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Substituted Ureas. Methods of Synthesis and Applications

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Systematic data on the method of synthesis of ureas by the interaction of compounds containing the amino-group with organic isocyanates, of amines and alkyl halides with alkali metal cyanates, and of primary and secondary amines with phosgene, carbon dioxide, urea, or nitrourea and by the carbonylation of amines are presented. The reactions involving the alkylation of urea and its interaction with various compounds containing functional groups are considered. The advantages and disadvantages of various methods are noted. The principal and practical applications of substituted ureas, including their applications as additives to organic materials, are discussed.
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I. INTRODUCTION

Substituted ureas have attracted attention because of the wide variety of their applications in industry, engineering, agriculture, and medicine;[1] they are widely used as pesticides and plant growth regulators, are effective additives, for different purposes, to hydrocarbon fuels and oils and polymeric materials, and they have found applications as medicinal preparations and dyes.

An enormous amount of factual data has now been accumulated on the methods of synthesis, properties, and applications of substituted ureas. However, hitherto there have been no review articles in the literature devoted to these compounds.

Kutepov's review[2] covers the literature up to 1961 and deals with the synthesis and reactions of only one group of compounds of this type—diarylureas. A review[3] dealing with the methods of synthesis, structure, and properties of a specific class of ureas, namely carbohydrate derivatives with carbamide fragments, was published in 1982. For this reason, carbohydrates containing derivatives of urea are not dealt with in this review.

The present communication is the first attempt at a survey and systematic account of the available literature data and the methods of synthesis and practical applications of substituted ureas.

II. METHODS OF SYNTHESIS OF SUBSTITUTED UREAS

The methods for the preparation of substituted ureas developed at the present time can be divided into eight principal groups.

1. The Interaction of Amino-compounds with Organic Isocyanates

In 1848 Würtz obtained symmetrical dimethylurea for the first time by treating methyl isocyanate with water.[4,5] Subsequently these results were confirmed: the corresponding symmetrical dialkylureas were obtained by decomposing methyl, ethyl, butyl, and isobutyl isocyanates with water.[6] The corresponding amines are formed as intermediates in these processes, reacting further with another isocyanate molecule:

$$RNCO \xrightarrow{H_2O} RNHCOOH \xrightarrow[-CO_2]{} RNH_2 \xrightarrow{RNCO} RNHCONHR .$$

The method has been used to synthesise substituted di(isocyanatophenyl)ureas by the reaction of 1-R-substituted 2,4-phenylene di-isocyanates with water in molar proportions of 2 : 1 and using ether as the solvent.[7]

The interaction of organic isocyanate with amines, for example, of phenyl isocyanate with methylaniline, ethylaniline, or diphenylaniline, leads to substituted ureas:[8]

$$C_6H_5NHR + C_6H_5NCO \rightarrow C_6H_5N(R)CONHC_6H_5 ;$$
$$R = CH_3,\ C_2H_5,\ C_6H_5 .$$

Table 1. The isocyanate method of synthesis of substituted ureas.

Initial compound	References
Amino-compounds	
Ammonia	[29—31]
Primary amines:	
saturated aliphatic	[12,15,32,33]
unsaturated aliphatic	[34]
aromatic	[8,23—25,32,35—39]
heterocyclic	[24,26,28,40—42]
Secondary amines:	
unsaturated aliphatic	[20]
saturated aliphatic	[12,14,15,18,20,43—53]
aromatic	[8]
heterocyclic	[28,54]
Alkoxyamines	[17—20]
Hydroxylamines	[9—16]
Aminophenols	[35,55—57]
Aminoalcohols	[57]
Diamines	[41,58,59]
Aminoethylbenzoxazole	[26]
Acid amides	[22,37]
Thiadazole	[27]
Organic isocyanates	
Saturated aliphatic	[4—6,10,26,27,29,31,32,35,40, 47—52,54,57]
Aromatic	[8,9,11,12,14—22,24,26,28,32,36—38, 41,43—45,53,55,56,58—60]
Saturated carbocyclic	[61]
Benzoyl isocyanate	[23,37,39]
Alkylphenylene isocyanates	[7]
Heterocyclic	[24]

The interaction of organic isocyanates with amines is nowadays the most widely used method of synthesis of asymmetric ureas. Various compounds containing the amino-group can enter into this reaction (Table 1). The reaction of alkyl isocyanates with hydroxylamines is widely used to obtain urea derivatives containing the hydroxy- or methoxy-group at one of the nitrogen atoms.[9-16]

The range of organic isocyanates used in this method is also extremely varied (Table 1).

The interaction of isocyanates with compounds containing the amino-group is as a rule carried out at room temperature or with cooling, sometimes with heating.[18,21-28] Equimolar amounts of the reactants or a slight excess of the organic isocyanates, more rarely an excess of the compounds containing the amino-group, are usually employed.

The process is normally performed in an organic solvent—benzene,[12,17-19,38] toluene,[14,25,39] xylene,[25] cresol,[23,24,53] chlorobenzene and dichlorobenzene,[12,25,52] methyl or ethyl alcohol,[54] dioxan,[23,52] tetrahydrofuran,[30,37,52,54,58] dimethylformamide (DMF),[19,22] ethanolamine,[27] acetonitrile,[13,30] and methylene chloride.[59,60] Water is sometimes used as the solvent because isocyanates react with water much more slowly than with amines.

