

CADMIUM PHOTSENSITIZED DECOMPOSITION OF ETHANE

E. J. McALDUFF and Y. H. YUAN*

St. Francis Xavier University, Antigonish, Nova Scotia (Canada)

(Received July 25, 1975; in revised form November 11, 1975)

Summary

The photosensitized decomposition of ethane has been carried out at temperatures of 533, 553, and 573 °K and over a pressure range from 3 to 40 Torr. The principal products were hydrogen, ethylene, butane and methane. A mechanism to account for the pressure and temperature dependence of the products is invoked which involves production of ethylene by unimolecular decomposition of ethyl radicals as well as by disproportionation of ethyl radicals. The formation of butane can be accounted for in terms of pressure dependent free radical recombination. Hydrogen is assumed to arise by H atom abstraction from reactant. Methane formation is shown to involve secondary processes. These results agree as to major products but differ in minor products from earlier work on the Cd photosensitized decomposition of ethane and also from the high temperature mercury photosensitized decomposition.

Introduction

A number of previous investigations [1 - 7] of the mercury photosensitized decomposition of ethane have been made. In 1939, Steacie and Potvin published results [8] of the cadmium (3P_1) photosensitized reactions of ethane. The results found and the mechanism suggested were similar to those of mercury (3P_1) photosensitized reactions of ethane [1 - 6]. The primary process was suggested to be C-H bond rupture with the resultant formation of an ethyl radical and cadmium hydride. The cadmium hydride is presumed to dissociate into a ground state cadmium atom and a hydrogen atom. The existence of cadmium hydride in the process was confirmed by the resonance emission of cadmium hydride bands observed in the quenching of cadmium (3P_1) by propane [9]. On

*Present address: Department of Chemistry, University of Ottawa, Ottawa, Ontario (Canada).

energetic grounds this suggestion is also favored since the reaction is exothermic by 26.3 kJ/mol. This process was further confirmed by the fact that hydrogen was found to be the main product at short exposure times.

However, the C–C bond splitting process, in which ground state cadmium and methyl radicals are formed, which is exothermic by 15.5 kJ/mol, cannot be completely excluded.

The mechanism of the formation of hydrogen [5, 6] has been believed to be by abstraction from reactant ethane.

According to Steacie and Potvin's study [8], methane and propane were found to be the major products besides hydrogen and secondary processes were suggested to account for their formation. Butane was found to be a relatively minor product and was presumed to be produced by the recombination of ethyl radicals. Trace amounts of ethylene were found but its mechanism of formation was not suggested.

In Steacie and Potvin's study [8], reactions with high percentage of ethane decomposition were studied. Obviously a considerable amount of secondary reactions of products would be expected and the rates of product formation were reported to be changing with the progress of reaction. This possibly makes the assumed mechanism of decomposition uncertain. From this point of view, it appeared that an investigation in the initial states of reaction at low percentages of ethane decomposition is worthwhile. Without the interference of the secondary reactions, a clearer picture of the mechanism might be revealed.

Experiment

Philips research grade ethane, stated to be 99.99 mol % pure, was used. The impurities were removed by distillation from a dry ice–acetone trap and from a solid n-pentane trap. Finally, the purified ethane was degassed in the storage bottle before use.

The reaction was investigated in a conventional static system. A cylindrical quartz reaction vessel, 150 mm long and 70 mm diameter, was enclosed in a concentric tubular furnace. A few small pieces of cadmium (Fischer, C-2) were placed in the reaction vessel for supplying cadmium vapor at reaction temperature. A Cole–Parmer temperature controller was used to maintain the furnace temperature constant to within $\pm 1^\circ$. Temperature was measured by a millivolt potentiometer (Leeds and Northrup Co.) through a Chromel P/Alumel thermocouple. Pressures of ethane were read on a mercury manometer.

The light source was a George W. Gates and Co. low pressure Cd spectral lamp with a quartz lens converging the light into a nearly parallel beam. A Corning 9863 filter excluded wavelengths less than 2300 Å.

After irradiation, the gas condensable by liquid N₂ was analyzed by gas chromatography. Flame ionization detection was preceded by product

separation on a 15.2 m long and 9.5 mm o.d. column of squalane (30% by wt) on 45/60 mesh Chromosorb P. Helium was used as the carrier gas with a flow-rate of 40 cm³/min. The peaks of propylene and propane, which were eluted after ethane, were distorted or concealed by the huge ethane peak and failed to be determined. Methane and ethylene, which were eluted before ethane, and butane, retained much longer than ethane, were readily determined. Known amounts of ethane were swept from a U-tube by the carrier gas and used as a reference for the quantitative measurements of the products.

