Some Decomposition Reactions of Acid Azides

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In the decomposition of benzenesulfonyl azides, the nitrene intermediate reacts with nitro substituents in the *ortho* position of the azide or in nitrobenzene solvent to produce tars and nitric oxide. The decomposition of benzenesulfonyl azides shows only small medium and substituent effects and no sensitivity to radical inhibitors. The reaction of benzoyl azides with triphenylphosphine in benzene to give the phosphine-imines and nitrogen is a *second-order* reaction with $\rho = +0.78$. A charge-transfer model is proposed for the transition state. The reaction of benzenesulfonyl azide with triphenylphosphine in *benzene* is a *first-order* decomposition of the 1:1 complex into the phosphine-imine and nitrogen. The reaction of benzenesulfonyl azide and triphenylphosphine in chloroform gives different products and consumes several moles of triphenylphosphine per mole of azide.

In the decomposition of azides the simple expulsion of nitrogen to form an intermediate nitrene must compete with various concerted processes. The occurrence of such processes can ordinarily be detected by the increase in reaction rate. Thus the decomposition of acyl azides, with simultaneous migration of the aryl or alkyl group from carbon to nitrogen, is several orders of magnitude faster than the decomposition of benzenesulfonyl azides. Other examples of induced decomposition of azides are the reaction of benzenesulfonyl azide with thiyl radicals in thiols,[1] with free radicals from decomposing *t*-butyl hydroperoxide,[2] and the reaction of all classes of azides (except ionic ones) with triphenylphosphine.[3]

In this paper we report on a search for azide decomposition induced by *ortho*-substituents and an investigation of the kinetics and mechanism of the reaction of triphenylphosphine with acid azides.

The Effect of Substituents on the Decomposition of Acid Azides.—The decomposition of *o*-substituted *benzoyl azides* has been studied for many substituents other than iodo by Yukawa and Tsuno.[4] We find that the rate of decomposition of *o*-iodobenzoyl azide in toluene at 42.2° is precisely first order with $k_1 = 23.2 \times 10^{-3}$ min.$^{-1}$. This is not appreciably different from the rate of other *o*-substituted azides at that temperature. The product is the usual isocyanate.[5]

The effects of various media, catalysts, inhibitors, and substituents on the decomposition of *benzenesulfonyl azide* are shown in Tables I and II. The rate of this reaction is first order and the rate constant is independent of moderate changes in initial concentration. The rate constant is also insensitive to changes in solvent, and is not appreciably affected by several radical chain inhibitors. Substituents, including *o*-iodo, also have very little effect on the rate constant.[6] There is probably some interaction between the nitrene and the iodo substituent in the steps immediately following the rate-determining step, since the products in mixed xylene consist of large amounts of an insoluble black

TABLE I

EFFECT OF POTENTIAL CATALYSTS, INHIBITORS, AND DIFFERENT MEDIA ON THE DECOMPOSITION OF BENZENESULFONYL AZIDE AT 126.8°[a]

Solvent	C_0, moles/l.	Remarks	$k_1 \times 10^3$ min.$^{-1}$
p-Xylene	0.046		1.47
	.067		1.45
	.045	Pre-saturated with O_2	1.41[b]
	.050	Quinone, 0.05 *M*	1.53
	.050	Hydroquinone, 0.05 *M*	1.46
Chlorobenzene	.050		1.51
	.050		1.48
	.028		1.48
	.066	[By the $(C_6H_5)_3P$ method]	1.49
	.050	Diphenyl disulfide, 0.025 *M*	1.51
	.050	Benzothiazoyl disulfide, 0.03 *M*	1.40
	.050	Stilbene, 0.05 *M*	1.51
	.050	Iodine, 0.01 *M*	1.48
Nitrobenzene		In nitrobenzene excess gas (NO) is evolved; k_1 increases slightly during the first 10% of the reaction, then becomes constant	
	.051	V_∞ 157%	1.58
	.043	V_∞ 154%	1.48
	.046	V_∞ 156%, iodine, 0.02 *M*	1.48

[a] By nitrogen or total gas evolution, unless otherwise noted. [b] For the first 25% of the reaction the kinetics was more nearly zero than first order. See ref. 2 for effect of hydroperoxides.

