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Reaction of 4-Nitrobenzenesulfenamide with Liquid Ammonia

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SHORT COMMUNICATION

Reaction of 4-Nitrobenzenesulfenamide with Liquid Ammonia

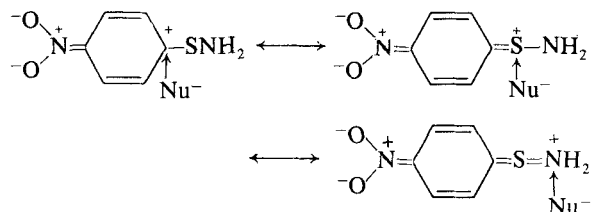
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Although numerous investigations on the chemistry of organic sulfenamides, for example, studies on the S-N torsional barrier,¹ the electronic nature of the S-N bond² and some nucleophilic substitutions on sulfur or nitrogen atom³ have been known, no example of nucleophilic substitution on arylcarbon of aromatic sulfenamides has been reported.

4-Nitrobenzenesulfenamide (1) possesses the following three potential reaction centers in the nucleophilic substitution.



When the sulfenamide (1) was treated with liquid ammonia at a relatively low temperature such as 30°C in a titanium autoclave, we obtained 4-nitroaniline (2) which is a product of the nucleophilic substitution on arylcarbon, besides such other products as 4,4'-dinitrodiphenyldisulfide (3), 4-nitrobenzenethiol (4) and 4-nitrobenzenethiosulfenamide (5), another interesting compound. The yields of the products of this reaction, determined by the nmr proton intensities of the products at a few intervals, are shown in the Table.

A few characteristic features of the data in the Table are following. (1) There is an induction period in this reaction; i.e., as illustrated in Run 1-4, the sulfenamide (1) did not react until *ca.* 90 min. and in Run 5, until 100 min. (2) The induction period shortened even at a lower temperature, 40°C, than in Run 1-4 when the substrate concentration was high as shown by Run 6. (3) The reaction seems to be

self-catalyzed. Once the reaction was initiated after a long induction period, the sulfenamide (1) disappeared within a short period, *ca.* 30 min. (4) 4-Nitrobenzenethiol (4) or 4,4'-dinitrodiphenyldisulfide (3) displays some catalytic activity in the reaction of the sulfenamide (1) with liquid ammonia, i.e., as illustrated in Run 8-9.⁴

These observations suggest that the reaction is not an unimolecular reaction of the sulfenamide (1), because the reaction has an induction period and depends on the substrate concentration. Thus, 4-nitroaniline (2) does not seem to be formed by the direct substitution of the sulfenamide group on arylcarbon of the sulfenamide (1) by ammonia, or by the intramolecular sulfur-extrusion reaction. Incidentally ordinary 4-nitroderivatives do not undergo such a facile nucleophilic substitution on arylcarbon at such a low temperature. For example, 4-nitrochlorobenzene and 4,4'-dinitrodiphenylsulfone do not react with liquid ammonia at such a low temperature.⁵

Since the reaction time is shortened by the increase of concentration of the original sulfenamide, the initial slow step of this reaction is considered to be the formation of the sulfonium intermediate by nucleophilic attack of sulfenyl sulfur

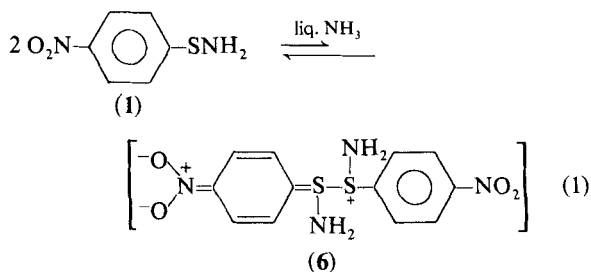


TABLE I
Reaction of 4-Nitrobenzenesulfenamide (1) with Liquid Ammonia

Run ^a	Reaction		Recovery Sulfenamide (%)	R-NH ₂	Products (%) ^b		
	Temp. (°C)	Time (min.)			R-SS-R	R-SSNH ₂ ^c	R-SH
1	60	120	100	—	—	—	—
2	60	150	25	30	31	10	4
3	60	180	—	49	31	4	8
4	60	240	—	62	22	8	8
5	40	240	100	—	—	—	—
6	40	240	2	35	7	45	10
7	30	120	—	50	—	44	6
8 ^d	20	120	58	14	28	—	72
9 ^e	20	120	67	20	3	—	10

^a Substrate concentration, Run 1–4: 0.08 mol/l, Run 5: 0.15 mol/l, Run 6: 0.23 mol/l, Run 7: 0.49 mol/l, Run 8–9: 0.13 mol/l.

