and ice listed by Kelley.[3] The net correction ranged from 0.48 to 1.11%, depending upon the temperature. The thermal behavior of the substance was regular and an entirely normal type of heat capacity curve was obtained.

TABLE I

HEAT CAPACITY OF ANALCITE

(Mol. wt., 220.17)

T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole
53.42	10.83	114.59	25.15	216.33	41.72
57.77	11.93	124.57	27.14	225.93	43.02
62.43	13.03	135.81	29.25	237.75	44.51
67.38	14.51	145.87	31.05	245.73	45.43
72.24	15.69	156.03	32.78	256.58	46.58
77.05	16.84	166.26	34.44	266.28	47.61
79.93	17.55	175.98	35.92	275.91	48.66
83.52	18.39	185.95	37.38	286.32	49.40
94.43	20.86	195.98	38.79	296.21	49.98
105.44	23.21	206.45	40.21	298.16	(50.17)

The measured portion of the entropy, between 51 and 298.16°K., was obtained in the usual manner by Simpson-rule integration of the C_p against log T plot, as $S^\circ_{298.16} - S^\circ_{51} = 49.64$ cal./deg. mole. Extrapolation below 51°K. was accomplished by the adaptation of the method of Kelley, Parks and Huffman[4] used previously[1] for treating heat capacity data of other alkali-aluminum silicates. The extrapolated portion of the entropy is $S^\circ_{51} = 6.39$ cal./deg. mole. The sum of the two increments gives $S^\circ_{298.16} = 56.0 \pm 0.6$ cal./deg. mole.

It is of interest to compare the entropy of analcite at 298.16°K. with those of albite, jadeite and nephelite, which are, respectively, 50.2 ± 0.4, 31.9 ± 0.3, and 29.7 ± 0.3 cal./deg. mole.[1] It was noted previously[1] that the entropy of jadeite is abnormally low in comparison with those of albite and nephelite, and this is to be associated with the higher atomic density of the jadeite and with the difference in mode of occurrence of the aluminum atoms in the crystals. The entropy of analcite is 24.1 units higher than that of jadeite and 16.0 units higher than the mean for albite and nephelite. Although both figures are larger than the entropy difference usually accompanying one mole of water difference in composition, they are entirely reasonable in view of the much looser structure of the analcite.

[3] K. K. Kelley, U. S. Bur. Mines Bull. 477 (1950).

[4] K. K. Kelley, G. S. Parks and H. M. Huffman, *J. Phys. Chem.*, **33**, 1802 (1929).

CONTRIBUTION FROM THE MINERALS
THERMODYNAMICS BRANCH, REGION III
BUREAU OF MINES
UNITED STATES DEPARTMENT OF THE INTERIOR
BERKELEY, CALIFORNIA

The Rate of Decomposition of Ethane into Methyl Radicals[1]

BY C. H. LEIGH, M. SZWARC AND J. BIGELEISEN

RECEIVED DECEMBER 6, 1954

The intention of this work is to determine the absolute rate of the dissociation of ethane into two methyl radicals. It is hoped that the continuation of this work will allow us to determine the activation energy of the dissociation process (1)

$$C_2H_6 \longrightarrow 2CH_3 \qquad (1)$$

and from this the C–C bond dissociation energy in ethane. An accurate value for this heat might enable one to calculate the entropy of methyl radicals within one-half an entropy unit and thus determine which of the two models (planar or pyramidal) describes more correctly the structure of methyl radicals.

The investigation of the dissociation of ethane into methyl radicals was carried out in a flow apparatus, using the toluene carrier technique.[2] Methyl radicals produced in such a system are expected to react rapidly with toluene, present in a great excess, and to form methane according to equation (2)

$$C_6H_5\cdot CH_3 + CH_3\cdot \longrightarrow C_6H_5\cdot CH_2\cdot + CH_4 \quad (2)$$

Since the pyrolysis of toluene produces even a greater amount of methane[3] than the pyrolysis of ethane, it is necessary to use ethane labeled by C^{14} in order to discriminate between the products of pyrolyses of toluene and of ethane. Consequently, the rate of reaction 1 was measured by the rate of formation of radioactive methane.

Experimental

The radioactive ethane was prepared from radioactive barium carbide containing 22% C^{14}. The hydrolysis of the latter compound produced labeled acetylene, and the hydrogenation of the acetylene led to the ethane. This high specific activity ethane was diluted by a factor of 10^5 with a non-active ethane, and then purified by scavenging it with non-active methane. The scavenging process was repeated until the ethane was found to contain no radioactive methane. The ethane was also scrubbed with an aqueous solution of cuprous ammonia chloride to remove unreacted acetylene.

