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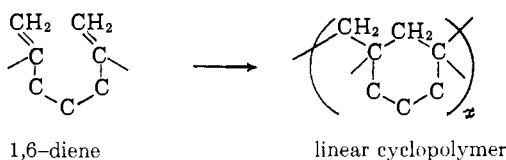
## Cyclopolymerization of Aliphatic 1,2-Diisocyanates

BY C. KING

RECEIVED JULY 2, 1963

The aliphatic 1,2-diisocyanates ethylene diisocyanate, 1,2-propylene diisocyanate, and 1,2-cyclohexylene diisocyanate have been cyclopolymerized to linear, high molecular weight products having regularly recurring 5-atom heterocyclic units. These polymers appear to have the structure of poly-[ketoethyleneureas] (formula I in text), as shown by infrared analysis. Glyceryl triisocyanate, a 1,2,3-vicinal triisocyanate, underwent analogous cyclopolymerization to give linear polymer having recurring units consisting of fused 5-atom ring heterocycles (formula II in text). The 1,3-diisocyanates oxydimethylene diisocyanate and trimethylene diisocyanate gave only minor amounts of 6-atom heterocycles by cyclopolymerization and the polymers were cross linked. It is concluded that cyclopolymerization for diisocyanates strongly favors formation of 5-atom rings, and thus differs from that for diolefins, where the preferred course is the formation of 6-atom rings. Synthesis of the diisocyanate monomers used in this work is described.

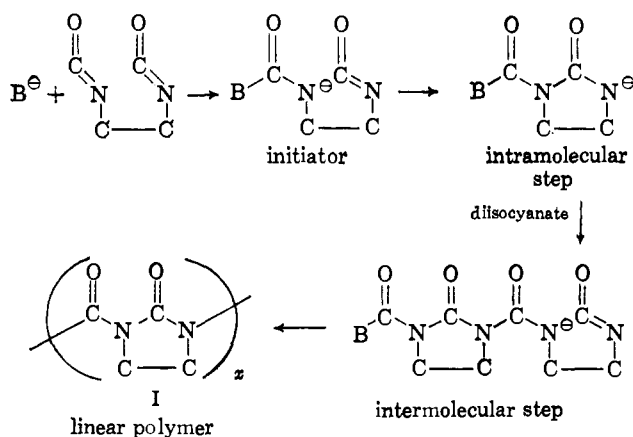
Cyclopolymerization of 1,6-dienes to linear polymers was first demonstrated by Butler<sup>1</sup> and has since been extended by many workers.<sup>2</sup> The polymers from such dienes consist of regularly recurring 6-atom ring units joined by methylene groups. Typically



This polymerization proceeds through stepwise intramolecular ring closure and intermolecular chain extension. Cyclopolymerization of diolefins is most efficient when the monomers are so constructed as to yield 6-atom rings.<sup>2</sup>

We now report an extension of cyclopolymerization to include monomers containing isocyanate groups as the polymerizable functions. Specifically, we have found that aliphatic 1,2-diisocyanates (vicinal diisocyanates) may be converted to linear high molecular weight cyclopolymer.<sup>3</sup> These differ from the diene cyclopolymer in that the recurring cyclic units consist of five atoms rather than six. The polymerization technique was essentially that developed in this laboratory for polymerizing monoisocyanates to linear N-alkyl "1 nylons."<sup>4,5</sup>

**Structure.**—It is proposed that the 1,2-diisocyanate polymers prepared in this work are poly-[N-ketoethyleneureas], which evidently arose from an alternating intra-intermolecular chain growth mechanism analogous to that postulated for 1,6-dienes.<sup>1</sup>

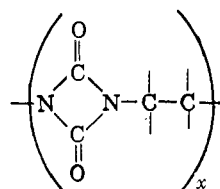


- (1) G. B. Butler and R. J. Angelo, *J. Am. Chem. Soc.*, **79**, 3128 (1957).
- (2) See, e.g., reviews by C. S. Marvel, *J. Polymer Sci.*, **48**, 101 (1960); G. B. Butler, *ibid.*, **48**, 279 (1960).
- (3) R. G. Beaman, U. S. Patent 3,048,566 (August 7, 1962), to du Pont.
- (4) V. E. Shashoua, *J. Am. Chem. Soc.*, **81**, 3156 (1959).
- (5) V. E. Shashoua, W. Sweeny, and R. F. Tietz, *ibid.*, **82**, 866 (1960).

