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Task No. NR055-398

Final Technical Report

by

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PART I. ORGANOBORON CHEMISTRY

Preparation and Decomposition of Dimesityl Boron Azide

See Technical Report No. 1 or Leffler and Todd, Chem. and Industry 1961 512.

Attempted Preparation of $Ar_3BN_3^-$

See Technical Report No. 1

Attempted Reaction $RN_3 + R_3B \rightarrow R_3\overset{-}{B}-\underset{R}{\overset{|}{N}}-\overset{+}{N}_2 \rightarrow R_2B-\underset{R}{\overset{|}{N}} + N_2$

See Technical Report No. 1

Attempted Preparation of $\phi_2BCH_2C_6H_4OCH_3$ (p)

See Technical Report No. 1

Reactions of Organoboron Compounds with Diazo Compounds

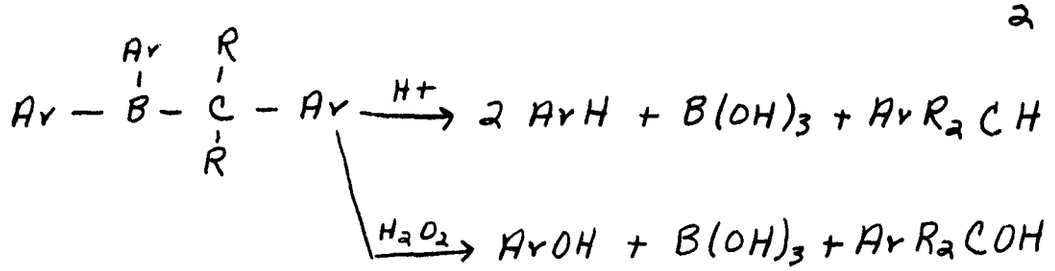
See Technical Report No. 1 and Leffler and Ramsey, Proc. Chem. Soc. 1961 117. The following information has not yet been published elsewhere.

Phenylboronic acid anhydride reacts with diphenyldiazomethane in ether to give products which on acid hydrolysis are isolable as triphenylmethane and triphenylcarbinol. Tolylboronic anhydride similarly gives diphenyltolylmethane.

These results are consistent with the following reaction mechanism:

$$Ar_3B + R_2CN_2 \longrightarrow Ar-\underset{\underset{Ar}{|}}{\overset{\overset{Ar}{|}}{B}}-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}-\overset{+}{N}\equiv N$$

$$Ar-\underset{\underset{Ar}{|}}{\overset{\overset{Ar}{|}}{B}}-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}-\overset{+}{N}\equiv N \longrightarrow Ar-\underset{}{\overset{\overset{Ar}{|}}{B}}-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}-Ar + N_2$$

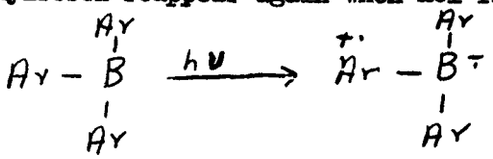


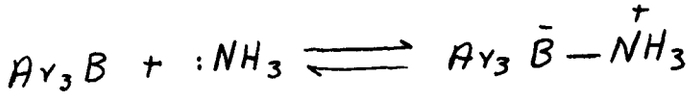
The first step is consistent with complexing of Ar_3B with various reagents having unshared pairs of electrons. (vide infra)

Triarylboron Absorption Spectra

See attached reprint, J. Chem. Phys. 35, 1502 (1961)

Triphenylboron in inert solvents such as methylcyclohexane has an intense band at λ max 2871 Å and ϵ 3.9×10^4. Tri-α-naphthylboron has intense bands at 2638 and 3526 Å. These have been tentatively identified as intramolecular charge-transfer bands. (see reprint). They vanish when dry ammonia is bubbled through the solution, but in the case of tri-α-naphthylboron reappear again when HCl is bubbled through.





The spectra of tritolylboron and trimesitylboron are like that of triphenylboron. The transition energy of the charge transfer band in Ar_3B is a roughly linear function of the first ionization potential of ArH (figure 1). A precisely linear relationship obtains between the intramolecular charge-transfer transition energy and the intermolecular charge-transfer transition energy for the $ArH \cdot I_2$ complex (figure 2).

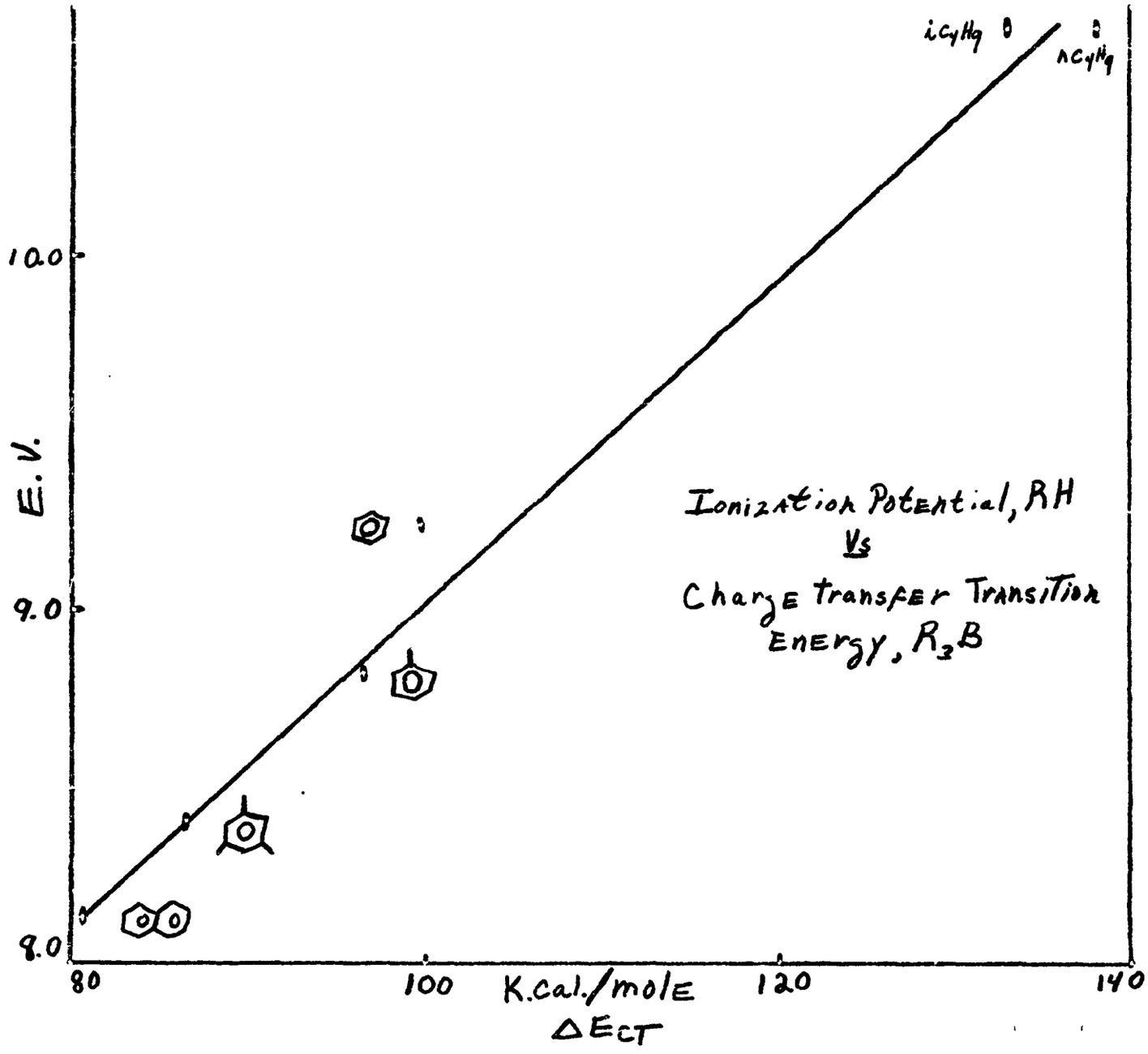

iCyHq
nCyHq
10.0
9.0
8.0
E. V.
80
100
120
140
K.cal./mole
ΔECT
Ionization Potential, RH
Vs
Charge transfer Transition
Energy, R3B

Fig. 2

ΔE Charge transfer ArB

Vs.

ΔE Charge transfer $ArH \cdot I_2$

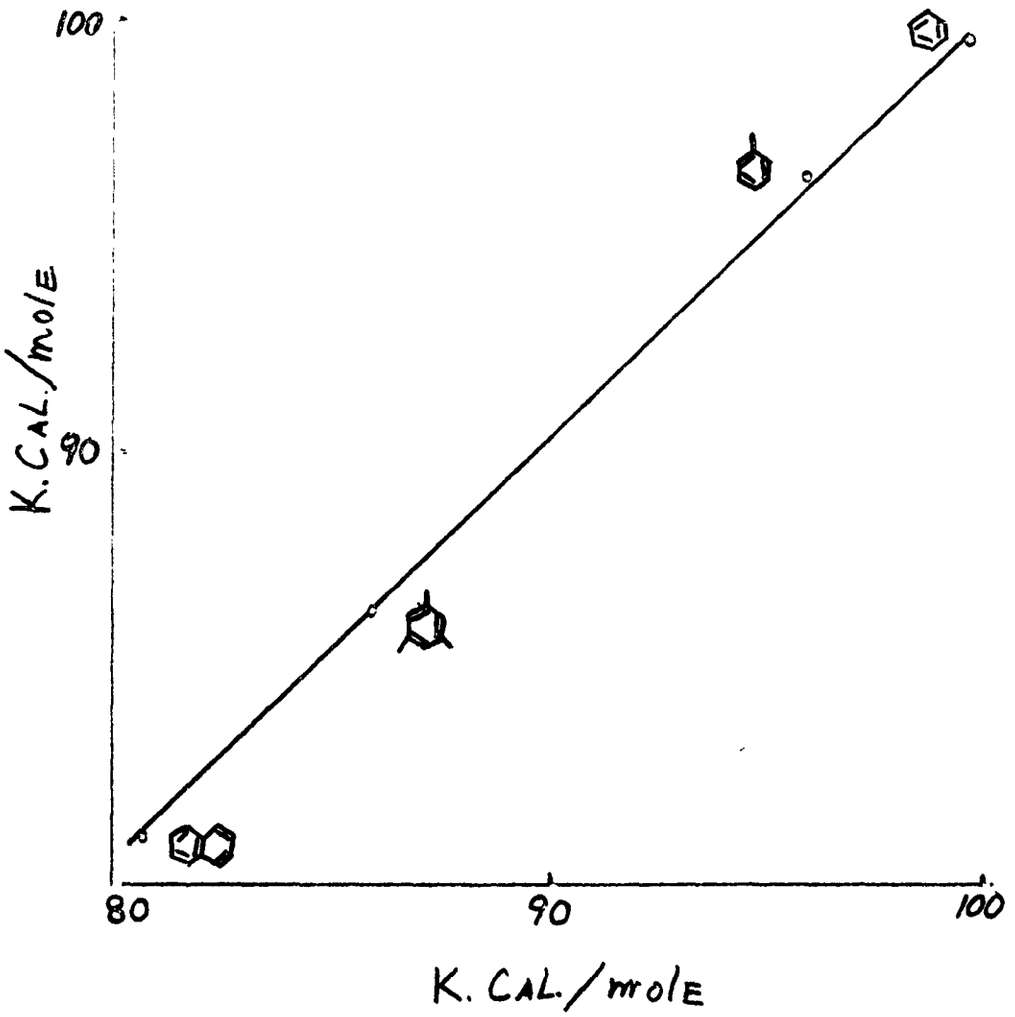


Table 1

Ultraviolet C. T. Maximum in Methylcyclohexane

Tri-1-naphthyl boron	3526	1.9×10^4
Trimesityl boron	3310	1.5×10^4
Tritolyl boron	2966	3.3×10^4
Triphenyl boron	2871	3.9×10^4

There are some anomalies in the earlier literature on the spectrum of triphenyl boron. Thus in acetonitrile it exists only in the complexed form and the C. T. band is missing.(1)

(1) D. Geske, J. Phys. Chem. 63 1067 (1959)

The C. T. bands of tri-α-naphthyl boron in that solvent are weakened (1/5 factor) and several intense new bands appear. The highly hindered trimesityl boron has its usual spectrum even in acetonitrile. The spectrum reported by Mikhailov(2) for triphenylboron is erroneous, and is probably the result of air-oxidation of the triphenyl boron.

(2) B. M. Mikhailov, Optika Spectroskopiza 7 644 (1959)

Boron Radicals and Triaryl Boron Photolysis

Photolysis of tri-α-naphthyl boron in toluene, using sunlight or ultraviolet light, gave naphthalene, α-naphthylboronic acid, and di-α-naphthylborinic acid. In dry CCl_4 under N_2 the products are hexachloroethane, binaphthyl, naphthalene, and 1-chloronaphthalene (trace) plus readily hydrolyzable CCl_3 or Cl derivatives. On hydrolysis the reaction mixture gives Cl^- (as AgCl) in large amounts plus α-naphthylboronic and di-α-naphthylborinic and α-naphthoic acids. The products fume in air. If the photolyzed solution is oxidized with air and then treated with small amounts of water, phosgene is evolved. These products are consistent with the following sets of reactions:

$(\alpha\text{-n})_3\,B \xrightarrow[CCl_4]{h\nu} (\alpha\text{-n})_2\,B\cdot$ + 

$(\alpha\text{-n})_2B\cdot + CCl_4 \longrightarrow (\alpha\text{-n})_2\,B\text{-Cl} + Cl_3C\cdot$

 $+ CCl_4 \longrightarrow$  $+ Cl_3C\cdot$

$(\alpha\text{-n})_2\,B\cdot + Cl_3C\cdot \longrightarrow (\alpha\text{-n})_2\,B\text{-}CCl_3$

 $+ Cl_3C\cdot \longrightarrow (\alpha\text{-n})_2\,B\text{-}CCl_3$

$(\alpha\text{-n})_2\,BX \xrightarrow{h\nu} \alpha\text{-n-B-X} +$  etc.

Protolysis of Tetraphenylborate Ion

This work was supported only in part under thi contract. It constitutes the dissertation of Verne Allen Simon, I. S. U. 1962, and will be published in full elsewhere. Tracer and kinetic studies have established the protolysis mechanism in 50% aqueous dioxane as a bimolecular reaction of

protons with the phenyl substituents at the carbon attached to boron. There is no detectable general acid catalysis.

Experimental Section, Organoboron Chemistry

Preparation of Tri-1-naphthylboron:

Tri-1-naphthylboron was prepared by the method of Brown and Sujishi[3] from the reaction of 1-naphthylmagnesium bromide with boron trifluoride etherate. M. p. 203-204° uncorr. % B - 2.6, % B calc. 2.7

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(3) H. C. Brown an S. Sujishi, JACS 70 2793 (1948)

Preparation of Triphenyl boron:

Triphenylboron was prepared from phenylmagnesium bromide and boron trifluoride according to the procedure of Wittig,[4] or was purchased from Aldrich Chemical Company.

The crude triphenyl boron was recrystalized to a white crystalline substance from benzene in a dry box under prepurified nitrogen. M.p. 146°-147° (evacuated).

The purity of ϕ_3B is tested by the absence of strong peaks at 1320-1400 and 1810-1820 cm^{-1} which are characteristics of oxidation products of triphenyl boron. The solutions were made up and the cells loaded in the nitrogen box.

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(4) G. Wittig et al. Ann. 563 110 (1949); Ber. 88 962 (1955)

Passage of ammonia through an ether solution of triphenyl boron gave a white crystalline adduct. M.p. 204-207° (dec) in air and 234° in an evacuated and sealed cappillary.

Preparation of Tritolylboron:

Tritolylboron was prepared in the following manner, using a procedure adapted from Wittig. (5)

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(5) G. Wittig, Ber. 88 962 (1955)

The Grignard reagent prepared from 34.2g of parabromotoluene was added under nitrogen to 9.5g of boron trifluoride etherate in 100 ml of ether at a rate sufficient to maintain reflux. After addition was complete, the reaction was refluxed an additional hour. The ether was removed by distillation and replaced by 75 ml of toluene. The toluene was heated to reflux and the solution filtered through a sintered glass disk into a flask, under a nitrogen atmosphere. The flask was stoppered and transferred to a nitrogen box where 30-40 ml of the toluene was evaporated off and the solution filtered and was allowed to stand overnight. A white srystalline product was obtained, which was recrystallized from toluene, and dried under N_2 at reduced pressure in the air lock of the nitrogen box. M. p. 149.5° -151°, reported M. p. 142°-44°. The product has the following strong to medium bands in the infrared, in units of cm^{-1}, in CCl_4: 3050, 2950, 2900, 1600, 1445, 1400, 1315, 1280, 1240, 1210, 1190, 910, 895. The spectrum was taken on an Infracord and the cells loaded under nitrogen.

Trimesityl boron:

Trimesityl boron was synthesized by the method of Brown and Dodson.(6) Mesityl magnesium bromide was reacted with borontrifluoride etherate, and the product recrystallized from acetone. M. p. 191°-192°.

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(6) H. C. Brown and V. H. Dodson, JACS 79 2304 (1957)

Reactions of triphenylboron with diazomethane:

Run I

Diazomethane (13×10^{-1} moles) in 200 ml ether was added slowly with vigorous stirring to 1.7×10^{-3} moles of triphenyl boron in 100 ml of ether, under a nitrogen atmosphere.

After addition of the diazomethane was complete, 100 ml of dilute hydrochloric acid was added and the mixture was stirred at room temperature for several hours.

The ether layer was separated, dried, and all but 20 ml distilled off. The ether was replaced by 40 ml of isooctane, (spectro grade). This was fractionally distilled and ultraviolet spectra taken of the four fractions obtained.

Fraction I - Identical with benzene

II - λ max= 242, 248, 254, 260, 267, 279 mμ

III - λmax = 248, 260, 261.5, 264.7, 268.3, 277 mμ

IV - λmax = 243 mμ, weak 277, 298

Fraction III was redistilled through a small column (helices) into fractions IIIa, IIIb, IIIc.

The ultraviolet spectrum of fraction IIIb was very nearly identical with that of toluene, the only difference being an additional weak absorption at λmax 248 mμ.

Run II:

An excess of diazomethane ($\approx 45 \times 10^{-3}$ moles) in ether was added, with rapid stirring under nitrogen, to (9.1×10^{-3} m, 2.21g) triphenylboron in 100 ml ether. Thirty ml. of 30% hydrogen peroxide was then added and the reaction stirred over night. The ether was then extracted with 75 ml of water and treated with lithium aluminum hydride until the ether no longer gave a peroxide test.

The ether was then extracted with 75 ml. of concentrated sodium hydroxide solution, and dried. Removal of the ether by distillation left a residue of 0.3 g. Vacuum distillation of the residue yielded 0.201 g. of benzyl alcohol. The infrared spectrum of the product and the spectrum of its phenylurethan derivative, M. p. 74°, were identical with spectra of known samples.

The solid residue left from the vacuum distillation showed an ultraviolet maximum at 246 mμ. Chromatography on alumina gave a waxy crystalline polymer whose infrared spectrum, λmax 3050 w, 2940 s, 2870 m, 1590 w, 1480 m, and 690 s (cm^{-1}) and ultraviolet spectrum, λmax 244 mμ would seem to indicate a polymer with ($\phi - \overset{O}{\overset{\|}{C}}$) end groups - or else contamination with very small amounts of benzaldehyde. Benzaldehyde has a strong band at 244 mμ.

