# The Photolysis of Sulfonyl Azides in Isopropyl Alcohol[1]

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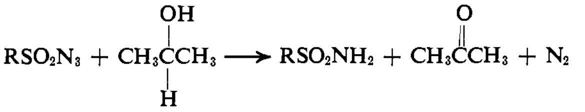
**Abstract:** Sulfonyl azides in isopropyl alcohol solution give the corresponding sulfonamides, acetone, and nitrogen either on direct irradiation of the azide or on selective irradiation of added benzophenone. Detailed studies with methanesulfonyl azide revealed high quantum yields and rates that showed complex dependences on the light intensity and on the concentrations of azide and benzophenone. A radical chain mechanism, evidently consisting of two propagation sequences, is involved. Chains appear to be terminated by radicals derived from isopropyl alcohol and from benzophenone.

We wish to report our discovery and mechanistic characterization of a photochemical reaction in which sulfonyl azides are reduced to sulfonamides by isopropyl alcohol solvent, according to eq 1. The reaction occurs in the absence of oxygen (1) on direct irradiation of the azide, (2) on selective irradiation of benzophenone added as a sensitizer, (3) on thermal treatment of the solution at its reflux temperature (80°), or (4) on addition of small amounts of ferrous chloride and hydrochloric acid to a solution of the azide in the alcohol.[3] We optimized the conditions only for the photochemical transformations 1 and 2, which are the chief topics of this paper.



$$RSO_2N_3 + CH_3\overset{OH}{\underset{H}{C}}CH_3 \longrightarrow RSO_2NH_2 + CH_3\overset{O}{\overset{\|}{C}}CH_3 + N_2 \quad (1)$$

Because of its representative behavior, methanesulfonyl azide was chosen as the substrate for most of our mechanistic investigations, although the reaction appears general for aliphatic and aromatic sulfonyl azides.

**Methods and Product Studies.** A deoxygenated solution of the azide in peroxide-free isopropyl alcohol was irradiated at *ca.* 20° with a mercury lamp. The acetone produced was isolated (as its 2,4-dinitrophenylhydrazone) from the distillate of the irradiated solution. The sulfonamide and benzophenone (in those cases where the latter was employed as a sensitizer) were obtained from the distillation residue.

A. **Direct Photolyses.** These irradiations were conducted with unfiltered light in both anhydrous and aqueous isopropyl alcohol. Methanesulfonyl azide, either in the anhydrous solvent or in the presence of 10 vol % water, reacted quantitatively, according to the stoichiometry of eq 1. The photolysis of *p*-methoxybenzenesulfonyl azide under anhydrous conditions gave the related sulfonamide in at least 94% yield, but the behavior of *m*-nitrobenzenesulfonyl azide, in anhydrous solvent, was anomalous. Prolonged irradiation gave an orange solution, but no gas was evolved, and the infrared spectrum of the product mixture showed diminution of the nitro band at 1397 cm$^{-1}$ and the appearance of a new band at 1540 cm$^{-1}$, while the azido band at 2132 cm$^{-1}$ remained moderately strong.

Arenesulfonyl azides appeared to be somewhat less reactive than compounds with the sulfonyl group attached to a saturated carbon atom. Direct photolysis of *p*-bromobenzene- and 2-naphthalenesulfonyl azides in isopropyl alcohol containing 8–10 vol % of water gave nearly quantitative yields of the respective crude sulfonamides, containing light pink impurities that turned red-black at the melting points, which were *ca.* 5° low. The tendency to form reddish side products was characteristic of arenesulfonyl azides and was accentuated by water. The *p*-methoxybenzenesulfonamide obtained from the photolysis of the corresponding azide in anhydrous isopropyl alcohol was slightly contaminated by a pink substance. Essentially the same results were obtained in 4% water, but when 27% water was used the reaction rate was appreciably depressed, and a massive quantity of red tar accompanied the expected products. The behavior of arenesulfonyl azides contrasts with that of methane- and $\alpha$-toluenesulfonyl azides, which were transformed rapidly and quantitatively to the respective sulfonamides, without detectable side-product formation, both in the anhydrous solvent and in the presence of 10% water.

The photolyses in aqueous isopropyl alcohol (and probably also in the anhydrous solvent) are markedly inhibited by oxygen. An oxygen-saturated solution of $\alpha$-toluenesulfonyl azide reacted at least 50 times slower than a nitrogen-swept solution. The most distinctive feature of the direct photolysis is that it showed a marked induction period, even in thoroughly deoxygenated solutions. Addition of a small amount of acetone to methanesulfonyl azide in isopropyl alcohol completely eliminated the induction period and shortened the photolysis half-life by a factor of *ca.* 10. Thus the direct photolysis is autocatalyzed by acetone, which absorbs the same wavelengths as does the azide ($\lambda$ 254 m$\mu$).

To test the possibility that the reaction proceeds through an N-isopropoxysulfonamide, we synthesized N-isopropoxy-$\alpha$-toluenesulfonamide (**3**) by the sequence shown in Chart I, which was modeled after

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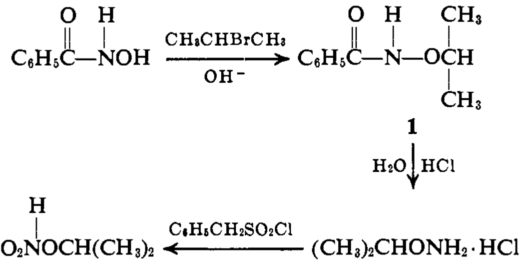
(1) (a) Abstracted from the dissertation submitted by M. T. R. in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (b) Presented in summary at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 13, 1965, Abstract 23S. (c) This work was supported by the National Institutes of Health (Grants GM-06304 and GM-9693) and by a grant-in-aid from the H. A. B. Dunning Foundation.

(2) To whom inquiries should be addressed.

(3) H. Kwart and A. A. Kahn, *J. Am. Chem. Soc.*, **89**, 1950 (1967), report that the reaction can be effected catalytically with copper.

Chart I



related procedures in the literature.[4] We excluded N-isopropoxysulfonamides as intermediates in the photolysis by recovering **3** in 96% yield after irradiation under conditions that effected quantitative conversion of α-toluenesulfonyl azide.

**B. Benzophenone-Sensitized Photolyses.** These experiments were conducted in anhydrous isopropyl alcohol with light from which all wavelengths below *ca.* 345 mμ were filtered so that benzophenone was the only absorbing species. No reaction occurred under these conditions when benzophenone was absent. As expected, the benzophenone-sensitized photolysis exhibited no induction period, and its rate steadily declined as the reaction progessed. The colored side products sometimes seen in the direct photolyses were not observed in the benzophenone-sensitized reaction. Yield data are summarized in Table I.

**Table I.** Photolysis of Sulfonyl Azides in Isopropyl Alcohol with Benzophenone

| $RSO_2N_3$<br>R | Yield, %<br>$N_2$ | <br>$RSO_2NH_2$ | <br>$Me_2CO$ | % recovery, benzophenone |
|---|---|---|---|---|
| $CH_3$[a] | 99.5 | 98.2 | 104[b] | 96.0 |
| $C_6H_5CH_2$ | 100.2 | 69.2 | 87.0 | 77.9 |
| *p*-$BrC_6H_4$ | 84.4 | 95.3 | 67.7 | 82.5 |
| *p*-$CH_3OC_6H_4$ | 90.0 | 82.0 | 88.3 | 56.6 |

[a] Each value is the best obtained in five experiments. In a control experiment designed to test the quantitative efficiency of product isolation, the losses of methanesulfonamide, acetone, and benzophenone were, respectively, 3, 0.2, and 6%. [b] One value as high as 109% was observed.

We took precautions to isolate the products from methanesulfonyl azide quantitatively, but the yields recorded for other azides do not imply optimum values.

Because benzophenone and isopropyl alcohol are known to undergo photoconversion to benzpinacol and acetone in the absence of azide,[5,6] a greater than quantitative yield of acetone and less than quantitative recovery of benzophenone might be expected when the azide is present. The product mixtures were not examined specifically for benzpinacol, but in one experiment with methanesulfonyl azide the recovered benzophenone was contaminated by a high-melting material, probably benzpinacol (lit.[7] mp 185–186°), and an unusually high yield of acetone (109%) was obtained. Clearly, however, little or no photoreduction of benzophenone takes place until decomposition of the azide is virtually complete. This claim is supported by the 96% recovery of pure benzophenone from an experiment in which the solution was irradiated no longer than necessary to obtain a quantitative yield of nitrogen. Moreover, the ultraviolet spectrum of benzophenone (examined in the region of its 326-mμ maximum) in a solution of isopropyl alcohol containing methanesulfonyl azide underwent no detectable change when the azide was photolyzed to half-decomposition.