Structure assignment is based on evidence from polymer solubility measurements and infrared absorption spectra. All the poly-[1,2-diisocyanates] prepared in this work were rapidly and completely soluble in sulfuric acid without degradation; this is good evidence that the polymers were linear. Poly-[1,2-propylene diisocyanate] and poly-[1,2-cyclohexylene diisocyanate] were completely soluble in polar organic solvents such as formic acid, nitromethane, N,N-dimethylformamide (DMF), and dimethyl sulfoxide. Some samples of the former had sufficiently high molecular weight that they afforded clear flexible films on evaporation of these solvents.

All the cyclopolymer showed carbonyl absorptions of equal intensity at 5.6 and 5.9  $\mu$ , consistent with the N-ketoethyleneurea structure. N-Acetyleneurea, a model compound which has a similar structure, has similar split carbonyl absorption at 5.7 and 6.1  $\mu$ .<sup>6</sup> The "1-nylon" polymers from monoisocyanates have only a single absorption at 5.85  $\mu$  due to carbonyl.<sup>4,5</sup>

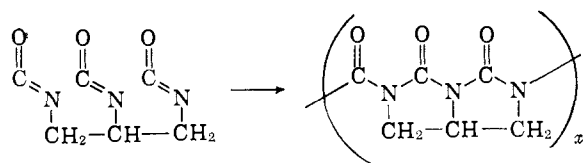
An alternative "poly-dimer" structure



appears unlikely because aliphatic isocyanates are not known to dimerize under these conditions, and phenyl isocyanate dimer has a single carbonyl absorption at 5.6  $\mu$ .

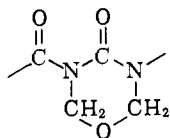
**Scope.**—No attempt was made to determine the maximum degree of alkyl substitution on the basic ethylene diisocyanate unit compatible with polymerizability. However, the examples provided in this work suggest that the degree of substitution permissible may be quite varied. We have found that ethylene diisocyanate, glyceryl triisocyanate, 1,2-propylene diisocyanate, and 1,2-cyclohexylene diisocyanate readily cyclopolymerize to high molecular weight products. The last two are structurally analogous to isopropyl isocyanate and cyclohexyl isocyanate in the monoisocyanate series. Prior work in this laboratory<sup>4,5</sup> showed that these  $\alpha$ -substituted monoisocyanates do not give high polymer. It therefore appears that formation of a 5-atom ring constitutes here a powerful driving force to effect polymerization through an otherwise poorly polymerizable structure. Glyceryl triisocyanate was used to demonstrate a case in which three vicinal isocyanate groups undergo cyclopolymerization.

- (6) H. K. Hall and R. Zbinden, *ibid.*, **80**, 6428 (1958).



This polymer was soluble in sulfuric acid and had the split carbonyl absorption characteristic of the 1,2-diisocyanate polymers.

Polymers were prepared from oxydimethylene diisocyanate,  $\text{OCN-CH}_2\text{-O-CH}_2\text{-NCO}$ , and trimethylene diisocyanate,  $\text{OCN-CH}_2\text{-CH}_2\text{-CH}_2\text{-NCO}$ , in the hope of preparing cyclopolymers with recurring 6-atom ring units, but the polymers obtained were insoluble in sulfuric acid and appeared to be cross linked. Polymers from trimethylene diisocyanate were insoluble, even when they were prepared in dilute solutions, which might be expected to favor cyclopolymerization.<sup>7</sup> Infrared analysis of these polymers disclosed only a single carbonyl absorption at  $5.9 \mu$ , characteristic of the N-alkyl "1-nylons."<sup>4,5</sup> One preparation of poly-[oxydimethylene diisocyanate] showed strong carbonyl absorption at  $5.85 \mu$ , accompanied by a shoulder at  $5.7 \mu$ , suggesting that some of the 6-atom ring unit may have been present. The evidence here indicates that for 1,3-



diisocyanates the reactive groups polymerize largely by an all-intermolecular path, giving cross-linked structures. Cyclopolymerization for diisocyanates is thus seen to proceed more efficiently when 5-atom rings can be formed rather than 6-atom rings, which are the preferred course for dienes.

