

Correlation of Urea Structure with Thermal Stability in Model Compounds

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Synopsis

Initial decomposition temperatures of various ureas have been determined using thermogravimetry and infrared analyses. Ranking of the compounds in order of thermal stability allows correlation between urea structure and resistance to thermal degradation. *N*-alkyl substitution of an arylurea results in the most significant lowering of thermal stability (50–70°C) as compared to the standard (*N,N*-diphenylurea) whereas orthosubstituent effects and electronic effects are present but lesser in magnitude. The large steric effect is postulated to indicate the necessity of rotation of the nitrogen–carbonyl bond during dissociation in order to establish the proper geometry for isocyanate bond formation.

INTRODUCTION

The effect of urea structure on thermal stability is of interest because of increasing demands for urea–urethane polymers which retain good mechanical properties at high temperatures.^{1,2} One example is the use of amine-extended RIM systems to enable the production of high modulus elastomers for automotive applications and elastomers which have better high temperature mechanical properties than their glycol-extended counterparts.^{3–5} Another example is the utilization of 10–30 wt% urea in a styrene–butadiene–urea block copolymer to significantly increase the high temperature tensile strength.⁶ The identification of suitable new polymers for high temperature applications is needed, and the consideration of model urea compounds is a useful initial step in this identification process.

In addition to the usage of urea components in polymer systems, there are other areas in which the relative thermal stabilities of ureas can be exploited. Thermolyses of substituted ureas as a method for preparing otherwise difficult to obtain isocyanates have been reviewed.^{7,8} Alkyl isocyanates have historically been prepared via this thermolytic route. A more recent example is that of a bicyclic urea which yields a diisocyanate and no volatile fragments on thermal dissociation.⁹

Of necessity (to ensure a sufficient yield of isocyanate) the temperatures at which these urea thermolyses were run exceeds the temperature at which dissociation begins.¹⁰ For example, *N,N*-diphenylurea and *N*-phenylurea are dissociated in the vapor phase at 370°C to an extent of 99% and 77%, respectively, allowing a recoverable yield of 57.6% phenyl isocyanate in the former case. Similarly, *N,N*-dicyclohexylurea yielded 71.6% cyclohexylisocyanate.¹¹ Lower temperatures (180–250°C) have been reported in the thermolyses of tertiary alkylureas to the corresponding alkyl isocyan-

ates.^{7,12,13} Urea itself has been studied, generally in the presence of aniline.^{14,15} At 180–190°C the ultimate product of this reaction (known as the "urea dearrangement") is *N,N'*-diphenylurea. The same product is found from thermolyzing phenylurea at 160°C. The lowest temperature at which *N,N'*-diphenylurea was reported to be formed from phenylurea is just above 100°C in aqueous solution at reflux. It can be seen from the above that no systematic, definitive study of initial urea dissociation temperatures has been done. Additionally, many of the experiments were run in solvent systems, allowing for the possibility of a solvent effect on the observed thermolytic temperatures.

The existence of this solvent effect has been conclusively demonstrated by a series of kinetic studies on the dissociation of *N,N'*-diphenylurea, a process shown to readily proceed at 100–140°C in large excesses of carboxylic acid solvent.^{16,17} The rate of dissociation of *N,N'*-diphenylurea varied as much as fourfold, depending on the carboxylic acid used as solvent. Other studies on the determination of initial dissociation temperatures of mono- and biscarbamates derived from substituted phenols and aromatic isocyanates have confirmed that the temperature at which initial thermolysis is observed is strongly influenced by the presence of a solvent.^{18–20} Thus, the use of a solventless method in determining initial urea dissociation temperature would be preferred, as it would avoid both the possible occurrence of side reactions with the solvent and the solvent effect.

One study which attempts to eliminate this solvent effect is that in which the relative stabilities of some hexamethylene diisocyanate-based ureas are determined using a suspension of the urea in a cellulose polymer.²¹ As isocyanate is liberated from the urea on heating, it reacts with the hydroxyl moieties of the cellulose, crosslinking it and rendering it insoluble in organic solvents. The aniline-derived urea has been found under these conditions to be more stable (no observed dissociation at 190°C) than the *N*-methyl aniline-derived adduct (dissociation occurred at 170–180°C). However, only a few ureas have been tested, and no systematic correlation of urea structure with thermal stability has been done using this method.

