axis projection does not permit the determination of interatomic distances since none of the bonds is believed to be directed exactly perpendicular to the c-axis. However, the sulfur–oxygen projection distance is equal to the reported value of 1.50 Å. for the sulfates.

Summary.—The primary result of this investigation of the crystal structure of trimethylamine sulfur trioxide using X-ray diffraction is that, in the crystalline state, the SO_3 groups rotate about the molecular axes while the $N(CH_3)_3$ groups rotate very little, if at all. The basic unit cell was found to be a rhombohedron with $a = 5.71$ Å. and $\alpha = 107°40'$ and containing one molecule. The space group is $C_{3v}^5 = R3m$ and the calculated density is 1.52 g./cm.^{3}.


The Oxidation Products of 2,5-Diphenyl-1,4-dithiadiene

BY H. HARRY SZMANT AND JAMES DIXON

RECEIVED JUNE 1, 1953

The recent publication concerning the chemistry of the 1,4-dithiadiene system[1] and the reports of the Diels–Alder type condensation reactions in the course of the oxidation of thiophene[2] and benzothiophene[3,4] prompts us to report the results obtained in the study of the oxidation of 2,5-diphenyl-1,4-dithiadiene (I).

(R = C_6H_5)
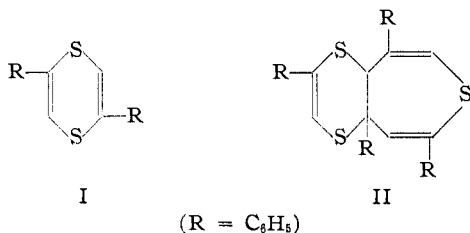
When I was treated with an equimolar amount of hydrogen peroxide, there was obtained a compound $C_{32}H_{24}S_3$. Analogy with reactions previously studied[2,3,4] leads to the tentative assignment of structure II to this compound.

Further study is planned, but the behavior of II on vigorous oxidation is in agreement with the structure assigned. With excess hydrogen peroxide acting for a long time, 0.11 g. of II gave 0.025 of the disulfone of I, 0.093 g. of benzoic acid and 0.051 g. of barium sulfate. These amounts are 34, 174 and 169% of the expected ones, if one molecule of the disulfone were formed from each molecule of II. The deficiency in the yield of the disulfone and the excess of benzoic acid and sulfate

(1) W. E. Parham, T. M. Roder and W. R. Hasek, THIS JOURNAL, **75**, 1647 (1953).

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ion indicates that the disulfone itself is not completely stable.

The disulfone was obtained directly from I, with excess hydrogen peroxide, but in only 50% yield, and accompanied by benzoic and sulfuric acids. This may indicate that even under these conditions II is an intermediate in the oxidation of I to its disulfone.

Experimental[5]

2,5-Diphenyl-1,4-dithiadiene-1,4-tetroxide.—I, 5.55 g., was heated with an excess of hydrogen peroxide in glacial acetic acid until the yellow color of the starting material faded. On cooling there was isolated 50.5% of desired disulfone of I, m.p. 232°.

Anal. Calcd. for $C_{16}H_{12}O_4S_2$: C, 57.82; H, 3.61. Found: C, 57.63; H, 3.78.

The filtrates from the oxidation reaction were concentrated and finally diluted with water in order to isolate additional material. There was obtained only benzoic acid and sulfate ion (precipitated as barium sulfate).

Oxidation of I with Equimolar Hydrogen Peroxide.—Equimolar amounts of I and hydrogen peroxide were heated in glacial acetic acid for one hour and the reaction mixture was poured on ice. The precipitate was crystallized repeatedly from isopropyl alcohol to give yellow crystals, m.p. 128° (II).

Anal. Found: C, 76.12; H, 4.64; S, 19.20; mol. wt. (Rast), 510–560. The repetition of this experiment gave the same results. Found: C, 76.28; H, 4.90. Calcd. for $C_{32}H_{24}S_3$: C, 76.16; H, 4.79; S, 19.09; mol. wt., 502.7.

Quantitative Oxidation of II with Hydrogen Peroxide.—II, 0.1094 g., was heated with an excess of hydrogen peroxide in glacial acetic acid, and nitrogen was used to sweep any carbon dioxide produced in the reaction into a solution of barium hydroxide. The reaction mixture gave on cooling 0.0247 g. (34%) of the disulfone of I, m.p. 232°. The filtrate on concentration gave no additional disulfone and was diluted with water. The aqueous solution was extracted with ether and the ether layer was dried and concentrated. The residual liquid was placed in a desiccator containing sodium hydroxide pellets, and after several days *in vacuo* the residue became solid and there was isolated 0.0928 g. of benzoic acid. The aqueous portion from the extraction was boiled to expel carbon dioxide and then was treated with barium hydroxide to give 0.0507 g. of barium sulfate.

