

geneous, fixed-bed acid catalysis, it is possible to convert trioxane vapors conveniently to anhydrous, gaseous formaldehyde in good yield. Conversions as high as 89% were obtained in the equipment shown in Fig. 1 at 220–230° and at

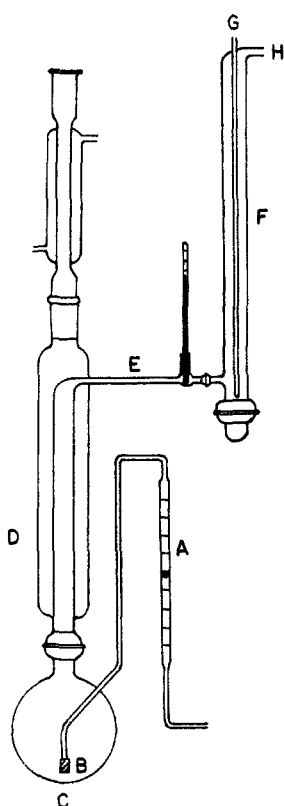


Fig. 1.

mass velocities of 0.3 to 0.4 g. trioxane/g. catalyst-hr. Since no by-products (such as carbon monoxide, carbon dioxide, hydrogen, other water insoluble gases, or methyl formate) and no unreacted trioxane were found in the product stream, it is possible that quantitative conversions were actually approached. Mechanical losses from paraformaldehyde formation in the water absorber used for calibration were noted but not corrected for.

Catalysts used included Amberlite IR-120 ion-exchange resin, potassium acid sulfate-on-activated charcoal, potassium acid sulfate-on-silicon carbide, and phosphoric acid-on-silicon carbide. Of these, the last was the most satisfactory, since the others either gave undesirable by-products (methyl

formate or sulfur compounds) or had a short life. A 32% phosphoric acid-on-silicon carbide catalyst was used intermittently for 50 hours with no detectable decrease in activity.

Experimental

Flow of trioxane vapors was regulated by controlled vaporization with an inert carrier gas. Nitrogen was metered (A) through a fritted glass gas dispersion tube (B) into boiling trioxane (C). Trioxane saturated nitrogen at 99.5° was obtained by cooling the vapors in a thermodynamic condenser (D) containing refluxing *s*-butyl alcohol in the jacket. The vapors were preheated (E) to 200° and passed into the electrically-heated depolymerizer (F) containing 106 g. (135 cc.) of 32% phosphoric acid-on-carborundum maintained at 220–230° as indicated by thermocouple (G). Formaldehyde evolved (H) should be kept at temperatures of 160° or above, or polymerization to paraformaldehyde catalyzed by traces of water may occur. The nitrogen flowmeter was calibrated in terms of the rate of trioxane delivered to the depolymerizer.

The catalyst was prepared by absorbing 185 g. of a 77% phosphoric acid solution on 297 g. of porous silicon carbide granules (4–8 mesh) and drying at 110° for 16 hours.

In a typical run 15.5 g. (0.172 mole) of trioxane was vaporized in 30 minutes, and the product gases were absorbed in water. Titration of the base liberated on the addition of sodium sulfite to a neutralized aliquot showed that 13.8 g. (0.469 mole, 89%) of formaldehyde had been formed. No water insoluble gases were formed, and analyses of the absorbate for trioxane and ester were negative.

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The Ignition Limits of 1–3 Mixtures of Carbon Disulfide and Oxygen^{1,2}

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In 1935, Semenoff³ summarized the status of the study of CS₂ oxidation by pointing out that "the experimental results are hardly reproducible, and the difficulties immense." The first extensive work⁴ had consisted of the determination of the boundaries in cylindrical flasks. Only a general picture resulted, owing to the great difficulties encountered in reproducing boundary points. A paper by Sagulin⁵ on this explosion system and one by Prettre and Lafitte,⁶ who studied CS₂-air mixtures, had presented rather limited observations of ignition limits.

It could be concluded from the published results cited that the greatest deterrent to reproducibility is the sensitivity of the reaction to surface conditions. To overcome this difficulty, a procedure was developed whereby each flask was cleaned without washing, using the heating process described in the experimental section. It was thus possible to reproduce most explosions within a few degrees centigrade and a few mm. pressure. Ignition limits were obtained for several sizes of Pyrex and quartz flasks, and include a third limit hitherto not reported. These data also resulted in orderly relationships between induction time, τ (period between mixing of gases and explosion) and temperature at constant pressure, and between τ and pressure at constant temperature. In past studies of CS₂-O₂ systems, induction times varied at random with pressure and temperature.