Thus the experimental work presented here represents an attempt to perform such a systematic study of the structural influence of model ureas on their initial dissociation temperatures in a solvent-free, uncatalyzed process. Thermogravimetry (TG)^{*,†} is used as the main experimental technique, with supplementary information obtained from heated-cell infrared spectroscopy, H-NMR, ultraviolet spectroscopy, and pyrolysis mass spectroscopy. The TG method involves heating the solid particulate urea at a constant rate under a dynamic nitrogen atmosphere. The volatile thermolytic products are thus swept away as formed, minimizing the occurrence of side reactions to form potentially more thermally stable products such as biurets, trimer, and carbodiimides. In this way, the onset of initial thermal dissociation can be observed.

* This temperature is a result of the procedure used and is not a fundamental property of the material.²²

† Following conventions for reporting TG data as specified by ICTA.²³

EXPERIMENTAL

Materials. All solvents used were anhydrous grade and were dried over 4 Å molecular sieves. Dimethylacetamide (DMAc) was additionally distilled from calcium hydride and stored over sieves. Chloroform was rendered ethanol-free by distillation from *p*-toluene sulfonyl isocyanate and stored in the dark under nitrogen. 2,6-Diisopropylphenylisocyanate was freshly prepared by a typical phosgenation procedure⁸ and distilled prior to use. Phenyl isocyanate, 4,4'-diphenylmethanediisocyanate (MDI), amines, and triethylene diamine (DABCO) catalysts were commercial products used as received without further purification. Melting points were determined using a Mel-Temp melting point apparatus and corrected using benzoic acid as a standard.

Model Compound Preparation. The ureas (see Tables I and II) were prepared by addition of isocyanate to a 5 mol % excess of the amine in an appropriate solvent, usually toluene or DMAc. In some cases, heating to 50–70°C and/or addition of 1% by weight DABCO were necessary to complete the reaction. The compounds were recrystallized to constant melting point and characterized by infrared and elemental analysis.

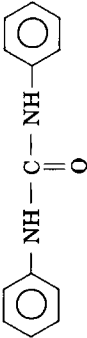
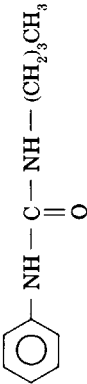
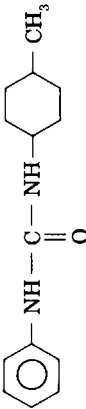
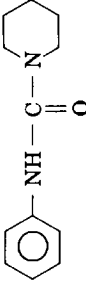
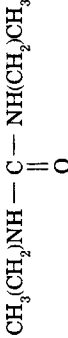
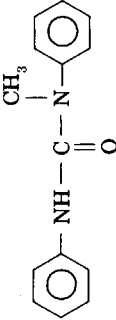
Thermogravimetric Studies. Thermogravimetric (TG) analysis was performed using a DuPont 951 TG unit with a DuPont 990 Recorder Unit. The furnace temperature was measured using a chromel–alumel thermocouple. Nitrogen was the purge gas. Heating rate for comparative studies was 5°C min⁻¹, sample size was 20–25 mg and the sample container was an open platinum boat.²³ For convenience in presenting the data, the temperatures corresponding to the 2%, 50%, and 100% weight losses were recorded. The precision of the method was determined to be ± 0.5°C (25–32 mg samples) at the 2% weight loss measurement.

For isothermal TG runs the heating rate was 5°C min⁻¹ to the isothermal temperature, at which point weight loss with time at that temperature was recorded (Table IV). Weight loss vs. temperature data for the isocyanates used in the study were also determined (Table V).

