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Urea Dissociation. A Measure of Steric Hindrance in Secondary Amines

John C. Stowell* and Stanley J. Padegimas

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70122

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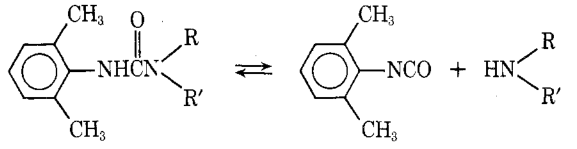
Most ureas are very stable compounds, sometimes used as characterizing derivatives of amines. Thermal dissociation may require high temperatures; *e.g.*, *N,N′*-diphenylurea was 99% dissociated into phenyl isocyanate and aniline at 370° in the gas phase.[1] Sufficient dissociation of some ureas occurs at 175° to give measurable rates of reaction with alcohols to give urethanes.[2] Similarly at 240–280° *N,N*-diphenyl-*N′*-methylurea dissociates enough to allow distillative removal of methyl isocyanate.[3] The possibility that lower temperature dissociation occurs in hindered cases is suggested by the room temperature rearrangement of *N-tert*-butyl-*N*-hydroxyureas to urethanes,[4] and the room temperature decomposition of 1,2-di-*tert*-butyl-4-isopropylsemicarbazide.[5]

We have found that ureas 1–8 dissociate appreciably in the range of 20–140° and that the equilibrium constants



1-8 **9**

1, R = R′ = *sec*-butyl
2, R = cyclohexyl; R′ = 3-pentyl
3, R = R′ = cyclohexyl
4, R = *tert*-butyl; R′ = isopropyl
5, R = *tert*-butyl; R′ = 3-pentyl
6, R = *tert*-butyl; R′ = cyclohexyl
7, R = 2,4,4-trimethyl-2-pentyl; R′ = isopropyl
8, NRR′ = 2,2,6,6-tetramethylpiperidyl

are readily measured by nmr spectroscopy. The equilibrium constants at two temperatures are given in Table I, and the thermodynamic values for variable-temperature measurements are given in Table II.

These equilibrium constants are a good indication of steric hindrance in secondary amines.[6,7] Polar effects should be very slight since we are not comparing relative rates, *i.e.*, stabilities of charged transition states, as in esterifications and hydrolyses.[8] It is interesting to note the very large difference between the disecondary alkyl amines and the secondary tertiary alkyl amines. This dramatic effect is similar to the one found in hydroboration of hindered olefins where the *tert*-butyl group exerts an extraordinary rate-retarding effect.[9] A scale of E^*_s values based on the hydroboration rates[10] was similar to the Taft E_s scale[8] except for the *tert*-butyl group, which showed greater hindrance in hydroboration.

Table I
Urea Dissociation Equilibrium Constants

	40°		127°	
Urea	K^a	% dissociation^c	K^a	% dissociation^c
1			0.017	12
2			0.032	16
3	$2.6 \times 10^{-5\,b}$	0.52^b	0.044	19
4	0.20	36	$72.^b$	99^b
5	0.34	42		
6	1.4	67	$117.^b$	99^b
7	2.1	74		
8	$(15.)^d$	$(95)^d$		

[a] K = [isocyanate][amine]/[urea]; ±10% of value. [b] Extrapolated values. [c] Calculated for 1 M initial urea concentration. [d] At 22°.

Table II
Thermodynamic Values for Urea Dissociation

Urea	$\Delta H°$, kcal/mol	$\Delta S°$, cal/deg mol
3	21.6 ± 0.5	48 ± 1
4	17.2 ± 0.4	51 ± 1
6	12.8 ± 0.2	41 ± 1

Our equilibria showed several inversions of order of steric hindrance in alkyl groups, compared to those indicated by E_s values. For example, we find the 3-pentyl group ($E_s = -1.98$) less hindering than the cyclohexyl group ($E_s = -0.79$).[11] In kinetic terms however, we find that urea formation for this pair is qualitatively in line with E_s values. At 40° the reaction of *tert*-butylcyclohexylamine with **9** (0.7 *M*) is at equilibrium (27% associated) in less than 1.5 hr, at which time the reaction of *tert*-butyl-3-pentylamine with **9** is only 14% associated. Even after 2 days, equilibrium is not yet reached (final value after 4 days is 47% associated). Similarly in the reverse direction, **2** required about 20 min to reach equilibrium at 140° by dissociation while **3** required only about 5 min.

