TABLE I

FORMATION OF PERHYDRO-*s*-TRIAZINES IN VARIOUS SOLVENTS

Solvent	Temp., °C.	Perhydro-*s*-triazine yield, % Propionitrile	Acrylonitrile	Benzonitrile
Carbon tetrachloride	77	86	89	95
Carbon disulfide	46	66	64	8
Chlorobenzene	100	64	37	78
Nitromethane	102	64	21	79
Trichloroethylene	87	63	38	56
Methyl chloroform	74	53	9	56
Ethylene dichloride	84	45	69	73
s-Tetrachloroethane	100	42	76	81

class are insoluble in this solvent and precipitate from solution as they are formed. Consequently, the quality of the crude perhydro-*s*-triazine obtained with carbon tetrachloride has been in every case superior to that obtained under any other conditions. It is interesting to note that Gresham and Steadman[5] reported that commercial acrylonitrile was a superior reactant for perhydro-*s*-triazine formation, while we have observed that freshly distilled acrylonitrile gives much better and more reproducible yields in carbon tetrachloride. Carbon disulfide is also of considerable interest since with this solvent the reaction may be carried out at relatively low temperatures and under mild conditions. Solvents in which the perhydro-*s*-triazines were obtained in low yield were nitrobenzene, dioxane, chloroacetic acid, trichloroacetic acid, and acetic acid. In ethyl acetate, formic acid and ethyl ether, no perhydrotriazine was isolated.

In order to test further the excellence of carbon tetrachloride as a solvent for this reaction, *p*-chlorobenzonitrile and *p*-methoxybenzonitrile (both solids) were converted to the previously unknown perhydro-*s*-triazines in yields of 88 and 98%, respectively. Vinylacetonitrile failed to react in carbon tetrachloride, probably due to the fact that it is relatively insoluble in this solvent.

Experimental[6,7]

Typical procedures for the experiments summarized in Table I are given below. Formaldehyde was introduced in every case as *s*-trioxane, and the experimental conditions were standardized insofar as was conveniently possible. The products were identified by infrared spectra and by melting point and mixed melting point where applicable. The procedures for preparation of tris-*p*-chlorobenzoylperhydro-*s*-triazine and tris-*p*-methoxybenzoylperhydro-*s*-triazine are also described.

1,3,5-Triacrylylperhydro-*s*-triazine.—A solution of 13.2 g. of freshly distilled acrylonitrile, 0.65 g. of sulfuric acid and 50 ml. of dry carbon tetrachloride was brought to reflux. A solution of 13.3 g. of acrylonitrile and 15.0 g. of *s*-trioxane in 50 ml. of carbon tetrachloride was then added dropwise with stirring over a 15-minute period. A white solid separated out before addition was complete. The mixture was then stirred one hour under reflux. After cooling to room temperature, the white amorphous solid was collected on a filter and washed with carbon tetrachloride, yield 37.0 g. (89%). The product did not melt before polymerization but its infrared spectrum was identical to that previously reported.[2]

1,3,5-Tripropionylperhydro-*s*-triazine.—To a boiling solution of 5.5 g. of propionitrile, 0.20 g. of sulfuric acid and 20 ml. of carbon disulfide was added over a 10-minute period 5.5 g. of propionitrile and 6.0 g. of *s*-trioxane in 20 ml. of carbon disulfide. The solution was stirred under reflux for two hours and then cooled to room temperature. The product was washed with carbon tetrachloride and 11.3 g. (66%) of white crystalline material was obtained. After recrystallization from ethyl acetate the perhydro-*s*-triazine melted at 170–173°. A melting point of 169–171° has been reported.[2] The infrared spectrum was identical to that reported in the literature.[2]

1,3,5-Tris-*p*-chlorobenzoylperhydro-*s*-triazine.—*p*-Chlorobenzonitrile (17.2 g.) was dissolved in 50 ml. of carbon tetrachloride containing 0.65 g. of sulfuric acid. To this solution under reflux was added with stirring over a 20-minute period 17.2 g. of *p*-chlorobenzonitrile and 7.5 g. of *s*-trioxane in 50 ml. of carbon tetrachloride. The resulting mixture was boiled for 75 minutes. No product separated out during this period. The solution was then cooled to −15° and 40.8 g. (98% yield) of light yellow solid separated, m.p. 208–213°. The product was recrystallized from a mixture of carbon tetrachloride and ether. After recrystallization, the melting point increased to 216–217°. The infrared spectrum of the compound was in agreement with the proposed structure and showed an amide carbonyl band at 1652 cm.$^{-1}$.

Anal. Calcd. for $C_{24}H_{20}N_3O_3Cl_3$: C, 57.29; H, 3.61; N, 8.35. Found: C, 57.74; H, 3.88; N, 8.16.