The reaction of organic isocyanates with substituted amines proceed as a rule with high yields of substituted ureas, which are frequently nearly quantitative. However, it has been noted that secondary aliphatic-aromatic amines react with isocyanates to form unstable products, which decompose on heating. Diphenylamine does not react with isocyanates.[8]

It has been established that the molecular weight of the initial amine is only slightly reflected in the rate of its reaction with isocyanates. Aliphatic amines react much faster than aromatic amines. The reactivity of the isocyanate increases with increase of the electrophilicity of the substituent in its molecule.[44]

In order to improve the mass exchange between the individual components of the reaction mixture, *N*-aryl-*N'N'*-dimethylureas, where aryl = phenyl or *p*-chlorophenyl, have been synthesised in the presence of surfactants.[43] The yield of, for example, *N*-phenyl-*N'N'*-dimethylurea then amounted to 97.5%.[44]

Kinetic studies of the reactions of isocyanates with amines have been carried out.[62-67] The influence of substituents in the molecules of the isocyanate and the amine on the rate of reaction has been described and the reaction kinetics have been determined. However, hitherto there is no unanimous view concerning the reaction mechanism. It is believed[68] that the reaction proceeds in two stages. The first stage involves the formation of an activated complex, which is subsequently converted into the substituted urea by reacting with the amine. By analogy with the scheme proposed by Zahradnik,[69] the rearrangement of the intermediate complex into urea may be regarded as possible in principle:

$$RNCO + R'NH_2 \rightleftarrows \left[RN{=}C^{+}{-}O^{-} \cdots H_2NR' \right] \rightleftarrows \left[RN{=}C(O^{-})(NH_2^{+}R') \right] \rightarrow RNHC(=O)NHR' .$$

The thermodynamic data presented by Vorob'ev et al.[70] allow the possibility of the formation of a four-centre activated intermediate complex:

$$\begin{matrix} RN{=}C{=}O \\ H{-}NH{-}R' \end{matrix} \rightarrow \left[\begin{matrix} R{-}N{-}C{=}O \\ H \cdots NHR' \end{matrix} \right] \rightarrow \begin{matrix} RN{-}C{=}O \\ H \quad NHR' \end{matrix} .$$

2. The Interaction of Amines and Alkyl Halides with Alkali Metal Cyanates

Cyanic acid and alkali metal cyanates are fairly frequently used to obtain substituted ureas.[71-75] Würtz proposed for the first time in 1851 the alkylureas be obtained by evaporating to dryness a solution of the sulphuric acid salt of the corresponding amine and potassium cyanate.[71]

Subsequently the cyanate method of synthesis of substituted ureas was used in a number of investigations.[72-75] In particular, a large number of arylureas were obtained[72,73] by the reaction of the arylamine hydrochloride with sodium cyanate at 30 °C in glacial acetic acid with their subsequent separation in the form of a water-insoluble precipitate.

The reaction of alkyl halides with cyanate in aqueous DMF, described for the first time by Fukui et al.,[76] is a variety of the cyanate method of synthesis. The authors established that the composition of the reaction product is determined mainly by the presence of water in the reaction mixture. Thus, when dried reagents are used, only tributyl isocyanurate was obtained from butyl bromide in 84% yield, while in the presence of added water (0.56 of a mole per mole of butyl bromide) the yield of tributyl isocyanurate was 7% and that of symmetrical dibutylurea was 75%.[76]

The influence of the structure of the initial alkyl halide on the yield of substituted ureas has been investigated[77] and it has been established that the best yields of the required products are achieved when primary alkyl halides with a straight chain are employed; tertiary alkyl halides do not react. For example, unbranched alkyl bromides and alkyl chlorides react with potassium cyanate at 100–130 °C in DMF in the presence of an equimolar amount of water to form *NN*-dialkylureas in 90–96% yield.

By treating an alkyl chloride with potassium cyanate in DMF containing 5% of water at 100 °C, Argabright et al.[78] obtained monosubstituted ureas as well as the *NN*-disubstituted derivatives. The 1,5-disubstituted biuret is then formed as a side product and the formation of the 1,3,5-trisubstituted isocyanurate is not observed.

3. The Interaction of Primary and Secondary Amines with Phosgene

Symmetrical dialkyl-, diaryl-, and alkylaryl-ureas are obtained by treating the corresponding amines with phosgene. Several reviews devoted to the chemistry of phosgene, in particular its interaction with amines, are available.[44,67,79-84]

By passing phosgene through a saturated aqueous solution of aniline, Hoffman obtained for the first time diphenylurea:[85]

$$C_6H_5NH_2 + COCl_2 \rightarrow C_6H_5NHCONHC_6H_5 + HCl .$$

The reaction of phosgene with aniline was investigated by Japanese workers,[86] who established that aniline hydrochloride and the chloride of phenylcarbamic acid are formed together with diphenylurea.

Starting in 1875, Michler[87-92] began publishing communications on the treatment of primary and secondary amines with phosgene. Thus, by treating diphenylamine with phosgene in ligroin, he obtained diphenylcarbamoyl chloride $(C_6H_5)_2N{-}C(=O){-}Cl$, which readily reacts with the initial amine to form a substituted urea. Thus it has been established that the reaction between the amine and phosgene proceeds in two stages, the hydrogen chloride evolved being combined with the amine to form the amine hydrochloride:

$$RR'NH + COCl_2 \rightarrow RR'NCOCl + RR'NH \cdot HCl ;$$
$$RR'NCOCl + RR'NH \rightarrow RR'N{-}CO{-}NRR' + RR'NH{\cdot}HCl .$$

Treatment of aqueous solutions of amines with a benzene solution of phosgene in the presence of alkali led to dimethyl-, diethyl-, and difurfuryl-ureas in quantitative yields.[93] In subsequent studies it was shown[94,95] that the reaction takes place successfully not only in aqueous solution but also in organic solvents.

In many instances it has been suggested that, in order to increase the yield of a substituted urea, the hydrogen chloride evolved during its synthesis be absorbed with the aid of special acceptor additives.[93,96-101] Alkalis, sodium and calcium carbonates, sodium acetate, and zinc and magnesium oxides[94,96-98] are used as hydrogen chloride acceptors in an aqueous medium, while in organic solvents the acceptors are triethylamine, dimethylaniline,[99-101] and other tertiary amines.

