**145.** *Complex Formation between Polynitro-compounds and Aromatic Hydrocarbons. Part V. The Effect of Methylation on the Stability of Tetranitromethane Complexes.*

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The colour density of mixtures of tetranitromethane in carbon tetrachloride with aromatic hydrocarbons increases as more hydrocarbon is added, and from measurements of the rate of increase of colour the relative stabilities of the coloured intermolecular complexes can be derived. In this way it is shown that stabilities increase

as the number of methyl groups attached to the benzene nucleus is increased to six. Introduction of methyl groups into the side chain of toluene, however, does not progressively increase the stability of the tetranitromethane complexes.

In Part III (J., 1936, 1463) it has been shown that the variation in colour density of a fixed volume of a solution of tetranitromethane with increase in the ratio of aromatic hydrocarbon to nitro-compound is proportional to the product $\varepsilon K$ of extinction coefficient and equilibrium constant for the interaction to form the coloured intermolecular complex. It was found that values of the product $\varepsilon K$ for a series of hydrocarbons were in the same order as the equilibrium constants for the interaction of the same hydrocarbons with picric acid (Moore, Shepherd, and Goodall, J., 1931, 1447; Dimroth and Bamberger, *Annalen*, 1924, **438**, 67). It was therefore concluded that the variation of $\varepsilon$ with the nature of the hydrocarbon is small and that the method might be used as a general method for comparing the stabilities of the coloured complexes formed by tetranitromethane with other aromatic and unsaturated substances.

In the present communication we give the results of an investigation of the effect of the progressive introduction of methyl groups into the benzene nucleus and into the side chain of toluene on the stability of the coloured complexes formed with tetranitromethane in carbon tetrachloride solution. We have included diphenyl- and triphenyl-methane among the hydrocarbons examined in order to make a comparison possible between the effect of the substitution of methyl and of phenyl into the toluene side chain on the stability of the complexes.

### EXPERIMENTAL.

*Materials.*—The tetranitromethane and carbon tetrachloride were prepared and purified as described in Part III (*loc. cit.*); the hydrocarbons were prepared by standard methods, their purity being checked by determinations of b. p. and refractive index. We are indebted to Professor R. Robinson for a specimen of *tert.*-butylbenzene.

*Measurement of Colour Density.*—The experimental procedure was as described in Part III, progressively increasing quantities ($b$ g.-mols.) of hydrocarbon being added from a micro-burette to a fixed amount ($a$ g.-mols.) of tetranitromethane in carbon tetrachloride, the mixture being made up in each case to a standard volume $V$ (4 c.c.) with carbon tetrachloride. The colour density $D$ was determined in a Hilger–Nutting spectrophotometer fitted with a device for circulating a thermostatically controlled stream of water around the observation tube.

In Part III it was shown that $(\partial D/\partial b)_{a,V} = aK\varepsilon d/V^2$ * if the amount of coloured complex is relatively small. For fixed $a, V$, and $d$ (depth of absorbing solution), the colour-density slopes $(\partial D/\partial b)_{a,V}$ are proportional to $K$, the equilibrium constants [$K = c/(a - c)(b - c)$ where $c$ = no. of g.-mols. of coloured complex], if $\varepsilon$ does not vary much with the nature of the hydro-carbon. In the present communication we record the results of our measurements in a slightly different form. We have not kept to the same number of molecules of tetranitromethane in every case, and in order to make our results comparable, we have determined and compared the slopes

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

(The colour density–concentration of hydrocarbon slopes recorded in Part III are converted into the present units by division by 0·177.) As before, determinations of colour density were made at two temperatures ($T_1$ and $T_2$), and estimates made of the heats of interaction $H$ of tetranitromethane with the various hydrocarbons. Results are collected in Table I.

### DISCUSSION.

The effect of the successive introduction of methyl groups into the benzene nucleus on the value of the product $K\varepsilon d$ at 25° is shown in Table II (*a*). The values of $K\varepsilon d$ for benzene, toluene, the xylenes, and mesitylene are taken from Part III (*loc. cit.*) and converted into the system of units used in the present communication.

* In Part III, this equation is given in error as $(\partial D/\partial b)_a, V = (a/V^2)(K/\varepsilon d)$.

