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*Mechanism of Reaction of
Isocyanate-Bisulfite Adducts
with
Primary Amines*

By

PETER D. HOAGLAND

and

PETER R. BUECHLER

Technical Note

MECHANISM OF REACTION OF ISOCYANATE-BISULFITE ADDUCTS WITH PRIMARY AMINES

PETER D. HOAGLAND AND PETER R. BUECHLER

*Eastern Regional Research Center**
Philadelphia, Pennsylvania 19118

Introduction

Organic isocyanate-bisulfite adducts carbamylate amines in water under mild conditions (1, 2). As a consequence, these adducts have application as tanning or retanning agents (3). One reviewer (4) of such an application study in our laboratory (3) questioned whether free isocyanates might not be important intermediates when the adducts react with a primary amine in water at room temperature. Even though aqueous solutions of organic isocyanate-bisulfite adducts are reported to be stable at room temperature (1, 2), this question is appropriate, since an appreciable concentration of free isocyanate was reported to be in a solution of potassium butylaminocarboxysulfonate, pH 6, after standing 1 hr at 80°C (1). Under these circumstances, we decided to investigate the mechanism of the tanning reaction at room temperature under conditions reported earlier (3). To this end we employed nuclear magnetic resonance (NMR) to look for free isocyanate intermediates.

Experimental

Proton-decoupled ^{13}C NMR spectra were obtained with a JEOL-FX-60Q spectrometer at 15.00 MHz, using an observation frequency of 37.50 KHz and an irradiation frequency of 47.65 KHz. The pulse width was 74° at a 5 s repetition rate. Free induction decays were acquired using 8 K data points, a 4 K spectral width, and were transformed to give 0.23 Hz resolution. Samples were dissolved in 20 percent D_2O (2 ml) to give 10 percent concentrations. Internal 1 percent p-dioxane was the reference.

Materials. Hexamethylene-1,6-di(aminocarboxysulfonate) was a gift of Mr. Edward Harris, Jr. and was prepared by a published procedure (1). Butylamine, hexamethylenediisocyanate, and triethylamine was obtained from Aldrich Chemical Company.

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Results and Discussion

To address the question of formation of free isocyanate both the stability of 1,6-hexamethylene di-(aminocarboxysulfonate) (1) in 20 percent D₂O at room temperature and its reaction with butylamine have been examined by ¹³C-NMR spectroscopy. Because the carbonyl carbons of isocyanates have long relaxation times and cannot benefit from the Nuclear Overhauser Effect, their resonances are weak and of little use for the detection of free isocyanate (6). However, the shift value for the α -methylene carbon of hexamethylene diisocyanate is sufficiently different from that for the α -methylene carbon of its bisulfite adduct (1) (Table I) to insure that any monoisocyanate (6), would be detected at concentra-

TABLE I

¹³C-SHIFT VALUES IN PPM AND (RELATIVE INTENSITIES) FOR WATER SOLUBLE,
HYDROLYTIC PRODUCTS OF HEXAMETHYLENE-1,6-Di-
(AMINOCARBOXYSULFONATE) (1) IN 20 PERCENT D₂O AND 1.8 PERCENT
TRIETHYLAMINE AT 33°C

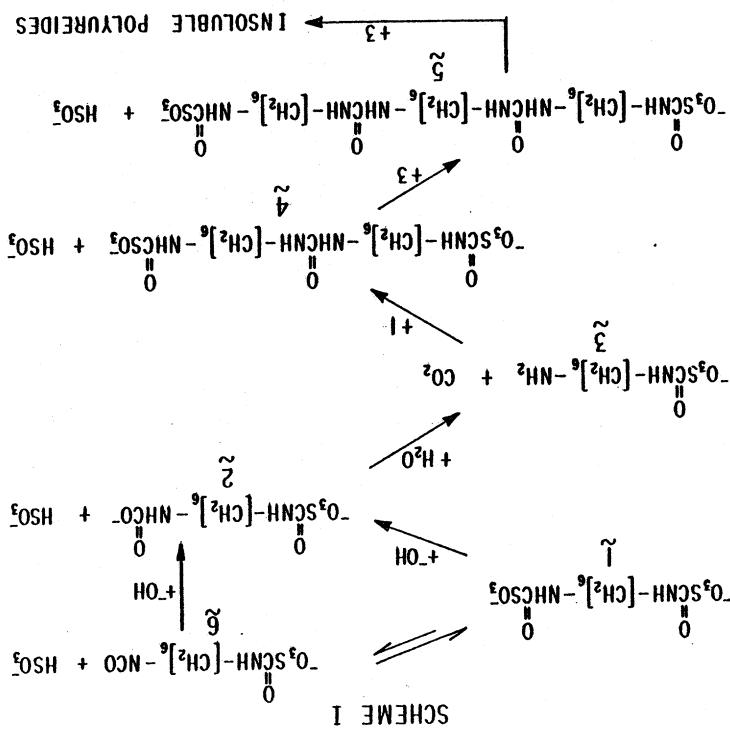
Carbon species	α -C	β -C	γ -C	C = 0
Product I (possible 4)	40.77 (619)	29.99 (631)	26.15 (761)	161.50 (190)
Product II (possible 5)	40.38 (454)	27.45 (447)	25.96 (426)	
Hexamethylene di- (aminocarboxysulfonate)	41.09 (3351)	28.75 (2756)	26.35 (3190)	166.31 (487)
Hexamethylene ^a diisocyanate	42.42	30.34	25.34	121.59