TABLE II

SUBSTITUENT EFFECTS IN THE DECOMPOSITION OF BENZENESULFONYL AZIDES AT 126.8°[a]

Substituent	Solvent	C_0, moles/l.	Remarks	$k_1 \times 10^3$ min.$^{-1}$
o-I	Mixed xylene	0.05		1.24
p-CH_3	Mixed xylene	.07		1.43
o-CH_3	Chlorobenzene	.047		1.19
o-I	Mixed xylene with 9% nitrobenzene	.047	V_∞ 100.2%	1.22
o-NO_2[b]	*p*-Xylene	.045	V_∞ 148%	2.40
	p-Xylene	.045	V_∞ 153%, 0.045 *M* I_2	2.15
	Chlorobenzene	.030	V_∞ 159%	2.38
	Chlorobenzene	.076	By $(C_6H_5)_3P$ method	1.43

[a] By total gas evolution unless otherwise noted. [b] The first-order rate constants for the evolution of N_2 + NO are greater than the first-order rate constant for the disappearance of the azide.

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(1) M. Takebayashi and T. Shingaki, private communication.

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

(3) (a) H. Staudinger and E. Hauser, *Helv. Chim. Acta*, **4**, 861 (1921); (b) H. Staudinger and J. Meyer, *ibid.*, **2**, 635 (1919); (c) L. Horner and A. Gross, *Ann.*, **591**, 117 (1955); (d) Diphenyliodonium azide is too ionic to give the triphenylphosphine reaction. On heating alone in solution it gives phenyl azide and iodobenzene. U. Honsberg, this laboratory.

(4) (a) Y. Yukawa and Y. Tsuno, *J. Am. Chem. Soc.*, **79**, 5530 (1957); (b) **80**, 6346 (1958); (c) **81**, 2007 (1959).

(5) J. E. Leffler and A. F. Wilson, *J. Org. Chem.*, **25**, 424 (1960).

(6) (a) This is in contrast to the effect of *o*-iodo substituents on the decomposition of benzoyl peroxides. J. E. Leffler, R. D. Faulkner, and C. C. Petropoulos, *J. Am. Chem. Soc.*, **80**, 5435 (1958); (b) W. Honsberg and J. E. Leffler, *J. Org. Chem.*, **26**, 733 (1961); (c) J. C. Martin and E. H. Drew, *J. Am. Chem. Soc.*, **83**, 1232 (1961).

solid[7] and only 0.26 mole of *o*-iodobenzenesulfonamide and traces of the sulfonxylidides.

The decomposition of benzenesulfonazide in the presence of nitro groups leads to the production of about 0.5 to 0.6 mole of nitric oxide as well as the usual 1.0 mole of nitrogen. The nitro group may either be attached to the azide in the *ortho* position or it may be part of the solvent nitrobenzene.[8a,b]

Benzenesulfonazide in Nitrobenzene.—The production of excess gas (nitric oxide) by attack of the nitrene on nitrobenzene is not inhibited by 0.02 *M* iodine, but it can be prevented entirely if the nitrobenzene is extensively diluted (1:10) with xylene. The first order rate constants calculated from the rate of total gas evolution (N_2 + NO) are constant within a few percent and are not very different from those calculated from nitrogen evolution rates in the other solvents. Total gas evolution will give the correct first order rate constant for the initial step of the azide decomposition if the partition of nitrene between reaction leading to NO and reaction not leading to NO is constant during the run. The products of the reaction of the nitrene with nitrobenzene are tars.[8a]

***o*-Nitrobenzenesulfonyl Azide.**—The amount of excess gas (NO) produced by the decomposition of *o*-nitrobenzenesulfonyl azide is the same in *p*-xylene solution as it is in chlorobenzene, even though the decomposition of *benzenesulfonyl* azide in nitrobenzene diluted with xylene produces no excess gas. The reaction leading to nitric oxide is therefore an intramolecular rather than an intermolecular one. Iodine at a concentration of 0.045 *M* also has no effect on the gas yield.

The other products of the reaction in *p*-xylene are major amounts of a black solid insoluble in organic solvents but slightly soluble in alkali, and only a 33% yield of *o*-nitrobenzenesulfonyl-*p*-xylidide. The total yield of the normal products (exclusive of the black solid) is somewhat less than the amount of nitrene not diverted into the NO-producing reaction as estimated from the yield of NO.

