Thermal Reactions of Sulfonyl Azides

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Abstract: *p*-Toluenesulfonyl azide has been shown by kinetic studies to decompose thermally in a variety of solvents by a clean first-order reaction. The rate-determining step is loss of nitrogen and formation of an electron-deficient nitrene species. Although aliphatic sulfonyl azides behave similarly in diphenyl ether, their decomposition in aliphatic hydrocarbon solvents is not first order. Although exactly 1 mole of gas is formed, it contains sulfur dioxide as well as nitrogen. Two simultaneous reactions occur: first-order elimination of nitrogen and formation of nitrene, and an apparent radical-chain reaction evolving sulfur dioxide. The other products expected of a radical reaction have been identified, and addition of radical inhibitors eliminates the radical reaction. The origin of the radical initiator is discussed. Sulfonylnitrenes insert into carbon–hydrogen bonds of saturated hydrocarbons, but they form little if any RSO_2NH_2 by hydrogen abstraction. They are less discriminating in their reactions with primary, secondary, and tertiary C–H bonds than are formylnitrenes. Benzene is twice as reactive as cyclohexane and half as reactive as *p*-xylene toward *p*-toluenesulfonylnitrene. The multiplicities responsible for the different reactions of nitrenes are discussed. It is concluded that singlet stability falls in the order sulfonyl > formyl > aryl, that insertion into the C–H bond of a saturated hydrocarbon and addition to an aromatic ring are singlet reactions, and that hydrogen abstraction from a saturated hydrocarbon is a triplet reaction.

In our continued search for new reactions of saturated hydrocarbons,[2] our attention was focused on the reactions of sulfonyl azides.[3] Here, as with the azidoformates, it was felt that if these materials decomposed by loss of nitrogen and formation of nitrene, the nitrene might insert into a carbon–hydrogen bond and allow the modification or cross-linking of hydrocarbon polymers by the use of sulfonyl azides. Although there was a considerable body of literature[4] on sulfonyl azide reactions when our work was initiated, it consisted almost entirely of descriptions of the reactions of aromatic sulfonyl azides with aromatic compounds.

Results and Discussion

Although nitrenes had been suggested as intermediates in the decomposition of sulfonyl azides, no evidence for their actual existence had appeared in the literature when this work was initiated. Therefore, the thermolysis of *p*-toluenesulfonyl azide was carried out in a variety of solvents; the results are shown in Table I. The reactions, as measured by gas evolution, gave clean, first-order plots generally to 90% reaction. In spite of the wide diversity in the nature of the solvent and in the complexity of the reactions with the sulfonyl azide, as evidenced by both the identity and the amount of gas evolved, there was surprisingly little variation in the rates of the reactions; the average half-life at 155° is 33 min. There can be little doubt from these results that the rate-determining step is the loss of nitrogen and the formation of an electron-deficient nitrene species. For the thermal decomposition, $\Delta H^{\ddagger}$ of 35.1 kcal/mole and $\Delta S^{\ddagger}$ of +7 eu were calculated, in good agreement with recently reported results for benzenesulfonyl azide.[5,6] Aliphatic sulfonyl azides, both mono- and difunctional, decompose appreciably more slowly in diphenyl ether, as shown in Table II. The tetramethylene and hexamethylene derivatives appear to be slightly less stable than 1-pentanesulfonyl azide, as do the *m*- and *p*-xylylene derivatives, but the differences in all cases are very small. For 1,9-nonanedisulfonyl azide $\Delta H^{\ddagger} = 36.5$ kcal/mole and $\Delta S^{\ddagger} = +9$ eu.

$$p\text{-}CH_3C_6H_4SO_2N_3 \xrightarrow{\Delta} p\text{-}CH_3C_6H_4SO_2\ddot{\underset{..}{N}} + N_2$$

Table I. Decomposition of *p*-Toluenesulfonyl Azide in Various Solvents[a]

Solvent	Temp, °C	$k_1 \times 10^4$ sec^{-1}	Rel rate	Gas evolved, % of theory
Diphenyl ether	155	3.43	1	100
Tetradecane	155	3.80	1.11	
Nitrobenzene	155	3.97	1.15	199[b]
1-Octanol	155	3.63	1.06	96
n-Hexanoic acid	155	2.97	0.86	114[c]
Dimethyl terephthalate	155	3.23	0.95	104
Diphenyl ether	145	1.44	1	
1,4-Dichlorobutane	145	1.70	1.18	140[d]
Diphenyl ether	130	0.330		

[a] Approximately 0.14 *M* in azide. [b] Contains NO and other gases. [c] Contains CO_2. [d] Contains a chlorobutene.

Because of our interest in aliphatic sulfonyl azides and saturated hydrocarbon polymers, we next turned our attention to the decomposition of 1-pentanesulfonyl azide in mineral oil. Here a good first-order plot was not obtained by following the gas evolution. However, as indicated in the first-order plot of the data (Figure 1), the points for the first half-life fell close to a straight line, and the rate constants in parentheses in

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(2) D. S. Breslow, T. J. Prosser, A. F. Marcantonio, and C. A. Genge, *J. Am. Chem. Soc.*, **89**, 2384 (1967).

(3) Reported in preliminary form: M. F. Sloan, W. B. Renfrow, and D. S. Breslow, *Tetrahedron Letters*, 2905 (1964); M. F. Sloan, T. J. Prosser, N. R. Newburg, and D. S. Breslow, *ibid.*, 2945 (1964).

(4) For an excellent review, see R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 178 (1964).