(5) All melting points are uncorrected. Microanalyses by Mr. George Stragand, University of Pittsburgh.

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Studies in Low Concentration Chemistry. IV. The Radiocolloidal Properties of Beryllium

BY GEORGE K. SCHWEITZER AND JAMES W. NEHLS

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In 1950, Haymond, Garrison and Hamilton[1] noted the radiocolloidal behavior of beryllium when they found that they could separate carrier-free[2] beryllium-7 from lithium solutions by making such solutions basic and then filtering them through a glass frit. This paper constitutes a further investigation of the radiocolloidal properties of beryllium, using beryllium-7 as a tracer nuclide.

Experimental

Materials.—All inactive chemicals were of analytical reagent quality. All water was triply distilled and was pre-

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(2) The term carrier-free is used to indicate that no inert beryllium has been intentionally added.

served in carbon dioxide-free air. About 0.5 ml. of dilute hydrochloric acid containing 2.0 mc. of beryllium-7 was obtained from Oak Ridge National Laboratory. Using 0.2 ml. of this solution, no indication of the presence of beryllium could be obtained by the method of Klemperer and Martin,[3] which will detect 0.05 microgram with ease. The remainder of the beryllium solution was diluted to one liter, setting a maximum concentration of about 10^{-9} M. As needed portions of this solution were treated with sodium hydroxide solution until the pH value was approximately 11.0, then filtered through a fine glass frit with the aid of suction, most of the activity being retained on the frit. After washing the filter with distilled water to remove the excess base, dilute nitric acid of the concentration desired for the particular experiment was slowly pulled through the frit, eluting the activity. Half-life and absorption determinations on samples of these solutions showed them to contain beryllium-7 as the only radioactive nuclide.

Radioactivity Measurements.—All determinations of radioactivity were made using a Tracerlab TGC-3A end-window tube attached to a conventional scaler. All activities were counted for a sufficiently long time to give a maximum standard deviation of 1%.

Preparation of Samples.—A small amount of the active beryllium solution was placed in a beaker, dilute nitric acid was added to increase the volume, other substances which were called for in the specific experiment were added and the pH was adjusted with dilute sodium hydroxide solution. After standing for 60 min., the solution was centrifuged in a Misco Electric Microcentrifuge for 30 min., filtered through Whatman No. 50 filter paper, or filtered through a fine glass frit. From the radioactivities of 0.100-ml. samples, which were taken before and after filtration or centrifugation, the amount removed could be calculated. The 0.100-ml. samples were measured with a 0.100-ml. micropipet, placed on metal planchets, evaporated to dryness and then counted.

Results

Coagulation Time.—Samples (originally 0.01 N in acid) at pH values of 8.0, 9.0 and 10.0 were prepared and were allowed to stand for lengths of time from one min. to 60 min. before being filtered. Quadruplicate experiments showed that beyond 5 min. standing time, the percentage of beryllium removed was constant within the standard deviation of 2.4 percentage points. Somewhat similar results have been reported for the radiocolloids of silver, yttrium and zirconium.[4]

pH Studies.—Figure 1 illustrates the results obtained as the pH values of various beryllium solutions are varied. Each point on the graph represents at least three determinations, the standard deviation in no case exceeding 3.0 percentage points. Results similar to the filter paper ones were obtained when a fine glass frit was used in filtration studies. These studies are in accord with previous observations on other radiocolloidal elements.[5]

Electrolyte Effects.—Solutions of beryllium 0.001 N in nitric acid were made up to various concentrations with different electrolytes, the pH was adjusted, and then they were centrifuged. All experiments were done in triplicate and the standard deviations did not exceed 2.8 percentage points. At a pH value of 5.0, the addition of sodium nitrate, sodium chloride, sodium bromide or sodium sulfate caused the percentage removal to decrease from 19 to about 1 as the electrolyte concentration increased
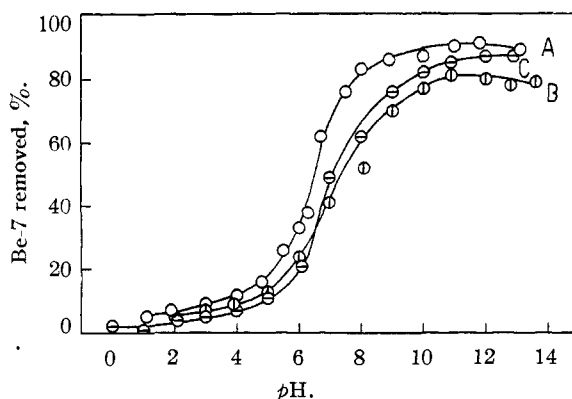
(3) F. W. Klemperer and A. P. Martin, *Anal. Chem.*, **22**, 828 (1950).