1,3,5-Tris-*p*-methoxybenzoylperhydro-*s*-triazine.—To 20 ml. of carbon tetrachloride was added 6.7 g. of *p*-methoxybenzonitrile and 0.20 g. of sulfuric acid. A solution of 6.6 g. of *p*-methoxybenzonitrile and 3.0 g. of trioxane in 20 ml. of carbon tetrachloride was added to this hot mixture over a 15-minute period. The solution was heated under reflux for one additional hour and was then cooled to −15°. The white crystalline material was collected on a funnel and washed with carbon tetrachloride; yield 14.3 g. (87%). The material was recrystallized from ethyl acetate, m.p. 216–217°. Infrared examination of the compound showed a typical spectrum for a 1,3,5-triacylperhydro-*s*-triazine with a carbonyl frequency at 1656–1659 cm.$^{-1}$.

Anal. Calcd. for $C_{27}H_{27}N_3O_6$: C, 66.20; H, 5.55; N, 8.59. Found: C, 65.95; H, 5.74; N, 8.61.

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[6] All melting points are uncorrected.

[7] We are indebted to Dr. Keith S. McCallum for infrared interpretations and to Mr. Al Kennedy for microcombustion data.

The Extent of Dimerization of Sulfur Monoxide[1]

BY ERSEL A. EVANS, ALLEN B. SCOTT AND JOHN L. HUSTON

RECEIVED MAY 19, 1952

Since the first reported preparation of a "monoxide" of sulfur by Schenk[2] a considerable body of controversial literature has been published[3] regarding the formula of the molecule in the vapor state. Kondrat'ev and Kondrat'eva[4,5] concluded that within a few seconds after sulfur monoxide was formed during the oxidation of H_2S, it exists entirely in the form of the dimer, S_2O_2, at room temperature. On the other hand, Schenk[6] found the molecular weight of the monoxide from the condensed electrical discharge through SO_2 to be about 70; from data of Kondrat'ev he also calculated[3] the molecular weight to be 45.3 for monoxide from the discharge; further he noted a volume decrease of about 25% when the gas was condensed with liquid air and decomposed to sulfur and SO_2 by warming.

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[1] Published with the approval of the Oregon State College Monograph Committee, Research Paper No. 207, Department of Chemistry, School of Science.

[2] P. W. Schenk, *Z. anorg. allgem. Chem.*, **211**, 150 (1933).

[3] See P. W. Schenk, *Chem. Z.*, **67**, 273 (1943), for an extensive bibliography.

[4] V. Kondrat'ev and E. Kondrat'eva, *J. Phys. Chem. U. S. S. R.*, **21**, 1251 (1948).

[5] E. Kondrat'eva and V. Kondrat'ev, *ibid.*, **14**, 1528 (1940).

[6] P. W. Schenk, *Z. anorg. allgem. Chem.*, **248**, 297 (1941).

The process

$$2SO = S_{solid} + SO_2$$

would thus result in a 50% contraction, while the same process for S_2O_2 would result in none. Schenk concluded that the gas was either a mixture of SO and S_2O_2 or of S_2O and SO_2. The latter possibility is ruled out by Kondrat'ev's observation that the gas other than SO_2 has the formula S_xO_x.

Jones[7] showed that diatomic SO cannot be responsible for the ultraviolet absorption of sulfur monoxide and presented evidence that the absorbing species was probably S_2O_2, an opinion previously shared by both Schenk and Kondrat'ev. The presence of SO in addition to S_2O_2 was not entirely excluded; however, an infrared absorption band expected for SO (calculated from its emission spectrum) did not appear.

Since the presence of monomeric SO in the gas during discharge was demonstrated by Henri and Wolff[8] and Martin,[9] it was of interest to determine whether the dimerization occurs with a measurable rate after withdrawal. Schenk explained the difference between his and the Russian data from which he calculated molecular weights by the fact that his samples were condensed "some minutes" after withdrawal from the discharge while the Russians took "fresher" samples. Further, it appeared that Schenk's experiment on contraction following decomposition offered no alternative to the conclusion that the dimer comprises not more than about 50% of the gas for an appreciable time after withdrawal, and was worth repeating.

Experimental

Sulfur monoxide was prepared by means of a 5000 v., 300 ma. discharge through a mixture of SO_2 and sulfur vapor. The apparatus is shown in Fig. 1. The discharge tube, A, contained hollow cylindrical aluminum electrodes of large area (9 cm. long and 6 cm. in diameter) so that no auxiliary cooling was necessary. The stopcock D, of 10 mm. bore, permitted A or E to be evacuated independently, by a mercury diffusion pump trapped with liquid N_2 to prevent decomposition of sulfur monoxide on the mercury. Also A and E could be disconnected from the pumping system and either connected or separated from each other. The connection from A to D was 20 cm. long and 12 mm. bore. E was a 2-liter flask in which gas samples were collected, F a condenser for the gas when immersed in liquid N_2, B a bulb for sampling the gas stream, H a large capacity liquid N_2 trap to retain most of the monoxide, and G a sensitive Bourdon gage. This type of gage was selected for its sensitivity, low response time, and freedom from materials known to decompose sulfur monoxide.