Experimental

To determine whether or not a given mixture of CS₂ and O₂ would explode, the ignition flask was first brought to the desired temperature in an air-stirred thermostat ($\pm 0.2^\circ$). Carbon disulfide was then admitted to the evacuated (0.1 μ) ignition flask through a stopcock connected to the vessel by 2-mm. bore capillary. The system back of the stopcock was evacuated and filled with oxygen to a calculated pressure. When the stopcock was opened, the mixture in the flask quickly attained the desired equilibration value.

Explosion, if it took place, could be observed visually by a brilliant violet flash, and was also detected and timed by a photomultiplier and associated circuit. A fairly heavy yellow deposit, probably of (CS)_n and S, was left on the flask by the explosion; a very light deposit could usually be found even when ignition did not occur. After observation, the flask was removed from the thermostat and cleaned of all surface impurities by repeatedly evacuating, filling with oxygen, and flaming to a red heat with a gas-oxygen flame. This treatment, which removed all products as SO₂ and CO₂, caused some distortion of Pyrex flasks but had very little effect upon quartz in which most of the explosions were carried out. After flaming, the flask was returned to the thermostat and maintained at 300° and a few tenths of a micron of pressure for three hours. The vessel was then

(1) This research was performed under Contract No. AF33(038)-20863 with Wright Air Development Center, Dayton, Ohio.

(2) Presented at the 123rd Meeting of the American Chemical Society at Los Angeles, California, March, 1953, and the Meeting-in-Miniature of the Philadelphia Section of the American Chemical Society, January, 1953.

(3) N. Semenoff, "Chemical Kinetics and Chain Reactions," Clarendon Press, Oxford, 1935, p. 280.

(4) H. W. Thompson, *Z. physik. Chem.*, **10B**, 273 (1930); H. W. Thompson and C. F. Kearton, *ibid.*, **14B**, 359 (1931).

(5) A. B. Sagulin, *ibid.*, **1B**, 275 (1928).

(6) M. Prettre and P. Lafitte, *Compt. rend.*, **190**, 796 (1930).

ready for another explosion, which occurred under almost identical conditions.

Long induction periods were usually observed, and were quite frequently of at least 15 seconds duration and as long as several minutes. Since even the longest induction times correlate so well with other ignition data, it can be concluded that the results are relatively free of pre-ignition and other effects of incomplete mixing.

A check was made on the temperature of the gases after admission of the cold O_2 to the CS_2 and flask at thermostat temperature. A very fine thermocouple was placed inside the ignition vessel and the temperature change was followed with a suspension galvanometer. Results indicated that upon addition of the oxygen the temperature dropped to a minimum of only a few tenths of a degree below the thermostat temperature in a very short time, and recovered slowly, in a matter of seconds (5-10). Thus as far as cooling effects are concerned, the boundary temperatures found can be considered to be high by not more than a few tenths of a degree centigrade.

The CS_2 used was purified by fractionating a C.P. grade of analyzed material in an 18-in. silvered Stedman column. A constant boiling ($\pm 0.1^\circ$) fraction was obtained using a reflux ratio of 15:1 and a reflux rate of 5 ml./min. The purified liquid was dried over $CaSO_4$ and kept in a tube ending in a packless valve to obviate air leakage. Pure oxygen was prepared by the thermal decomposition of $KClO_3$ using Fe_2O_3 as a catalyst. Airco spectrometrically pure O_2 was also used with no difference in results.

Results

The ignition limits obtained are shown in Fig. 1, and are characteristic of a branched chain explosion. In the pressure range of the first limit it is generally accepted that the probability of an active center diffusing to and being destroyed at the wall is inversely proportional to the pressure. This leads to a first boundary relationship between total initial pressure p and flask diameter d , such that pd^2 is a constant. For the two smaller flasks, $d_1^2/d_2^2 = 0.71$, while $p_2/p_1 = 0.72 \pm 2\%$ over the range 115 to 140° to satisfactorily confirm this relationship. The data for the two large flasks, relative to the data for the smaller, are qualitatively but not quantitatively, in accord with this relationship.

The second limits of the two smaller flasks show the convergence expected for a homogeneous gas phase process. This would correspond to chain breaking in three-body collisions, as postulated by Lewis and von Elbe for the H_2-O_2 explosion. However, it can be noted that the second limits of the two larger flasks of essentially equal size do not converge with the limits of the smaller flasks. If the lack of convergence were due to surface effects, the coincidence of the second boundaries of the two smaller flasks of unequal size would be rather improbable. This low probability is especially likely for smaller flasks with their greater surface-to-volume ratio. The explanation for the lower second limits of the larger flasks thus would seem to involve the increasing importance of thermal explosion. Further experiments with vessels coated with inorganic materials should help to elucidate this phase, since the surface will be identical for all vessel sizes.

