4-Oxa-A-homofriedelan-3-one (Friedelolactone) (VI).—Peracetic acid (40%, 7.5 ml.) was added to a solution of friedelin (1.525 g.) in chloroform (70 ml.) and the mixture maintained at 58° for 17 hr. It was then concentrated until solid started to precipitate, methanol added, and the precipitate collected. This was dissolved in benzene, filtered to remove a little insoluble material, washed with water, and concentrated to yield well formed needles (1.34 g., m.p. 279–293°). Chromatography of this product (265 mg.) and elution with benzene (150 ml.) gave a solid (198 mg.) which was recrystallized once from ethyl acetate and once from chloroform–methanol to give friedelolactone as long felted needles, m.p. 303–306° (softens 294°), $[\alpha]_D$ +38° (*c* 1.9), undepressed by specimen obtained from friedelolactam.

Friedonic Acid (VII).—A solution of chromium trioxide (600 mg.) in water (10 ml.) and concentrated sulfuric acid (7.5 ml.) was added to a solution of friedelolactone (550 mg.) in acetic acid (300 ml., freshly distilled from potassium permanganate) and the mixture stirred at room temperature for 16 hr. Methanol was then added, the solution concentrated, diluted with water, and extracted with ether. Sodium hydroxide solution (15%, 200 ml.) was added to precipitate the salt at the interface. Much of the aqueous layer was run off and the ether removed by decantation. The precipitate was washed several times by decantation with water, then warmed on the steam bath to form a gel which gave a granular precipitate on acidification with hydrochloric acid. Two recrystallizations from aqueous ethanol gave friedonic acid (250 mg.) as fine felted needles, m.p. 205–207°, $[\alpha]_D$ −3° (*c* 1.6), λ^{CHCl_3} 2.85, 3.42, 5.88 (broad), 6.85, 7.20, 7.40, 7.79, 8.80 μ (reported,[23] m.p. 206–207°).

Methyl Friedonate.—Excess diazomethane in ether solution was added to friedonic acid (360 mg.) in ether (10 ml.), the solvent removed after 16 hr., and the residual solid crystallized from methanol to yield methyl friedonate as needles (300 mg.), m.p. 155–157°, $[\alpha]_D$ −2° (*c* 1.7), λ^{CHCl_3} 3.42, 5.79, 5.90, 6.88, 7.20, 7.40, 8.55, 8.95, 9.44, 10.10 μ (reported,[24] m.p. 153–154°, $[\alpha]_D$ +12°).

Friedonic Acid Oxime (VIII).—Friedonic acid (260 mg.) was added to a solution of hydroxylamine hydrochloride (355 mg.) in water (1 ml.) and pyridine (8 ml.). After the mixture had been heated under reflux for 20 hr., the solvents were removed under reduced pressure, the residue taken up in ether, washed with water, and dried (sodium sulfate). Removal of the ether gave a solid which crystallized from ethyl acetate to give friedonic acid oxime as stout needles (175 mg.), m.p. 238–240°.

Anal. Calcd. for $C_{30}H_{51}O_3N$: C, 76.06; H, 10.85; N, 2.96. Found: C, 75.43; H, 10.81; N, 2.87.

Acknowledgment.—The award of a research grant (A-3439) from the National Institute of Arthritis and Metabolic Diseases, Public Health Service, is gratefully acknowledged.

[23] N. L. Drake and W. P. Campbell, *J. Am. Chem. Soc.*, **58**, 1681 (1936).

[24] L. Ruzicka, O. Jeger, and P. Ringnes, *Helv. Chim. Acta*, **27**, 972 (1944).

The Mutual Decomposition of Benzenesulfonyl Azide and *t*-Butyl Hydroperoxide[1]

J. E. LEFFLER AND Y. TSUNO

Department of Chemistry, Florida State University, Tallahassee, Florida

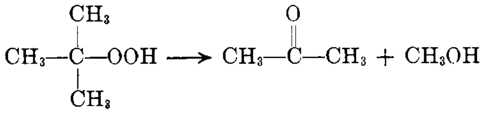
Received September 4, 1962

The system benzenesulfonyl azide–*t*-butyl hydroperoxide exhibits mutually induced decomposition of both reagents. The same system in the presence of iodine gives no induced decomposition of the azide, but shows two additional peroxide decomposition reactions, both of which involve both the azide and iodine.