Infrared Studies. Infrared spectra were obtained using a Beckman Acculab 4 Spectrometer. A Valley Forge Instruments Model PC6011 Temperature Programmer was the source of temperature control for the heated cell. Temperature was measured with an iron–constantan digital thermometer. The KBr heated-cell infrared technique consisted of rapidly heating a pellet, consisting of 6% by weight urea in KBr, between 2-mm salt plates. Absorbance at 2250 cm⁻¹ was followed continuously, and when an increase was seen, the region 2000–2400 cm⁻¹ was scanned, and a measurement of absorbance made relative to the baseline. The temperature limit of the cell was 225–230°C.

H-NMR and Ultraviolet Spectra. H-NMR spectra were obtained on a Varian T60 (60 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm) downfield from internal tetramethylsilane. The ureas were dissolved in D₆DMSO at a 15–20 wt % level. Ultraviolet spectra were recorded using a Cary 14 Spectrophotometer. Each of the ureas was dissolved in absolute ethanol to a known concentration (which was in the range of 0.00001–0.00002M).

TABLE I
 Characterization of Model Monoureas

No.	Name	Structure	Melting Point (°C)		Elemental Analysis	
			Experimental (Literature)	Theory	Experimental	Theory
			%C	%H	%N	%N
1	N,N'-diphenylurea		241-2 (235 ³⁵)		73.39 5.88 13.50	73.58 5.66 13.21
2	N-n-butyl-N'-phenylurea		130-1 (129-30 ³⁶)		68.49 8.17 14.41	68.75 8.33 14.58
3	N-(<i>cis</i> , <i>trans</i> -4-methyl cyclohexyl)-N'-phenylurea		150-186 (176 <i>cis</i> 210-11 <i>trans</i> ³⁷)		71.72 8.84 12.85	72.41 8.62 12.07
4	N,N-pentamethylene -N'-phenylurea		167-8 (171-2 ³⁸)		70.50 7.74 13.53	70.59 7.84 13.73
5	N,N'-di-n-butylurea		69-9.5 (70.5-1 ²¹)		62.58 11.61 15.92	62.79 11.63 16.28
6	N-methyl-N,N'-diphenyl urea		102 (104-5 ³⁸)		74.40 6.06 12.14	74.34 6.19 12.39

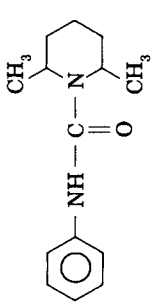
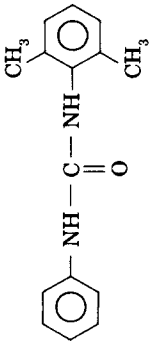
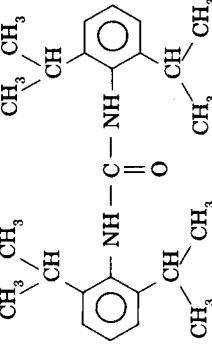
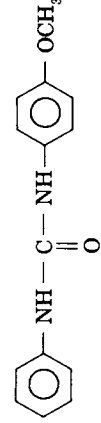
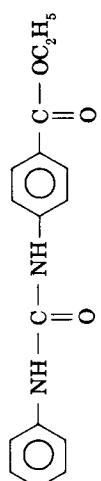
7	N,N-(1,5-dimethylpenta- methylene)-N'-phenylurea		149.5-50	73.98 74.01 6.56 6.61 12.64 12.33
8	N-phenyl-N'-(2,6-dimethyl phenyl)urea		237	75.08 75.00 6.88 6.67 12.17 11.67
9	N,N'-bis(2,6-diisopropyl phenyl)urea		229.5	75.08 75.00 9.39 10.42 7.23 7.29
10	N-phenyl-N'-4-methoxy phenyl)urea		194.5-5.5 (192 ⁸⁹)	68.46 69.42 6.08 5.79 11.57 11.27
11	N-phenyl-N'-(4-ethoxy carbonylphenyl)urea		170.5-2 (169 ⁸⁹)	67.82 67.61 5.71 5.63 9.69 9.86