#### Polymerization and Properties of the Cyclopolymers.

High yields of high molecular weight cyclopolymers were obtained when sodium cyanide was added to a 10-15% solution of a 1,2-diisocyanate in DMF at from  $-30$  to  $-50^\circ$ . Heat of polymerization usually raised the temperature to about  $15^\circ$ , and the polymerizations were essentially complete after 0.5 hr. With soluble polymers, the polymerization mixtures became viscous after about 5 min. Polymers insoluble in DMF settled out as swollen white particles. Polymers were isolated by precipitation into methanol.

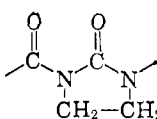
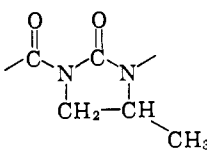
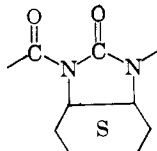
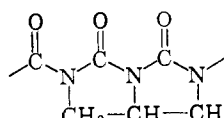
Polymerization of ethylene diisocyanate required no added initiator, since rapid polymerization occurred immediately upon mixing the monomer with solvent at  $-30^\circ$ . Occasionally, samples of 1,2-diisocyanates stored for extended times at  $0^\circ$  slowly polymerized. In this manner, ethylene diisocyanate gave cloudy solid objects; bulk polymers from 1,2-propylene diisocyanate were hard and brilliantly clear. Polymers thus "spontaneously" formed were also completely soluble and showed split carbonyl absorption at  $5.6$  and  $5.9 \mu$ . It is remarkable that cyclopolymerization should be so favored in this system so as to predominate even in bulk.

The molecular weights of the polymers relative to each other were conveniently determined by measuring their inherent viscosities at  $30^\circ$  on 0.5% solutions in tetrachloroethane-phenol (40/60 wt.). Some samples of poly-[1,2-propylene diisocyanate] had values as high as 1.35. A sample of polymer having an inherent vis-

cosity of 0.56 was found by osmometry to have a number average molecular weight of 45,000.

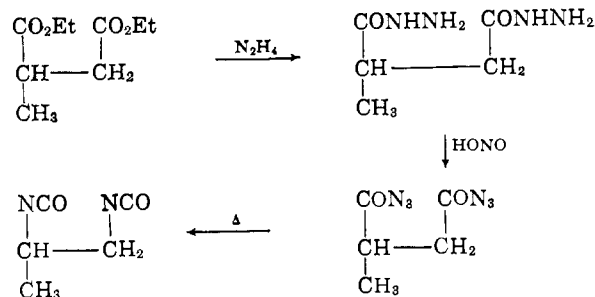
Polymer melt temperatures were substantially higher than those reported previously for the N-alkyl "1-nylons."<sup>4,5</sup> The integral ring structures of the cyclopolymers doubtless stiffen the polymer chains and increase melt temperatures over those of the monoisocyanate polymers. Melting was accompanied by decomposition to monomer, as is the case for the N-alkyl "1-nylons." When the cyclopolymers were decomposed at reduced pressure in a distillation apparatus, monomeric diisocyanate could be recovered in 50-70% yield. Table I summarizes polymer properties.

TABLE I  
CYCLOPOLYMERS FROM 1,2-DIISOCYANATES

Polymer	Melt or de-compn. temp., $^\circ\text{C}.$ <sup>a</sup>	Soluble in	Carbonyl absorption, $\mu$
	365	Sulfuric acid, tetrachloroethane-phenol (40/60 wt.)	5.6, 5.9
	287	Formic acid, nitromethane, dimethyl sulfoxide, dimethylformamide	5.6, 5.9
	303	Pyridine, nitromethane, dimethyl sulfoxide	5.6, 5.9
	365-400	Sulfuric acid	5.5, 5.9

<sup>a</sup> Temperature at which the polymer first left a clear molten trail on a temperature-gradient bar; see R. G. Beaman and F. B. Cramer, *J. Polymer Sci.*, **21**, 223 (1956).

**Monomer Preparation.**—The required 1,2-diisocyanate monomers were easily prepared by decomposing the appropriate succindiazide in refluxing benzene or carbon tetrachloride. The diazides were prepared from nitrous acid treatment of the dihydrazides, which were obtained from hydrazinolysis of the corresponding esters. This reaction sequence is shown below for 1,2-propylene diisocyanate.



