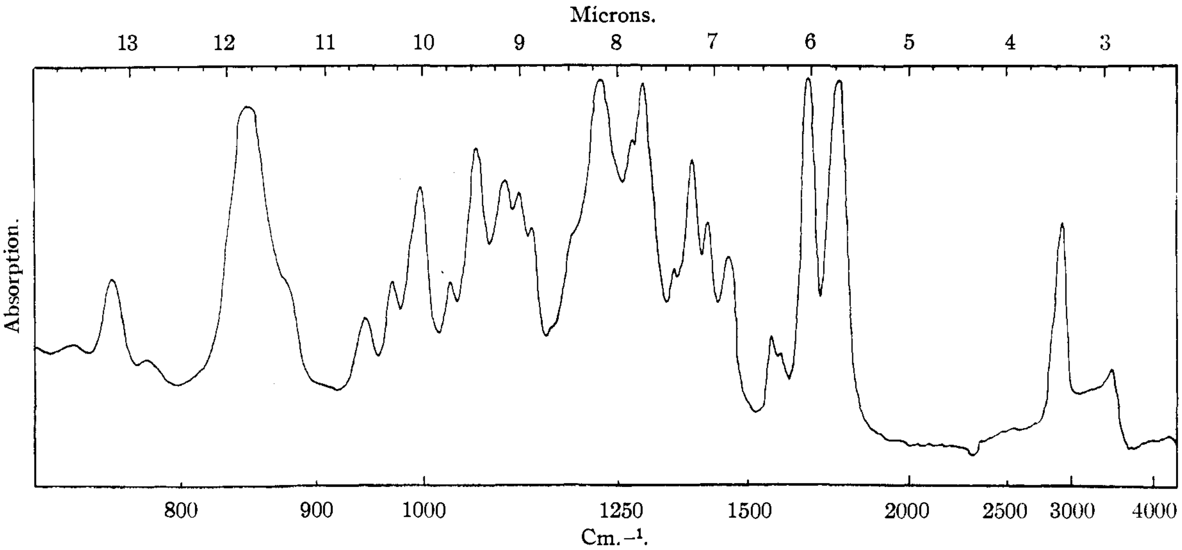

Fig. 1.—*s*-Butylglycolate nitrate, $O_2NO—CH_2\overset{\overset{O}{\|}}{O}—OCH—\overset{\overset{CH_3}{|}}{C}—CH_2—CH_3$.

at 2.96 μ. The height and breadth of this band are neither as great with respect to the C–H band as they are in the case of *s*-butylglycolate nitrate. Since the number of C–H bonds differ only by one in the two compounds the relative height and breadth of the bands near 3 μ should give an indication of the amount of enol in the compounds. On this basis one would conclude that there is somewhat more enol in liquid *s*-butylglycolate nitrate than in liquid ethylacetoacetate.

If this 3 μ band is due to enol then it should change on being measured in dilute solution in a solvent such as carbon tetrachloride. The broad character of the band in the liquid is attributed to hydrogen bonding, and mainly intermolecular hydrogen bonding because the ring formed by intramolecular hydrogen bonding would be seven membered and therefore relatively unstable. In Fig. 3 the plot of the spectrum for this region for a 0.42% solution of the compound in carbon tetrachloride in a 2-mm. cell shows all of these predictions are fulfilled. The band is considerably narrower and is of lower extinction, the total amount of absorption having been reduced to about one-fourth of that shown by the pure liquid in this region. The maximum has shifted from 2.93 to 2.88 μ, close to the wave length characteristic of a free OH. All of these changes are the expected result of the suppression of intermolecular hydrogen bonding in dilute solution.

The strong band at 5.73 μ or 1745 cm.$^{-1}$ is attributed to the carboxylic ester C=O and the one at 6.04 μ or 1656 cm.$^{-1}$ to the nitrate group. Ethyl nitrate for example has a strong band at 6.10 μ or 1639 cm.$^{-1}$. Any absorption in the range 1600–1660 cm.$^{-1}$ expected from C=C present in the enol, would thus be obscured by this nitrate band.