TABLE II
 Characterization of Model Bisureas

No.	Name	Structure	Melting Point (°C) Experimental	Elemental Analysis	
				Experimental	Theory
				%C	%H
12	Methylene bis(N,N'-diphenyl)urea		330	74.30 6.21 13.17	74.31 5.50 12.84
13	Methylene bis(N'-cis,trans-4-methylcyclohexyl)-phenylurea		331 ³³	72.10 8.11 10.68	73.73 7.63 11.86
14	Methylene bis(N,N'-piperidyl)urea		254-55	71.59 7.24 11.88	71.43 7.62 12.07
15	Methylene bis(N-methyl-N,N'-diphenyl)urea		166-7	74.86 5.87 11.88	75.00 6.03 12.07
16	Methylene bis(N-phenyl-N'-4-methoxyphenyl)urea		319 ³³	71.86 5.28 10.82	70.16 5.64 11.29
17	Methylene bis(N-phenyl-N'-4-ethoxyphenyl)urea		290	68.27 5.18 9.90	68.04 5.15 9.62
18	Methylene bis(N-phenyl-N'-2-nitrophenyl)urea		239-240 ³³	61.57 3.97 15.89	61.83 3.82 16.00

TABLE III
Thermogravimetric Analysis of Ureas

No.	Temperature (°C) at weight loss of		
	2%	50%	100%
1	232	266	277
2	185	245	> 265
3	187	248	275
4	182	241	262
5	170	239	255
6	165	225	252
7	162	182	197
8	230	263	303
9	214	259	270
10	210	252	275
11	207	269	302
12	241	322	> 450
13	247	303	> 450
14	230	343	> 450
15	192	266	287
16	257	313	> 450
17	205	334	> 450
18	217	292	—

Pyrolysis Mass Spectroscopy. Spectra were obtained on a Hewlett-Packard 5985A GC/MS system using a direct insertion probe. The initial temperature was 30°C and was increased at a programmed rate of 30°C min⁻¹ up to 300°C. The electron beam potential was 20 eV.

RESULTS

Two groups of ureas have been studied: The first group consists of structural variation of *N,N'*-diphenylurea,

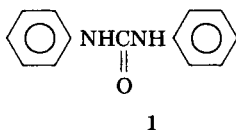


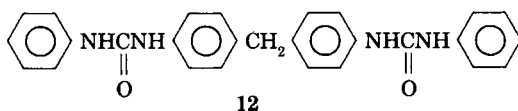
TABLE IV
Analysis of Ureas by Isothermal TG

Compound	Isothermal temperature (°C)	Weight loss on 5°C min ⁻¹ heating to isothermal temperature (%)	Weight loss after 1 h at isothermal temperature (%)
<i>N</i> -methyl- <i>N,N'</i> -diphenylurea	115	0	4.5
	164	4	82.5
<i>N,N'</i> -bis(2,6-diisopropyl phenyl)urea	129	0.5	0.5
	164	0.5	1.5
Methylene bis(<i>N'</i> -methyl- <i>N,N'</i> -diphenylurea)	130	0	0
	170	0	6

TABLE V
Weight Loss of Isocyanates by TG

Compound	Temperature (°C) at weight loss of			
	1%	2%	50%	85%
Phenyl isocyanate	25	27	77	89
Methylene bis(4-phenyl isocyanate)	158	170	248	265

and the second group includes modifications of the corresponding 4,4'-diphenylmethane diisocyanate (MDI)-based urea,



Three types of structural variations have been examined: (1) substitution of an alkyl group for an amine hydrogen or a terminal phenyl group; (2) substitution of an alkyl group for a ring (aliphatic or aromatic) hydrogen; (3) other aromatic ring substitution

In the first case, it can be seen (Tables I-III) that substitution of an alkyl group for a proton causes the major destabilizing effect. For example, the 2% weight loss temperature by TG ($T_{2\%}$) of compound **6** is 165°C. This is 67°C below the $T_{2\%}$ of compound **1**. The corresponding MDI derivative, **15**, is also much less thermally stable than its unsubstituted analog **12**. Evidence supporting the $T_{2\%}$ temperatures as the initial dissociation temperatures of compounds **6** and **15** is by observation of the isocyanate absorption in the infrared at these temperatures (Fig. 1). However, while replacement of the phenyl group in compound **1** by either *n*-butyl (**2**) or 4-methylcyclohexyl (**3**) appears to produce a destabilization comparable to that just described, the same result is not seen with the higher-melting MDI analogues **13** and **14**.