Diazide solutions separated from the nitrous acid-dihydrazide reaction were approximately 3-4 M in diazide. It was expedient to dilute these solutions immediately with benzene to concentrations of 1 M, or preferably less, since the diazides decomposed slowly

(7) A recent communication has appeared claiming trimethylene diisocyanate cyclopolymers which are soluble in sulfuric acid and cresol: W. L. Miller and W. B. Black, *Division of Polymer Chemistry Preprints*, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962, p. 345.

TABLE II

## DIHYDRAZIDE INTERMEDIATES FOR 1,2-DIISOCYANATES

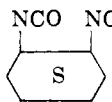
Hydrazide from, acid	M.p., °C. (lit.)	Yield, %
Succinic	164-166 (167-167.5 <sup>a</sup> )	80
Diglycolic	160-162	60
Glutaric	174-176 (176 <sup>b</sup> )	82
Hexahydrophthalic	230-231 (245 <sup>c</sup> )	90
Tricarballic	196-197.5 (195-196 <sup>d</sup> )	95

<sup>a</sup> K. A. Jensen and B. Bak, *Z. anorg. Chem.*, **228**, 85 (1936).

<sup>b</sup> R. F. Peschke and D. H. Wheeler, *J. Am. Oil Chemists' Soc.*, **26**, 637 (1949). <sup>c</sup> H. Wieland, O. Schlichting, and W. V. Langsdorff, *Z. physiol. Chem.*, **161**, 74 (1926). <sup>d</sup> H. O. L. Fischer and G. Dangschat, *Helv. Chim. Acta*, **17**, 1204 (1934).

TABLE III

## PROPERTIES OF ISOCYANATE MONOMERS

Isocyanate	B.p.		Yield, %	M.p., °C.	Formula	Bis-phenylurea		Hydrogen, %		Nitrogen, %	
	°C.	mm.				Calcd.	Found	Calcd.	Found	Calcd.	Found
OCNCH <sub>2</sub> CH <sub>2</sub> NCO	75	14	47	251-252	C <sub>16</sub> H <sub>18</sub> N <sub>4</sub> O <sub>2</sub>	64.41	63.9	6.08	6.0	18.78	18.6
OCNCH(CH <sub>3</sub> )CH <sub>2</sub> NCO <sup>a</sup>	83.5	25	42	238-240	C <sub>17</sub> H <sub>20</sub> N <sub>4</sub> O <sub>2</sub>	65.36	65.4	6.45	6.5	17.94	17.7
OCNCH <sub>2</sub> OCH <sub>2</sub> NCO <sup>b</sup>	90-91	28	34	193-194	C <sub>16</sub> H <sub>18</sub> N <sub>4</sub> O <sub>3</sub>	61.5	61.0	5.77	5.7	17.82	17.7
OCNCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NCO	85-86	14	62								
	119-120	15	52	275-276	C <sub>20</sub> H <sub>24</sub> N <sub>4</sub> O <sub>2</sub>	68.16	68.1	6.86	7.0	15.89	15.7
NCO NCO NCO <sup>d</sup>       CH <sub>2</sub> -CH-CH <sub>2</sub>	140-141	14	10	186-194							

<sup>a</sup>  $n_D^{20}$  1.4398. <sup>b</sup>  $n_D^{27}$  1.4465. <sup>c</sup>  $n_D^{27}$  1.4750. <sup>d</sup> Polymerization occurred in pot during distillation.

and exothermically during drying of the solutions at room temperature. A relatively large amount of solvent provides sufficient capacity for heat dissipation to prevent overheating, which can cause sudden vigorous decomposition of azide.

## Experimental

**I. Polymerizations.** **A. Poly-[1,2-propylene diisocyanate]. Polymerization in Solution.**—A 100-ml., three-neck flask equipped with a mechanical stirrer, calcium chloride tube, and low temperature thermometer was charged with 50 ml. of dry DMF and then cooled to  $-40^\circ$  in a Dry Ice-acetone bath. 1,2-Propylene diisocyanate, 5.2 g., precooled to  $-38^\circ$ , was stirred into the flask; 1 ml. of a saturated solution of sodium cyanide in DMF was then added to the stirred mixture by means of a hypodermic syringe over a period of 3 min. The temperature rose to  $-14^\circ$  within 6 min. after addition of the initiator, and the polymerization mixture thickened to a smooth, viscous dope. The cold bath was removed and the mixture stirred for 0.5 hr. Polymer was isolated by precipitation in methanol stirred vigorously in a Waring Blender. Dried polymer weighed 4.6 g. (89%) and melted at  $287^\circ$ . The inherent viscosity of the polymer was 1.35. A similarly prepared sample having an inherent viscosity of 0.56 was found to have a number average molecular weight of 45,000 by osmotic pressure measurement on a solution in nitromethane. Infrared analysis showed carbonyl absorptions of equal intensity at 5.63 and 5.88  $\mu$  (run as Nujol mull). No absorption due to isocyanate was present.

