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THE EFFECT OF ADDITIVES ON THE REACTIONS OF ETHYL AZIDOFORMATE WITH CYCLOHEXANE

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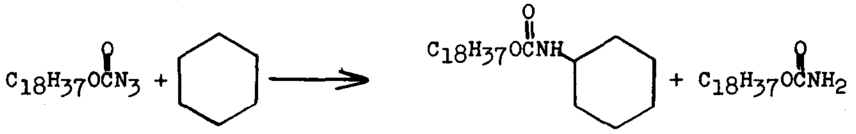
There are several reports in the literature (1-4) concerning the effect of the inert diluent, methylene chloride, on the reactions of ethyl azidoformate with various substrates. The effect has been explained by assuming that the initially formed formylnitrene singlet has more time to decay to ground state triplet before reacting with substrate, thus accounting for increased yields of the products presumably derived from the triplet.

Some time ago we found that the presence of a small amount of *m*-dinitrobenzene during the thermal decomposition of *n*-octadecyl azidoformate in cyclohexane led to an increased yield of the C-H insertion product, N-cyclohexyl *n*-octadecyl carbamate, and a decreased yield of the hydrogen abstraction product, *n*-octadecyl carbamate (5). Since the evidence is quite conclusive that the insertion product is derived from the nitrene singlet (1-3,5), this effect is the reverse of the dilution effect. Inasmuch as we know of no other instance of what appears to be singlet stabilization, this phenomenon has been investigated in greater detail.



Experiments were carried out by heating a 1% solution of ethyl azidoformate in cyclohexane in a sealed system under nitrogen. As shown in Table I, a variety of compounds, which might be broadly classified as radical traps, show the same type of activity as *m*-dinitrobenzene. It is quite apparent from the

TABLE I

Decomposition of Ethyl Azidoformate in Cyclohexane[a]

Additive	Conc., Mole % of Azidoformate	Yield, %[b]		
		Insertion	Abstraction	Total
None	-	52 ± 3[c]	25 ± 3[c]	77
m-Dinitrobenzene	19	74	17	91
Nitrobenzene	14	70	17	87
2-Nitropropane	87	59	19	78
Sulfur	34	76	14	90
2,6-Di-_t_-butyl-_p_-cresol	7	59	16	75
Hydroquinone	8	65	17	82
_p_-Quinone	7	65	17	82

[a] Azidoformate concentration 0.087 _M_ (1%). Solutions heated under nitrogen for 20 hrs. at 120°. [b] Analysis by v.p.c. [c] Average of six runs. Standard deviation of the average is 0.66%.

total yield figures that in most cases the insertion yield increases at the expense of both the abstraction product and an undetermined side reaction. The effect of concentration of additive is shown for three of these in Table II. In

TABLE II

Effect of Additive Concentration on the Decomposition of Ethyl Azidoformate in Cyclohexane[a]

Additive	Concentration		Yield, %	
	g./100 ml. Soln.	Mole % of Azidoformate	Insertion	Abstraction
None			52 ± 3	25 ± 3
Nitrobenzene	0.15	14	70	17
	0.46	43	70	15
	1.24	116	69	15
	2.37	221	65	13
	6.17	577	61	14
_m_-Dinitrobenzene	0.05	3.70	61	21
	0.13	8.73	70	17
	0.27	18.7	74	17
	1.09	75.0	71	14
	2.43	166	67	12
Sulfur	0.06	20.8	72	18
	0.10	34.2	76	14
	0.53	192	65	15
	0.99	354	61	13
	2.35	845	56	14

[a] See Table I footnotes.

each case there is an optimum concentration of additive for obtaining a maximum yield of insertion product; this is well below an equimolar amount, roughly 0.1-0.4 mole per mole of azidoformate. The yield of abstraction product, however, decreases with increasing additive concentration, but seems to level off at about 12-14%.

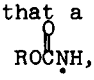
To determine the effect of the additives on the reaction kinetics, the decomposition of n-octadecyl azidoformate in diphenyl ether was investigated (5). As shown in Table III, sulfur and m-dinitrobenzene have no effect on the rate of the reaction, and the theoretical amount of gas is evolved; the reaction is still cleanly first order.

TABLE III

Decomposition of n-Octadecyl Azidoformate in Diphenyl Ether[a]

Additive	Conc., Mole % of Azidoformate	First-Order Rate[b] sec.$^{-1}$ x 10^4	Gas Evolved, % of Theory
None		4.45	98
Sulfur	40.4	4.28	100
	430	4.28	98
m-Dinitrobenzene	19	4.28	98
	213	5.03	98

[a] Approximately 0.08 M. [b] At 124°. Calculated from first-order plot.

Many points require explanation, the most important being the increased amount of insertion product derived from singlet nitrene. The simplest explanation would be that a radical, perhaps the presumed intermediate in the abstraction reaction,  $RO\overset{O}{\overset{\|}{C}}\underset{\bullet}{N}H$, can catalyze singlet-triplet intersystem crossing. Reaction with the additive would decrease the radical concentration, resulting in a slower singlet to triplet conversion and therefore a higher yield of the product derived from singlet. The decrease in insertion yield with increasing additive concentration is undoubtedly due to some reaction of the singlet with the additive; the fact that in the initial experiment involving n-octadecyl azidoformate plus m-dinitrobenzene in cyclohexane all the azidoformate could be accounted for by reaction with the cyclohexane or with itself can be attributed to the low concentration of m-dinitrobenzene used.

Several alternative explanations are available to explain why the yield of abstraction product appears to level off at a constant value independent of the nature of the additive or of its concentration. If the assumption is made that both singlet and triplet nitrenes are capable of abstraction, the 12-14% yield of urethan could be attributed to the singlet portion of the reaction. If the assumption is made that urethan results only from triplet nitrene, the levelling off must be attributed to inefficient trapping of the radicals, either because of the low additive concentrations used or, more likely, because of a solvent cage effect. In an attempt to differentiate between these possibilities, the condensation of ethyl azidoformate with cyclohexane was run in the presence of increasing amounts of tetrachloroethylene, reported to be relatively inert to nitrene reactions (6). Since the yield of abstraction product, urethan, dropped to practically zero while the yield of insertion product, N-cyclohexyl ethyl carbamate, was still fairly high (Table IV), it seems quite reasonable to conclude that tetrachloroethylene traps triplet nitrene much more efficiently than it reacts with singlet, and that hydrogen abstraction is a triplet reaction.

TABLE IV

Effect of Tetrachloroethylene on the Ethyl Azidoformate-Cyclohexane Reaction[a]

	Yield, %	
Cyclohexane, Mole %	Insertion	Abstraction
89.4	65	12
73.9	54	10
48.6	42	2.5
23.9	33	1.1
9.5	25	0.9

[a] See Table I footnotes.

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