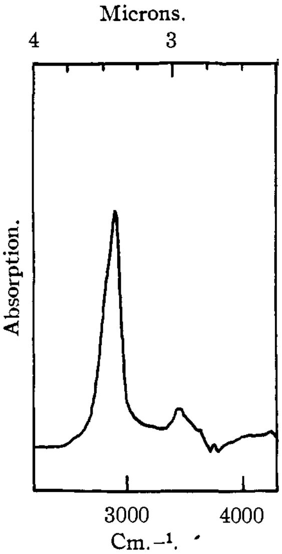

Fig. 2.—Ethyl acetoacetate.

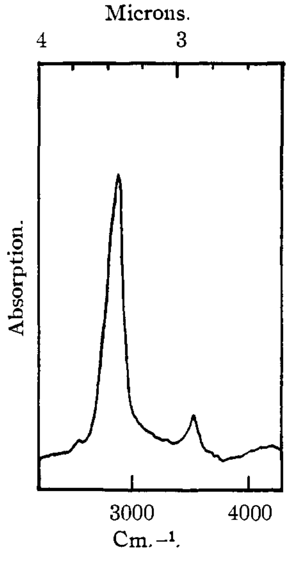

Fig. 3.—*s*-Butylglycolate nitrate, 0.210 g. in 50 ml. of CCl_4, 20-mm. cell.

I wish to thank Dr. Harry K. Iwamoto for supplying the glycolate nitrate esters and Dr. Louis A. Strait and Mr. M. K. Hrenoff for measuring ethyl nitrate. I am especially indebted to Professor Richard M. Badger for his expert advice and counsel during the investigation.

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Vapor Phase Depolymerization of Trioxane

BY ARTHUR W. SCHNIZER, GENE J. FISHER AND ALEXANDER F. MACLEAN

RECEIVED APRIL 14, 1953

Liquid phase homogeneous acid-catalyzed depolymerization of trioxane has been described as an *in situ* source for formaldehyde.[1] Using hetero-

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[1] J. F. Walker and A. F. Chadwick, *Ind. Eng. Chem.*, **39**, 974 (1947).

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 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.

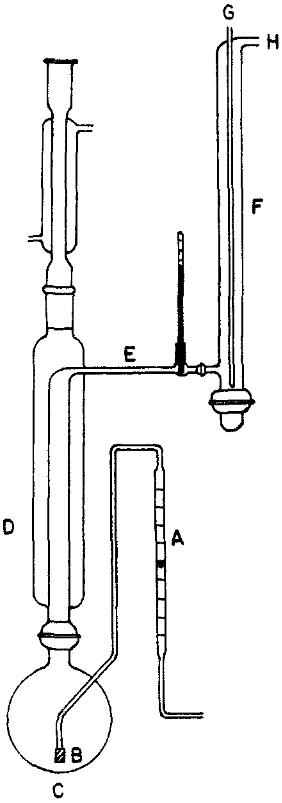

Fig. 1.

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 thermostatic 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]

BY ALBERT L. MYERSON AND FRANCIS R. TAYLOR

RECEIVED JANUARY 12, 1953

In 1935, Semenoff[3] summarized the status of the study of CS_2 oxidation by pointing out that "the experimental results are hardly reproducible, and the difficulties immense." The first extensive work[4] 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 Sagulin[5] on this explosion system and one by Prettre and Lafitte,[6] who studied CS_2–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 cleansed 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 CS_2–O_2 systems, induction times varied at random with pressure and temperature.

Experimental

To determine whether or not a given mixture of CS_2 and O_2 would explode, the ignition flask was first brought to the desired temperature in an air-stirred thermostat (±0.2°). 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 SO_2 and CO_2, 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

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[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).