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THERMAL REACTIONS OF SULFONYL AZIDES WITH ALIPHATIC HYDROCARBONS

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Although there is considerable literature on both thermal and photochemical reactions of sulfonyl azides, most of it is concerned with the reaction of aromatic sulfonyl azides with aromatic compounds (1).

In an attempt to compare the chemistry of sulfonyl azides with that of azidoformates (2), a study was made of the thermal decomposition of aliphatic sulfonyl azides in aliphatic hydrocarbons. Reactions were followed either by measuring the increase in pressure at constant volume (2) or the more usual increase in volume at constant pressure. The decomposition of 1-pentanesulfonyl azide in mineral oil at 165° failed to exhibit good first-order kinetics. That is, the integrated first-order rate constants dropped continuously during the run. However, in a first-order plot of the data the points for about the first 50% of the reaction fell close to a straight line. The rate constant in parentheses in Table I was calculated from the slope of this line. The calculated quantity of gas was evolved. Furthermore, the infrared spectrum of the solution showed a strong azide peak, in spite of the reaction being heated for up to 24 hours. Mass spectroscopic analysis of the gas showed the presence of nitrogen, sulfur dioxide and a small amount of n-pentane. As shown in Table I, the amount of sulfur dioxide evolved (determined by absorption in caustic and titration) was lowered only slightly by lowering the temperature; a somewhat greater effect was observed by lowering the concentration. 2-Propanesulfonyl azide gave off slightly more sulfur dioxide than the 1-pentane derivative, while p-toluenesulfonyl azide gave off very little and decomposed in a clean first-order reaction. On the assumption that sulfur dioxide evolution might be a radical reaction, free radical traps, such as hydroquinone and sulfur, were added. Under these conditions the amount of sulfur dioxide was decreased to 3-4%, good first-order kinetics were observed and the rate was reduced. It appears, therefore, that two simultaneous reactions are taking place: in one reaction nitrogen is evolved, leaving a nitrene, i.e., an intermediate containing an electron-deficient nitrogen with six valence electrons, while in the other sulfur dioxide is evolved in a radical chain decomposition. Inasmuch as the alkyl azide formed is stable under these conditions, each molecule gives off either nitrogen or sulfur dioxide, thereby accounting for the quantitative evolution of gas.

$$C_5H_{11}SO_2N_3 \longrightarrow C_5H_{11}SO_2\underset{\cdot\cdot}{\ddot{N}} + N_2$$

$$R\cdot + C_5H_{11}SO_2N_3 \longrightarrow C_5H_{11}SO_2\cdot + RN_3$$

$$C_5H_{11}SO_2\cdot \longrightarrow C_5H_{11}\cdot + SO_2$$

$$C_5H_{11}\cdot + RH \longrightarrow C_5H_{12} + R\cdot$$

It is interesting that Leffler and Tsuno (3) report that t-butyl hydroperoxide accelerates the rate of decomposition

TABLE I

Thermal Decomposition of Sulfonyl Azides

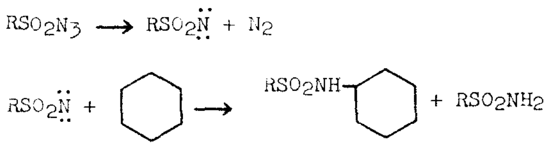
Azide	Conc. M	Solvent	Additive	Conc. M	Temp. °C.	$k_1 \times 10^4$ sec.$^{-1}$	%SO_2
n-Pentane	0.27	Mineral oil			175.0	-	20.5
n-Pentane	.27	Mineral oil			165.3	(8.0)[a]	19.2
n-Pentane	.24	Mineral oil			155.8	-	18.0
n-Pentane	.12	Mineral oil			163.0	-	16.5
2-Propane	.28	Mineral oil			165.0	-	22.0
n-Pentane	.25	Mineral oil	Hydroquinone	0.045	166.0	4.80	5.7
n-Pentane	.25	Mineral oil	Hydroquinone	0.091	165.5	4.46	3.2
n-Pentane	.25	Mineral oil	Sulfur	0.32	165.0	4.10	3.1
n-Pentane	.26	Diphenyl ether			165.9	4.46	4.2
p-Toluene	.26	Tetradecane			154.0	3.80	1.3

[a] Not first order

of benzenesulfonyl azide.

The source of the initiator is puzzling. Although the mineral oil was difficult to purify, a carefully distilled sample of tetradecane resulted in only slightly less sulfur dioxide. However, the surprising fact that decomposition was first order in diphenyl ether, with only a small amount of sulfur dioxide, would indicate that the free radical reaction is catalyzed by traces of hydroperoxide, formed by attack of adventitious oxygen on the solvent. Yet a run in the presence of air gave even less sulfur dioxide than a run under nitrogen. The lack of radical character in the decomposition of p-toluenesulfonyl azide is probably related to the relative difficulty with which the arylsulfonyl radical abstracts a hydrogen from the solvent to propagate a chain, the radical losing sulfur dioxide only with difficulty (4).

To determine the fate of the nitrene intermediate, decompositions were carried out in cyclohexane under pressure at 175°. 1-Pentane-, 2-propane- and p-toluenesulfonyl azides all gave about 60% yields of insertion product. Quite surprising was the almost total absence of abstraction product, 3% being obtained from 2-propanesulfonyl azide, 5% from the p-toluene derivative, and none being identified with certainty from the 1-pentane derivative.



$$RSO_2N_3 \longrightarrow RSO_2\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}} + N_2$$

With the aliphatics, including the 20-25% yields of sulfur dioxide, 80-90% of the azides were accounted for; no attempt was made to isolate the other products resulting from the radical reaction. Addition of a small amount of sulfur to the reaction of 1-pentanesulfonyl azide with cyclohexane raised the yield of insertion product from 61% to 72%. Thus, sulfur can interfere with the radical chain reaction and thereby raise the yield of the nitrene reaction.

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