The non-condensable fraction, which was found to contain traces of methane and ethane along with hydrogen, was collected through a Toepler pump into a U-tube with calibrated volume into the gas chromatograph after the pressure was read. For the measurement of pressure, a vacuum gauge (Consolidated Vacuum Corporation, Type GIC-110A, thermocouple gauge tube GTC-004) was used and calibrated for hydrogen by a McLeod gauge. A correction for the trace of methane and ethane in the non-condensable fraction was applied in the following manner. The partial pressures of methane and ethane were calculated from the amount of the gases determined by chromatographic analysis. The partial pressure of hydrogen was then calculated by subtracting the partial pressure of methane and ethane from the total pressure of non-condensable gases. Finally, the data of hydrogen pressure and volume led to the amount of hydrogen in moles.

Results

The cadmium photosensitized decomposition of ethane was studied at 533, 553, and 573 K. At each temperature the reactions were examined at ethane pressures from 3 to 40 Torr and at saturated vapor pressure of cadmium at the respective temperature. In this initial stage of reaction less than 0.2% ethane was consumed. The results are presented in Tables 1, 2, and 3.

The major products of reaction are hydrogen, butane, ethylene, and methane. Propylene, propane, isobutane, and 1-butene were found to be minor products of reactions at higher temperatures and pressures. For some runs it was possible to analyze approximate quantities of propylene and propane. However, the difficulty involved in the separation of propylene and propane from large quantities of ethane by gas chromatography make their analysis unreliable. A search by chromatography revealed no further products of reaction.

Dark reactions have been carried out at extremes of pressure and temperature and no significant products are observed indicating that no appreciable thermal decomposition occurred.

TABLE 1

Rates* of formation of the products of the ethane decomposition at 533 K. $[Cd] = 7.7 \times 10^{-3}$ Torr. Exposure = 1 h.

C_2H_6 (Torr)	CH_4	C_2H_4	C_4H_{10}	H_2
3	0.1094	0.3876	—	2.260
4	0.1378	0.5152	—	3.391
5	0.2670	0.5512	—	4.005
6	0.2411	0.5944	0.0689	4.778
8	0.2584	0.7237	0.1551	6.296
12	0.3230	0.9803	0.3962	8.397
18	0.3962	1.529	2.820	10.82
24	0.4220	1.593	3.015	7.076
30	0.4652	1.753	4.264	10.01
40	0.6544	1.891	5.339	14.46

*Rates are given in $\text{mol m}^{-3} \text{s}^{-1} \times 10^9$.

TABLE 2

Rates* of formation of products of the ethane decomposition at 553 K $[Cd] = 1.9 \times 10^{-2}$ Torr. Exposure = 1 h.

C_2H_6 (Torr)	CH_4	C_2H_4	C_4H_{10}	H_2
3	0.4392	1.593	0.1723	6.820
4	0.7901	1.680	0.4134	8.222
5	0.6026	1.830	0.6247	8.579
6	0.9488	2.153	0.9991	11.79
8	0.9131	2.550	3.075	15.17
12	1.516	5.984	10.85	27.73
18	1.551	6.893	23.12	29.67
24	1.206	7.838	30.41	33.74
30	2.023	12.92	60.93	55.87
40	1.826	17.23	89.98	68.47

*Rates are given in $\text{mol m}^{-3} \text{s}^{-1} \times 10^9$.

Discussion

The results will be interpreted in terms of the following mechanism.

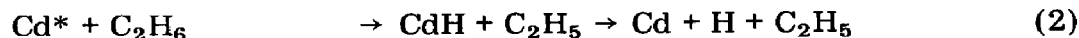
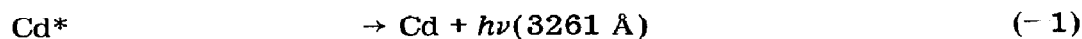
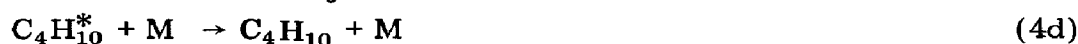
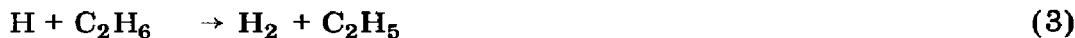


TABLE 3

Rates* of formation of products of the ethane decomposition at 573 K. $[Cd] = 4.3 \times 10^{-2}$ Torr. Exposure = 1 h.