The literature data[84,102-107] show that the rate of reaction of amines with phosgene is extremely high and increases with increasing basicity of the initial amine. Kutepov and Rozanova were the first to investigate the mechanism of the reaction between phosgene and amines.[108,109] They believe that in the first stage of the reaction the nucleophile (the amine) adds to the powerful electrophile (phosgene) to form a 1:1 or 2:1 complex depending on the reactant ratio. The complex, being unstable, decomposes to form an *N*-substituted carbamoyl chloride or a di-*N*-substituted symmetrical urea. The carbamoyl chloride formed from the 1:1 adduct can split off hydrogen chloride to form the isocyanate. At the same time the carbamoyl chloride and the isocyanate formed from it interact with the amine to form a di-*N*-substituted symmetrical urea.

Japanese investigators[110] showed that the interaction of phosgene (in 10% excess) with aromatic amines (aniline, *p*-toluidine, and *p*-nitroaniline) and their hydrochlorides results in the rapid formation of the *N*-arylcarbamoyl chloride and the amine hydrochloride even at −15 °C. Only at temperatures above 0 °C do appreciable amounts of the diarylurea appear.

Other communications have also been devoted to the treatment of amines and their hydrochlorides with phosgene.[111-115] The most thorough studies on the treatment of primary, secondary, and tertiary amines with phosgene have been carried out by Strepikheev and co-workers,[67,116] who investigated the kinetics of the interaction of amines with phosgene and established that it is a complex chemical process consisting of several parallel-consecutive reactions.

In contrast to Kutepov and Rozanova, the authors believe that amines are not acylated directly on treatment with carbamoyl chlorides, but convert the latter into isocyanates:

$$RNHCOCl + RNH_2 \rightarrow RNH_3Cl + RNCO .$$

The free isocyanate then reacts with the excess amine to form a disubstituted urea.

The formation of ureas on treatment of amines with phosgene proceeds in accordance with the following scheme:

$$RNH_2 + COCl_2 \rightarrow RNHCOCl + HCl ; \quad (1)$$

$$RNH_2 + HCl \rightarrow RNH_3Cl ; \quad (2)$$

$$RNH_2 + RNHCOCl \rightarrow RNH_3Cl + RNCO ; \quad (3)$$

$$RNHCOCl \rightleftarrows RNCO + HCl ; \quad (4)$$

$$RNHCOCl + RNH_2 \rightarrow [RNCO] \rightarrow (RNH)_2CO ; \quad (5)$$

$$RNH_2 + RNCO \rightarrow (RNH)_2CO . \quad (6)$$

The amine hydrochlorides and disubstituted symmetrical ureas also react with phosgene to form the corresponding carbamoyl chlorides:

$$RNH_3Cl + COCl_2 \rightarrow RNHCOCl + HCl ; \quad (7)$$

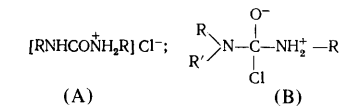
$$(RNH)_2CO + COCl_2 \rightarrow RNHCOCl . \quad (8)$$

In addition the isocyanates can polymerise [reaction (9)] and in certain cases the NCO group can be replaced by chlorine:

$$n\,RNCO \rightarrow (RNCO)_n . \quad (9)$$

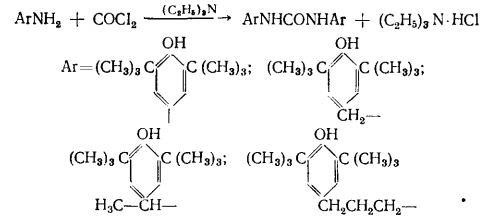
In the presence of an excess of phosgene substituted ureas are absent from the reaction mixture, which indicates a relatively low rate of reactions (5) and (6) compared with reactions (1) and (2). Consequently, in order to increase the yield of substituted ureas, it is necessary to use an excess of the amine and, in order to increase the rate of reaction, a hydrogen chloride acceptor must be employed.

Thus substituted ureas are obtained on treatment with phosgene as a result of the interaction of amines with intermediates—isocyanates and carbamoyl chlorides. Reviews concerning the mechanism of the last reaction are contradictory. The ammonide salts (A)[109] or the dipolar ions (B)[117,118] have been proposed as intermediates:



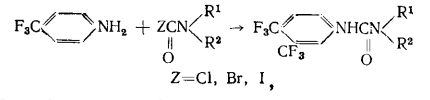
(A) (B)

Symmetrically disubstituted ureas can be obtained by treating sterically hindered aminophenols with phosgene in solution in benzene in the presence of triethylamine as the hydrogen chloride acceptor:[56]



The yield of substituted ureas decreases from 85 to 66% on passing from 4-aminophenol to 4-hydroxyphenylpropylamine. Together with substituted ureas, carbamoyl chlorides ArNHCOCl were isolated; the reaction proceeds via the intermediate formation of these compounds.

Some workers have suggested that substituted ureas be obtained by the reaction of amines with carbamoyl chlorides.[45,87,92,119] Thus *N'*-alkyl-*NN*-diphenylureas have been obtained in 90–98% yields from diphenylcarbamoyl chloride in an aqueous solution of C_2–C_4 alkylamines in acetone or toluene using hydrogen chloride acceptors—a tertiary amine or inorganic bases.[119] The corresponding ureas have been synthesised by the reaction of 3,4-bis(trifluoromethyl)aniline with dialkylcarbamoyl halides:[45]



where R^1 = H, a lower alkyl, alkenyl, or alkoxy-group and R^2 = a lower alkyl or alkenyl.

Substituted ureas containing a hydroxy-group at one of the nitrogen atoms have been obtained in satisfactory yields by the reaction of arylhydroxylamines with dialkylcarbamoyl chlorides.[9]

4. The Interaction of Amines with Urea and Nitrourea

Substituted ureas have been obtained in 50–80% yields by fusing urea together with amine hydrochlorides at ~180 °C or by refluxing in aqueous solution.[120-123] It has been

established that urea dissociates into ammonia and isocyanic acid, which reacts with the primary amine to give a monosubstituted urea; the latter splits off ammonia and is converted into the isocyanate, which again reacts with the amine to form a disubstituted urea:

$$H_2NCONH_2 \xrightarrow[-NH_3]{} HNCO \xrightarrow{RNH_2} RNHCONH_2 \xrightarrow[-NH_3]{} RNCO \xrightarrow{RNH_2} RNHCONHR .$$

It has been noted[124] that, by varying the amine : urea ratio, it is possible to obtain predominantly monosubstituted ureas.