On heating a chlorobenzene solution of benzenesulfonyl azide and *t*-butyl hydroperoxide, intermediates from the decomposing azide induce the decomposition of the peroxide, and intermediates from the peroxide induce the decomposition of the azide. Since a dozen or so different free radicals or diradicals and a correspondingly large number of chain-carrying and chain-breaking steps might plausibly be important in this system, readily interpretable kinetics are not to be expected. We undertook the investigation reported here as the result of a chance observation and were kept from discontinuing it immediately by certain interesting features which we now report.

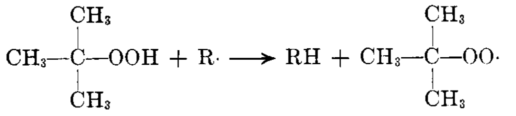
The decomposition of benzenesulfonyl azide to the nitrene and nitrogen is a well known reaction.[2] It is known both to be accelerated by free radicals[2b] and to induce vinyl polymerization.[2c] The decomposition of *t*-butyl hydroperoxide[3] has two free radical paths, one leading to acetone and methanol, the other to oxygen and *t*-butyl alcohol.

$$\mathrm{C_6H_5SO_2N_3 \longrightarrow C_6H_5SO_2N\colon + N_2} \qquad (1)$$



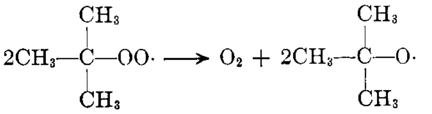
(2)

$$\mathrm{CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}OOH \longrightarrow CH_3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_3 + CH_3OH}$$



(3a)

$$\mathrm{CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}OOH + R\cdot \longrightarrow RH + CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}OO\cdot}$$



(3b)

$$\mathrm{2CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}OO\cdot \longrightarrow O_2 + 2CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}O\cdot}$$

Induced Decomposition of the Azide in the Presence of the Peroxide.—The decomposition of the azide in chlorobenzene at 126.7° can be followed by total gas evolution or by analysis for azide by means of the triphenylphosphine method described in the Experimental. Fig. 1 shows the results of some total gas evolution experiments. The gas evolution rate is equal to that expected from the uncatalyzed azide decomposition at the beginning of the reaction and at the end, but there is an intervening period of very fast nitrogen-plus-oxygen evolution lasting for about forty-five minutes. Extrapolation of the linear portion of the gas evolution curve back to zero time gives an azide concentration considerably less than the actual initial azide concentration. Fig. 2 shows the decrease in azide concentration as determined by the triphenylphosphine

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[1] This investigation was supported under a contract with the Office of Naval Research.

[2] (a) O. C. Dermer and M. T. Edmison, *J. Am. Chem. Soc.*, **77**, 70 (1955); (b) M. Takebayashi and T. Shingaki, private communication; (c) J. F. Heacock and M. T. Edmison, *J. Am. Chem. Soc.*, **82**, 3460 (1960).

[3] (a) B. K. Morse, *ibid.*, **79**, 3375 (1957); (b) V. Stannett and R. B. Mesrobian, *ibid.*, **72**, 4125 (1950); (c) N. A. Milas and D. M. Surgenor, *ibid.*, **68**, 205 (1946).

method. Superimposed on the same figure is the decrease in iodometric peroxide concentration for a similar run. Again we find a period of normal azide decomposition rate, a period of accelerated decomposition, and a return to the normal rate.

The induced decomposition of the azide can be prevented entirely either by adding iodine to the chlorobenzene solution or by using *p*-xylene as the solvent. Fig. 3 shows the evolution of nitrogen plus oxygen in the presence of iodine. The experimental points fall on a theoretical curve calculated from the usual first-order rate constant for the azide decomposing in chlorobenzene alone and a first-order rate constant for the peroxide determined iodometrically.

The products of the azide decomposition in chlorobenzene plus *t*-butyl hydroperoxide are the usual benzenesulfonanilides plus benzenesulfonamide and tar. In *p*-xylene plus *t*-butyl hydroperoxide, the product is benzenesulfonyl *p*-xylidide, almost quantitatively.

Induced Decomposition of the Peroxide in the Presence of the Azide.—The reaction induced by the simultaneous decomposition of benzenesulfonyl azide in chlorobenzene at 126.7° is reaction 3, nitrogen being evolved quantitatively and oxygen in 90% yield or better. Reaction 3 in the absence of azide proceeds at a negligible rate; the observed reaction under those conditions is (2). The rate of reaction 2, expressed as a first-order rate constant, is about 1.04×10^{-3} min.$^{-1}$ for an initial peroxide concentration of 0.065 M.

Iodometric titration of the peroxide in chlorobenzene in the presence of the azide shows peroxide decomposition occurring by a process of nearly zero order within the run, especially at low azide concentrations. A typical run is shown in Fig. 4.

