22. *Compound Formation between Nitrobenzenes.*

By Dalziel Llewellyn Hammick, Leslie W. Andrew, and John Hampson.

Although stable compounds between aromatic hydrocarbons and aromatic nitro-compounds are numerous and well known, compound formation between aromatic nitro-derivatives themselves

has apparently not been noticed hitherto. The observation, however, that a faint though definite colour change occurs on mixing pure nitrobenzene with pure molten *m*-dinitrobenzene led us to investigate solid–liquid equilibria in the system. The discovery of a stable solid phase of the composition $C_6H_5{\cdot}NO_2,C_6H_4(NO_2)_2$, with an incongruent m. p. at about 26°, suggested the possibility that similar compounds might be formed between other nitrobenzenes. We have accordingly also examined the systems nitrobenzene–*s*.-trinitrobenzene, *m*-dinitrobenzene–*s*.-trinitrobenzene, and nitrobenzene–trinitrotoluene. In the first of these we find a compound of the composition $2C_6H_5{\cdot}NO_2,C_6H_3(NO_2)_3$, having a congruent m. p. at about 67°. The melting-point curves for the last two systems show no indication of the existence of stable solid complexes.

Experimental.

Temperatures of solid–liquid equilibria in the various systems were determined by the synthetic method, weighed quantities of the carefully purified components being sealed in bulb tubes, and the temperatures $T°$ at which the last trace of solid phase disappeared being observed in a variable thermostat.

Table I.

Nitrobenzene (M.N.B.) (*m. p.* 5·7°)–m-*dinitrobenzene* (D.N.B.).

T.	D.N.B., mols. %.		*T*.	D.N.B., mols. %.	
8·5°	9·46	Solid phase = complex $C_6H_5{\cdot}NO_2,C_6H_4(NO_2)_2$.	26·5°	33·09	Solid phase = $C_6H_4(NO_2)_2$.
19·0	18·45		31·0	35·25	
21·5	23·31		32·0	36·00	
22·5	24·98		46·5	46·43	
23·5	26·93		56·0	54·79	
24·5	29·43		69·5	69·55	
25·7	31·64		91·0	100·0	

The results are recorded in Table I and plotted in Fig. 1; they clearly indicate the existence of a compound with an incongruent m. p. at about 26°.

Owing to the absence of a congruent m. p. and the flatness of the curve where the compound is the solid phase, it is not possible to determine the composition of the compound from the diagram. A mixture of nitrobenzene and *m*-dinitrobenzene melting at about 24° was therefore made, and allowed to cool to room temperature. The solid phase that separated was rapidly filtered off at the pump and pressed on a porous tile for a few minutes. A portion was then added to a weighed amount of *m*-dinitrobenzene in a weighed bulb tube, the whole being again weighed and sealed. The "melting point" (temperature at which the last trace of solid just disappeared) of the mixture was found as before, and the composition

of the mixture in the bulb read off from the diagram. Thus 0·6925 g. of compound added to 0·6215 g. of *m*-dinitrobenzene gave a mixture melting at 70·0°, which corresponds to 70·0 mols. % of *m*-dinitrobenzene. From this result we find that the compound contains 47·0 mols. % of *m*-dinitrobenzene. In a second experiment, a specimen of the solid phase separating at room temperature was pressed on a porous tile, sealed in a bulb tube and found to melt at 47·5°, which from the diagram corresponds to a composition of

FIG. 1.