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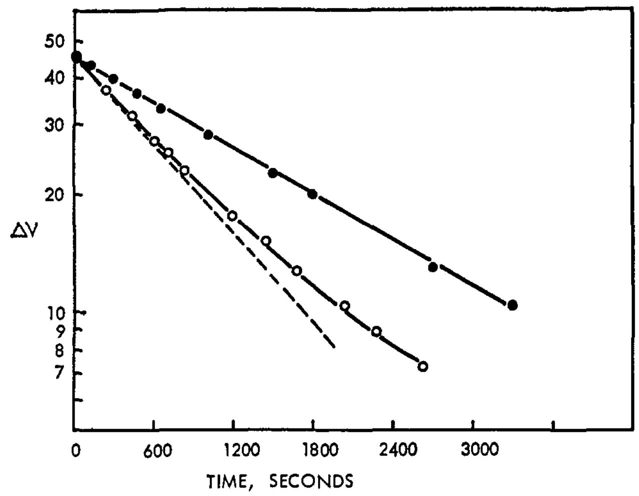

Figure 1. Decomposition of 0.25 *M* 1-pentanesulfonyl azide in mineral oil at 165.3°: ○, no additive; ●, 0.091 *M* in hydroquinone.

Table II. Decomposition of Various Sulfonyl Azides in Diphenyl Ether[a]

Sulfonyl azide	Temp, °C	$k_1 \times 10^4$ sec^{-1}	Gas evolved, % of theory
1-Pentane-	166	4.46	102
1,4-Butanedi-	163	5.02	99
1,6-Hexanedi-	163	5.02	98
1,9-Nonanedi-	170	4.45	
	160	2.25	
	150	0.884	
1,10-Decanedi-	163	4.45	100
1,4-Dimethylcyclohexane-α,α′-di-	163	4.82	98
m-Xylene-α,α′-di-	163	6.09	101
p-Xylene-α,α′-di-	163	5.78	96

[a] Approximately 0.1 *M* in azide.

Table III were calculated from the slope of this line. In spite of the fact that the calculated quantity of gas was evolved, mass spectroscopic analysis of the gas showed the presence of nitrogen, sulfur dioxide, and a small amount of *n*-pentane. In addition, the solution contained azide (absorption at 2100 cm^{-1}) even after being heated for 24 hr (about 60 half-lives). As shown in Table III, the amount of sulfur dioxide evolved (determined by absorption in sodium hydroxide) 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 (Figure 1). It appears, therefore, that two simultaneous reactions are taking place: in one reaction, nitrogen is evolved, leaving a nitrene; 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. As further proof

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

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

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

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

of this mechanism a 10% solution of 1-pentanesulfonyl azide in an ethylene–propylene copolymer was heated at 175° for 2 hr under nitrogen. The product, after purification by dissolving and reprecipitating twice, still showed a strong azide peak in the infrared; it was demonstrated that one precipitation was sufficient to remove unreacted 1-pentanesulfonyl azide from the elastomer.

Because of several puzzling features in the reaction, the evolution of sulfur dioxide was investigated in greater detail. As the temperature was increased there was a small but significant increase in the amount of sulfur dioxide evolved. A secondary sulfonyl azide, 2-propanesulfonyl azide, evolved slightly more sulfur dioxide than the primary azide. *p*-Toluenesulfonyl azide under these conditions gave only traces of sulfur dioxide. Not only did radical traps, such as hydroquinone, 2,6-di-*t*-butyl-*p*-cresol, and sulfur, decrease the sulfur dioxide evolution and convert the decomposition to a clean, first-order reaction, but they also slowed down the rate. Thus at 165° in mineral oil, the straight-line portion of the 1-pentanesulfonyl azide decomposition gave a k_1 of 8.00×10^{-4} sec^{-1}. In the presence of 0.045 *M* hydroquinone a k_1 of 4.80×10^{-4} sec^{-1} was obtained. The course of the reaction was followed by quenching a sulfonyl azide decomposition at various times and determining the extent of decomposition and the amount of sulfur dioxide formed. As shown in Table IV, the sulfur dioxide formation is not a first-order reaction and it is virtually complete by the time half the sulfonyl azide has decomposed. The puzzling question is the source of the initiator for the free-radical decomposition. One possibility would be impurities, presumably hydroperoxides, in the solvent. Most of the kinetic runs were carried out under nitrogen in a commercial mineral oil used without additional purification. Therefore, a comparable run was done in tetradecane which had been carefully purified by distillation and subsequently handled in a nitrogen atmosphere; the amount of sulfur dioxide was reduced from 19 to 16%, from which result it is difficult to draw any conclusion. Inasmuch as sulfur dioxide evolution ceases when only half the azide has been decomposed, it would appear that some if not all of the initiator would be consumed by the end of a run. To investigate this point, a normal run was carried out in mineral oil at 165°, the gas was vented at the end of the run, and a second azide sample was injected. Rate constants calculated from the slopes of the lines drawn through the points for the first 50% of reaction were 7.63×10^{-4} sec^{-1} for the first run and 7.08×10^{-4} sec^{-1} for the second. Thus, although the rate did drop slightly in the second run, the change is very small and the reaction is still considerably faster than in the presence of an inhibitor. In another run, the air was not displaced by nitrogen.

Table III. Thermal Decomposition of Sulfonyl Azides

Azide	Concn, *M*	Solvent	Additive	Concn, *M*	Temp, °C	$k_1 \times 10^4$ sec^{-1}	% SO_2
1-Pentane	0.27	Mineral oil			175.0		20.5
1-Pentane	0.27	Mineral oil			165.3	(8.0)[a]	19.2
1-Pentane	0.24	Mineral oil			155.8		18.0
1-Pentane	0.12	Mineral oil			163.0		16.5
2-Propane	0.28	Mineral oil			165.0		22.0
1-Pentane	0.25	Mineral oil	Hydroquinone	0.045	166.0	4.80	5.7
1-Pentane	0.25	Mineral oil	Hydroquinone	0.091	165.5	4.46	3.2
1-Pentane	0.25	Mineral oil	Sulfur	0.32	165.0	4.10	3.1
1-Pentane	0.24	Mineral oil	Air		165.7	(7.7)[a]	13.8
1-Pentane	0.26	Diphenyl ether			165.9	4.46	4.2
p-Toluene	0.26	Tetradecane			154.0	3.80	1.3

[a] Not first order.