**Quantum Yield and Rate Studies.** These experiments were conducted with methanesulfonyl azide in anhydrous isopropyl alcohol. Reaction rates were measured gas volumetrically, and light intensities were determined by ferrioxalate actinometry.[8]

**A. Direct Photolysis.** Several features of the direct photolysis of methanesulfonyl azide made it unsuitable for a kinetic study. The acetone produced is both an inner filter and a sensitizer, and the molar absorptivities of both the azide (ε 13.1) and the acetone (ε 8) at the most favorable wavelength available (254 mμ) are so low that a suitable range of concentrations ensuring total light absorption was not attainable. Our study was therefore limited to quantum yield determinations. In each experiment a 0.8 *M* solution of the azide was photolyzed at 22° to 20% completion with monochromatic light. The average quantum yield over the initial 20% of the reaction ranged from 20 to 75, and the values calculated from the instantaneous rate at 20% completion ranged from 110 to 150 mol/einstein. The appreciable variation in quantum yield from one run to another was not unexpected because the technique used to degas the solution before photolysis left varying unknown amounts of oxygen.

**B. Photolysis with Benzophenone.** The benzophenone-sensitized reaction was amenable to a kinetic study because the benzophenone concentration remains effectively constant throughout the reaction, and it was possible to use wavelengths (*ca.* 366 mμ) at which benzophenone was the only absorbing species. We studied the reaction rate at 24° as a function of the light intensity and of the concentrations of benzophenone and the azide. The technique employed (see Experimental Section) effectively eliminated oxygen from the system, as evidenced by the satisfactory reproducibility of the results. Studies of the rate dependence on the azide concentration covered a tenfold range of initial azide concentrations but were conducted at a single benzophenone concentration (0.162 *M*). Light intensities were not determined but were held constant in each individual run. Intensity variations over the entire set of experiments caused a *ca.* 2.5-fold spread in the apparent rate constants. Solutions with the lower initial azide concentrations were irradiated with polychromatic light suitably filtered to exclude absorption

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(4) (a) O. L. Brady and F. H. Peakin, *J. Chem. Soc.*, 226 (1930); (b) P. Mamalis, J. Green, and D. McHale, *ibid.*, 229 (1960); (c) M. Murakami and T. Nashima, *Mem. Inst. Sci. Ind. Res. Osaka Univ.*, **10**, 175 (1953); *Chem. Abstr.*, **49**, 6864*d* (1955).

(5) W. E. Bachman in "Organic Syntheses," Coll. Vol. II, A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p 71.

(6) (a) J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Rechtenwald, and R. B. Martin, *J. Am. Chem. Soc.*, **81**, 1068 (1959); (b) W. M. Moore and M. D. Ketchum, *J. Phys. Chem.*, **68**, 214 (1964).

(7) N. A. Lange, "Handbook of Chemistry," 4th ed, Handbook Publishers, Inc., Sandusky, Ohio, 1941: (a) p 298; (b) p 296.

(8) (a) C. A. Parker, *Proc. Roy. Soc.*, (London), A220, 104 (1953); (b) C. G. Hatchard and C. A. Parker, *ibid.*, **A235**, 518 (1956); (c) J. H. Baxendale and N. K. Bridge, *J. Phys. Chem.*, **59**, 783 (1955); (d) J. Lee and H. H. Seliger, *J. Chem. Phys.*, **40**, 519 (1964).

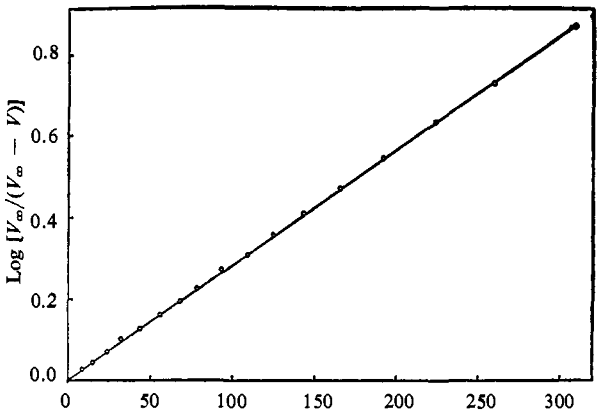

Figure 1. Photolysis of methanesulfonyl azide (0.0191 *M*) with benzophenone (0.160 *M*) in isopropyl alcohol.

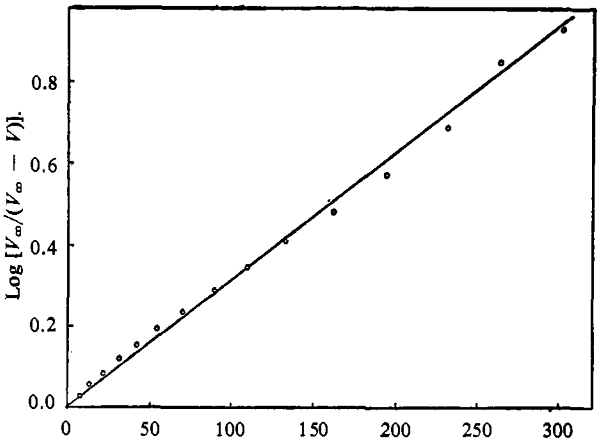

Figure 2. Photolysis of methanesulfonyl azide (0.183 *M*) with benzophenone (0.158 *M*) in isopropyl alcohol.

by species other than benzophenone. Solutions with the higher initial azide concentrations were irradiated with 365- and 366-mμ lines isolated from a spectral lamp. The two methods gave data that overlap with respect to initial azide concentrations.

At the lowest initial azide concentration the data gave an excellent first-order rate plot (Figure 1). When the initial azide concentration was increased by as much as a factor of 5, we continued to observe fairly good first-order kinetics, but a tenfold increase revealed a modest, but unmistakable, departure from first-order behavior, shown in Figure 2, in which the distribution of experimental points shows the contribution of a greater-than-first-order term, which becomes significant only at high azide concentrations. A graphical examination of the data based on eq 2, where *n* is the apparent order in azide, led to the same conclusion. At initial azide concentrations up to 8.8 × $10^{-2}$ *M*, plots of log ($V_\infty - V$) *vs.* log ($dV/dt$) gave straight lines with slopes

$$\log (dV/dt) = n \log (V_\infty - V) + \log k \qquad (2)$$

(*n*) averaging 1.00 ± 0.04, but at higher concentrations such plots showed upward concavity with slopes distinctly above unity for the initial phases of the reaction.

We studied the quantum yield and half-life dependence of the photolysis on a tenfold range of intensities of 365–366-mμ light. The experiments were all conducted at the same initial concentrations of methanesulfonyl azide (0.0894 *M*) and benzophenone (0.167 *M*). The results (Table II) reveal that the average quantum yield in the first half-life is much greater than unity and, within experimental error, is an inverse function of the light intensity.[9] With run 1 as a reference, Table II shows the rate dependence on the intensity by a comparison of the observed half-lives with those calculated for a first-order and for a half-order light dependence. The observed order in intensity is clearly between one-half and unity, and almost certainly reflects a rate law containing both half-order and first-order light intensity terms (see below).

**Table II.** Half-Life Dependence of Sensitized Photolysis of Methanesulfonyl Azide on Light Intensity

| Run | Intensity × $10^7$, einstein $l.^{-1}$ $sec^{-1}$ | Av quantum yield in first half-life | Half-life, min Obsd | Half-life, min Calcd Half-order | Half-life, min Calcd First-order |
|---|---|---|---|---|---|
| 1 | 1.86 | 57 | 69 | ... | ... |
| 2 | 1.84 | 56 | 72 | 69 | 71 |
| 3 | 0.58 | 68 | 188 | 124 | 220 |
| 4 | 0.57 | 65 | 201 | 125 | 225 |
| 5 | 0.21 | 101 | 353 | 207 | 620 |
| 6 | 0.19 | 112 | 356 | 218 | 690 |

Because of the low molar absorptivity of benzophenone (ε 51) at the wavelength used the requirement of total light absorption limited the range of concentrations available for our study of the rate dependence on the benzophenone concentration. We determined the effect of a fivefold change in the benzophenone concentration on the half-life. In each run, two solutions identical except for the benzophenone concentration were irradiated under the same conditions. In each run the azide concentration was *ca.* 0.09 *M*, but light intensities ranging from *ca.* 2 × $10^{-8}$ to 6 × $10^{-8}$ einstein $l.^{-1}$ $sec^{-1}$ were employed. There was no *detectable* dependence of the results on the light intensity. Data from three typical experiments, summarized in Table III, demonstrate an inverse, and apparently complex, dependence of the rate on the benzophenone concentration. For a strict reciprocal first-order dependence one would predict a value of unity for *Q* in Table III, and for a recip-

**Table III.**[a] Half-Life Dependence of Sensitized Photolysis of Methanesulfonyl Azide on the Benzophenone Concentration

| Intensity × $10^8$ [b] | $[Ph_2CO]_A$, *M* | $[Ph_2CO]_B$, *M* | $[CH_3SO_2N_3]_0$, *M* | $\tau_A$, min | $\tau_B$, min | *Q*[c] |
|---|---|---|---|---|---|---|
| 6 | 0.0464 | 0.207 | 0.0879 | 54.1 | 203 | 0.84 |
| 6 | 0.0411 | 0.221 | 0.0918 | 66.5 | 285 | 0.80 |
| 2 | 0.0417 | 0.228 | 0.0905 | 135 | 645 | 0.87 |

[a] Data for solutions dilute in benzophenone (A) are distinguished from those for concentrated ones (B) by subscripts. Half-lives are τ. [b] Approximate, in einsteins $l.^{-1}$ $sec^{-1}$. [c] $\tau_B[Ph_2CO]_A/\tau_B[Ph_2CO]_B = Q$.

