

An Efficient Preparation of 4-Nitrosoaniline from the Reaction of Nitrobenzene with Alkali Metal Ureates

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ABSTRACT. This paper describes the synthesis of alkali metal salts of urea (ureates) and their application to the direct preparation of 4-nitrosoaniline from nitrobenzene *via* nucleophilic aromatic substitution of hydrogen. Sodium and potassium ureates were readily prepared from the reaction of urea with sodium hydride, metal methoxides, and metal hydroxides. The effect of ureates as nucleophiles on the conversion of nitrobenzene to 4-nitrosoaniline was investigated and compared with that of a urea-metal hydroxide mixture. It was found that the ureates were superior for producing 4-nitrosoaniline owing to their higher thermal stability of the ureate. The ureate obtained from the treatment of urea with sodium hydride gave the highest yield for the preparation of 4-nitrosoaniline. The ureates generated from the reaction of urea with metal hydroxide also gave high yields of 4-nitrosoaniline. Catalytic hydrogenation of 4-nitrosoaniline afforded polymer-grade 1,4-benzenediamine in quantitative yield.

Key words: 4-Nitrosoaniline, Ureate, Nitrobenzene, Urea, 1,4-Benzenediamine

INTRODUCTION

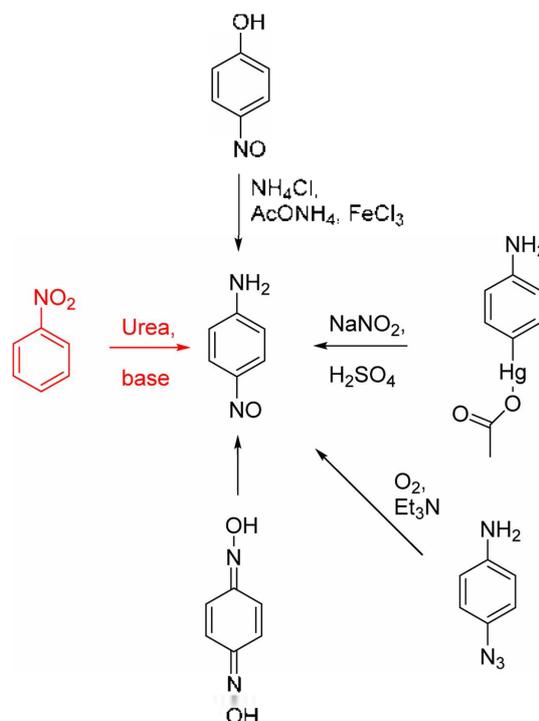
4-Nitrosoaniline and its derivatives find their applications as radical polymerization inhibitors, additives in the polymer processing, and as part of the vulcanization compounds in rubber processing.^{1,2} They can be also used as mediators in glucose monitoring devices.^{3,4} 4-Nitrosoaniline is also the precursor of other useful compounds, such as fluorescent dyes⁵ and 1,4-diaminobenzene.^{6,7} The latter material can be prepared from 4-nitrosoaniline by catalytic hydrogenation.

There are several ways to prepare 4-nitrosoaniline (*Scheme 1*). One of the ways is based on the reaction of 4-nitrosophenol and ammonium carbonate.⁸

The main drawback of this method is the thermal instability of 4-nitrosophenol as an intermediate. Safety measures must be taken to avoid an explosion. Another method using 1,4-quinonedioxime can be used, but it produces a low yield of 4-nitrosoaniline.⁹ 4-Nitrosoaniline can also be synthesized by the photolysis of 4-azidoaniline,¹⁰ or the treatment of mercury aniline with nitrosylsulfuric acid.¹¹ However, the former gives a low yield of both 4-nitrosoaniline and 4-nitroaniline, while the latter requires several steps to get 4-nitrosoaniline.

Development of the synthetic methods based on the nucleophilic aromatic substitution of hydrogen (NASH) process

opens further possibilities for the preparation of 4-nitrosoaniline from nitrobenzene.^{12,13} For example, the reaction of the amides with nitrobenzene in the presence of a base provides 65% yield of 4-nitrosoaniline accompanied with



Scheme 1. Synthetic routes of 4-nitrosoaniline.