Table IV. Rate of Sulfur Dioxide Formation from 1-Pentanesulfonyl Azide in Mineral Oil at 165°

Time, min	Azide reacted mmoles	%	SO_2 formed, mmoles
3	0.34	13.1	0.155
8	0.79	30.4	0.318
15	1.23	47.4	0.445
25	1.66	64.0	0.440
∞	2.60	100	0.510

The rate behavior was unchanged, but the sulfur dioxide yield was lowered to 14%; if anything, air seems to inhibit the reaction. Furthermore, since sulfur dioxide is known to be a good decomposer for hydroperoxides,[7] it does not seem very likely that peroxidic impurities in the solvent are the initiators of the radical decomposition. A second possibility is impurities in the azides, but this does not appear to be very likely either. Although 1-pentanesulfonyl azide is a liquid and the sample used contained traces of chlorine, a sample purified by low-temperature recrystallization from *n*-hexane gave identical results. Furthermore, 1,10-decanedisulfonyl azide, which is a crystalline solid, and 2-propanesulfonyl azide both gave similar amounts of sulfur dioxide, and it does not appear to be very likely that all three azides would contain the same impurities at the same levels. The thermal cleavage of a sulfonyl azide to radicals is a third possibility.

$$RSO_2N_3 \longrightarrow RSO_2\cdot + N_3\cdot$$

This would be analogous to the cleavage of sulfonyl chlorides, which is considered to be a radical reaction,[8] although the S–N bond would not be expected to break as readily as the S–Cl bond. A more interesting possibility is that the nitrene triplet or a radical formed from it, catalyzes the radical decomposition, although other evidence discussed below indicates that little if any triplet is formed in sulfonylnitrene reactions.

In light of the finding that aliphatic sulfonyl azides undergo induced free-radical decomposition to give sulfur dioxide, one might question whether the nitrogen-forming reaction is also induced by free radicals, for example

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

Extrapolation of the data in Table IV shows that at zero time 48% of the gas produced from 1-pentanesulfonyl azide is sulfur dioxide. As shown in Figure 1, the reaction follows reasonably good first-order kinetics for the first half of the reaction in the absence of an inhibitor, and an average value of 8.0 × 10^{-4} sec^{-1} can be calculated for k_1. If we assume that the initial formation of both sulfur dioxide and nitrogen occur by first-order reactions, the relative amounts of the two products should be proportional to the relative magnitude of the individual rate constants for their formation. Applying this reasoning, we calculated a k_1 of 4.11 × 10^{-4} sec^{-1} for the nitrogen-forming reaction, which is in fairly good agreement with the actual value of 4.45 × 10^{-4} sec^{-1} found for the average of three inhibited runs in which the free-radical reaction has been almost completely suppressed. From this admittedly rough estimation it would appear that the evolution of nitrogen and the formation of a nitrene are not affected by the free radicals present in the system.

Recently, Leffler and Tsuno[9] reported that the decomposition of benzenesulfonyl azide is accelerated by *t*-butyl hydroperoxide and concluded that the decomposition to nitrene is induced by free radicals. In order to resolve this apparent disagreement, we investigated the decomposition of *p*-toluenesulfonyl azide. As mentioned previously, this compound decomposes in a strictly first-order fashion in tetradecane. The amount of sulfur dioxide was 0.75–1.3% of the evolved gas, and this was not changed by the addition of an equivalent amount of *t*-butyl hydroperoxide; neither was the rate. Since benzenesulfonyl radicals are reported[10] not to lose sulfur dioxide but to give other products, such as benzenesulfinic acid, *p*-toluenesulfonyl azide was decomposed in mineral oil at 130° in the presence of an equivalent amount of *t*-butyl hydroperoxide; calcium oxide was added to trap any sulfinic acid that might be formed. From the calcium salts present at the end of the reaction there was isolated an 11% yield of *p*-toluenesulfonic acid as its *p*-toluidine salt. No sulfinic acid was found, and no sulfonic acid was formed in the absence of hydroperoxide. These results indicate that the sulfur–nitrogen bond can be cleaved by the hydroperoxide; the expected sulfinic acid is undoubtedly oxidized to sulfonic acid before it can be trapped. Consequently, an aromatic sulfonyl azide will undergo free-radical

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(7) W. L. Hawkins and H. Sutter, *J. Polymer Sci., Part A*, **1**, 3499 (1963).

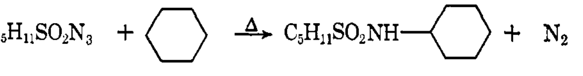
(8) C. Walling, "Free Radicals in Solution," John Wiley and Sons Inc., New York, N. Y., 1957, p 395; F. A. Drahowzal in "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961, p 372.

(9) J. E. Leffler and Y. Tsuno, *J. Org. Chem.*, **28**, 190 (1963).

(10) A. J. Rosenthal and C. G. Overberger, *J. Am. Chem. Soc.*, **82**, 108, 117 (1960).

decomposition if a source of radicals is provided but not in its absence. It is conceivable that the lack of radical decomposition of an aromatic sulfonyl azide or of an aliphatic sulfonyl azide in an aromatic solvent is due to the formation of the corresponding sulfonanilide which, being an aniline derivative, is probably a fairly good radical trap.