^b Based on recovery % of benzene ring. R = p-O₂N-C₆H₄-.

^c Compound R-SSNH₂, mp. 86–88°C, S%: Found 32.0. Calcd. 31.7. nmr (CDCl₃) = 8.18 (2H, d, J = 9 Hz), 7.70 (2H, d, J = 9 Hz), 3.29 (2H, broad, NH₂).

^d In the presence of 0.13 mol/l of 4-nitrobenzenethiol.⁴

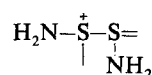
^e In the presence of 0.013 mol/l of 4-nitrobenzenethiol.⁴

of one sulfenamide on sulfonyl sulfur of one sulfenamide on sulfonyl sulfur of another sulfenamide (Eq. 1). This reaction would be quite slow, since the sulfonyl sulfur in the sulfenamide (1) would not be a good electron acceptor, although it would not be a bad nucleophile.

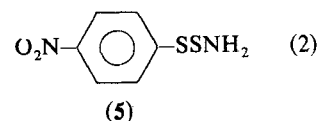
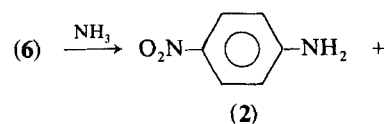
The dependence on the substrate concentration may be readily explained by this mechanism, which may also explain the occurrence of the induction period, since the induction period seems to be the time required to generate enough concentration of catalytically active species, such as 4-nitrobenzenethiol (4) or the disulfide (3).⁶

Once this sulfonium intermediate (6) is formed, its arylcarbon would be readily attacked by ammonia to give 4-nitroaniline (2) and 4-nitrobenzenethiosulfenamide (5), an interesting product, since both the 4-nitro group and another electron withdrawing

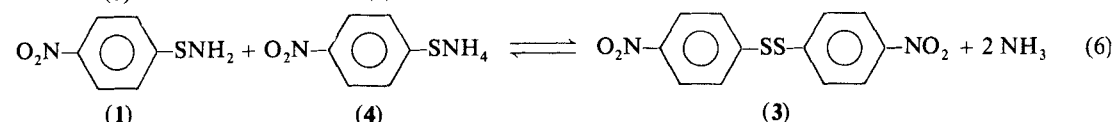
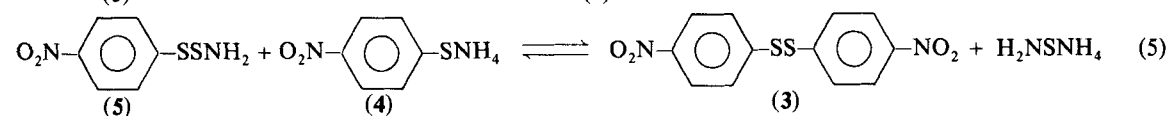
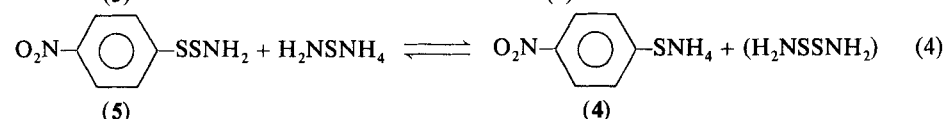
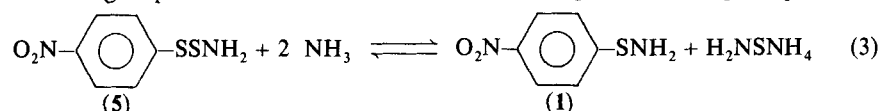
group i.e., the heterosulfonic group,



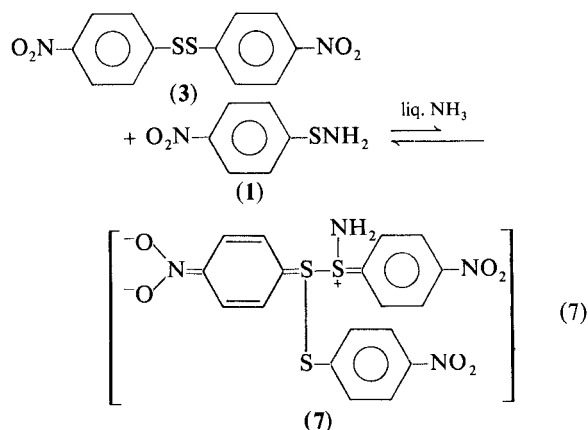
are activating the arylcarbon of the intermediate (6). (Eq. 2)