At higher initial azide concentrations the behavior is more complicated, the zero-order rate constant k_{op} increasing during the run. The zero-order rate constants for runs of constant initial peroxide concentration (0.05 M) depend on the initial azide concentration as shown in Fig. 5. The upper branch at high azide concentration shows the rates late in the run, the lower branch the initial rates.

The effect of changing initial peroxide concentration at a constant initial azide concentration of 0.01 M is shown in Fig. 6.

The combined effect of changes in initial azide and peroxide concentration on k_{op} in chlorobenzene at 126.7° is given by equation 4, in which only runs of clearly zero order ($[\text{A}]_0 \leq 0.017$ M) were used to evaluate the parameters.

$$k_{\text{op}} = 3.1 \times 10^{-3}[\text{A}] + 26 \times 10^{-3}[\text{P}][\text{A}]^{1/2} + 0.45 \times 10^{-3}[\text{P}] \; M^{-1}\ \text{min.}^{-1} \quad (4)$$

The coefficient of the first term, 3.1×10^{-3}, is equal within experimental error to twice the normal first-order rate constant for the decomposition of the azide alone. That rate constant is 1.5×10^{-3} min.$^{-1}$ in chlorobenzene at 126.7°.

Equation 4 gives a clue to the general nature of the induced peroxide decomposition, but we have not been able to derive any entirely satisfactory mechanism. This may be partly the result of the purely mathematical difficulty of a system in which at least a dozen different radical intermediates are likely and partly the result of such complications as the partial sweeping

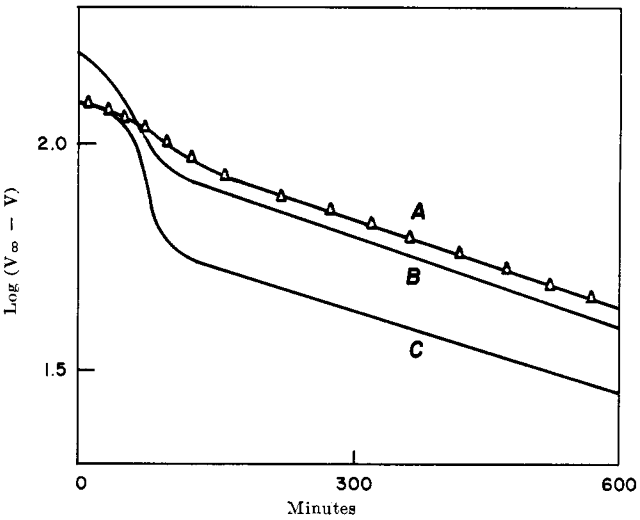

Fig. 1.—A. 0.05 M azide, 0.025 M peroxide; B. 0.05 M azide, 0.05 M peroxide; C. 0.033 M azide, 0.05 M peroxide.

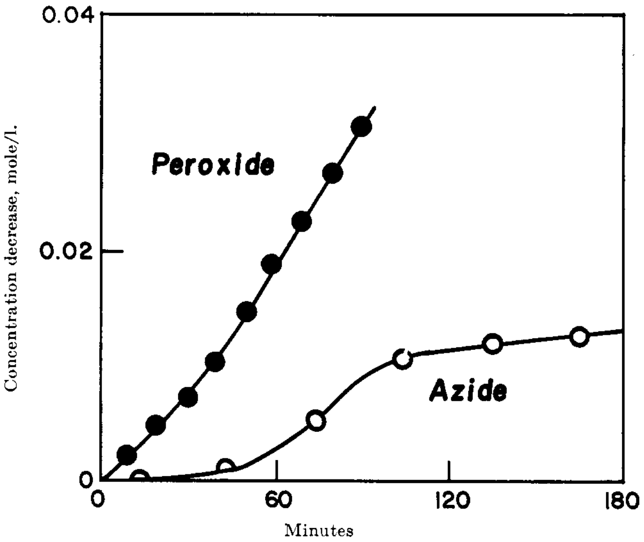

Fig. 2.—Two runs, both of initial azide concentration 0.033 M and initial peroxide concentration 0.05 M, chlorobenzene, 126.7°.