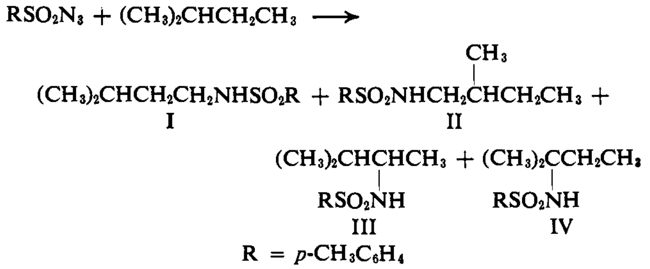
Both aliphatic and aromatic sulfonyl azides have been found to insert into the carbon–hydrogen bond of saturated hydrocarbons. Thus, the thermolysis of 1-pentanesulfonyl azide in cyclohexane gave a yield of N-cyclohexyl-1-pentanesulfonamide of 54 ± 5% from an average of three experiments. In one run analyzed chromatographically on the "Scanalyzer,"[2,11] the yield of insertion product was 56%, in excellent agreement with the isolated yield. In marked contrast to the reactions of azidoformates,[2] no hydrogen-abstraction product, 1-pentanesulfonamide, could be isolated, although a 2% yield of a compound with a similar but not identical infrared spectrum was obtained.



Since about 20% of the sulfonyl azide would have been expected to decompose by loss of sulfur dioxide, about one-fourth of the sulfonyl azide was not accounted for; the presence of cyclic sultams, formed by intramolecular carbon–hydrogen insertion, would be expected by analogy with the reaction of azidoformates,[2] but no pure compounds could be isolated. Addition of sulfur as a radical trap to the reaction mixture increased the yield of insertion product to 72%, indicating that essentially all of the free-radical portion of the reaction had been inhibited.

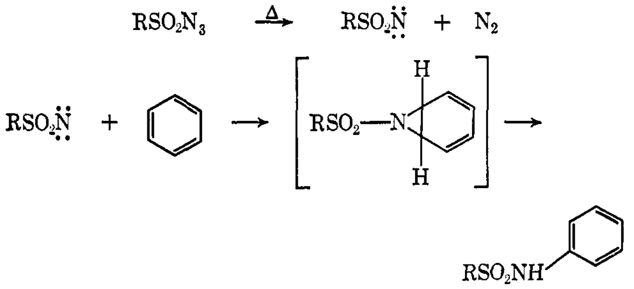
2-Propanesulfonyl azide reacted with cyclohexane to give, by infrared analysis, a 60% yield of N-cyclohexyl-2-propanesulfonamide and a maximum of 3% of 2-propanesulfonamide. The latter was not isolated but a material with a similar spectrum appeared to be present in small quantities. *p*-Toluenesulfonyl azide gave a 58% yield of insertion product, but with this azide a 5% yield of the abstraction product was definitely isolated. Since there is almost no loss of sulfonyl azide by sulfur dioxide evolution, the amount of unidentified material is larger from aromatic than from aliphatic sulfonyl azides.

Attempts to determine the relative reactivity of primary, secondary, and tertiary carbon–hydrogen bonds to sulfonylnitrenes had only limited success. The sulfonamides formed by the reaction of *p*-toluenesulfonyl azide with 2-methylbutane were found to be barely volatile and stable enough for gas chromatographic analysis, and no quantitative hydrolytic procedure could be found. Although complete separations could not be made, vpc showed a ratio of (III + IV):(I + II) of 1.53. Since this ratio for azidoformates is 5.6,[2] it is apparent that sulfonylnitrenes are less selective reagents than formylnitrenes. It seems reasonable to assume that the resonance forms available to the formylnitrene would stabilize it and make it more selective; no resonance forms, other than those involving d-orbital expansion on the sulfur, are available to the sulfonylnitrene. *p*-Toluenesulfonyl azide was treated with an equimolar mixture of benzene and cyclohexane by heating a 2% solution for 4 hr at 165°. The solvent was removed, the residue was hydrolyzed with a mixture of phenol and hydrobromic acid,[12] and the resulting amines were determined by vpc. Although the values obtained are not very precise, benzene was found to be about twice as reactive as cyclohexane. If the reaction with benzene is considered to involve addition followed by rearrangement,[13] a benzene "double bond" can be considered to be eight times more reactive with a sulfonylnitrene than a carbon–hydrogen bond in cyclohexane. By a similar competitive experiment, ring substitution in *p*-xylene has been shown to take place 2.2 times as rapidly as in benzene with a sulfonylnitrene. This is in reasonable agreement with the results of Abramovitch, Roy, and Uma,[14] who found toluene to be 1.86 times as reactive as benzene toward methanesulfonyl azide, in accord with a sulfonylnitrene being a highly electrophilic but nondiscriminating intermediate. For comparison, *p*-xylene is 2500 times more reactive than benzene in electrophilic bromination.[15]



$$\mathrm{RSO_2N_3 + (CH_3)_2CHCH_2CH_3 \longrightarrow \underset{I}{(CH_3)_2CHCH_2CH_2NHSO_2R} + \underset{II}{RSO_2NHCH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_3} + \underset{III}{(CH_3)_2CH\underset{\underset{RSO_2NH}{|}}{C}HCH_3} + \underset{IV}{(CH_3)_2\underset{\underset{RSO_2NH}{|}}{C}CH_2CH_3}}$$

$\mathrm{R} = p\text{-}\mathrm{CH_3C_6H_4}$



Azidoformates, sulfonyl azides, and aryl azides differ in their chemistry, in spite of the fact that loss of nitrogen is the rate-determining step[2,16] in many of their reactions.[17] These differences can be rationalized by assuming that in each case a singlet nitrene is formed, which reacts with substrate or undergoes intersystem crossing and the resulting triplet than reacts with substrate.[2] The more possibilities for resonance stabilization of the species, the more rapid intersystem crossing should be;[18] consequently, the order of singlet sta-

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(11) We are indebted to Dr. C. A. Genge for this analysis.