C_2H_6 (Torr)	CH_4	C_2H_4	C_4H_{10}	H_2
3	1.568	5.650	5.253	15.48
4	1.843	6.116	5.926	19.14
5	2.300	6.865	7.188	20.99
6	2.635	8.950	13.41	26.79
8	1.964	10.70	29.20	38.76
12	2.429	14.82	60.70	74.32
15	3.626	17.14	77.96	82.01
18	3.281	18.95	65.90	74.60
21	5.054	18.74	91.94	79.43
24	3.799	20.72	96.91	82.99
27	2.697	23.32	108.1	74.32
30	6.400	26.70	126.6	114.7
33	14.32	23.65	111.2	101.4
36	6.107	29.63	174.4	137.9
40	7.586	28.00	157.7	139.2

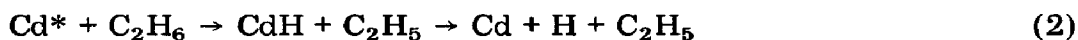
*Rates are given in $\text{mol m}^{-3} \text{s}^{-1} \times 10^9$.



The foregoing results show that the hydrogen production is much more than that of methane. It therefore appears that the main primary process involves a C-H bond split in the cadmium photosensitized reaction, which occurs after production of $Cd(5^3P_1)$ in reaction (1):



In the absence of complete quenching $Cd(5^3P_1)$ can return to the ground state by re-emission of 3261 Å or formation of $Cd(5^3P_0)$ [11] may result. For purposes of the present discussion it is sufficient to identify the excited species as Cd^* and note that more than one excited state of Cd may be involved. Reaction (2) is the quenching reaction and hydrogen results from reaction (3).





Ethylene and butane formation

Butane is formed by the combination of ethyl radicals:

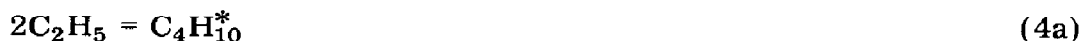


and this gives further evidence of the C–H bond split in the primary process. Disproportionation leads to ethylene production in reaction (5):



Roquitte and Futrell [12] reported the ratio of disproportionation/combination of ethyl radicals is a constant with the value of 0.117 in the flash photolysis of azoethane. In other words, the ratio combination/disproportionation has a constant value of 8.55 independent of pressure. In Fig. 1, $R_f(\text{C}_4\text{H}_{10})/R_f(\text{C}_2\text{H}_4)$ is plotted against the pressure of ethane and shows an abrupt fall-off in the region of low pressures. It also appears that, at high pressures this ratio tends towards a constant with a value of 5 to 6 which is less than that evaluated by Roquitte and Futrell. This indicated that either butane production is reduced by some process or a pressure dependent enhanced production of ethylene accounts for the changing ratio.

We shall first examine the possible third body effect if an intermediate $\text{C}_4\text{H}_{10}^*$ is assumed to be formed in the process of the combination of ethyl radicals, viz.:



There might be two mechanisms of the decomposition of the unstable $\text{C}_4\text{H}_{10}^*$:



However, if reaction (4c) occurs, pentane should then result from recombination of C_3H_7 and C_2H_5 . No C_5 hydrocarbons were detected and therefore reaction (4c) can be excluded. The stabilization of $\text{C}_4\text{H}_{10}^*$ by a third body which may be assumed to be C_2H_6 is:



In the steady state:

$$[\text{C}_4\text{H}_{10}^*] = \frac{k_{4a}}{k_{4b} + k_{4d} [\text{C}_2\text{H}_6]} [\text{C}_2\text{H}_5]^2 \quad (\text{I})$$

$$\begin{aligned} R_f(\text{C}_4\text{H}_{10}) &= k_{4d} [\text{C}_2\text{H}_6] [\text{C}_4\text{H}_{10}^*] \\ &= \frac{k_{4a} [\text{C}_2\text{H}_6]}{k_{4b}/k_{4d} + [\text{C}_2\text{H}_6]^2} \end{aligned} \quad (\text{II})$$

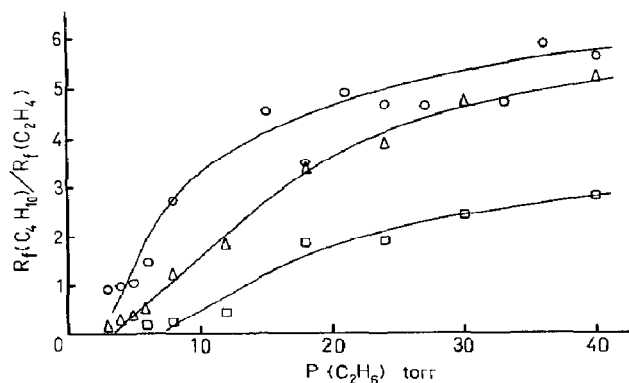


Fig. 1. Rate of formation of butane/ethylene as a function of pressure. \circ , 573 K; Δ , 553 K; \square , 533 K.

