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The Mercury ($^3P_1$) Photo-Sensitized Reaction of Ethane at High Temperatures*

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The mercury photo-sensitized decomposition of ethane has been carried out with particular emphasis on the high temperature reaction. Evidence is given that under these experimental conditions the ethyl radical becomes unstable around 400°C. An activation energy of 39.5 kcal is assigned to the reaction

$$C_2H_5 = C_2H_4 + H$$

on the basis of the proposed mechanism.

INTRODUCTION

THE mercury photo-sensitized reaction of propane at high temperatures and moderate pressures has yielded[1] information on the stability of the propyl radical.

It seemed therefore profitable to investigate the thermal stability of the ethyl radical by producing ethyl radicals at high temperatures by a mercury photo-sensitized reaction of ethane. Various investigations have been carried out[2–4] on the mercury photo-sensitized decomposition of ethane but in no case was the reaction investigated at a sufficiently high temperature that the ethyl radical would be expected to be unstable.

EXPERIMENTAL

Ethane was obtained in cylinders from the Phillips Petroleum Company (Research Grade). This was stated to be 99.9 percent pure and was therefore used without purification except for a simple bulb-to-bulb distillation and rigorous degassing. The reaction was investigated in a static system. The reaction was carried out in a cylindrical quartz cell inside a tubular furnace and the cell illuminated by unreversed λ2537 obtained from a low pressure mercury lamp with neon as carrier gas. Actinometry using uranyl oxalate gave a light input of 1.38×10^{-5} Ein./hr. After reaction the products were frozen out with liquid nitrogen and the hydrogen pumped off and analyzed for traces of methane by combustion over copper oxide. A few typical experiments were completely analyzed using a modified Ward still. The apparatus used was exactly as described by Bywater and Steacie[1] and thus needs no further description.

TABLE I. Rate of hydrogen production.

Temp. (°C)	cc/hr NTP	cc/hr (non-chain)	cc/hr (chain)
27	0.106	...	...
100	0.154	..	...
200	0.202	...	...
300	0.229	...	...
400	0.270	...	...
425	0.380	0.269	0.111
450	0.582	0.277	0.305
475	1.144	0.283	0.861
500	2.184	0.289	1.895

RESULTS

Experiments were carried out at a pressure of 40 cm of ethane. This relatively high pressure was used to eliminate unwanted side reactions, particularly those leading to the formation of methane, and also to eliminate the quenching of excited mercury by the reaction products. Some of these have a much larger quenching cross section than has ethane.

Below 400°C these experiments confirm that hydrogen and butane are the only significant reaction products at high pressures (Tables I and II, Figs. 1 and 2). Between room temperature and 400°C the rate of hydrogen production increases slightly corresponding to an apparent activation energy of 0.9 kcal per M. The quantum yield thus rises from 0.34 at 27°C to 0.87 at

TABLE II. The products of the reaction (cc NTP).

Run	Temp. (°C)	Time (min)	H_2	CH_4	C_2[a]	C_3	C_4	C_5^+
200	200	90	0.299	0.000	72.0	0.00	0.247	0.003
203	400	60	0.270	0.009	55.6	0.007	0.153	0.006
227	425	40	0.262	0.008	55.7	0.000	0.123	0.004
209	450	45	0.402	0.014	53.8	0.000	0.094	0.007
218	500	7.5	0.299	0.002	52.1	0.000	0.073	0.002

[a] C_2 includes unchanged ethane.

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[1] S. Bywater and E W. R. Steacie, J. Chem. Phys. **19**, 172 (1951).

[2] E. W. R. Steacie and N. W. F. Phillips, J. Chem. Phys. **6**, 179 (1938). Can. J. Research **B16**, 303 (1938).

[3] E. W. R. Steacie and R. L. Cunningham, J. Chem. Phys. **8**, 800 (1940).

[4] B. deB. Darwent and E. W. R. Steacie, J. Chem. Phys. **16**, 381 (1948).

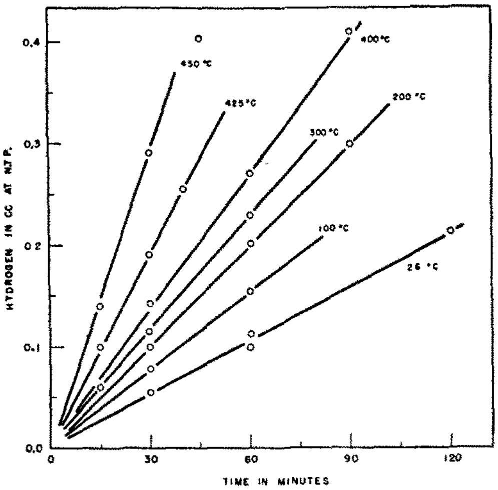

FIG. 1. Rate of hydrogen production at various temperatures.