(12) H. R. Snyder and R. E. Heckert, *J. Am. Chem. Soc.*, 74, 2006 (1952).

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(15) H. C. Brown and L. M. Stock, *J. Am. Chem. Soc.*, 79, 1421 (1957).

(16) (a) M. Appl and R. Huisgen, *Chem. Ber.*, 92, 2961 (1959); (b) P. A. S. Smith and J. H. Hall, *J. Am. Chem. Soc.*, 84, 480 (1962); (c) P. Walker and W. A. Waters, *J. Chem. Soc.*, 1632 (1962).

(17) This discussion is limited to saturated and aromatic hydrocarbon reactions. There are numerous reactions of these azides, with olefins and acetylenes, for example, which obviously do not involve nitrenes.

(18) For example, carbene can react as a singlet, while diphenyl-

bility of the three nitrenes would be sulfonyl > formyl > aryl. If insertion into a carbon–hydrogen bond is a singlet reaction,[21] the expected order of singlet stability is followed: sulfonyl azides and azidoformates give comparable yields of N-cyclohexyl derivatives with cyclohexane, and aryl azides give very little,[22,23] high yields of C–H insertion products being obtained only in intramolecular reactions,[24] where favorable geometry might make addition faster than conversion to triplet.

Evidence has been presented that hydrogen abstraction by formylnitrenes is a triplet reaction.[25] To investigate this latter phenomenon more thoroughly, a number of azides were decomposed in cumene; the formation of dicumyl (2,3-dimethyl-2,3-diphenylbutane) is a good indication of the presence of radicals. *p*-Toluenesulfonyl azide gave no dicumyl, 1-pentanesulfonyl azide gave 1%, and *n*-octadecyl azidoformate 3%. Since Walker and Waters[16c] reported a 20% yield of dicumyl from *p*-methoxyphenyl azide, the predicted order is observed. Yields of the other expected abstraction products, the unsubstituted amine derivatives, from reactions with saturated hydrocarbons give comparable results: 0–3% sulfonamide from sulfonyl azides,[26] 20–25% carbamate from azidoformates,[2] and as high as 97% from an aryl azide.[16b] The preponderance of evidence, therefore, favors hydrogen abstraction being a reaction of the triplet nitrene.

Indirect evidence suggests that addition of a nitrene to an aromatic system is a singlet nitrene reaction.[27] Good yields are obtained with both azidoformates[28] and sulfonyl azides,[14] whereas aryl azides add successfully only in intramolecular reactions.[16b,29] Although azidoformates give azepines and sulfonyl azides give anilides, both are likely to result from the same type of intermediate; N-ethoxycarbonylazepine is known, for example, to undergo acid-catalyzed rearrangement to the corresponding anilide.[30]

Azobenzenes are often the major products in aryl azide thermolysis.[31] This probably involves a triplet nitrene reaction, although it does not follow that the product is formed by nitrene dimerization.

Experimental Section

Materials. The azides used in this work were all prepared in similar fashion by reaction of the appropriate sulfonyl chloride with sodium azide in aqueous acetone. The sulfonyl chlorides were either purchased or prepared by reaction of the corresponding thiols with chlorine.[32a] A typical preparation of 1-pentanesulfonyl azide is given below. Properties of the azides are summarized in Table V. Purity was ascertained by measurement of the gas evolved upon heating the azide in diphenyl ether; in this solvent the gas is almost completely nitrogen, with only traces of sulfur dioxide.

Table V. Sulfonyl Azides

Sulfonyl azide	Mp, °C	Recrystn solvent	Gas evolved, % of theory
1-Pentane-	−9	*n*-Hexane (−80°)	102
2-Propane-	<20	Not recrystallized	100
p-Toluene-		Methanol	192
1,4-Butanedi-	85–86	Ethanol	99
1,6-Hexanedi-	88.5–91	Ethanol	98
1,9-Nonanedi-	44.6–45.5	Ethanol	99
1,10-Decanedi-	89.5–91.5	Ethanol	100
1,4-Dimethylcyclohexane-α,α′-di-	126–129.5	Ethanol	98
m-Xylene-α,α′-di-	129–131	Ethanol	101
p-Xylene-α,α′-di-	164–165	Ethanol	96

All sulfonyl azides decompose more or less vigorously and exothermally on heating, and arenesulfonyl azides have been reported to detonate above 165°.[32b] In this laboratory the stability of sulfonyl azides has been found to be a function of purity. For example, a slightly impure sample of methanesulfonyl azide was extremely shock sensitive, whereas pure material was not. However, even the pure compound is comparable to TNT in its explosive power, and compounds with high azide contents should be handled in solution whenever possible.

1-Pentanesulfonyl Azide. Chlorine was bubbled through a solution of 104.2 g (1.0 mole) of 1-pentanethiol in 500 ml of acetic acid and 45 ml of water, maintained at 10–15°, until the yellow-green color persisted (3 hr). Nitrogen was bubbled through the solution to remove excess chlorine, and the resulting mixture was poured onto ice and then extracted with three 300-ml portions of methylene chloride. The methylene chloride solution was washed with water, 5% sodium hydroxide, again with water, and then dried over magnesium sulfate. Distillation of the methylene chloride followed by distillation of the residue yielded 154.4 g (90%) of 1-pentanesulfonyl chloride, bp 87–88° (7 mm), $n^{30}\text{D}$ 1.4520; lit.[33] $n^{25}\text{D}$ 1.4547, bp 77–78° (3 mm).