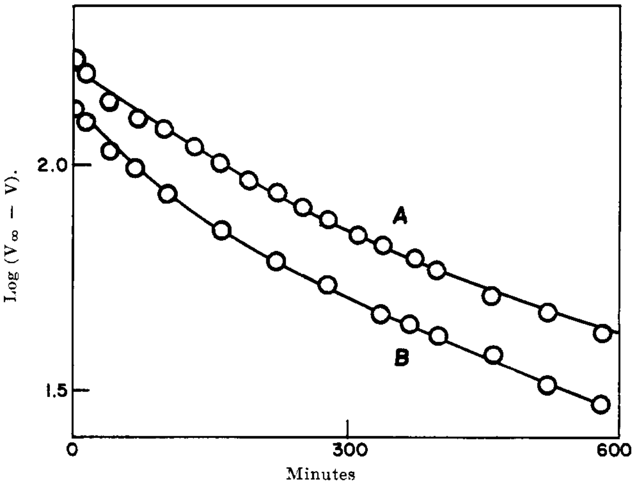

Fig. 3.—Gas Evolution with 0.01 M I_2 in C_6H_5Cl. *Experimental* points and *theoretical* curve: A. For 0.0497 M azide and 0.0499 M peroxide; B. For 0.0336 M azide and 0.0503 M peroxide.

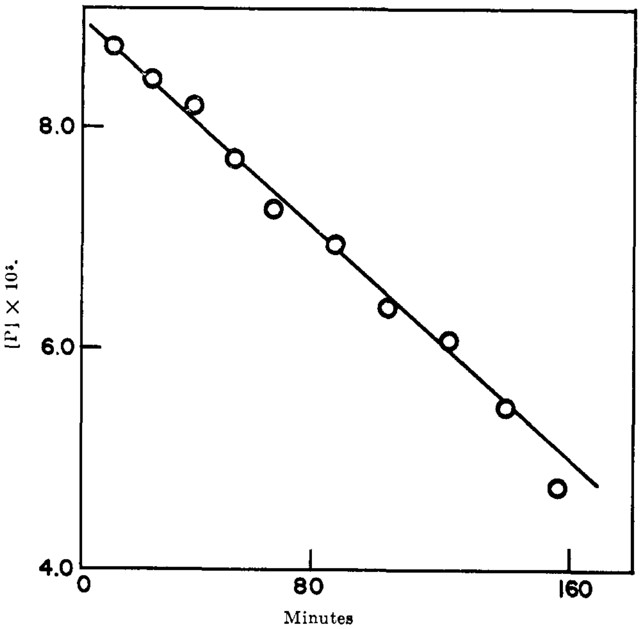

Fig. 4.—0.05 *M* peroxide and 0.006 *M* azide in C_6H_5Cl at 126.7°.

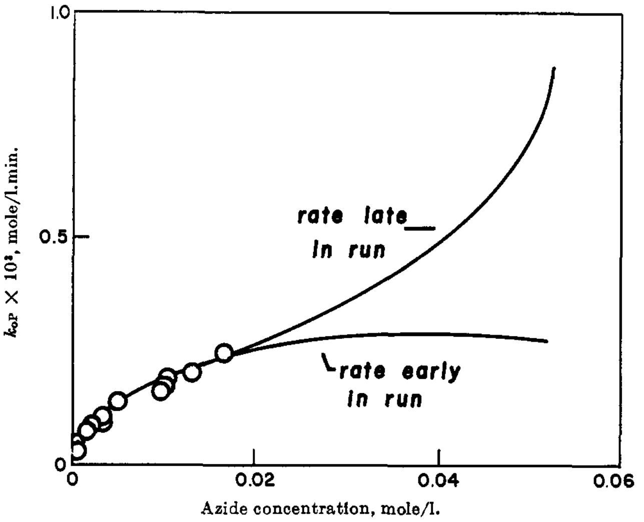

Fig. 5.—Dependence of peroxide decomposition rate on azide concentration for initial peroxide concentration 0.05 *M* in C_6H_5Cl at 126.7°.

out of oxygen by the evolved nitrogen.[4] We note, however, that several mechanisms involving *t*-butoxy radicals, *t*-butylperoxy radicals, benzenesulfonyl nitrene, and substituted nitrogen-free radicals predict the $2k_1$[A] term and terms in [P] $[A]^{1/2}$ and [P].

One such mechanism, involving chain transfer from the nitrene to a benzenesulfonanilide and chain-breaking by bimolecular reaction of *t*-butoxy radicals, gives the bk_1[A] and [P] $[A]^{1/2}$ terms but cannot account for the term in [P]. The latter is too large for an accompanying unimolecular decomposition of the peroxide.