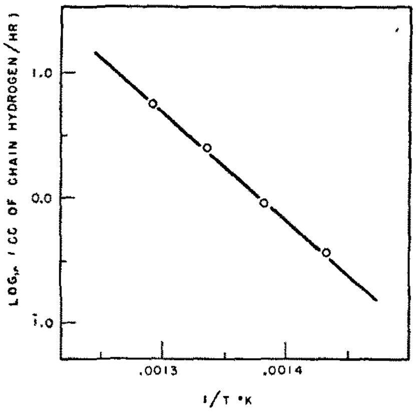

FIG. 3. Activation energy plot for the chain step.

400°C. This slight rise may correspond to greater efficiency in the quenching of excited mercury by ethane at higher temperatures or to the fact that radical recombination reactions are less likely at higher temperatures or to the occurrence of a disproportionation step between ethyl radicals. In any of these cases it can be easily shown that this is formally equivalent to a primary step with a variable quantum yield, dependent both on pressure and temperature. Most interest attaches to those experiments above 425° where the basic quantum yield is almost unity. It follows that here the other reaction steps are unimportant and in fact can be corrected for by using the rise in quantum yield at low temperatures.

Above 400° the hydrogen production increases rapidly giving quantum yields above unity which indicate a chain mechanism. Such a chain mechanism requires a new elementary reaction which will regenerate a chain carrying hydrogen atom. The apparent activation energy of this step has been calculated from the results (Table I and Fig. 3) by subtracting the amount of hydrogen produced by the non-chain mechanism (using an extrapolation from the low temperature experiments (Fig. 4)) from the total hydrogen produced at each temperature. In this calculation quantities of gas evolved were expressed in cc of gas at NTP. In practice the experiments were carried out at constant total pressure rather than constant concentration; since, however, separate experiments showed that at such high pressures the rate of hydrogen production is almost independent of concentration of ethane, the error particularly in a calculation of an activation energy will be negligible. The apparent activation energy for this step is 40±1 kcal.

DISCUSSION

The low temperature measurements are consistent with the mechanism postulated earlier[2,3,4]

$$Hg(^1S_0)+h\nu = Hg(^3P_1) \qquad I_a$$

$$Hg(^3P_1)+C_2H_6 = Hg(^1S_0)+C_2H_5+H \qquad \Phi I_a \qquad (1)$$

$$H+C_2H_6 = C_2H_5+H_2 \qquad k_2[C_2H_6][H] \qquad (2)$$

$$2C_2H_5 = C_4H_{10} \qquad k_3[C_2H_5]^2, \qquad (3)$$

where Φ is a function of temperature. Here the low quantum yield has been attributed to inefficiency in the ethane quenching step. If recombination of hydrogen

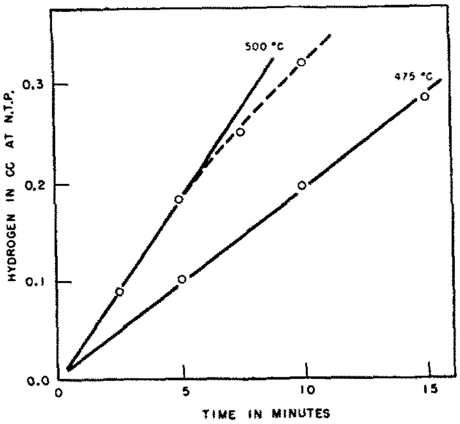

FIG. 2. Rate of hydrogen production at high temperatures.

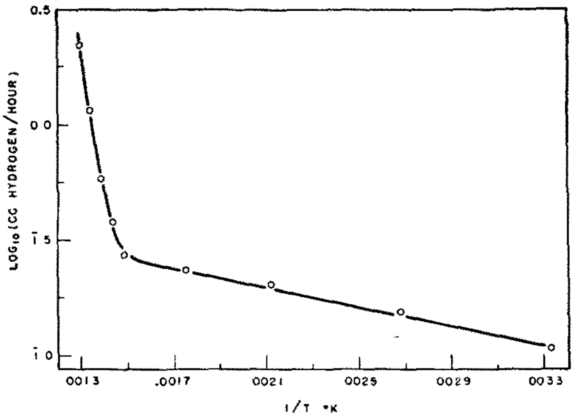

FIG. 4. Activation energy plot for the total hydrogen production.

atoms and ethyl radicals, or disproportionation of ethyl radicals rather than recombination, is responsible for the low Φ value, it is easily shown that the over-all effect is still formally equivalent to a variable primary quantum yield.