The definite existence of a third limit can be noted on Fig. 1. That this was not reported by Thompson and Kearton³ can be ascribed to the inhibition caused by reaction products. The latter could easily accumulate under the conditions used for determinations at the higher pressures of the third limit. In this method, a cold vessel

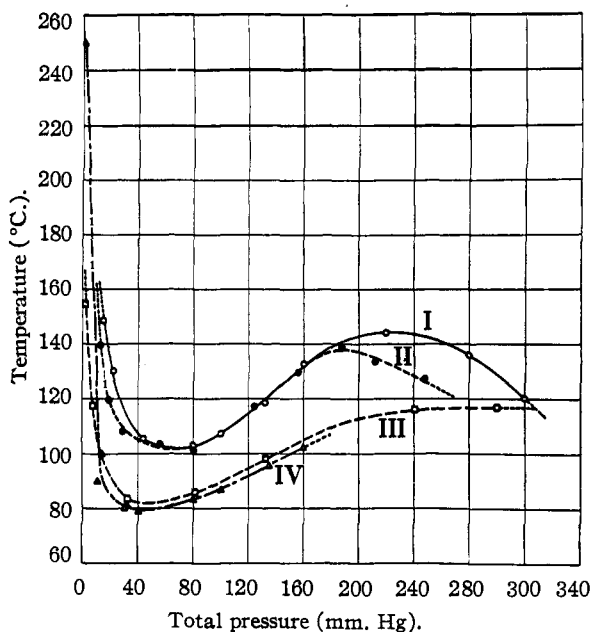


Fig. 1.—Ignition limits of $CS_2 + 3O_2$ as a function of total pressure and temperature. Curve I of flask I, 4.15 cm. diam., quartz; II, 5.05 cm. diam., quartz; III, 6.05 cm. diam., quartz; IV, 5.85 cm. diam., Pyrex.

containing the mixture was plunged into the heated thermostat, allowing ample time for slow reaction before thermostat temperature was attained. In the present experiments, it has been shown that a non-explosive mixture formed at the higher pressures of the 3rd limit will not explode at the boundary when heated thereafter; in fact, not until a much higher (by 50° or more) temperature is reached. A relatively dark coating, probably of S and $(CS)_n$, on the vessel surface gives evidence that a considerable reaction is present.

As previously mentioned, it was possible to observe logical variations in induction time as a function of temperature and pressure. Thus in a series of observations at constant pressure at varying temperatures, in the vicinity of a boundary, the curves shown on Fig. 2 were obtained. The induction time (τ) can be considered to be the time interval of the approximately linear or zero-order section of the curve describing the increase in chain carriers from the time of mixing to explosion. One would therefore expect a relationship such as

$$\tau e^{-E^\ddagger/RT} = \text{constant}$$

such as is given by Semenov.⁷ Thus a plot of $\log \tau$ as a function of $1/T$ ($^\circ K.$) should result in a straight line. Such a graph for the data of Fig. 2 follows such a formula, and exhibits deviations from a straight line which seem to be random in nature. In view of the difficulties entailed in reproducing an induction time in some boundary regions, these deviations are within the limit of experimental error.

In the region of the first limit, data showing the variation in induction time as a function of pressure (at constant temperature) are even more

(7) See. ref. 3, pp. 85-87.

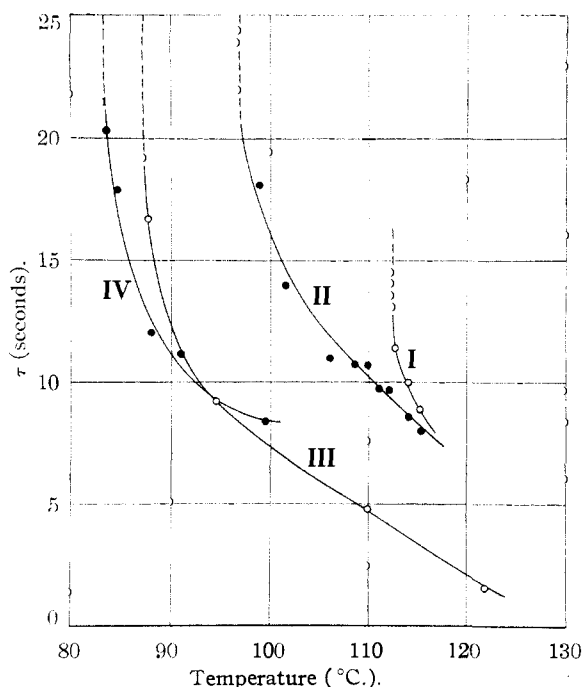


Fig. 2.—Variation of induction time with temperature: curve I, flask I, $p = 32$ mm.; II, flask II, 32 mm.; III, flask IV, 101 mm.; IV, flask IV, 80 mm.

satisfactory. We believe that these data can be satisfactorily interpreted through consideration of the basic processes of chain propagation. This will be considered in future publications when more data are available.