Experimental Section

3-Pentylcyclohexylamine was prepared by a modification of the method of Skita and Keil.[12] Platinum oxide (25 mg) and one drop of concentrated HCl were added to 9.9 g (0.10 mol) of cyclohexylamine and 17.2 g (0.20 mol) of 3-pentanone. This was hydrogenated in a Parr shaker at 50 psi initial pressure for 2 days. The solution was decanted, about 200 mg of Na_2CO_3 was added, and then the solution was distilled on a spinning band column to give 11.0 g (65%) of the secondary amine, bp 95° (13 mm) (lit. yield 31%, bp 208–209°).

Di-*sec*-butylamine was prepared similarly from *sec*-butylamine and 2-butanone.

Commercial dicyclohexylamine was purified by distillation.

The secondary alkyl tertiary alkyl amines were prepared as described previously.[13]

All amines were dried over 4A molecular sieves before use.

2,6-Dimethylphenyl isocyanate[14] was prepared by phosgenation of 2,6-dimethylaniline hydrochloride and purified by spinning band distillation, bp 112–113° (35 mm) [lit.[14] bp 90–91° (13 mm)].

Anisole was purified by distillation and dried over 4A molecular sieves. Anisole was chosen as solvent for the higher boiling point (155°). Moreover, the difference in nmr chemical shift between the methyl groups on the isocyanate and those on the ureas (Table IV) were greater than in, *e.g.*, *o*-dichlorobenzene.

Equilibrium Measurements. 2,6-Dimethylphenyl isocyanate (303 mg, 2.06 mmol) was added to a solution of *tert*-butylisopropylamine (217 mg, 0.189 mmol) in 2 ml of pentane under nitrogen. The resulting white solid (**4**) was filtered, washed with pentane, and dried under nitrogen in a glove bag. A sample of the dry urea (97.4 mg) was dissolved in 307.2 mg of anisole under nitrogen in a well-dried nmr tube equipped with a tight cap. The tube was heated in the variable-temperature probe of an A-60 nmr spectrometer at each temperature until the ratio of isocyanate to urea remained constant. The peaks for the benzylic methyl

Table III
Equilibrium Constants for Variable-Temperature Dissociation of Ureas

Urea 6		Urea 4		Urea 3	
Temp, °C	K	Temp, °C	K	Temp, °C	K
32	0.70	44.5	0.31	103	8.3×10^{-3}
34.5	0.89	48.5	0.40	109	1.25×10^{-2}
39	1.10	52.5	0.55	120.5	2.8×10^{-2}
50	2.4	61	0.94	127	4.1×10^{-2}
55	2.6	65	1.57	134	7.0×10^{-2}
59	4.0	69	2.1	138	1.0×10^{-1}
65.5	5.5	73.5	2.7	143	1.3×10^{-1}
		81.5	4.5		

Table IV
Chemical Shift Values[a] of the Benzylic Methyl Groups in Each Urea and the Isocyanate at 34°

Compd	δ	Compd	δ
1	1.29	**6**	1.23
2	1.27	**7**	1.24
3	1.26	**8**	1.22
4	1.26	**9**	1.36
5	1.26		

[a] In parts per million upfield from anisole OCH_3.

groups of the isocyanate and the urea were recorded at 100-Hz sweep width and measured with a planimeter. In the case of this particular urea, the concentration of the amine could be measured as well. The *tert*-butyl groups and the methyls of the isopropyl groups were at δ 2.44 and 2.51. The corresponding peaks in the urea were at δ 2.12 and 2.25 ppm upfield from anisole OCH_3.

