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SOLID GAS REACTION OF HYDRAZOBENZENE WITH METHYL IODIDE

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Summary: Solid-gas reactions are used as a new approach to the study of solvolysis reactions. The reaction of solid hydrazobenzene with gaseous methyl iodide yields a different product distribution from the solution reaction and the possible mechanisms of these reactions are discussed.

Earlier we attempted to prepare hydrazobenzene dihydroiodide from solvolysis of hydrazobenzene in methyl iodide as Pongratz reported[1]; instead we isolated phenylammonium iodide and azobenzene as major products, as well as a small amount of trimethylphenylammonium iodide and other products[2]. We suspected that the final products resulted from the further reactions of initial products such as $PhNCH_3NHPh$, $PhNCH_3NCH_3Ph$, $PhNH_2$, $PhNHCH_3$ and I_2. However, the solvolysis reaction has been stopped at an early stage but unsatisfactory results were obtained. Since it is known that the solid state reactions are often unique due to crystal packing[3], and in most cases the reaction in solid state is slower than the corresponding reaction in solution. We report the application of solid gas reactions to the study of the solvolysis of hydrazobenzene in methyl iodide.

No significant amount of the suspected initial products can be found during or after reaction of solid hydrazobenzene with methyl iodide vapor. The reaction was run at room temperature, room light and in air for 10 days and during the reaction the solid became slightly wet and orange brown in color. Reaction of this solid with ammonia gas gave aniline, N-methylaniline, N,N-dimethylaniline, azobenzene and trimethylphenylammonium iodide. While extraction of this solid with water gave a mixture of phenylammonium iodide, N-methylphenylammonium iodide and trimethylphenylammonium iodide, the extracted residue consisted of azobenzene, a small amount of iodine complex with N-substituted phenylammonium iodide and unidentified compound (∿4%). The results are shown in Table 1.

Apparently the solid gas reaction gives a different product distribution from that solution. This might indicate that the different mechanisms are operative. First of all, $PhNHNCH_3Ph$ and $PhNCH_3NCH_3Ph$ do not play a major role in these reactions since they are less reactive than PhNHNHPh which we studied earlier[2]. In addition no significant amount of them is found. The different product distributions in the solid state and in solution can be rationalized in terms of two different pathways. We suggest that in solution, the major route leading to the products aniline and azobenzene is the same as that used to explain the

Table 1

Reaction of Hydrazobenzene with Methyl Iodide

Reaction conditions and reaction time	Yield % of Products Formed					
	$Ph\overset{+}{N}H_3I^-$	$Ph\overset{+}{N}H_2CH_3I^-$	$Ph\overset{+}{N}(CH_3)_2I^-$	$Ph\overset{+}{N}(CH_3)_3I^-$	$Ph\overset{+}{N}(CH_3)_3I_3^-$	PhN=NPh
CH_3I solution for 4 days[8c]	46.2	<1.0	<1.0	23.8	1.7	27.0
Gas solid for 10 days	30.7	17.5	18.7	6.2	2.6	18.6

disproportionation reaction which accompanies the benzidine rearrangement (equation 1)[4].

$$2\ PhNHNHPh \longrightarrow PhN{=}NPh + 2\ PhNH_2 \qquad (1)$$

Further reaction of aniline with methyl iodide solvent gives phenylammonium iodide and trimethyl-phenylammonium iodide (equation 2)

$$3\ PhNH_2 + 3\ CH_3I \longrightarrow 2\ Ph\overset{+}{N}H_3I^- + Ph\overset{+}{N}(CH_3)_3I^- \qquad (2)$$

calcd. product ratio:	2	1
Found:[8a] aniline in methyl iodide solution (4 days)	2.3	1
Found:[8b] aniline with methyl iodide vapor (10 days)	2.3	1

This suggestion is supported by the fact that the reaction of aniline in methyl iodide solution gives the same products but in somewhat different mole ratio as shown under equation (2), the mole ratio obtained from solvolysis, $Ph\overset{+}{N}H_3I^-/PhN{=}NPh$ is 1.4 (calcd. 1.3) and $Ph\overset{+}{N}H_3I^-/Ph\overset{+}{N}(CH_3)_3I^- + Ph\overset{+}{N}(CH_3)_3I_3^-$ is 2.2 (calcd. 2.0), both approximate to the theoretical value.

Furthermore the fact that no significant amount of $Ph\overset{+}{N}H_2CH_3I^-$ and $Ph\overset{+}{N}H(CH_3)_2I^-$ is formed gives more evidence to support the above suggestion. Similar N-N bond cleavage of N-substituted hydrazobenzene in liquid SO_2 [5] and acetonitrile[6] leading to amines has been reported. An intermediate cation radical is probably involved in the solvolysis of hydrazobenzene in methyl iodide.

