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THERMAL REACTIONS OF AZIDOFORMATES

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In the past several years, there has been considerable interest in the chemistry of azidoformates. In 1962, Lwowski and Mattingly (1) reported that the photolysis of ethyl azidoformate in cyclohexene gives 7-carbethoxy-7-azabicyclo /4.1.0/ heptane, while under the same conditions in cyclohexane the major product is N-cyclohexylurethane. The reactions were shown to involve a nitrene intermediate, i.e., a compound containing an electron-deficient nitrogen atom with six electrons in its valence shell, by demonstration that the rate of nitrogen evolution equaled the rate of disappearance of azide and that the same products are formed when the intermediate is generated by a base-catalyzed α-elimination from N-p-nitrobenzenesulfonoxyurethane (2). Hafner and König (3) found that the photolysis of ethyl azidoformate in benzene yields N-carbethoxy-1H-azepine, while Cotter and Beach (4) reported that the same reaction takes place in the thermal decomposition of several azidoformates. Berry, Cornell and Lwowski (5) have shown by flash photolysis that ethyl azidoformate decomposes into cyanate radicals when photolyzed in the vapor phase.

Inasmuch as none of this information was available when we started our work, we set out first to determine the kinetics of decomposition of an azidoformate in a variety of solvents. n-Octadecyl azidoformate was used in most of this work because of its ease of purification, its low volatility and its safety (ethyl azidoformate is shock sensitive and explosions have been reported during attempted distillations (4)). Reactions were carried out at constant volume, the increase in pressure being measured by a transducer connected to a recorder; individual points could be determined by means of a read-out device. In diphenyl ether, the thermal decomposition of n-octadecyl azidoformate followed strict first-order kinetics to 95% reacted. As shown in Table I the rate constant is independent of concentration at several temperatures, and the evolution of nitrogen is essentially quantitative. An activation energy of

TABLE I

Decomposition of Azidoformates in Diphenyl Ether

Azidoformate	Conc., M	Temp., °C.	$k_1 \times 10^4$ sec.$^{-1}$	N_2 evolved, % of theory
n-Octadecyl	0.02	133.3	8.70	98.5
"	0.10	133.3	9.00	99.5
"	0.02	120.0	2.44	97.4
"	0.10	120.0	2.40	100
"	0.10	100.0	0.267	102.7
Tetramethylene	0.10	120.0	2.34	98.2
2,2-Bis(4-hydroxyphenyl)propane	0.02	120.0	3.46	97.5

31.3 kcal./mole has been determined from a normal Arrhenius plot. Tetramethylene bis(azidoformate) yielded practically identical results, while the bis(azidoformate) of 2,2-bis(4-hydroxyphenyl)propane was slightly less stable.

Clean first-order kinetics were observed in the decomposition of n-octadecyl azidoformate in a number of solvents, including aliphatic hydrocarbons, olefins, ethers, esters, ketones, and phenols. As shown in Table II, the rates are almost independent of solvent (6). The largest effect was found in indene, the azidoformate decomposing 2.5 times faster than in diphenyl ether. Only in 2-heptanone was the amount of gas evolved somewhat less than theory. There would appear to be little doubt, therefore, that in these solvents the rate-determining step is the loss of nitrogen and the formation of a nitrene intermediate.

TABLE II

Decomposition of n-Octadecyl Azidoformate in Different Solvents[a]