Although the total gas evolution from the decomposition of *o*-nitrobenzenesulfonyl azide appears to be very nearly first order, the gasometric rate constants do not represent the true rate of decomposition of this azide. The rate of azide decomposition as determined by the triphenylphosphine method is considerably lower and about the same as that for the other benzenesulfonyl azides. It appears, therefore, that there is no direct reaction between the *o*-nitro and sulfonazide groups *during the rate-determining* step. Fig. 1 and Fig. 2 show first-order plots for total gas evolution and for azide disappearance by the triphenylphosphine method, respectively. The lack of interaction between the *o*-nitro and sulfonazide groups during the rate-determining step is in contrast to the behavior of *o*-nitrophenyl azide.[8c] That compound apparently gives benzfurazane oxide and nitrogen in the rate-determining step.

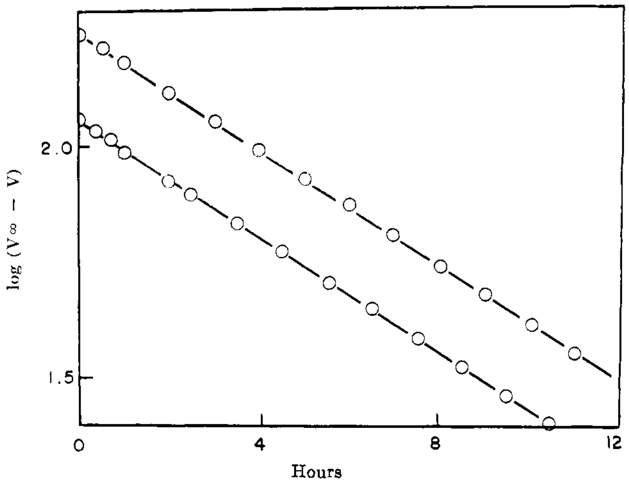

Fig. 1.—*o*-Nitrobenzenesulfonyl azide, total gas at 126.7°: upper, .05 *M*, *p*-xylene; lower, .032 *M*, in mixed xylene.

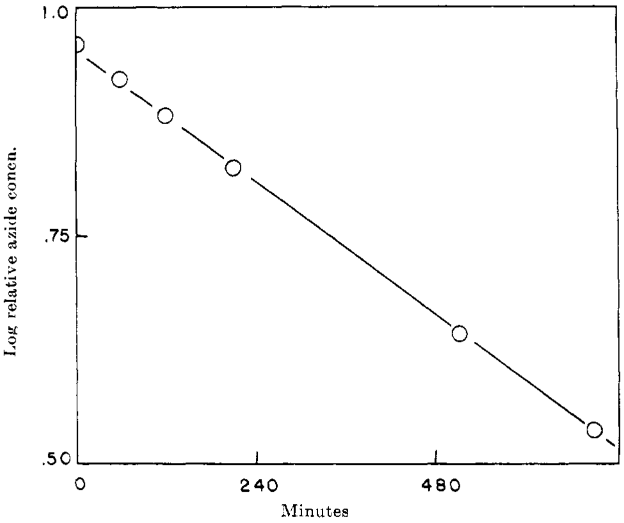

Fig. 2.—*o*-Nitrobenzenesulfonyl azide decomposition in chlorobenzene at 126.7° followed by the triphenylphosphine method.

The Reaction of Acid Azides with Triphenylphosphine.—The mechanism of the triphenylphosphine–azide reaction[3] has been investigated kinetically only for trityl and 9-phenylfluorenyl azides.[9] The carbonium ion mechanism suggested for those azides is obviously a special one and unlikely to apply to other classes of azides.

Benzazides.—The reaction of *meta* and *para* substituted benzazides with triphenylphosphine gives nitrogen and the corresponding phosphine-imine quantitatively and directly. No intermediate complex is isolable nor is there any indication of the existence of such a complex from the reaction kinetics, which remain cleanly second-order for all of the benzoyl azides investigated. There is also no sign of the marked acid catalysis and the heterogeneous reaction observed in the case of the trityl azide reaction.[9] Only a moderate acceleration is produced by a change to a more polar solvent. The rate constants are given in Table III.

Fig. 3 illustrates the fit to a second-order rate expression within a run and the insensitivity of the second-order rate constant to changes in the initial concentration is shown in the table.

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[7] An experiment with a model compound suggests that any product resulting from bonding of the nitrene to the adjacent iodine atom probably decomposes at the temperature of the azide decomposition experiment.

