unlikely that ionic dissociation of the ethane would take place in a solvent of low dielectric constant such as benzene. However, diphenyl-2-thienylchloromethane appears to be much less stable than triphenylchloromethane. Probably, the ionic dissociation of diphenyl-2-thienylchloromethane is catalyzed by the presence of silver amalgam. Minnis apparently was misled by the ease of formation of this cation and arrived at the erratic conclusion that diphenyl-2-thienylmethyl was responsible for the red color of the solution.

In the present investigation, phenyl-α-naphthyl-2-thienylchloromethane also was synthesized. Its reduction with silver amalgam in benzene also gave a red solution which was diamagnetic; white crystals of 1,2-diphenyl-1,2-di-α-naphthyl-1,2-di-2-thienylethane, m.p. 140°, were isolated from this solution in almost quantitative yield.

As a conclusion, no evidence of paramagnetism was found during the reduction of diphenyl-2-thienylchloromethane or phenyl-α-naphthyl-2-thienylchloromethane with silver amalgam in benzene solution. The diamagnetic hexasubstituted ethanes which were isolated showed no tendency to dissociate in solution.

Acknowledgment.—We wish to thank the Research Corporation of America for the financial assistance in carrying out this work.

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Aluminum Suboxide Formed in Reaction of Aluminum with Alumina

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RECEIVED DECEMBER 13, 1954

The existence of an aluminum suboxide has been proposed by many early workers.[1] More recently the volatility of alumina in the presence of aluminum was attributed by Zintl and co-workers[2,3] to the formation of gaseous AlO. Grube, Schneider Esch and Flad[4] determined from the distillate composition that silicon reacted with alumina at 1800° to form Al_2O along with SiO. Brewer and Searcy[5] reasoned that gaseous Al_2O is formed when alumina is heated with a reducing agent whereas gaseous AlO and atomic oxygen are the principal products when alumina is heated alone. The bands in the blue and green regions of the spectrum from an aluminum discharge in air were ascribed to AlO by Mulliken.[6] Baur and Brunner[7] ascribed a lowering of the melting point of alumina mixed with aluminum to Al_8O_9. Beletskii and Rapoport[8] on heating a pelleted mixture of aluminum and alumina above 1800° under 1 mm. pressure obtained coarse crystals which were thought to be Al_2O. Using a high temperature X-ray technique Hoch and Johnston[9] reported solid Al_2O between 1100 and 1500°, solid Al_2O and AlO between 1500 and 1600° and solid AlO above 1600°.

Weight Loss Experiments.—About 0.3 g. of 99.99% aluminum in a tantalum carbide-lined tantalum boat was covered with a 1-g. loose fitting lid of pure sintered alumina, with no contact between the aluminum and alumina. The boats were held in a 12″ long, 1″ o.d. graphite tube centered in a 1.5″ i.d. graphite susceptor heated by a 10″ long induction coil. Overlapping tantalum sheets lined the inside of the graphite tube through the reaction zone. The susceptor was insulated from an outer Pyrex envelope by a $^1/_2$″ thick layer of outgassed lampblack. The boats and contents were held at temperature for at least 15 minutes. Temperature readings with a Leeds and Northrup optical pyrometer sighted on the boat were corrected for window absorption but not for lack of black body conditions.

In four runs at 1700–1500° and with total pressures less than 1 mm. the weight losses corresponded to aluminum to oxygen atomic ratios of 2.8 to 3.1. To further increase the equilibrium between the aluminum vapor and the alumina, sintered alumina 100 to 250 mesh was heaped over the aluminum for the fifth and sixth of these runs. About three quarters of the alumina weight loss was from the powder over the aluminum, the balance was from the alumina lid. The atomic ratios for the volatile products in these runs approach Al_2O. The aluminum to oxygen atomic ratios for the volatile reduction products were calculated from Brewer and Searcy[5] for the equation

TABLE I

ALUMINA-ALUMINUM WEIGHT LOSS

Alumina-covered tantalum carbide boat containing aluminum, tantalum shielded graphite charge tube

°C.	Residual pressure, mm.	G. loss		Al:O atomic ratio	
		Al_2O_3	Al	Exp.	Calcd.[a]
1700	1	0.09	0.18	3.0	2.2
1690	1	.11	.19	2.8	2.2
1650	1	.08	.15	3.0	2.2
1500	1	.07	.13	3.1	2.3
1510	0.4	.12	.17	2.4	2.3
1700	10[b]	.20	.24	2.2	2.2

[a] Aluminum at its vapor pressure reacting with alumina to form Al_2O, data of Brewer and Searcy. [b] Pressure of added argon.

$$4Al(v) + Al_2O_3(s) \longrightarrow 3Al_2O(v)$$

These are listed in the table for comparison with the experimental values.

Spectroscopic Investigations.—The emission spectra from aluminum arcs in nitrogen, argon and oxygen atmospheres were compared using a quartz prism Gaertner spectrograph. In the range from 2700 to 8700 Å. no extra bands were found in the oxygen atmosphere that had not been previously ascribed to AlO.

The absorption spectrum of the vapors from the alumina-aluminum reaction was investigated with a Cenco replica grating spectrograph, Catalog No. 87102, from 3400 to 7500 Å. and with a Model DU Beckman spectrophotometer from 2800 to 3400 Å. Charges consisted of two $^3/_8$″ diameter pellets made from a mixture of calcined alumina and atomized aluminum. The pellets were heated at temperatures up to 2200° in tantalum carbide boats in the same induction heated system as used for the weight loss experiments. A continuum was projected through quartz windows at both ends of the 5 ft. long Pyrex envelope which enclosed the susceptor. Argon at 1 atmosphere pressure flowed slowly through the envelope during measurements.