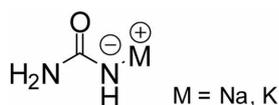


Figure 1. Structure of alkali metal ureates.

4-nitroaniline.¹⁴ The reaction of nitrobenzene with a mixture of urea and a base also gives up to 87% yield of 4-nitrosoaniline.^{15,16} In this last case, the reaction is performed by the semi-continuous addition of nitrobenzene to the mixture of urea and a base dissolved in a polar solvent at 90 °C.

However, it is generally known that urea decomposes in the presence of hydroxide to form ammonia and carbonate. The significant extent of the decomposition reaction reduces the efficiency of the process.^{14,15} It is therefore advantageous to replace the mixture of urea and a base with other reagents that are able to react with nitrobenzene to give 4-nitrosoaniline by the NASII mechanism, and not be decomposed to ammonia and carbonate during the reaction. The salts of urea (ureates) can be an alternative to the mixture of urea and a base (Fig. 1).

Ureates are distinguished by their high thermal stability of up to 120 °C.¹⁷ This feature is in distinct contrast to the instability of the equimolar mixture of urea and alkali hydroxide. Thus, this study examined the usefulness of alkali metal ureates as a reagent for preparing 4-nitrosoaniline by the NASH process.

Herein the detailed procedure for the preparation of thermally stable alkali metal ureates and the efficient route for the direct formation of 4-nitrosoaniline from nitrobenzene using the ureates is described.

EXPERIMENTAL

General

Commercially available reagents and anhydrous solvents were obtained from Sigma Aldrich Korea and the Tokyo Chemical Industry Co., Ltd., and were used without further purification. Xylene was used as a mixture of isomers. High performance liquid chromatography (HPLC) was performed with a Shimadzu LC 10AD VP system equipped with a ZORBAX 300SB-C18 column (250 × 4.6 mm) eluting with a mixture of CH₃CN/water. Potentiometric titration was performed using a Mettler Toledo G-20 potentiometric titrator.

Preparation of ureate

Sodium ureate from urea and NaH. This preparation was performed in a 250 mL three-necked flask equipped

with a stirrer, condenser, thermometer, and CaCl₂ tube. The flask was filled with urea (15 g, 0.25 mol), NaH (9 g, 0.3 mol), and toluene (100 g, 1.28 mol). The mixture was stirred at 500 rpm. The reaction temperature was increased from 25 °C to 85–90 °C within 30 min while the vigorous evolution of hydrogen gas occurred. The reaction was continued for an additional 60 min, and considered complete when the formation of bubbles ceased. The mixture was then cooled to 50–60 °C. The solid product was filtered and dried to yield sodium ureate (24 g, ~100%), a white powder.

Sodium ureate from urea and NaOMe. A five-necked flask was equipped with a stirrer, addition funnel, thermometer, gas inlet, and column. A second thermometer, condenser, and glass valve were placed on the column head. The electrical heater's power was controlled by the precise rheostat. Xylene (400 mL) was placed in the flask. A solution of urea and NaOMe was prepared by the dissolution of urea (33.3 g, 0.56 mol) in a methanolic NaOMe solution (100 g, 0.56 mol, 30% strength). The solution was transferred to the addition funnel. The content of the flask was stirred at 500 rpm and heated from 25 to 120 °C for 30 min. The addition of the urea-NaOMe solution started when the N₂ gas started to flush through the inlet (180 mL/min). The addition rate was adjusted to keep the temperature of the reaction mixture between 115–120 °C. The temperature on the column head varied from 60–70 °C. After the addition was completed, the temperature of the reaction mixture was increased to 125 °C. At this time, the temperature of the column head decreased gradually indicating the absence of volatile MeOH. The preparation took 90 min total, and produced 99 g of the xylene-MeOH mixture on the column head. A total of 69.7 g of wet solid beads was also collected. The potentiometric titration confirmed the absence of ammonia and Na₂CO₃ in the product, which contained 59.1 wt % of ureate with xylene. This amount corresponds to 41.2 g of the pure sodium ureate (91% yield).