Clear, flexible films were obtained when 10% solutions in formic acid or nitromethane were spread on a glass plate and solvent was evaporated.

**B. Poly-[1,2-propylene diisocyanate], Bulk Polymerization.**—Freshly distilled 1,2-propylene diisocyanate was maintained under dry nitrogen in a round-bottom flask for 2 weeks at  $0^\circ$ . The monomer gradually polymerized to a hard, colorless, transparent mass. The infrared spectrum of this polymer was identical with that in A, and the inherent viscosity was 0.72.

**C. Poly-[ethylene diisocyanate].**—An apparatus similar to that described in A was charged with 30 ml. of freshly distilled dry DMF and cooled to  $-30^\circ$ . Ethylene diisocyanate, 5.0 ml., was stirred in, and polymerization began immediately. The temperature rose to  $-15^\circ$  while polymer separated. The cold bath was removed and the stirring continued for 20 min. while the mixture was allowed to warm to room temperature. Methanol, 50 ml., was added, and stirring was continued for 15 min. White fibrous polymer, which had separated, was collected on a filter and then dried at  $40^\circ$  under reduced pressure. The poly-

mer, 5.2 g., melted at  $365^\circ$  and had an inherent viscosity of 0.85. The infrared spectrum showed equal absorptions at 5.6 and 5.9  $\mu$  due to carbonyl. A portion of this polymer, after reflux for 2 hr. in methanol, showed no change in inherent viscosity.

**D. Poly-[glyceryl triisocyanate].**—To 8.0 ml. of dry DMF cooled to  $-30^\circ$  was added 2.0 g. of glyceryl triisocyanate; 0.5 ml. of a saturated solution of sodium cyanide in DMF was added, and the solution was stirred for 15 min. at  $-30^\circ$ . The polymerization mixture was poured into 200 ml. of 95% ethanol, and the polymer, 1.7 g. (85%), was collected by filtration. This polymer had an inherent viscosity of 0.28 (in sulfuric acid) and showed split absorption in the infrared at 5.53 and 5.87  $\mu$ .

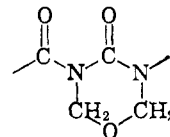
**E. Poly-[1,2-cyclohexylene diisocyanate].**—Dry DMF, 25 ml., was cooled to  $-35^\circ$ , and 5.0 ml. of 1,2-cyclohexylene diisocyanate was added. The mixture was stirred, and 1.0 ml. of a saturated solution of sodium cyanide in DMF was added. After

0.5 hr. at  $-35^\circ$ , there was obtained 5.4 g. of white polymer which melted at  $303^\circ$  and had an inherent viscosity of 0.38. Infrared absorption showed split carbonyl absorption at 5.63 and 5.88  $\mu$ .

**F. Poly-[trimethylene diisocyanate].**—Dry DMF, 75 ml., was cooled to  $-50^\circ$  and then mixed with 1.5 ml. of trimethylene diisocyanate. The temperature rose to  $-44^\circ$  soon after addition of 0.5 ml. of a saturated solution of sodium cyanide in DMF. The mixture was stirred at  $-45^\circ$  for 0.5 hr., and polymer, 1.8 g., was isolated by thorough washing with 95% ethanol. Infrared analysis of the polymer showed only a single carbonyl absorption at 5.93  $\mu$ . The polymer melted at  $338^\circ$  with decomposition to monomer and was not soluble in DMF, dimethyl sulfoxide, or tetrachloroethane-phenol mixture (40/60 wt.). Dissolution was effected with hot sulfuric acid, but degradation apparently occurred, as evidenced by considerable frothing.