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(9) In runs conducted at very similar intensities (runs 1 and 2, and 3 and 4), there is an apparent reversal of the intensity–quantum yield relationship shown by the experiments taken as a whole. These discrepancies may be due to experimental error or to trace impurities to which reactions of high quantum yield are often very sensitive.

rocal half-order dependence, $Q = 0.44$ if $[Ph_2CO]_B = 5[Ph_2CO]_A$. The observed values of $Q$ show the apparent kinetic order in benzophenone to be between minus one and minus one-half.

## Discussion

The high quantum yields in the reaction of methanesulfonyl azide with isopropyl alcohol, both in the direct photolysis and in the benzophenone-sensitized process, leave no doubt that a chain mechanism is involved. Ample analogies for such a mechanism exist.[10] The complicated rate dependences displayed by our reaction point to a mechanism of considerable complexity. More than 20 different simple radical chain mechanisms, each consisting of a single initiation process, a single propagation sequence, and a single termination step, can be devised for the benzophenone-sensitized reaction. Under the high quantum yield conditions of our experiments, in which the rate of product formation by the initiation step can be neglected, the rate laws for all these simple mechanisms would be closely approximated by one-termed expressions in which the kinetic orders in azide, benzophenone, and light intensity are each an integral multiple of one-half. None of these simple rate laws can account for our data, but a systematic examination of them guided our consideration of the kinetic consequences of multiple initiation, propagation, and termination processes, which are too numerous to be considered here fully.

The mechanism of the benzophenone-sensitized photolysis of methanesulfonyl azide can be discussed in terms of eq 3–11. Steps 3–6 represent the accepted mechanism of the photolysis of benzophenone in isopropyl alcohol in the absence of azide.[6] In eq 3, B represents the relatively long-lived lowest triplet state of benzophenone (formed by intersystem crossing from the photoexcited singlet). Because of the extremely short life-times of other excited states of benzophenone, B is the only one that exhibits chemical reactivity.[6a]

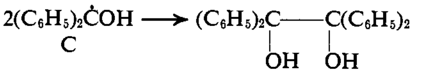
There are at least two conceivable fates of B that could initiate a chain reaction of the azide. The first, *direct initiation*, is simply the reaction of B with the alcohol that occurs in the absence of azide (eq 4). The other possibility is that of *energy transfer initiation* in which B returns to the ground state by transferring its triplet energy to the azide (E).[17] The resulting azide triplet then loses nitrogen, forming a triplet sulfonyl nitrene F. This two-step conversion of E to F is represented in the compressed form of eq 7. Actual initiation is accomplished by the nitrene's abstraction of hydrogen from a solvent molecule (eq 8).

Two propagation sequences can be envisaged. The first ("chain 1") consists of reactions 9 and 10, and the other ("chain 2") consists of reactions 9, 5, and 11. Chain 1 involves only two radicals (D and G) as carriers, but a striking feature of chain 2 is that its propagation entails the repetitive destruction and regeneration of three radicals (C, D, and G), and of the benzophenone molecule (A). Interestingly, reactions 5 and 6 each have a different relationship to the two chains. Reaction 6 is independent of chain 1 (as evidenced by the absence of its rate constant in the rate laws for mechanisms involving chain 1 alone), but its occurrence terminates chain 2. Reaction 5 terminates chain 1 but is a step in the propagation of chain 2.

$$\underset{A}{(C_6H_5)_2CO} + h\nu \longrightarrow \underset{B}{(C_6H_5)_2CO^*} \qquad (3)$$

$$\underset{B}{(C_6H_5)_2CO^*} + (CH_3)_2CHOH \longrightarrow \underset{C}{(C_6H_5)_2\dot{C}OH} + \underset{D}{(CH_3)_2\dot{C}OH} \qquad (4)$$

$$\underset{A}{C_6H_5)_2CO} + \underset{D}{(CH_3)_2\dot{C}OH} \longrightarrow \underset{C}{(C_6H_5)_2\dot{C}OH} + (CH_3)_2CO \qquad (5)$$



$$\underset{C}{2(C_6H_5)_2\dot{C}OH} \longrightarrow (C_6H_5)_2\underset{OH}{\underset{|}{C}}-\underset{OH}{\underset{|}{C}}(C_6H_5)_2 \qquad (6)$$

$$\underset{B}{(C_6H_5)_2CO^*} + \underset{E}{CH_3SO_2N_3} \longrightarrow \underset{A}{(C_6H_5)_2CO} + \underset{F}{CH_3SO_2\underset{\cdot\cdot}{\dot{N}}\cdot} + N_2 \qquad (7)$$

$$\underset{F}{CH_3SO_2\underset{\cdot\cdot}{\dot{N}}\cdot} + (CH_3)_2CHOH \longrightarrow \underset{G}{CH_3SO_2\underset{\cdot\cdot}{\dot{N}}H} + \underset{D}{(CH_3)_2\dot{C}OH} \qquad (8)$$

$$\underset{G}{CH_3SO_2\underset{\cdot\cdot}{\dot{N}}H} + (CH_3)_2CHOH \longrightarrow CH_3SO_2NH_2 + \underset{D}{(CH_3)_2\dot{C}OH} \qquad (9)$$

$$\underset{E}{CH_3SO_2N_3} + \underset{D}{(CH_3)_2\dot{C}OH} \longrightarrow \underset{G}{CH_3SO_2\underset{\cdot\cdot}{\dot{N}}H} + (CH_3)_2CO + N_2 \qquad (10)$$

$$\underset{E}{CH_3SO_2N_3} + \underset{C}{(C_6H_5)_2\dot{C}OH} \longrightarrow \underset{G}{CH_3SO_2\underset{\cdot\cdot}{\dot{N}}H} + \underset{A}{(C_6H_5)_2CO} + N_2 \qquad (11)$$

We now consider the detailed mechanism in the light of our results. A characteristic of chain reactions is that their kinetics are controlled largely by the termination processes. The observed inverse rate dependence on the benzophenone concentration can be reasonably attributed only to the destruction of a propagating radical by benzophenone, as shown in reaction 5, which also occurs in the absence of azide. The alternative possibility of "self-quenching" of photoexcited benzophenone by its ground state can be excluded, since the quantum yields of reactions in which excited benzophenone acts only as an energy transfer agent, and does not react chemically, are known to be independent of the

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(10) For example the reactions of sulfonyl azides (a) with *t*-butyl hydroperoxide,[11] with triphenylphosphine,[12] and with phenyl sulfide,[13] (b) the decomposition of sulfonyl azides in mineral oil,[14] (c) the photolysis of acyl and carbamoyl azides in alcohols,[15] and (d) the reaction of arenediazonium ions with methanol.[16]

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

(12) J. E. Leffler and Y. Tsuno, *ibid.*, 28, 902 (1963).

(13) M. Taketayaski, T. Shingaki, and T. Mitsuyama, *Sci. Rept. Osaka Univ.*, 10, 35 (1961); *Chem. Abstr.*, **59**, 9493*g* (1963).

(14) W. F. Sloan, W. B. Renfrow, and D. S. Breslow, *Tetrahedron Letters*, 2905 (1964).

(15) (a) R. Puttner and K. Hagner, *ibid.*, 3119 (1964); (b) R. Kreher and G. H. Berger, *ibid.*, 369 (1965).

(16) (a) D. F. DeTar and M. N. Turetsky, *J. Am. Chem. Soc.*, **77**, 1745 (1955); (b) *ibid.*, 78, 3925 (1956).

(17) Energy transfer to the azide from a benzophenone singlet can be safely discounted, since photoexcited benzophenone crosses over quantitatively to the lowest triplet before transferring energy to other molecules, even when such energy transfers are diffusion controlled.[18]

(18) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964).

benzophenone concentration.[19] A notable feature of the scheme under discussion is that it gives no role to sulfonylamido radicals (G) in chain breaking. This is suggested by the approximately unit order of the reaction in azide, since termination of either chain by reactions involving G should depress the kinetic order in azide toward its limiting value of zero for the case in which G is the only chain-breaking species. Since the accepted mechanism for the photoreduction of benzophenone in isopropyl alcohol in the absence of azide does not involve reactions between C and D, we assume that such reactions do not occur when azide is present.

Noyes and Leighton pointed out that the rate variation of a photochemical chain reaction with the light intensity provides a valuable clue to its mechanism.[20] The orders with respect to intensity almost always lie between one-half and one. Half-order intensity dependence is characteristic of a chain that is terminated by reaction between two of its propagating radicals, but when a chain is broken by the reaction of a propagating radical with some nonpropagating species, a first-order intensity dependence results. Simultaneous operation of both types of termination steps gives an apparent order between one-half and one.

The observed complex rate dependence of the sensitized azide photolysis on the intensity almost surely results from the contribution of both half-order and first-order terms and shows that both types of termination steps mentioned by Noyes and Leighton are operative. The first-order intensity component can be accounted for by eq 5, which terminates chain 1 by the removal of only one of its propagating radicals (D). The involvement of reaction 5 in chain termination is suggested also by the observed inverse rate dependence on the benzophenone concentration.