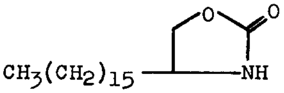
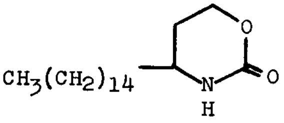
Solvent	$k_1 \times 10^4$ sec.$^{-1}$	Relative rate	Gas evolved, % of theory
Diphenyl Ether	2.40	1	100
Mineral Oil	2.15	0.90	103
1-Octadecene	3.76	1.57	97.7
Indene	5.88	2.45	100.8
Phenol	3.74	1.56	97.4
Diglyme	3.32	1.39	101.2
2-Heptanone	2.96	1.23	93.8
Diethyl Sebacate	2.52	1.05	101.0

a - 0.1 M conc. at 120.0°

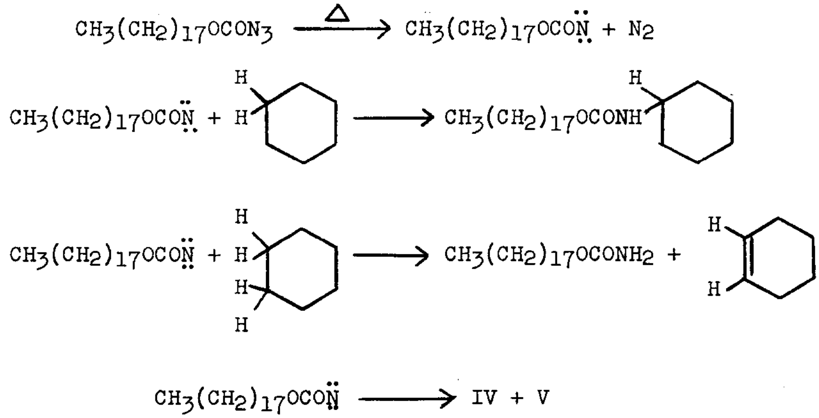
Since a good material balance has not been reported in an azidoformate reaction, the reaction of n-octadecyl azidoformate with cyclohexane was investigated. A 1% solution of the azidoformate in cyclohexane was heated at 130° under pressure, the solvent was removed and the residue was separated by means of a scanalyzer (7), modified to monitor fractions by infrared rather than by ultraviolet. In this way, 95% of the azidoformate was accounted for, as shown in Table III. Fraction I was shown to be a small amount of carbonate formed in the azidoformate synthesis and not removed by recrystallization. Fraction II, the insertion product, and Fraction III, the hydrogen abstraction product, were identified by comparison with authentic samples.

TABLE III

Reaction of n-Octadecyl Azidoformate with Cyclohexane at 130°

Fraction	Product	Wt. %	Mole % of initial azide
I	$[CH_3(CH_2)_{17}O]_2CO$	1.9	-
II	$CH_3(CH_2)_{17}OCONHC_6H_{11}$	62.6	59.8
III	$CH_3(CH_2)_{17}OCONH_2$	18.7	22.6
IV		4.1	5.0
V		6.7	7.7
		94.0	95.1

Fractions IV and V have been shown by analysis to be isomers, $C_{18}H_{37}NO_2$, and have been tentatively assigned cyclic carbamate structures resulting from "back-biting". Cyclohexene was identified in the distillate, although not in sufficient quantity to account for all the octadecyl carbamate. It appears, therefore, that the major course of the reaction is as follows:



REFERENCES

1. W. Lwowski and T. W. Mattingly, *Tetrahedron Letters* No. 7, 277 (1962).
2. W. Lwowski, T. J. Maricich and T. W. Mattingly, *J. Am. Chem. Soc.*, **85**, 1200 (1963).
3. K. Hafner and C. König, *Angew. Chem.*, **75**, 89 (1963).
4. R. J. Cotter and W. F. Beach, *J. Org. Chem.*, **29**, 751 (1964).
5. R. S. Berry, D. Cornell and W. Lwowski, *J. Am. Chem. Soc.*, **85**, 1199 (1963).
6. Recent results by Huisgen and Blaschke [*Tetrahedron Letters* No. 22, 1409 (1964)] for the decomposition of ethyl azidoformate at 130° in tolane, phenylacetylene, diphenyl ether, benzonitrile, mesitylene, and paraffin are in good agreement.
7. W. C. Kenyon, J. E. McCarley, E. G. Boucher, A. E. Robinson and A. K. Wiebe, *Anal. Chem.*, **27**, 1888 (1955).