Potassium ureate from urea and KOMe. Potassium ureate was prepared in an analogous way to the aforementioned sodium ureate. The solution of the KOMe was initially prepared by the dissolution of the metal potassium (63.9 g, 1.63 mol) in dry MeOH (530 g, 16.54 mol) which gave 592 g of the methanolic KOMe solution (19.3 wt % of KOMe). Urea (33 g, 0.55 mol) was dissolved in the prepared KOMe solution (200 g). The mixture was placed into the addition funnel and added into a hot xylene. The reaction conditions were identical to the preparation of the sodium ureate. The potassium ureate did not form the crystalline precipitate, but the formation of the liquid phase was observed. The liquid was immiscible with xylene. It was then

separated from xylene at the end of the process and formed crystalline solid product (48 g, 85%) after cooling to room temperature overnight.

Sodium ureate from urea and NaOH. The three-necked flask was equipped with a distillation condenser, vacuum adapter, and thermometers that measured the temperature of the reaction mixture in the flask and on the head of the condenser. DMSO (120 g, 1.54 mol) was added to the flask and immersed in a water bath at room temperature. Urea (48 g, 0.8 mol) and a finely ground NaOH (7.2 g, 0.18 mol) were successively added with stirring. The pressure was reduced to 0.4 kPa and the temperature of the mixture was slowly heated up to 70 °C. A part of the liquid was distilled off and collected until the temperature on the head of the condenser started to decrease. NaOH was dissolved into the reaction mixture as heating continued. The distillation was interrupted to collect 101 g of the wet DMSO (3.16 wt % water). The total amount of water in the distillate was 3.2 g (0.18 mol). This value corresponds with the molar amount of the NaOH added to the reaction. The solution of the sodium ureate in the DMSO-urea mixture was obtained in the form of the homogeneous viscous liquid (60.2 g). The pressure in the flask was increased to the atmospheric value. A sample of the viscous liquid was taken, and the fraction of the ureate (14.03 g, 96%, 23.3 wt %) was determined by titration. No formation of Na₂CO₃ was detected.

Potassium ureate from urea and KOH. Potassium ureate was prepared from the reaction of urea and KOH in the same way as it was prepared from urea and KOH (above). Finely ground KOH (11.8 g, 0.18 mol) was added to a stirred solution of urea (48 g, 0.8 mol) in DMSO (120 g, 1.54 mol). The reaction mixture was slowly heated up to 70 °C at 0.4 kPa. A part of the liquid was distilled off and 102 g of wet DMSO (3.13 wt % water) was collected. The total amount of water in the distillate was 3.2 g (0.18 mol). The solution of potassium ureate in the urea-DMSO mixture was obtained in the form of a homogeneous, viscous liquid (64.3 g, 92%).

Preparation of 4-nitrosoaniline

Ureate method. Urea (15.4 g, 0.26 mol) was dissolved in DMSO (73.4 g, 0.94 mol) in a 150 mL four-necked flask equipped with a stirrer, condenser, thermometer, addition funnel, and a gas inlet capillary. Sodium or potassium ureate (0.26 mol) were dispersed in the urea-DMSO solution in the flask. Nitrobenzene (10.5 g, 0.085 mol) dissolved in DMSO (11.5 g, 0.15 mol) was placed in the addition funnel and continuously added to the urea-DMSO solution for 120 min. The reaction temperature was kept at 90 °C. Part of the ureate in the reaction mixture was dissolved to form

a saturated solution, the remainder was dispersed in a solid state. As the reaction proceeded, the dissolved ureate was consumed and replenished by the further dissolution of a solid ureate.

After the addition was completed, the reaction was continued for an additional 120 min at 90 °C. The N₂ gas was bubbled through the capillary into the reaction mixture throughout the reaction. The solid product was separated from the liquid fraction and both fractions were analyzed by HPLC.

Hydroxide method. An equimolar hydroxide-urea mixture was used instead of the metal ureate. All reaction conditions were the same as those of the metal ureate procedure. Metal ureate was prepared from an equimolar mixture of extra urea (13.3 g, 0.22 mol) and metal hydroxide (0.22 mol). The reaction product was separated into the solid and liquid fraction, and each fraction was analyzed by HPLC.