The half-order component of the rate–intensity relationship is best accounted for by reaction 6, the only conceivable chain-breaking step that has not been at least tentatively rejected on the basis of previous considerations. If we accept both reactions 5 and 6 as chain-breaking steps, we must also conclude that chains 1 and 2 are simultaneously operative, since reactions 5 and 6 each terminate only chain 1 and chain 2, respectively.

The exact form of the predicted rate law depends on which of the two initiation processes actually operates. If initiation occurs by triplet energy transfer (eq 3, 7, and 8), the rate law is that shown in eq 12, whereas initiation *via* hydrogen abstraction by excited benzophenone (eq 4) would lead to eq 13.[1a] In eq 12 and 13, $\mathrm{d}V/\mathrm{d}t$ and $I$ symbolize the rate of nitrogen evolution and the light intensity, respectively.

$$\frac{\mathrm{d}V}{\mathrm{d}t} = k_3I + k_{10}[\mathrm{E}]\left\{\frac{k_{11}\left(\frac{k_3I}{k_6}\right)^{1/2}[\mathrm{E}] + 2k_3I}{k_5\,[\mathrm{A}]}\right\} + k_{11}[\mathrm{E}]\left(\frac{k_3I}{k_6}\right)^{1/2} \quad (12)$$

$$\frac{\mathrm{d}V}{\mathrm{d}t} = k_{10}[\mathrm{E}]\left\{\frac{k_{11}\left(\frac{k_3I}{k_6}\right)^{1/2}[\mathrm{E}] + k_3I}{k_5[\mathrm{A}]}\right\} + k_{11}[\mathrm{E}]\left(\frac{k_3I}{k_6}\right)^{1/2} \quad (13)$$

Comparison of eq 12 and 13 shows that the rate behaviors predicted by the two initiation schemes are in practice indistinguishable under the high quantum yield conditions of our experiments. The two rate laws differ essentially only in the appearance of $k_3I$ as the first term in eq 12 and the absence of this term in eq 13. The term $k_3$ expresses the rate of chain initiation, which is negligible compared to the total rate in a reaction of high quantum yield. Our studies do not uniquely define the initiation process, and competitive initiation by both mechanisms mentioned above cannot be excluded. It is even conceivable that initiation might be due to abstraction of solvent hydrogen by an azide triplet, although no such reactions appear to be known in the photochemistry of azide-like substances.

We found that the decomposition of methanesulfonyl azide in isopropyl alcohol could be effected by selective irradiation of 2-acetonaphthone instead of benzophenone. In the naphthone case, at least, initiation must occur *via* transfer of excitation energy to the azide, since 2-acetonaphthone triplets are incapable of hydrogen abstraction from isopropyl alcohol.[21] It follows that benzophenone also is energetically capable of transferring triplet excitation to the azide, since the triplet energy of benzophenone is 9.2 kcal/mol greater than that of 2-acetonaphthone.[22] However, sensitization by 2-acetonaphthone differed strikingly from that by benzophenone in that, with former sensitizer, the reaction was extremely slow, gave a nitrogen yield of only 68%, and produced a yellow solution.

In summary, we suggest that the benzophenone-sensitized photolysis of methanesulfonyl azide in isopropyl alcohol occurs by the mechanism shown in eq 3–11, with the possible exclusion of eq 4 or of eq 7 and 8. Our data do not permit a convincing quantitative test of the rate law, but qualitative agreement with both eq 12 and 13 is evident. Since the rate of chain initiation can be neglected, both expressions are compatible with the observed first-order azide kinetics that increases slightly at high azide concentrations, and with the mixed half- and first-order dependence on the light intensity, as well as the reciprocal first-plus-zero-order dependence on the benzophenone concentration.

Reactions 10 and 11 probably consist of several steps each, but for simplicity we have treated them formally as one-step processes, with the assumption that none of the intermediates is diverted. Sloan, *et al.*, found that radicals derived from saturated hydrocarbon solvents attack 1-pentanesulfonyl azide with the formation of sulfur dioxide and an alkyl azide, as shown in eq 14[14] (R· = saturated hydrocarbon radical). The analogous reaction of an alcohol radical (C or D) with methane-

$$\mathrm{C_5H_{11}SO_2N_3 + R\cdot \longrightarrow RN_3 + [C_5H_{11}SO_2\cdot] \longrightarrow SO_2 + C_5H_{11}\cdot} \quad (14)$$

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[19] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

[20] W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, p 197.

[21] G. S. Hammond and P. A. Leermakers, *J. Am. Chem. Soc.*, **84**, 207 (1962).

[22] J. R. Fox and G. S. Hammond, *ibid.*, **86**, 4031 (1964).

sulfonyl azide would give a methyl radical, sulfur dioxide, and a (probably unstable) $\alpha$-azido alcohol. We found no mass spectral evidence of sulfur dioxide in the gas produced in the photolysis of $\alpha$-toluenesulfonyl azide, and this, together with our quantitative yields of methanesulfonamide from methanesulfonyl azide, shows that sulfur–carbon scission like that in eq 14 does not occur in our reactions. We suggest that this striking dissimilarity between the reactions of alkyl radicals and radicals from alcohols with sulfonyl azides reflects a difference in mechanism. Whereas hydrocarbon radicals probably attack the azido group directly, those from alcohols may first transfer an electron to it, forming a cation–radical anion pair, which then collapses in one or more steps as shown in eq 15. This mechanistic dichotomy can be rationalized on the basis of the higher polarity of an alcohol solvent compared to that of a hydrocarbon solvent, and on the stabilization conferred by a hydroxyl group on a cationic center to which it is bonded. The mechanism of eq 15 is analogous to that proposed by DeTar and Turetzky for the reaction of the hydroxymethyl radical with arenediazonium ions,[16a] and by Leffler and Tsuno for the action of triphenylphosphine on acyl azides.[12]

$$\mathrm{CH_3SO_2N_3} + \mathrm{R_2\dot{C}OH} \longrightarrow [\mathrm{CH_3SO_2}\underset{\cdot\cdot}{\overline{\ddot{\mathrm{N}}}}\ddot{\mathrm{N}}{=}\ddot{\mathrm{N}}\cdot\ \mathrm{R_2C^+OH}] \xrightarrow{-\mathrm{N_2}} \mathrm{CH_3SO_2}\underset{\cdot\cdot}{\dot{\mathrm{N}}}\mathrm{H} + \mathrm{R_2C{=}O} \quad (15)$$

The direct photolysis of sulfonyl azides in isopropyl alcohol is mechanistically similar to the benzophenone-sensitized reaction. The basic differences are (a) that in the direct photolysis the azide must be directly involved in chain initiation, at least during the initial induction period before any acetone has accumulated to sensitize the reaction, and (b) that chain 2 is inoperative in the absence of benzophenone.

**Effect of Solvent.** We conducted some exploratory experiments on the direct photolysis of sulfonyl azides in ethanol and in methanol. In all cases the reaction rate was markedly lower in ethanol than in isopropyl alcohol, and lowest in methanol. For example, methanesulfonyl azide decomposed at least 50 times faster in anhydrous isopropyl alcohol than under comparable conditions in methanol. Furthermore, when the solvent was changed from isopropyl alcohol to ethanol to methanol, increasingly complex product mixtures were obtained. The photolysis of *p*-bromobenzenesulfonyl azide in 95% ethanol gave mainly *p*-bromobenzenesulfonamide and acetaldehyde along with unidentified side products. We did not characterize the variety of products obtained from photolyses in methanol, but Lwowski and Schieffele report[23] that irradiation of benzenesulfonyl azide–anhydrous methanol gave a mixture of which methyl phenylsufamate (formed in 23% yield *via* a Curtius rearrangement) was the chief component. Their yield of benzenesulfonamide was only 4.5%, which indicates that the reaction in methanol has little or no chain character. Lwowski found initial quantum yields of the order of unity for the photolysis of benzenesulfonyl azide in methanol.[24] This low quantum yield is not necessarily incompatible with the decomposition of a portion of the azide by a chain mechanism, but may only indicate an initiation process of low quantum efficiency. Our observation of strong autocatalysis by acetone in the direct photolysis of sulfonyl azides in isopropyl alcohol shows that chain initiation *via* direct excitation of the azide is relatively inefficient.

The dependence of the rate on the solvent is probably due in part to changes in reactivity of the species involved in chain propagation and termination. An additional source of solvent effects was discovered by Lwowski and coworkers. Their Curtius rearrangement of benzenesulfonyl azide in methanol is only one of several recent illustrations that many azides formerly thought to be incapable of rearrangement during photolysis do give rearranged products in media of high hydroxyl group content.[25] Thus the decrease in the rate of direct photolysis in the solvent series isopropyl alcohol, ethanol, methanol is evidently due in part to an increasing tendency of the excited azide to undergo rearrangement rather than to initiate a kinetic chain. Therefore our finding that added water weakly retards the direct photolysis of *p*-methoxybenzenesulfonyl azide in isopropyl alcohol and causes the formation of (unidentified) side products is consistent with Lwowski's results.