Diphenylureas have been obtained by heating one part of urea with three parts of aniline at 150–170 °C.[125]

The study of various methods of synthesis of *NN'*-dimethylurea showed that the highest yield of the latter (80–90%) is obtained when methylamine reacts with urea.[126]

The method developed by Davis and co-workers[120–122] was subsequently widely used to synthesise *N*-alkyl(aryl)- and *NN'*-dialkyl(diaryl)ureas.[127–130] In order to increase the yield of substituted ureas, some workers recommend that the reaction be carried out between urea and amines in high-boiling solvents (cyclohexanol, phenol, or decalin[131–133]) or that the initial urea be made to interact with aqueous solutions of amine hydrosulphates or hydrophosphates.[134] Sometimes,[135] in order to obtain *NN*-dialkylureas of high purity, the reaction between urea and dimethyl- or diethyl-amine is carried out in an aqueous medium at 120–140 °C under pressure.

Asymmetric ureas are synthesised by transamination, for example, by the reaction of diarylurea with dimethylamine.[136]

A convenient method of synthesis of substituted ureas involves the reaction of amines with nitrourea.[137–140] Like urea, nitrourea is cleaved on heating with formation of isocyanic acid and nitramide:[137]

$$NH_2CONHNO_2 \rightarrow HNCO + H_2NNO_2 .$$

Since the nitro-group is an electron acceptor, nitrourea decomposes faster than urea. The corresponding substituted ureas have been obtained in 80–90% yields by the reaction of primary and secondary amines with nitrourea,[137] the yields being 10–30% higher than in the case of urea. It is noteworthy that nitramide, which decomposes into water and nitrous oxide under the conditions of the synthesis, promotes the shift of the equilibrium towards the formation of isocyanic acid and ultimately the formation of substituted ureas. Various substituted ureas have been obtained in 75–95% yields by the interaction of equimolar amounts of nitrourea with monoalkyl-, dialkyl-, and alkyl-aryl-amines in water.[138]

If the reaction between amines and nitrourea is carried out in 95% ethanol instead of water, then the yields of substituted ureas increase by 20–40%. The method is particularly effective when the solubilities of the initial amines in water are limited.[139]

N-Substituted ureas having the general formula $C_6H_5ZCH_2NHCONH_2$ (Z = cyclopropylene, cycolhexylene, or cyclopentylene) have been obtained by the method of Davis and Blanchard[137] in 30–50% yields.[140] A large number of substituted ureas have been synthesised by the reaction of sterically hindered aminophenols with nitrourea.[141]

Nitrosomethylurea also reacts with amines analogously to urea and nitrourea.[142] A series of *N*-alkylureas have been obtained in 70–90% yields with its aid:[142]

$$CH_3N(NO)CONH_2 \rightarrow CH_3NHNO + HNCO ;$$
$$CH_3NHNO \rightarrow N_2O + CH_3OH ;$$
$$HNCO + RNH_2 \rightarrow RNHCONH_2 .$$

5. The Interaction of Urea with Various Compounds

The methods of synthesis of *N*-alkyl and *NN*-dialkyl-ureas by the reaction of aldehydes and ketones with urea under oxygen pressure in the presence of nickel and cobalt catalysts are of interest.[143–145] The reaction is carried out at 60–150 °C, *N*-alkylurea and *NN*-dialkylurea being formed preferentially at 60–100° and 100–150 °C respectively. Thus 4-octadecylurea has been obtained in 75% yield from stearaldehyde[143] and s-butylurea has been obtained from ethyl methyl ketone in 77% yield.[145]

Mono- and di-alkylureas with an alkyl substituent having the iso-structure can by synthesised by the direct alkylation of urea with alcohols or olefins.[146–151] Thus a patent[146] suggests that urea be alkylated by tertiary alcohols using urea : alcohol : sulphuric acid (concentration 94% and above) molar ratios of 1 : 2 : 2. According to another patent,[147] the initial urea is to be alkylated by olefins containing a double bond at a tertiary carbon atom at 0 °C and using olefin : urea : sulphuric acid (90–100%) molar ratios of 1 : 4–5 : 2–2.5.

Different t-alkylureas have been obtained by the direct alkylation of urea with olefins in the presence of concentrated sulphuric acid as the catalyst,[148,149,152] The study of the reaction conditions showed that the best yield of alkylation products is achieved at temperatures between 0° and −5 °C, a sulphuric acid concentration of 96%, for molar ratios of urea, sulphuric acid, and the olefin of 1 : 2 : 4, and for a reaction time of 4–5 h.

The authors suggest that the alkylation of urea by olefins in the presence of sulphuric acid proceeds in two stages: an alkylsulphuric acid is formed in the first stage and alkylates urea further with regeneration of sulphuric acid.

In order to reduce the amount of sulphuric acid necessary for the reaction, it has been suggested[150] that some of it be replaced by $FeSO_4.7H_2O$.