Tri-1-naphthylboron and diazomethane:

Diazomethane (2×10^{-2} moles) in anhydrous ether was added under nitrogen to 8 grams (2×10^{-2} moles) of tri-1-naphthylboron. The reaction proceeded with very rapid evolution of nitrogen and formation of polymer. The products were oxidized with 30% hydrogen peroxide, the ether then freed of peroxide and distilled off. Vacuum distillation of the residue did not yield any of the expected 1-naphthylmethanol. Chromatography on alumina of the residue and elution with hexane gave a low molecular wt. hexane-soluble polymer whose infrared spectrum in carbon tetrachloride showed only $-CH_2-$ absorption. The ultraviolet spectrum in methylcyclohexane, conc. = 160 mg/liter, however, showed the presence of 1-naphthyl end groups when compared with the spectra of 1-ethylnaphthalene (7), 1,2-di-1-naphthylethane (8) and 1-methylnaphthalene in isooctane.

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(7) Ramart-Lucus, Bull. Soc. Chim. France 19, 424, 1952.

(8) R. Adams and E. Kirkpatrick, JACS 60 2180 (1938)

TABLE 2

Compound	λ max	ϵ	λ max	ϵ	λ max	ϵ	λ max	ϵ	λ max	ϵ	λ max	ϵ
Polymer [a]	313	(0.32[a])[b]	294	1.57[a]	289	1.50[a]	283	1.81[a]	273	1.47[a]	225	15.95[a]
α-naphthylethane	316	3.2×10^2	293	4×10^3	-	-	282	6×10^3	272	5×10^3	263	4×10^3
1,2-di(α-naphthyl) ethane [c]	315	10^3	305	10^3	295	10^4	282	10^4	---		---	
α-methylnaphthalene	314	3.2×10^2	293	b	288	b	282	5.2×10^3	272	5.1×10^3	225	27×10^3

a. optical density for polymer

b. a shoulder

c. In dioxane

The insoluble polymer from the reaction of diazomethane and tri-1-naphthylboron was washed with water, acetone, and dried. The infrared spectrum in a KBr disk had bands characteristic of 1-naphthyl end groups[9] at 778 and 790 cm $^{-1}$, other bands at 2930, 2850, 1465, 732, 720 are characteristic of $(CH_2)_4$. There was no other absorption. The polymer was then placed in a Soxhlet extractor and extracted with chloroform for 24 hours. After this time the spectrum of the remaining polymer showed no changes in position or intensity of the bands. Evaporation of the chloroform gave a small amount of hexane-soluble polymer. The infrared spectrum of this polymer, λ max 2930, 2850, 1730, 1460, 795, 776, 730, and 720 cm^{-1} showed a strong relative increase in the 776, 795 bands as compared to the $(CH_2)_4$ maximum at 720 cm^{-1}.

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(9) R. L. Werner et al., Australian J. Chem. 8 346 (1955)

Reaction of ϕ_3B and ϕ_2CN_2:

Triphenylboron (2.28g, 9.4 X 10^{-3} moles) and diphenyldiazomethane in 400 ml of ether were stirred under a nitrogen atmosphere for 12 hours. After this time approximately 200 ml of nitrogen had been evolved and the purple color of ϕ_2CN_2 had been replaced with an orange color. Twenty ml of H_2O_2 (30%) was added to the reaction and allowed to stand overnight. Filtration gave 2.7g of azine. The ether was removed and replaced with 30 ml of hexane. Filtration of this gave an additional gram of azine. Total yield of azine 3.7g, m.p. 162°. Evaporation of the hexane gave 4.5 g of a black tar.

Chromatography of the black tar on alumina gave triphenylmethane, m. p. 92° , yield 0.40g, 1.6 X 10^{-3} moles and triphenylcarbinol, m. p. 162°, yield 0.16g, 0.6 X 10^{-3} moles. The infrared spectra of these products were identical with those of known samples. The combined yield $\phi_3CH + \phi_3$ COH is 23%.

Reaction of Phenylboronic Acid Anhydride and Diphenyldiazomethane

To a refluxing solution of 0.755g (6.52 X 10^{-3}m) of phenylboronic anhydride (m.p. 216.5° - 217°) under nitrogen was added 1.4g of ϕ_2CN_2 dissolved in 100 ml of hot toluene.

There was a very rapid evolution of nitrogen and disappearance of color. Concentrated hydrochloric acid was added (75 ml), and the solution refluxed for 45 minutes. The two-phase solution was cooled and filtered, 30 mg of boric acid being collected. The toluene layer was separated, after washing with water, and on standing overnight gave another 40 mg of boric acid. Evaporation of the aqueous portion gave further boric acid, making the total 0.22 g, or 3.6 X 10^{-3} moles.

The toluene solution was concentrated to 5-8 ml and chromatographed on an alumina column to give triphenylmethane, m.p. 92 ° , yield 0.22 g, 0.91 X 10^{-3}m, triphenylcarbinol, m.p. 161°, yield 0.41g, 1.6 X 10^{-3} moles, (combined % yield = 40%) and ϕ_2C = O, 0.61g.

Paratolylboronic Anhydride and Diphenyldiazomethane:

The product from the reaction of 1.41g of ϕ_2CN_2 and 0.606g (3.8 X 10^{-3}m) of paratolylboronic anhydride in toluene under nitrogen was hydrolyzed with HCl and chromatographed. Diphenylparatolylmethane (0.34g, 1.3 moles, 34% yld.) was identified by comparison of its infrared spectrum with that of an authentic sample. Diphenyl carbinol (.05g) was also isolated. The diphenyl carbinol probably arises from a small amount of boronic acid present.

Photolysis of Tri-1-naphthylboron:

Run I

A solution of 1.16g of tri-1-naphthylboron in 20ml of toluene was irradiated in a "Vicor" tube with an ultraviolet lamp for three days. During this time a steady flow of nitrogen was bubbled through the solution.

Fractional crystallization from toluene and hexane gave .024g (0.14×10^{-3} moles) of naphthylboronic acid, 0.16g recovered tri-1-naphthylboron, and 0.121g of dinaphthyl borinic acid (m.p. 115°-116° % C 84.7 % H 5.33). Chromatography of the residue from the mother liquors, 0.71g of a mixture of naphthalene and borinic acid, gave .0126 grams of naphthalene.

Photolysis in Carbontetrachloride:

Run II

A sealed degassed ampule containing 1.07g of tri-1-naphthylboron in 20 ml of carbon tetrachloride was irradiated for 12 hours with light from an AH-6 Hg arc lamp, using a filter of λmax 355 mμ and 0% T<300 mμ and >400 mμ.

Exposure of the photolysized solution to moist air resulted in fuming and production of hydrogen chloride gas.

A five ml sample of the carbon tetrachloride solution was evaporated to dryness and the crude tarry product taken up in hexane. On standing the mixture precipitated naphthylboronic acid, which was filtered off. The hexane mother liquor was evaporated to a few drops and put through a silicone grease-on-firebrick V.P.C. column. Three peaks were obtained at 170°, flow 30cc/min. These were identified by comparison of retention times and infrared spectra as hexachloroethane, naphthalene, and 1-chloronaphthalene.

Run III

Spectrograde carbontetrachloride, 49 ml, was distilled from P_2O_5 into an ampule containing 3.0g of tri-1-naphthylboron.

This sample was irradiated with U. V. light, λmax 355 mμ, from an AH-6 mercury arc lamp. Vapor phase chromatography as previously described gave a yield of 21 mg of hexachloroethane. The presence of unreacted trinaphthylboron obscured the detection of naphthalene or chloronaphthalene. Ten ml of water was injected into the sample through a syringe cap and after shaking for 15 minutes the ampule was opened to the air. A precipitate of 0.11 grams of phenylboronic anhydride was immediately filtered off. The aqueous layer after separation was strongly acidic and gave a positive test for chloride ion.

The carbon tetrachloride solution was separately extracted with water over a period of several days and continued to give positive tests for chloride ion. The combined aqueous extracts gave 0.798 grams of silver chloride, or 5.6×10^{-3} moles.

Extraction of the carbon tetrachloride solution with dilute potassium hydroxide gave 0.10g of a dark brown precipitate ($KOB[\alpha C_{10}H_2]_2$) and an aqueous solution which on reacidification and chloroform extraction yielded 0.2g of a mixture of naphthalene boronic anhydride and α naphthol.

Run IV

Sample identical to that used in Run II was photolyzed for two days in sunlight. The carbon tetrachloride solution was swept out with nitrogen. The nitrogen stream then gave a positive boron flame test, and after passing

through a solution of methanol, caused the methanol solution also to give a positive flame test, attributed to the formation of methyl borate from boron trichloride.

Oxidation of the sample by air, followed by hydrolysis, resulted in the formation of phosgene, detected with a Prägerwerk Lubeck Gas detector model 19/31. The phosgene was swept with air through an Et_2O solution of aniline with the resultant formation of phenylurea, m.p. 235°.

Sodium Tetraphenylboron and NaN_3:

Sodium tetraphenylboron (0.5g) and sodium azide(0.11g) were refluxed for 12 hours in 10 ml of water. At the end of this time two phases were evident. Distillation to dryness gave a distillate whose u. v. spectrum was identical to that of benzene in water.

The residue from the distillation did not give a green flame test, burn, or melt, but decomposed explosively in a flame. An u. v. spectrum was blank to 210 mμ.

The residue on solution in dilute hydrochloric acid and evaporation to dryness to remove azide ion now melted to give a borax bead and on addition of H_2SO_4 and EtOH gave a green flame test. An u.v. spectrum of the material was blank to 210 mμ. This characterizes $B(OH)_3$.

Control 1.0g of $Na\phi_4B$ was refluxed for a day in 40 ml of slightly basic water. At the end of this time the solution still gave a voluminous white ppt. with NH_4OH, showing presence of (ϕ_4B^-). Distillation gave no benzene detectable in the distillate by u.v. spectra. A second control experiment using an equal ionic strength of NaCl in place of the NaN_3 showed that the effect of the NaN_3 is merely a salt effect.

Phenylboronic Acid and Hydrazoic Acid

Phenylboronic acid (or more probably the anhydride), 1.0g (10^{-2}moles), was dissolved in 30 ml of $CHCl_3$ and 7 ml of conc. H_2SO_4. To this was added 1.30g (2 X 10^{-2}m) of sodium azide and the reaction was stirred at room temperature for a day.

After a day 25 ml of H_2O was added, the aqueous phase separated, made basic with sodium hydroxide, and extracted with ether. The ether on evaporation gave 0.055g of an oil whose spectrum was identical to that of aniline. Distillation of the $CHCl_3$ gave 0.61g (7.9 X 10^{-3}moles) of benzene, determined by u.v. spectroscopy.

One ml of benzene (0.78g) (10^{-2} moles) in a control experiment under the same conditions also gave aniline.

Sodium Tetraphenylboron and Hydrazoic Acid:

Sodium tetraphenylboron (0.7g, 2 X 10^{-3}moles) and sodium azide (0.65g, 10^{-2}moles) were dissolved in 50 ml of 0.1 N hydrochloric acid and allowed to stand overnight at room temperature with stirring. The next day the solution was a clear yellow, The solution was made basic to litmus and extracted with $CHCl_3$.

Distillation of the $CHCl_3$ gave an oily residue whose infrared spectrum showed an azide band. The oil was redissolved in ether, washed repeatedly with water, the ether solution dried and again evaporated to dryness. A small drop of the same oil was obtained. The infrared spectrum had strong peaks at 2140 cm^{-1}, 1600 cm^{-1}, 1490 cm^{-1}, and 1290 cm^{-1}, corresponding to peaks in the spectrum of phenyl azide.

The oil could not be induced to form an adduct by mixing with a drop of dicyclopentadiene. However, it was much decomposed by this time.

The ultraviolet spectrum of the $CHCl_3$ distillate from the above shows the presence of benzene. The spectrum of the aqueous solution after extraction (λ max = 266 mμ) is very similar to that of $\phi B(OH)_2$ (λ max 266 mμ).

Ultraviolet Spectra:

All spectra were done on the Cary model 11 recording spectrophotometer. In the case of ϕ_3B and $(pCH_3\phi)_3$ B, the solutions were prepared under nitrogen, and the u.v. cells loaded and sealed under nitrogen.

Compound: $(\alpha C_{10}H_7)_3$ B, m.p. 205°-206°

Solvent: methylcyclohexane

conc.: 3×10^{-4} molar

Path length: 1 mm.

λ max	O. D.	ϵ
3526 Å	0.566	1.9×10^{-1}
2888 Å	0.277	9.4×10^{3}
2638 Å	0.577	1.92×10^{4}
2214 Å	4.43	1.5×10^{5}

Sample: Same as above with ammonia bubbled through, $(\alpha\text{-}C_{10}H_7)_3$ BNH_3.

Path	λ max	O. D.	ϵ
1 mm	3215	.092	3.1×10^{2}
1 mm	2891	0.773	2.6×10^{4}
0.1 mm	2282	0.498	1.7×10^{5}

Compound $(\alpha\text{-}C_{10}H_7)_3B$

Solvent: CH_3CN

Conc: 1.3 mg in 150 ml, path 1 cm.

λ max	O. D.	ϵ
3775	0.31	0.40×10^4
3200	0.34	0.44×10^4
2850	1.9	2.5×10^4
2562	1.0	1.3×10^4

Compound ϕ_3B, m.p. 146-147°

Solvent: methylcyclohexane

Conc: 5.7×10^{-4} molar, Path- 0.1 mm

λ max	O. D.	ϵ
2871 Å	0.223	1.9×10^4
2757 Å	0.198	3.5×10^4
2380 Å	0.108	1.9×10^4

Same as above, NH_3 (dry) bubbled through sample; path length 1 cm

λ max	O. D.	ϵ
2720	0.82	1.4×10^3
2630	1.08	1.9×10^3
2570	0.87	1.5×10^3
2480	0.82	1.4×10^3

ϕ_3B in CH_3CN; solution prepared, and cells loaded, in nitrogen box. Only end absorption below 230 mμ.

Tritolylboron, m.p. 149.5° - 151°

Solvent: methylcyclohexane

Conc.: 2×10^{-4} molar, path 1mm

λ max	O. D.	ϵ
2966 Å	0.66	3.3×10^4
2820	0.38	1.9×10^4
2490	0.41	2.0×10^4
2350	0.31	1.5×10^4

Addition of triethylamine caused the disappearance of the C. T. band, 2966 Å.

Trimesitylboron, m.p. 190.5°- 191.5°

Solvent: Methylcyclohexane

Conc: 1.84 mg. /50 ml

Path: 1 mm

Max	O. D.	ϵ
3310 Å	0.61	1.5×10^4
2830 (shoulder)	(0.11)	
2470 (shoulder)	(0.27)	

The spectrum in acetonitrile is identical.

Tri-α-naphthylboron and n-butylazide:

Tri-α-naphthylboron (4g, 10^{-2} moles) and 1.8 ml of n-butyl azide (1.6×10^{-2}m) in 30 ml of chlorobenzene were heated in a sealed, degassed ampule for $2\frac{1}{2}$ days at 150°.

Addition of 5 ml of hexane to the ØCl solution and storage in a refrigerator for 2 days gave back 3g of $(\alpha C_{10}H_7)_3B$. Vacuum distillation of the mother liquor gave a solid crystalline mass whose infrared spectrum was that of a mixture of $(\alpha Cl_{10}H_7)_3B$ and $(\alpha C_{10}H_7)B(OH)_2$.

Tri-α-naphthylboron and Aluminum Azide:

One gram of $(\alpha C_{10}H_7)_3B$ and two moles of $Al(N_3)_3$ generated in situ from $AlCl_3$ and NaN_3 were refluxed in tetrahydrofuran for 24 hours.

The solid residue after distillation of the THF and washing with ether gave only tri-α-naphthylboron.

Tri-α-naphthylboron and Triphenylmethylazide:

Tri-α-naphthylboron (2.0g) and triphenylmethyl azide (1.7g) were refluxed overnight in tetralin under nitrogen. The tetralin was removed by vacuum distillation and the residue chromatographed on alumina.

The products isolated and identified by infrared spectra were benzophenone anil (1.06g), m.p. 112°, α-naphthol (0.147g), and α-naphthylboronic acid (1.39g). The spectra of these compounds were identical in every respect to those of known samples.

Tri-α-naphthylboron and Ethylene Glycol

Tri-α-naphthylboron (1.00g) was refluxed in 25 ml of $HOCH_2CH_2OH$ for 10 minutes. The ethylene glycol was diluted with 25 ml of water and extracted twice with 30 ml of hexane and twice with 30 ml of benzene. The extracts were combined, dried, and evaporated to dryness to give 0.8g of white crystalline material.

This material was chromatographed on alumina to give naphthalene (0.42g), α-naphthylboronic acid m.p. 205°(vac.), and a third white crystalline material which melted 146-149° (crude). Repeated recrystallization of the latter substance from EtOH gave α-naphthylboronic acid.

An infrared spectrum of the material melting at 146-149° showed bands at 3.4 μ, 3.5 μ and 6.9 μ characteristic of $-CH_2-$. The compound is probably an ethylene glycol ester of α-naphthylboronic acid.

In a second experiment 1.0 grams of $(\alpha C_{10}H_7)_3B$ was refluxed under N_2 in 35 ml of $HOCH_2CH_2OH$ for 6 hours. 0.7 grams of naphthalene was isolated.

Tri-α-naphthylboron-phenylhydrazine complex:

Tri-α-naphthylboron (2.0g) and phenylhydrazine (0.552g) (1:1 mole ratio) were refluxed under nitrogen in 30 ml of toluene for 7 hours. The toluene was evaporated to about 15 ml by a stream of nitrogen. White crystals were collected and washed once with cold toluene; m.p. 122.5°-123.5°.

Part II. The Fluorenyl-Nitrogen System

In an attempt at synthesizing the nitrogen analog (I) of Koelsch's free radical (II)[10], we prepared compound (III)[11] as a precursor. We also prepared the alleged tetrafluorenyl hydrazine (IV) by the methods

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(10) Koelsch, J. Am. Chem Society 79 4439 (1957)

(11) Ingold and Wilson, J. Chem. Soc. 1933 1493

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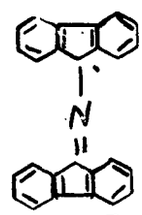
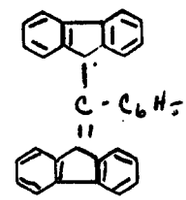
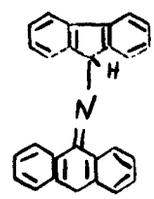
in the literature.[12] [13] These consist of autoxidizing or photo-oxidising 9-fluorenyl amine.



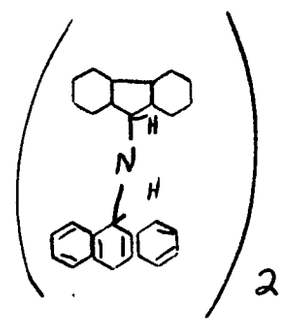
I



II



III



IV

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(12) Goldschmidt and Reichel, Ann. 456 152 (1927)

(13) Chu and Weismann, J. Am. Chem. Soc. 76 3787 (1954)

The product reported in the literature as IV proved to be III.[14] The temperature and concentration-dependent color changes of the alleged

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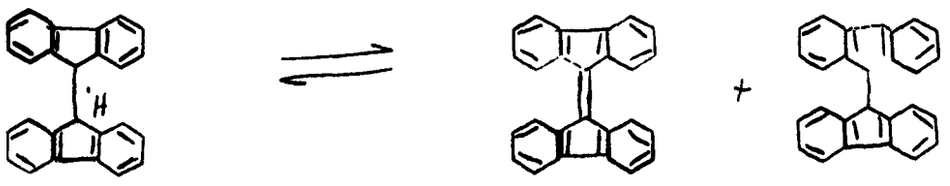
14. Infra-red, n m r, mixed melting point, cryoscopic molecular weight in benzene.

"IV" are apparently due to impurities. Compound III, prepared by either route, contains a free radical, the same in either case. This radical is detected by its ESR signal, figure 3 . The radical is removable by crystallization, chromatography or by boiling in alcohol. It seems to be fairly stable in solution at room temperature, even when exposed to air, although we have not been able to isolate a pure sample. Some concentration of the radical can be achieved by extration with ether, then extracting the extracted material with benzene. The fine structure of the ESR spectrum would seem to preclude I as the radical, since I should be a triplet. Structure V should have the observed doublet with hyperfine splitting, but it is hard to see why V would not rapidly disporportionate as in equation (V).