**Thermal and Ferrous Chloride-Induced Decompositions.** Our investigation of nonphotochemical means of effecting reaction 1 was cursory, but our findings may be of value to others engaged in related experiments. When methane- or *p*-bromobenzenesulfonyl azide was refluxed (80°) a few hours in 90 vol % isopropyl alcohol, the related sulfonamide was obtained in >95% yield. A chain mechanism is evidently involved because we found that sulfonyl azides in refluxing isooctane (100°), which is less susceptible to homolysis than is isopropyl alcohol, decomposes only very slowly, with half-lives of 4–5 days. These thermal experiments were conducted before the ability of sulfonyl azides to undergo chain reactions was known. Consequently we took no special precautions to remove the peroxides which may be adventitious in isopropyl alcohol, and our thermal results must be regarded with caution in view of the known ability of peroxides to engage in chain reactions with sulfonyl azides.[11]

Finally we draw attention to the catalytic effect of ferrous chloride–hydrochloric acid mixtures on the reaction of sulfonyl azides with isopropyl alcohol. Strong catalysis was observed for a variety of azides at temperatures from 25 to 75°. The reaction was usually conducted by dropwise addition of ferrous chloride in the aqueous acid to the azide solution. The yellow color characteristic of chloride-complexed ferric iron developed during the reaction, and appropriate control experiments established that the oxidizing agent was the azide, and not adventitious oxygen. The yields of sulfonamide and acetone sometimes approached the theoretical values, and the molar ratio of azide consumed to ferric chloride formed was typically of the order of 20 to 1.

The reaction rates and nitrogen yields were markedly irreproducible, which suggests an impurity-sensitive chain mechanism. Attempts to improve reproducibility by careful purification of the materials were unsuc-

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(23) W. Lwowski and E. Scheiffele, *J. Am. Chem. Soc.*, **87**, 4359 (1965).

(24) W. Lwowski, private communication.

(25) W. Lwowski, R. DeMauriac, T. W. Mattingly, Jr., and E. Schieffele, *Tetrahedron Letters*, 3285 (1964).

cessful. We did, however, exclude the possibility that catalysis is due to peroxidic impurities in the isopropyl alcohol. This finding is important, since alcohols are known to suffer homolysis of their α-C–H bonds in the presence of ferrous salts and hydrogen peroxide.[26]

The ferrous chloride evidently initiates a chain reaction by electron transfer to the azide, possibly to form a radical-anion intermediate. Loss of molecular nitrogen and capture of a solvent proton could then furnish a sulfonylamido radical, a propagating species of the chain. The over-all initiation reaction is shown in eq 16. Catalysis by ferrous chloride has analogy in the

$$RSO_2N_3 + FeCl_2 + HCl \longrightarrow RSO_2\overset{\cdot}{\underset{\cdot\cdot}{N}}H + FeCl_3 + N_2 \quad (16)$$

impurity-sensitive, metal ion catalyzed radical chain reduction of diazonium salts by hypophosphorous acid.[27]

## Experimental Section[28]

Nitrogen (Seaford grade) was freed of oxygen by passage through pyrogallol in aqueous sodium hydroxide[29] or, in kinetic work, by passage through spongy copper heated at *ca.* 350°, and was dried with a mixture of standard drying agents. Unless otherwise stated, isopropyl alcohol was used as received. Where purified solvent was used, the isopropyl alcohol was refluxed overnight with stannous chloride to destory peroxides,[30] then was distilled twice in a nitrogen atmosphere from barium oxide and calcium turnings. It was stored in deoxygenated, sealed ampoules.

**A. Compounds. Methanesulfonyl Azide.** To a stirred solution of methanesulfonyl chloride (Eastman White Label; 56.19 g, 0.491 mol) in anhydrous methanol (270 ml) was slowly added saturated aqueous sodium azide (Fisher "Laboratory Chemical"; 40.10 g, 0.617 mol) in small portions. The reaction was held at room temperature by a water bath. After 90 min the mixture was combined with water (1000 ml) and extracted with ether (USP, four 300-ml portions). The extract was filtered through anhydrous $Na_2SO_4$, and the residue obtained on evaporation of the solvent was solidified in a freezer and recrystallized by dissolving it in 95% ethanol at room temperature and cooling in a chloroform–Dry Ice bath. It was washed with cold water and stored in a desiccator with $P_2O_5$ in a cold, dark room for several weeks. Finally the desiccator was continuously evacuated until the azide began to sublime appreciably (*ca.* 2 days), yield 41.46 g (54.9%), specific gravity (20°) 1.42856. The product was recrystallized to constant mp 18–20° (lit.[31] 18°). The infrared spectrum ($CCl_4$ solution) had bands at 2146 ($N_3$), 1374 and 1177 ($SO_2$), and 1202 cm$^{-1}$. The ultraviolet spectrum (95% ethanol solution) showed a single, broad unsymmetrical maximum (λ 254 mμ (ε 13)), and the nmr spectrum (deuteriochloroform solution) showed a δ 3.34 singlet.

*Anal.* Calcd for $CH_3N_3O_2S$ (121.12): C, 9.92; H, 2.49. Found: C, 10.10; H, 2.42.

Our general procedure for preparation of other azides has been described in detail[32] and differed only in minor respects from that employed for methanesulfonyl azide. In the following summary of data on our azides, melting points are the constant values obtained by repeated recrystallizations from 95% ethanol. Infrared spectra were taken in carbon tetrachloride. Ultraviolet and nmr spectra were obtained in 95% ethanol and deuteriochloroform, respectively. Physical data are listed for the following azides.

***p*-Bromobenzenesulfonyl azide**, mp 54.5–56°, yield, 56%; ir: 2128 ($N_3$), 1395 and 1181 ($SO_2$), and 818 and 752 cm$^{-1}$ (aromatic C–H); uv: λ 240 mμ (ε 1.79 × 10$^4$); nmr: δ 7.78 singlet.

*Anal.* Calcd for $C_6H_4BrN_3O_2S$ (262.11): C, 27.49; H, 1.54. Found: C, 27.57; H, 1.27.

***p*-Methoxybenzenesulfonyl azide**, mp 51.5–52°, yield, 95%; ir: 2114 ($N_3$), 1591, 1365 and 1160 ($SO_2$), 1256 (C–O), and 835 cm$^{-1}$ (aromatic C–H); uv: λ 247 mμ (ε 1.61 × 10$^4$); nmr: δ 3.89 singlet ($CH_3$–O) and 7.1 and 7.8 doublets (aromatic C–H, $J \simeq 9$ Hz).

*Anal.* Calcd for $C_7H_7N_3O_3S$ (213.22): C, 39.43; H, 3.31. Found: C, 39.73; H, 3.30.

**2-Naphthalenesulfonyl azide**, mp 44–44.5° (lit.[32] mp 45°), yield, 51%; ir: 2132 ($N_3$), 1385 and 1182 ($SO_2$), and 1078, 901, and 656 cm$^{-1}$; uv: λ 235 mμ (ε 6.35 × 10$^4$); nmr: δ 7.9 multiplet (6 H) and 8.52 singlet (1 H, α-hydrogen).

***m*-Nitrobenzenesulfonyl azide**, mp 80.5–81°, yield, 92%; ir: 2132 ($N_3$), 1397 and 1355 ($NO_2$ and $SO_2$), 1183 ($SO_2$), and 882, 772, and 732 cm$^{-1}$ (aromatic C–H); uv: λ 248 mμ (ε 7.47 × 10$^3$); nmr: complex absorption between δ 7.75 and 8.75.

*Anal.* Calcd for $C_6H_4N_4O_4S$ (228.20): C, 31.58; H, 1.77. Found: C, 31.80; H, 1.82.

***p*-Nitrobenzenesulfonyl azide**, mp 101.5–102°, yield, 75%; ir: 2137 ($N_3$), 1391 and 1346 ($NO_2$ and $SO_2$), 1175 (SO), and 853 cm$^{-1}$ (aromatic C–H); uv: λ 250 mμ (ε 1.21 × 10$^4$); nmr: δ 8.20 and 8.45 doublets (C–H, $J \simeq 9$ Hz).

*Anal.* Calcd for $C_6H_4N_4O_3S$ (228.20); C, 31.58; H, 1.77. Found: C, 31.60; H, 1.57.

**α-Toluenesulfonyl azide**, mp 53.5–54°, yield, 98%; ir: 2132 ($N_3$) and 1385, 1193, and 1170 cm$^{-1}$ ($SO_2$); uv: λ 269, 263, and 258 mμ (ε 408, 603, and 699, respectively); nmr: δ 4.51 singlet (2 H, $CH_2$) and 7.41 (5 H, aromatic H).

*Anal.* Calcd for $C_7H_7O_2N_3S$ (197.22): C, 42.63; H, 3.58. Found: C, 42.72; H, 3.48.