Isolation and purification of the crude product

After the production of 4-nitrosoaniline, the solid fraction was dissolved in the amount of cold water equal to three-fold excess over the amount of the liquid fraction. The liquid fraction was subsequently poured into the solution. The pH was kept at 12.0. The precipitate was then filtered off. The pH of the filtrate was subsequently adjusted to 9.5 by adding conc. HCl. Crude 4-nitrosoaniline precipitated in the form of a dark green solid, which was then filtered and dried. The crude product was dissolved in MeOH and decolorized with activated charcoal. After filtration, the filtrate was concentrated under reduced pressure until a slurry of dark green crystals formed. The filtration and drying provided pure 4-nitrosoaniline (mp 173 °C).

Hydrogenation of 4-nitrosoaniline

4-Nitrosoaniline (112 g, 0.92 mol) was dissolved in EtOH (500 mL). The solution was placed into a pressure reactor. Pd/C (1.5 g, 5% Pd on activated charcoal) was added and the mixture was hydrogenated at 80 °C under 2.0–3.0 MPa of H₂. The solvent was evaporated and the crude product was fractionally distilled under 0.33 kPa.

Solubility and thermal stability test of sodium ureate

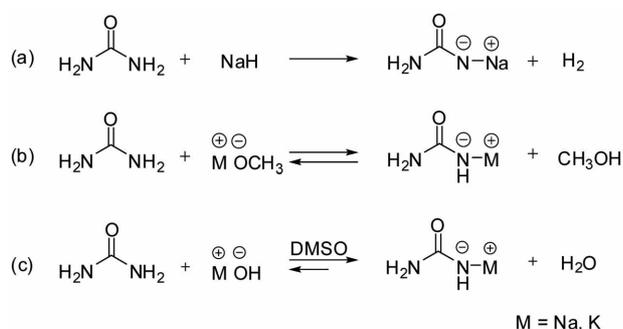
Sodium ureate (2.0 g, 0.024 mol) and NaOH (1.93 g, 0.048 mol) were dispersed in DMSO (30 mL) and heated at 90 °C for 120 min with sufficient stirring. Dissolution of the ureate was performed either in pure DMSO or in the mixture of urea and DMSO. The suspension was left to settle, and the liquid and solid fractions were separated and analyzed by HPLC.

RESULTS AND DISCUSSION

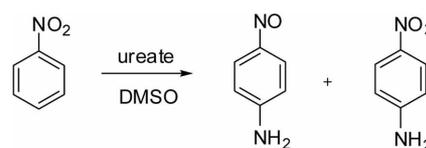
The ureate can be prepared in several ways. One of these preparation methods is based on the reaction of urea with metallic sodium,¹⁸⁻²⁰ sodium hydride²¹ (*Scheme 2(a)*), and sodium or potassium methoxide¹⁷ (*Scheme 2(b)*). In this work, sodium/potassium ureates were prepared with a slight modification to traditional literature methods using sodium hydride, sodium/potassium methoxide, and sodium/potassium hydroxides (*Scheme 2(c)*). The synthesis of the ureate using sodium hydride was rather simple and gave an excellent yield within a short reaction time. The synthetic method using methoxides was based on the dissolution of urea in a methoxide solution and dosing of this solution in the hot xylene. The yield of the ureate was increased by the evaporation of the methanol solvent, or formed during the reaction. However, the methods using sodium hydride and methoxides have economic challenges for large-scale production, because of the comparatively high price of sodium hydride or sodium/potassium methoxides. Hydroxides offer a much cheaper alternative. The importance of maintaining the dry reaction condition during the whole reaction process is another requirement for a high yield production.