The Schiff's base prepared from fluorenone and benzhydryl amine also contains a free radical by-product, but in too low a concentration to permit resolution of the finestructure. It is not the same radical as that found in the other Schiff's base, however, since its ESR signal occurs at a different field strength. The Schiff's base prepared from benzophenone and benzhydrylamine gives no signal at all.

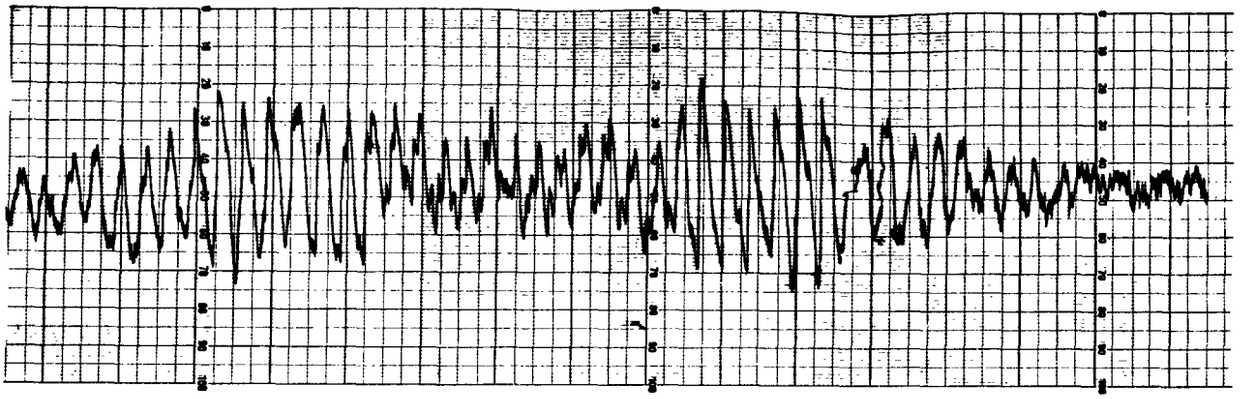
The Koelsch radical (II) did not show resolvable fine structure.

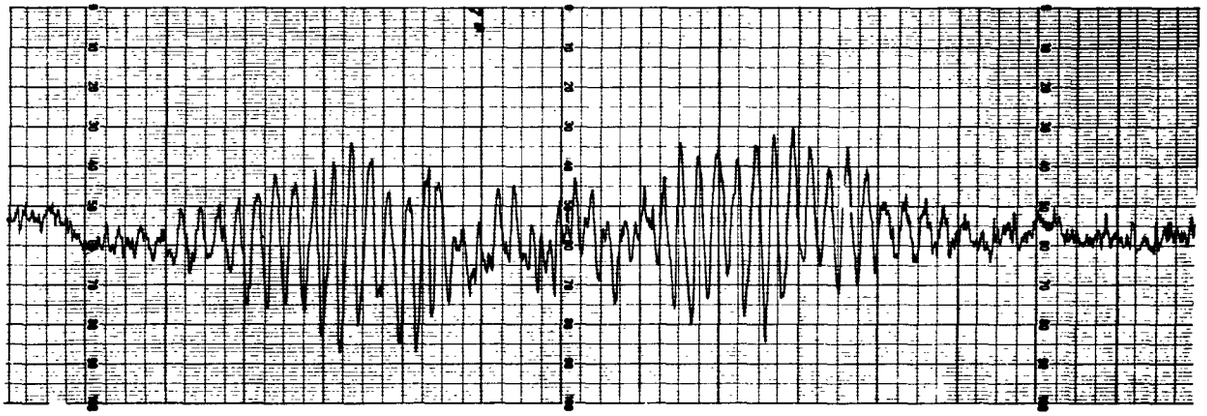


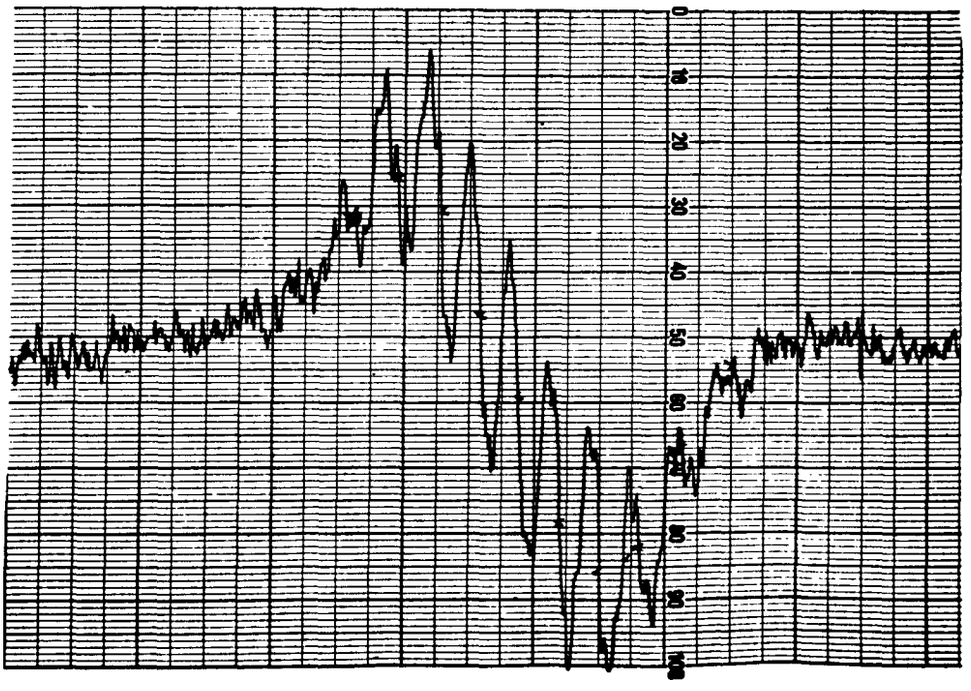
Equation V

Figure 3

ESR Spectra of the Radical from III in benzene at 25° (upper curve), in pyridine at 17°C (middle curve) and in pyridine at 100° (bottom curve).







PART III. THE CHEMISTRY OF PHOSPHINE-AZIDE COMPLEXES

For the acid-catalyzed decomposition of the triphenylphosphine-trityl azide complex, see Technical Report No. 2 or J. E. Leffler, U. Honsberg, Y. Tsuno and I. Forsblad, J. Org. Chem 26 4810 (1961). Work on other phosphine-azide complexes is described here.

Introduction

Tertiary phosphines react with covalent azides either to give stable complexes, isolable but unstable complexes, or nitrogen and phosphine-imines.(15)

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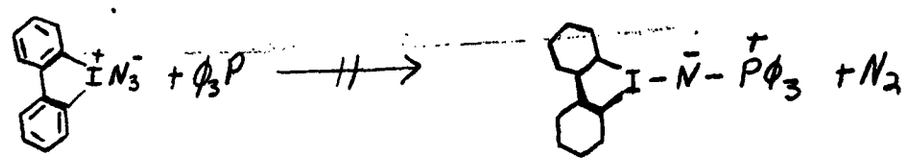
(15) (a) H. Staudinger and E. Hauser, Helv. Chim. Acta, 4 861 (1921)

(b) H. Staudinger and I. Meyer, Helv. Chim. Acta, 2 635 (1919)

(c) L. Horner and A. Gross, Ann. 591 117 (1955)

$$R\text{-}N_3 + R'_3P \longrightarrow [R\text{-}N{=}N\text{-}\bar{N}\text{-}\overset{+}{P}\text{-}R'_3] \longrightarrow N_2 + R\text{-}\bar{N}\text{-}\overset{+}{P}R'_3$$

Ionic azi es, for example, biphenylene iodonium azide, do not give the reaction.



Reaction of Triphenylphosphine with Substituted Benzazides

The rate at 25°, determined by nitrogen evolution, follows the second order law. The second order rate constants (Table 3) are independent of changes in the initial concentration of the reagents. The rate of decomposition of the azide at 25° in the absence of triphenyphosphine is entirely negligible.

There is a small solvent effect on the rate, $CHCl_3$ being faster than benzene and 10% acetic acid in benzene also being slightly faster than benzene (see Table 3).

In contrast to the decomposition of the triphenylphosphine-trityl azide complex[16] and with the decomposition of the azides alone,[17] this reaction does not seem to be acid-catalyzed.

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(16) J. E. Leffler, U. Honsberg, Y. Tsuno and I. Forsblad, J. Org. Chem 26 4810 (1961)

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(17) Y. Yukawa and Y. Tsuno JACS 81 2007 (1959)

The substituent effect on the rate is correlated with σ [18] as shown in Figure 4, electron-withdrawing substituents accelerating and electron-donating substituents decelerating the reaction. The value of ρ is +0.78.

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(18) The sigma values are taken from D. H. McDaniel and H. C. Brown, J. Org. Chem. 23 420 (1955) and are primary sigma values, that is, they are based directly on benzoic acid ionization in water.

Table 3

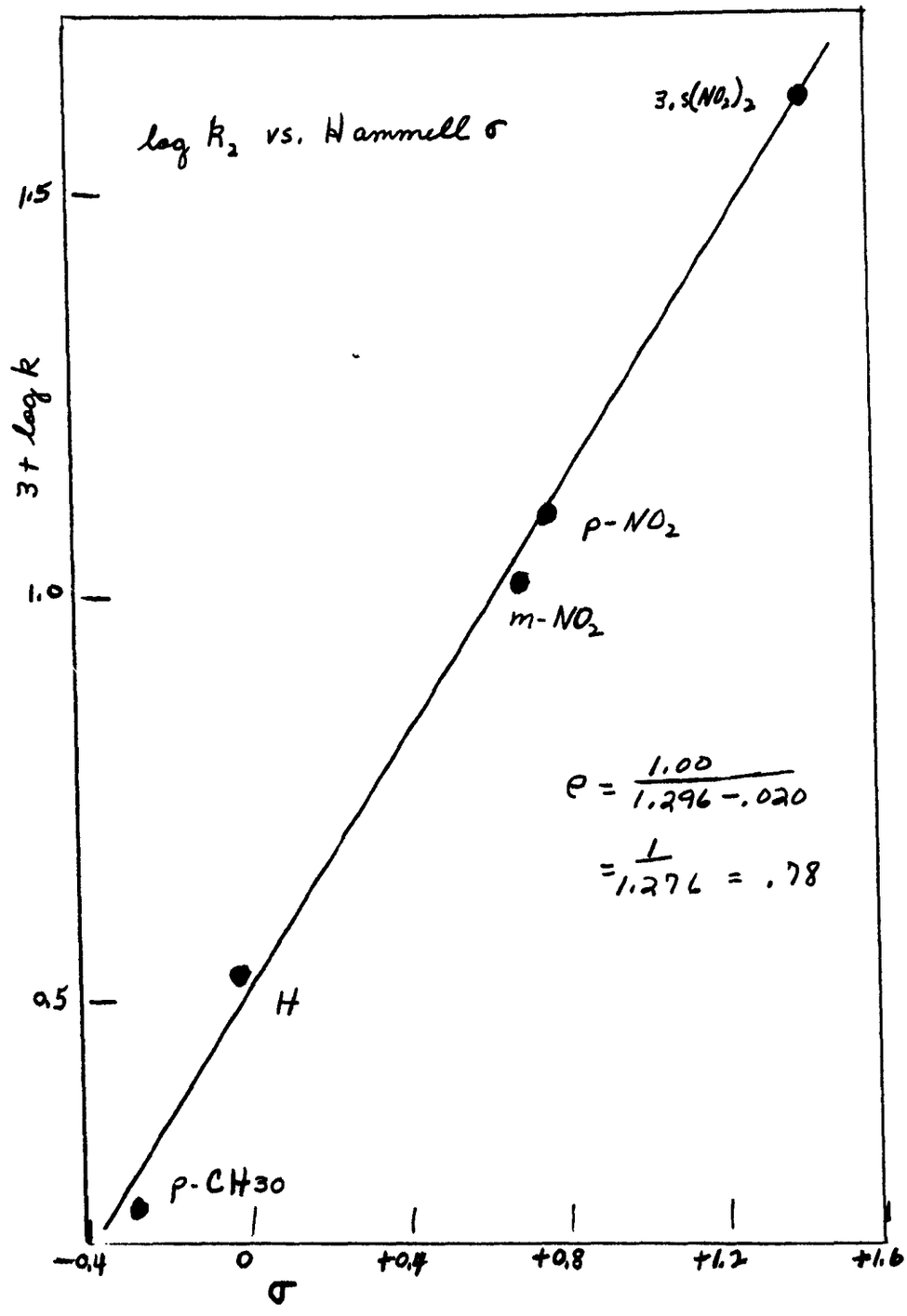
THE RATE OF THE REACTION OF SUBSTITUTED BENZAZIDES WITH TRIPHENYLPHOSPHINE IN BENZENE AT 25.00°

Y.T. Notebook Page	Subst.	Initial Conc. M/L [Azide]₀	Initial Conc. M/L [Ph_3P]₀	k_2 X 10^2 L/M sec.
200	H	0.0491	0.0491	0.333 ± 0.003
202		.0488	.0494	.345 ± .008
204		.0487	.0970	.313 ± .006
208		.0470	.1856	.339
206		.0472	.1886	.330 ± .006
210		.0238	.1903	.286 ± .005
212		.0983	.0493	.330 ± .002
			av.	.332
220	p-CH_3O	.0493	.0494	.167
222		.0485	.1462	.170
224		.0454	.3637	.171
			av.	.170
230	p-NO_2	.0467	.0490	1.235
234		.0450	.0970	1.20
232		.0459	.1441	1.20
			av.	1.21
240	m-NO_2	.0481	.0490	0.970
238		.0479	.1473	1.018
			av.	1.00
244	3,5-$(NO_2)_2$	.0330	.0330	4.04 ± .03
246		.0488	.0487	3.96 ± .02
			av.	4.00

Page	Subst.	Initial Conc. M/L		k_2 X 10^2 m/l.sec.
		[Azide]$_o$	[Ph_3P]$_o$	
214	H (in $CHCl_3$)	.0487	.0970	.678
216	H **	.0487	.0971	.413
226	p-$CHO_3\phi$ **	.0492	.0492	.267

** In Acetic acid 10 ml and benzene 90 ml

Figure 4


log k_2 vs. Hammett σ
3,5-$(NO_2)_2$
p-NO_2
m-NO_2
H
p-CH_3O
$\rho = \frac{1.00}{1.296 - .020}$
$= \frac{1}{1.276} = .78$
3 + log k
1.5
1.0
0.5
−0.4
0
+0.4
+0.8
+1.2
+1.6
σ

There are marked contrasts between substituent effects on the decomposition of benzazides alone and on their reaction with triphenylphosphine. The substituent effects in the former reactions are the net result of counteractive and linearly correlated changes in the enthalpy and entropy of activation.[19] The direction of the effect on the rate is determined by

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(19) Y. Yukawa and Y. Tsuno, JACS 79 5530 (1957)

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the enthalpy changes. Both meta and para substituents give points on a single enthalpy-entropy or isokinetic line. The sequence of meta points on the line, and the corresponding rates, is correlated with σ . The value of ρ is -0.33. The sequence of para points on the line, and their rates, is <u>not</u> correlated with σ . Apparently any para substituent capable of resonance decreases the rate, regardless of its electron-releasing or electron-withdrawing nature. In the present reaction both meta and para substituent effects are correlated with σ . The rate of the former reaction is considerably accelerated by increases in the polarity of the solvent, while the present reaction is relatively insensitive to such changes.

The behavior of para substituents in the decomposition of azides in the absence of triphenylphosphines is unexpected and difficult to explain. It also differs from the behavior of substituents in the rearrangement of diazoketones. We will not attempt to discuss the mechanism of the azide decomposition here except to note that it obviously differs from that on the present reaction.

A mechanism for the present reaction in accord with the available data is as follows:

$$X\phi-\overset{\overset{O}{\|}}{C}-N_3 + \phi_3P \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X-\phi-\overset{\overset{O}{\|}}{C}-\bar{N}-N=\overset{+}{N}-P\phi_3$$

$$X-\phi-\overset{\overset{O}{\|}}{C}-\bar{N}-N=\overset{+}{N}-P\phi_3 \xrightarrow{k_2} X-\phi-\overset{\overset{O}{\|}}{C}-\bar{N}-\overset{+}{P}\phi_3 + N_2$$

The rate would follow a second order law if step 1, foreward, were rate-determining and k_2 were fast. Since both the azide and the complex (or transition state of structure resembling the complex) have about the same degree of polarity, no very large medium effect is to be expected. Electron-withdrawing substituents should increase the rate of reaction with triphenylphosphine by stabilizing transition state structures having a formal negative charge on the N adjacent to the carbonyl; para substituents should not be exceptional in their behavior since no special resonance interaction is foreseen. Further tests of the mechanism would be desirable, including a nitrogen isotope experiment and an attempt to convert to first order kinetics, step 2 rate-determining. The latter effect might be expected in the presence of very strong electron-withdrawing substituents on the azide, since such substituents should increase K and decrease k_2. Examining the data for the 3,5-dinitro-substituted azide, we find that the reaction is still quite precisely second order. However, the reaction between benzenesulfonyl azide and triphenylphosphine does follow first order kinetics.

The Reaction of Benzenesulfonyl Azide with Triphenylphosphine in Benzene

The reaction of benzenesulfonylazide with triphenylphosphine in benzene is first order with respect to the concentration of the complex. Since the complex is almost entirely associated in benzene solution, the rate is simply proportional to the nominal concentration of whichever reagent is not in excess. The products are nitrogen and the phosphine-imine, quantitatively.

$$\phi SO_2N_3 + \phi_3P \rightleftharpoons \phi SO_2\bar{N}-N=N-\overset{+}{P}\phi_3$$

$$\phi SO_2\bar{N}-N=N-\overset{+}{P}\phi_3 \xrightarrow{k_1} \phi SO_2\bar{N}-\overset{+}{P}\phi_3 + N_2$$

m.p. 152-4°

Table 4 shows the rate constants obtained by the nitrogen evolution method.

Table 4

REACTION OF BENZENESULFONYL AZIDE WITH TRIPHENYLPHOSPHINE IN BENZENE AT 25.00°

Initial Conc. M/L $[Azide]_o$	$[Ph_3P]_o$	$k_1 \times 10^3$ sec.
.0502	.0501	1.02[a]
.0496	.0500	1.02[a]
.0500	.0500	ca.0.8
.0500	.0505	slow
.0500	.1000	1.00[b]
.1003	.0500	1.01[b]
.0502	.2003	1.02[a]

(a) With stirring

(b) With boiling tips

In two runs not shown in Table 4 the reaction was considerably slower, k_1 decreased during the run, and a precipitate appeared. The complex is quite insoluble in benzene at 25°, but remains in supersaturated solution in the runs having good first-order kinetics.

Thus the reaction of benzenesulfonyl azide with triphenylphosphine in benzene behaved as anticipated. The reaction in more polar solvents is quite different, however.

The Reaction of Benzenesulfonyl Azide with Triphenylphosphine in Chloroform and in Polar Solvents

Experiments in solvents other than benzene used both the complex and the azide and phosphine added separately. The solid complex is light yellow, melts at 87-88° with gas evolution, and has no 2130cm^{-1} azide band (Nujol mull).

Solutions of the complex in chloroform show the 2130cm^{-1} azide band steadily increasing in intensity for the first 45 min. after which the intensity becomes constant. During the same period, nitrogen is evolved but the yield never becomes quantitative. The nitrogen yield can be raised from its usual 60% to about 97% by adding 1 mole excess triphenylphosphine after nitrogen evolution has stopped.(20) The missing nitrogen is therefore present as a covalent azide.