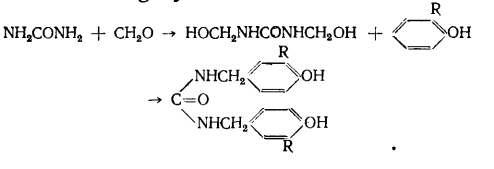
The use of a mixture of concentrated H_2SO_4 and methyl sulphate as the catalyst made it possible to obtain, by alkylating urea with isobutene, *NN'*-di(t-butyl)urea in 76.7% yield or *N*-t-butylurea in 29.6% yield relative to the initial urea.[151]

Certain symmetrical dibenzylureas are obtained by condensing phenols with urea and formaldehyde in the presence of acid catalysts.[152,155] The condensation of urea with formaldehyde to form mono(hydroxymethyl)urea in the first stage has been suggested:[155]

$$NH_2CONH_2 + CH_2O \rightarrow NH_2CONHCH_2OH .$$

The subsequent condensation with phenol in the presence of formic acid leads to *NN'*-di(4-hydroxybenzyl)urea.[155] Under these conditions, di(4-hydroxyphenyl)-methane is formed as a side product. The authors note that *N*-4-hydroxybenzylurea was not detected in any of the experiments.[155] On raising the temperature of the synthesis or on employing as the catalyst an acid stronger than formic, for example, hydrochloric, the formation of polymeric products sparingly soluble in organic solvents was observed.[155]

Alkylphenols have been condensed with urea and formaldehyde[153–155] in dearomatised petrol at 96–98 °C using 0.01% of concentrated hydrochloric acid as the catalyst. A large number of different *NN'*-dibenzylureas have been synthesised by this method in high yields:



An analogous reaction has been carried out with 2,6-di(t-butyl)phenol (DTBP).[56] In this process di[3,5-di(t-butyl)-4-hydroxyphenyl]methane and di(hydroxymethyl)urea polycondensation products are formed as side products. By varying the reaction conditions, namely the temperature (50–100 °C), the di(hydroxymethyl)urea : DTBP molar ratio (1 : 2.5–10), and the catalyst (HCOOH, KU-2 resin, HCl, sulphopolyphenyl ketone), the yield of substituted urea was raised only to 24%. The replacement of di(hydroxymethyl)urea by its dimethyl ether in this reaction (in order to prevent polycondensation) resulted in only a slight improvement of the yield of the required product—to 31%.

Table 2. Synthesis of substituted ureas by the catalytic carbonylation of amines.[164]

Amine	Catalyst	T, °C	Yield, %
Diethylamine	NiI_2	280	72
Butylamine	NiI_2	200	40–45
Ditto	$Mn_2(CO)_{10}$	180–200	47
Cyclohexylamine	$Mn_2(CO)_{10}$	180–200	58
Hexamethyleneamine	Co	200	—
Aniline	Co	200	75
Ditto	$Mn_2(CO)_{10}$	190	6
"	NiI_2	160	26
" *	Pd, Pd/C, $PdCl_2$	180	—
" **	Te	140	—

*See Tsuji and Iwamoto.[156]
**See Kambe et al.[165]

6. The Synthesis of Substituted Ureas by the Carbonylation of Amines

(a) Catalytic carbonylation of amines. Substituted ureas can be obtained by the catalytic carbonylation of amines,[156–162] using transition metals and their salts and carbonyls as catalysts (Table 2). The reaction is performed at 150–280 °C and a carbon monoxide pressure of 100–300 atm. Its products are *N*-formylureas and other substituted urea derivatives. This method has significant advantages over the method involving the treatment of amines by phosgene, used at present in industry, since it makes it possible to avoid the use of a poisonous component (phosgene) and in addition the carbonylation of amines results in the formation of hydrogen[156] and water[159–161] together with the required products and not hydrochloric acid as in the reaction with phosgene. The catalytic carbonylation of amines yields substituted ureas in a single stage under mild conditions.[163]

The large set of chemical substances of different kinds tested as catalysts shows that a purely empirical approach has been used. This is because the amine carbonylation process has been inadequately investigated.

Numerous mechanisms have been proposed for this reaction. They are as a rule contradictory and have not been confirmed by kinetic data. Thus it has been shown[166–168] that amines react with transition metal compounds to form charge-transfer complexes, which, on heating and on treatment with oxidants, are capable of undergoing deprotonation and homolytic decomposition with formation of the aminyl radical and a change in the oxidation state of the complex-forming agent. A chain reaction mechanism has been proposed in which the metal salts serve as the sources of radicals at the instant of reaction.[166] It has been suggested[169] that, in the presence of I_2 and $KMnO_4$, the reaction proceeds in accordance with an analogous mechanism.

Another carbonylation mechanism has been discussed by Dombek and Angelici,[170] who believe that $Fe(CO)_5$ reacts with the amine to form a carbamoyl complex, which is of key importance in the catalytic process. The reaction with $Mn_2(CO)_{10}$ [162] and certain other transition metal compounds, which are reduced to the metal under the reaction conditions (100–200 °C, 100 atm CO) and are capable of forming carbonyls, apparently proceeds analogously. The reaction results in the formation of either formamides or, when NiI_2, Co, or $Mn_2(CO)_{10}$ are used as catalysts, a mixture of formamides and substituted ureas; the latter are formed preferentially in the presence of $Mn_2(CO)_{10}$.

The composition of the products depends significantly on the nature of the amine. Thus it has been shown[156] that the carbonylation of lower aliphatic amines gives rise to only a small amount of ureas together with formamides, while aromatic amines produce only ureas.

It has been suggested[171,172] that ureas are formed in two stages via an intermediate formamide:

$$RNH_2 + CO \rightarrow RNHCOH \ ;$$

$$RNHCOH + H_2NR \rightarrow (RNH_2)_2CO \ .$$

Analysis of the views expressed in the literature on the mechanism of the amine carbonylation reaction shows that they require careful checks and investigation. Thus essentially the same mechanism has been proposed[158,166] for severe and mild conditions, although the reaction products are completely different. The high selectivity of the reaction as regards the formation of formamides under severe conditions and of urea under mild conditions is incompatible with a radical mechanism.

(b) Oxidative carbonylation of amines. In the amine carbonylation reactions examined above the catalyst either does not undergo a change in valence or is reduced with transfer of one electron. An interesting method of synthesis of substituted ureas involves the oxidative carbonylation of amines, which takes place on reduction of the metal complex (transfer of two electrons) or in a catalytic process in the presence of an additional oxidant. Apart from metal complexes, the reaction is catalysed by elemental sulphur and selenium. The oxidative carbonylation of amines is carried out under mild conditions, which is of practical interest.