To circumvent such problems, the synthetic methods for the ureates using sodium and potassium hydroxides were established. DMSO was a suitable solvent for this synthesis, because it enhances the basicity of the OH⁻ anion. This increased basicity shifts the reaction equilibrium in favor of the ureate formation (*Scheme 2(c)*). After the completion of the reaction, the ureate was obtained in a high yield by the azeotropic removal of water-DMSO from the reaction mixture under reduce pressure. The solubility of the ureate in pure DMSO was increased by the addition of an excess of urea, and the desirable ratio of urea/DMSO was within in a suitable range (1/10 to 1/2.5).

Next, the reaction of nitrobenzene with the ureates was performed to investigate the effects of the ureates on the



Scheme 2. Formation of ureates.



Scheme 3. Production of 4-nitroso- and 4-nitroaniline from nitrobenzene.

formation of 4-nitrosoaniline (*Scheme 3*). Results are summarized in *Table 1*.

When a three-fold excess amount of metal ureates dispersed in DMSO were used to prepare 4-nitrosoaniline, the conversions of nitrobenzene were 100% and the yields of 4-nitrosoaniline were higher than in the mixture of urea and NaOH (*Table 1*, entries 1-5). This was due to the sufficient amount of sodium ureate that remained in the reaction mixture throughout both the reaction and post reaction periods, and enabled the full conversion of nitrobenzene into 4-nitrosoaniline. It was also found that the weight ratio of ureate/DMSO varied from 1/10 to 1/2, preferably from 1/6 to 1/2.5, and the desired molar ratio of nitrobenzene/ureate was from 1/7 to 1/2.5.

As a comparison, the preparation of 4-nitrosoaniline was carried out using the mixture of urea and NaOH. The conversion of nitrobenzene decreased to 87% and the yield of 4-nitrosoaniline was 59% (*Table 1*, entry 6). This result shows that the majority of NaOH was converted to Na₂CO₃ during the reaction. Ammonia, a by-product of the decomposition reaction of urea, was also seen escaping from the reaction mixture with the stream of nitrogen at 90 °C. It thus is evident that the side reaction between urea and NaOH causes the deficiency of NaOH resulting in the incomplete conversion of nitrobenzene into 4-nitrosoaniline along with the increased yield (4.6%) of 4-nitroaniline.

When sodium ureate derived from urea and NaH was used, 4-nitrosoaniline was produced in 82% yield (*Table 1*, entry 1). In the case of the reactions with the sodium or potassium ureates obtained by the use of methoxides, the yield of 4-nitrosoaniline decreased to 63% and 56%, respectively (*Table 1*, entries 2 and 3). The reaction with potassium ureate gave a slightly increased yield (5.5%) of the byproduct 4-nitroaniline (entry 3).

When the ureate generated from urea and hydroxides was used, the yield of 4-nitrosoaniline was increased and the yield of the by-product was decreased compared to the case using methoxides (*Table 1*, entries 4 and 5). The urea and hydroxides process is therefore beneficial owing to the easy preparation of ureates using a relatively inexpensive hydroxide. The synthetic mechanism is not clear, but would

Table 1. Production of 4-nitrosoaniline from nitrobenzene using ureates

Entry	Ureate	Conversion of nitrobenzene (%)	Yield of 4-nitrosoaniline ^a (%)	Yield of 4-nitroaniline ^a (%)	Yield of Na ₂ CO ₃ ^a (%)
1	Sodium ureate based on NaH ^b	100	82	2.8	0
2	Sodium ureate based on NaOMe ^c	100	63	2.8	0
3	Potassium ureate based on KOMe ^d	100	56	5.5	0
4	Sodium ureate based on NaOH ^e	100	76	1.4	0
5	Potassium ureate based on KOH ^f	100	75	0.7	0
6	Urea – NaOH ^g	87	59	4.6	100

^aYields are calculated based on the amount of nitrobenzene.

^bSodium ureate from the reaction of urea with NaH.

^cSodium ureate from the reaction of urea with NaOMe.

^dPotassium ureate from the reaction of urea with KOMe.

^eSodium ureate from the reaction of urea with NaOH.

^fPotassium ureate from the reaction of urea with KOH.

^gA mixture of urea and NaOH.