At higher temperatures, the only feasible mechanism which will meet the requirements of regeneration of a hydrogen atom and a high activation energy seems to be

$$C_2H_5 = C_2H_4 + H \quad k_4[C_2H_5]. \tag{4}$$

Application of the stationary state hypothesis to this reaction scheme gives for the rate of production of hydrogen

$$\frac{d[H_2]}{dt} = \Phi I_{\text{abs}} + \frac{k_4}{(k_5)^{\frac{1}{2}}}(\Phi I_{\text{abs}})^{\frac{1}{2}}.$$

It is clear that the low temperature rate is simply equal to ΦI_{abs}. Therefore the activation energy obtained as above is equal to $E_4 + \frac{1}{2}E_\Phi - \frac{1}{2}E_3$. $\frac{1}{2}E_\Phi = 0.5$ kcal. Making the usual assumption that $E_3 = 0$, $E_4 = 39.5$ kcal.‡

The mechanism quoted requires that an amount of ethylene equivalent to the extra chain hydrogen should be produced. Normal methods of analysis are not accurate enough to detect ethylene in the large quantity of unchanged ethane. Attempts were therefore made to detect this small amount of ethylene by infrared analysis using the strong ethylene band at 949 cm^{-1} and using the total C_2 fraction as removed by a Ward still fractionation. The accuracy of these measurements is limited by the low concentration of ethylene and the pressure broadening of the peak caused by the high pressure of ethane present. However, roughly correct amounts of ethylene are present (Table III).

TABLE III. Production of ethylene (cc NTP).

Run	Temp. (°C)	Chain H_2	Measured C_2H_4
203	400	0.024	0.1^{0}
227	425	0 088	0.1^{5}
209	450	0.248	0.2^{0}
218	500	0.242	0.2^{0}

Previous experimental evidence for the activation energy of reaction (4) is scanty.

Rice[5,6] assigned a value of 49 kcal to this reaction in order to explain the over-all activation energy for the thermal decomposition of ethane. The activation energy was assessed on a purely speculative basis and so was not claimed to be more than a rough estimate.

Bawn[7] has estimated the activation energy for the decomposition of the ethyl radical by a transition state calculation and has obtained a value of 48–50 kcal.

A minimum value for the activation energy of reaction (4) can be assessed on thermochemical grounds since the reaction is endothermic. Numerically the heat of reaction is equal to the bond strength in hydrogen plus the heat of hydrogenation of ethylene minus the carbon-hydrogen bond strength in ethane. All these values have been established with reasonable certainty giving a heat of reaction of 37.5 kcal. Thus the activation energy of the reaction will be 37.5 kcal plus the activation energy of the reverse reaction. This would suggest an activation energy of 38–43 kcal.[8] The value of 39.5 kcal obtained would require an activation energy of 2 kcal for the back reaction. This value is in agreement with the experimental fact that the back reaction proceeds rapidly at room temperatures. The value 2 kcal can have a large error since it has been obtained by the differences of two large energy terms.

The reaction between hydrogen atoms and various olefins has been investigated at room temperature by Robb and Melville.[9] The value of the collision yield for the reaction of hydrogen atoms with ethylene is given as 8.5×10^{-4} at room temperature. If we assume the usual value (0.1) for the steric factor of this reaction the activation energy corresponds to about 3 kcal. This must be regarded as a maximum value, since there is evidence that similar reactions can have a lower steric factor.

Frost[10] has given thermodynamic arguments why the ethyl radical should be stable even at 600°C. He obtains an equilibrium constant for the reaction

$$C_2H_5 \rightleftharpoons C_2H_4 + H$$

at 900°K expressed as $(P_H \cdot P_{C_2H_4})/P_{C_2H_5}$ and gives a value of 2×10^{-4} at this temperature. The value obtained appears reasonable and has been checked using more recent values of thermodynamic constants. The argument however overlooks the fact that at an elevated temperature the hydrogen atoms produced by decomposition of the ethyl radical will react more readily with ethane than with ethylene under usual reaction conditions. Thus, using the data of Trost and Steacie[11] for the reaction of hydrogen atoms with ethane, and Robb and Melville's collision yield for the reaction of hydrogen atoms with ethylene, and assuming that the activation energy for this reaction is at the most 3 kcal, hydrogen atoms react 6×10^4 times faster with ethylene than ethane at room temperature and standard concen-

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‡ Inhomogeneity of light absorption will cause an error here, if it is temperature dependent. However, pressure broadening of the resonance line is so great that Doppler broadening is negligible, and the change in absorption with temperature will be small.