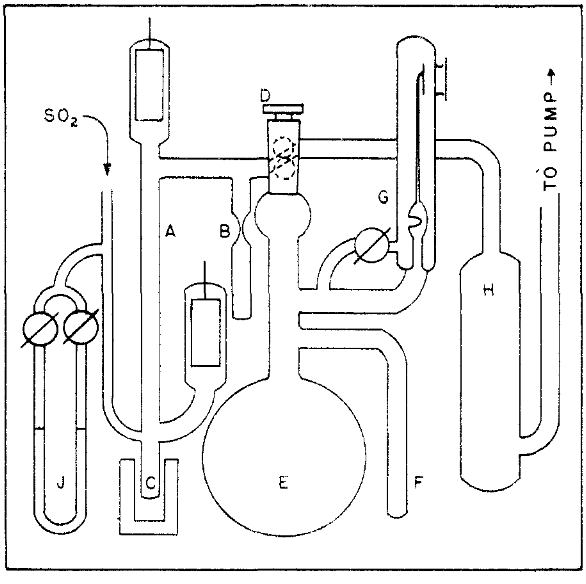

Fig. 1.—Apparatus for preparation of sulfur monoxide and measurement of pressure changes.

Deflections of the gage were followed by means of a mirror, lamp filament image, and scale. The gage was frequently calibrated against the differential H_2SO_4 manometer, J; four different Bourdon gages were used during this investigation and the magnification was usually adjusted so that 1 mm. on the scale represented a pressure difference of about 0.005 mm. The gage deflections were linear with pressure in the range 0–4 mm.

With A connected to the pump and E evacuated, SO_2 was admitted until its pressure in the tube almost quenched the glow discharge. Sulfur was vaporized from C by means of an electric heater and from the tube walls by a hand torch. The exit gas stream was analyzed several times during the discharge under these conditions by freezing out a quantity in B, by means of liquid nitrogen and obtaining the weight of S and SO_2 produced by decomposition of the solid on warming. The ampoule was sealed off and weighed. It was reopened and heated at 60° for several hours and the resulting sulfur was then melted to drive off any remaining SO_2. The ampoule was reweighed. Finally, the sulfur was removed by vaporization and the empty ampoule was weighed. Some loss of sulfur as the monoxide is possible during the process, which would lower the reported proportion of sulfur monoxide in the exit stream, but the elevated temperature at which the decomposition was carried out should minimize this error. Analyses made at four different times showed that the sulfur monoxide content was not very reproducible, but lay between 62 and 95%, averaging 75%. The remainder may safely be assumed to be unconverted SO_2. The analytical method was insufficiently accurate to permit analysis of each sample of gas taken for pressure studies, due to the low pressure (1 mm.), though such analytical data would be desirable in obtaining a quantitative value for the extent of dimerization.

Experiments to detect if polymerization occurred after the gas left the discharge tube were made by admitting a sample of the exit gas to the flask E and observing its pressure by means of the Bourdon gage. Initial readings were made within three seconds in many cases, and observations were continued for periods up to 45 minutes.

To ascertain if there were a pressure decrease during the decomposition to sulfur and SO_2, the procedure was the same except that after obtaining the initial pressure in the flask E, the contents were frozen in F, the pressure was noted, and then the orange-red solid deposited in F was decomposed by flaming until all of the sulfur had sublimed and was redeposited at new locations in the tube. There is uncertainty in the completeness of this decomposition; at temperatures between 0° and 100° some monoxide is resublimed and some oxygen is retained by the sulfur.[6] The sublimation of sulfur should avoid the latter possibility, but it is likely some monoxide was returned to the flask which would of course result in no over-all pressure change. The final pressure, initial pressure and pressure when the gas was solidified were used to compute the relative decrease in pressure during the process.

Results and Discussion

Forty-four attempts were made to detect a decrease in pressure following withdrawal of sulfur monoxide from the discharge tube. The shortest time for opening D, allowing sufficient gas to stream into E, closing D and obtaining an initial pressure reading was three seconds. The pressure was then observed continually for several minutes, in most cases from 3–15 minutes and in one case 45 minutes. Total pressure of the admitted gas was varied from

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(7) A. V. Jones, *J. Chem. Phys.*, **18**, 1263 (1950).

(8) V. Henri and F. Wolff, *J. Phys. Rad.*, [6] **10**, 81 (1929).

(9) E. V. Martin, *Phys. Rev.*, **41**, 167 (1932).