<div align="center">TABLE I.</div>

$V = 0.004$ l.; values of $D$ found either directly at $\lambda = 4300$ A. or converted into $D_{4300}$ from absorption curves; $a/V$ and $b/V$ are the numbers of g.-mols. of tetranitromethane and of hydrocarbon per l. in the standard volume $V$ l. of carbon tetrachloride solution; $d$ was 2 cm. in all cases; $- \Delta H$ is the heat absorbed on formation of 1 g.-mol. of coloured complex assumed to be 1 : 1 in composition.

Durene.  $T_1 = 25°$;  $T_2 = 60°$;  $a/V = 0.419$ g.-mol./l.

| | | | | | | |
|---|---|---|---|---|---|---|
| $b/V$ .............. | 0.0025 | 0.0050 | 0.9974 | 0.0124 | 0.0149 | 0.0248 |
| $D_{25°}$ .............. | 0.304 | 0.499 | 0.653 | 1.136 | 1.380 | 2.35 |
| $D_{60°}$ .............. | 0.231 | 0.432 | 0.557 | 0.940 | 1.112 | — |
| $D_{25°}/(a/V)$ ...... | 0.73 | 1.19 | 1.56 | 2.71 | 3.29 | 5.61 |
| $D_{60°}/(a/V)$ ...... | 0.55 | 1.02 | 1.33 | 2.24 | 2.66 | — |

$D_{25°}/(a/V) = 226b/V + 0.02$;  $D_{60°}/(a/V) = 175b/V + 0.02$;  $- \Delta H = 1.4$ kg.-cals./g.-mol.

Pentamethylbenzene.  $T_1 = 25°$;  $T_2 = 60°$;  $a/V = 0.423$ g.-mol./l.

| | | | | | | |
|---|---|---|---|---|---|---|
| $b/V$ .............. | 0.0021 | 0.0042 | 0.0062 | 0.0083 | 0.0104 | 0.0125 |
| $D_{25°}$ .............. | 0.289 | 0.575 | 0.782 | 1.114 | 1.412 | 1.596 |
| $D_{60°}$ .............. | 0.230 | — | 0.665 | 0.831 | 1.099 | 1.243 |
| $D_{25°}/(a/V)$ ...... | 0.684 | 1.360 | 1.850 | 2.635 | 3.340 | 3.777 |
| $D_{60°}/(a/V)$ ...... | 0.544 | — | 1.573 | 1.966 | 2.601 | 2.941 |

$D_{25°}/(a/V) = 308b/V + 0.03$;  $D_{60°}/(a/V) = 233b/V + 0.07$;  $- \Delta H = 1.7$ kg.-cals./g.-mol.

Hexamethylbenzene.  $T_1 = 25°$;  $T_2 = 60°$;  $a/V = 0.423$ g.-mol./l.

| | | | | | | |
|---|---|---|---|---|---|---|
| $b/V$ .............. | 0.0019 | 0.0038 | 0.0057 | 0.0076 | 0.0095 | 0.0114 |
| $D_{25°}$ .............. | 0.291 | 0.694 | 1.054 | 1.371 | 1.64 | 2.07 |
| $D_{60°}$ .............. | 0.230 | 0.559 | 0.848 | 1.036 | 1.346 | 1.54 |
| $D_{25°}/(a/V)$ ...... | 0.689 | 1.643 | 2.494 | 3.243 | 3.880 | 4.900 |
| $D_{60°}/(a/V)$ ...... | 0.544 | 1.322 | 2.006 | 2.445 | 3.184 | 3.649 |

$D_{25°}/(a/V) = 430b/V + 0.04$;  $D_{60°}/(a/V) = 329b/V + 0.04$;  $- \Delta H = 1.5$ kg.-cals./g.-mol.