[8] (a) O. C. Dermer and M. T. Edmison, *J. Am. Chem. Soc.*, **77**, 70 (1955); (b) J. F. Heacock and M. T. Edmison, *ibid.*, **82**, 3460 (1960); (c) E. A. Birkhimer, B. Norup, and T. A. Bak, *Acta Chem. Scand.*, **14**, 1894 (1960).

[9] J. E. Leffler, U. Honsberg, Y. Tsuno, and I. Forsblad, *J. Org. Chem.*, **26**, 4810 (1961).

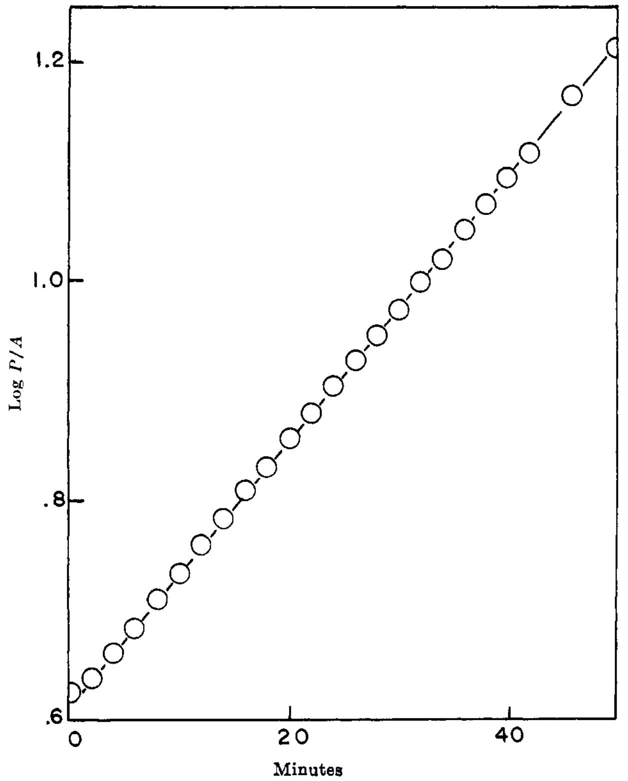


Fig. 3.—$C_6H_5CON_3$ (0.047 *M*) with $(C_6H_5)_3P$ (0.189 *M*) in benzene at 25.0°.

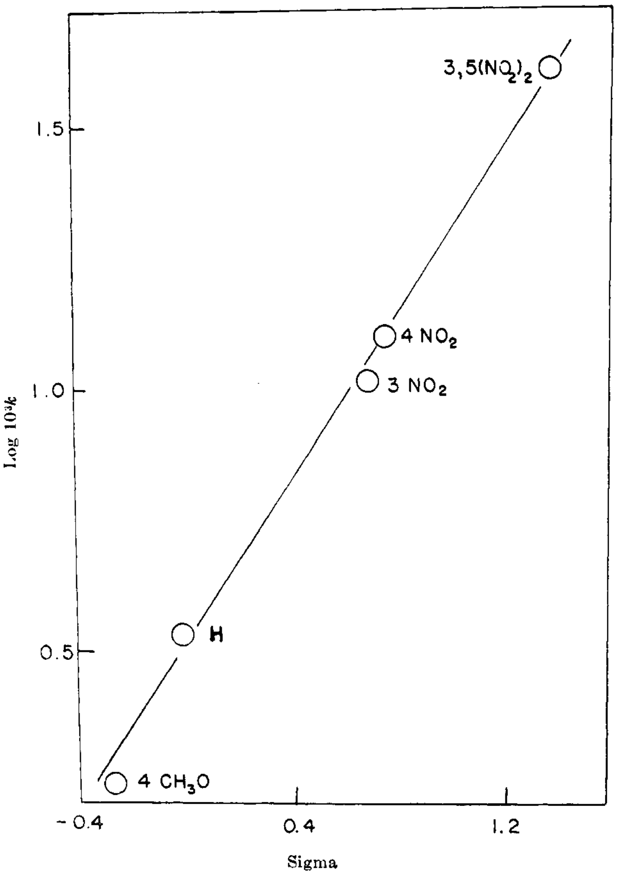


Fig. 4.—Benzoyl azides with $(C_6H_5)_3P$ in benzene at 25°.

