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.

[10] R. F. Geller and P. J. Yavorsky, *J. Research Natl. Bur. Standards*, **34**, 395 (1945).

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Acetone Formation in the Biacetyl Pyrolysis[1]

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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.

[2] F. E. Blacet and W. E. Bell, *Discs. Faraday Soc.*, No. 14, 70 (1953); THIS JOURNAL, **76**, 5332 (1954).

[3] (a) F. O. Rice and W. D. Walters, *J. Chem. Phys.*, **7**, 1015 (1939); (b) W. D. Walters, THIS JOURNAL, **62**, 880 (1940).

[4] (a) M. Szwarc, *Chem. Revs.*, **47**, 75 (1950); (b) F. O. Rice and W. D. Walters, THIS JOURNAL, **63**, 1701 (1941).

[5] J. Pitts, Jr., R. Stolberg and T. W. Martin, *ibid.*, **76**, 2843 (1954).

[6] The purification was performed by Dr. H. D. Batha in this Laboratory.

[7] C. J. Fisher, A. F. MacLean and A. W. Schnizer, *J. Org. Chem.*, **18**, 1055 (1953).

[8] Perkin–Elmer infrared cell, Model 12-064.

[9] D. Price, *J. Chem. Phys.*, **9**, 725 (1941); API Research Project 44, Infrared Curve Serial No. 1222.

[10] F. Halverson and V. Z. Williams, *J. Chem. Phys.*, **15**, 553 (1947); W. R. Harp, Jr., and R. S. Rasmussen, *ibid.*, **15**, 778 (1947).

[11] These analyses were made by R. C. Wilkerson and R. M. Guedin of the Celanese Corporation of America and by CEC Instruments, Incorporated.

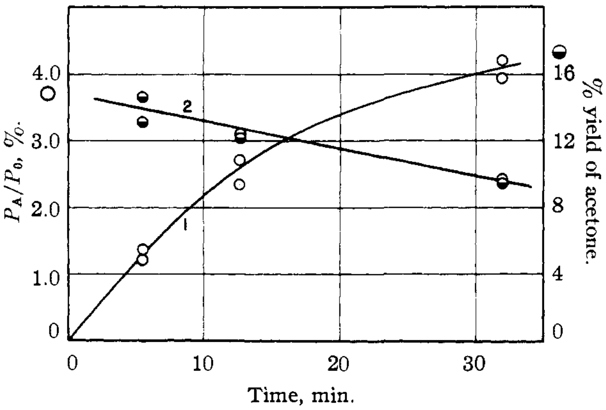

Fig. 1.—Acetone present during the decomposition of biacetyl at 436°. Initial pressure in the vicinity of 200 mm. (1) P_A is the pressure of acetone and P_0, the initial pressure of biacetyl. (2) The % yield represents the pressure of acetone divided by the pressure of biacetyl decomposed.

added to 205 and 142 mm. biacetyl, the value of the pressure of acetone after 12.7 min. divided by the initial pressure of biacetyl averaged 2.5% in comparison with 2.5% from two experiments with biacetyl alone. From these results it does not appear that acetone is formed by secondary reactions involving ketene.

Comparison of the results of the previous investigation[3b] with the present data shows that the amount of ketene is considerably larger than the amount of acetone in the initial stages of the decomposition. Under these conditions the ketene appears to result mainly from the reaction

$$\cdot CH_3 + CH_3COCOCH_3 \longrightarrow CH_4 + \cdot CH_2COCOCH_3 \quad (2)$$

