Interaction between Polynitro-compounds and Aromatic Hydrocarbons and Bases. Part XIV. Stabilities of Some Solid Complexes of Trinitrobenzene and Trinitrotoluene.*

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The relative stabilities of some solid complexes of 1 : 3 : 5-trinitrobenzene and of 2 : 4 : 6-trinitrotoluene with various aromatic hydrocarbons have been investigated by measuring the concentration of trinitrobenzene or trinitrotoluene in aqueous solution in equilibrium with the complex. Values of the free energy of formation of the complexes from their parent solids are derived.

THE equilibrium concentration of picric acid obtained when solid naphthalene picrate and other hydrocarbon picrates are shaken with excess of hydrocarbon in water has been used as a measure of the stability of the solid hydrocarbon picrates (Behrend, *Z. physikal. Chem.*, 1894, **15**, 183; Brönsted, *ibid.*, 1911, **78**, 284; Dimroth and Bamberger, *Annalen*, 1924, **438**, 67; Bell and Fendley, *Trans. Faraday Soc.*, 1949, **45**, 121). Values of the free energy of formation of naphthalene picrate obtained from measurements by Brönsted (*loc. cit.*) and by Bell and Fendley (*loc. cit.*) are in agreement with cryoscopic measurements (Brown, *J.*, 1925, **127**, 345). In the analogous systems of the trinitrobenzene and trinitrotoluene complexes the concentrations of trinitrobenzene (TNB) and of trinitrotoluene (TNT) so obtained are very much less than in the case of picric acid, but correspond in the same way to the stabilities of the hydrocarbon–polynitro-compound complexes, the more stable complex giving rise to the smaller concentration of TNB or TNT in solution.

EXPERIMENTAL

Materials.—The hydrocarbons were obtained from laboratory sources and were purified by recrystallization from ethanol. We are indebted to Dr. J. K. Marsh for a specimen of spectroscopically pure anthracene. 1 : 3 : 5-Trinitrobenzene was obtained as pale cream-coloured

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rhombs by recrystallization from ethanol [m. p. 121° (corr.)]; 2 : 4 : 6-trinitrotoluene was recrystallized from ethanol [m. p. 82° (corr.)]. Complexes were made by mixing hot solutions of the components and allowing them to cool. The m. p.s of the complexes so prepared agree with accepted values, where these are known.

Estimation of Trinitrobenzene.—Lobry de Bruyn and van Leent (*Rec. Trav. chim.*, 1895, **14**, 150) found that solutions of trinitrobenzene gave with strong alkali an orange-red colour, and this has been used as a basis for its colorimetric estimation in aqueous solution. The concentration of an unknown solution was determined by adding to it an equal volume of N-potassium hydroxide and comparing the colour so produced with the colour developed by a standard solution of trinitrobenzene of similar concentration treated in the same way. The colours were compared in a DuBosq colorimeter. The colours so produced are liable to slow fading, but by preparing coloured solutions from the unknown and the known solutions simultaneously the effect of fading was eliminated and reproducible estimations obtained.

Estimation of Trinitrotoluene.—2-Diethylaminoethanol in the presence of acetone develops a colour with aqueous solutions of trinitrotoluene (Golding and Rushman, *J. Ind. Hyg.*, 1943, **25**, 164). The concentration of an unknown solution was determined by adding to it an equal volume of a solution of diethylaminoethanol (5 g.) in acetone (100 c.c.) and comparing (DuBosq) the colour so produced with that developed by a standard solution of trinitrotoluene of similar concentration treated in the same way. When the aqueous trinitrotoluene and the reagent solution are first mixed, a purple colour is produced, which changes in about 10 min. to a red colour. This persists for 24 hr., but the comparison of the colours of the unknown and the standard solution was made 30 min. after the solutions were mixed.

Procedure.—A complex (*ca.* 0·2 g.) and its parent hydrocarbon (*ca.* 0·2 g.) were sealed into an ampoule containing distilled water (*ca.* 15 c.c.). Ampoules were rotated end-over-end in a thermostat at 25·0° until the solutions attained equilibrium; as this process was slow, measurements on a given system were repeated at intervals of about a week until consistent results were obtained; their consistency and reproducibility indicate that true equilibria were in fact established. The aqueous solution (5 c.c.) was removed from the ampoule by suction through a glass-wool filter, and either suitably diluted or used direct in the colorimetric estimation. The solubility of trinitro-benzene and -toluene was measured analogously.