The apparent zero-order rates within runs at low initial azide concentrations and the acceleration within runs at higher initial azide concentrations may be due to catalysis by some accumulating product of the azide decomposition reaction. A partly decomposed solution of the azide was found to give a faster peroxide

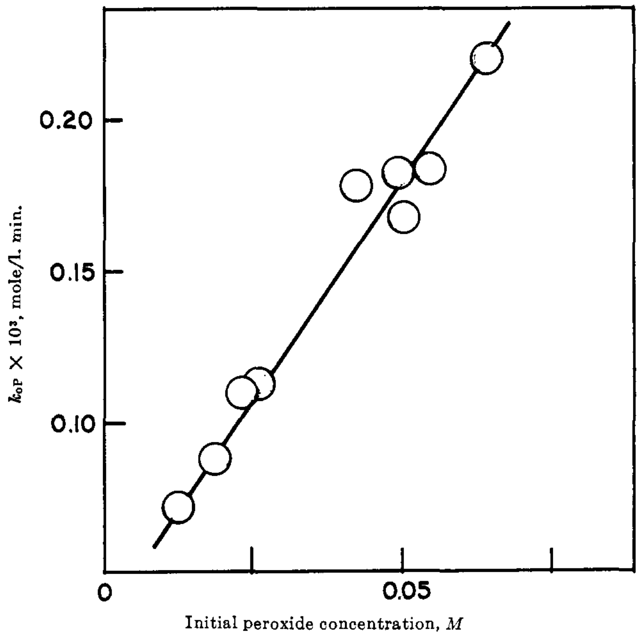

Fig. 6.—Dependence of peroxide decomposition rate on initial peroxide concentration in 0.01 *M* azide solutions in C_6H_5Cl at 126.7°.

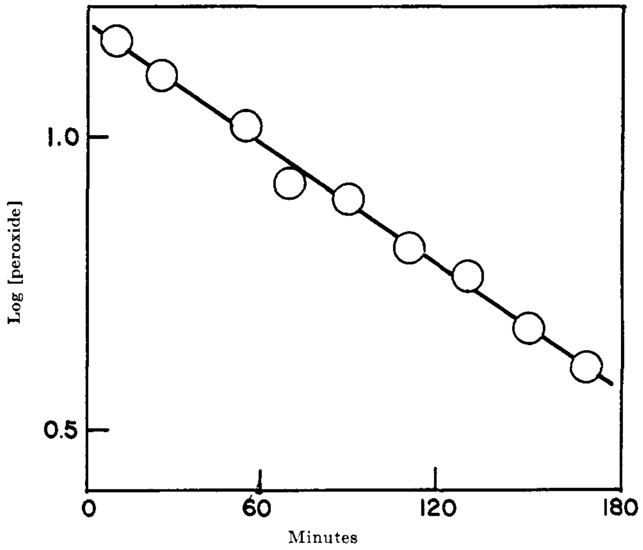

Fig. 7.—A first-order plot for a C_6H_5Cl, solution of iodine (0.01 *M*), azide (0.05 *M*), and peroxide (initially 0.05 *M*).

decomposition than that for an otherwise comparable run in which both the azide and peroxide were added at the same time. Neither benzenesulfonamide nor benzenesulfonyl-*p*-chloroanilide is a catalyst, however.

Induced Decomposition of the Peroxide in the Presence of Iodine and the Azide.—In an attempt to divert some of the intermediates and simplify the kinetics we added iodine to the medium. The decomposition of the peroxide (without azide) in chlorobenzene in the presence of 0.01 *M* iodine is a reaction of apparently first order for which the rate constant k_{IP} is 3.4 × 10^{-3} min.$^{-1}$, about three times as great as that obtained without iodine. This reaction gives little or no gas. In the presence of iodine and the azide we observe two reactions, depending on the initial azide concentration.

At *high* initial azide concentrations ($\geq$0.0124 *M*) the peroxide decomposition is clearly first order, as

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[4] Vigorous sweeping with nitrogen during the reaction increases the rate by about a factor of two, much less than the effect reported in ref. 3a for the decomposition of the peroxide alone.