(4) G. K. Schweitzer and J. W. Nehls, THIS JOURNAL, **74**, 6186 (1952); J. D. Kurbatov and M. H. Kurbatov, *J. Phys. Chem.*, **46**, 441 (1942); M. H. Kurbatov and J. D. Kurbatov, *J. Chem. Phys.*, **13**, 208 (1945).

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Fig. 1.—The effect of pH upon the removal of Be-7 from solutions neutralized with sodium hydroxide: A, samples originally 0.01 N in nitric acid, centrifuged; B, samples originally 0.01 N in nitric acid, filtered; C, samples originally 1 N in nitric acid, centrifuged.

from 0.001 N to over 1.0 N. At a pH value of 7.0, the addition of these same electrolytes resulted in a decrease in percentage removed from 63 to about 50 as the salt concentration increased from 0.001 N to over 1.0 N. The addition of sodium hydrogen carbonate at a pH of 7.0 caused a much more marked decrease in percentage removed, only 11% being removable from a 1.0 N solution. At a pH value of 9.0, the addition of sodium nitrate, sodium chloride, sodium bromide, or sodium nitrate again decreased the percentage removed from 85 to 0.001 N to less than 80 at concentrations above 1.0 N. Sodium hydrogen carbonate caused a marked decrease in removal, only 51% being centrifuged at a concentration of 1.0 N. Similar trends were observed when the activity was removed by filtration, either through filter paper or a glass frit. The effects of added electrolytes on other radiocolloids agree with these observations.[5]

Solvent Effects.—Figure 2 indicates the effects of the composition of the solvent upon the per cent. radiocolloid centrifuged. Each point on the graph represents at least three determinations, the standard deviation never exceeding 2.9 percentage points. Similar results were obtained when removal of the radiocolloid was effected by filtration.
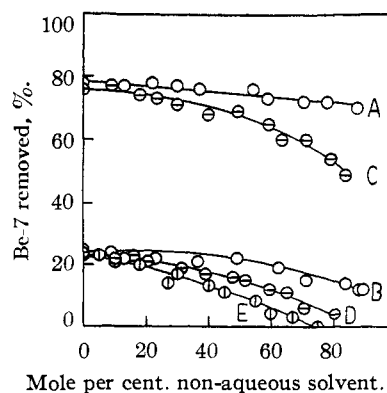

Fig. 2.—The effect of the presence of a non-aqueous solvent upon the removal of Be-7: A, ethanol at pH 10; B, ethanol at pH 6; C, 2-methylpropanol-2 at pH 10; D, 2-methylpropanol-2 at pH 6; E, 1,4-dioxane at pH 6.

These results compare favorably with those previously reported on silver[4] and polonium.[6]

Filtration Efficiency.—Filter papers of various relative retentivities and glass frits of various degrees of porosity were used to separate the radiocolloids at pH values of 7.0 and 10.0. As the relative retentivities of Schleicher and Schnell filter papers decreased and as the porosity of the frits increased, the per cent. radiocolloid removed decreased.

Effect of Stirring.—To test the effect of previous agitation upon the extent of radiocolloid removal, a series of samples originally 0.01 N in nitric acid was rapidly stirred for 60 min. after adjustment of the pH, and the removable activity was compared to that for similar samples which were not stirred. At a pH value of 7.0, 27% of the activity could be removed from the stirred samples by filtration through filter paper as compared to 38% for those not stirred. These values are the averages for four determinations, the standard deviations being 2.1 and 2.6 percentage points, respectively. Similar results were obtained for filtration through a glass frit and for centrifugation. Results showing a decrease in removal for stirred samples were also obtained at a pH value of 10.01. These results might be interpreted as the breaking up of the radiocolloidal aggregates into smaller groups which were not removed with as great an efficiency.