Substituted ureas have been obtained in high yields by the reaction[173–175]

$$CO + S + RNH_2 \rightarrow RNHCONHR + H_2S \ .$$

The reaction involving aromatic amines takes place under mild conditions (100–160 °C, 20–40 atm), while that of aliphatic amines requires more severe conditions. The yield of ureas increases on raising the temperature and when a solvent (ethanol) is employed.

When selenium is used instead of sulphur, the reaction conditions become much milder (20 °C, 1 atm CO).[176] The yield of substituted ureas formed from primary amines is 95–99%, but that formed from secondary amines is much lower. Seleno-carbamates have been isolated as intermediates. It has been shown that the active carbonylating agent is selenium carbonyl.[177,178] An excess of oxygen in the $CO + O_2$ mixture leads to the precipitation of elemental selenium and the cessation of the catalytic reaction. It is believed[176] that the reaction takes place in at least two stages:

$$RNH_2 + Se + CO \rightarrow (RNH_3)^+ (RNHC(=O)Se)^- \ ;$$

$$(RNH_3)^+ (RNHC(=O)Se)^- + O_2 \rightarrow (RNH_2)_2CO + H_2O + Se \ .$$

Carbonylation of primary amines in the presence of silver acetate under mild conditions (0–25 °C, 55–100 atm) afforded *NN*-dialkylureas in almost quantitative yields.[157] Copper, zinc, cadmium, cobalt, and nickel acetates are inactive, while $Pd(Ac)_2$ is weakly active.

In the presence of $CuCl_2$, substituted ureas are obtained at room temperature and atmospheric pressure of CO:[179,180]

$$R^1R^2NH + CO + Cu^{II} \rightarrow R^1R^2NCONR^1R^2 + H_2O + Cu^I .$$

Since univalent copper complexes are readily reoxidised by oxygen, the overall reaction has the following form:

$$R^1R^2NH + CO + O_2 \xrightarrow{Cu^{I,II}} R^1R^2NCONR^1R^2 + H_2O .$$

The reaction can be performed in many solvents and in their absence. Piperidine and morpholine show the highest reactivity, while diethylamine, pyrrolidine, cyclohexylamine, and butylamine are less reactive.

It has been found[158] that, in the temperature range 25–110 °C at atmospheric pressure, the carbonylation of certain primary and secondary amines in the presence of $PdCl_2$ and $Hg(CH_3COO)_2$ is a stoichiometric oxidation-reduction reaction, which takes place in four stages:

(1) the formation from the amine and the metal salt of a compound having the character of a charge-transfer complex:

$$R_2NH + Hg(CH_3COO)_2 \rightarrow (R_2NH)_2Hg(CH_3COO)_2 .$$

(2) The interaction of the complex formed with CO accompanied by the insertion of the latter in the metal–nitrogen bond:

$$(R_2NH)_2Hg(CH_3COO)_2 + CO \rightarrow R_2NCHg(CH_3COO) + R_2NH \cdot CH_3COOH .$$

(3) The redox decomposition of the carbamoyl complex with formation of active radical species and the reduction of the metal ion:

$$R_2NCHg(CH_3COO) \rightarrow R_2NC\cdot + Hg(CH_3COO) .$$

(4) The recombination of the active species to the reaction products:

$$2R_2NC\cdot \rightarrow R_2NC{-}CNR_2 \xrightarrow{\Delta} R_2NCNH_2 + CO .$$

In a complex system comprising organic phosphines, quaternary ammonium bases, and tetraethylammonium chloride, palladium complexes effect the catalytic carbonylation of amines to *NN'*-disubstituted ureas in the presence of nitro-compounds as oxidants at 90 °C and a CO pressure of 1 atm.[181]

The synthesis of substituted ureas by the oxidative carbonylation of n-butylamine and piperidine in the presence of palladium(II) complexes, copper(I, II) complexes, or the highly active catalytic system comprising both copper(II) and palladium(II) complexes has been investigated.[163] The last catalytic system retains its activity in reactions with different amines in a number of solvents (dioxan, ethanol, pyridine, and acetonitrile). It has been established[163] that, in the presence of palladium complexes, the reaction proceeds via the formation of a carbonyl complex, which is subsequently converted, as a result of nucleophilic attack by the amine on the coordinated carbon monoxide, into a carbamoyl intermediate, whose redox decomposition is the rate-limiting stage of the process. The amine-copper(II) complexes greatly accelerate this decomposition. When bivalent palladium and copper complexes are used, a synergistic effect is observed.

Thus the oxidative carbonylation of amines is an effective and promising method of synthesis of substituted ureas. However, this reaction has so far been inadequately investigated. The studies which have been made are in the main preparative and the reaction mechanism has been scarcely investigated.

Symmetrical dialkyl- or diaryl-ureas have been obtained in 50–90% yields by condensing the corresponding amine with carbon dioxide at 100–300 °C and a pressure of 100–300 atm.[182–187]

7. Synthesis of Substituted Ureas and Acid Amides (Hofmann Rearrangement)

Hofmann found in 1881 that the reaction of amides with bromine in the presence of alkali results in the formation of 1,3-alkylacylureas, which are converted into alkylureas on subsequent treatment with nitric acid:[188,189]

$$CH_3CONH_2 \xrightarrow[-HBr,\,-H_2O]{NaOH+Br_2} CH_3CONa \xrightarrow[-NaNO_3,\,-HBr]{HNO_2} CH_3NCO \rightarrow$$
$$\rightarrow CH_3NHCONHCOCH_3 \xrightarrow[-CH_3COOH]{H_2O} CH_3NHCONH_2 .$$

The corresponding *NN*-dialkyl-*N'*-arylureas have been obtained in 20–60% yields from aromatic acid amides and secondary amines in the presence of potassium hypochlorite.[190]

III. APPLICATIONS OF SUBSTITUTED UREAS

Substituted ureas, which constitute some of the most important classes of chemical compounds, have found extensive applications in agriculture as plant growth regulators and pesticides, particularly herbicides. This question has been widely dealt with in the literature. A systematic account and a survey of data on the effectiveness of ureas as plant growth regulators and herbicides have been given in a review,[191] in which certain regularities in the herbicidal activity of substituted ureas as a function of their structure have been established. A bibiographic index of recommended pesticides and plant growth regulators, covering the literature up to 1979, has been published;[192] much space in it has been devoted to substituted ureas.