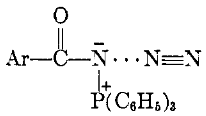
The effect of substituents in the *meta* and *para* positions is correlated by the Hammett ρ–σ relationship with a ρ value of +0.78, as shown in Fig. 4. It would be difficult to explain this value of ρ on the basis of transition state structures such as I, even though such structures place a negative charge in the required position.

TABLE III

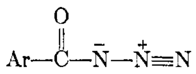
REACTION OF SUBSTITUTED BENZAZIDES WITH TRIPHENYLPHOSPHINE AT 25.00°[a]

Substituent	Initial concn., moles/l. Azide	Initial concn., moles/l. Ph_3P	$k \times 10^2$, l./mole sec.
H	0.0491	0.0491	0.33
	.0488	.0494	.345
	.0470	.186	.34
	.0487	.0970	.31
	.0472	.189	.33
	.0238	.190	.29
	.0983	.0493	.33
p-CH_3O	.0493	.0494	.167
	.0485	.146	.170
	.0454	.364	.171
p-NO_2	.0467	.0490	1.23
	.0450	.0970	1.20
	.0459	.144	1.20
m-NO_2	.0481	.0490	0.97
	.0479	.147	1.02
3,5-$(NO_2)_2$	.0330	.0330	4.04
	.0488	.0487	3.96
H[b]	.0487	.0970	0.68[b]
H[c]	.0487	.0971	.41[c]
p-CHO_3[c]	.0492	.0492	.27[c]

[a] In benzene unless otherwise noted. The rates were determined by nitrogen evolution. [b] In chloroform. [c] In acetic acid–benzene, 1:9 by volume.

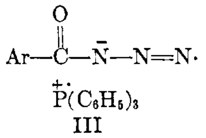

$\mathrm{Ar{-}\overset{O}{\overset{\|}{C}}{-}\underset{\overset{|+}{P(C_6H_5)_3}}{\bar{N}}\cdots N{\equiv}N}$

I

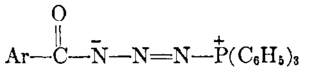

$\mathrm{Ar{-}\overset{O}{\overset{\|}{C}}{-}\bar{N}{-}\overset{+}{N}{\equiv}N}$

II

Although canonical structure I, if important, might increase the charge density near the ring over that represented by canonical structure II for the reagent, it could only be sufficiently important if the bond-breaking and making processes were nearly completed at the transition state. Since the *azide is a species of much higher energy than the phosphine-imine* produced, it is unlikely that the transition state would resemble I enough to account for the ρ value.[10] On the other hand a charge transfer structure such as III could account for the ρ value and resembles the reagents, as is to be expected.


$\mathrm{Ar{-}\underset{\overset{+\cdot}{P(C_6H_5)_3}}{\overset{O}{\overset{\|}{C}}}{-}\bar{N}{-}N{=}N\cdot}$

III


$\mathrm{Ar{-}\overset{O}{\overset{\|}{C}}{-}\bar{N}{-}N{=}N{-}\overset{+}{P}(C_6H_5)_3}$

IV

There are good analogies for III in the formation of charge-transfer complexes between triphenylphosphine and quinone[11] and possibly with the transition state for the reaction of triphenylphosphine with benzoyl peroxide. Intervention of a metastable *intermediate* IV between the reagents and the phosphine-imine would also be compatible with the observed ρ value. It

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(10) (a) According to a well known postulate of organic chemistry, the transition state should resemble both reagent and product in some degree, but should more closely resemble the species of higher energy—in this case, the reagent. J. E. Leffler, *Science*, **117**, 340 (1953); (b) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(11) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 856 (1957).

should be noted, however, that no kinetic evidence was obtained for such an intermediate even in the case of the nitro-substituted azides.

Benzenesulfonyl Azide.—The reaction of triphenylphosphine with benzene–sulfonyl azide in benzene leads to the formation of a rather insoluble 1:1 complex.[12] Occasionally the complex remains in supersaturated solution in benzene and it is possible to measure its decomposition rate by the nitrogen evolved. The reaction is precisely first order and gives the rate constants in Table IV. Excess of either reagent has no effect.

Table IV

Reaction of Benzenesulfonyl Azide with Triphenylphosphine in Benzene at 25.00°

Initial concn., moles/l.		$k_1 \times 10^3$ sec.
Azide	Ph_3P	
0.0502	0.0501	1.02[a]
.0496	.0500	1.02[a]
.0500	.1000	1.00[b]
.1003	.0500	1.01[b]
.0502	.2003	1.02[a]

[a] With stirring. [b] With boiling chips.