Diphenylmethane.  $T_1 = 25°$;  $T_2 = 60°$  $a/V = 0.4425$ g.-mol./l.

| | | | | | |
|---|---|---|---|---|---|
| $b/V$ .............. | 0.051 | 0.102 | 0.203 | 0.254 | 0.305 |
| $D_{25°}$ .............. | 0.236 | 0.458 | 0.854 | 1.068 | 1.312 |
| $D_{60°}$ .............. | 0.216 | 0.399 | 0.730 | 0.963 | 1.158 |
| $D_{25°}/(a/V)$ ...... | 0.533 | 1.035 | 1.931 | 2.413 | 2.966 |
| $D_{60°}/(a/V)$ ...... | 0.488 | 0.902 | 1.650 | 2.176 | 2.622 |

$D_{25°}/(a/V) = 9.52b/V + 0.02$;  $D_{60°}/(a/V) = 8.65b/V + 0.02$;  $- \Delta H = 0.5$ kg.-cal./g.-mol.

Triphenylmethane.  $T_1 = 25°$;  $T_2 = 60°$;  $a/V = 0.4125$ g.-mol./l.

| | | | | | | |
|---|---|---|---|---|---|---|
| $b/V$ .............. | 0.0168 | 0.0338 | 0.0506 | 0.0675 | 0.0844 | 0.1161 |
| $D_{25°}$ .............. | 0.184 | 0.353 | 0.498 | 0.689 | 0.851 | 1.161 |
| $D_{60°}$ .............. | 0.172 | 0.323 | 0.454 | 0.602 | 0.757 | 1.050 |
| $D_{25°}/(a/V)$ ...... | 0.446 | 0.857 | 1.208 | 1.671 | 2.065 | 2.817 |
| $D_{60°}/a/V$ ......... | 0.417 | 0.784 | 1.102 | 1.461 | 1.837 | 2.548 |

$D_{25°}/(a/V) = 24.25b/V + 0.22$;  $D_{60°}/(a/V) = 21.53b/V + 0.03$;  $- \Delta H = 0.66$ kg.-cal./g.-mol.

Ethylbenzene.  $T_1 = 25°$;  $T_2 = 60°$;  $a/V = 0.3540$ g.-mol./l.

| | | | | | |
|---|---|---|---|---|---|
| $b/V$ .............. | 0.060 | 0.120 | 0.180 | 0.241 | 0.301 |
| $D_{25°}$ .............. | 0.222 | 0.440 | 0.645 | 0.86 | 1.05 |
| $D_{60°}$ .............. | 0.186 | 0.380 | 0.551 | 0.698 | 0.90 |
| $D_{25°}/(a/V)$ ...... | 0.627 | 1.24 | 1.82 | 2.43 | 3.05 |
| $D_{60°}/(a/V)$ ...... | 0.525 | 1.07 | 1.56 | 1.97 | 2.54 |

$D_{25°}/(a/V) = 10.10b/V + 0.01$;  $D_{60°}/(a/V) = 8.33b/V + 0.04$;  $- \Delta H = 1.08$ kg.-cals./g.-mol.

*iso*Propylbenzene.  $T_1 = 25°$;  $T_2 = 60°$;  $a/V = 0.4125$ g.-mol./l.

| | | | | | | |
|---|---|---|---|---|---|---|
| $b/V$ .............. | 0.0488 | 0.0975 | 0.1464 | 0.1972 | 0.2440 | 0.2928 |
| $D_{25°}$ .............. | 0.159 | 0.300 | 0.430 | 0.549 | 0.713 | 0.861 |
| $D_{60°}$ .............. | 0.145 | 0.252 | 0.355 | 0.456 | 0.619 | 0.698 |
| $D_{25°}/(a/V)$ ...... | 0.386 | 0.728 | 1.041 | 1.332 | 1.730 | 2.088 |
| $D_{60°}/(a/V)$ ...... | 0.352 | 0.611 | 0.902 | 1.109 | 1.502 | 1.693 |

$D_{25°}/(a/V) = 6.97b/V + 0.02$;  $D_{60°}/(a/V) = 5.68b/V + 0.05$;  $- \Delta H = 1.15$ kg.-cals./g.-mol.