0.40 to 3.24 mm. In only three attempts was any decrease in pressure whatsoever observed and the average of these three decreases was only 0.02 mm. It may be concluded that no rapid polymerization occurs during the period 3 seconds-45 minutes after the gas leaves the discharge. It was not possible to detect any long-time (one or two days) pressure changes arising from slow decomposition, because of insufficient stability of the Bourdon gage over long periods.

The results of several measurements of the pressure change resulting from the decomposition of the monoxide to sulfur and SO_2 are summarized in Table I.

TABLE I

PRESSURE DECREASE ON DECOMPOSING SULFUR MONOXIDE

Initial P(mm.)	Final P(mm).	Decrease, %
0.14	0.09	36
.26	.21	19
.44	.32	18
.56	.38	32
.63	.57	10
.64	.44	31
.70	.64	9
.70	.54	23
.71	.62	13
.94	.63	33
1.15	.48	58
	Average	26

To ensure that the changes were really due to the presence of sulfur monoxide, seven measurements were made on SO_2 alone, three on SO_2 passed through the discharge in the absence of sulfur vapor, and one on SO_2 to which was added sulfur vapor in the absence of the discharge. The average change for these eleven experiments was a decrease of 0.1% with a probable error of 1%.

The large variation between samples in the observed pressure changes is mainly the result of variation in sulfur monoxide content. Qualitatively it was noted that when the deposit in F was more intensely colored, the pressure decrease was greater. Also the relative proportion of molecular species in the gas might be quite variable in a mixture suddenly withdrawn from the reaction zone and "frozen" in a metastable condition. Thus the average decrease of 26% has no quantitative significance other than to show that the change is far greater than the experimental error of the control experiments and to demonstrate that a considerable part of the gas is responsible for the effect. From the average sulfur monoxide content it may be estimated that a typical gas sample contains about 70% monomeric SO, but a wide variation from this typical value is probable.

It is strongly indicated by these experiments that the product from the discharge is a mixture of SO and S_2O_2 which undergoes no appreciable further dimerization after removal from the discharge tube and holding at room temperature 45 minutes. It is not surprising that Kondrat'ev's contention of complete dimerization is contradicted; his arguments rest almost entirely upon experiments conducted in the presence of H_2S and O_2 at total pressures as high as 100 mm. and catalysis of the dimerization may be very important. The existence of monomeric SO should not be considered established, however, until the uncertainties in the analytical methods for the gas mixture and decomposition products are entirely removed and until the question of the absence of a characteristic infrared absorption is solved.

Experiments upon the paramagnetism of the gas would be instructive, if such measurements could be carried out on a compressed sample before it underwent decomposition. Such experiments are projected for the near future.

Acknowledgment.—We are indebted to the Research Corporation for generous support of this project, to T. M. Cromwell, who carried out some of the preliminary experiments, and to Dr. E. N. Marvell, who originally suggested this problem.

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A New Approach to δ-Phenylvaleric Acids

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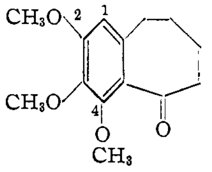
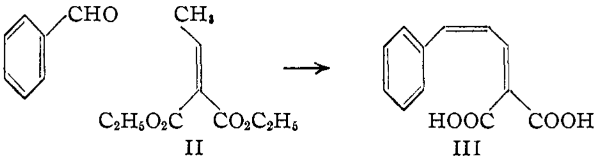
Investigations in progress in this Laboratory on the synthesis of compounds having the carbon ring system of colchicine have encouraged us to seek a method for the preparation of 2,3,4-trimethoxybenzosuberone (I) a needed intermediate. The original synthesis[3,4] was found laborious and a more recent method[5] gave us a mixture of products.



I

Ethylidenemalonic ester (II) has previously been condensed with several aromatic aldehydes by means of concentrated sulfuric acid.[6] Saponification of the condensation products gave cinnamylidenemalonic acids. We have found that potassium hydroxide in absolute alcohol, benzyltrimethylammonium hydroxide in methanol or choline in methanol may replace sulfuric acid in this



II III

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[1] Public Health Service Research Fellow of the National Cancer Institute.

[2] From the Master's Dissertation of R. R. Twelves.

[3] R. D. Haworth, B. P. Moore and P. L. Pauson, *J. Chem. Soc.*, 1045 (1948).

[4] The Haworth procedure has been improved by A. G. Anderson, Jr., and H. F. Greef, THIS JOURNAL, **74**, 2923 (1952).

[5] E. C. Horning, M. G. Horning, J. Koo, M. S. Fish, J. A. Parker, G. N. Walker, R. M. Horowitz and G. E. Ullyot, *ibid.*, **72**, 4840 (1950).

[6] L. Higginbotham and A. Lapworth, *J. Chem. Soc.*, **121**, 2823 (1922).