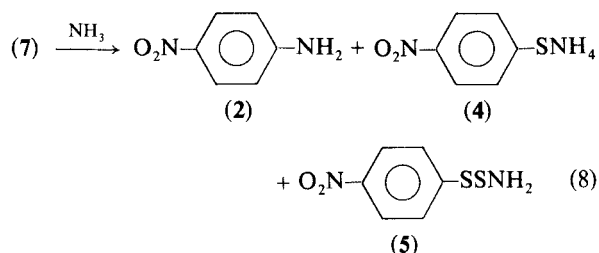
Subsequent possible reactions are as shown below.⁷



In this reaction, the self-catalytic reaction is illustrated by the Eqs. (3) and (6). The catalytic action of 4-nitrobenzenethiol (4) or 4,4'-dinitro-diphenyldisulfide (3) is illustrated by that 4-nitrobenzenethiol (4) reacts with the thiosulfenamide (5) and the sulfenamide (1) to give the disulfide (3) shown in Eqs. (5) and (6). It is considered that the nucleophiles may attack the sulfur atom of disulfide (3) more easily than the sulfur atom of the sulfenamide (1). Consequently, the sulfenamide (1) can react with the disulfide (3) to form the following sulfonium intermediate (7) (Eq. 7).



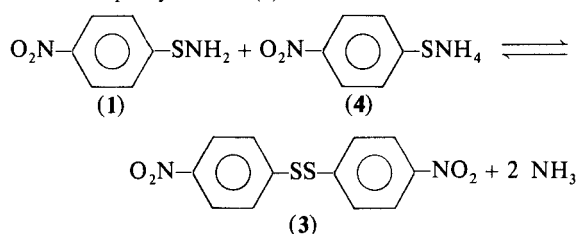
The sulfonium intermediate (7) also would react with ammonia rapidly to give the aniline (2), the thiol (4) and the thiosulfenamide (5) (Eq. 8).



All the reactions presented above were repeated and the results were found to be reproducible. The results given in the Table can be readily interpreted by the mechanism involving the sulfonium intermediate (7). Each of the reactions of Eq. 3–6 was confirmed by comparing the physicochemical behaviours with those of the authentic sample.⁷ In this work, we found a new nucleophile, H_2NSNH_4 , which could be obtained from S_8-NH_3 solution. Further detailed studies on it are now in progress.

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4. There is a following equilibrium between 4-nitrobenzenesulfenamide (1) with 4-nitrobenzenethiol (4) and 4,4'-dinitrodiphenyldisulfide (3).

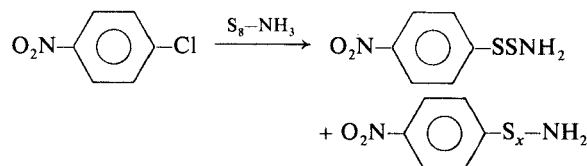


Therefore when 4-nitrobenzenethiol (4) was added into the reaction system, we are observing the catalytic activities of both the thiol and the disulfide.

5. The rate constants for the reaction of 4-nitrochlorobenzene and 4,4'-dinitrodiphenylsulfone with liquid ammonia were $1.52 \times 10^{-6}/\text{s}$. (at 100°C) and $4.52 \times 10^{-5}/\text{s}$. (at 80°C) respectively.
6. The referee has suggested that 4-nitroaniline (2) might be formed by direct substitution of ammonia on the disulfide (3), which is formed during the reaction, with concurrent formation of 4-nitrobenzenedisulfane, $\text{p-O}_2\text{NC}_6\text{H}_4\text{SSH}$. However, this reaction is quite unlikely in view of the scant reactivity of the more reactive 4-nitrochlorobenzene with liquid ammonia under the present reaction condition (see ref. 5). Preliminary experiments with the disulfide (3) indicate that the initial products of the reaction are only the expected sulfenamide (1) and 4-nitrobenzenethiol (4). Details of this reaction will be reported in future.
7. The species, H_2NSNH_4 , could be obtained from S_8-NH_3 solution as following.



K. M. Herlem and A. Thiebault, *Anal. Lett.* **6**, 171 (1973). Further, we could observe the following reaction.



R. Sato and S. Takizawa, Abstr. No. 1S01, 36th National Meeting of the Chemical Society of Japan, Osaka, April 1977.