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(20) If the 1 mole excess ϕ_3P is present from the beginning, the yield of N_2 is not affected. If 2 moles excess ϕ_3P is present from the beginning, the N_2 yield is raised only to 82%.

The products in chloroform are ϕSO_2NH_2 (which precipitates out), and ϕ_3PO (isolated by chromatography on alumina). The infrared spectrum of the $CHCl_3$ solution after N_2 evolution has ceased can be accounted for by assuming a mixture of ϕSO_2N_3, ϕSO_2NH_2 and ϕ_3PO. The spectrum does not suffice to rule

out the presence of $\phi_3PNSO_2\phi$, but it is not isolated. A control experiment shows that $\phi_3PNSO_2\phi$ (from the reaction in benzene) is easily isolated and is recovered quantitatively from an alumina column.

The initial zeroth order rates of N_2 evolution in chloroform are reproducible within about 10 per cent, but conform to no simple reaction order. Excess ϕ_3P seems to have no effect on the rate; excess ϕSO_2N_3 increases it. Acetic acid increases both the N_2 yield and rate, but a more polar solvent (DMF or nitrobenzene in place of the $CHCl_3$) decreases both the N_2 yield and the rate. At present we have no explanation of this behavior, except that some side reaction is consuming ϕ_3P. Whatever that reaction may be, it is not able to compete in the presence of $\phi\overset{O}{\overset{\|}{C}}N_3$. The decomposition of $\phi_3PN_3SO_2\phi$ in the presence of $\phi\overset{O}{\overset{\|}{C}}N_3$ gives 96.7% of the N_2 expected from the reaction below:

$$\phi_3PN_3SO_2\phi \rightleftharpoons \phi_3P + \phi SO_2N_3$$

$$\phi_3P + \phi\text{-}\overset{O}{\overset{\|}{C}}\text{-}N_3 \longrightarrow \phi_3PN\overset{O}{\overset{\|}{C}}\phi + N_2$$

Free radical reactions of ϕSO_2N_3 have been noted by Takebayashi[21]. A free radical $\phi_3P^{\dagger}$ derived from ϕ_3P has been postulated by Bartlett[22].

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(21) M. Takebayashi, private communication. $ArS\cdot + \phi SO_2N_3 \longrightarrow ArS\text{-}\overset{\cdot}{N}SO_2\phi + N_2$

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(22) P. D. Bartlett, E. F. Cox and R. E. Davis, JACS 83 103 (1961)

IV. The Decomposition of o-Substututed Benzazides and Benzenesulfonazides

The free radical decomposition of benzoyl peroxide and of t-butyl perbenzoates is very much accelerated by certain o-substituents.[23] [24] This is not the usual steric effect, but a concerted reaction involving a cyclic transition state, and, in the case of o-iodobenzoyl peroxide, leading to a cyclic product[23].

(23) J. E. Leffler, R. D. Faulkner and C. C. Petrupoulos, JACS 80 5435 (1958)

(24) J. C. Martin and E. H. Drew, JACS 83 1232 (1961)

Benzazides

Similarly, the o-hydroxyl substituent decelerates the decomposition of benzazide in marked contrast to the acceleration by other ortho substituents.[25]

(25) Y. Yukawa and Y. Tsuno, JACS 80 6346 (1958)

The usual accelerative effect is attributed to steric inhibition of resonance in the ground state of the o-substituted benzazide. The deceleration by the o-hydroxyl substituent is attributed to intramolecular hydrogen bonding with the azide group. No special effects were noted for ortho methyl, bromo, chloro or nitro, the points for all of which fall on a single isokinetic line.[25]

In previous work in this laboratory, we have shown that the benzazide rearrangement still gives the usual isocyanate in the presence of an ortho-iodo substituent. In the present work we show that the reaction rate is also normal and that there is no indication of iodine-nitrogen bonding in the transition state. Table 5 shows the rates of decomposition (by nitrogen evolution) for various o-substituted benzazides.

Table 5

Benzazide Decomposition in Toluene

Substituent	Temp.	$k_1 \times 10^2 (min^{-1})$
o-Cl[a]	44.50	1.87
o-Br[a]	45.00	2.72
o-I [b]	46.0	3.10
	42.2	2.32
	43.0	2.52

[a] Reference (25)

[b] This work

Experimental

o-Iodobenzazide was obtained by the reaction of the acid chloride with NaN_3 in 50% aqueous acetone.(26)

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(26) P. A. S. Smith, Organic Reactions, Vol III, Wiley, (1946)

It melted at 29-30° and gave at least 99% of the theoretical amount of N_2 on decomposition. The rate of decomposition was determined by the nitrogen evolution method. (25)

Part V. The Decomposition of Benzenesulfonylazides

As part of our research on the intramolecular interaction of iodo-substituents with free radicals of various types, we have found acceleration and the formation of a cyclic product in the decomposition of o-iodobenzoyl peroxides[27] but not in the decomposition of o-iodophenylacetyl peroxide[28] or of o-iodobenzazide. (see Part IV)

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(27) (a) W. Honsberg and J. E. Leffler, J. Org. Chem. 26 733 (1961)

(b) J. E. Leffler, R. D. Faulkner and C. C. Petropoulos, JACS 80 5435 (1958)

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

The Curtius rearrangement of benzazides probably involves a concerted reaction and a cyclic transition state rather than a nitrene intermediate[32] and therefore formation of a cyclic iodine compound is possible only if the iodo substituent attacks the azide group in a reaction which is faster than the normal attack of the migrating phenyl on the azide group. Since the decomposition of benzenesulfonyl azides[29] apparently involves an actual intermediate nitrene or nitrogen diradical which selectively attacks solvent molecules[30], we still considered it likely that nitrogen-iodine bond formation might take place at some step in the decomposition of o-iodobenzenesulfonyl azide. To test this hypothesis it is necessary to examine the product (which proved to be normal although certain other experiments showed that cyclic nitrogen-iodine structures are capable of existence) and to compare the rate with those of other benzenesulfonyl azides. The rate also proved to be normal.

Benzenesulfonyl azide was first prepared by Curtius[29] and the

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

decomposition products in various aromatic solvents were studied by Dermer and Edmison [30]. However, no kinetic study of the decomposition has been available,

(30) O. C. Dermer and M. T. Edmison, J. Am. Chem. Soc. 77 70 (1955)

in contrast to numerous studies of the decomposition of benzazides.[31] [32]

(31) M. S. Newman, S. H. Lee, Jr. and A. B. Garrett, ibid. 69, 113 (1947)
M. S. Newman and H. V. Gildenhorn, ibid., 70, 317 (1948).
R. A. Coleman, M. S. Newman and A. B. Garrett, ibid., 76,4534 (1954).

(32) Y. Yukawa and Y. Tsuno, ibid. 79, 5530 (1957); ibid., 80, 6346 (1958); ibid., 81 2007 (1959).

Recently, we have learned that Takebayashi and Shingaki have studied the decomposition kinetically and that the decomposition was found to be accelerated by thiophenols and also by radical sources.[33].

(33) M. Takebayashi and T. Shingaki, Private communication. The authors are indebted to Prof. Takebayashi who kindly made his data available to us prior to publication.

Our own study has been extended to the decomposition in the presence of peroxides. (Part VI)

EXPERIMENTAL

Benzenesulfonyl azide The method of preparation of benzenesulfonyl azide was essentially the same as that reported by Dermer and Edmison[29] Benzenesulfonyl chloride was allowed to react with sodium azide in an aqueous alcohol or aqueous acetone solution. 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-petrol 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 (5g in 75 ml), 15g of o-nitrobenzenesulfonyl chloride dissolved in 75ml acetone was added dropwise with stirring at -10°. The stirring was then continued for one hour at this temperature and another hour at room temperature. The solution was filtered and diluted with 500ml icewater to precipitate a yellow solid, which was collected on a filter, washed with cold water and dried. The product was dissolved in 150ml of warm alcohol and insoluble material was removed. 12g of yellow needles having m.p. 68-71° was obtained on cooling. Recrystallizations 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 a Nujol mulls had a characteristic azide band at 2170 cm^{-1}.

o-Iodobenzenesulfonyl azide Seven grams of o-iodobenzenesulfonyl chloride in 20 ml ethanol was added in several portions to the cold solution of 5g sodium azide in 70 ml aqueous ethanol (30%). The solution was stirred for 2 hours at this temperature, 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, 4.5g of an almost colorless oil remained. The oil solidified at -30°, and the solid was recrystallized from ether-petrol ether solution, giving colorless needles which had a m.p. 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°.

Mixed xylene which had been purified for kinetic purposes was used without further purification.

p-Xylene was freshly prepared by refluxing the sulfur-free xylene with sodium for 20 hrs, follwed by distillation, b.p. 137-8°.

Chlorobenzene was dried over calcium chloride and distilled, b.p. 130.5-1.0°

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

Kinetic Experiments The rates of decomposition of benzenesulfonyl azides were estimated by following the rate of evolution of nitrogen. The procedure and apparatus were the same as those described previously[30][31] The temperature of the bath was maintained at 126.68 ± 0.03°. One hundred ml 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 into the bath, in order to avoid the effect of supersaturation.

The weighed amount of the azide, 0.01-0.005 moles, was poured into the flask in 10ml of the solvent. The flask was connected to the azotometer through a small condenser and a stop-cock and the reading of volume was adjusted to zero. The stop-cock 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 20 readings during subsequent two half-lives of the reaction. The infinity volume of gas was determined by the reading at the time after 8-9 half-lives of the reaction proceeded and an additional reading was made after another half-live in order to assure that no leakage of gas occurred.

Decomposition of benzenesulfonyl azide Several preliminary experiments were made and the products of rate runs were treated in a similar manner.

Benzenesulfonyl azide, 2.54g, was decomposed under reflux in 25ml p-xylene for 20 hrs. 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, 2.79g of yellow needles having m.p. within 129-38° was obtained. On recrystallization from alcohol, the substance gave 2.40g of colorless needles (m.p. 136-8°), identified as benzenesulfonyl-p-xylidide. From the alcohol eluent 0.38g of solid, m.p. 135-147°, containing some oily matter was obtained. The mixed melting point with the xylidide was depressed and showed 138-52° with benzenesulfonyl amide.

The product from 2.36g azide in chlorobenzene was separated by the chromatographic method into 0.49g of oily crystals, 1.1g of needles having m.p. 123-8° and 0.36g of plates, m.p. 114-20°. The first product gave crystals having m.p. 116-20° by the recrystallization from ether. The second was recrystallized from alcohol, giving needles m.p. 127-9°. From the third product, colorless plates having m.p. 119-21° were obtained. The first product was identified as the m-chloroanilide. The second was identified as o-chloranilide and the third as the p-chloranilide, by mixed melting points.

In one experiment, oxygen was passed into p-xylene for 22 hrs. at room temperature and 0.9232g of the azide was decomposed in this solvent. The chromatography of the product gave 0.58g of benzenesulfonyl-p-xylidide and 0.07g of oil from the benzene eluent, and a large amount of black material from the alcohol eluent.

Decomposition in nitrobenzene gave a large amount of black tar, 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 probably contains nitrogen oxide derived from the nitrobenzene.(29)

The decomposition of benzenesulfonyl azide in the presence of t-butyl hydroperoxide in p-xylene solution proceeded quantitatively and gave a colorless solution. On removing the solvent, benzenesulfonyl-p-xylidide was obtained in quantitative yield. (See Part VI)

Decomposition of o-Iodobenzenesulfonyl azide The product of the decomposition of 2.72g of the azide in mixed xylene was chromatographed and gave 0.80g of o-iodobenzenesulfonyl amide, m.p. 161-3° and small amount of crystals , m.p. 81-116°, which would be a mixture of the o-iodobenzenesulfonyl-

xylidides. A large amount of black solid was also obtained.

Decomposition of o-Nitrobenzenesulfonyl azide Two grams of o-nitrobenzenesulfonyl azide was decomposed at 130-40° in 25ml of p-xylene. The gas evolved was mixed with air and passed into a potassium iodide solution containing a small amount of acetic acid. After about one hour, the solution gradually became red. The amount of iodine liberated corresponded to 14.26ml of 1-N sodium thiosulfate solution. This may be due to nitrogen oxide.

In another experiment, 1g of the azide was decomposed in 20ml p-xylene, and the product was chromatographed. The benzene eluent gave a small amount of brown crystals, m.p. 177-80° (mixed m.p. with o-nitrobenzenesulfonamide, 167-74°). The alcohol eluent gave 0.44g of colorless plates of o-nitrobenzenesulfonyl-p-xylidide, m.p. 141-2.5° 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 conc. alkali.

The decomposition of 1.55g of the azide in mixed xylene gave a large amount of black solid, a small amount of tar and 0.68g of crystalline product. The latter was treated with charcoal in ethereal solution and recrystallized from ether-petrol ether solution, m.p. 100-114°. This product is presumably a mixture of isomeric o-nitrobenzenesulfonyl-xylidides.

Results

Benzenesulfonylazide and the substituted benzenesulfonyl azides all decomposed at moderate rates at 126.68° in every solvent.

In mixed xylene, the decomposition occurred quantitatively giving nearly the theoretical amount of nitrogen, except for o-nitrobenzenesulfonyl

azide. The decomposition of benzenesulfonyl azide followed the first order kinetic law except for initial 10-15% period of the reaction in one sample of mixed xylene, during which the rate was markedly higher than the subsequent first order part, as shown in Figure 5. Such a higher rate at the initial step was also observed in the cases of the o-iodo and p-CH_3 derivatives in that sample of mixed xylene. (Figure 6)

On the other hand, completely first order rate constants were obtained in freshly prepared p-xylene, chlorobenzene and crude xylene from a different source. In the presence of molecular iodine, the decomposition did not show the initial fast reaction but gave a straight first order plot even in the mixed xylene, although the rate was lowered to some extent. The decomposition in the product solution also did not indicate such an irregularity (Fig. 7). The pecularities of the reaction in the one mixed xylene sample lead to the investigation of the reaction with peroxides described in part VI.

In all cases, the first order rate constants obtained were independent of the initial concentration of the azides. These results are summarized in Table 6.

The decomposition of o-nitrobenzenesulfonyl azide in xylene yielded a gas in about 166% of the theoretical amount of nitrogen. The change of gas volume followed the first order kinetic law and the rate was higher than that of benzenesulfonyl azide. Changes of the initial concentration showed no effect on either the excessive gas yield or the rate constant (Figure 8). The addition of iodine also had no effect. The decomposition of benzenesulfonyl azide in nitrobenzene gave the same results as the decomposition of the o-nitro-compound except that the reaction followed the first order kinetics only after the first 15% of reaction. The rate constant was equal to that in mixed xylene (Figure 9).

Table 6

The Results of Decomposition of Benzenesulfonyl Azides at 126.68°

Subst.	Solvent	Init. Conc.	$k_1 \times 10^3 min^{-1}$	Remarks	Gas Yield.%
4	mixed xylene[a]	.075	1.541 ± 0.013[c]		
		.051	1.543 ± 0.016[c]		
		.051	1.453 ± 0.013	in product. soln.	
		.052	1.400 ± 0.012	O_2 passed for 1.5 hr.	
		.051	1.538 ± 0.04	I_2, $5X\ 10^{-3}M$	
		.051	1.405 ± 0.014	I_2, $2.5 \times 10^{-3}M$	
		.051	1.437 ± 0.009	I_2, $1.25 \times 10^{-3}M$	
		.049	1.65 ± 0.03	10 ml $C_6H_5NO_2$ per 100cc xylene	100
	crude xylene[b]	.050	1.617 ± 0.014		

(a) Sample that gives initial fast reaction

(b) Sample that does not give initial fast reaction

(c) Runs with initial fast part

Table 6 (cont'd)

Subst.	Solvent	Init. Conc.	$k_1 \times 10^3 min^{-1}$	Remarks	Gas Yield %
H	p-xylene	.051	1.467 ± 0.005		
		.074	1.446 ± 0.012		
		.050	1.411 ± 0.007	O_2 passed for 22 hrs.	
		.050	1.534 ± .016	+ hydroquinone	
		.051	1.46 ± .046	+ benzoquinone	
	chlorobenzene	.0503	1.507		
		.0500	1.48 ± .03		
		.0280	1.481 ± .012		
		.0657	1.49 (d)		
		.0505	1.48 ± .023	I_a, 0.0099 M/L	
		.0495	1.511 ± .022	stilbene; .0501 M/L	
		.0496	1.511 ± .015	Phenyldisulfide .0250 M/L	
		.0498	1.40 ± .02	Benzothiazoyl-disulfide	
		.0497	1.612 ± .017	Tetraphenyl-hydrazine .0250 M/L	

(d) Dete mined by the Triphenylphosphine method

Table 6 (cont'd)

Subst.	Solvent	Init. Conc.	$k_1 \times 10^3 min^{-1}$	Remarks	Gas Yield, %
H	Nitrobenzene	.051	1.576 ± 0.005		157.0
		.043	1.48 ± 0.03		156.8
		.046	1.54 ± 0.04	2.5×10^{-3}M, I_2	158.4
o-NO_2	mixed xylene[a]	.056	2.37 ± 0.03		166.9
		.041	2.18 ± 0.04		159.6
		.032	2.35 ± 0.03		168.5
		.027	2.19 ± 0.04		166.4
	Chlorobenzene	.0756	1.43 ± .03[d]		
		.0302	2.379 ± .014		160
	p-xylene	.050	2.399 ± 0.011		
		.049	2.15 ± 0.02	1×10^{-2}M, I_2	153.0
o-I	mixed xylene[a]	.049	1.234 ± 0.009[c]		
		.048	1.263 ± 0.008[c]		
		.044	1.223 ± 0.019	10ml $C_6H_5NO_2$ per 100cc xylene	100
p-CH_3	mixed xylene[a]	.073	1.43 ± 0.02[c]		
o-CH_3	chlorobenzene	.0465	1.19 ± .02		

Discussion

As can be seen from the data in Table 6, the decomposition of benzenesulfonyl azide is rather insensitive both to the nature of the solvent or of the substituent. For example, the rates differ very little in p-xylene, chlorobenzene and nitrobenzene. A para methyl group seems to decelerate only very slightly (at 126.68°). The o-nitro substituent accelerates the gas evolution moderately, but obviously leads to a different reaction since more than one mole of gas is evolved. If the rate of disappearance of azide is measured[34] rather than the rate of appearance of gas, the o-nitro group is found to decelerate slightly. So do the o-methyl and o-iodo substituents.

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(34) By the triphenylphosphine method, Part VI

In contrast to the benzenesulfonyl azide decomposition, the decomposition of benzoyl azides[32] is accelerated by one or two orders of magnitude by ortho substituents. Para substituents decelerate the decomposition of benzoyl azide[32] but do not follow the ρ σ relationship established by meta substituents in the same reaction.

The behavior of the o-iodo substituents was of special interest because of the possibility of attack of the nitrogen diradical on the iodine atom either during the rate-determining step or later. Since the rate and product are normal, this does not occur. In this respect the decomposition of benzenesulfonyl azide resembles the decomposition of benzoyl azide rather than the decomposition of benzoyl peroxides.[27][35]

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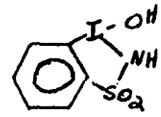
(35) Chlorination of o-iodobenzenesulfonamide gives a yellow iodo-dichloride m.p. 110° which decomposes to the original amide.

Treatment of the iodo-dichloride with dilute alkali, followed by neutralisation gives a yellow substance, probably



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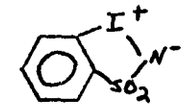

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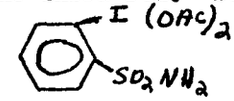
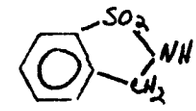
melting at 130-132°with decomposition. The latter compound reacts with acetic acid to give a substance decomposing at 103-106° and having the usual amide bands in the infra-red. It is probably



We plan to investigate the decomposition products of o-toluenesulfonyl azide for signs of intramolecular hydrogen transfer. The expected cyclization product,



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appears to be unknown.