A mixture of 70 g (0.41 mole) of 1-pentanesulfonyl chloride, 35.2 g (0.54 mole) of sodium azide, 430 ml of acetone, and 300 ml of water was refluxed for 3 hr and then stirred at room temperature for 4 hr. A large quantity of cold water was added, and the liberated oil was taken up in ethylene dichloride. The ethylene dichloride solution was washed with water and dried over magnesium sulfate. Distillation of the solvent left the azide as a colorless oil, which contained 0.13% Cl. Recrystallization from hexane at −80° yielded a chlorine-free material of unchanged infrared spectrum, mp −9 to −8.5°.

Anal. Calcd for $C_5H_{11}SO_2N_3$ (177.2): C, 33.9; H, 6.26; N, 23.7. Found: C, 34.2; H, 6.19; N, 24.2.

Kinetic Experiments. Kinetic experiments were carried out in two ways. In some, a previously described[2] constant-volume

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methylene reacts only as a triplet.[19] Similarly, benzophenone singlet undergoes intersystem crossing very rapidly, whereas dialkyl ketones appear to be able to undergo singlet reactions.[20]

(19) P. P. Gaspar and G. S. Hammond in "Carbene Chemistry," W. Kirmse, Ed., Academic Press, New York, N. Y., 1964, pp 235–272.

(20) D. C. Neckars, "Mechanistic Organic Photochemistry," Reinhold Publishing Corp., New York, N. Y., 1967, p 168; N. J. Turro, P. Wriede, J. C. Dalton, D. Arnold, and A. Glick, *J. Am. Chem. Soc.*, **89**, 3950 (1967).

(21) There is considerable evidence that formylnitrenes insert only in the singlet state: see, for example, W. Lwowski and J. Simson, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 10–14, 1967, 163–O.

(22) J. H. Hall, J. W. Hill, and H. Tsai, *Tetrahedron Letters*, 2211 (1965).

(23) There is recent evidence that phenylnitrene inserts in low yield into the tertiary C–H bond of isobutane as a triplet: J. H. Hall, J. W. Hill, and J. M. Fargher, *J. Am. Chem. Soc.*, **90**, 5313 (1968).

(24) (a) G. Smolinsky, *ibid.*, **83**, 2489 (1961); (b) G. Smolinsky and B. I. Feuer, *ibid.*, **86**, 3085 (1964).

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(32) (a) G. Geisler and F. Asinger, *ibid.*, **89**, 1100 (1956); (b) G. P. Balabanov, Y. I. Dergunov, and V. G. Golov, *Zh. Fiz. Khim.*, **40**, 2171 (1966); *Chem. Abstr.*, **65**, 19974 (1966).

(33) I. B. Douglass and J. B. Johnson, *J. Am. Chem. Soc.*, **60**, 1486 (1938).

apparatus utilizing a pressure transducer was used to measure evolved gas. In others, gas volume was measured at constant pressure by means of a conventional mercury buret. Rate data were plotted either by the first-order rate equation or by the Guggenheim method[34] using time intervals of approximately two half-lives. Rate constants were determined from the slopes of the lines obtained.

When the sulfur dioxide evolved during a kinetic run was to be determined, the evolved gas was passed into a solution of sodium hydroxide which was analyzed for total sulfur by oxidation to sulfate, which was then determined turbidimetrically as barium sulfate. A typical rate experiment on 1-pentanesulfonyl azide is plotted in Figure 1.

Rate of Decomposition of 1-Pentanesulfonyl Azide. A decomposition tube fitted with a magnetic stirring bar was charged with 10.0 ml of white mineral oil (USP, Fractol) and sparged with nitrogen for 1 hr. The tube was then placed in a heating bath at 165.3° and, after temperature equilibration, 0.35 ml of 1-pentanesulfonyl azide was injected into the oil; the gas evaluation was followed by a gas buret jacketed at 29.6°. The data are plotted by the Guggenheim method in Figure 1 using a Δt of 30 min. A first-order rate constant of 8.0×10^{-4} sec^{-1} was calculated from the slope of the line drawn through the points for the first half-life.

The volume of gas evolved during the experiment was 66.3 ml (59.7 ml at STP). The gas was absorbed into 25.0 ml of 1 *N* sodium hydroxide solution. The resulting solution was shown to contain 16.25 mg of sulfur, equivalent to 0.51 mmole of sulfur dioxide or 19.2% of the evolved gas.

In a similar experiment, an infrared spectrum of the mineral oil solution at the end of gas evolution exhibited a strong peak assigned to azide at 2085 cm^{-1}.

Decomposition of *p*-Toluenesulfonyl Azide in the Presence of *t*-Butyl Hydroperoxide. A mixture of 100 ml of mineral oil, 3.0 ml (20 mmoles) of *p*-toluenesulfonyl azide, 3.0 g of calcium oxide, and 1.98 g of 90% *t*-butyl hydroperoxide (Lucidol) was stirred and heated for 26.5 hr at 127–132°. After cooling, the solids were separated by centrifugation, washed with benzene, and extracted with 250 ml of hot water. The resulting water solution was filtered and evaporated to dryness. The residue was dissolved in hydrochloric acid, the solution was filtered, and the filtrate was treated with *p*-toluidine.[35] The yellow solid obtained was recrystallized twice from water, with large losses, to yield 0.60 g (11%) of the *p*-toluidine salt of *p*-toluenesulfonic acid, mp 190.5–192°. The melting point of an authentic sample of the salt was 200–201°, mmp 199–199.5°. The infrared spectra of the product and of the authentic material[35] were identical. In a control experiment, in which the hydroperoxide was omitted, no sulfonic acid derivative was isolated.

Reaction of 1-Pentanesulfonyl Azide with Ethylene–Propylene Copolymer Rubber. A 4% solution of 118 g of ethylene–propylene rubber (reduced specific viscosity 1.1) in chloroform was mixed with 11.8 g of 1-pentanesulfonyl azide and the resulting solution was evaporated to dryness at room temperature. The residual rubber was placed in a flask which was evacuated and flushed with nitrogen and then heated in a nitrogen atmosphere for 2 hr at 175°. The product was dissolved in chloroform and precipitated by pouring into acetone, then redissolved in toluene and reprecipitated by pouring into acetone. After drying, the product weighed 101 g. The infrared spectrum had a strong absorption at 2100 cm^{-1}.