Apparently the complex is not sufficiently dissociated in benzene to cause deviation from first-order kinetics; this is in contrast to the benzoyl azide–triphenylphosphine complexes, which if they exist at all, must be highly dissociated.

The solid complex is yellow and has no band in the 2100-cm.$^{-1}$ region where azides usually absorb.

The product of the decomposition of the complex in benzene is nitrogen and the phosphine-imine.

$$Ph_3P + PhSO_2N_3 \xrightarrow{C_6H_6} \underset{\substack{\text{light yellow} \\ \text{m.p. 87–88° dec.}}}{PhSO_2N_3{\cdot}Ph_3P} \xrightarrow{C_6H_6} N_2 + PhSO_2\overset{-}{N}\text{—}\overset{+}{P}Ph_3$$

Benzenesulfonyl Azide in Chloroform.—In chloroform and other polar solvents, the reaction of benzenesulfonyl azide and triphenylphosphine (or the decomposition of the complex) takes an entirely different course from that in benzene. The nitrogen evolution rates fit no single reaction order and are only about one-fifth of those in benzene. No phosphine-imine is produced but benzenesulfonylamide precipitates during the reaction and triphenylphosphine oxide can be isolated by chromatography. Nitrogen is evolved in only 65% yield and azide is left over at the end of the reaction. The remaining azide can be decomposed, raising the nitrogen yield to nearly 100%, by adding additional triphenylphosphine *after nitrogen evolution has stopped.* However, if up to one mole of excess triphenylphosphine is present *from the beginning,* the nitrogen yield is still only 65%. Two moles of excess triphenylphosphine present from the beginning raise the nitrogen yield to 82%.

If the complex, synthesized in benzene, is dissolved in chloroform, the azide band of $C_6H_5SO_2N_3$ at 2130 cm.$^{-1}$ slowly increases in intensity for about forty-five minutes and then becomes constant. Apparently the dissociation of the complex to azide and triphenylphosphine takes place at a rate somewhat faster than the reaction destroying the azide.

The consumption of excess triphenylphosphine in polar solvents suggests reaction by a radical chain transfer mechanism. Benzenesulfonyl azide has been observed to participate in several free radical reactions, as already noted.[13] The ion radical $Ph_3P^{\dot{+}}$ has been postulated to be an intermediate in the reaction of triphenylphosphine with sulfur[14] as well as an ingredient of charge-transfer complexes. If the benzenesulfonamide which precipitates from chloroform solution during the reaction gets its hydrogen by attack of nitrene, or of nitrogen radical, or of ion-radical intermediates on the solvent, several plausible mechanisms can be written to account for the consumption of up to three moles of triphenylphosphine and their eventual isolation in the form of triphenylphosphine oxide. However, further evidence will be required before a detailed mechanism can be proposed.

Experimental

Kinetics.—Nitrogen evolution rates were measured by the method of Overberger.[15] One hundred milliliters of solvent in a 124-ml. long-necked flask was immersed in the constant temperature bath and allowed to reach the equilibrium temperature and pressure. Several boiling chips were added before immersing the flask in the bath, in order to avoid the effect of supersaturation.

A weighed amount of the azide, 0.01–0.005 mole, was poured into the flask in 10 ml. of the solvent. The flask was connected to the azotometer through a small condenser and a stopcock and the reading of volume was adjusted to zero. The stopcock was closed, the solution was shaken well and the measurement was started immediately. The volume change of gas was followed over a period of 75–80% reaction. Six or more readings were made during the initial 20% reaction and at least twenty readings during the next two half-lives of the reaction. The infinity volume of gas was determined by the reading at eight to nine half-lives and an additional reading was made after another half-life in order to assure that no leakage of gas occurred.

Rates of azide disappearance using its reaction with *triphenylphosphine* were determined as follows: A sample is removed from the reaction mixture and the reaction quenched by cooling. A quenched aliquot is then transferred to a flask equipped with a magnetic stirrer, a rotatable side-arm containing triphenylphosphine in acetic acid–chloroform, and a connection to an azotometer. The magnetic stirrer is started, the azotometer adjusted to zero volume reading, and the excess triphenylphosphine and acetic acid added by rotating the side arm. Nitrogen evolution is complete in about 15 min. at room temperature.

o-Iodobenzazide.—This azide was obtained by the reaction of the acid chloride with sodium azide in 50% aqueous acetone.[16] It melted at 29–30° and gave 99% of the theoretical yield of nitrogen on decomposition.