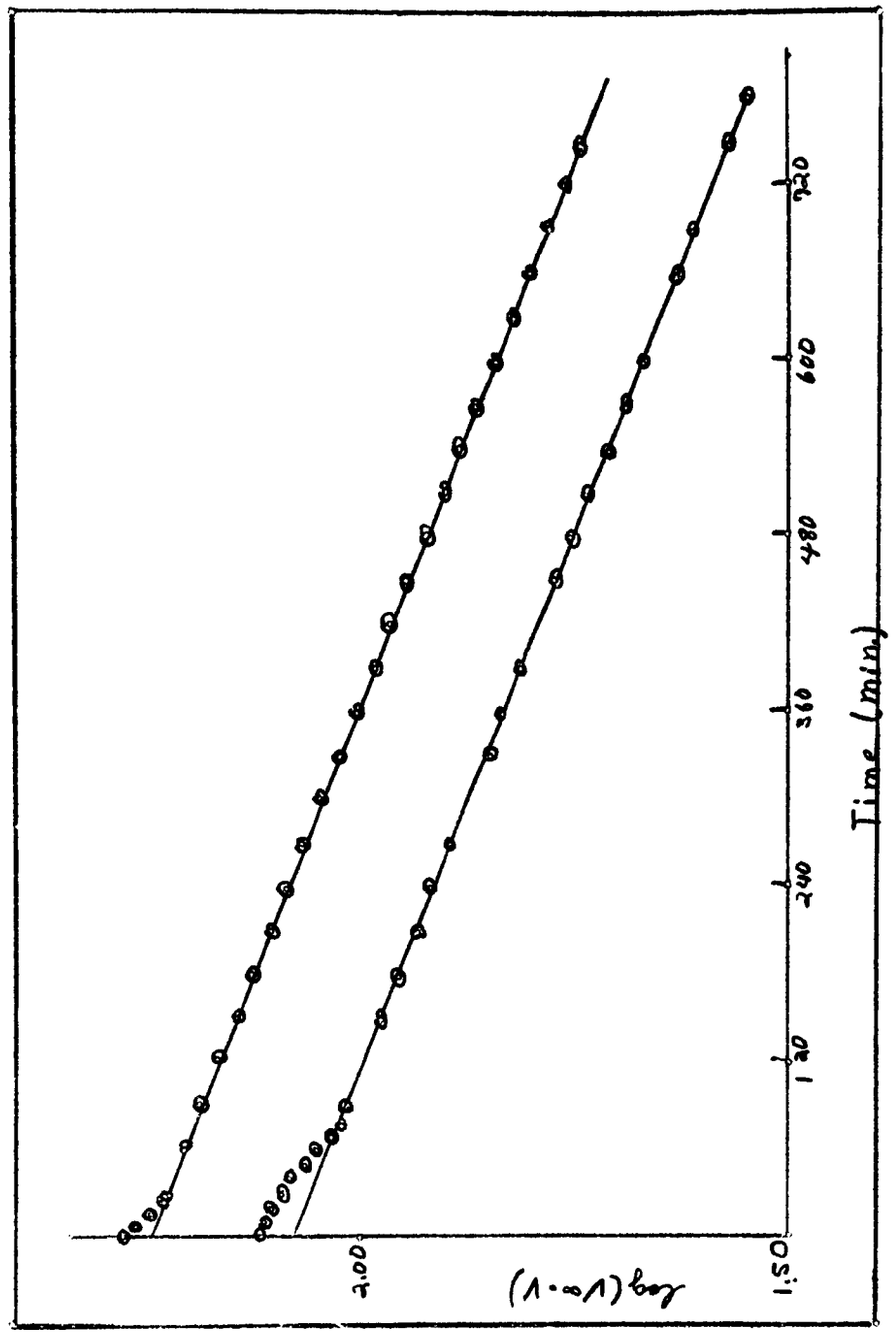


Fig. 5 Decomposition of Benzenesulfonylazide in Mixed Xylene

A, conc. = $0.75 \times 10^{-2} M$

B, conc. = $0.51 \times 10^{-2} M$

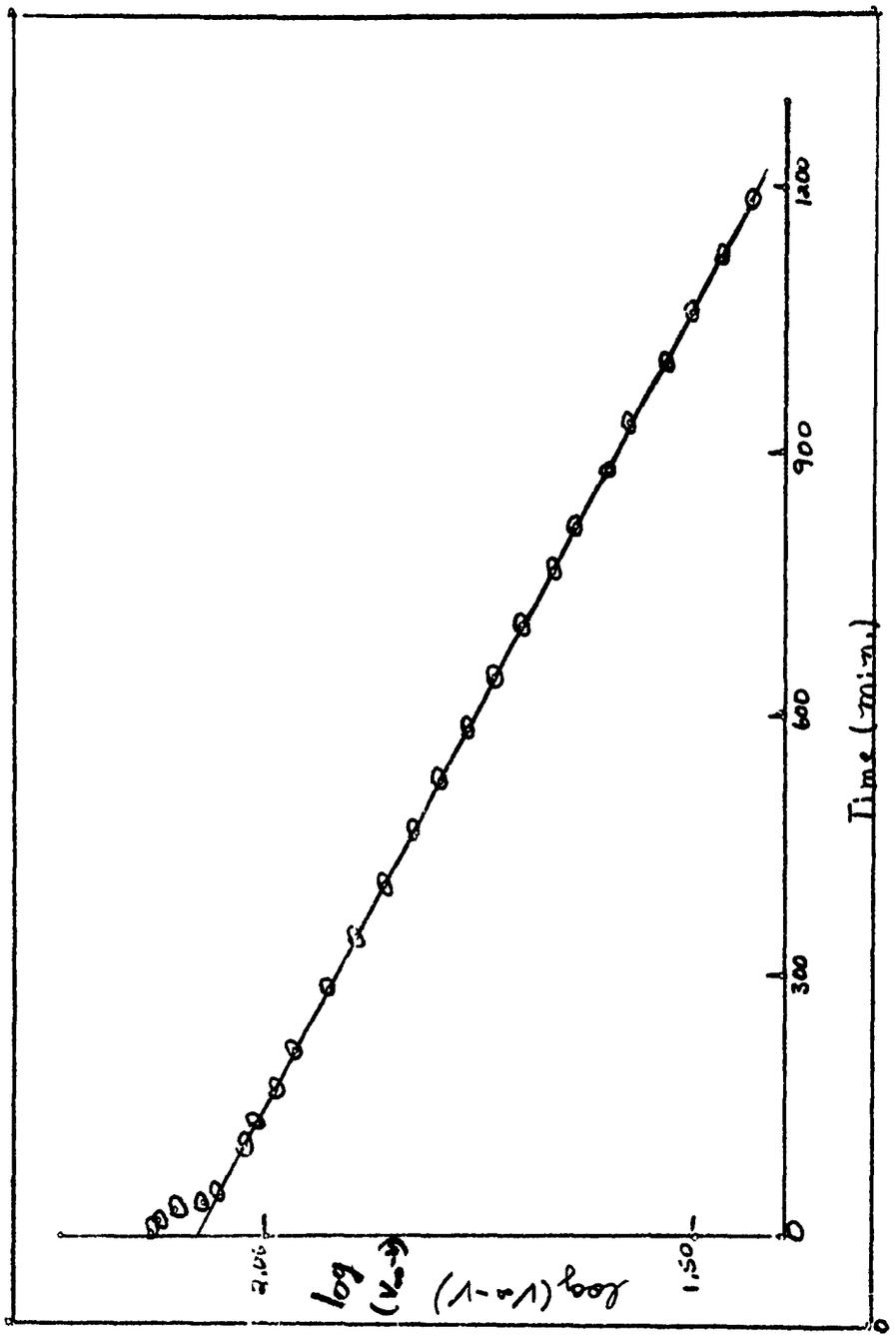


Fig. 6 Decomposition of o-Iodobenzenesulfonylazide in mixed xylene

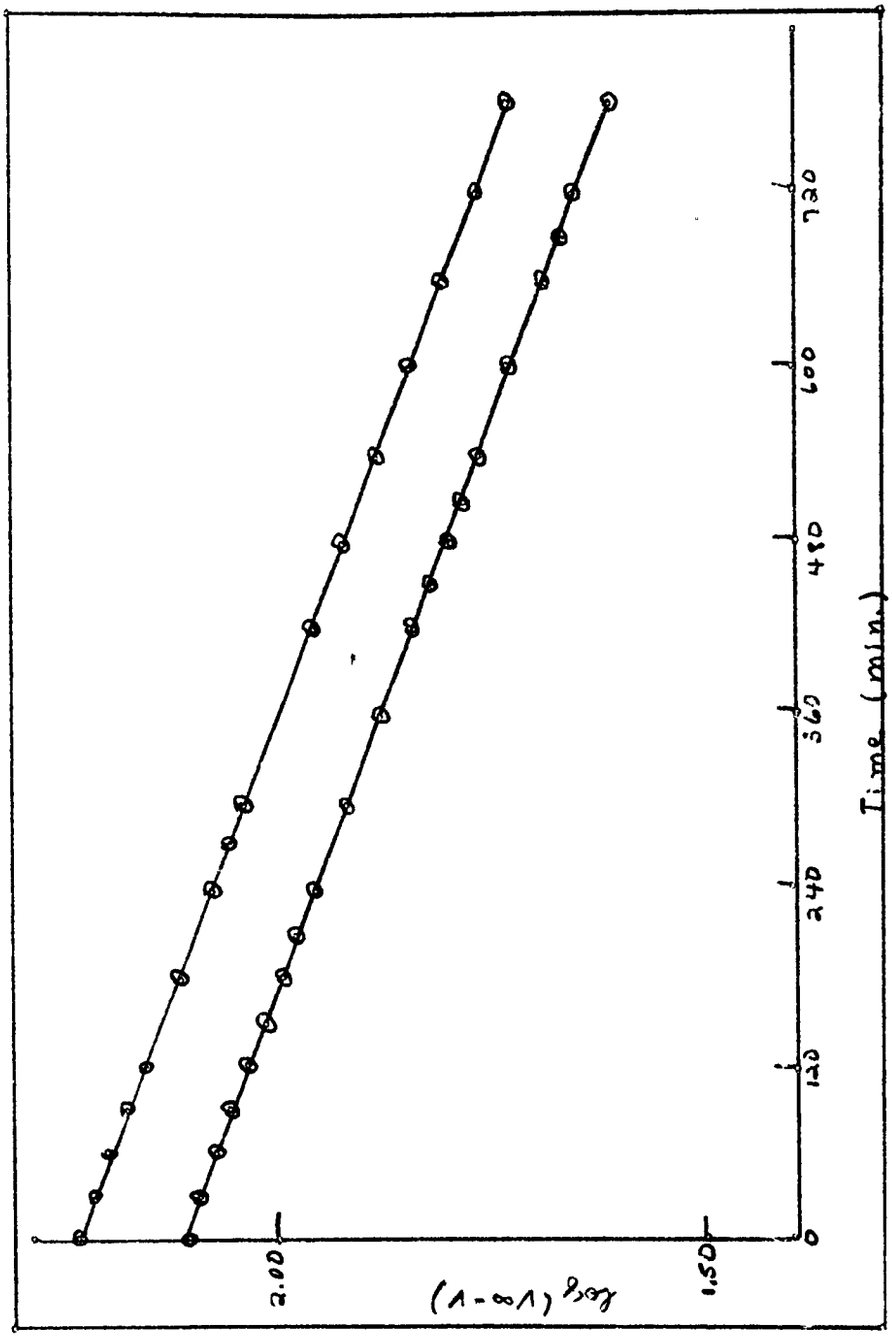


Fig. 7 Decomposition of Benzenesulfonylazide

A, in p-xylene and B in product solution.

i.e. in mixed xylene* with products of a previous run in that solvent

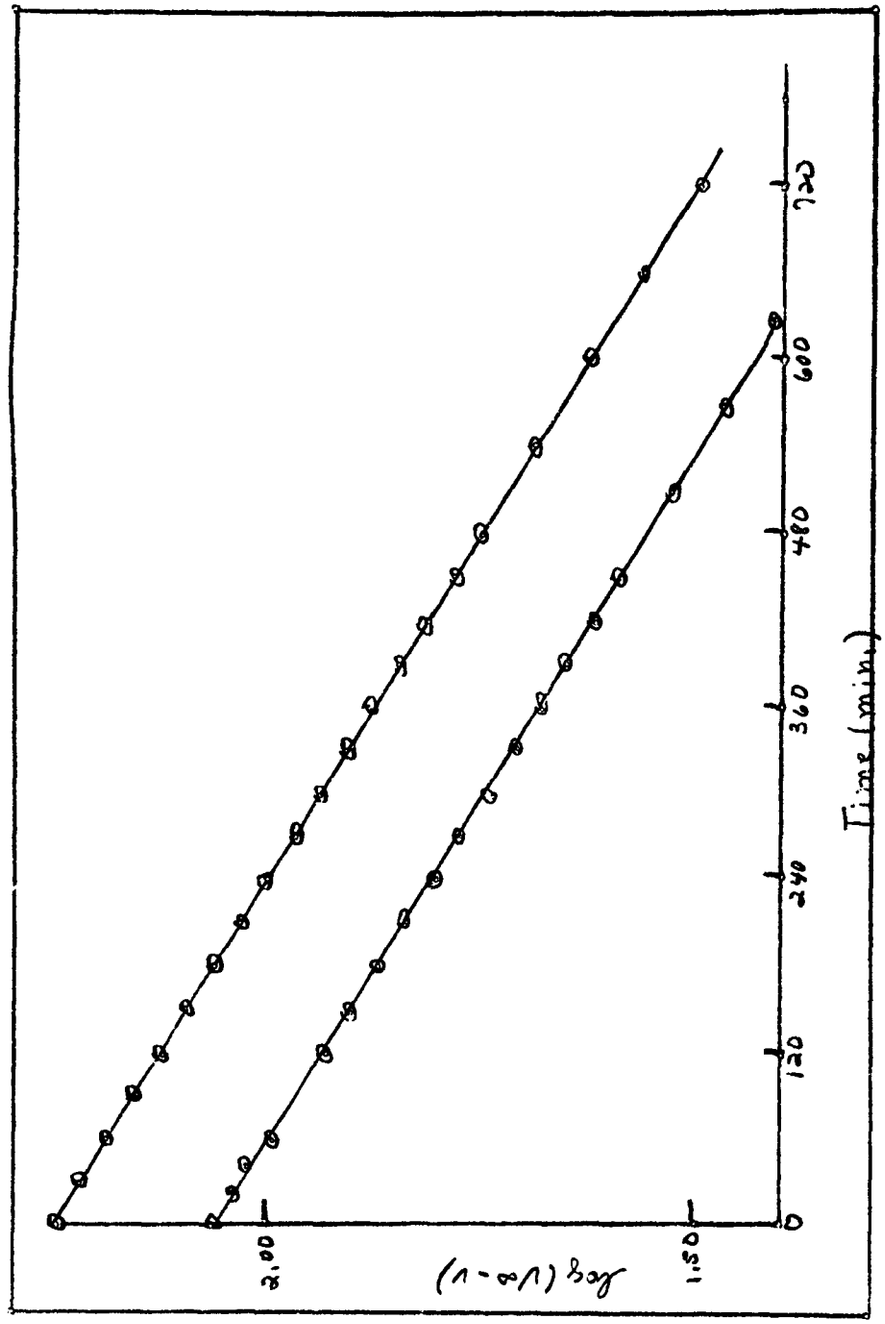


Fig. 8 Decomposition of o-Nitrobenzenesulfonylazide

A. in p-xylene, $0.500 \times 10^{-2} M$

B. in mixed xylene* $0.319 \times 10^{-2} M$

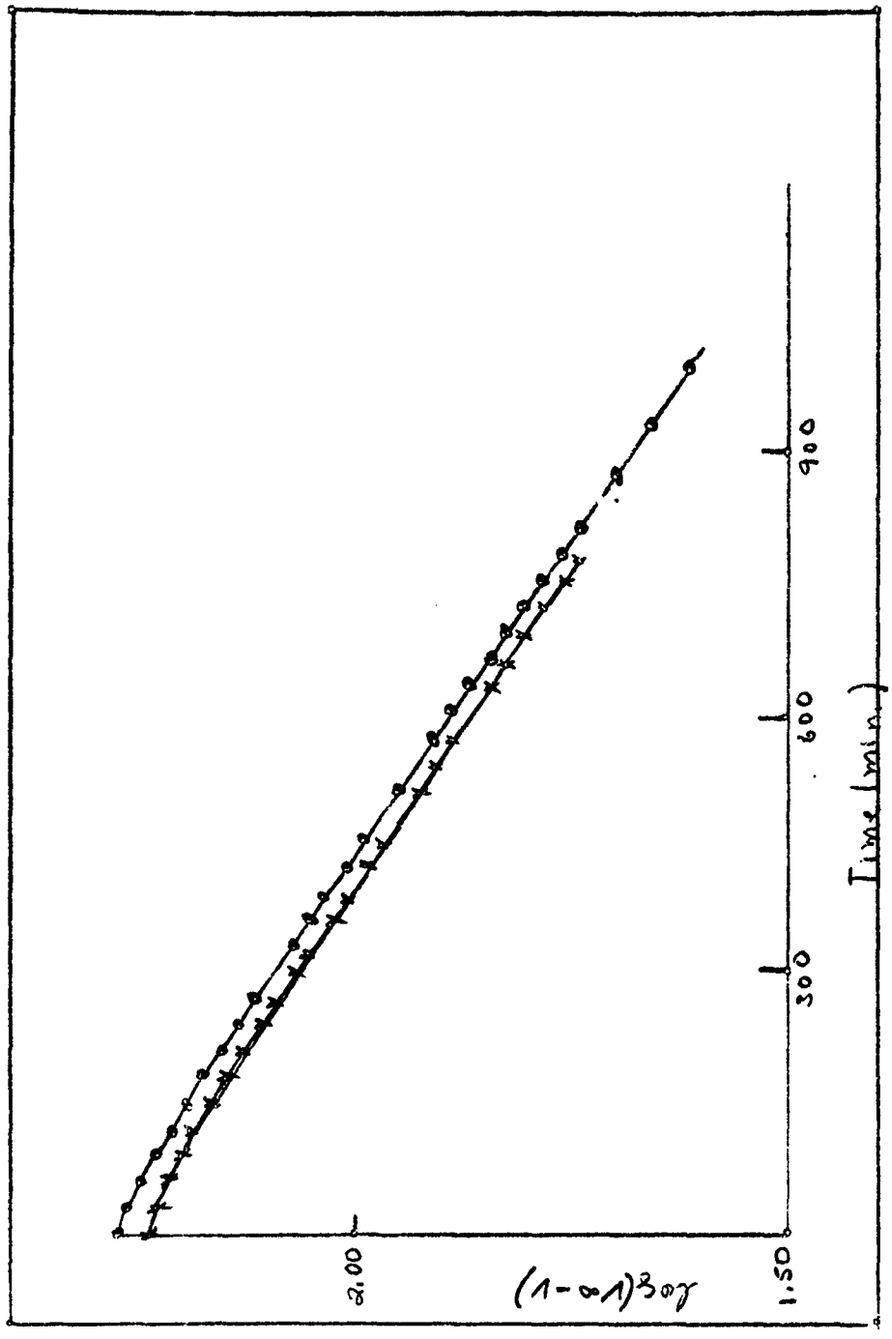


Fig. 9 Decomposition of Benzenesulfonylazide

A. In nitrobenzene, 0.509×10^{-2} M

B. In nitrobenzene in the presence of Iodine, 0.459×10^{-2}, $I = 0.250 \times 10^{-2}$ M

Part VI. The Mutual Acceleration of the Decomposition of Benzenesulfonylazide and t-Butyl Hydroperoxide

In part V we reported that in certain samples of xylene the rate of decomposition of benzene sulfonylazide was accelerated by some impurity. The impurity was soon consumed, and the rate became accurately first order. Because we suspected that the impurity might be a hydroperoxide[36] we did some experiments on the simultaneous decomposition of benzenesulfonazide and t-butyl hydroperoxide. We have been able to show the existence of several distinct reactions in this system. However, even though we carried out more than one hundred kinetic runs, the behavior of the system proved to be too complicated for a complete analysis of the reaction mechanisms. Intermediates from the azide accelerate the decomposition of the hydroperoxide, and intermediates from the hydroperoxide accelerate the decomposition of the azide in chlorobenzene, but not in p-xylene. Both compounds are known to be subject to decomposition induced by certain radicals, sulfur radicals in the case of the azide[37] and carbon radicals in the case of the hydroperoxide.[38] In addition, the decomposing azide is known to initiate vinyl polymerization.[39]

[36] See H. Heck and S. Lary, Ber. 76B, 169 (1943) for xylene autoxidation.