**G. Poly-[oxydimethylene diisocyanate].**—Polymerization of 5.0 g. of oxydimethylene diisocyanate was carried out in 50 ml. of dry DMF with 1.0 ml. of a saturated solution of sodium cyanide in DMF as initiator. Polymerization was slow, and after 20 min., white solid separated which was washed thoroughly with methanol and then collected. Dry polymer amounted to 4.4 g. and melted with decomposition at  $345^\circ$ . It was insoluble in a wide variety of solvents, including DMF, dimethyl sulfoxide, *m*-cresol, and tetramethylene sulfone. Its behavior with sulfuric acid was similar to that of poly-[trimethylene diisocyanate].

Infrared analysis showed carbonyl absorption at 5.85  $\mu$ . A weak shoulder indicated that some of the 6-atom ring unit



may have been present.

**II. 1,2-Diisocyanate Monomer.**—The synthesis of 1,2-propylene diisocyanate is treated here in some detail. All other monomers in this work were prepared in a similar manner, and pertinent data are summarized in Table III.

**A. 1,2-Propylene Diisocyanate. 1. 2-Methylsuccinic Dihydrazide.**—Hydrazine hydrate, (545 g., 10.9 moles), dissolved in 7 l. of 95% ethanol and 1 l. of water, was mixed with 429 g. (2.7 moles) of dimethyl 2-methylsuccinate. The ester, b.p.  $85-86^\circ$  at 16 mm., was obtained from catalytic hydrogenation of dimethyl itaconate. The mixture was refluxed overnight and then concentrated, giving 367 g. (84%) of 2-methylsuccinic dihydrazide, m.p.  $160-162^\circ$ .

In like manner, other hydrazides were prepared, and melting points and yields are summarized in Table II.

2. **1,2-Propylene Diisocyanate**.—A 2-l. beaker equipped with a thermometer and a mechanical stirrer and externally cooled in an ice bath was charged with 600 g. of ice, 100 ml. of carbon tetrachloride, 70 ml. of concentrated hydrochloric acid, and 57 g. (0.36 mole) of 2-methylsuccinic dihydrazide. A solution of 50 g. (0.73 mole) of sodium nitrite in 100 ml. of water pre-cooled to 0° was added dropwise to the stirred mixture over a period of 20 min. The temperature of the reaction mixture was maintained below 8° by addition of pieces of ice, and stirring was continued for 0.5 hr. after completion of the addition. The layers were separated, and the azide solution combined with two benzene extractions of the aqueous layer. The final volume<sup>8</sup> amounted to about 400 ml. The solution was dried overnight over anhydrous calcium chloride and then refluxed for 4 hr. to complete decomposition of the azide. The refluxing solution developed a blue color which disappeared when the decomposition was essentially complete. Solvent was removed and the diisocyanate was then distilled at reduced pressure. After a short forerun, 19.6 g. (42%) of pure 1,2-propylene diisocyanate was collected as a lachrymatory liquid which had b.p. 83.5° (25 mm.) and  $n_D^{20}$  1.4398.

Treatment with aniline gave a bis-phenylurea, m.p. 238–240°.

(8) It is essential that the solution be dilute at this stage, so that the heat generated by the slowly decomposing azide may be safely dissipated. More concentrated solutions retain sufficient heat to cause sudden and violent decomposition of the remaining azide.

*Anal.* Calcd. for  $C_{17}H_{20}N_4O_2$ : C, 65.36; H, 6.45; N, 17.94. Found: C, 65.41; H, 6.45; N, 17.65.

Table III summarizes the properties and yields of the other isocyanates prepared in this work. All the isocyanates were extremely moisture-sensitive, so no elemental analyses were performed on the monomers themselves. Several monomers were derivatized with aniline, and the bis-phenylureas serve well to identify the isocyanates. 1,2-Propylene diisocyanate, 1,2-cyclohexylene diisocyanate, and glyceryl triisocyanate apparently have not been prepared previously.

III. **Infrared Analysis of Phenyl Isocyanate Dimer (1,3-Diphenyluretidinedione)**.—Although dimers of aromatic isocyanates (uretidinediones) have been known for many years,<sup>9</sup> the carbonyl absorption of the four-membered heterocycle has not apparently been reported in the literature. The infrared absorption spectrum determined on a chloroform solution of phenyl isocyanate dimer, m.p. 177–178° (lit.<sup>10</sup> 175–176°), showed a single sharp band at 5.60  $\mu$  due to carbonyl.