The present work represents the initial efforts of a more extensive study of the $\text{CS}_2\text{-O}_2$ system, which will include spectroscopic as well as ignition data.

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The Irradiation of Crystalline Vitamin B_{12} with Neutrons

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The widespread interest in the biological role of vitamin B_{12} makes its availability in radioactive form for tracer studies highly desirable. Microbiological synthesis of vitamin B_{12} labeled with Co-60^{1-3} and P-32^3 has been described. However, isolation of substantial quantities of crystalline vitamin B_{12} from fermentation broths is a fairly tedious operation, and an easier route to the labeled vitamin would be desirable.

A recent communication⁴ has claimed the forma-

(1) L. Chalet, C. Rosenblum and D. T. Woodbury, *Science*, **111**, 601 (1950).

(2) C. Rosenblum and D. T. Woodbury, *ibid.*, **113**, 215 (1951).

(3) E. L. Smith, D. J. D. Hackenschull and A. R. J. Quilter, *Biochem. J.*, **52**, 387 (1952).

(4) R. C. Anderson and Y. Delabarre, *THIS JOURNAL*, **73**, 4051 (1951).

tion of vitamin B_{12} labeled with Co-60 by the irradiation of vitamin B_{12} with thermal neutrons. Since the completion of our work another report⁵ has appeared, describing the results of experiments similar to those of Anderson and Delabarre.⁴ Such a procedure, if successful, would offer an attractive alternate route to the preparation of the labeled vitamin even if the specific activities obtained were not as high as those obtainable by microbiological synthesis.

In an effort to duplicate this method of preparation of Co-60 labeled vitamin B_{12} we have had a sample of the crystalline vitamin irradiated with neutrons. Our results, which differ from those published,^{4,5} are based on the use of countercurrent distribution for the establishment of the identity of the Co-60 labeled material.

Experimental

Fifty milligrams of anhydrous crystalline vitamin B_{12} , sealed in an evacuated quartz vial, was irradiated for 19 days in the Brookhaven National Laboratory reactor through the courtesy of Dr. R. C. Anderson, Chemistry Department, Brookhaven National Laboratory, Upton, Long Island, New York. The irradiation was carried out at a temperature of $30\text{-}35^\circ$ in a special "cold-hole" in the Brookhaven pile at a flux density of 2.7×10^{12} neutrons/cm.²/sec. The exact energy spectrum of the irradiation flux was not known; besides the predominantly thermal neutron flux there were present also undetermined epithermal neutron and gamma radiation fluxes.

After irradiation the quartz vial was allowed to stand for two months to allow the decay of short-lived isotopes. The vial was then opened and the contents dissolved in water. Bioassays of an aliquot of this solution indicated that about one-third of the original biological activity remained. Another portion of the solution, when tested for Co^{++} ions using dithizone in chloroform, and α -nitroso- β -naphthol, gave negative results.

The irradiated material was purified by extraction into benzyl alcohol, after formation of the dicyanide complex, according to the procedure of Rudkin and Taylor.⁶ Water was added to the benzyl alcohol extract and the vitamin B_{12} then transferred to the aqueous phase by the addition of chloroform. After decomposition of the dicyanide complex, the aqueous layer was then evaporated to a small volume and vitamin B_{12} crystallized by the addition of acetone.⁶ Recrystallization was also carried out from aqueous acetone. Twenty-one milligrams of crystalline material was obtained representing 42% of the weight of the starting material. Five milligrams of this material was used in a countercurrent distribution with the system benzyl alcohol-water.¹ Each tube of the distribution was assayed for biological activity and for radioactivity.

Beta radioactivity was determined with a flow counter operating in the Geiger region; gamma radioactivity was determined with a scintillation counter.

All paper chromatograms were carried out on Whatman #1 paper. The two-dimensional chromatogram of the crystals isolated after irradiation is shown in Fig. 1. The vitamin B_{12} spot, though devoid of radioactivity, is still close to the point of application of the sample at the origin of the chromatogram. In the hope that a longer development time would result in a greater separation of the vitamin B_{12} from the other materials, a unidimensional chromatogram was carried out in which development was continued until the vitamin B_{12} spot had moved 14 cm. from the origin. An autoradiograph of this paper was made, with the results shown in Fig. 2. There are dense areas of radioactivity at the origin and at distances of 1.5, 5 and 6.7 cm. from the origin.

Countercurrent distribution of the purified crystallized sample of vitamin B_{12} was also employed to characterize the material isolated from the irradiated crystals. If Co-60 labeled vitamin B_{12} were present, the distribution of radioactivity/tube should parallel the distribution of bioactivity/

(5) E. L. Smith, *Biochem. J.*, **52**, 384 (1952).

(6) G. O. Rudkin and R. J. Taylor, *Anal. Chem.*, **24**, 1155 (1952).