**Isopropyl Benzohydroxamate (1).** To a mixture of sodium hydroxide (6.15 g, 0.154 mol), dissolved in a little water, and benzohydroxamic acid[33] (20.56 g, 0.148 mol) was added just enough water (*ca.* 65 ml) to obtain solution while the mixture was warmed strongly. This solution was added to isopropyl bromide (63.34 g, 0.515 mol) in absolute ethanol (170 ml), and the mixture refluxed for 5 hr. The viscous residue left on evaporation of the solvent was mixed with water (100 ml) and extracted with chloroform (two 200-ml portions). The extract was dried with anhydrous $MgSO_4$ and was concentrated until the product solidified. Recrystallization from 1:1 ethyl acetate–Skellysolve gave 18.32 g (69%), mp 81.5–85.5°. Further recrystallizations from 3:7 ethyl acetate–benzene gave constant mp 88–89°, unchanged by sublimation. The infrared spectrum ($CH_2Cl_2$ solution) had bands at 3367 (N–H), 2924–2865 (C–H), 1681 (carbonyl), 1460, 1384, 1149, and 1118 cm$^{-1}$. The nmr spectrum ($CCl_4$ solution) had complex multiplets centered at δ 1.2 ($CH_3$) and 7.4 and 7.7 (aromatic H).

*Anal.* Calcd for $C_{10}H_{11}NO_2$ (179.22): C, 67.02; H, 7.31. Found: C, 67.28; H, 7.26.

**O-Isopropylhydroxylamine Hydrochloride (2).** Isopropyl benzohydroxamate (39.16 g, 0.219 mol) in absolute ethanol (320 ml) and concentrated hydrochloric acid (55 ml) was refluxed for 15 min. The bulk of the solvent was removed at reduced pressure with gentle heat. The liquid residue was mixed with ether (700 ml) and extracted with water (two 50-ml portions), and the extract was concentrated with gentle heat. The concentrated aqueous solution was continuously evacuated for 10 hr in a desiccator containing $P_2O_5$. The white platelets left after vigorous effervescence were recrystallized from ethyl acetate, washed with benzene, and dried at 25° *in vacuo* over $P_2O_5$; 15.5 g (63.4%), mp 84.5–91°. Repeated recrystallizations gave material with constant mp 84–88° (sealed capillary). The salt was too hygroscopic to be rigorously characterized and decomposed on attempted sublimation. The infrared spectrum ($CHCl_3$ solution) showed bands at *ca.* 3250, 3050, and 2800–2650 (N–H stretch), 1590 (N–H deformation), and 1540, 110, and 1010 cm$^{-1}$.

**N-Isopropoxy-α-toluenesulfonamide (3).** O-Isopropylhydroxylamine hydrochloride (11.77 g, 0.105 mol) in a flask with a KOH drying tube was dissolved in dry pyridine (250 ml). α-Toluene-

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(26) J. H. Merz and W. A. Waters, *J. Chem. Soc.*, S15 (1949).

(27) N. Kornblum, G. D. Cooper, and J. E. Taylor, *J. Am. Chem. Soc.*, 72, 3031 (1950).

(28) Melting points were taken with total immersion thermometers calibrated against a set from the National Bureau of Standards. Infrared spectra, calibrated with polystyrene, were recorded on a Perkin-Elmer Model 21 or Model 137 spectrophotometer, each equipped with sodium chloride optics, or on a Perkin-Elmer Model 337 grating spectrophotometer. A Cary Model 14 or Beckman Model DU spectrophotometer was used for quantitative visible and ultraviolet spectral measurements. Nmr spectra were obtained on a Varian A-60 spectrophotometer with tetramethylsilane as an internal standard. Solvents and chemicals were reagent grade unless stated otherwise.

(29) A. I. Vogel, "Practical Organic Chemistry," 3rd ed, John Wiley and Sons, Inc., New York, N. Y., 1956, p 186.

(30) (a) Reference 29, p 886; (b) A. R. Burgess, C. F. Cullis, and E. J. Newitt, *J. Chem. Soc.*, 1844 (1960).

(31) L. Horner and A. Christman, *Chem. Ber.*, **96**, 338 (1963).

(32) T. Curtius, *J. Prakt. Chem.*, **125**, 303 (1930).

(33) C. R. Hauser and W. B. Renfrow, Jr., in ref 5, p 67.

sulfonyl chloride (19.03 g, 0.100 mol) was added, and the mixture was stirred for 2 hr at 0°, then for 20 hr at room temperature. The mixture was greatly concentrated with gentle warmth at reduced pressure, then mixed with water (200 ml). An orange oil was deposited, and the mixture was extracted with ether (five 100-ml portions). The extract was dried with anhydrous $Na_2SO_4$, and evaporation of the solvent gave the product. Recrystallization from 1:2 water–95% ethanol yielded 15.1 g (77%), mp 84–86°. Repeated recrystallizations from water–ethanol, then from carbon tetrachloride, gave white crystals with constant mp 84.5–85°, raised by sublimation to 85–85.5°. The infrared spectrum ($CH_2Cl_2$ solution) had bands at 3300 (N–H), 2933 (C–H), 1377 and 1166 ($SO_2$), and 1399 cm$^{-1}$. The nmr spectrum ($CCl_4$ solution) showed a $\delta$ 1.22 doublet ($CH_3$), a 4.24 singlet (aromatic H), and a weak 6.72 singlet.

*Anal.* Calcd for $C_{10}H_{15}NO_3S$ (229.31): C, 52.38; H, 6.59. Found: C, 52.47; H, 6.43.

**B. Photolytic Apparatus and Technique.**[34] Azides were photolyzed with magnetic stirring in an air-tight vessel consisting of vertical Vycor outer tube (3.2 × 30 cm). The temperature was held at *ca.* 20° by circulation of water through a concentric Pyrex inner tube extending nearly to the bottom of the outer one. Before an experiment the contents were degassed by passage of nitrogen through a sintered disk at the bottom of the inner tube. The gas was vented through a one-way valve consisting of a few millimeters of mercury layered over a sintered glass disk. To protect the photolyte from mercury vapor, the gas was passed through 5 ml of water before being led to the mercury valve.

For collection of the gas produced by the photolysis, the vessel was connected to a water-jacketed buret by means of a stopcock located between the valve and the buret. The solution was then irradiated with a Hanovia 30600 high-pressure mercury arc. The light was unfiltered in the direct photolyses, but a uranium glass filter and a Hanovia No. 16223 filter were employed in the sensitized reaction to remove all light of wavelengths below approximately 345 m$\mu$.

After recrystallization to constant melting point, the identity of each sulfonamide produced, and of benzophenone recovered from sensitized reactions, was established by the undepressed melting point of admixtures with authentic samples. The acetone produced in photolyses in isopropyl alcohol was similarly identified as its 2,4-dinitrophenylhydrazone (DNP). Infrared spectra of products were identical with those of authentic samples.

**Benzophenone-Sensitized Photolysis of Methanesulfonyl Azide in Isopropyl Alcohol.** The procedure used for methanesulfonyl azide was typical and was essentially the same as for the other azides. Methanesulfonyl azide (0.5648 g, 0.0046 mol) and benzophenone (1.346 g, 0.00748 mol) in isopropyl alcohol (42 ml, purified as described) were irradiated until the yield of nitrogen was 99.5% (90 min).

The work-up procedure was designed for quantitative isolation of the acetone produced and of the benzophenone. The contents of the irradiation vessel and the water trap were rinsed with water (15 ml) into a distillation apparatus whose receiver was chilled in chloroform-Dry Ice. The mixture was distilled until the temperature reached 84°. Isopropyl alcohol (20 ml) was added to the cooled residue, and the mixture was distilled again until the temperature reached 84°. The latter procedure was repeated and the distillate was washed with water (10 ml) into 2,4-dinitrophenylhydrazine solution prepared from 2.3 g (0.012 mol) of the reagent.[35a] The mixture stood overnight at room temperature and, after being chilled in a freezer, a first crop was collected and washed with water (100 ml). Cooling (*ca.* 0°) of the filtrate from the first crop, combined with the washings, gave a second crop. The crops were dried with warmth *in vacuo* to constant weights 1.0788 g (mp 123.5–125°) and 0.0794 g (mp 120.5–122°); total yield of acetone–DNP, 104%. Several recrystallizations from 95% ethanol gave constant mp 124.5–125° (lit.[35b] mp 126°).

The distillation residue was mixed with water (7 ml) and extracted with ether (five 20-ml portions). The combined extracts were dried with anhydrous $Na_2SO_4$ and evaporated to give benzophenone, 1.310 g (96%), mp 46–48° (lit.[7b] mp 45–48°). Evaporation of the layer that had been extracted left methanesulfonamide, 0.2458 g (81%), mp 88.5–91°, recrystallized from 1:1 absolute ethanol-benzene to constant mp 90.5–91.5° (lit.[36] mp 89–91°).

Methanesulfonamide was quantitatively isolated in another experiment in which methanesulfonyl azide (0.5678 g, 0.00468 mol) and benzophenone (1.3485 g, 0.00740 mol) were irradiated in purified isopropyl alcohol (42 ml). The residue from the evaporated reaction mixture was taken up in carbon tetrachloride (10 ml) and the solution was extracted with water (four 5-ml portions). The white crystals left by evaporation of the combined extracts were dried with warmth *in vacuo* to constant weight 0.4592 g and then triturated with hexane to remove any benzophenone. This left 0.4422 g of methanesulfonamide, mp 89.5–90.5°. An ultraviolet spectrum of the product revealed that it was still contaminated by 0.7 mole % benzophenone. The yield of methanesulfonamide, corrected for benzophenone content, was 98.2%.