The apparatus used in these studies was similar to one described previously.[2] The radioactive ethane is introduced into the toluene flow through a needle valve and a capillary, and its rate of flow was determined by the pressure drop across the capillary. The toluene vapor mixed with ethane flows through a silica reaction vessel heated electrically to the desired temperature. The gases emerging from the reaction vessel pass through one trap cooled by a carbon dioxide–acetone mixture and then through a second trap cooled by liquid nitrogen. The non-condensed products ($H_2 + CH_4$) are pumped by means of two mercury vapor pumps into storage flasks. A small trap, cooled by liquid nitrogen and introduced at the exit of the second mercury pump, prevents the presence of any C_2 hydrocarbons in the storage flasks.

This separation process is insufficient to yield a $CH_4 + H_2$ mixture free of radioactive contaminants, *e.g.*, unreacted ethane and other C_2's which may have been present as contaminants in the stock radioethane or formed in the pyrolysis. These were removed by a rigorous decontamination procedure, which was based on a repetitive dilution and extraction process.

The amount and the composition of the originally collected mixture of $H_2 + CH_4$ were determined by standard methods. Thereafter, a mixture of non-active ethane, ethylene and acetylene was admitted into the storage flasks. The ratio of scavenger gas to CH_4–H_2 mixture was about fifteen to one. The mixture of all these gases was circulated for a few minutes to provide adequate mixing, and thereafter they were circulated through a trap cooled by liquid nitrogen, until all the C_2 hydrocarbons were condensed out. The uncondensed $H_2 + CH_4$ was then returned to the storage

---

[1] Research carried out at the Brookhaven National Laboratory under the auspices of the U. S. Atomic Energy Commission.

[2] M. Szwarc, *J. Chem. Phys.*, **17**, 431 (1949); *Proc. Roy. Soc. (London)*, **98A**, 267 (1949).

[3] M. Szwarc, *J. Chem. Phys.*, **16**, 128 (1948).

flasks. Since some amount of methane remained dissolved in the liquid C_2 hydrocarbons, the latter were distilled from a trap to trap under continuous pumping. By this procedure the dissolved methane was removed and combined with the other gas in the storage flasks. The mixture of the C_2 hydrocarbons used for the scavenging was then pumped out, and a fresh portion of C_2 hydrocarbons admitted into the storage flasks. The scavenging process was thus repeated five times. Methane, separated from a synthetic mixture of radioactive ethane and dead methane, which was subjected to this decontamination cycle, showed no activity. Likewise, ethane–methane–hydrogen mixtures from pyrolytic experiments under conditions where there was no ethane decomposition showed no activity in the methane. The composition of the methane–hydrogen mixture and the recovery yield was determined after the scavenging process. A sample of the decontaminated gas was transferred into a proportional counter, which was then filled with P-10 gas, 90% A-10% CH_4, to a pressure of one atmosphere. The gas was then counted. The statistical error of the total count was usually of the order of 1%. The counting efficiencies and effective volumes of the counters were determined by the use of standards.

The fraction of decomposition of ethane was calculated by dividing the total activity of the collected gas ($H_2 + CH_4$) into the total activity of the introduced ethane. It is obvious that by this procedure we measure the rate of reaction 1 only, and do not observe the rate of decomposition of ethane into ethylene and hydrogen (even if such a reaction does take place under our experimental conditions).

Results

The experimental results are given in Table I. The specific activity of ethane used in our work was 6.59×10^5 c.p.m./mmole. In a typical experiment, the collected gas had a net count of 70–1500 c.p.m.

TABLE I

RATE CONSTANTS FOR THE DECOMPOSITION OF ETHANE

Run	T, °K.	P_{total}, mm.	$P_{C_2H_6}$, mm.	Time of contact, sec.	Decomp., %	$k \times 10^4$, sec.$^{-1}$
8[a]	1039	13.7	0.16	0.56	0.071	12.7
3[a]	1045	10.5	.026	.26	.083	32.2
9[a]	1047	13.7	.055	.55	.087	15.9
4[a]	1050	10.6	.039	.26	.029	11.3
21	1051	13.9	.20	.65	.072	19.4
12[a]	1052	16.6	.16	.55	.055	22.5
20	1063	14.0	.20	.63	.143	23.0
16	1070	17.4	.13	.47	.119	38.1
15	1075	13.6	.067	.54	.131	49.8
19	1076	6.3	.39	.79	.387	57.7
14	1077	13.6	.25	.54	.152	55.9
10[a]	1079	13.6	.061	.50	.385	77.0
5[a]	1080	10.6	.055	.25	.113	44.6
17	1080	6.3	.225	.82	.264	34.0
13[a]	1085	13.5	.20	.52	.298	57.4
11[a]	1109	13.6	.092	.53	1.13	212