followed by the decomposition of the $\cdot CH_2COCOCH_3$ radical to form ketene. The sum of the yields of ketene and acetone in the early portion of the reaction are closer to 100% than the yield of ketene alone.[3b] Blacet and Bell[2] have reported energies of activation for reactions (1) and (2) and the ratio of the steric factors obtained from their data for the range 100–200°. From their values it can be calculated that reaction (2) should occur about three times as often as reaction (1) at 436°. The experimental results obtained in the thermal work confirm the greater importance of reaction (2); the ketene observed after 5.5 min. at 436° (67% yield) in the earlier work[3b] is about five times the amount of acetone found in the present study. It is to be noted that the latter comparison does not provide an exact measure of the importance of reactions (1) and (2) since both ketene and acetone undergo subsequent reactions. The decreasing yield of acetone with time (curve 2, Fig. 1) can be explained by the loss of acetone in secondary reactions.[12] Moreover, the comparison will be affected if an appreciable fraction of the $\cdot CH_2COCOCH_3$ radicals do not form ketene or if acetone or ketene results from reactions other than (1) or (2).

The mass spectrometric results and the ultraviolet data indicated the presence of small amounts of products other than those mentioned above, but the data did not provide an unequivocal identification of such products in the liquid mixture. Further investigation is needed to determine the identities and possible modes of formation of the minor products. By means of such information it may be possible to make a decision concerning the suggestion of Darwent[13] that reaction (1) proceeds by the addition of the methyl radical to a carbonyl carbon atom of biacetyl.

[12] The data of J. A. Leermakers, THIS JOURNAL, **56**, 1899 (1934), and F. O. Rice, E. L. Rodowskas and W. R. Lewis, *ibid.*, **56**, 2497 (1934), indicate that although radicals may react with acetone molecules, a radical induced chain decomposition of acetone does not occur at 350–400°. Likewise the recent results of S. Kodama and Y. Takezaki, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **73**, 82 (1952), at 309° with methyl radicals do not show an induced chain decomposition.

[13] B. deB. Darwent, *Discs. Faraday Soc.*, 129, No. 14 (1953).

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Low Temperature Heat Capacity and Entropy at 298.16°K. of Analcite

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The mineral analcite ($NaAlSi_2O_6 \cdot H_2O$) has the chemical composition of jadeite ($NaAlSi_2O_6$), except for the water content. Structurally, of course, they are not similar. One very pertinent difference is the occurrence of aluminum as separate Al^{+++} ions in jadeite, whereas in analcite it occurs as AlO_4-tetrahedra, replacing SiO_4-tetrahedra in the silicate network. In this respect analcite is similar to albite ($NaAlSi_3O_8$) and nephelite ($NaAlSiO_4$). The geochemical relationship of analcite to albite, jadeite and nephelite (which has been under investigation elsewhere) required a knowledge of its entropy, thus furnishing the incentive for the present work. The entropies of albite, jadeite and nephelite have been reported previously.[1]

Materials and Method.—The analcite was furnished by H. S. Joder, Jr., Geophysical Laboratory, Washington, D. C. Chemical analysis of a portion of the same sample was conducted by S. S. Goldich, Department of Geology, University of Minnesota, who obtained the following results: 13.44% sodium oxide, 22.36% alumina, 56.05% silica, 8.13% combined water, 0.10% potassium oxide, 0.02% magnesia, 0.01% titania, 0.03% ferric oxide, 0.01% adsorbed water, and less than 0.005% lime. These results are to be compared with the theoretical 14.08% sodium oxide, 23.15% alumina, 54.59% silica and 8.18% water. The material for the heat capacity measurements was dried 4 hours at 110° before use. For the purpose of correcting the heat capacity data, the sample was considered as containing 96.5% analcite, 3.3% silica and 0.2% water—an approximation based upon the analysis.

The heat capacity measurements were made with previously described apparatus.[2] The sample mass was 162.39 g.

Results

The measured heat capacity values, expressed in defined calories (1 cal. = 4.1840 abs. joules) per deg. mole, are in Table I. These values have been corrected for the major impurities (as indicated above) through use of heat capacity data for silica

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[1] K. K. Kelley, S. S. Todd, R. L. Orr, E. G. King and K. R. Bonnickson, U. S. Bur. Mines Rept. of Investigation 4955 (1953).

[2] K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper 686 (1946).