Studies in this field are developing vigorously; new communications on the efficiency of substituted ureas as herbicides,[12–14,17–19,36,38,41,42,193–210] and plant growth stimulators,[38,211–213] as well as fungicides,[17,19,22,205,213–215] insecticides,[23,24,37,39,216–218] bactericides,[60,213,219] and other pesticides,[16,34,220] promising for practical applications, are being published systematically.

Yet another field in which substituted ureas are widely employed is that of the manufacture of physiologically active substances[34,221–225] and medicinal preparations, mainly with tranquillising and anticonvulsant activities.[226–231] Various *N*-alkyl-*N'*-aminophenoxyureas are used in the treatment of asthma and other diseases of the respiratory tract[59,232] and substituted ureas are used as components of medicinal preparations for the treatment of cardiac diseases.[233]

Certain nitroureas exhibit anticancer and antileukaemic properties,[54,234–242] heterylcarbonylureas dissolve gall stones,[243] while indolylureas, amidinoureas, *N*-aryl-*N'*-imidazolidineureas, aminoethylureas, and piperidinylureas possess hypotensive properties.[58,244–248]

Sulphonylureas and 1-amidino-3-phenylureas exhibit dermatological properties.[249,250] The latter can also be used to reduce blood pressure[245] and in the treatment of

increased acidity and stomach ulcers;[251,252] *N*-alkyl-*N'*-dialkylaminoethylureas[253] and pyrazinylureas can also be employed in the treatment of gastrointestinal diseases;[254] certain substituted ureas are used as agents for the protection of the skin against boils.[255]

Certain phenylureas are capable of inhibiting the degradation of connective tissues in warm blooded animals and in man.[256] Ureas with nitrogen-containing heterocycles can be used as regulators of immune responses,[28] as antihelminthic preparations,[26,257] and as hypoglycaemic substances.[258,259]

Data concerning the use of substituted ureas for the dyeing of hair and keratin and cellulose fibres have been described in the literature;[260,261] 3-hydroxy-2,4-dimethylphenylurea is the most effective.[103,262] Substituted ureas are able to form complexes with certain metal ions and they are used in analytical chemistry as complex forming agents.[263,268] Certain urea derivatives (for example, the symmetrical diethylphenylurea under the name centramit) serve as stabilisers of smokeless powders;[152] 1,3-dialkylureas are used in the synthesis of sweetening agents and as sugar substitutes.[269]

Tetramethylurea is used as a solvent in polarography.[270] Urea derivatives are also employed as solvents for quinone or hydroquinone in the manufacture of hydrogen peroxide[271] and as solvents and catalysts in chlorination reactions.[164]

Substituted ureas can serve as the starting materials for the synthesis of polymers[61,221,222,272-276] and also surfactants.[277]

Substituted ureas have assumed special importance recently as effective additives to hydrocarbonfuel oils and polymeric materials. They have been studied in detail as antioxidants in various types of petrol for automobiles.[32,33,278-280] Thus the study of various derivatives of *p*-hydroxyphenylurea showed[278-280] that the substitution of hydrogen at the nitrogen atom by various aliphatic and aromatic groups leads to the appearance of an appreciable antioxidant effect, while *p*-hydroxyphenylurea itself does not inhibit the oxidative processes in petrols. *N*-Alkyl-*N'*-(*p*-hydroxyphenyl)ureas, *N*-(4-hydroxy-3-methylphenyl)-*N'*-phenylurea, and *N*-butyl-*N*-phenyl-*N'*-(*p*-hydroxyphenyl)urea, used at a concentration of 0.06%, exhibit the highest effectiveness.

The influence of *N*-(*p*-hydroxyphenyl)-*N'*-pentylurea and *NN'*-dipentylurea on the thermo-oxidative stability of TS-1 and T-2 reactive fuels has been investigated.[281] In contrast to their effect on petrols,[55] in reactive fuels the test compounds proved to be relatively ineffective; in their presence the decrease in deposit formation was only by 20–30% (the concentration of the additive was 0.05 wt.%).

The study of the influence of various alkyl- and alkylarylureas on the thermo-oxidative stability of straight-run reactive fuels of the T-1 type showed that *N*-alkyl and *NN*-dialkylureas are the most effective and reduce deposit formation in the fuel by 80–90%.[141,282] It has been established that substituted ureas which effectively reduce deposit formation in the fuel have almost no influence on the oxygen absorption process; this apparently shows that the antideposit formation function of the test compound is not associated with the antioxidant activity and is due to a dispersing type of activity. Compounds in which a urea fragment, with its dispersing activity, and a typical antioxidant fragment, namely 2,6-di(t-butyl)phenol, are combined in one molecule are effective stabilisers of reactive fuels.[156,283-285] Certain *N'*-acylaminoacyl derivatives of *N*-substituted ureas are also highly effective in stabilising reactive fuels obtained by hydrogenation processes.[286]

Kuliev and co-workers[152-154] proposed *NN'*-di(alkylbenzyl)-ureas as antioxidant additives to energy oils. For example, the additive obtained by condensing a mixture of C_8–C_{12} alkylphenols with urea and formaldehyde (AZNII-11) has antioxidant properties in oils which are not inferior to those of antioxidants such as ionol and *p*-hydroxydiphenylamine.

Apart from antioxidant properties, some of the substituted ureas behave as corrosion inhibitors when added to fuels and oils.[287-288] Thus *N*-alkyl-*NN'*-di(carboxymethyl)ureas containing 15–45 carbon atoms, preferably with an unbranched hydrocarbon chain, for example *N'N'*-di(carboxymethyl)-*N*-octadecylurea $C_{18}H_{37}NHCON(CH_2COOH)_2$ have been proposed as effective corrosion inhibitors in light distillate fuels.[287]

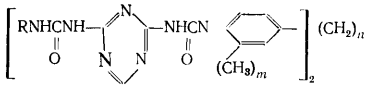
The alkenylsuccinimide based on urea (SIM), obtained by aminating alkenylsuccinic anhydride with urea, is used as a corrosion inhibitor in engine conservation oils for different purposes.[288,289] Its use ensures a high protective capacity and effective operating properties of the oils.

