Chemistry of Aryl Isocyanates: Rate of Decomposition of Some Arylalkyl Biurets and Ethyl α,γ-Diphenylallophanate

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The NH groups of alkyl or arylalkyl ureas and carbanilates exhibit absorption in the region of 6750 cm.$^{-1}$ of the near infrared spectrum. Recent studies of the near infrared spectrum of ethyl α,γ-diarylallophanate and tetraarylalkyl biurets showed that absorption for the NH group in the region of 6750 cm.$^{-1}$ was absent. This was interpreted as evidence for intramolecular hydrogen bonding between the NH and carbonyl groups.[1] This difference in absorption permits a study of the decomposition of ethyl α,γ-diphenylallophanate and some tetraarylalkyl biurets to carbanilate or urea and isocyanate.

EXPERIMENTAL

Materials. Ethyl α,γ-diphenylallophanate,[2] m.p. 94° was prepared by the method of Kogon and recrystallized from absolute ethyl alcohol. 1,3,5-Triphenyl-1-methylbiuret m.p. 133° and 1,3-diphenyl-5,5-diethylbiuret m.p. 115° were prepared by the method of Baker.[3] 1-Phenyl-3,5,5-triethylbiuret m.p. 113.5–114° was obtained from E. J. Goldberg.[4]

"Kel F" Alkane, grade 695 [$Cl(CF_2—CFCl)_3Cl$] and "Kel F" Alkane, grade 464 [$Cl(CF_2—CFCl)_2Cl$] were obtained from the M. Kellogg Co.

Measurements were made with the Cary Spectrophotometer Instrument Model No. 14, using a thermostatically heated cell holder.

Kinetic Method. The rate of increase of carbanilate or urea was determined at regularly timed intervals by the increase in absorption in the region of 6750 cm.$^{-1}$ The concentration of carbanilate or urea at time t was determined by the Beer-Lambert formula. The molar absorptivity for 1,3-diphenyl-1-methylurea, 1,1,3-triethylurea, 1-phenyl-3,3-diethylurea, and ethyl carbanilate at 131–145° were 0.699, 0.490, 0.464, and 1.192, respectively.

Solutions. For a kinetic run 25.0 ml. of "Kel F" grade 494 or grade 695 was added to a 100-mm. quartz cell and heated in the instrument until the required temperature was obtained. To the hot solvent was then added 0.5 gm. of arylalkylbiuret or ethyl α,γ-diphenylallophanate and the mixture was shaken for ten seconds before the spectrum was obtained. The measurements were then made on the sample at successive time intervals.

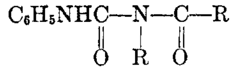
Calculations. The rate constants were calculated from the customary first order rate expression

$$K = 1/t \ln \frac{a}{a\text{-}x}$$

where a is equal to the initial concentration of allophanate or biuret and x is the concentration of allophanate or biuret decomposed to carbanilate or urea and a-x is the concentration of remaining allophanate or biuret. In the case of ethyl α,γ-diphenylallophanate the assumption is made that although the reaction is reversible the rate of the decomposition of allophanate is much greater than the rate of formation which can be neglected.[5]

The first order rate constants are listed in Table I.

TABLE I

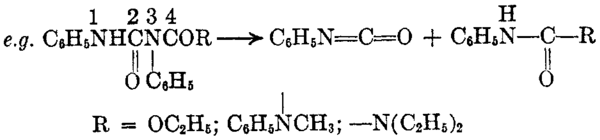


$$C_6H_5NH\underset{\underset{O}{\|}}{C}—\underset{\underset{R}{|}}{N}—\underset{\underset{O}{\|}}{C}—R'$$

No.	R	R′	Temp., ° C.	$k \times 10^4$ sec.$^{-1}$	ΔE Kcal.
1	C_6H_5	OC_2H_5	132	0.39	
2	C_6H_5	OC_2H_5	150	1.65	26.2
3	C_6H_5	$N(CH_3)C_6H_5$	131	6.8	
4	C_6H_5	$N(CH_3)C_6H_5$	145	15.0	17.8
5	C_6H_5	$N(C_2H_5)_2$	138	0.9	
6	C_6H_5	$N(C_2H_5)_2$	145	1.5	20.0
7	C_2H_5	$N(C_2H_5)_2$	131	0.2	
8	C_2H_5	$N(C_2H_5)_2$	150	1.32	34.2

DISCUSSION

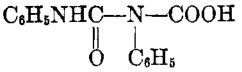
For this study, the molecules were chosen so that cleavage to isocyanate and carbanilate or urea could occur at only one point, between 2 and 3.[6]



$$e.g.\ C_6H_5\overset{1}{N}H\underset{\underset{O}{\|}}{\overset{2}{C}}\underset{\underset{C_6H_5}{|}}{\overset{3}{N}}\overset{4}{C}OR \longrightarrow C_6H_5N{=}C{=}O + C_6H_5\overset{H}{N}—\underset{\underset{O}{\|}}{C}—R$$

$$R = OC_2H_5;\ C_6H_5\overset{|}{N}CH_3;\ —N(C_2H_5)_2$$

An examination of these molecules indicates that they are derivatives of α,γ-diphenylallophanic acid (I). The rate constants indicate that the rate of decomposition of a biuret containing a phenyl group on the 1 and 3 nitrogen atom in greater than ethyl α,γ-diphenylallophanate. The increased thermal stability of ethyl α,γ-diphenylallophanate compared to 1,3-diphenyl-5,5-diethylbiuret or 1,3-5-triphenyl-5-methylbiuret is due to the apparently greater stabilization afforded to the allophanic acid derivative by an ethoxy group compared to the diethylamino or methylanilino group. A comparison of the biurets studied shows that substitution of a phenyl group by an ethyl group on the 3 nitrogen atom increases the thermal stability of the biuret.



$$C_6H_5NH\underset{\underset{O}{\|}}{C}—\underset{\underset{C_6H_5}{|}}{N}—COOH \quad (I)$$

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[1] I. C. Kogon, *J. Am. Chem. Soc.*, **79**, 2253 (1957).

[2] I. C. Kogon, *J. Am. Chem. Soc.*, **78**, 4911 (1956).

[3] J. W. Baker and J. B. Holdsworth, *J. Chem. Soc.*, 724 (1945).

[4] Kindly supplied by E. J. Goldberg, E. I. du Pont de Nemours & Company, Inc., Elastomer Chemicals Department, Wilmington, Del.

[5] Recent studies by I. C. Kogon, to be published, have shown this to be true.

[6] The referee has suggested that dismutation could occur between atoms 1 and 2 and possibly effect the apparent rate of dismutation between atoms 2 and 3. This is highly unlikely since the energy of dissociation between atoms 1 and 2 is far greater than the energy of dissociation between atoms 2 and 3.