**Acknowledgments.**—The author is indebted to Dr. R. Zbinden and Miss Mary Schick for interpretation of the infrared spectra, and to Mrs. Raila M. Mason for determination of molecular weight by osmometry.

(9) J. H. Saunders and R. J. Slocumbe, *Chem. Rev.*, **43**, 211 (1948).

(10) J. S. Blair and G. E. P. Smith, Jr., *J. Am. Chem. Soc.*, **56**, 909 (1934). We are indebted to Dr. K. C. Smeltz for a sample of pure phenyl isocyanate dimer.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, IND.]

## Displacement Reactions. V. The Reaction of Cyanide Ion with Tetramethylthiuram Disulfide<sup>1</sup>

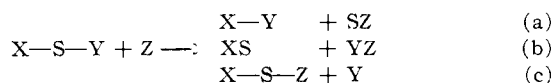
BY ROBERT EARL DAVIS<sup>2</sup> AND ARNOLD COHEN<sup>3</sup>

RECEIVED JULY 17, 1963

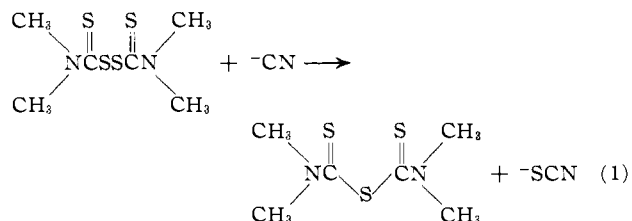
The reaction of tetramethylthiuram disulfide with cyanide ion has been found to be a two-step process in which the dimethyldithiocarbamate intermediate rises to concentrations allowing spectral analysis or isolation. The two S<sub>N</sub>2 displacement reactions are discussed in terms of the oxibase scale relating oxidation electrode potential and basicity of the nucleophile to its reactivity. An estimate of  $2.12 \pm 0.04$  Å. is given to the S-S bond length in the disulfide by the correlation of activation energy with bond distance.

### Introduction

The displacement reactions on a divalent sulfur atom divide into three stoichiometric classes.<sup>4,5</sup>



Numerous examples of kinetic and mechanistic studies have been reported for type c reactions.<sup>4-6</sup> While the reaction of cyanide ion with tetramethylthiuram disulfide has the same stoichiometry<sup>7</sup> as the type a,



it is unlikely from the work of Cambron<sup>8</sup> that reaction 1 represents the *mechanism* as well as the over-all reaction. Indeed Cambron's work and suggested

mechanism have been found to be correct in the present study. In continuation of a series of studies on the S<sub>N</sub>2 reaction at divalent sulfur atoms, we wish to present a detailed kinetic and mechanistic investigation of this reaction of an excellent thiophilic<sup>9</sup> reagent, cyanide ion, with a compound containing a thiuram disulfide sulfur-sulfur bond.

### Results

**Ultraviolet Spectra.**—The ultraviolet spectrum of the nearly colorless tetramethylthiuram disulfide (TMTD) is characterized by strong absorption increasing below 300 m $\mu$  with a plateau between 280 and 240 m $\mu$  and finally increasing toward 200 m $\mu$ .<sup>10</sup> The monosulfide (TMTM) is yellow and has one strong maximum near 275 m $\mu$  in methanol and a minimum near 240 m $\mu$ .<sup>10</sup> In Fig. 1 the spectrum of a mixture of TMTD and TMTM each at  $5 \times 10^{-5}$  M in methanol is reproduced. Also in this figure is the spectrum of a solution containing initially  $10 \times 10^{-5}$  M in TMTD and some cyanide ion after 50% reaction. From this figure one concludes, in accord with Cambron's results, that the reaction is not a one-step process but that intermediates are present in measurable concentrations. Also presented in Fig. 1 is the spectrum of the dimethyldithiocarbamate with its characteristic double camel hump near 285 and 250 m $\mu$ .

**Isolation of an Intermediate.**—Cambron<sup>8</sup> suggested and demonstrated that a dithiocarbamate could react with a thiocarbamyl thiocyanate to produce a thiuram monosulfide and thiocyanate ion. It seemed most reasonable to suggest that reaction 1 has a two-step

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