[37] M. Takebayashi and T. Shingaki, private communication.

[38] (a) B. K. Morse, JACS, 79, 3375 (1957). (b) V. Stannett and R. B. Mesrobian, JACS, 72, 4125 (1950)

[39] J. F. Heacock and M. T. Edmison, JACS, 82, 3460 (1960)

The peroxide by itself can decompose by two paths, one leading to t-butyl alcohol and oxygen and the other, a β-cleavage reaction, leading to acetone, methanol, and only traces of gas.[38,40] The β-cleavage reaction is

[40] N. A. Milas and D. M. Surgenor, JACS, 68, 205 (1946).

the usual one in the gas phase and in dilute solutions, the oxygen-generating reaction being favored by high peroxide concentration, for example in the neat peroxide. It is the oxygen-generating reaction which is induced by the intermediates from the decomposing azide.

The products of the decomposition of the azide are changed only slightly by the presence of t-butyl hydroperoxide. In p-xylene the yield of benzenesulfonyl xylidide becomes nearly quantitative at the expense of the benzene sulfonamide. The solution also remains colorless rather than developing the usual dark color. In chlorobenzene plus t-butyl hydroperoxide the main product is still a mixture of substituted benzene sulfonanilides, but the yield is lowered, and there is some benzenesulfonamide as well as considerable tar.

Reaction Rates in p-Xylene

The decomposition of the azide plus t-butyl hydroperoxide in p-xylene solution gives nitrogen plus oxygen. The oxygen can be removed by means of alkaline pyrogallol, and the volume of the remaining gas corresponds to a theoretical yield of nitrogen. The initial rate of nitrogen evolution is very closely equal to the initial rate of total gas evolution, since the decomposition of the peroxide is initially very slow, as determined by titration. In xylene solution the presence of the peroxide has little or no effect on the initial rate of nitrogen evolution and certainly no large effect on the nitrogen evolution rate at any time. Using the first order rate constant $1.44 \times 10^{-3} min^{-1}$, obtained for the decomposition of the azide in p-xylenealone at 126.7°, the rate of oxygen evolution may be estimated as a difference between total gas evolved and nitrogen evolved. The results of

such a calculation indicate considerably less net evolution of oxygen than expected on the basis of the hydroperoxide titer and suggest that oxygen is being consumed by solvent radicals. With excess peroxide the rate of total gas evolution steadily increases during the run, eventually becoming too rapid to measure.

The rate of peroxide decomposition as determined by iodometric titration is slow and nonreproducible for the first five hours or so. This corresponds to about 5% decomposition of the peroxide and about 35% decomposition of the azide. The rates in the latter part of the run are four or five times as fast and are reproducible (table 7). They appear to be a linear function of the initial azide concentration. The point for zero azide concentration falls well below the line, however.

Most of our experiments were done in chlorobenzene in order to avoid the complication of solvent autoxidation. The results for the chlorobenzene experiments are described in the following sections.

Table 7

THE REACTION OF BENZENESULFONYLAZIDE WITH t-BuOOH IN p-XYLENE AT 126.7°, BY IODOMETRY

Initial Conc. M/L		$k_o \times 10^4$
$[Azide]_o$	[t-BuOOH]	M/L. Min
0	(.05)	.03[a]
.0504	.0503	.82
.0507	.0498	.78
.0507	.0499	.86
.0177	.0503	.50
.0333	.0698	.62

[a]Initial rate. The apparent rate-law in absence of azide is first order. It was used to estimate on initial k_o for a run of initial concentration .05 molar.

Effect of the Hydroperoxide on the Azide Decomposition in Chlorobenzene

Figure 10 is a first-order plot of the gas evolution rate in the presence of various amounts of hydroperoxide. After a period of about 30 minutes during which the gas evolution rate is about that expected for the azide alone, there is a period of about 45 minutes during which gas evolution is very rapid, followed by gas evolution at the expected rate for the azide alone during the rest of the run. The period of rapid gas evolution overlaps the period during which the hydroperoxide is decomposing, and the gas evolved during this period is a mixture of nitrogen and oxygen. However, it can also be shown that there has been a temporary acceleration of the azide decomposition. Extrapolation of the linear portion of the curve in figure 10 back to zero time gives an azide concentration considerably less than the actual initial azide concentration.

We were also able to confirm the rapid azide decomposition rate by direct analysis for azide. The method used is reaction with triphenyl phosphine and is described in the experimental section. Again we find a decomposition at the normal slow rate for the azide alone, followed, first, by a period of rapid decomposition, and then by a period of decomposition at the normal rate. A typical run is shown in figure 11, which also shows the decrease in iodometric titer of the peroxide. It can be seen that the beginning of the period of accelerated azide decomposition coincides with an acceleration of the peroxide decomposition. The peroxide decomposition rate in typical runs remains constant from the time of the sharp break in the curve to the end of the reaction.

The decomposition of approximately equal concentrations of the azide and peroxide in chlorobenzene in the presence of iodine gives the usual mixture of benzene sulfonanilides, but without the black tar. The rate of

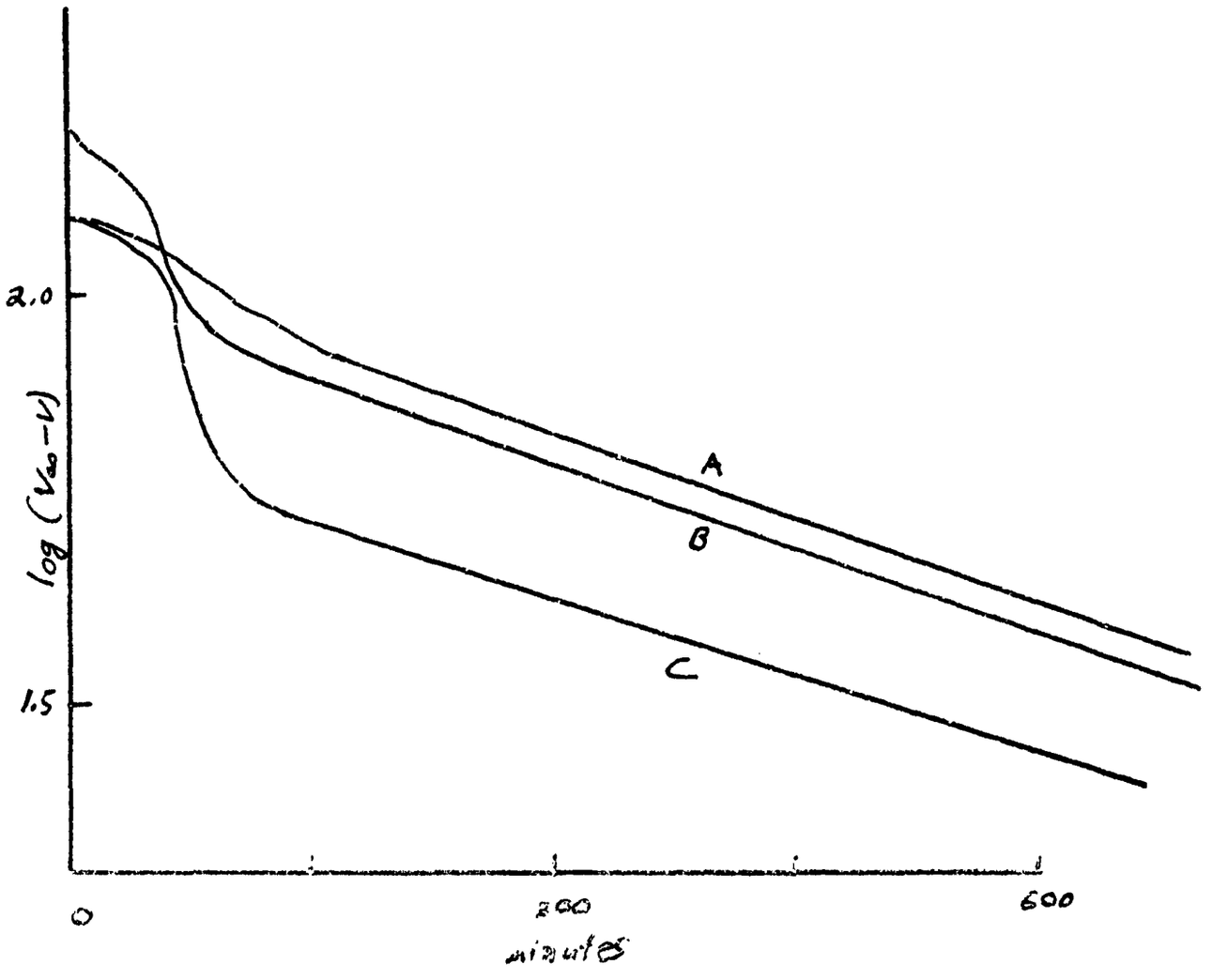


Figure 10. Decomposition of the azide in chlorobenzene in the presence of t-butyl hydroperoxide.

A. Azide, 0.05M; hydroperoxide, 0.025M.

B. Azide, 0.05M; hydroperoxide, 0.05 M.

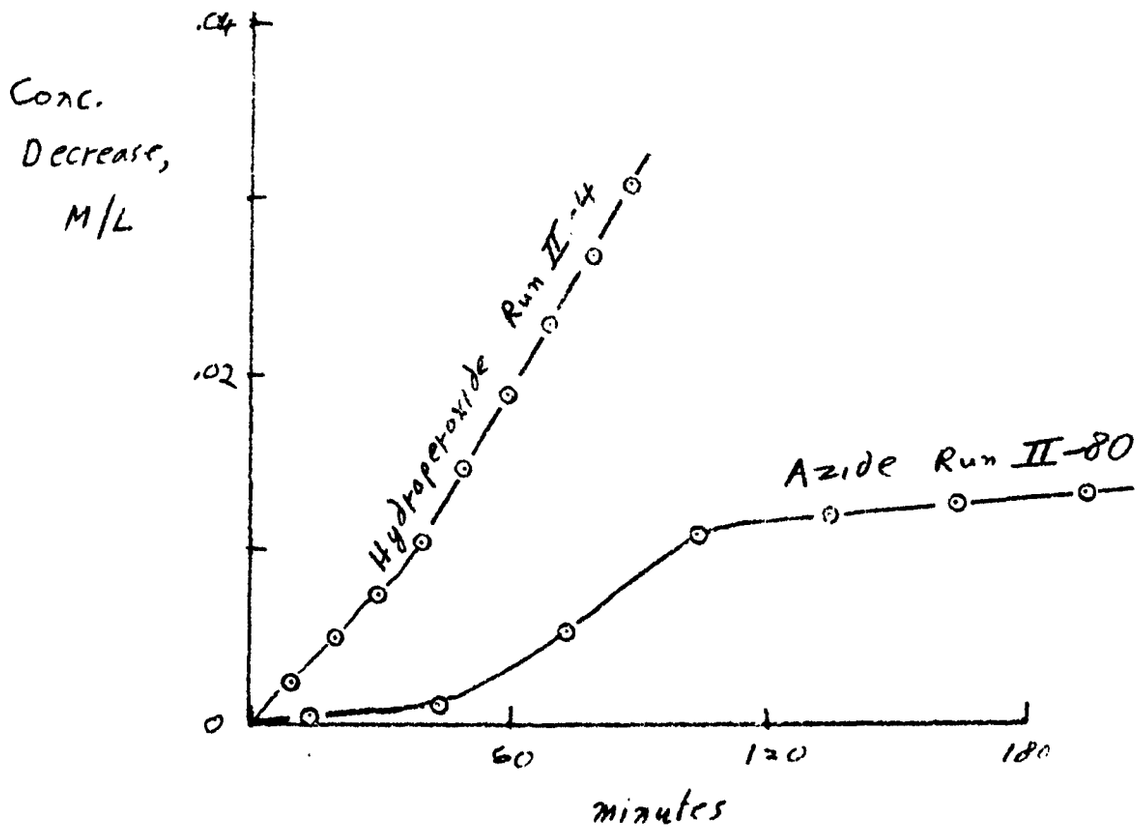
C. Azide, 0.033M; hydroperoxide, 0.05M.

Figure 11

$[A]_0 = .033\ M$

$[P]_0 = .050\ M$

Chlorobenzene at 126.7°



total gas evolution fits two simultaneous first-order processes, one for the azide and one for the peroxide. The first-order rate constant for peroxide decomposition under these conditions can be obtained independently by iodometric titration. The k_A for the azide decomposition used to calculate the curve shown in figure 10 for the azide-peroxide-iodine system is the same as that observed for the azide or the azide plus iodine. The k_{1p} used for the peroxide, however, is a function of the initial concentration of azide. At very low azide concentration the rate of peroxide disappearance is initially very fast, becoming first order only at a later stage of the reaction.

Figure 13 shows a first-order plot for the disappearance of peroxide in a system containing iodine and also azide in concentration about equal to that of the peroxide.

In summary we can say that the acceleration of the azide decomposition by the peroxide appears to be due to attack by radicals which can be diverted either by reaction with p-xylene (solvent) or by reaction with iodine in chlorobenzene. In the next section we will examine the effects of the azide on the peroxide decomposition rates.

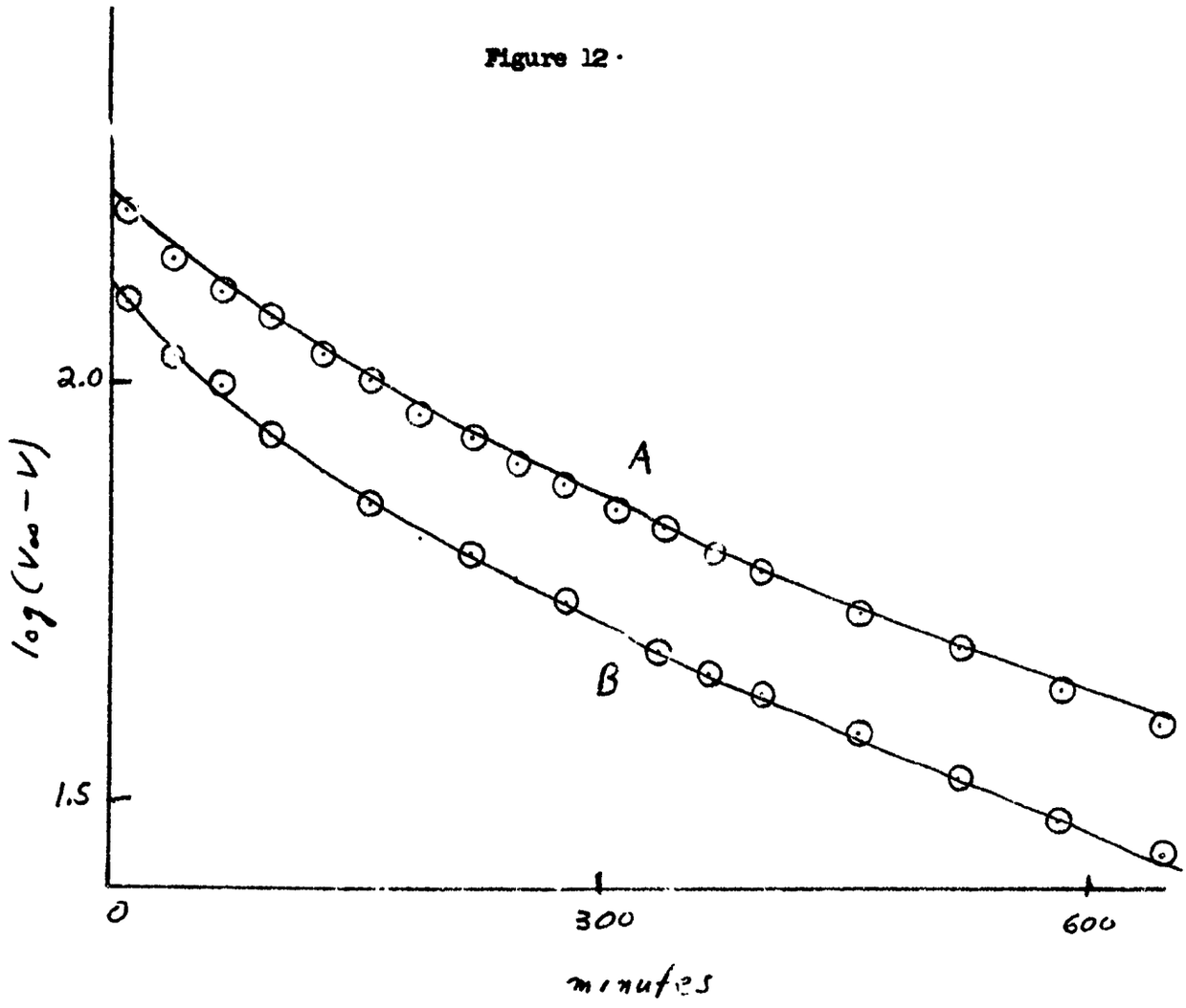
The Effect of the Azide on the Peroxide Decomposition

t-Butyl hydroperoxide in chlorobenzene solution in the absence of azide decomposes by a first-order process into products that are largely non-gaseous. The first-order rate constant at 126.7° is about 1.04×10^{-3} min^{-1}, for runs of initial peroxide concentration near .065 molar.[41] In the presence

[41] The rate can probably be changed by scavenging of O_2 from the system by means of a nitrogen stream. See reference 38a.

of the azide the gas evolved is nitrogen in the theoretical amount plus oxygen in 90% or better of the theoretical amount. The gas mixture is

Figure 12.