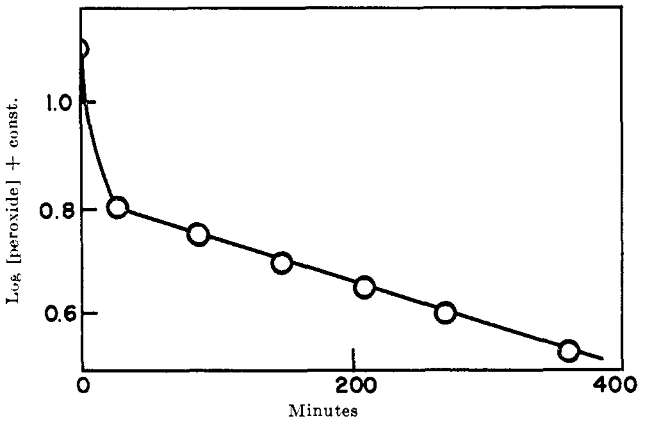


Fig. 8.—First order plot for peroxide decomposition in C_6H_5Cl at 126.7° with 0.01 *M* I_2 and 0.05 *M* initial peroxide concentration and a *low* (0.0016 *M*) azide concentration.

shown in Fig. 7. It is also clearly first order if benzenesulfonyl *p*-chloroanilide is added, even at lower azide concentrations.

At *low* initial azide concentrations (≤ 0.0124 *M*) there is an extremely fast peroxide decomposition whose half-life is about five minutes or so. This reaction, like that of the peroxide plus iodine alone, gives no gas. It is much faster, however.

The initial fast peroxide decomposition soon stops, as shown in Fig. 8, and is succeeded by the first-order process leading to oxygen. Fig. 9 shows the linear relationship between k_{1P} for that process and the square root of the initial azide concentration. Initial iodine and peroxide concentrations were 0.01 and 0.05 *M*.

Fig. 10 shows a plot of k_{1P} against the reciprocal of the initial peroxide concentration for runs initially 0.01 *M* in iodine and 0.0164 *M* in azide.

The data of Fig. 9 and 10 are best fitted by equation 5 (in the presence of I_2, chlorobenzene, 126.7°).

$$k_{1P} = 0.4 \times 10^{-3} \frac{([A]_0)^{1/2}}{[P]} + 23 \times 10^{-3}([A]_0)^{1/2} \qquad (5)$$

It appears that the iodine-*t*-butyl hydroperoxide system is able to react in at least three ways. The first of these, in the absence of azide, is very likely a polar decomposition of the peroxide catalyzed by the iodine acting as a Lewis acid. The *fast initial peroxide decomposition* observed in the presence of low concentrations of *azide* might be a polar decomposition of the peroxide catalyzed by the positive halogen of N,N-diiodobenzenesulfonamide, *i.e.*, the nitrene diiodide. The inhibition of this initial fast reaction by benzenesulfonyl-*p*-chloroanilide might be explained by conversion of the nitrene and sulfonanilide to two nitrogen radicals by hydrogen transfer. The third reaction is the one whose rate constants are correlated by equation 5.

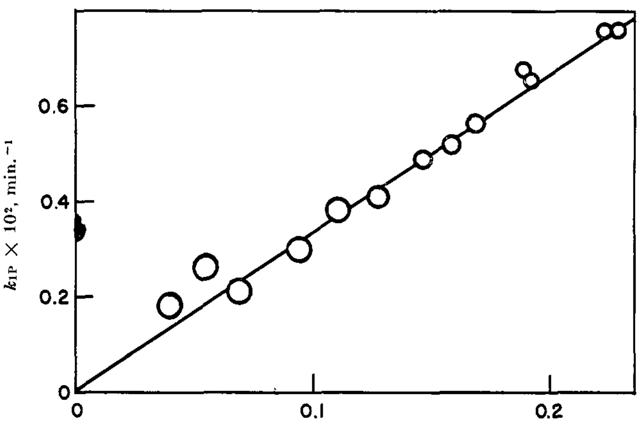


Fig. 9.—Dependence of k_{1P} on the square root of the azide concentration. The large circles are for runs having an initial fast part, like that of Fig. 8. The I_2 concentration is 0.01 *M* and the initial peroxide concentration is 0.05 *M*. The rate with *no azide* is shown by the filled circles.

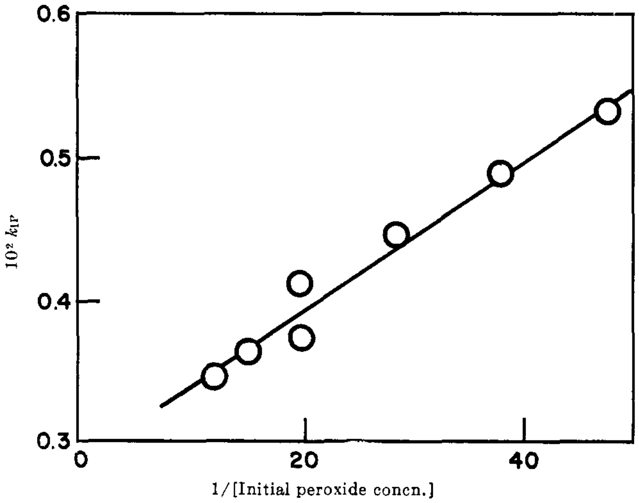


Fig. 10.—Dependence of k_{1P} for azide concentration 0.0164 *M* and I_2 concentration 0.01 *M* on 1/[P].