Table 2. Stability of reagents and occurrence of by-products

Entry	Reagents and by-products	Sodium ureate in DMSO		Sodium ureate in DMSO/urea		Mixture of NaOH/urea in DMSO	
		Before heating (mol)	After heating ^a (mol)	Before heating (mol)	After heating ^a (mol)	Before heating (mol)	After heating ^a (mol)
1	Sodium ureate ^b	0.244	0.212	0.244	0.212	–	–
2	NaOH ^c	–	–	–	–	0.74	0
3	NH ₃ ^b	0	0	0	0.02	0	0.533
4	Na ₂ CO ₃ ^c	0	0	0	0.013	0	0.369
5	Urea ^b	–	–	0.217	0.217	0.667	0.234
6	DMSO ^b	0.962	0.962	1.089	1.089	0.962	0.962

^aThe reagent dispersed in DMSO was heated at 90 °C for 120 min.

^bThe amount of the compound was analyzed by HPLC.

^cAnalyzed by potentiometric titration.

involve the nucleophilic attack of the ureate at the *para*-position of nitrobenzene, and the intermolecular disproportionation of nitroarene to nitrosoarene.¹³

To find out the effects of the reagents and the reaction media on the progress of the NASH reaction, the solubility and thermal stability of sodium ureate and the mixture of sodium hydroxide and urea were examined in either DMSO or a mixture of DMSO and urea (*Table 2*).

Sodium ureate was not well dissolved in pure DMSO even at 90 °C, but remained stable and did not convert to sodium carbonate (*Table 2*, entry 1). The addition of the appropriate amount of urea readily solubilized the ureate in DMSO. The optimal ratio of urea/DMSO was about 1/6.5, and the solubility of sodium ureate increased five times in this solvent system. However, the presence of urea in DMSO caused the unwanted decomposition of sodium ureate to sodium carbonate (*Table 2*, entry 4), whereas 90% of the ureate still remained even after heating. In the case of the sodium hydroxide-urea mixture, all NaOH was converted to sodium carbonate within 120 min at 90 °C (*Table 2*,

entry 4). These decomposition reactions proceeded independently in the presence or absence of the nitrobenzene in the reaction mixture. This result indicates that sodium ureate is more stable at 90 °C and thus suppressed side reactions. DMSO was not consumed in all of the reaction conditions (*Table 2*, entry 6).

To obtain a pure 4-nitrosoaniline from the reaction mixture, the crude product was purified by adjusting pH in an aqueous solution and decolorizing in a methanolic solution. Analysis of the purified product by GC revealed that the contents of 4-nitrosoaniline and 4-nitroaniline were 99.1% and 0.9%, respectively. This 4-nitrosoaniline containing 0.9% of 4-nitroaniline was quantitatively hydrogenated on Pd/C under H₂ pressure to 1,4-benzenediamine (99.9% purity) that was suitable for the preparation of aramid fibers.²²

CONCLUSION

Metal ureates were synthesized in high yields by reacting urea with sodium hydride in toluene, sodium or potassium

methoxide in methanol, and sodium or potassium hydroxide in DMSO. These metal ureates were used as nucleophiles for the direct formation of 4-nitrosoaniline from nitrobenzene *via* the NASH mechanism.

When compared to the mixture of urea and alkali metal hydroxide, the ureates showed better performance on the preparation of 4-nitrosoaniline, likely due to the thermal stability of the ureates. The sodium ureate generated by the use of NaH afforded 82% of 4-nitrosoaniline along with 2.8% of 4-nitroaniline. The ureates generated from the reaction of urea with NaOH and KOH gave 76% and 75% of 4-nitrosoaniline, respectively. In these cases, the by-product 4-nitroaniline was formed in 1.4% and 0.7% yields, respectively. This supports the notion that process based on metal hydroxides could be more beneficial than those using the ureates derived from NaH or metal methoxide. Sodium ureate generally gave better results than potassium ureate. Crude 4-nitrosoaniline was readily purified to 99.0% purity, and the catalytic hydrogenation of the purified 4-nitrosoaniline furnished 1,4-benzenediamine quantitatively in polymer-grade. Therefore, the present synthetic method using the ureates provides an efficient route for the producing 4-nitrosoaniline from nitrobenzene.

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