In cases where there is a discrepancy between the results obtained for phenylisocyanate-based and MDI-based ureas, the latter are taken to be correct as the higher melting bisureas are less subject to volatilization during to the TG experiment. Thus, in conclusion for the first group of compounds studied, ureas based on primary aliphatic amines are more stable than their aniline analogues when the isocyanate is MDI, and less stable when the isocyanate is phenyl isocyanate. In contrast, *N*-alkyl group substitution exerts a *major* destabilizing effect regardless of the isocyanate used.

For the second case, it can be seen that increasing the degree of steric hindrance about the amine hydrogen by adding two *o*-methyl (**8**) or four *o*-isopropyl (**9**) groups decreases the $T_{2\%}$. This decrease is negligible (within experimental error) in the former case and slight in the latter case. The isocyanate from compound **9** has also been seen to initially appear in the infrared spectrum (as the urea is being heated) at 217°C. This agrees well with the $T_{2\%}$ of 219°C and confirms that dissociation is indeed commencing at this temperature.

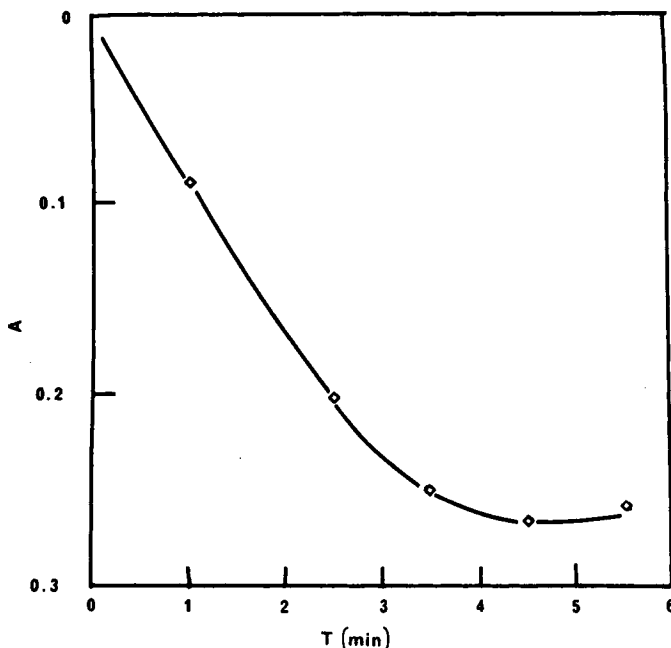


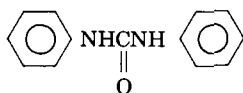
Fig. 1. Infrared absorbance at 2250 cm^{-1} as a function of temperature for urea no. 15, methylene bis(*N*-methyl)-*N,N'*-diphenylurea.

In the third case of aromatic ring substitution other than *o*-alkyl group substitution, it can be seen that for the phenyl isocyanate-based ureas, both the electron-donating *p*-methoxy group and the electron-withdrawing *p*-methoxy group caused a decrease in the $T_{2\%}$. For the MDI-derived analogues, however, the *p*-ethoxy carbonyl group again decreases the $T_{2\%}$ compared to the $T_{2\%}$ of compound 12, but the *p*-methoxy group this time increases the $T_{2\%}$ relative to 12. Thus, electron withdrawing group definitely decreased the urea thermal stability. Due to the suspected impurity of the *p*-methoxy derivatives (see Table I), no conclusions are drawn for the electron-donating case.