The characteristic absorption lines of trace elements, aluminum vapor and aluminum hydride were noted. The spectrum of AlO was not noted nor any unidentified spectrum.

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Melting Points of Alumina–Aluminum Mixture.—Melting points were determined by placing the material on a support centered in the equipment described previously for weight loss experiments with the addition of radiation plugs on both sides of the charge. An atmosphere of argon in the system slowed the evaporation of volatile materials. With a constant furnace setting, the time of sample melting was noted and the corresponding temperature interpolated on a time–temperature curve for the run. The emissivities of the alumina–aluminum charge and the pure alumina used for standardization were the same inasmuch as both gave the same temperature readings below the melting point.

With the readings corrected to a melting point of 2030°[10] for sintered alumina, the apparent melting point of a 50 wt. % alumina–aluminum mixture on a tungsten support was 1945°. With 33 wt. % aluminum in alumina supported on tungsten, the melting point was 2005°. An alumina–aluminum pill containing 52% alumina by weight held in a tantalum cup began to sink at 1700° and disappeared at 1960°. A pellet containing 21 wt. % aluminum was placed on alumina and melted at 2005°. In all of these determinations about half of the alumina–aluminum pill disappeared during the run.

The empirical formulas for the equilibrium volatile products calculated from the Brewer and Searcy data for Al_2O check well with the weight loss results. The absence of the spectrum of AlO from the vapors over the alumina–aluminum reaction supports the belief that this molecule is not involved in the reaction. The lowered melting points of alumina mixed with aluminum indicate subcompound formation in the condensed phase but are much too scattered for construction of a phase diagram for this system.

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Acetone Formation in the Biacetyl Pyrolysis[1]

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RECEIVED DECEMBER 16, 1954

A re-examination of the homogeneous thermal decomposition of biacetyl for possible acetone formation was suggested by the recent discovery of acetone in the biacetyl photolysis at 100–200°.[2] Previous studies of the thermal decomposition of biacetyl[3] had shown that the major products between 383 and 470° are carbon monoxide, methane and ketene. However since methyl radicals are probably present during the thermal decomposition,[3,4] it seemed that acetone might be formed by the skeleton-breaking reaction suggested in the photochemical research[2]

$$\cdot CH_3 + CH_3COCOCH_3 \longrightarrow CH_3COCH_3 + \cdot COCH_3 \quad (1)$$

A rather similar type of reaction by a methyl radical also has been proposed recently to account for the products of the photolysis of *trans*-methylpropenyl ketone.[5]

Experimental

The biacetyl, which was Eastman Kodak Co. white-label grade, was dried over anhydrous calcium sulfate. The sample for all experiments, except one, had been fractionally distilled three times under vacuum; the middle third was taken for each subsequent distillation.[6] It was stored in the dark at −78° under vacuum between uses and was degassed before each experiment. For one of the experiments carried to 12.7 min. at 436° a new sample of biacetyl was given two trap-to-trap distillations under vacuum and then distilled at atmospheric pressure in dry nitrogen in a 90-cm. Lecky–Ewell column. The middle third had a boiling point of 88.3–88.4° at a pressure of 746 mm. The ketene was made by the pyrolysis of acetic anhydride at 500–520°[7] and analyzed 99.4–99.9% pure by titration after conversion into acetic acid.

The experiments were performed by the static method in a 0.5-liter Pyrex bulb contained in an electrically heated furnace. The temperature was measured with a platinum, platinum–13% rhodium thermocouple standardized at the melting point of zinc. Infrared analyses were made on the Perkin–Elmer Model 12AB spectrometer with a gas cell of one meter path length.[8] The fact that acetone was present in the products at 436° was shown by the presence of an absorption in the region of 8.2–8.3 μ which corresponded to an absorption reported for acetone in the literature[9] and agreed with that observed for a prepared mixture of biacetyl and acetone. The biacetyl did not have appreciable absorption in this region. Known mixtures of biacetyl and acetone were used to establish a calibration curve for the relation of the transmission at 8.25 μ to the acetone pressure over the range used. The analyses were reproducible to within 10% of the pressure of acetone. Ketene may have a weak absorption at this wave length[10]; therefore, it was removed by pumping the products through a spiral kept at −100°. After the ketene had been removed, the contents of the spiral could be warmed and expanded into the infrared cell or into a sample bulb for mass spectrometric analysis. The presence of acetone in the decomposition products from biacetyl at 436° was confirmed in five mass spectrometric analyses[11] which indicated amounts of acetone of the same order of magnitude as those measured in the infrared method. For a preliminary observation of the ultraviolet absorption, the products after removal of ketene were dissolved in 95% ethanol and the absorbance measured on a Beckman DU spectrophotometer.

Results and Discussion

The results of the infrared analyses are shown in Fig. 1. Curve 1 represents the amount of acetone (in terms of the percentage of the initial pressure) present during the pyrolysis of biacetyl at 436°. On the basis of the previous study under the same conditions, in which the amounts of biacetyl disappearing were determined by analysis,[3b] it was possible to calculate the amount of biacetyl decomposed in each of the present experiments from the observed pressure increase. Thus, the % yield of acetone could be determined and is shown as curve 2 in Fig. 1.

Since ketene is a product of the decomposition, two experiments were performed at 436° in order to find out whether a reaction involving ketene (*e.g.*, a reaction sequence beginning with an addition of a methyl radical to ketene) might be responsible for the formation of acetone. With 21 mm. ketene

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[1] This work has been supported by a grant from the Celanese Corporation of America.

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