The solution was concentrated under nitrogen, leading to a colorless compound, m.p. 214–217° from chloroform and from ethanol-acetone, m.p. depressed on mixture with tetraphenylethane and with tetraphenylethylene, 0.065 g., 35% yield.

*Anal.* Calcd. for $C_{28}H_{24}$: C, 93.3; H, 6.7; Found: C, 93.2; H, 6.8; N, 0.

The filtrates were concentrated and extracted with ether, leading to a solid which was crystallized from chloroform and ethanol, *p,p'*-dimethylbenzophenone, m.p. and mixed m.p. 90–92°, infrared spectrum in chloroform identical with that of an authentic sample, 0.060 g., (0.29 mmole) 56% yield. This product was also characterized as the oxime, m.p. 159–162°, reported[12] m.p. 161–162°.

*Tetraphenylethylene* was made by treatment of diphenylmethane with diphenyldichloromethane under reflux, m.p. 220–222°, reported[13] m.p. 223–224°.

*Tetraphenylethylene oxide.* Diphenyldichloromethane, 21 g. (0.09 mole) was treated with 28 g. (0.18 mole) of sodium iodide in 100 ml. of acetone for 2 days, leading to tetraphenylethylene dichloride, 12 g. (0.03 mole), 76% yield, m.p. 182°, reported[14] m.p. 182°. Treatment of the dichloride, 1.5 g. (3.7 mmoles) with 25 ml. of water under reflux for 18 hr. led to the epoxide, 0.8 g. (2.3 mmoles), 62% yield, m.p. 204–205°, reported[6] m.p. 203°.

*1,1-Diphenyl-2,2-di-p-tolylethylene.* Di-*p*-tolyl ketone (Eastman Kodak, m.p. 90–92°), 20 g. (0.095 mole) and phosphorus pentachloride, 15 g. (0.072 mole) were heated at 110° for 16 hr. Phosphorus oxychloride was removed in vacuum and the residue was treated with diphenylmethane (Matheson, b.p. 262–264°), 15 g. (0.09 mole) at 165° for 16 hr. The product was treated with 50 ml. of 1:1 benzene-ethanol and chromatographed over alumina, leading to 1,1-diphenyl-2,2-di-*p*-tolylethylene, 6.2 g. (0.017 mole), m.p. 161–163°, reported[15] m.p. 161°.

*Acknowledgment.* We are indebted to Alfred Stern for the preparation of tetraphenylethylene dichloride, tetraphenylethylene oxide, and tetraphenylethylene.

WALTHAM 54, MASS.

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[12] H. Goldschmidt, *Ber.*, **23**, 2747 (1890).

[13] O. Lohse, *Ber.*, **29**, 1789 (1896).

[14] H. Finkelstein, *Ber.*, **43**, 1533 (1910).

[15] E. Bergmann and D. Wagenberg, *Ber.*, **63B**, 2585 (1930).

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[CONTRIBUTION FROM THE LION OIL CO., A DIVISION OF THE MONSANTO CHEMICAL CO.]

# A New Urea Synthesis. I. The Reaction of Ammonia, Carbon Monoxide, and Sulfur[1]

RAYMOND A. FRANZ AND FRED APPLEGATH

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Urea was prepared by a novel method based on two moles of ammonia to one each of carbon monoxide and sulfur. One mole of urea and one of hydrogen sulfide was produced. A mechanism, supported by experimental evidence, has been hypothesized for this reaction.

In spite of the fact that more than 125 years have passed since the synthesis of the first organic compound from inorganic materials, urea has again been made by a new method.[2] It was found that when a mixture of ammonia, carbon monoxide, and sulfur was heated at 120° for several hours in the presence of a suitable solvent, such as methanol, urea was formed in good yields. The stoichiometic equation is

$$CO + S + 2\,NH_3 \longrightarrow H_2NCONH_2 + H_2S$$

Although the mechanism of this reaction is still open to question, the one that is preferred by the authors is shown as follows:

$$\begin{tikzcd}
CO + S \arrow[r] & COS \arrow[r, "2\,NH_3"] & H_2NCOSNH_4 \arrow[d] & \\
H_2NCONH_2 & HNCO + NH_4HS \arrow[l, "NH_3"'] \arrow[r] & H_2S + NH_3
\end{tikzcd}$$

Experimental evidence for the proposed mechanism is as follows: The presence of as high as 30% carbonyl sulfide has been found by infrared in the product gases when the reaction was run at 150°. Ammonium thiocarbamate has been obtained in large quantities when the temperature of the reaction was held overnight at approximately 25–30° using carbon monoxide pressures of about 700 pounds per square inch gauge. Experimental evidence in support of isocyanic acid is based on the detection of the isocyanate group by infrared. An alcoholic solution of ammonium thiocarbamate was closely followed by infrared at room temperature for seven days. At the end of three days, a trace of a band at 4.63 μ showed up, which after five days had increased to a maximum. At the end of seven days this band had completely disappeared, while the urea band had grown progressively stronger, reaching its maximum in seven days. When a solution of known ammonium isocyanate in methanol was followed similarly by infrared, a very strong band was found at 4.65 μ, but after one day it almost disappeared with the simultaneous appearance of urea bands. Urea itself was identified by a mixed melting point with a known sample and quantitatively determined by the urease method.[3] The conversion of alcoholic

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[1] Presented at 16th Southwest Regional Meeting of the American Chemical Society, at Oklahoma City, December 1, 1960.