The form of equation 5 plus the effects of iodine and benzenesulfonyl-*p*-chloroanilide noted above suggest that the reaction consists of formation of the nitrene, chain transfer to form nitrogen-free radicals, some further chain transfer and chain-propagating steps, and one or more bimolecular termination steps. There are, unfortunately, a very large number of such mechanisms. Some of them lead to simple rate expressions incompatible with equation 5, others to rate expression of considerable mathematical complexity which might approximate (5) under special conditions. There is also at least one mechanism giving a *simple* rate expression compatible with (5). Although we do not wish to propose it as the mechanism of the reaction, we give it here as an example of the features which seem to be required. For convenience we let the azide be repre-

$$A \xrightarrow{1} N: + N_2$$

$$N: + NH \xrightarrow{2} 2N\cdot$$

$$N\cdot + I_2 \xrightarrow{3} (NI + I\cdot) \longrightarrow N\cdot + 2I.$$

$$I\cdot + P \xrightarrow{\text{fast}} HI + ROO\cdot$$

$$2ROO\cdot \xrightarrow{\text{fast}} 2RO\cdot + O_2$$

$$HI + P \xrightarrow{\text{fast}} H_2O + ROI$$

$$2N\cdot \xrightarrow{4} \text{chain breaking}$$

$$RO\cdot + P \xrightarrow{5} ROH + ROO\cdot$$

$$RO\cdot + I_2 \xrightarrow{6} ROI_2\cdot$$

$$2ROI_2\cdot \xrightarrow{\text{fast}} 2ROI + I_2$$

sented by A, the peroxide by P and by ROOH, the nitrene by N:, and the radicals $C_6H_5SO_2NH\cdot$ or $C_6H_5SO_2NAr\cdot$ indiscriminately by $N\cdot$.

Assuming that ROI decomposes by an iodine-catalyzed polar mechanism and applying the steady-state approximation, the above mechanism gives an equation 6 of the required form.

$$k_{1P} = 4k_2[I_2]\left(\frac{k_1}{k_3}\right)^{1/2}\frac{[A]^{1/2}}{[P]} + \frac{2k_4k_2}{k_5}\left(\frac{k_1}{k_3}\right)^{1/2}[A]^{1/2} \qquad (6)$$

Experimental

Triphenylphosphine Method for the Azide.—A 5-ml. aliquot of the azide solution is added to 10 ml. of benzene in an azotometer equipped with a magnetic stirrer and a rotatable sidearm for adding a mixture of 5 ml. of triphenylphosphine reagent and 3 ml. of acetic acid. The triphenylphosphine reagent consists of 13.12 g. of triphenylphosphine in 50 ml. of chloroform. The gas buret is adjusted to zero, the sidearm is rotated so as to add the reagent, and the volume of nitrogen from the azide is read. Nitrogen is evolved quantitatively. A considerable excess of triphenylphosphine is used in order to destroy any unchanged peroxide.

$$(C_6H_5)_3P + C_6H_5SO_2N_3 \longrightarrow N_2 + (C_6H_5)_3\overset{+}{P}\text{—}\overset{-}{N}SO_2$$

$$(C_6H_5)_3P + (CH_3)_3COOH \longrightarrow (C_6H_5)_3PO + (CH_3)_3COH$$

Iodometry.—To a 10-ml. aliquot diluted with 25 ml. of isopropyl alcohol are added 5 ml. of acetic acid and 5 ml. of aqueous saturated potassium iodide solution, and the mixture is shaken and warmed for 20 min. at 60–70°. The solution is then diluted with water and titrated with 0.05 *N* thiosulfate.

For free iodine, the sample in isopropyl alcohol is titrated with thiosulfate without adding potassium iodide and acetic acid or warming.

Benzenesulfonylazide.—The method of preparation was essentially the same as that reported by Dermer and Edmison.[2a] Benzenesulfonyl chloride was allowed to react with sodium azide in an aqueous alcohol or aqueous acetone solution at about 0°. The product was taken up in ether, washed well with ice–water, and dried over sodium sulfate. If the solution was dried over calcium chloride, it became warm, bubbled, and turned pink or red. After the solvent was removed under reduced pressure at room temperature, the remaining oil was solidified by cooling in Dry Ice. It was then twice recrystallized from ether–petroleum ether (low boiling) and dried *in vacuo* at 30–40°. The azide melted at 13–14° and decomposed with bubbling at about 135°. The decomposition in chlorobenzene or xylene gave closely the theoretical amount of nitrogen.