Benzenesulfonyl Azide.[8a]—Benzenesulfonyl chloride was allowed to react with an aqueous alcohol or aqueous acetone solution of sodium azide. The product was taken up in ether, washed well with ice–water and dried over sodium sulfate. (When the solution was dried over calcium chloride, the solution bubbled and the drying agent turned pink or red, with evolution of heat.) After the solvent was completely removed at reduced pressure, the remaining oil solidified on cooling in an ice–salt bath. The product was recrystallized from ether–petroleum ether mixture twice and the solvent contained in crystals was removed as completely as possible at 30–40° under reduced pressure. The azide melted at 13–14°, and decomposed with bubbling at about 135°.

o-Nitrobenzenesulfonyl Azide.—To an aqueous acetone solution of sodium azide (5 g. in 75 ml.), 15 g. of *o*-nitrobenzenesulfonyl chloride dissolved in 75 ml. of acetone was added dropwise with stirring at −10°. The stirring was then continued for 1 hr. at this temperature and another hour at room tempera-

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[12] Certain aryl and alkyl azides also react with tertiary phosphines to give isolable 1:1 complexes (ref. 3a and 3c).

[13] See also the initiation of polymerization of vinyl monomers (ref 8b).

[14] P. D. Bartlett, E. F. Cox, and R. E. Davis, *J. Am. Chem. Soc.*, **83**, 103 (1961).

[15] C. G. Overberger, M. T. O'Shaughnessy, and H. Shalit, *ibid.*, **71**, 2661 (1949); Y. Yukawa and Y. Tsuno, *ibid.*, **79**, 5530 (1957).

[16] P. A. S. Smith, *Org. Reactions*, **III**, 337 (1946).

ture. The solution was filtered and diluted with 500 ml. of ice-water to precipitate a yellow solid, which was collected on a filter, washed with cold water and dried. The product was dissolved in 150 ml. of warm alcohol and insoluble material was removed. Cooling gave 12 g. of yellow needles, m.p. 68–71°. Recrystallization from alcohol gave big needles, m.p. 71–73°.

Anal. Calcd. for $C_6H_4N_4O_4S$: C, 31.58; H, 1.76; N, 24.56. Found: C, 32.15; H, 1.99; N, 24.75.

Infrared spectra in Nujol mulls had characteristic azide band at 2170 cm.$^{-1}$.

***o*-Iodobenzenesulfonyl Azide.**—Seven grams of *o*-iodobenzenesulfonyl chloride in 20 ml. of ethanol was added in several portions to a cold solution of 5 g. of sodium azide in 70 ml. of 30% aqueous ethanol. The solution was stirred for 2 hr. with cooling, and then gradually warmed to room temperature. The mixture was diluted with an equal amount of cold water and extracted with ether. The ether solution was washed well with cold water and dried over anhydrous sodium sulfate. After removing the solvent *in vacuo,* 4.5 g. of an almost colorless oil remained. The oil solidified at −30°, and the solid was recrystallized from ether–petroleum ether solution, giving colorless needles which melted at 30–32° and decomposed above 115°. Infrared spectra in chloroform solution showed characteristic bands at 2120 and 2330 cm.$^{-1}$.

***p*-Methylbenzenesulfonyl azide** was prepared in the same manner in 60% yield; colorless needles, m.p. 19–20°.

***p*-Xylene** was freshly prepared by refluxing sulfur-free xylene with sodium for 20 hr., followed by distillation, b.p. 137–138°.

Chlorobenzene was dried over calcium chloride and distilled, b.p. 130.5–131.0°.

Nitrobenzene, dried over calcium chloride, was distilled under reduced pressure, b.p. 126°/32 mm.

Decomposition of Benzenesulfonyl Azide.—Several preliminary experiments were made and the products from rate runs were treated in a similar manner.

