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).

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

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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.

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[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*.

Peroxide in the dioxane was determined by titrating the iodine liberated from sodium iodide in glacial acetic acid, using 0.0811 *N* sodium thiosulfate solution. (A blank correction was made, using 10 ml. of water instead of 10 ml. of dioxane, with the same period of heating, to allow for air oxidation of iodide.) An old sample of dioxane showed about one milliequivalent of peroxide per liter. Air was bubbled through a sample of treated dioxane, using a fine frit to ensure small bubbles. After 30 min., the dioxane contained 0.81 meq./l. peroxide, and after 1 hr., 1.10 meq./l. Apparently an equilibrium between formation and decomposition of peroxide was then reached, because the titer remained unchanged after bubbling air through the dioxane for an additional 30 min.

In another experiment, 1.18 g. of polyvinylpyridine was dissolved in 10 ml. of methanol, and precipitated with untreated dioxane. The precipitate was allowed to stand in contact with the dioxane for a week. The volume of the precipitate was 3.0 ml. The dioxane was decanted carefully and 55 ml. of methanol was added; the precipitate expanded in 2 days to 6.0 ml. This methanol (plus extracted dioxane) was decanted and 50 ml. of fresh methanol was added. After 5 days, the volume of precipitate had expanded to 8 ml. The methanol was decanted and combined with the first portion; evaporation under vacuum gave a residue of 0.724 g. for the soluble polymer. The gel portion was also dried under vacuum; it weighed 0.457 g., so approximately 40% of the polymer had been insolubilized. The specific volumes of the gel were 6.5, 13 and 18 cc./g. as first precipitated, and after the first and second soakings in methanol, respectively. As the precipitating liquid was extreated with methanol, the gel naturally expanded while it imbibed good solvent.

It is therefore clear that dioxane which is to be used in polymer work should be carefully freed from oxygen and peroxides, and further that polymers should not be allowed to stand in contact with dioxane and air.

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Activity Coefficient of Gallium Perchlorate in Water at 25°[1]

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Extensive compilations of activity coefficients by Stokes and Robinson[2,3] indicate that for a strongly hydrated cation the salts exhibiting the highest activity coefficients are usually those of large anions. The iodide and perchlorate of lithium, for example, reach the greatest value. With potassium, on the other hand, which is not so highly hydrated, the perchlorate and nitrate have low values. Where there is evidence of a chemical nature for complex halide formation, as with zinc, the polyatomic anions of strong acids, especially the perchlorate, give the largest activity coefficient. This behavior is presumably due to the fact that there is the least possible amount of complex or ion-pair formation between perchlorate ion and cations. Thus, perchlorates are widely used to study the chemistry of cations.

We have measured the osmotic coefficients of aqueous solutions of pure gallium perchlorate by the isotonic method of Sinclair and Robinson[4,5] as part of a study of the hydrolysis–polymerization of gallium ion produced by added base. The activity coefficients have been calculated over the concentration rate, 0.05 to 2.0 molal gallium perchlorate.

Experimental

Materials.—Gallium perchlorate was prepared by the method of Foster[6] from gallium metal. One sample of gallium was obtained from the Aluminum Company of America; another was donated by the Eagle-Picher Company. The most satisfactory method found for drying the salt was to place it in a glass tube, the closed end of which fitted into the drying chamber of an Abderhalden drying pistol. The tube was made long enough for perchloric acid to condense between the sample and a sodium hydroxide trap. The tube was evacuated through this trap by a vacuum pump. A solvent with a b.p. of 125° was used, and the sample was heated under vacuum overnight. Dry air was then admitted and the tube sealed between the condensed acid and the sample. The tube was opened in a dry-box and the sample stored in a weighing bottle until used. All weighings were done in the dry-box. The material was analyzed for perchlorate by precipitation with tetraphenylarsonium chloride solution saturated with tetraphenylarsonium perchlorate after solution in water saturated with tetraphenylarsonium perchlorate. Following digestion on a hot plate, the solution was brought back to its volume after precipitation by the addition of distilled water.[7] The precipitate was filtered at room temperature on a sintered glass crucible, washed with water saturated with tetraphenylarsonium perchlorate and then with ice-cold distilled water. It was dried at 110° and weighed as tetraphenylarsonium perchlorate. Triplicate samples run in this manner agreed to within a few tenths of 1%. Analysis for gallium was made both by precipitation as the hydrous oxide and ignition to the oxide, and by direct ignition of the hydrated perchlorate to the oxide. The results of both methods agreed.

Anal. Calcd. for $Ga(ClO_4)_3\cdot 6H_2O$: Ga, 14.64; ClO_4, 62.66. Found: Ga, 14.96; ClO_4, 63.78; ratio, ClO_4/Ga, 2.989; formula, $Ga(ClO_4)_3\cdot 5.5H_2O$.

The sample prepared in this manner is thus somewhat less hydrated than the stoichiometric 6-hydrate.

Potassium chloride of reagent grade was recrystallized repeatedly from water and dried at 120°. This material was found to give the same results as that taken directly from the bottle without further purification.

Calcium chloride 2-hydrate of reagent grade was analyzed for chloride by precipitation with silver nitrate. The calcium chloride content was found to be 75.62%, the remainder being water. The stoichiometric 2-hydrate is 75.49% $CaCl_2$.

Apparatus and Procedure.—The apparatus was similar to that described by Mason.[8] The cups of 25-ml. capacity were machined out of silver rod. A nickel collar was soldered around the outside top of each cup, fitting a tapered stainless steel lid. The cups were made to fit tightly into six holes in a copper block 7.5 in. in diameter by 2.5 in. thick. Slight depressions around the edge of the block fitted the lids, so that they could be quickly placed on the proper cup upon opening the unit. Platinum gauze strips stood up in the cups to give increased surface area. A magnetically driven fan with two 3 × 5 cm. flat blades was fastened vertically in the center of the block and ran at about 60 r.p.m. The fan hastened equilibrium, especially in the more dilute solutions where the time required without it became excessive. The container was a 250-mm. glass vacuum desiccator. The whole assembly was clamped on a flat brass rack which rocked back and forth at seven round trips per min. in a 45-gal. thermostat. Temperature was controlled at 25 ± 0.005°. The fluctuations in the region of the samples was doubtless much less than this limit.

At the beginning of a series of runs, samples of gallium perchlorate were weighed directly into the cups. For the more concentrated solutions, the calcium chloride was also

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(1) From the doctoral research of C. S. Patterson.

(2) R. H. Stokes, *Trans. Faraday Soc.*, **44**, 295 (1948).

(3) R. A. Robinson and R. H. Stokes, *ibid.*, **45**, 612 (1949).

(4) D. A. Sinclair, *J. Phys. Chem.*, **37**, 495 (1933).

(5) R. A. Robinson and D. A. Sinclair, THIS JOURNAL, **56**, 1830 (1934).

(6) L. S. Foster, *Inorg. Syntheses*, **2**, 26 (1946).

(7) The authors are grateful to Professor W. T. Smith, Jr., for informing them of this way of increasing the accuracy of the procedure described by H. H. Willard and G. M. Smith, *Ind. Eng. Chem., Anal. Ed.*, **11**, 305 (1939), for perrhenate.

(8) C. M. Mason, THIS JOURNAL, **60**, 1638 (1938).