Gas Evolution with .01 M I_2 in ϕCl

A. Experimental points and calculated curve for .0497 M azide and .0499 M peroxide.

B. Same for .0336 M azide and .0503 M peroxide.

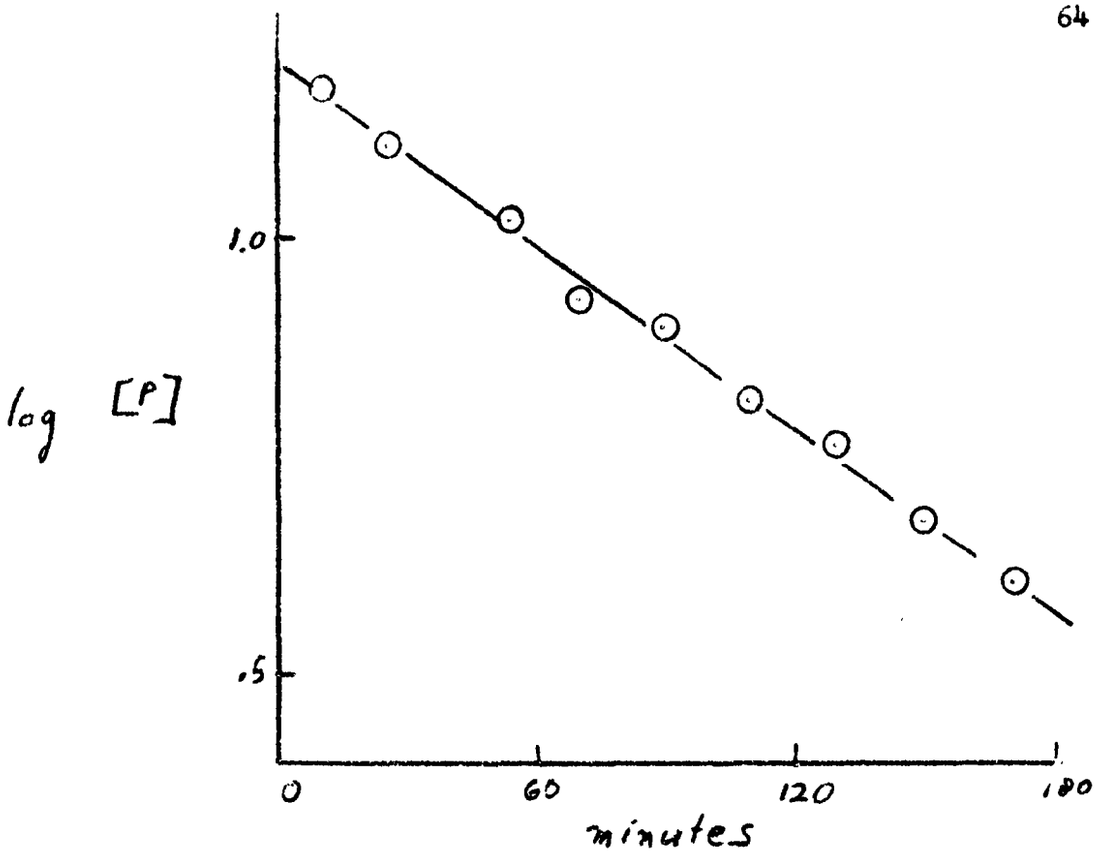


Figure 13. Change of the concentration of t-butyl hydroperoxide in the reaction of the azide [.05 molar] and the hydroperoxide [.05 molar] in the presence of iodine [.01 molar].

evolved rapidly at first, then decreases to the first-order rate of nitrogen evolution characteristic of the azide by itself.

Iodometric titration of the peroxide in chlorobenzene in the presence of the azide shows decomposition occurring by a process of nearly zeroth order, especially at low azide concentration. A typical run is shown in figure 14. However, at high concentration of the azide the rate of peroxide decomposition (k_{op}) increases with time, and we have used both the initial and final zeroth order rate constants. The zeroth order rate constants are related to the initial azide concentration (the azide concentration does not change drastically during the peroxide decomposition)

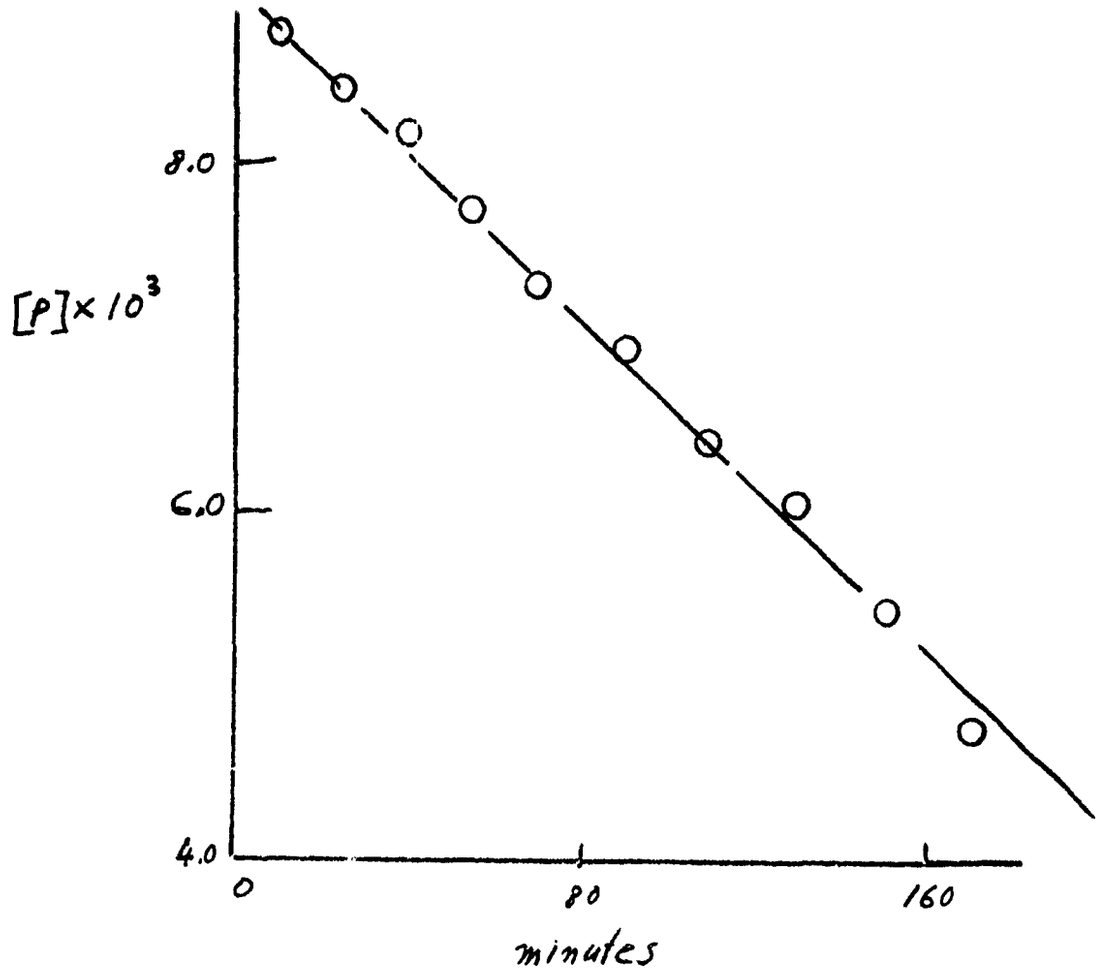


Figure 14. Zeroth order plot of the decomposition of t-butyl hydroperoxide in chlorobenzene at 126.7°.

Azide--.0060 molar
Peroxide--.050 molar

as shown in figure 15 for runs of initial peroxide concentration equal to .05 molar. The upper branch at high azide concentration shows the rates late in the run; the lower branch shows the initial rates.

The effect of changing initial peroxide concentration at a constant initial azide concentration of .01 molar is shown in figure 16.

The combined effect of changes in azide and peroxide concentrations on the peroxide decomposition rate can be approximated equally well by

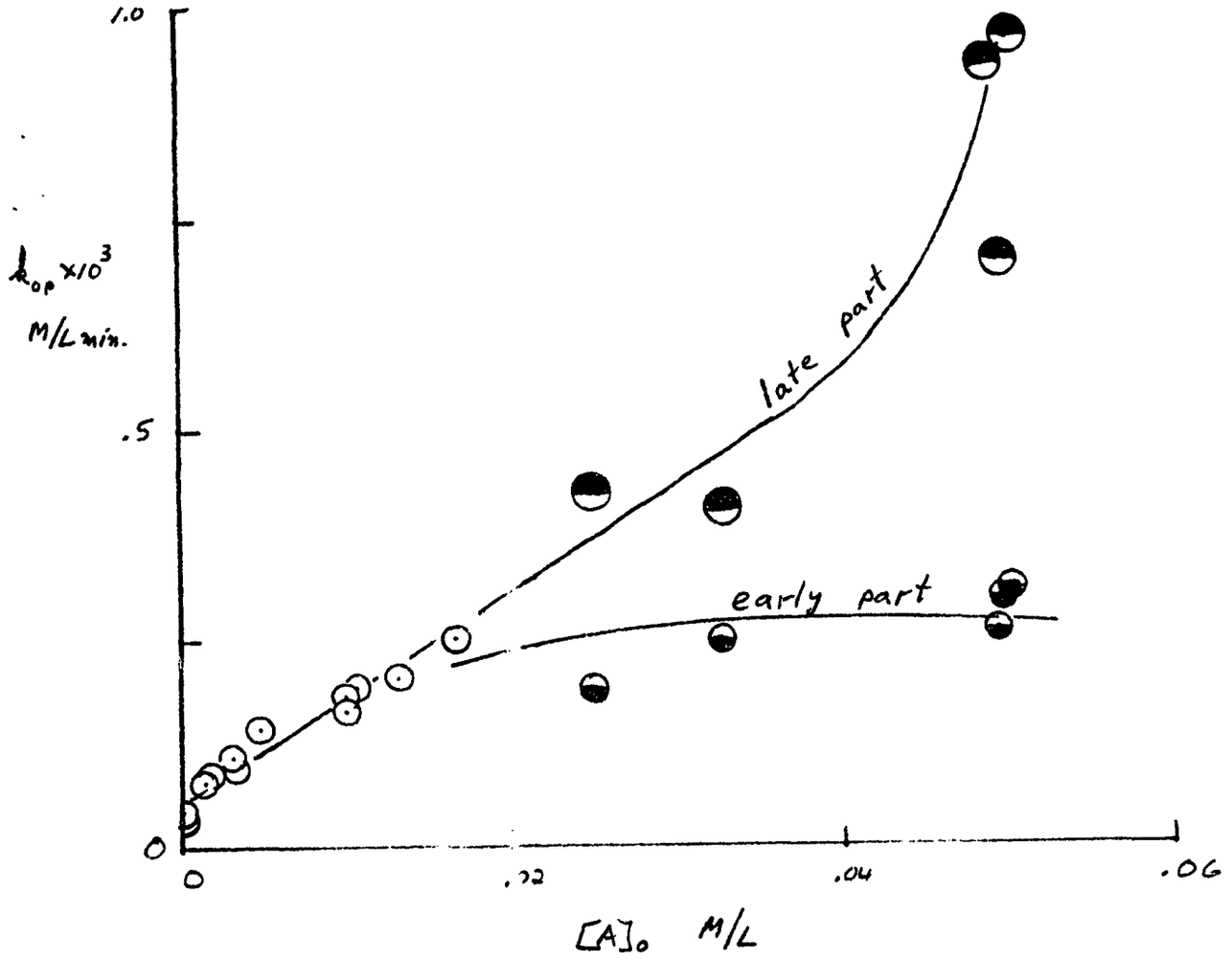


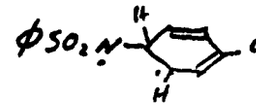
Fig. 15 $[P]_o = .05$, dependence of titrimetric peroxide rate on azide conc.

several equations. One of these is equation (1), which uses only rates from runs of low enough azide concentration so that the runs are fairly accurately zero order (i.e., $[A]_o \leq .017$).

$$k_o \frac{M}{L \text{ min}} = .45 \times 10^{-3} [P] + 26 \times 10^{-3} [P][A]^{1/2} + 3.1 \times 10^{-3}[A] \qquad \text{(Equ 1)}$$

The constant 3.1×10^{-3} is approximately twice the first-order rate constant, 1.5×10^{-3} min^{-1}, for the decomposition of the azide alone.

By using the steady-state approximation and assuming interplay between such species as $CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-O\cdot$, $CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-OO\cdot$, $\phi SO_2N:$, $\phi SO_2\dot{N}H$,



, etc.,

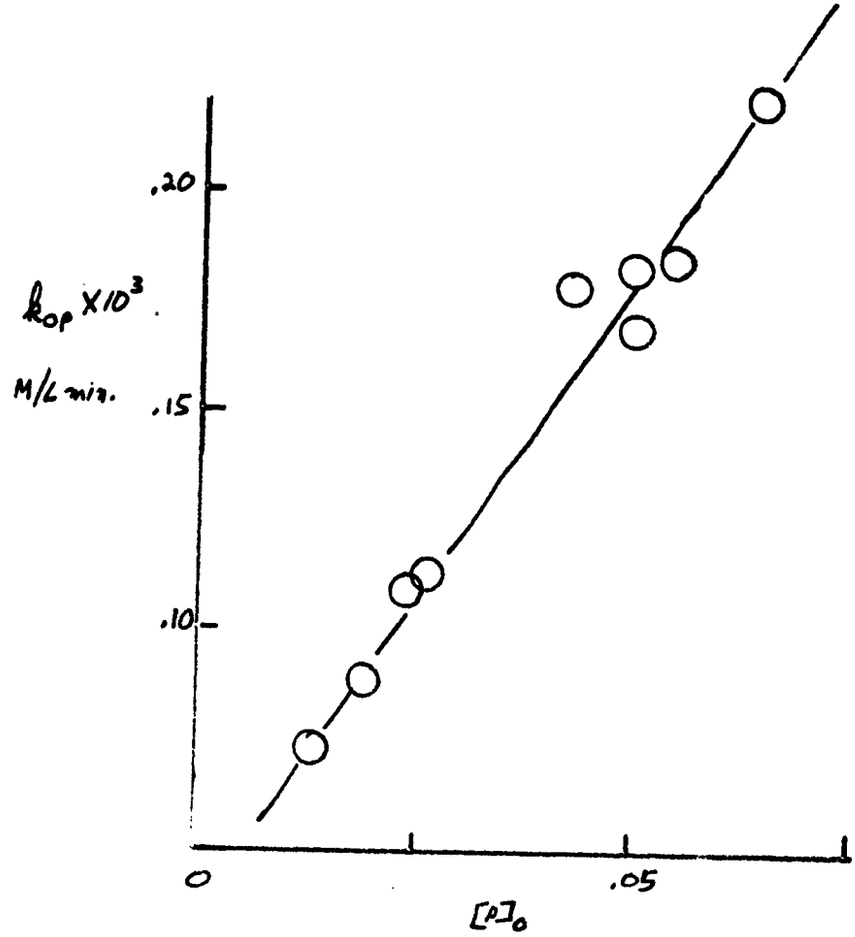


Fig. 16 $[A]_o = .01$, dependence of titrimetric peroxide rate on initial peroxide conc.

as well as the azide and the peroxide, it is possible to derive several kinetic equations which feature a cross term containing both the azide and peroxide concentrations and a $2k_{1A}[A]$ term. The reaction scheme shown below is an example of such a mechanism. It explains the term proportional to [P] in equation (1) as a unimolecular rate of peroxide decomposition. The observed k_1 for the peroxide decomposition in the absence of azide is about twice as great as the proportionality constant in equation (1), however.[42] Like the other simple mechanisms it is not completely satisfactory.

[42] This may be an effect due to sweeping out of O_2 by the gas evolved from the azide. See table 8.

An additional defect is that this mechanism neglects the induced decomposition of the azide; however, this is less important at low concentrations.

Steady State Derivation for a Simplified Mechanism

(Special symbols are written under the corresponding species in the chemical equations.)

$$\underset{A}{\phi SO_2N_3} \xrightarrow{1} \underset{N:}{\phi SO_2N:} + N_2$$

$$N: + \phi SO_2NH\text{-}C_6H_4\text{-}\phi \xrightarrow{2} \underset{NH\cdot}{\phi SO_2NH\cdot} + \underset{N\phi\cdot}{\phi SO_2N\phi}$$

$$NH\cdot + \underset{P}{CH_3\text{-}C(CH_3)_2\text{-}OOH} \xrightarrow{3} \underset{NH_2}{\phi SO_2NH_2} + CH_3\text{-}C(CH_3)_2\text{-}OO\cdot$$

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

$$N\phi\cdot + P \xrightarrow{4} N\phi H + ROO\cdot$$

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

$$2RO\cdot \xrightarrow{6} ROCH_3 + CH_3\text{-}\overset{O}{C}\text{-}CH_3$$

$$P \xrightarrow{7} CH_3\text{-}\overset{O}{C}\text{-}CH_3 + CH_3OH$$

$$-\frac{d[P]}{dt} = k_3[P][NH\cdot] + k_4[P][N\phi\cdot] + k_5[P][RO\cdot] + k_7[P]$$

$$0 \cong \frac{d[N:]}{dt} = k_1[A] - k_2[NH\phi][N:]$$

$$0 \cong \frac{d[NH\cdot]}{dt} = k_2[NH\phi][N:] - k_3[P][NH\cdot]$$

$$0 \cong \frac{d[N\phi\cdot]}{dt} = k_2[NH\phi][N:] - k_4[P][N\phi\cdot]$$

$$0 \cong \frac{d[RO\cdot]}{dt} = k_3[P][NH\cdot] + k_4[P][N\phi\cdot] - 2k_6[RO\cdot]^2$$

$$\therefore \quad -\frac{d[P]}{dt} = 2k_1[A] + k_5[P]\sqrt{\frac{k_1}{k_6}[A]} + k_7[P]$$

The Effect of the Azide on the Peroxide Decomposition Rate in the Presence of Various Added Substances

The rate of decomposition of t-butyl hydroperoxide by itself in dodecane[38a] depends on the rate at which the oxygen produced is removed from the system, apparently because oxygen diverts radicals which are particularly effective in inducing the decomposition of the peroxide. The effect of sweeping with helium is an acceleration by a factor of 40 to 50. We find that the effect of nitrogen-sweeping on the rate of decomposition of the peroxide in the presence of azide is very much less, as can be seen from Table 8.

Allowing the azide (.0246 molar) to decompose for one hour (about 7.5% decomposition) before adding the peroxide (.0507 molar) gave a peroxide decomposition rate about twice that of a comparable run in which both azide and peroxide were added at the same time. On the other hand, the major azide decomposition products, benzenesulfonamide (.003 molar) and benzenesulfonyl-p-chloroanilide (.0009 molar), had no effect.

We next studied the decomposition of the peroxide and azide in the presence of iodine as a trap for radicals, in the hope that the peroxide decomposition kinetics would be simplified.

Table 8

Effect of N_2 Sweeping on Rate of Decomposition of t-Butyl Hydroperoxide in Chlorobenzene with Benzenesulfonyl Azide

Initial Conc.		$k_o \times 10^3$ Moles/L.Min.	
Peroxide	Azide	Under N_2+O_2	Swept by N_2
.05	.0015	.08	.24 to .34
.05	.0044	.13	.21
.05	.012-.013	.20	.35
.05	.025	.42	.36

The Effect of the Azide on the Peroxide Decomposition Rate in the Presence of Iodine

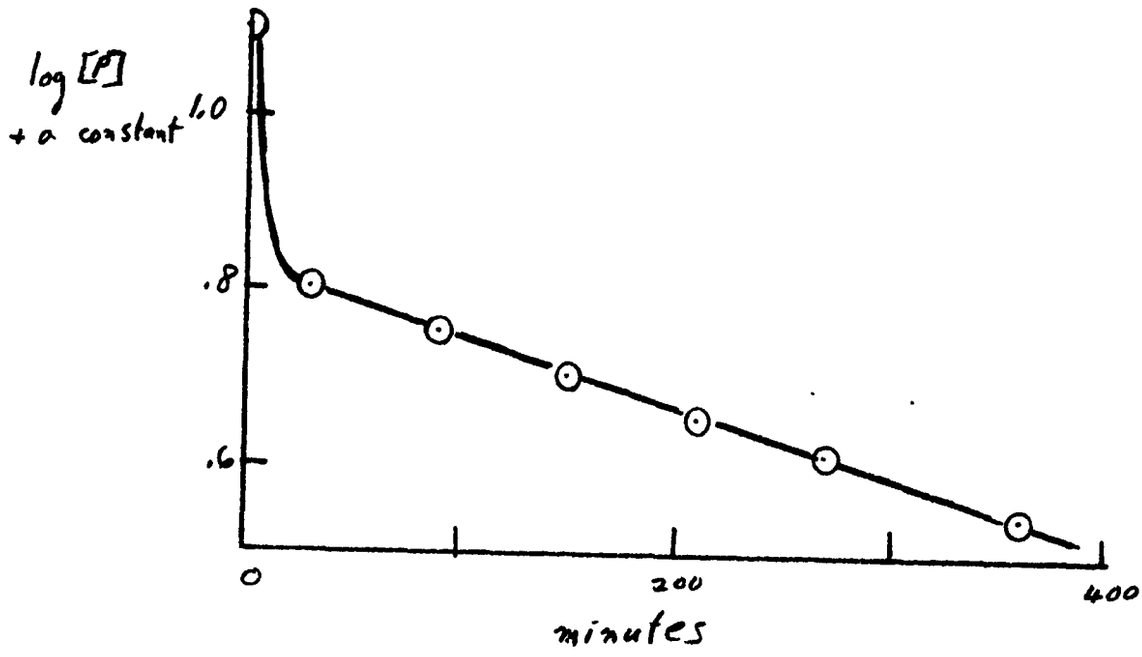
The decomposition rate of the peroxide in the absence of azide is dependent, as we have seen, on various factors. For example, it is much slower in p-xylene than in chlorobenzene and is somewhat faster in nitrogen-swept chlorobenzene than in chlorobenzene in the presence of the evolved oxygen. The decomposition in chlorobenzene, unswept, in the presence of .01 molar iodine is a first-order reaction with $k_{1p}=3.4 \times 10^{-3} min^{-1}$, about three times as fast as the decomposition of the peroxide alone. However, this reaction of the peroxide alone is attended by little or no gas evolution and is not the same as the apparent first-order decomposition of the peroxide in the presence of iodine plus the azide.