RESULTS AND DISCUSSION

The results are collected in the Table in order of increasing stability of the trinitrobenzene complex. The order of stability follows directly from the decreasing concentrations of nitro-compound (c_2, g./l.). Values of the free energy of formation ($\Delta G°$, kcal./mole) are determined from the relation $\Delta G° = \boldsymbol{R}T \ln c_2/c_1$, where c_1 (g./l.) is the solubility of the nitro-compound and c_2 is the concentration thereof in equilibrium with solid complex and solid hydrocarbon. The assumption is made that the solutions are sufficiently dilute for activities to be proportional to concentrations.

Stabilities of solid polynitro-compound–hydrocarbon complexes at 25·0°.

	1 : 1 TNB Complexes			1 : 1 TNT Complexes		
Parent hydrocarbon	M. p.	c_2	$\Delta G°$	M. p.	c_2	$\Delta G°$
Anthracene	162°	0·100	−0·84	(*a*) 159°	0·107	−0·14
Durene	101	0·099	−0·84	(*b*)		
Fluorene	105	0·091	−0·89	89	0·034	−0·83
Hexamethylbenzene	173	0·043	−1·34	(*c*) 123	0·085	−0·28
Pentamethylbenzene	119	0·0279	−1·59	(*c*) 81	0·045	−0·66
Acenaphthene		(*d*)		111	0·0151	−1·30
Naphthalene	152	0·0114	−2·08	97	0·0123	−1·43
Phenanthrene	164	0·0070	−2·41	102	0·0142	−1·34
2-Methylnaphthalene	123	0·0062	−2·48	(*c*) 74	0·0079	−1·69
Fluoranthene	204	0·0030	−2·91	132	0·0096	−1·57
1 : 3 : 5-Trinitrobenzene		c_1 = 0·404 (*e*)				
2 : 4 : 6-Trinitrotoluene					c_1 = 0·135 (*f*)	

(*a*) Incongruent m. p. (*b*) Durene–TNT complex is not stable. (*c*) These substances have not been previously reported, but they have not been fully characterised in this work. (*d*) Equilibrium was not attained in this system. (*e*) Lobry de Bruyn and van Leent (*loc. cit.*) report 0·40 g./l. (*f*) Taylor and Rinkenbach (*J. Amer. Chem. Soc.*, 1923, **45**, 47) report 0·120 g./l. at 20·0°.

Dimroth and Bamberger (*loc. cit.*) found a similar sequence for the stabilities of solid hydrocarbon picrates at 24·1°, *viz.*, benzene<fluorene<anthracene<indene<naphthalene<1-<2-methylnaphthalene. Bell and Fendley (*loc. cit.*) found for naphthalene picrate $\Delta G^\circ = -2{\cdot}075$ kcal./mole, which is very close to the value (—2·08) found here for the naphthalene–trinitrobenzene complex. This leads to the conclusion that there is no very great difference in the stability of the solid picrates and the corresponding trinitrobenzene derivatives, while the trinitrotoluene derivatives are rather less stable (naphthalene TNT, $\Delta G^\circ = -1{\cdot}43$ kcal./mole).

The free energies of formation obtained by this method refer to the reaction $\mathrm{M_{cryst.}} + \mathrm{N_{cryst.}} = \mathrm{MN_{cryst.}}$ and are therefore distinct from the free energies of formation (or equilibrium constants) determined by various methods involving equilibrium in solution, as these depend on the interaction of the species in solution with the solvent molecules. Nevertheless certain parallels can be found. Moore, Shepherd, and Goodall (*J.*, 1931, 1447) found naphthalene picrate less stable than 2-methylnaphthalene picrate, and Anderson and Hammick (*J.*, 1950, 1089) found durene picrate less stable than hexamethylbenzene picrate. These relative stabilities are paralleled in both the trinitrobenzene and the trinitrotoluene derivatives in the solid state.

The facts that the order of the stabilities is broadly similar for the three series of nitro-compounds, and that the values of the free energy of formation of the three derivatives of naphthalene are of the same order of magnitude, indicate that the same sort of molecular interaction is operative in all cases. Individual discrepancies, *e.g.*, the near equality of the stabilities of the trinitrobenzene and the trinitrotoluene derivatives of fluorene, or the inversion of the relative stabilities of naphthalene and phenanthrene in the two series here examined may be attributable to differences of packing of the molecules in the crystals.

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