Anal. Found: N, 0.4; S, 0.67; reduced specific viscosity, 2.2.

In a control experiment, a solution of 1.0 g of the rubber and 0.11 g of 1-pentanesulfonyl azide in 50 ml of chloroform was precipitated by pouring into acetone. The dried, recovered rubber exhibited an infrared spectrum identical with that of untreated rubber.

Decomposition of 1-Pentanesulfonyl Azide in Cyclohexane. A titanium-lined pressure vessel, charged with 3.0 g of 1-pentanesulfonyl azide and 250 ml of cyclohexane, was heated at 170–175° for 6 hr, the mixture was washed out with chloroform, and the resulting solution was evaporated to dryness to yield 3.55 g of a dark brown solid exhibiting a peak in its infrared spectrum at 2085 cm^{-1}. The material was recrystallized once from methanol–water to yield 2.47 g of off-white solid; this was triturated with water to remove any 1-pentanesulfonamide and then recrystallized again from methanol–water. The yield of white solid was 2.12 g (53% based on azide). The melting point, 55–56°, and the infrared spectrum were identical with those of authentic N-cyclohexyl-1-pentanesulfonamide.

The product from a similar experiment was analyzed chromatographically on the Infrared Scanalyzer.[2,11] Two columns were found suitable for the separation, grade III alumina with 6% added water and Florisil with 10% added water. A gradient solvent mixture of carbon tetrachloride and acetonitrile was used; *i.e.*, the acetonitrile content of the solvent delivered to the column was very low at first but increased rapidly toward the end of the run to a maximum value of about 13–15 vol %. After completion of the run, the column was washed with pure acetonitrile to recover any polar fractions. The results from the alumina and Florisil columns were similar. In a typical separation on alumina the results in Table VI were obtained. The amounts of material isolated between fractions 2 and 3, between fractions 3 and 4, after fraction 4, and in the column wash were not identified. The 84.3 wt % yield of N-cyclohexyl-1-pentanesulfonamide corresponds to a 58% yield based on 1-pentanesulfonyl azide. Analysis of mixtures of pure compounds indicated that 1-pentanesulfonamide would have been detected if present in amounts larger than 0.5–1 wt %.

Table VI. Chromatographic Separation of Product from Reaction of 1-Pentanesulfonyl Azide and Cyclohexane

Fraction	Wt %	Identificztion
1	1.4	Unidentified hydrocarbon, mol wt ~500
2	0.8	Unidentified; contains C=O, probably as ketone
	1.7	
3	84.3	N-Cyclohexyl-1-pentanesulfonamide
	2.9	
4	2.7	Unidentified; infrared spectrum suggested a substituted sulfonamide
	1.8	
Column wash	1.5	
Total	97.1	

Decomposition of 1-Pentanesulfonyl Azide in Cyclohexane Containing Sulfur. A solution of 4.01 g of 1-pentanesulfonyl azide in 250 ml of cyclohexane containing 0.50 g of sulfur was heated in a stainless steel pressure vessel for 6 hr at 175°. Removal of the solvent from the product left a bright yellow solid. The solid was dissolved in methanol, treated with charcoal, and then filtered to remove unreacted sulfur. The resulting solution was concentrated, and water was added to cause crystallization, giving 3.40 g of crystals; a second crop weighed 0.39 g. The infrared spectra of both were identical with that of N-cyclohexyl-1-pentanesulfonamide. The total yield was 72% based on azide.

Decomposition of *p*-Toluenesulfonyl Azide in Cyclohexane. A solution of 4.00 g of *p*-toluenesulfonyl azide in 250 ml of cyclohexane was heated at 165° for 5 hr in a pressure vessel. The resulting mixture was filtered and evaporated to dryness. The residue was taken up in chloroform and the resulting solution was continuously extracted with water for 6 days. Evaporation of the water left 0.18 g of solid, the infrared spectrum of which was the same as that of *p*-toluenesulfonamide. The yield was 5% based on azide.

In another experiment, using 68 mg of *p*-toluenesulfonyl azide and 2 ml of cyclohexane, the residue after evaporation of the cyclohexane was stirred with 1 ml of 10% sodium hydroxide solution followed by two 1-ml portions of 10% potassium hydroxide. The residue solidified but did not dissolve. Acidification of the alkaline extracts precipitated small quantities of pasty material. The alkali-insoluble residue was stirred with dilute hydrochloric acid, washed with water, and allowed to dry. The dried material (50.6 mg, 58% yield based on azide) was identical with N-cyclohexyl-*p*-toluenesulfonamide, mp 83–85°, mmp 85°.

Decomposition of 2-Propanesulfonyl Azide in Cyclohexane. A solution of 4.07 g of 2-propanesulfonyl azide in 200 ml of cyclohexane was heated at 175° for 6 hr in a titanium-lined pressure vessel. The mixture was evaporated to dryness, the residue was dissolved in hexane, and the hexane solution was filtered to remove the insoluble portion (0.034 g) and then evaporated to dryness to

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(34) E. A. Guggenheim, *Phil. Mag.*, 2, 538 (1926).

(35) N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," T. Y. Crowell Co., New York, N. Y., 1947, p 322.

give 3.48 g of tan crystals. The infrared spectrum appeared to be identical with that of a mixture of 2-propanesulfonamide and N-cyclohexyl-2-propanesulfonamide. Under the assumption that only these two compounds were present, the mixture was analyzed by infrared using a published method.[36] The bands used for analysis were at 1535 and 995 cm^{-1}. The results indicated that the mixture contained 94–95 mole % N-cyclohexyl-2-propanesulfonamide, a 60% yield based on 2-propanesulfonyl azide. A synthetic mixture containing 92 mole % N-cyclohexyl-2-propanesulfonamide analyzed 93%.