***t*-Butyl Hydroperoxide.**—The commercial product was purified by fractional distillation through a short column, and the fraction, b.p. 38.5–39.5°/18 mm., was used for the rate measurements.

Chlorobenzene was dried over calcium chloride and distilled, b.p. 131–131.5°.

The Products of the Decomposition.—The product from the decomposition of 2.36 g. of the azide in chlorobenzene at 126° was chromatographed on alumina after evaporation of the solvent, giving 0.49 g. of oily crystals, 1.1 g. of needles, m.p. 123–128°, and 0.36 g. of plates, m.p. 114–120°. The first fraction melted at 116–120° after recrystallization from ether. The second melted at 127–129° after recrystallization from alcohol. The third fraction gave colorless plates, m.p. 119–121°. These products were identified by mixed melting points as the *m*-, *o*-, and *p*-chloroanilides of benzenesulfonic acid, respectively. The total yield was about 56% of the theoretical before purification.

In the presence of *t*-butyl hydroperoxide, the yield of these products was decreased. The low molecular weight material from 2.62 g. of azide and 1.16 g. of *t*-butyl hydroperoxide amounted to only 1.47 g. after chromatographic separation from tars, and the total yield of chloroanilides was less than 35%. *o*-Chloroanilide was the main product, and a small amount of unsubstituted benzenesulfonylamide was also obtained. There was a considerable amount of black material, insoluble in the usual organic solvents.

Reaction of Carbon Disulfide with Azide Ion[1]

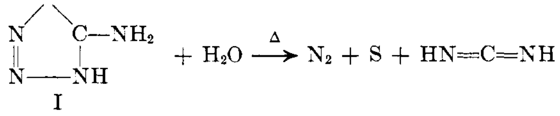
EUGENE LIEBER,[2a] EDWIN OFTEDAHL,[2b] AND C. N. R. RAO[2c]

Departments of Chemistry, Roosevelt University, and DePaul University, Chicago, Illinois

Received November 8, 1960

Carbon disulfide reacts with azide ion to form the 1,2,3,4-thiatriazolinethionate ion and not the acyclic azidodithiocarbonate ion as previously reported. A series of salts of thiatriazoline have been prepared and none shows evidence for the presence of the azido group. Esters of thiatriazolinethione prepared by the reaction of the sodium salt with alkyl or acyl halides have been found to be either 5-(substituted) mercapto-1,2,3,4-thiatriazoles or 4-substituted 1,2,3,4-thiatriazoline-5-thiones. These structures have been assigned on the basis of degradative and spectroscopic evidence. The chemistry of the so-called azidodithiocarbonates has been reinterpreted in terms of the thiatriazole structure.

During the course of the investigations[3] on the 1,2,3,4-thiatriazole ring system, Lieber and co-workers were struck by the similarity in their chemistry with that reported for substances described in the literature[4] as azidodithiocarbonates. For example, 5-amino-1,2,3,4-thiatriazole (I)[5] and azidodithiocarbonic acid (II. R = H), respectively, decompose on warming[6] in water.



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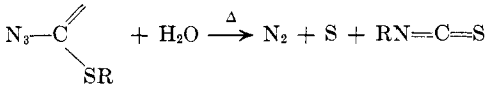

II[7]

Other similarities in the chemistry of the so-called II led to a preliminary re-examination[5] of the structure of the products obtained by the condensation of azide ion with carbon disulfide. The absence of the characteristic azido group frequencies in the infrared spectra

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[1] The authors gratefully acknowledge the support of this research by he U. S. Army Research Office.

[2] (a) To whom all correspondence should be addressed; (b) taken in part from M.S. thesis, DePaul University, 1960; (c) presently at the Indian Institute of Science, Bangalore, India.

[3] E. Lieber, J. Ramachandran, C. N. R. Rao, and C. N. Pillai, *Can. J. Chem.*, **37**, 563 (1959), which cites previous references in this series.

[4] L. F. Audrieth, *Chem. Rev.*, **15**, 169 (1934).

[5] E. Lieber, C. N. Pillai, J. Ramachandran, and R. D. Hites, *J. Org. Chem.*, **22**, 1750 (1957).

[6] Both structures I and II will slowly decompose in aqueous solution and room temperature.

[7] This is the structure corresponding to the descriptive name for this substance.