In many instances substituted ureas are used as detergent additives and additives preventing the formation of carbon deposits.[290,291] Monosubstituted ureas with an overall number of carbon atoms between 5 and 25 are used to remove carbon, varnish, and other deposits formed in the injection system of an internal combustion engine. Octadecyl-, dodecyl-, and 9-octadecynyl-ureas are the most effective (they are recommended for use in hydrocarbon fuels with a boiling range of 38–400 °C).

A reduction of the extent of deposition in the carburettor of an internal combustion engine is achieved by introducing into petrol additives which are products of the interaction of air-oxidised liquid paraffin and a substituted urea having the general formula $RNH(CH_2)_xNHCONH(CH_2)_xNHR'$, where $x = 2$–4 and R and R' are saturated secondary aliphatic C_{10}–C_{15} groups.[291]

Some investigors have successfully solved the problem of reducing the setting temperatures of diesel fuels with the aid of substituted ureas.[292,293] Compounds have the general formula $\begin{matrix}R_1\\R_2\end{matrix}\!\!>\!NCONH_2$ ($R^1 = C_3$–C_{20} alkyl groups, R^2 = phenyl), particularly *N*-phenyl-*N*-propylurea, produced a satisfactory result.[292] Alkylisoureas RNHCOR, where R = $\begin{matrix}\\||\\NH\end{matrix}$ C_{16}–C_{20} alkyl groups, have also proved to be more effective depressors of the setting temperatures of diesel fuels.[293]

Compounds of urea and triazine having the general formula



where R = C_{16}–C_{22} aliphatic group and *m* and *n* = 0 or 1 have been proposed as thickening additives to high-temperature plastic lubricants,[40] while halogenoarylureas are effective hardening agents for epoxy resins.[294-296]

It has been suggested that benzylureas be used as antioxidants for certain polymers.[297] It has been established that 3-alkylbenzyl-1-phenylurea at a concentration of 0.1% is the most effective in tests in polypropylene.

An important problem which has been solved successfully with the aid of substituted ureas is that of the prevention of the cracking of rubbers under the influence of ozone.[298-300] Substituted ureas having the general formulae ArNHCONHAr' (Ar and Ar' are various aromatic groups), for example, *N*-naphthyl-*N'*-*p*-tolylurea,[298] and $R^1R^2NCONR^3R^4$ (R^1, R^2, R^3, and R^4 are hydrogen or hydrocarbon groups, two of which are alicyclic) have been proposed.[209] For example, *NN*-dicyclohexyl-*N'*-phenylurea at a concentration of 1.5% reacts with butadiene–styrene raw rubber to form a vulcanised rubber which hardly cracks under the influence

of ozone. Substituted ureas with the above structure do not dye or decolorise the raw material to which they are added.

Urea derivatives have been proposed as anti-ageing agents[301] and thermal stabilisers[302] for synthetic rubbers. Diphenylurea prevents the cross-linking of synthetic rubbers to a high degree of unsaturation.[303] It has also been stated that urea derivatives with aromatic and aliphatic acyl groups can function as thermal stabilisers not only for rubbers but also for plastics and oils,[304] while dihydroxyalkylureas can be used as modifying agents (chain lengthening agents) for urethane thermoelastoplastics.[305]

Derivatives containing urea residues have been patented as stabilisers preventing changes in the mechanical properties and colour of polyurethane resins, foam plastics, fibres, synthetic leather, and elastomers under the influence of sunlight, ultraviolet irradiation, or heat.[306]

It has been suggested that substituted ureas be used as stabilisers for higher ketone peroxides (vulcanising agents for polyester resins)[307] and as stabilisers preventing the formation of a sludge from hydrocarbons, lubricating materials, and fuels.[308]

Substituted ureas are used for the bleaching[309] of fabrics and for imparting hydrophobic properties to the latter,[310] for the impregnation[311] of synthetic fibres, and for the improvement of their formation.[312]

Data have appeared recently in the literature[313] demonstrating the possibility of using substituted ureas as additives imparting fire resistance to synthetic fibres. For example, for this purpose polyamide fibres have been impregnated with a solution containing urea or some of its derivatives, such as *NN*-diphenylurea, *N*-α-naphthylurea, and *NN*-dimethyl-*N'*-phenylurea.[313] *N*-Substituted derivatives of ethyleneurea can be used as ink stabilisers.[314] Inks containing substituted ureas are highly stable during use and storage and possess satisfactory physical properties.

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Analysis of the literature data on the methods of synthesis of substituted ureas demonstrates their wide variety, but many of them suffer from various disadvantages which limit their application. Thus the amide method is characterised by low yields and the use of isocyanates for synthesis is difficult because they are not readily available, the condensation of hydroxymethylurea with phenols is accompanied by the formation of a large number of side products, while treatment of amines with phosgene makes it possible to obtain substituted ureas in high yields but the high toxicity of phosgene makes it difficult to work with this substance. From the standpoint of the ready availability of the starting material and simplicity, the interaction of urea or nitrourea with amines constitutes a convenient method of synthesis of substituted ureas but even this procedure suffers from certain limitations, because, depending on the amine employed, it gives rise to mono- or *NN*-disubstituted ureas. All these disadvantages and limitations must be taken into account in selecting the methods for the synthesis of particular urea derivatives.

The literature data which have been published recently show that, together with the traditional applications of substituted ureas (pesticides, medicinal preparations, and dyes), these compounds are highly effective as modifying and stabilising agents for various organic materials. One of the aims of the review is to draw the attention of investigators, working in the field concerned with the improvement of the quality of polymers and petroleum products with the aid of additives, to this promising class of compounds.

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