[a] Runs uncorrected for possible change in CH_4/H_2 ratio during scavenging. Most of these runs had high recovery yields of the original $CH_4 + H_2$ mixture.

Inspection of Table I shows that the percentage of decomposition was below 1%. In some experiments it was as low as 0.03%. Consequently, the occurrence of other reactions is irrelevant for our measurements. The reproducibility of results leads to rate constants which are probably reliable within 50% or less. Admittedly, the accuracy of the work must be improved if one wishes to determine the activation energy of the process accurately. At present our results indicate a reasonable activation energy, namely, within the range 85–89 kcal./mole. Comparison of experiments 8 and 9, and 14 and 15 shows that the decomposition is first order in respect to ethane. The partial pressure of ethane varies by a factor of 3 in experiments 8 and 9 while the first-order rate constants (interpolated for a middle temperature) are 15.1×10^{-4} sec.$^{-1}$ and 13.3×10^{-4} sec.$^{-1}$, respectively. Similarly, a variation in partial pressure of ethane by nearly a factor of 4 in experiments 14 and 15 gives values of 52.0×10^{-4} and 53.5×10^{-4} sec.$^{-1}$ for the first-order rate constants (the results are again interpolated to the middle temperature).

It is interesting to note that the frequency factor for this decomposition is calculated at: 5×10^{15} sec.$^{-1}$ if $E = 89$ kcal./mole; 7×10^{14} sec.$^{-1}$ if $E = 85$ kcal./mole. These frequency factors, although rather high, are much lower than the value of 10^{17} calculated by Trotman-Dickenson.[4]

A detailed description of this work is available from the authors and will be published when data leading to a more precise value of the activation energy are available.

---

[4] A. F. Trotman-Dickenson, *J. Chem. Phys.*, **21**, 211 (1953).

CHEMISTRY DEPARTMENTS
BROOKHAVEN NATIONAL LABORATORY
UPTON, L. I., N. Y.
STATE UNIVERSITY OF NEW YORK
COLLEGE OF FORESTRY
SYRACUSE, N. Y.

Cross-linking of Polymers by Peroxides in Dioxane[1,2]

BY ROBERT MACFARLANE, JR., AND RAYMOND M. FUOSS

RECEIVED DECEMBER 11, 1954

We have frequently used dioxane to precipitate polyvinylpyridine and its salts from various solvents; occasionally the precipitate resisted redissolution and evidently was cross-linked. Aliphatic ethers are known to form peroxides in the presence of air and free radicals from decomposing peroxides can reactivate dead polymer; the latter can then cross-link when several molecules react at several sites. Some exploratory experiments were made which confirmed the hypothesis that peroxides in the dioxane were responsible for the insolubilization; the purpose of this note is to summarize our results.

One sample of dioxane was freed from oxygen and peroxides by mixing 900 ml. with 100 ml. of an aqueous solution of acidified (0.001 N sulfuric acid) ferrous sulfate (0.04 N) and distilling at 30 mm. pressure. The distillate gave only a trace of yellow tint after 10 ml. was heated for 10 min. with 10 ml. of glacial acetic acid containing 0.05 g. of sodium iodide; untreated dioxane from a freshly opened bottle gave a deep red immediately. A sample of polyvinylpyridine (0.4 g.) was then dissolved in 25 ml. of methanol, and the solution was divided into two equal portions. The polymer was precipitated by adding 150 ml. of untreated dioxane to one portion and an equal amount of treated dioxane to the other. After 72 hr., the dioxane was decanted from the precipitates and 10 ml. of methanol was added to each. The first swelled considerably but did not dissolve while the second dissolved rapidly.

---

[1] Project NR 051-002 of the Office of Naval Research; Paper No. 47. Contribution No. 1270 of the Sterling Chemistry Laboratory, Yale University.

[2] Results presented in this note will be included in a thesis to be presented by Robert MacFarlane, Jr., to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of *Doctor of Philosophy*.