The equilibrium constants (Table I) were calculated using a correction for the density of anisole at each temperature.[15] The thermodynamic values (Table II) were obtained by a least-squares treatment of log K *vs.* $1/T$. The temperatures could be measured quickly after each equilibration if a very fine sealed capillary of ethylene glycol was placed in the nmr tube with the sample. The ethylene glycol peaks occur in an otherwise clear area of the spectrum.

Urea **6** was prepared similarly, although the pentane solution required cooling for crystallization of the product.

Urea **3** gave no precipitate; so it was prepared by transferring the amine, isocyanate, and anisole with syringes in a glove bag under nitrogen to the nmr tube, weighing after each addition.

Equilibrium constants (Table III) were determined from solutions of each of the above ureas at two different concentrations to check reproducibility.

Ureas **1**, **2**, **5**, **7**, and **8** were measured at only one temperature owing to very slow equilibration, or their dissociating near the upper limit of the usable temperature range. They were each prepared in the nmr tubes as described above for **3**. See Table IV for chemical shift values.

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Registry No.—**1**, 51608-96-9; **2**, 51608-97-0; **3**, 51608-98-1; **4**, 51608-99-2; **5**, 51609-00-8; **6**, 51609-01-9; **7**, 51609-02-0; **8**, 51609-03-1; **9**, 28556-81-2; di-*sec*-butylamine, 626-23-3; cyclohexyl-3-pentylamine, 51609-04-2; dicyclohexylamine, 101-83-7; *tert*-butylisopropylamine, 7515-80-2; *tert*-butyl-3-pentylamine, 51609-05-3; *tert*-butylcyclohexylamine, 51609-06-4; isopropyl(2,4,4-trimethyl-2-pentyl)amine, 51609-07-5; 2,2,6,6-tetramethylpiperidine, 768-66-1; cyclohexylamine, 108-91-8; 2-butanone, 78-93-3; 2,6-dimethylaniline hydrochloride, 21436-98-6.

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Heterodienophiles. VI.[1] The Structure of Protonated Aldimines

Grant R. Krow,* C. Pyun, C. Leitz, and J. Marakowski

Temple University, Philadelphia, Pennsylvania 19122

Kermit Ramey

ARCO Chemical Company, Glenolden, Pennsylvania 19036

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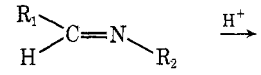
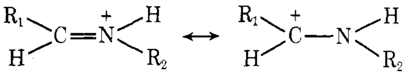
A nuclear magnetic resonance study[2] of protonated aldimines **1–3** with fluorosulfonic acid–antimony pentafluoride in sulfur dioxide solution has indicated a predominance of *E*-immonium structure I, with only limited contribution of aminocarbonium ion form II. We have extended this study in strongly acidic solution to aldimines having electron-withdrawing *N*-carbamyl, acyl, and *p*-toluenesulfonyl substituents.

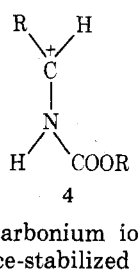


1, $R_1 = Ph; R_2 = CH_3$
2, $R_1 = Ph; R_2 = Ph$
3, $R_1 = Ph; R_2 = Ph\text{-}p\text{-}Cl$



I II

A literature survey indicates that reactions of *N*-carbethoxyl imines have been variously described as polar cycloadditions,[3] Diels–Alder reactions,[4] pseudo-Diels–Alder reactions,[5] α-amidoalkylations,[6] or stabilized carbonium ion reactions.[7] The reactive species in these reactions has been depicted as an azacarbonium ion[3] **4**, an



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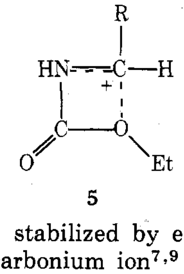

5

$RCH\overset{+}{=\!=}NHCOOEt$

6

azacarbonium ion stabilized by ester oxygen[8] **5**, a resonance-stabilized carbonium ion[7,9] **6**, an N-protonated *Z*-immonium ion[5] **7**, and a carbonyl-oxygen protonated *E*-iminourethane **9**. One might in addition postulate an *E*-immonium ion **8** similar to **7**, as well as significant contri-