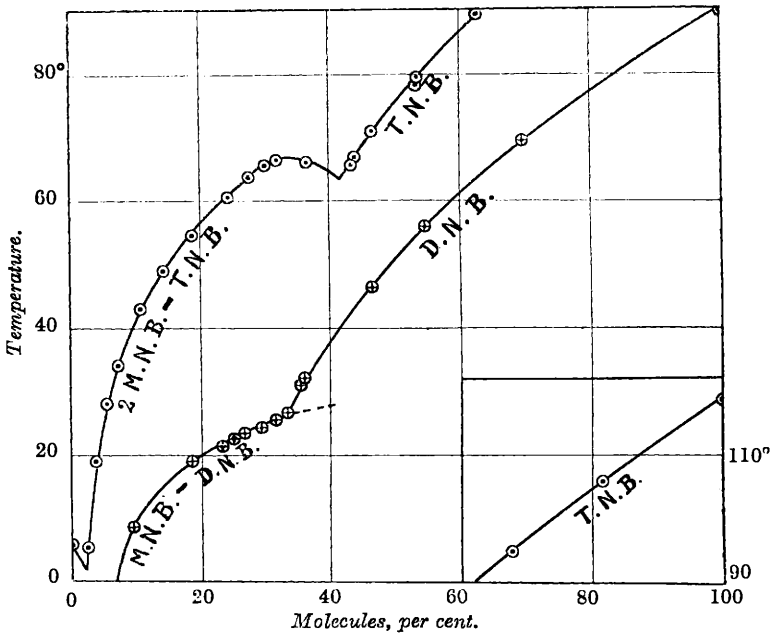

TABLE II.

Nitrobenzene (M.N.B.)–s.-*trinitrobenzene* (T.N.B.).

T.	T.N.B., mols. %.		*T.*	T.N.B., mols. %.	
5·5°	2·52	Solid phase = $C_6H_5 \cdot NO_2$.	65·5°	43·44	Solid phase = $C_6H_3(NO_2)_3$.
19·0	3·79	Solid phase = compound $2C_6H_5 \cdot NO_2, C_6H_3(NO_2)_3$.	67·0	43·92	
26·0	5·06		71·0	46·65	
28·0	5·40		78·0	53·27	
34·0	7·20		79·5	53·59	
43·0	10·85		89·5	62·92	
49·0	14·31		95·0	67·76	
54·5	18·74		106·0	81·56	
60·5	24·22		121·0	100·00	
63·5	27·47				
65·5	29·95				
66·3	32·04				
66·0	37·71				

47·5 mols. % of *m*-dinitrobenzene. There is thus no doubt that the compound is equimolecular, $C_6H_5{\cdot}NO_2,C_6H_4(NO_2)_2$, the slightly higher percentage of nitrobenzene being due to incomplete removal of liquid phase by the porous tile.

The above data for nitrobenzene and trinitrobenzene (Table II) are plotted in Fig. 1 and show clearly the existence of a solid phase with a congruent m. p. at about 66° and having the composition $2C_6H_5{\cdot}NO_2,C_6H_3(NO_2)_3$.

TABLE III.

Nitrobenzene (M.N.B.)–*trinitrotoluene* (T.N.T.).

T.	T.N.T., mols. %		*T.*	T.N.T., mols. %	
5·7°	0·00	Solid phase = $C_6H_5{\cdot}NO_2$.	44·0°	42·56	Solid phase = $C_7H_5(NO_2)_3$.
2·0	6·86		49·0	47·62	
2·75	13·95	Solid phase = $C_7H_5(NO_2)_3$.	53·0	52·61	
15·5	20·54		56·5	57·45	
22·5	24·51		60·5	63·72	
30·5	29·91		67·0	74·03	
37·5	36·22		81·0	100·00	

TABLE IV.

m-*Dinitrobenzene*–s.-*trinitrobenzene* (T.N.B.).

T.	T.N.B., mols. %		*T.*	T.N.B., mols. %	
91·0°	0·00	Solid phase = $C_6H_4(NO_2)_2$.	62·5°	44·3	Solid phase = $C_6H_3(NO_2)_3$.
86·2	7·3		63·7	44·5	
74·2	25·5		64·5	45·8	
69·2	31·5		69·0	48·6	
68·0	33·8		71·0	50·0	
66·8	34·0		71·3	50·5	
65·0	36·0		79·0	55·3	
62·0	39·7		91·0	65·2	
62·4	40·0		94·8	69·4	
61·9	41·0		97·0	72·2	
			104·0	79·2	
			121·0	100·0	

The results of Tables III and IV when plotted show no indication of the existence of any stable solid complex.

Summary.

Solid–liquid equilibria have been investigated in the systems nitrobenzene–*m*-dinitrobenzene, nitrobenzene–*s*.-trinitrobenzene, *m*-dinitrobenzene–*s*.-trinitrobenzene, and nitrobenzene–trinitrotoluene. In the first of these systems a compound $C_6H_5{\cdot}NO_2,C_6H_4(NO_2)_2$, with an incongruent m. p. at about 26° has been found; in the second, the compound $2C_6H_5{\cdot}NO_2,C_6H_3(NO_2)_3$, m. p. *ca.* 66°, has been obtained. No solid compounds apparently exist in the last two systems.

THE DYSON PERRINS LABORATORY,
OXFORD.

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