[5] F O. Rice and K. F. Herzfeld, J. Am. Chem. Soc. **56**, 284 (1934)

[6] F. O. Rice, J. Am. Chem. Soc. **56**, 488 (1934).

[7] C. E. H Bawn, Trans. Faraday Soc. **31**, 1536 (1935).

[8] E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York, 1946).

[9] J. C. Robb and H. W. Melville, Proc. Roy. Soc. (London) **A196**, 494 (1949).

[10] A. V. Frost, Zhur. Fiz. Khim **8**, 290 (1936).

[11] W. R. Trost and E. W. R. Steacie, J. Chem. Phys **16**, 361 (1948).

trations. At 850°K, however, this ratio is reduced to about 25 and since the ethane concentration is one to two hundred times greater than the ethylene concentration in the aforementioned experiments, the reaction is weighted at least ten to twenty times in favor of the ethane reaction. Thus the equilibrium will be pushed over by removal of hydrogen atoms from the system, and decomposition products of the ethyl radical will be observed.

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The Reactions of Methyl Radicals. IV. The Abstraction of Hydrogen Atoms from Cyclic Hydrocarbons, Butynes, Amines, Alcohols, Ethers, and Ammonia*

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The photolysis of acetone in the presence of various compounds has been investigated between 70°C and 340°C. If the reaction

$$CH_3+CH_3=C_2H_6$$

has no activation energy, then the activation energies in kcal for the reactions of the type

$$CH_3+RH=CH_4+R$$

are cyclopropane 10.3, cyclobutane 9.3, cyclopentane 8.5, cyclohexane 8.3, benzene 9 2, toluene 8 3, 1-butyne 9.1, 2-butyne 8.6, methanol 8.2, ethanol 8.7, iso-propanol 7 3, methyl ether 9 5, iso-propyl ether 7.3, monomethyl amine 8.4, dimethyl amine 7.2, trimethyl amine 8.8, and ammonia 10 0 The collision theory steric factors are of the order of 10^{-3} or less for all these reactions.

A table is presented summarizing the results so far obtained on methyl radical reactions by the photolysis of acetone in the presence of other compounds. The accuracy of the method and some of the general implications of the results are discussed.

INTRODUCTION

THIS paper is the fourth of a series describing a quantitative survey of the reactions of methyl radicals. The experiments described here were carried out to determine the rate of abstraction of hydrogen atoms from a variety of compounds by methyl radicals formed in the photolysis of acetone. We have determined the rate constants, k_1, of these reactions of type (1),

$$CH_3+RH=CH_4+R, \qquad (1)$$

relative to the square root of the rate constant, k_2, for the combination of methyl radicals (reaction 2);

$$CH_3+CH_3=C_2H_6. \qquad (2)$$

This was done by two methods: Method I, where the value of $k_1/k_2^{\frac{1}{2}}$ is determined directly using ordinary acetone and Method II, where the ratio is found indirectly using deuterated acetone. These Methods are fully described in the second paper[1] (Part II) of this series.

EXPERIMENTAL

Apparatus

The apparatus was the same as that used in Part II. In the experiments on cyclohexane, cyclopentane, methanol, and methyl ether, which were carried out with ordinary acetone, a chlorine filter five cm long filled with gas at one atmosphere pressure and a light beam collimated with quartz lenses were used. The experiments on cyclopentane using heavy acetone and on toluene, benzene, the butynes, iso-propanol, iso-propyl ether, the amines, and ammonia were carried out with a light beam collimated roughly with a polished aluminum cylinder and a 1 mm Corex *D* (also known as 9–53 or 9700) filter. The same method of collimation was employed for the experiments with cyclobutane and cyclopropane, but no filter was used. The experiments with ethanol were carried out using a light beam roughly collimated with a polished aluminum cylinder and a Corex *A* (also known as 9–54 or 7910) filter, with 50 percent transmission at 2450A.

Materials

The acetone was a Mallinckrodt Reagent Grade product which had been refluxed over potassium permanganate, distilled, and dried with drierite.

The heavy acetone, which mass spectrometer analysis showed to be 68 percent acetone-d_6 and 32 percent acetone-d_5, was made for us by Dr. L. C. Leitch of this laboratory.

Cyclohexane, toluene, and benzene were Phillips Petroleum Company (Research Grade) and were stated to have a purity of 99.8 percent or better. Cyclopropane

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[1] Trotman-Dickenson, Birchard, and Steacie, J. Chem Phys. 19, 163 (1951).