Reaction of *p*-Toluenesulfonyl Azide with a Mixture of Cyclohexane and Benzene. A solution of 3.50 g of *p*-toluenesulfonyl azide in 87.9 g (1.13 moles) of benzene and 97.3 g (1.16 moles) of cyclohexane was heated in a titanium-lined pressure vessel for 4 hr at 165°. The mixture was filtered and the filtrate was diluted to 500 ml with chloroform. A 200-ml aliquot was evaporated to to dryness, and the residue refluxed overnight with a mixture of 5.0 g of phenol and 35 ml of 48% hydrobromic acid.[12] The reaction mixture was continuously extracted with ether overnight, made basic with sodium hydroxide, and continuously extracted again with benzene.

Analysis of the benzene extract by gas chromatography (28% Dowfax-9N10 on 5% potassium hydroxide loaded Chromosorb W, 1-ft column) indicated 73% aniline and 27% cyclohexylamine. Repetition of the hydrolysis step yielded values of 63.5% aniline and 36.5% cyclohexylamine. In a control experiment, a mixture of 0.503 g of N-cyclohexyl-*p*-toluenesulfonamide and 0.502 g of N-phenyl-*p*-toluenesulfonamide was hydrolyzed and analyzed by the above procedure. The results were 52% aniline and 48% cyclohexylamine. Converted to mole per cent, these values are aniline, 53.5%, and cyclohexylamine, 46.5%; theoretical values are aniline, 50.5%, and cyclohexylamine, 49.5%. Correcting the average of the experimentally found values for the control, the ratio of N-phenyl-*p*-toluenesulfonamide to N-cyclohexyl-*p*-toluenesulfonamide in the azide decomposition is 1.95.

Reaction of *p*-Toluenesulfonyl Azide with a Mixture of Benzene and *p*-Xylene. A solution of 4.038 g of *p*-toluenesulfonyl azide in 78.1 g (1 mole) of benzene and 106.2 g (1 mole) of *p*-xylene was heated in a titanium-lined pressure vessel for 5 hr at 165°. The resulting mixture was filtered and evaporated to dryness. The residue, a dark semisolid mass, was cleaved with phenol and hydrobromic acid, as in the previous experiment, to give 29% aniline and 71% 2,5-dimethylaniline. In a control experiment, equal weights of the two product sulfonamides were hydrolyzed to give 56.5 mole % aniline and 43.5 mole % dimethylaniline (theoretical values are 52.5 and 47.5%). Correcting the experimentally found value for the control, the ratio of N-2,5-dimethylphenyl-*p*-toluenesulfonamide to N-phenyl-*p*-toluenesulfonamide is 2.2.

Reaction of *p*-Toluenesulfonyl Azide with Isopentane. A solution of 5.00 g of *p*-toluenesulfonyl azide in 200 ml of isopentane (Phillips Research Grade) was heated for 7 hr at 155°. The resulting solution was evaporated to dryness, the residue was dissolved in hot carbon tetrachloride, and the solution was filtered to remove black, tarry material. The carbon tetrachloride was removed under vacuum. The residue was taken up in benzene, and the resulting mixture was filtered to remove insolubles (0.252 g, 6% based on *p*-toluenesulfonyl azide), whose infrared spectrum spectrum was identical with that of *p*-toluenesulfonamide. Evaporation of the benzene left 2.00 g of an amber oil. Gas chromatography on the same column used in the above experiments indicated that 50.6% of the material was a mixture of the *p*-toluenesulfonamides of 2-amino-2-methylbutane and 2-amino-3-methylbutane, and 33% was a mixture of the *p*-toluenesulfonamides of 1-amino-2-methylbutane and 1-amino-3-methylbutane.

Decomposition of Azides in Cumene. Pressure bottles containing (a) 0.75 g of 1-pentanesulfonyl azide in 12.5 ml of cumene, (b) 1.5 g of *n*-octadecyl azidoformate[2] in 25 ml of cumene, (c) 1.0 g of *p*-toluenesulfonyl azide in 17 ml of cumene, and (d) 25 ml of cumene were flushed with nitrogen and then heated at 150° overnight. The contents of the bottles were analyzed by gas chromatography for dicumyl with the following results: a, 0.89 μg/μl; b, 1.31 μg/μl; c, none detected; d, <0.01 μg/μl. For a and b, these values correspond to 1.2 and 3.2 mole % (based on azide), respectively.

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Hydrogen Bonding between Phenol and the Cyclopropane Ring[1]

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Abstract: The hydrogen-bond interaction between phenol and the cyclopropane ring has been studied by the infrared method. The hydrogen-bond shifts of the ν_{OH} frequency of phenol are in the order of 40 cm^{-1} and the enthalpy changes for the phenol–cyclopropane complex formation are in the range of 1.3–1.5 kcal/mole. From the $-\Delta F°$ *vs.* $\Delta\nu$ plot, which is established to be a good criterion to decide the type of π base, the cyclopropane ring has been confirmed to have olefinic character. The cyclopropane ring in the bicyclic compounds has been found to be more basic than that in the alkylcyclopropanes from a comparison of the frequency shifts and the hydrogen-bond energy. The ultraviolet spectra of the iodine–cyclopropane derivatives system show the presence of a charge-transfer band at about 250 mμ.

During the past 20 years the characteristics of the cyclopropane ring were reported by using the spectroscopic methods: ultraviolet,[2] infrared,[3] nuclear magnetic resonance spectra,[4] and others.[5] Of particular interest is the fact that the cyclopropane derivatives behave as compounds having "double-bond

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