*tert.*-Butylbenzene.  $T_1 = 25°$;  $T_2 = 60°$;  $a/V = 0.3540$ g.-mol./l.

| | | | | | | |
|---|---|---|---|---|---|---|
| $b/V$ .............. | 0.046 | 0.092 | 0.137 | 0.183 | 0.229 | 0.275 | 0.321 |
| $D_{25°}$ .............. | 0.255 | 0.457 | 0.668 | 0.90 | 1.08 | 1.29 | 1.48 |
| $D_{60°}$ .............. | 0.215 | 0.400 | 0.583 | 0.754 | 0.94 | 1.10 | 1.28 |
| $D_{25°}/(a/V)$ ...... | 0.720 | 1.292 | 1.888 | 2.544 | 3.052 | 3.644 | 4.200 |
| $D_{60°}/(a/V)$ ...... | 0.607 | 1.13 | 1.65 | 2.13 | 2.66 | 3.11 | 3.62 |

$D_{25°}/(a/V) = 13.07b/V + 0.07$;  $D_{60°}/(a/V) = 10.98b/V + 0.10$;  $- \Delta H = 0.98$ kg.-cal./g.-mol.

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TABLE II.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| (a) { | $C_6H_6$ 0·4 | $C_6H_5Me$ 7·7 | $C_6H_4Me_2$ 55* | $s\text{-}C_6H_3Me_3$ 180 | $1:2:4:5\text{-}C_6H_2Me_4$ 226 | $C_6HMe_5$ 308 | $C_6Me_6$ 430 |
| (b) { | $C_6H_6$ 0·4 | $C_6H_5Me$ 7·7 | $C_6H_5Et$ 10·10 | $C_6H_5Pr^\beta$ 6·97 | $C_6H_5Bu^\gamma$ 13·07 | $CH_2Ph_2$ 9·52 | $CHPh_3$ 24·25 |

* Mean for *o*-, *m*-, and *p*-xylene.
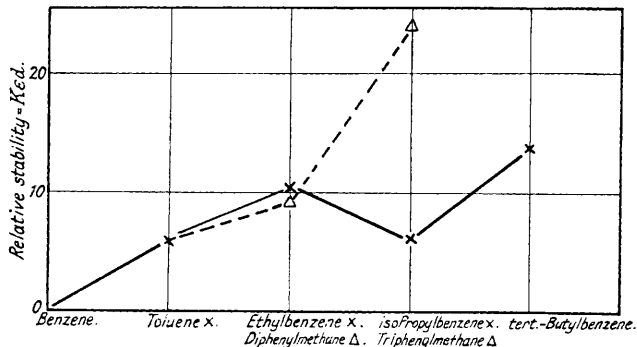


If the reasons we have given for the view that ε does not vary much throughout the series are valid, it appears that the stability of the coloured complexes resulting from the interaction of tetranitromethane with these hydrocarbons increases steadily as the number of methyl groups increases.

The effect on stability of successive replacement by methyl groups of the side-chain hydrogens in toluene is, however, different. As is shown in Table II(*b*) and the figure, stability increases from benzene through toluene to ethylbenzene, falls with *iso*-propylbenzene and rises again at *tert.*-butylbenzene. On the other hand, each successive phenyl group introduced into the methyl group of toluene increases stability.

It is generally agreed that the part played by the hydrocarbon in forming complexes with polynitro-compounds is that of an anionoid reagent or electron donor. It therefore seem reasonable to connect the increased stability of the complexes of the methylated benzenes with the increase in anionoid reactivity that the nucleus might be expected to derive from successive replacements of hydrogen atoms by the electron-repelling ($+ I$) methyl groups. Replacement of the hydrogen atoms in the toluene side chain by successive methyl groups might *a priori* be expected to produce a similar though less marked effect. The drop in stability on passing from ethyl- to *iso*propyl-benzene implies therefore that the side-chain methylation of toluene not only increases the anionoid character of the nucleus but also has some other effect that lessens the stability of the tetranitromethane complexes. In other words, the anomalous effects of the substitution of methyl groups for alkyl hydrogen atoms observed in other fields (*e.g.*, Hughes and Ingold, J., 1935, 244; Baker and Nathan, *ibid.*, p. 1844) appear to be manifested on the decomposition side of the nitro-compound–aromatic hydrocarbon interaction. Further, in this connexion we may mention that analogous abnormalities in stability have been detected by preliminary experiments in the picric acid–aromatic hydrocarbon series.