Again, we find a change in the kinetics of peroxide within a run at a critical azide concentration (about .0124 molar). This time, however, the kinetics are more complex at low azide concentrations rather than at high azide concentrations. At low azide concentrations there is a very fast initial peroxide decomposition, not leading to gas, which quickly subsides and is followed by a slower, gas-evolving, first-order peroxide decomposition. A typical run of this type is shown in figure 17.

The initial fast peroxide decomposition (figure) has rate constants of the order 10×10^{-3} to 60×10^{-3} min^{-1} as compared to the later rate constants of the order of 2×10^{-3} to 6×10^{-3} $min.^{-1}$ The initial fast peroxide decomposition requires the presence of some azide but is absent at higher concentrations of azide. Tables 9 and 10 show the rate of the fast initial reaction, if any, expressed as a first-order rate constant. It can be seen from the tables that the initial fast reaction is regularly observed whenever the initial azide concentration is below about .015 molar. It is absent or slower than usual, however, if benzenesulfonyl p-chloroanilide

Figure 17

Peroxide Decomposition in the Presence of .01 M I_2 and .0016 molar initial azide concentration



(a product of the azide decomposition) is added at the beginning of the run. We therefore have an induced decomposition of the peroxide dependent on iodine and azide but inhibited by the anilide. The second stage of the reaction in the presence of iodine exhibits fairly precise first-order rates.

Figure 18 shows how these rate constants are related to the square root of the initial azide concentration at constant initial iodine and peroxide concentrations. Neglecting the rates for runs without azide (which are too high, see the figure) the plot passes through the origin.

Figure 19 is a plot of initial zeroth order rate constants for the peroxide obtained by multiplying the observed first-order rate constants by the initial peroxide concentration for runs of constant initial concentration of iodine (.01 M) and azide (.0164M).

Table 9

Iodometric Rates of Peroxide Decomposition
t-BUTYLHYDROPEROXIDE AND BENZENESULFONYL AZIDE IN
CHLOROBENZENE AT 126.7°; IN THE PRESENCE OF IODINE

	Initial Conc. M/L			$k_1 \times 10^2$ min.$^{-1}$		$\Delta[I_2]/\Delta[P]$
	$[t\text{-BuOOH}]_o$	$[Azide]_o$	$[I_2]_o$	First Order Part	Initial Fast Reaction	
II-74	.0500	.0000	.0100	.33	absent	.15
II-75	.0500	.0000	.0101	.35	absent	.16
II-61	.0501	.0124	.0101	.375	2.0	.27
II-14	.0503	.0164	.0101	.415	1.0	.24
II-65	.0502	.0248	.0100	.506	absent	
II-17	.0500	.0249	.0046	.518	absent	.23
II-64	.0501	.0287	.0101	.562	absent	.20
II-15	.0505	.0348	.0102	.684	absent	.20
II-63	.0501	.0364	.0100	.665	absent	.20
260	.0502	.0500	.0101	.766	absent	.21
II-62	.0502	.0514	.0101	.761	absent	.20
II-72	.0211	.0164	.0100	.537	absent	.28
II-71	.0263	.0164	.0100	.493	absent	.27
II-69	.0347	.0164	.0100	.447	absent	.30
II-66	.0507	.0164	.0100	.375	absent	.28
II-67	.0564	.0164	.0101	.32	absent	.30
II-68	.0680	.0164	.0101	.364	1.8	.30
II-70	.0832	.0164	.0100	.350	2.5	.38
$II\text{-}17_b$	.0497	.0255	.0194	.607	absent	
II-60	.0499	.0016	.0101	.184	3.5	.45
II-58	.0501	.0031	.0100	.265	2.8	.45
II-18	.0501	.0049	.0099	.202	4.0	.40
II-16	.0502	.0091	.0100	.297	2.4	.23
II-59	.0822	.0031	.0100	.18	5.8	.40

Table 10

The Reaction of ϕO_2N_3 with t-BuOOH

in Chlorobenzene at 126.7° Involving I_2, Iodometry

page	Initial Conc. M./L			$k_1 \times 10^2$ min.$^{-1}$		$\Delta[I_2]/\Delta[P]$	Additives
	$[t\text{-BuOOH}]_o$	$[Azide]_o$	$[I_2]_o$	First Order Part	Initial Fast Reaction		
II-84	.0500		.0101	.248	absent	.13	benzenesulfonyl-p-chloro anilide; .0020 M/L
II-85	.0501	.0031	.0101	.27	absent		anilide; .0050 M/L
II-92	.0500	.0046	.0101	.276	.33	.23	anilide; .0009 M/L
II-93	.0500	.0047	.0101	258	32	.20	anilide; .0036 M/L
II-102	.0500	.0248	.0101	.50	absent	.10	under nitrogen

Figure 18

First-order rate constant for peroxide decomposition in chlorobenzene at 126.7° in the presence of .01 M I_2 and .050 M. initial peroxide concentration. The solid points represent runs having an initial fast part whose rate is not plotted.

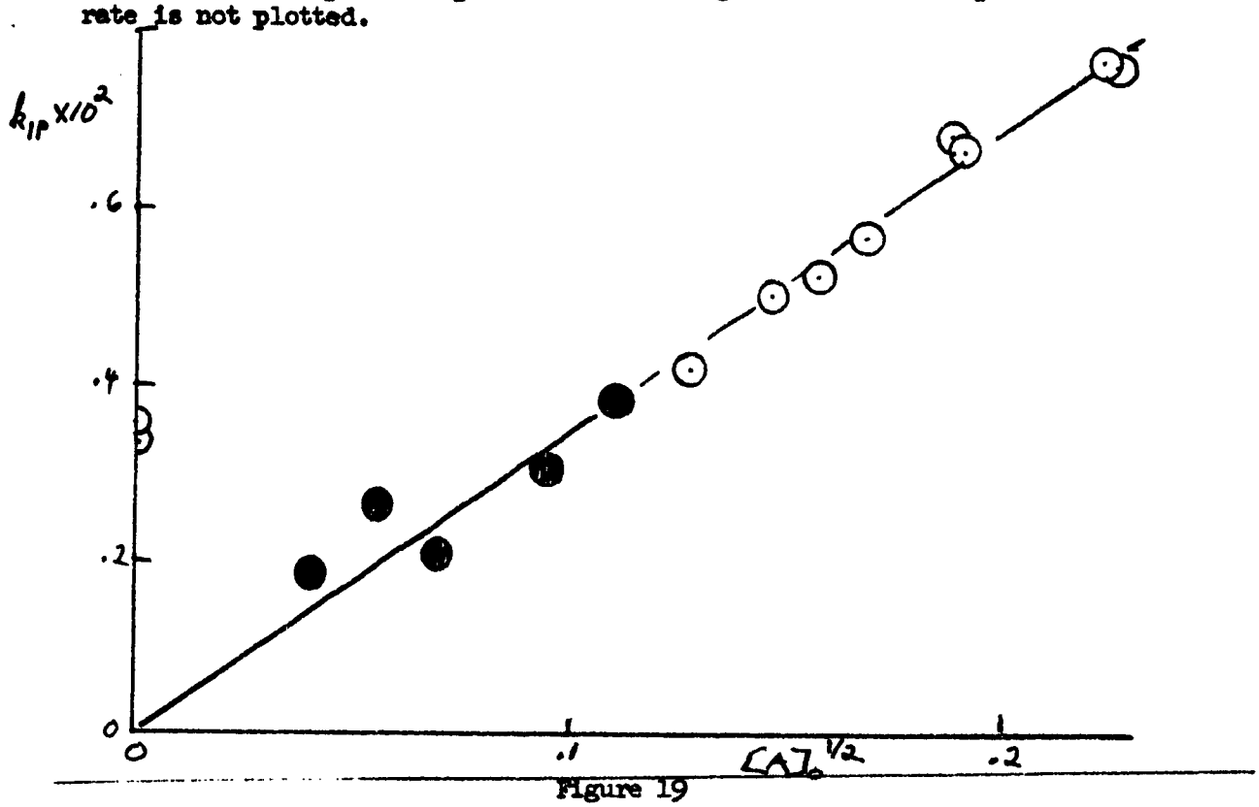
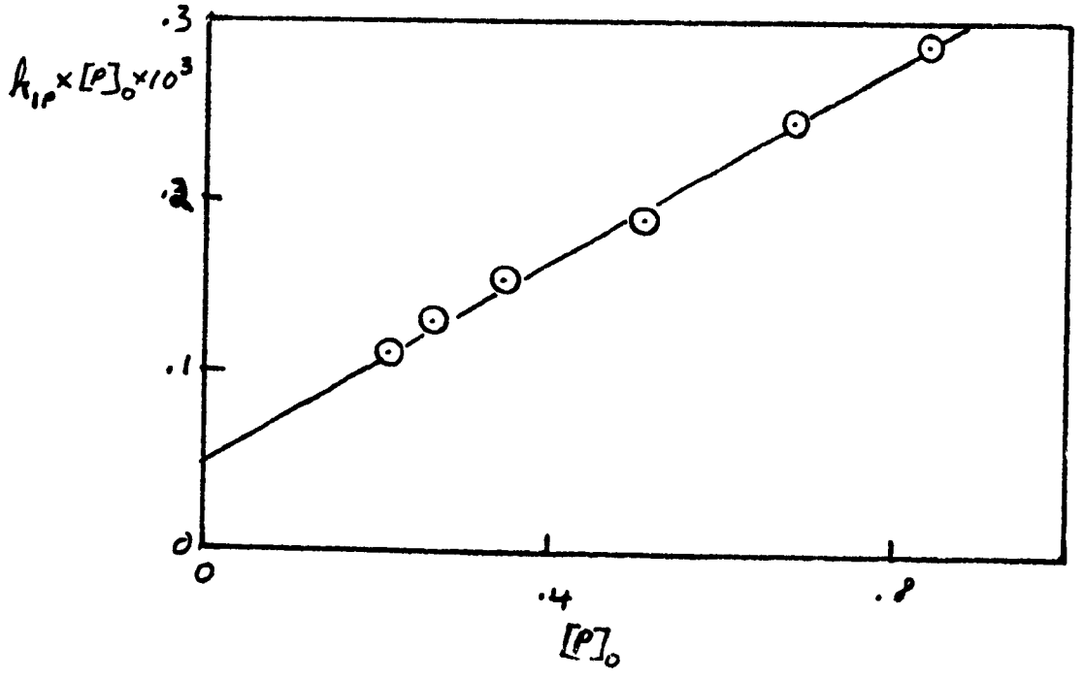


Figure 19

Initial zeroth order rate constants and peroxide concentrations for runs having constant initial concentration of iodine (.01 M) and azide (.0164 M).



The data of figures 18 and 19 can be summarized by equation (2):

$$k_o \cong .4 \times 10^{-3}[A]_o^{\frac{1}{2}} + 23\,[P]_o[A_o]^{\frac{1}{2}} \qquad \text{(Equ. 2)}$$

Since equation (2) differs from equation (1) in having a half-order term in azide in place of a first-order term, we tested the fit of the data to an equation more nearly like (1) and found a fair degree of fit using the coefficients in equation (3).

$$k_o(\text{M/L min}) \cong (0 \text{ to } 1\text{x}10^{-3}) \times [P] + (15\text{x}10^{-3} \text{ to } 22\text{x}10^{-3})[P][A]^{\frac{1}{2}} + 3.1 \times 10^{-3}[A] \qquad \text{(Equ. 3)}$$

In view of the experimental uncertainty in the rates at low azide concentration in the presence of iodine, we believe that equation (3) merits just as much consideration as (2). If so, the main effect of iodine (except for the initial fast reaction) is to reduce the importance of the term in $[P][A]^{\frac{1}{2}}$, perhaps by diversion of t-butyloxy free radicals. The reason for the shift from zeroth to first-order kinetics within a given run remains obscure.

Experimental Part

Triphenylphosphine Method for the Azide

A five 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 triphenyl phosphine reagent consists of 13.12 G of ϕ_3P in 50 ml. of $CHCl_3$. The gas b rette 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 ϕ_3P is used in order to destroy any unreacted peroxide.

$$\phi_3P + \phi\,SO_2N_3 \longrightarrow N_2 + \phi_3\overset{+}{P}\text{-}\overset{-}{N}SO_2\phi$$

$$\phi_3P + (CH_3)_3COOH \longrightarrow \phi_3PO + (CH_3)_3COH$$

Iodometry

A 10 ml. aliquot is diluted with 25 ml. isopropyl alcohol, 5 ml. acetic acid and 5 ml. of aqueous sat. KI are added, and the mixture is shaken and warmed for 20 min. at 60-70°. The solution is then diluted with water and titrated with .05 N thiosulfate.

For free iodine, the sample in isopropyl alcohol is titrated with thiosulfate before adding the KI and acetic acid and warming.

Part VII

Triphenylphosphine Oxide Peroxide

Attempted oxidation of the phosphine imines from triphenylphosphine and benzoyl azide or benzenesulfonyl azide[43] with peracids or hydroperoxides gave unchanged starting material from the sulfonyl phosphine-imine and benzamide, benzonitrile, and triphenylphosphine oxide from the benzoyl phosphine-imine. However, treatment of the benzoyl phosphine-imine with hydrogen peroxide in warm acetic acid gave a new substance which we will tentatively call the triphenylphosphine oxide peroxide. It was subsequently found that the new peroxide could be prepared directly from triphenyl phosphine oxide.

[43] Analogous oxidation of ylides gives alkenes. See
H. J. Bestmann, Angew. Chem., 72, 34 (1960);
D. B. Denney and L. C. Smith, JACS, 82, 2396 (1960).

Preparation and Properties of Triphenylphosphine Oxide Peroxide

To 4.0 g. of ϕ_3PO dissolved in 30 ml. of dioxane is added 15 ml. of 30% H_2O_2 cooling in ice water. The mixture is then allowed to stand for 24 hours and diluted with ice water. The peroxide which precipitates melts at 127-130° with gas evolution. It may be dried by treatment with Na_2SO_4 in hot benzene; it crystallizes on cooling the filtered solution. Yield, 3.5 g., m.p. 130-131° with gas evolution. The reaction may also be carried out in acetic acid, but t-butyl hydroperoxide may not be used in place of H_2O_2.

Equivalent Weights by Iodometry

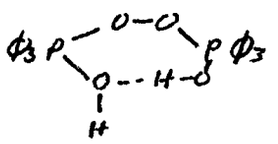
311
277
281
290
or 290 ± 10

Equivalent weight by O_2 evolved from the decomposition in ØCl is 282.

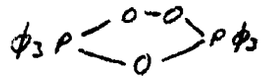
The $Ø_3PO$ obtained on removal of the ØCl melted at 154.5° without any further purification. Oxygen was identified by the glowing splint test and absorption in alkaline pyrogallol.

CHP Analyses by Clark Microanalytical Laboratory

	C	H	P
	73.73	6.01	10.53
	73.85	5.82	10.50
	73.80	5.03	
Av.	73.79	5.62	10.52

Theory for 

C	H	P	Equ. wt.
73.21	5.47	10.49	304

Theory for 

C	H	P	Equ. wt.
75.51	5.29	10.82	286

Infrared Spectrum

The infrared spectrum (in Nujol) is very much like that of $Ø_3PO$, except for a band at 3.2 μ (- OH dimer) and the following slight shifts:

Band in ϕ_3PO	Band in $(\phi_3PO)_2H_2O_2$
absent	3.2
8.4-8.5	8.5-8.7
10.85	10.8
13.2-13.4	13.1
	13.35

Reactions of Triphenylphosphine Oxide Peroxide

Although a quantitative evolution of oxygen is observed in chlorobenzene at 126.7°, a sample of the peroxide added to a solution of anthracene in xylene at the same temperature evolves no gas at all. The products of the decomposition in the presence of anthracene have not yet been investigated.

The peroxide (.10 g.) dissolved in 15 ml. of styrene and warmed at 60° for 15 hours gives considerable methanol-insoluble polymer. A control experiment without the peroxide gave no polymer.

Refluxing the peroxide (2.32 g.) with styrene (0.40 g.) in 50 ml. $CHCl_3$ for three days gave an oil having a carbonyl peak in the infrared at 1700 $cm.^{-1}$ It does not appear to be acetophenone.

The peroxide dissolves only very slowly in refluxing cyclohexene. Besides ϕ_3PO, the product is a small amount of an oil having a carbonyl absorption at 1670 cm^{-1}. (Cyclohexanone absorbs at 1710 cm^{-1}.) V.P.C. with a silicone-firebrick column shows only one major fraction, probably cyclohexenone.

The peroxide (6.00 g.) and benzhydrol (1.85 g.) in 25 ml. of benzene was refluxed for three days, at the end of which the peroxide had been almost completely consumed. After removal of the benzene and extraction of the residue with ether an insoluble residue of 4.05 g. of ϕ_3PO was obtained. The ether-soluble material was chromatographed on alumina, giving 1.1 g. of benzophenone and a small further amount of ϕ_3PO.

The peroxide in benzene does not appear to oxidize benzophenone, benzil, or l-menthol.

Part VIII.

Trapping of Carbenes by Triphenylphosphine

The generation of dichlorocarbene (from $CHCl_3$) in the presence of triphenylphosphine results in the formation of the corresponding ylide. This substance is readily hydrolyzed to triphenylphosphine oxide. It will react with carbonyl compounds to form terminal alkenes. Since parallel results have in the meantime been published by Seyferth, Grim, and Read[44]

[44] D. Seyferth, S. O. Grim, and T. O. Read, JACS, 82, 1511 (1960).

we discontinued this part of our program.

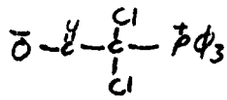
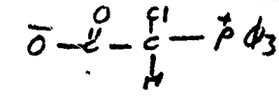
Part IX.

Miscellaneous Exploratory Experiments

(1) Reactions of silyl azides and azo compounds were discontinued.

(2) Negative results were obtained in attempts at trapping anthracene triplet states or diradicals with triphenylphosphine.

(3) The electron-deficient intermediate from the photolysis of β-naphthalenesulfonyl azide in iodobenzene is not trapped by the iodobenzene with formation of trivalent iodine-nitrogen compounds.

(4) The reaction of triphenylphosphine with sodium trichloroacetate in ethyleneglycol dimethyl ether gives a product which appears to be a mixture of  and 

(5) An attempt at inducing the decomposition of a sulfonyl azide by means of dichlorocarbene (from sodium trichloroacetate) had negative results.

(6) The reaction of diphenylphosphonyl chloride with diazomethane appears to give the chloromethyl derivative rather than the desired

diazomethyl derivative.

(7) The decomposition of diphenyliodonium azide does not proceed by the diphenyliodine-nitrene path, but only by way of the iodoazidobiphenyl.