Diffusion.—The diffusion coefficients of the beryllium were determined at several pH values using the method of Anderson and Saddington.[7] At a pH at 2.0 the diffusion coefficient was 0.34 cm.^{2}/day; at pH 6.0 it was 0.29 cm.^{2}/day; the value was 0.13 cm.^{2}/day at a pH of 8.0 and 0.11 cm.^{2}/day at pH 10.0. Each determination was made in triplicate and no standard deviation exceeded 0.02 cm.^{2}/day. Assuming the validity of the Einstein–Stokes equation, the average radii of the aggregates were calculated to be 7 Å. at pH 2.0 increasing to 22 Å. at pH 10.0. Similar results are reported by Hevesy and Paneth for polonium,[8] and Schubert and Conn for zirconium and barium.[9]

Acknowledgment.—The authors wish to express their gratitude to the U. S. Atomic Energy Commission for the grant of funds which made this work possible.

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3-Methyl-5-anisyl-4-carbethoxy-2-cyclohexene-1-one

BY WALTER T. SMITH, JR., AND DANIEL S. P. EFTAX

The preparation of 3-methyl-5-substituted-4-carbethoxy-2-cyclohexene-1-ones by the acid-catalyzed monodecarbethoxylation of 3-methyl-5-substituted-4,6-dicarbethoxy-2-cyclohexene-1-ones

has been reported only in those cases in which the 5-substituent is alkyl.[1] Various earlier attempts to accomplish the monodecarbethoxylation have been unsuccessful in those cases in which the 5-substituent is aryl.[2,3]

Horning and Field[4] devised an alternate method for the preparation of 3-methyl-4-carbethoxy-5-anisyl-2-cyclohexene-1-one. The final step in their method was the cyclization of ethyl α,γ-diacetyl-β-anisylbutyrate with phosphoric acid in acetic acid. On this final step the yield of crude product was 22%.

A reinvestigation of the action of sodium ethoxide on ethyl anisal-bis-acetoacetate has shown that the product of this reaction is not 3-methyl-5-anisyl-2-cyclohexen-1-one as previously reported,[5] but that this reaction provides a new and improved method for the synthesis of 3-methyl-5-anisyl-4-carbethoxy-2-cyclohexene-1-one. The yield in the last step is 47%. The method has the further advantage that the starting material can be prepared in good yield in only one step from anisaldehyde.[5]

The identity of the product is established by comparison with the melting points previously reported[4] for the compound itself and for its dinitrophenylhydrazone. The p-nitrophenylhydrazone was also prepared. In addition, the monoester was converted to the known 3-methyl-5-anisyl-2-cyclohexene-1-one by alkaline saponification, followed by decarboxylation.

By the procedures described here, together with methods previously reported,[6] it is possible to use ethyl anisal-bis-acetoacetate as the common starting material for the preparation not only of 3-methyl-5-anisyl-2-cyclohexen-1-one, but also for the 4-carbethoxy derivative and the 4,6-dicarbethoxy derivative.

Experimental

3-Methyl-4-carbethoxy-5-anisyl-2-cyclohexene-1-one.—Ethyl anisal-bis-acetoacetate (60 g., 0.16 mole) was dissolved in 240 ml. of absolute ethanol containing 1.9 g. (0.082 mole) of sodium and refluxed for five hours. At the end of this period a small amount of sodium carbonate (4.8 g.) precipitated on cooling and was separated by filtration. The remaining orange solution was poured into 250 ml. of water containing chipped ice and 15 ml. of concd. hydrochloric acid; 40 g. (87%) of pale yellow solid separated. Subsequent recrystallizations from 95% ethanol yielded 21.5 g. (47%) of colorless crystals, m.p. 71–73°. The 2,4-dinitrophenylhydrazone melted at 182.5–183.5°.[4]

The yellow p-nitrophenylhydrazone[7] was recrystallized from 95% ethanol and melted at 195–196°.

Anal. Calcd. for $C_{23}H_{25}O_5N_3$: C, 65.25; H, 5.96; N, 9.92. Found: C, 65.16; H, 5.98; N, 10.06.

3-Methyl-5-anisyl-2-cyclohexene-1-one.—3-Methyl-4-carbethoxy-5-anisyl-2-cyclohexene-1-one (13 g., 0.043 mole) was dissolved in 100 ml. of 95% ethanol and the solution was added to 60 ml. of water containing 8 g. of sodium hydroxide; the mixture was refluxed for one-half hour, cooled to room temperature, acidified with 40 ml. of 1:1 hydro-

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