Control experiments with artificial mixtures of benzophenone, methanesulfonamide, and acetone in isopropyl alcohol showed our isolation procedures to be quantitative with respect to all three components. Results of other sensitized photolyses are presented in Table I.

**Direct Photolysis of Methanesulfonyl Azide in Isopropyl Alcohol.** The procedure was typical of those for other photolyses, both in anhydrous and in aqueous isopropyl alcohol. The gas collection apparatus was not used in this experiment, but the gas outlet on the reaction vessel was connected to a series of two cold traps immersed in chloroform–Dry Ice.

Methanesulfonyl azide (1.503 g, 0.0124 mol) in isopropyl alcohol (45 ml) and water (5 ml) was irradiated until gas evolution subsided (80 min). A slow stream of nitrogen was maintained through the solution throughout the reaction. The contents of the reaction vessel and cold traps were washed with 95% ethanol into a distillation apparatus whose receiver was chilled in chloroform–Dry Ice. The acetone was quantitatively distilled and converted to its DNP essentially by the method described above. Two crops of acetone–DNP were obtained and dried to constant weights 2.631 g (mp 124.5–125.5°) and 0.327 g (mp 121.5–123°) (100% total). Evaporation of the distillation residue left methanesulfonamide (1.177 g, 99.8%), mp 89–90.5°. An experiment with an artificial mixture of methanesulfonamide and acetone in isopropyl alcohol showed the isolation technique to be quantitative.

Typical results of other direct photolyses of sulfonyl azides in isopropyl alcohol are summarized below. In each case acetone was identified as a product as its DNP, but quantitative isolation of the acetone was, in general, not attempted.

***p*-Bromobenzenesulfonyl azide** in the presence of 10 vol % water gave *p*-bromobenzenesulfonamide, mp 161–164.5°, in 97% yield. Recrystallization from 1:1 95% ethanol–water, then from 3:7 hexane–ethyl acetate gave mp 166.5–167.5° (lit.[35c] mp 166°).

**Methanesulfonyl azide** in the absence of water gave methanesulfonamide, mp 89.5–90.5° in 99% yield.

***p*-Methoxybenzenesulfonyl azide** in 4 vol % water gave *p*-methoxybenzenesulfonamide, mp 110–111°, in 100% yield (lit.[37] mp 110°). The photolysis of 27% water gave a wine-colored solution whose evaporation left white needles inextricably mixed with red tar. The mixture dissolved in chloroform and had an infrared spectrum that was nearly superposable on that of *p*-methoxybenzenesulfonamide. Photolysis in anhydrous isopropyl alcohol gave the sulfonamide in 94% yield, mp 104–107°.

**2-Naphthalenesulfonyl azide** in 10 vol % water gave a 93% yield of 2-naphthalenesulfonamide, mp 213.5–215°. Several recrystallizations from absolute ethanol gave constant mp 216–217° (lit.[35c] mp 217°).

**$\alpha$-Toluenesulfonyl azide** in 10 vol % water gave a 100% yield of $\alpha$-toluenesulfonamide, mp 100–102.5°, recrystallized from 1:1 hexane–ethyl acetate to constant mp 103–103.5° (lit.[35c] mp 105°).

**Effect of Added Acetone on the Photolysis of Methanesulfonyl Azide in Isopropyl Alcohol.** Several runs were conducted, and the one described is typical. Methanesulfonyl azide (0.432 g, 0.0036 mol) in purified isopropyl alcohol (50 ml) was irradiated at 25.0 ± 0.1° until gas evolution subsided (15 min). The induction period was *ca.* 6 min and the half-life was 10.4 min. This run was immediately followed by another which was identical with the first except that acetone (1.27 g, 0.022 mol) was added to the solution along with the azide (0.410 g, 0.0034 mol). There was no induction period, and the half-life was 1.0 min, yield of nitrogen, 103%.

**Irradiation of N-Isopropoxy-$\alpha$-toluenesulfonamide.** A nitrogen-swept solution of N-isopoxy-$\alpha$-toluenesulfonamide (1.341 g, 0.0059

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[34] Several slight modifications were used at different stages. For details, see ref 1a.

[35] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956: (a) p 241; (b) p 227; (c) p 327.

[36] L. Field and F. A. Grunwald, *J. Am. Chem. Soc.*, **75**, 934 (1953).

[37] M. H. Carr and H. P. Brown, *ibid.*, **69**, 1170 (1947).

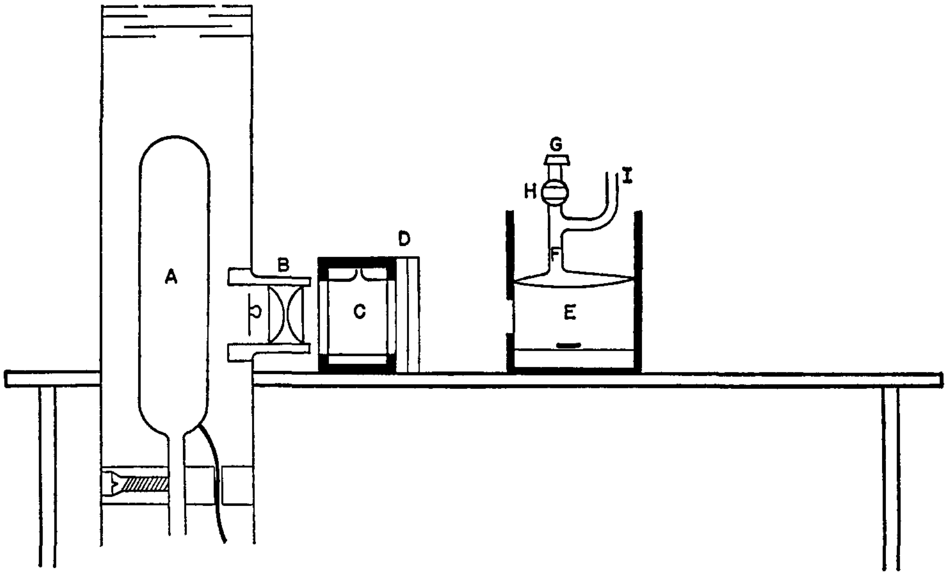

Figure 3. Kinetics apparatus: A, lamp; B, lenses; C, filter solution cell; D, glass filters; E, photolysis cell; F, filling tube; G, rubber septum; H, stopcock; I, side arm to gas buret.

mol) in isopropyl alcohol (45 ml) and water (5 ml) was irradiated for 90 min at *ca.* 20° (50% longer than necessary to effect complete reaction of α-toluenesulfonyl azide under similar conditions). Evaporation of the solvent left material (1.285 g, 96%), mp 83–83.5°, whose infrared spectrum was identical with that of the unirradiated isopropoxysulfonamide. Recrystallization from carbon tetrachloride gave constant mp 84.5–85°, not depressed by mixture with pure N-isopropoxy-α-toluenesulfonamide.

C. **Rate and Quantum Yield Studies.** These were conducted in a dark room illuminated with red light because of the sensitivity of the actinometer solution[8] and of sulfonyl azides in the presence of benzophenone to daylight. Photolysis lamps were operated through a Sola 23-22-125 constant-voltage transformer.

**Kinetics Apparatus for Sensitized Photolysis.** The apparatus (Figure 3) was a 13 × 30 cm optical table with an Osram mercury arc, type Hg, mounted in a ventilated cylindrical housing at one end. After passage through quartz lenses to decrease its divergence, the beam was directed through a filter solution (10% copper sulfate pentahydrate in 0.01 *N* aqueous sulfuric acid) in a cell with quartz windows of 2.0-cm optical depth, then through a pair of Corning glass filters (No. CS-1-69 and CS-7-37) to isolate the 365- and 366-mμ lines.[8d] The beam entered a Pyrex 2.5 × 4 cm cylindrical photolysis cell through an aperture (1.34 cm diameter) in its window. The cell was equipped with a micromagnetic stirrer, and the cell's upper wall ballooned outward, providing a sizable interface between its contents and the overlying gas space. A filling tube at the cell top had a side arm leading to the gas collection apparatus described earlier. The filling tube was capped by a rubber septum, just below which was located a high-vacuum stopcock. The photolysis cell was mounted in a brass box through which water thermostated at 24.0 ± 0.1° was circulated. The box was held in a track milled in the surface of the table, and could be reproducibly located at any desired distance from the lamp.

**Kinetic Procedure.** The following method was used unless stated otherwise. A solution of methanesulfonyl azide and benzophenone in purified isopropyl alcohol was deoxygenated on a vacuum train by at least four cycles of being frozen in liquid nitrogen, highly evacuated, and gradually thawed. Then nitrogen was admitted, and the solution was magnetically stirred to ensure homogeneity and saturation with nitrogen. The photolysis cell was purged with nitrogen *via* a hypodermic needle inserted through the septum. A gas-tight syringe with a Chaney adaptor was used to transfer the azide solution (17.99 ± 0.02 ml) from the vacuum train to the photolysis cell. The stopcock below the septum was closed and, after equilibration, the lamp shutter was opened and the gas volumetric reaction rate was recorded.