[2] U. S. Patent **2,857,430.**

[3] *Methods of Analysis AOAC*, 7th ed. (1950), p. 345.

solutions of ammonium cyanate has been studied by a number of investigators[4] who found that the rate of reaction was much greater in alcohol than in water. They also found that increasing the temperature from 33° to 57° caused the rate to increase fifty times.

The effect of variables on reaction time (*cf.* Table I) was found by making a series of runs in which the reaction mixtures were sampled at specified intervals of time. The results are given as the time for one half of the sulfur to react and the time to obtain one fourth of the theoretical yield of urea. One half of the sulfur had reacted in fourteen minutes and one fourth of the theoretical urea was obtained in nineteen minutes in the run used as a basis of comparison in Table I. Decreasing the temperature to 70° caused only a slight increase in the time for the reaction of the sulfur, but resulted in a very large increase in the time for the yield of urea. This indicates that the formation of the isocyanic acid intermediate is more dependent upon temperature than is the reaction of sulfur in the formation of carbonyl sulfide. Even at 50° the sulfur continued to react in a reasonable time. When the ammonia was reduced to one fifth of the theoretical amount, fifty-eight minutes were required for one fourth of the ammonia to be converted to urea compared to nineteen minutes in the base case. This is consistent with free ammonia appearing as one of the reactants in two of the steps of the proposed mechanism. The reaction times were actually decreased when the sulfur and then the carbon monoxide were reduced to one fifth of the theoretical amounts. Again, this agrees with sulfur and carbon monoxide each appearing just once in the reactions of the proposed mechanism. Additional hydrogen sulfide, probably by combining with the ammonia, not only increased the time for the formation of urea as predicted by the proposed mechanism, but also increased the time for the reaction of the sulfur. The addition of urea had no effect on the sulfur reaction time, but the reaction time for the formation of urea was increased. This result is interpreted as being due to the dilution of the preferred solvent with 10% of a less suitable solvent, rather than to the mass action effect of urea. The stability of urea at the reaction conditions precludes any mass action effect.

Although different types of solvents may be used, compounds containing alcohol groups were the most effective solvents. The ease of separation and the high concentration of reactants obtained by the use of methanol make it the preferred solvent. The optimum solvent ratio was found to be 4.6 g. of methanol per gram of sulfur.

TABLE I[a]

EFFECTS OF VARIABLES ON REACTION TIME

| Conditions Altered | Time for $^1/_2$ of Sulfur to React, Min. | Time for $^1/_4$ Theoretical Yield of Urea, Min. |
|---|---|---|
| None | 14 | 19 |
| 70° | 21 | 60 |
| 50° | 60 | 60 |
| $^1/_5$ of theoret. $NH_3$ | — | 58 |
| $^1/_5$ of theoret. S | 8 | 12 |
| $^1/_5$ of theoret. CO | — | 13 |
| 0.8 mole of $H_2S$ | 18 | 47 |
| 0.6 mole of urea | 14 | 36 |

[a] The basis of comparison was the reaction in a 2-l. Parr Bomb at 100° of 0.1 mole of hydrogen sulfide, 300 g. of methanol, and theoretical ammonia, sulfur, and carbon monoxide to produce 0.6 mole of urea.

It should be pointed out that this new urea synthesis is of practical interest because carbon monoxide is available as a by-product in the manufacturing of ammonia. The reaction is of academic interest because it adds to the very limited number of known reactions which carbon monoxide will undergo under mild conditions of temperature and pressure.

Experimental work has been done to apply this new urea synthesis in the preparation of substituted ureas. This, is, however, beyond the scope of this paper and will be reported at a later date.

## EXPERIMENTAL

The reaction was carried out in a batch manner using a 1.8-l. war-surplus oxygen container, Type A-4, Spec. 94-40376, volume 104 cu. in., nonshatterable stainless steel with maximum pressures of 400 p.s.i. This vessel had one $^1/_4''$ pipe opening which was closed by a stainless steel "Hoke" valve and a pressure gauge connected by a tee. The bomb was agitated by clamping in a Burrell Wrist Shaker, Model BB, and heated by wrapping with flexible tape. The temperature was measured by a thermocouple installed next to the shell of the bomb.

Before the stainless steel bomb was closed, 9.8 g. of sulfur and 44.8 g. of methanol were charged to it. The gases, 0.6 g. of hydrogen sulfide, 10.9 g. of ammonia, and 8.7 g. of carbon monoxide, were individually introduced under pressure and measured by the increase in gross bomb weight. After 1 hr. at 100°, the bomb was vented and rinsed with additional methanol. The product solution and washings were evaporated to dryness. The crude urea was then dissolved in water. Elemental sulfur, 1.4 g. (14%), was recovered as the water-insoluble portion of the product. Evaporation of the aqueous solution gave 13.7 g. of crude urea, or 13.5 g. (73%) of urea by analysis.[3]

EL DORADO, ARK.

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(4) H. E. Williams, *Cyanogen Compounds*, 2nd ed. (1948), p. 48.