Benzenesulfonyl azide, 2.54 g., was decomposed under reflux in 25 ml. of *p*-xylene for 20 hr. The resulting dark-colored solution was concentrated and the residue chromatographed through alumina with benzene, benzene–ether, ether, and alcohol, successively. Each fraction was treated with charcoal in ether. From the first three solvent fractions, 2.79 g. of yellow needles (m.p. 129–138°) was obtained. On recrystallization from alcohol, this substance gave 2.40 g. of colorless needles (m.p. 136–138°), identified as benzenesulfonyl-*p*-xylidide. From the alcohol eluent 0.38 g. of solid (m.p. 135–147°) containing some oily matter was obtained. The mixed melting point with the xylidide was depressed and showed 138–152° with benzenesulfonylamide.

The product from 2.36 g. of benzenesulfonyl azide in chlorobenzene was separated by the chromatographic method into 0.49 g. of oily crystals, 1.1 g. of needles, m.p. 123–138°, and 0.36 g. of plates, m.p. 114–120°. The first product gave crystals m.p. 116–120° by recrystallization from ether. The second was recrystallized from alcohol, giving needles m.p. 127–129°. From the third product, colorless plates, m.p. 119–121°, were obtained. The first product was identified as the *m*-chloroanilide. The second was identified as the *o*-chloroanilide and the third as the *p*-chloroanilide, by mixture melting points.

Decomposition in nitrobenzene gave a large amount of black tar, a black solid which was insoluble in organic solvents and had no m.p., and a small amount of needles. This reaction resulted in about 60% excess amount of gas. The gas liberated iodine from potassium iodide solution and was insoluble in alkali; hence it is very probably nitric oxide derived from the nitrobenzene.

Decomposition of *o*-Iodobenzenesulfonyl Azide.—The product of the decomposition of 2.72 g. of the azide in mixed xylene was chromatographed and gave 0.80 g. of *o*-iodobenzenesulfonylamide, m.p. 161–163° and a small amount of a mixture of the *o*-iodobenzenesulfonyl xylidides, m.p. 81–116°. A large amount of black solid was also obtained.

Decomposition of *o*-Nitrobenzenesulfonyl Azide.—One gram of *o*-nitrobenzenesulfonyl azide was decomposed at 130–140° in 20 ml. of *p*-xylene, and the product was chromatographed. The benzene eluent gave a small amount of brown crystals, m.p. 177–180° (m.m.p. with *o*-nitrobenzenesulfonamide, 167–174°). The alcohol eluent gave 0.44 g. of colorless plates of *o*-nitrobenzenesulfonyl-*p*-xylidide, m.p. 141–142.5°, on recrystallization from ether. A considerable amount of black solid remained in the column. This material was insoluble in the usual organic solvents and in water but seemed to be soluble to some extent in concentrated alkali.

The decomposition of 1.5 g. of the azide in mixed xylene gave a large amount of black solid, a small amount of tar and 0.68 g. of crystalline product. The latter after treatment with charcoal in ether and recrystallization from ether–petrol ether solution, melted at 100–114°. This product is presumably a mixture of isomeric *o*-nitrobenzenesulfonyl-xylidides.

***p*- and *m*-Nitrobenzoyl Azides.**—These were prepared by the aqueous acetone–sodium azide method.[16]

3,5-Dinitrobenzoyl Azide.—This azide was prepared by the method of Blanksma and Verberg.[17] It melted at 107° and gave a phosphine-imine derivative with triphenylphosphine melting at 180–183°.

Benzenesulfonylazide–Triphenylphosphine Complex.—To 6.56 g. of triphenylphosphine in 30 ml. of cold benzene was added a seed crystal of the complex. A cold solution of 4.58 g. of benzenesulfonyl azide in 20 ml. of benzene was then added in several portions with shaking and stirred. The yellow precipitate was washed with cold benzene and then with dry ether. Yield 10.7 g., m.p. 87–88° dec. The infrared spectrum in a Nujol mull had no 2130-cm.$^{-1}$ band (azide), but such a band appears immediately and grows during a period of 45 min. when the complex is dissolved in chloroform. In benzene solution the complex decomposes to nitrogen (100 ± 1%) and $C_6H_5SO_2\overset{+}{N}\overset{-}{P}(C_6H_5)_3$, m.p. 154–157°.

The decomposition of the complex in chloroform gives nitrogen (60% yield), unchanged azide, benzenesulfonamide, and on chromatography, triphenylphosphine oxide. The phosphine-imine seems not to be among the products; a control experiment showed that it is easily isolated by chromatography on alumina.

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[17] J. J. Blanksma and G. Verberg, *Rec. trav. chim.*, **53**, 988 (1934).