**Rate Dependence on the Azide Concentration.** The benzophenone concentration was 0.162 *M* in all seven runs and the initial azide concentration ranged from 0.019 to 0.19 *M*. Solutions with initial azide molarities >0.088 were treated by the procedure just described. Solutions with initial molarities up to 0.093 were photolyzed in the reaction vessel described in part B. When the latter apparatus was used in kinetic work, water thermostated at 24.0 ± 0.1° was circulated through the inner tube. The yield of nitrogen after nine half-lives averaged 99.7 ±0.8%, and *ca.* 50 readings were taken in the first three half-lives. Because the light intensity was not the same in all runs, the apparent first-order rate constants varied from 0.94 to 1.95 $\sec^{-1}$.

**Half-Life Dependence on Light Intensity.** The procedure used for actinometry has been described in detail.[8] The actinometer solution, $6.00 \times 10^{-3}$ *M* ferrioxalate ion in 0.1 *N* aqueous sulfuric acid, was prepared just before use by dilution of measured amounts of acid and standard ferric ammonium sulfate and potassium oxalate solutions.

Each run consisted of three immediately successive irradiations, all in the same photolysis cell positioned at the same distance from the lamp. In the first and third irradiations actinometer solution (20.00 ml) was exposed long enough to effect *ca.* 2% reaction. In the second, 17.99 ml of a stock solution of 0.0894 *M* methanesulfonyl azide and 0.0167 *M* benzophenone in isopropyl alcohol was irradiated until the nitrogen yield was 50%. Ferrous ion in the exposed actinometer solutions was assayed spectrophotometrically as its *o*-phenanthroline complex.[8b] Each intensity recorded in Table II is the average of values found before and after the azide photolysis. The two intensity values usually agreed with each other within 5%. We varied the intensity from run to run by changing the irradiation distance.

**Half-Life Dependence on the Benzophenone Concentration.** In each run two isopropyl alcohol solutions (A and B) with accurately known concentrations of benzophenone (0.04 *M* in solution A; 0.2 *M* in solution B) and methanesulfonyl azide (0.09 *M* in both solutions) were photolyzed until the yield of nitrogen was 50%. The photolyses were conducted in immediate succession in the same cell at the same distance from the lamp. The results appeared to be independent of whether solution A or B was photolyzed first. Typical data are given in Table III. The experiments were not accompanied by actinometry, and the approximate intensities were estimated from the dependence of intensity on irradiation distance observed in the quantum yield experiments.

**Quantum Yield of Direct Photolysis.** The quantum yield of the direct photolysis of methanesulfonyl azide in anhydrous isopropyl alcohol was measured at 22.0° with an apparatus and procedure that differed importantly from those used for the sensitized photolysis only in the following respects. Experiments were conducted with 253.7-mμ light isolated from an Osram mercury lamp, type Hgs, by passage through a 4.0-cm layer of solution of nickelous sulfate hexahydrate (300 g) and cobaltous sulfate hexahydrate (56 g) diluted to 1 l. with water.[8b,38] Most of the oxygen was removed from the azide solution before photolysis by passage of nitrogen

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[38] M. Kasha, *J. Opt. Soc. Am.*, 38, 929 (1948).

under its surface. The photolysis cell had a quartz window. The quantum yields given in Table IV were calculated from the instantaneous rate of the azide photolysis at 20% completion. Because of adventitious oxygen, quantum yields calculated from initial rates are of little quantitative significance.

**Table IV.** Quantum Yield (Φ) at 20% Completion in Direct Photolysis of Methanesulfonyl Azide in Isopropyl Alcohol

| Intensity × $10^6$, einstein $l.^{-1}$ $sec^{-1}$ | $[CH_3SO_2N_3]_0$, *M* | Φ, moles $einstein^{-1}$ |
|---|---|---|
| 1.05 | 0.083 | 111 |
| 1.08 | 0.088 | 124 |
| 1.21 | 0.082 | 126 |
| 0.85 | 0.092 | 153 |

**D. Thermolysis of *p*-Bromobenzenesulfonyl Azide in Aqueous Isopropyl Alcohol.** The results obtained with *p*-bromobenzenesulfonyl azide were similar to those with other azides. The azide (0.715 g, 0.0028 mol) in isopropyl alcohol (72 ml) and water (8 ml) in a foil-wrapped flask was degassed by passage of nitrogen under its surface and refluxed (78°) with stirring until infrared spectra of aliquot residues showed no unchanged azide (5 hr). Evaporation left *p*-bromobenzenesulfonamide, 0.615 g (98%, corrected for aliquot removal), mp 165.5–166.5°. Repeated recrystallizations from 1:1 95% ethanol-water gave constant mp 166–167.5°, not depressed by mixture with authentic *p*-bromobenzenesulfonamide.

**E. Ferrous Chloride Induced Reaction of α-Toluenesulfonyl Azide with Isopropyl Alcohol.** To preclude interference from peroxides, freshly purified isopropyl alcohol was distilled (in a system gently swept with nitrogen) from anhydrous stannous chloride into a fraction cutter, from which 60 ml of the alcohol was measured into a nitrogen-purged flask separated from the atmosphere by a mercury trap. The flask was equipped with a reflux condenser and a dropping funnel containing a nitrogen-washed aqueous solution of 0.33 *M* ferrous chloride[39] in 2.4 *M* hydrochloric acid. A Teflon bucket containing α-toluenesulfonyl azide (0.736 g, 0.00373 mol) was suspended in the condenser. The stirred alcohol was heated to 75°, and the azide was dropped into the liquid; it dissolved with no sign of reaction. Addition of ferrous chloride solution (0.75 ml, $5 \times 10^{-4}$ mol) caused vigorous nitrogen evolution lasting *ca.* 1 min. The cooled reaction mixture was diluted with water to 100 ml, and a portion (40 ml) was combined with 2,4-dinitrophenylhydrazine solution prepared from 1.2 g (0.006 mol) of the reagent. The mixture stood overnight and was chilled, and acetone–DNP (0.426 g; 98% corrected) was collected. Recrystallization from 95% ethanol gave constant mp 125–126°, not depressed by mixture with an authentic sample.

Evaporation of the remaining portion of the reaction mixture left a solid which was triturated and centrifuged with warm aqueous 5% NaOH (4 ml, then five 2-ml portions) to precipitate the iron. The combined supernatants, after being acidified with concentrated hydrochloric acid and chilled, gave α-toluenesulfonamide, which was washed with a little ice water, 0.253 g (78%, corrected), mp 103.5–104°, unchanged by recrystallization from 2:3 Skellysolve–ethyl acetate, and not depressed by mixture with an authentic sample.

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[39] K. H. Gayer and L. Woontner in "Inorganic Syntheses," Vol. V, T. Moeller, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1957, p 179.

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# The Kinetics of the Photochemically Initiated Condensation Reaction between Tetrachloroethylene and *n*-Pentane[1a]

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**Abstract:** The kinetics of the photochemically initiated radical chain condensation reaction between tetrachloroethylene and *n*-pentane, resulting in the formation of pentyltrichloroethylene and HCl have been studied at 25°. The absolute rate constant for the rate-determining step, the addition of pentyl radicals to tetrachloroethylene, is estimated as $6.6 \times 10^2$ $M^{-1}$ $sec^{-1}$, by combining rate constant ratios from kinetics with alkyl radical combination data.

The addition of alkyl radicals to substituted olefins is known to be affected both sterically and by polar effects. Szwarc, *et al.*,[1b] have found that in the case of addition of methyl radicals to ethylene, the substitution of all hydrogen by fluorine atoms resulted in a tenfold increase in the rate of addition. This enhanced rate of addition was attributed by the authors to the fact that electron-withdrawing substituents weaken the repulsion between the negative cloud of π electrons of the olefin and of the p electrons of the attacking radical thus lowering the activation energy of the addition reaction. However, in the case of methyl radical addition to tetrachloroethylene the rate of addition was found to only $^1/_{90}$ of that observed in the case of ethylene. The pronounced lack of reactivity of tetrachloroethylene toward methyl radical addition was attributed to steric hindrance, the bulky chlorine obstructing the approach of the alkyl radical.

The facts that no polymerization of tetrachloroethylene was observed under free radical initiation[2] and that very limited copolymerization with other monomers was obtained[3] seem to support Szwarc's finding that the process of addition of alkyl radical to tetrachloroethylene proceeds very sluggishly.

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[1] (a) This paper is based upon a dissertation to be submitted by A. Horowitz in partial fulfillment of the requirement for the Ph.D. degree in chemistry, at the Hebrew University, Jerusalem; (b) R. P. Buckley and M. Szwarc, *J. Am. Chem. Soc.*, **78**, 5696 (1956).

[2] K. W. Doak, *ibid.*, 70, 1525 (1948).

[3] A. Turner and S. Grenberg, *J. Polymer Sci.*, **3**, 237 (1948).