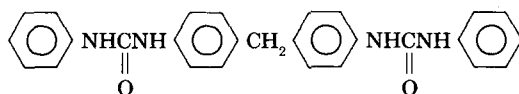
Supplementary information on selected compounds was provided by ultraviolet spectroscopy, ¹H-NMR and pyrolysis mass spectroscopy. Relative to compound 1, the ultraviolet spectra in (Fig. 2) absolute ethanol of compounds 6 and 9 showed hypsochromic shifts. Compounds 10 and 11 conversely demonstrated bathochromic shifts. In the ¹H-NMR spectrum of compound 9 the N-H shift appears at 7.78 ppm while in compound 1 the resonance is at 8.71 ppm. Similar upfield shift relative to compound 1 occurs for compounds 4 and 7. Pyrolysis mass spectroscopy of ureas 12, 16, and 17 indicates that all possible products (i.e., diisocyanate, diamine, and mixed isocyanate-amine) form, and no definitive conclusions about products of dissociation can be reached.

DISCUSSION

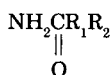
In an attempt to determine the characteristics of a thermally stable urea, the basic structures of *N,N'*-diphenylurea 1,



and methylene bis(*N,N'*-diphenylurea) **12**,



has been varied in three ways: (1) substitution of aliphatic for aromatic groups; (2) substitution of an alkyl group for hydrogen on the nitrogen atom; and (3) addition of substituents to the aromatic ring. Unsubstituted ureas, monoureas, and disubstituted ureas of the form



are not of interest because polymers cannot be formed from them. Tetra-substituted ureas (lacking an active hydrogen) decompose by a mechanism altogether different than that undergone by di- and trisubstituted ureas,³⁰ and in fact are thus considerably more stable than the latter to thermolysis. Therefore, the focus of the study here is with di- and trisubstituted ureas exclusively.

One item which becomes apparent in comparing the melting points (Tables I,II) and the 2% weight loss TG temperatures (Table III) is that while the carbanilide structure **1** is desirable as a basis for comparison to our own efforts and literature results, the use of compounds of this type may lead to ambiguous results if thermogravimetry is employed. Compounds which melt below the temperature at which 2% weight loss occurs during

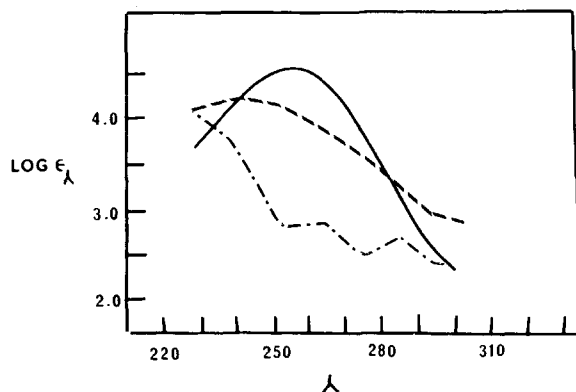


Fig. 2. Molar absorptivity ξ vs. wavelength λ plots of the ultraviolet spectra of ureas nos. **1** (—), **6** (---), and **9** (- · -).

the TG experiment may have sufficient vapor pressure to be swept away by the nitrogen purge in an undissociated form. Solids exhibiting weight loss may do so in an undissociated or a dissociated form. Corroborative evidence from heated cell infrared spectroscopy indicates that, for the ureas tested, the $T_{2\%}$ coincides with the temperature at which one observes initial generation of isocyanate from the urea in the infrared spectrum. In these cases, the TG is actually measuring relative temperatures of dissociation, not merely volatilization. However, other factors can influence the TG curve such as crystal lattice forces, which we have no way of measuring. It is possible that crystal lattice forces are stronger than chemical bonds in the bisureas. The observation that the melting points of trisubstituted ureas derived from phenyl isocyanate or MDI are lower than the melting points of other symmetrical aromatic ureas (nos. 1,12-14,16-18) suggests that the lattice forces of the former are weaker than those of the latter. Additionally, in the series of ureas based on phenyl isocyanate, the melting points of the aliphatic ureas are much lower than that of *N,N'*-diphenylurea 1. This may be due to their specific substituent effects or to their unsymmetrical nature. Both factors could affect the lattice structure of the urea, but we have no way based on current data to assess lattice forces. Another possible factor to consider in the interpretation of TG results is the influence of intermolecular hydrogen bonding.^{31,32} Factors which increase the hydrogen bonding capability are expected to increase the thermal stability of the resulting urea.