There is an alternate way to obtain similar products which we believe is not a major pathway. The reaction of iodine with hydrazobenzene in ether solution gives $Ph\overset{+}{N}H_3I^-$ and $^-IH_3\overset{+}{N}PhPh\overset{+}{N}H_3I^-$ in a 4:1 ratio and an equivalent amount of azobenzene. However, no significant amount of $^-IH_3\overset{+}{N}PhPh\overset{+}{N}H_3I^-$ was found in the solvolysis reaction. We cannot rule out the possibility that a small amount of iodine is present which could serve as an initiator. In addition it should be noted that iodine will react quickly with $Ph\overset{+}{N}H(CH_3)_2I^-$ or $Ph\overset{+}{N}H_2CH_3I^-$ to form a liquid complex and with $Ph\overset{+}{N}(CH_3)_3I^-$ to form a solid complex.

In the solid gas reaction, besides the same major products as in solution there are significant amounts of $Ph\overset{+}{N}H(CH_3)_2I^-$ and $Ph\overset{+}{N}H_2CH_3I^-$. We suggest that the major route leading to products is according to equation (3) or related reactions.

$$2\ PhNHNHPh + CH_3I \longrightarrow PhNHCH_3 + Ph\overset{+}{N}H_3I^- + PhN{=}NPh \qquad (3)$$

Further reaction of N-methylaniline with methyl iodide occurs according to equation (4) to give three products

$$3\ PhNHCH_3 + 3\ CH_3I \qquad Ph\overset{+}{N}H(CH_3)_2I^- + Ph\overset{+}{N}H_2CH_3I^- + Ph\overset{+}{N}(CH_3)_3I^- \qquad (4)$$

Calcd. product ratio:	1.0	:	1.0	:	1.0
Found:[8a] N-methylaniline in methyl iodide (4 days)	1.7	:	1.4	:	1.0
Found:[8b] N-methylaniline with methyl iodide vapor (10 days)	3.3	:	1.0	:	1.0

The reactions of N-methylaniline in methyl iodide or with methyl iodide vapor have been found to give the same products but in a somewhat different mole ratio as shown under equation (4).

The mole ratios obtained from the solid gas reaction are: $Ph\overset{+}{N}H_3I^-/PhN{=}NPh$, 1.2 (calcd. 1.0); $Ph\overset{+}{N}H(CH_3)_2I^-/Ph\overset{+}{N}H_2CH_3I^-$, 1.0 (calcd. 1.0); and $Ph\overset{+}{N}H_3I^-/Ph\overset{+}{N}(CH_3)_3I^- + Ph\overset{+}{N}(CH_3)_3I_3^-$, 4.8 (calcd. 3).

The nature of the solid gas reaction seems more complicated than the solution reaction. From the limited data at hand now we can only assume that the initial addition of methyl iodide to hydrazobenzene leads to the intermediate $Ph\overset{+}{N}HCH_3NHPhI^-$. A similar intermediate has been suggested by Shine[6] to explain the formation of N-methylaniline from the acid-catalyzed benzidine rearrangement,

$$Ph\overset{+}{N}HCH_3NCH_3Ph \longrightarrow PhNHCH_3 + Ph\overset{+}{N}CH_3$$

and also by Lukashevich[7a] to interpret the formation of phenylammonium chloride from hydrazobenzene hydrochloride.

$$2\ Ph\overset{+}{N}H_2NHPhCl^- \longrightarrow 2\ Ph\overset{+}{N}H_3Cl^- + PhN{=}NPh$$

On the other hand the same intermediate[7b] has been reported in the low $[H^+]$ catalyzed rearrangement of $PhNCH_3NHPh$ to lead to rearrangement products, thus the solvent may link these different mechanisms and cause changes from one to another.

Finally the solvent effect on the methyl iodide reaction was examined, the reactions of hydrazobenzene with two equivalent amounts of methyl iodide were carried out in benzene solution, ether solution and methanol solution, respectively. The former two solutions give the same products as in methyl iodide solution, but the methanol solution gives besides the solution reaction products, solid gas reaction products and also benzidine rearrangement products. In conclusion, the solid gas reaction demonstrates that the solid state reaction would provide an elegant approach to study the facile solution reaction.

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8. a) 5 drops of amine was added into 5 ml of methyl iodide
   b) Amine was absorbed in paper to react with methyl iodide vapor
   Vary reaction time might give different product distributions.
   c) Reaction of hydrazobenzene (1g) with methyl iodide (10ml) at room temperature, room light and in air.

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