ь		0.00		102 0	0153	0.0204
D <sub>20'8°</sub>	0.247	0.484	0.72	3 0.9	68	$D_{2}$	20.8° •	0.26	0 0.2	24 Ö·	780	1.045
$D_{61 \cdot 0^{\circ}} \dots D_{b}$	0.217	0.423	0.64	3 0.8	61 0		32·3° ·	0.21	8 0.4	35 0.	658 ( 08 5	D·859 1.99
$D_{20\cdot8^{\circ}}/b$ $D_{61\cdot0^{\circ}}/b$	44.02	42.91	43.47	43.6	<i>5</i> 6	$D_{e}$	<sub>20·8°/0</sub> . <sub>32·3°</sub> /b.	30 38 42.74	42.6	4 43.	00 4	2.10
NT:4		1	90.1	00								
a-Nitroi	$T_{\bullet} = 6$	$3.0^{\circ}$ .	1 = 20.3	5⁻.		A	nthrac	cene. T	1 = 21.0	0°. T.	= <b>54</b> ·0°	
ь	. 0.06	48 0.1	296	0.216	ь			0.0129	0.02	57 0.0	0386	0.0514
$D_{20^{\circ}8^{\circ}}$	. 0.18	7 0.3	82	0.650	D	21·0°	•••••	0.330	0.65	9 0.9	990	1.337
$D_{63 \cdot 0^{\circ}} \dots \dots$	2.89	7 0.3 2.7	41 4	0°280 3•01	מ	54·0°		0°204 25.58	25.64	o 0. 25.1	153 64 2	1.002 8.01
$D_{63 \cdot 0^{\circ}}/b$	2.73	2.6	3	2.68	$\tilde{D}$	54·0°/b		19.69	19.26	19-	50 1	9.55
(The dat	ta for t	the syste	em a-n	itronaph	thalen	e-tetra	.nitrom	nethane	have b	een corr	rected i	for the
absorption d	lue to th	ne nitron	aphthal	ene.)								
Mesitylene. $T = 20.8^{\circ}$ .												

			2					
b	0.0043	0.0086	0.0172	0.0258	0.0344	0.0428	0.0600	0.0856
D	0.090	0.198	0.412	0.295	0.740	0.860	1.08	1.50
D b	20.93	23.05	24.12	22.94	21.21	20.09	18.00	17.5

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### 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.

m	
ADTE	
IADLE	11.

	Benzene.	Toluene.	a-Nitro- naphthalene.	o-, m-, p-Xylenes.	Mesityl- ene.	Naphthal- ene.	$\beta$ -Methyl- naphthalene.
$\partial D / \partial b_{\mathbf{a}, \mathbf{V}} \dots$	0.02	0.892	2.88	5.64, 5.65, 8.73	21.0 *	34.6	39.73
$K_{\text{Pic.}}$	0.09	0.15	[1.02]	0.12	0.18	2.17	3.44
			* From in	nitial slope.			

It is seen that, with one exception ( $\alpha$ -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  $\alpha$ -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 :

			β-Methyl-	[2:4-Dimethy]-	
Benzene.	Anthracene.	Naphthalene.	naphthalene.	naphthalene.]	$[\beta$ -Naphthol.]
0.02	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,  $C_6H_5R$ .

			Тав	le III.			
R	H	СН <sub>3</sub>	О•СО•СН <sub>3</sub>	OH	O•C <sub>4</sub> H <sub>5</sub>	O-CH <sub>3</sub>	O·C <sub>2</sub> H <sub>5</sub>
<i>K</i>	0·05	0-90	1∙ <b>6</b> 8	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.

	Т	ABLE IV.		
Substance.	<i>p</i> -Xylene.	Diphenyl ether.	Naphthalene.	β-Methyl- naphthalene.
H (kgcais.)	0.72	1.99	0.00	0.11
Substance.	naphthalene.	$\beta$ -Naphthol.	naphthalene.	Anthracene.
H (kgcals.)	0.28	0.86	1.69	1.29

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.

		TA	ABLE V.			
b	0·0065	0·0129	$0.0215 \\ 1.314$	0·0 <b>301</b>	0·038 <b>6</b>	0·0514
$\log (\partial D / \partial b)$	1·400	1·402		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 Kwill be of the order 10<sup>-4</sup>, which implies that in a molar solution of the constituents in carbon tetrachloride the concentration of coloured molecules will be about 10<sup>-4</sup> g.-mol. per litre.

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