The combined results of thermogravimetry and heated-cell infrared spectroscopy lead us to the conclusions that (1) trisubstituted ureas are much less stable than disubstituted ureas and (2) steric and electronic effects are present but are much lesser in magnitude.

We believe that our results are best interpreted by a transition state in which the two segments of the molecule (termed for convenience, an "amine" and an "amide") are at or near right angles to one another, as shown in Figure 3. This geometry is closest to that required for formation of the heterocumulene system of the isocyanate, since in that molecule the two systems are mutually perpendicular. This transition state not only allows for easy transfer of the proton from oxygen to nitrogen but also aligns the bonds necessary to form the C-O system by a rehybridization process. While it is conceivable that enolization may not occur, we have no evidence to deny the possibility. In fact, previous workers have supported this idea.^{16,33} Figure 4 shows that even if enolization does not occur, the proton transfer can take place from the amide nitrogen to the amine nitrogen and that the same geometry applies. In addition, the rate of ring

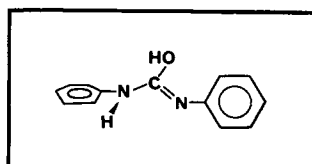


Fig. 3. "Amine" transition state for *N,N'*-diphenylurea.

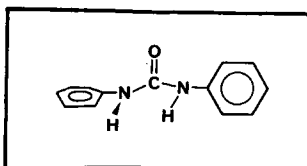


Fig. 4. "Amide" transition state for *N,N'*-diphenylurea.

opening of cyclic polymethylene ureas reaches a maximum in the eight-membered ring; the ring contains one C–N–H three atom system perpendicular to the N–C–O portion of the urea as shown in Figure 5.³⁴ This and our evidence support a mechanism for urea dissociation which involves rotation of one segment out of coplanarity with the second (Fig. 5).

Additional evidence to support this mechanism comes from (1) consideration of models, (2) prediction of relative coplanarity from ¹H-NMR spectra, and (3) determination of relative extent of conjugation in diaryl ureas by ultraviolet spectroscopy. While models suggest interference between the *o*-substituents and either the amide hydrogen (N–H) or urea carbonyl, the upfield shift of the N–H proton in the ¹H-NMR spectrum of these compounds provides some evidence for the lack of coplanarity of the two segments of the molecule. Ultraviolet spectroscopy was utilized in an attempt to determine the relative extent of conjugation³⁵ of five diaryl ureas: **1**, **6**, **9**, **10**, **11**, and one monoaryl urea, **4**. Picard and McKay have shown that extension of conjugative systems in general is manifested by a bathochromic (shift of absorption to longer wavelength), hyperchromic (increase in absorption intensity) shift, as seen, for example, in comparing acetanilide to aniline or 1,3-diphenyl-urea to acetanilide.³⁶ We find that, relative to carbanilide as a standard, *N*-methyl substitution significantly decreases the extent of conjugation. The spectrum of *N*-methyl, *N,N'*-diphenyl urea is similar to that of acetanilide. The same decrease in extent of conjugation is seen for *N,N'*-di(2,6-diisopropylphenyl) urea, whose spectrum is similar to that of simple urea.³⁷

In closing, it must be mentioned that, to fully assess substituent effects, one would like to know the structures of the products formed upon thermolysis. TG does not provide this information, and heated-cell infrared spectroscopy does not yield complete results. In an attempt to characterize the products of dissociation, pyrolysis mass spectroscopy was utilized. It was hoped that the initial products of dissociation could be elucidated; instead no definitive conclusion could be reached on the *mechanism* of urea thermolysis since all possible products form.

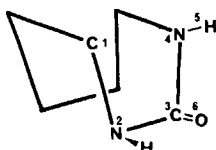


Fig. 5. A model of a cyclic polymethylene urea containing an eight-membered ring, showing the coplanarity of atoms nos. 1, 2, 3, 4, 5, and 6.

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