^aIn DMSO-d₆ at 33°C,

tion levels above about 0.5 percent. A 10 percent solution of 1,6-hexamethylene di-(aminocarboxysulfonate) (1) in 20 percent D₂O (pH 4.79) after standing at room temperature for 24 hr presented no spectroscopic evidence for the formation of either isocyanate or of any hydrolytic products. When triethylamine (1.5 percent) was added to effect alkaline hydrolysis of (1), no free isocyanate could be detected in spectra obtained using a 24-hr period. However, seen in these spectra were new resonances with shift values significantly different from those for hexamethylene-1,6-diisocyanate (Table I). These resonances probably derive from dimer and trimer ureas (4) and (5), as shown in Scheme I. The insoluble material has been reported to be the expected polyureide material (1).

With spectroscopic data on the alkaline hydrolysis of (1) in hand, the reaction of (1) with butylamine in water at 33°C was next examined (Scheme II). Within a minute after addition of a 1.1 equivalent amount of butylamine to a 10 percent

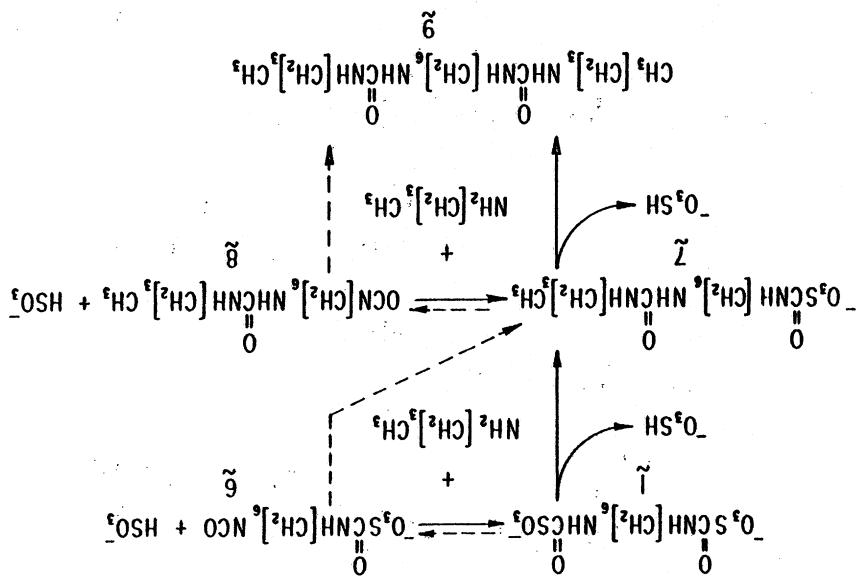
solution of (1) in 20 percent D₂O in a standard 10-mm NMR tube, cloudiness developed. Thereafter, the expected N⁺-N⁺-diisobutyl-N⁺-N⁺-hexane-diylbis-diurea (9) (confirmed by IR spectroscopy, m.p. 192.5-193°, lit. 192-194°, (5) slowly precipitated from solution. ¹³C-NMR spectra were acquired during the first hour of reaction. At no time did resonances for a carbon *a* to an isocyanate group appear. In order for the reaction to proceed through isocyanate intermediates (6 and 8), which would have to exist below detectable concentrations, an unobserved great rate of adduct reversal (1 → 6) is demanded in addition to the requirement that (1) cannot appreciably react directly with primary amine. The observed data do strongly support nucleophilic attack by the amine on the bisulfite ion. Hence, organic disocyanate-bisulfite adducts have expulsion of bisulfite ion.



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- Department of Agriculture over others of a similar nature not mentioned.
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Scheme II