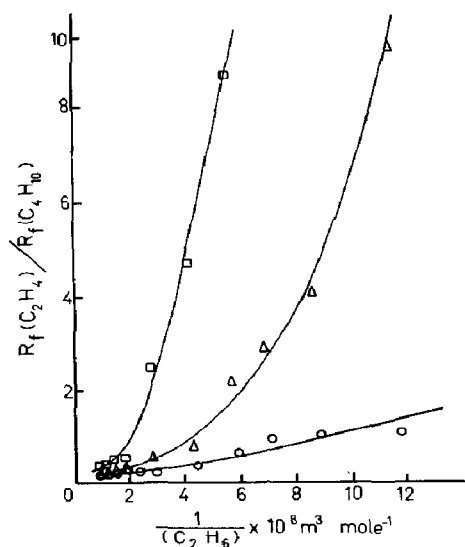


Fig. 2. Rate of formation of ethylene/butane vs. reciprocal of ethane concentration. \square , 533 K, Δ , 553 K, \circ , 573 K.

if ethylene is produced only from the reaction (5), its rate of formation is:

$$R_f(C_2H_4) = k_5 [C_2H_5]^2 \quad (III)$$

and then the ratio of the rate of disproportionation to combination becomes:

$$\frac{R_f(C_2H_4)}{R_f(C_4H_{10})} = \frac{k_5}{k_{4a}} + \frac{k_{4b}k_5}{k_{4a}k_{4d}[C_2H_6]} \quad (IV)$$

This ratio is plotted against the reciprocal of ethane concentration in Fig. 2. The curves do not show linear behaviour as predicted by eqn. (IV) but seem to have a common intercept with a value in the range 0.10 to 0.15. This is of the order of magnitude expected for the true disproportionation/

combination ratio and corresponds to the ratio of k_5/k_{4a} . The limiting slopes of the curves in Fig. 2 are also approximately constant with a value of 2.5. The slope should correspond to $(k_{4b}k_5)/(k_{4a}k_{4d})$ in terms of eqn. (IV) and since the k_5/k_{4a} ratio is known from the intercept k_{4b}/k_{4d} becomes approximately 25. This prediction represents the amount of decomposition of hot butane relative to its stabilization. This ratio is several orders of magnitude greater than that calculated by Rabinovitch and Setser [13] where they have predicted the decomposition/stabilization ratio for butane at 573 K to be 3.8×10^{-2} with activation by ethyl radical combination. The curves in Fig. 2 also show a rapid increase in C_2H_4/C_4H_{10} at lower pressures of ethane. This non-linear behaviour makes the attempted fit of the results to eqn. (IV) a dubious procedure at even the higher pressures of ethane. It also indicates an extra source of ethylene formation, other than that from the disproportionation process, which becomes significant at low pressures of ethane.

Bywater and Steacie [14] reported that the ethyl radical becomes unstable at around 400 °C and may decompose by:



Loucks and Laidler [15] made a more thorough investigation of ethyl radical decomposition and reported that a significant ethylene formation from reaction (6) was found at 673 K. In the present study in the temperature range 533 - 573 K, reaction (6) may also be assumed to occur to a certain extent. The following arguments show a general agreement of this assumption with the results shown in Fig. 1.

At high pressure of ethane, since a high concentration of ethyl radical results, the bimolecular reactions of combination and disproportionation are more favored than the unimolecular reaction of ethyl radical decomposition. Thus the ratio $R_f(C_4H_{10})/R_f(C_2H_4)$ tends towards a constant value nearly equal to the ratio combination/disproportionation which is pressure independent. While at low pressure, the resulting low concentration of ethyl radical minimizes reactions (4) and (5) and causes reaction (6) to become significant. Therefore, the relative increase of ethylene formation from reaction (6) reduces the ratio $R_f(C_4H_{10})/R_f(C_2H_4)$ rapidly as shown in Fig. 1 in the low pressure region.

Secondly, let us examine the effect of temperature on $R_f(C_2H_4)$. Both combination and disproportionation reactions have been found to possess zero activation energy [16] and their ratio should be temperature independent. As shown in Table 4 the variation in $R_f(C_4H_{10})/R_f(C_2H_4)$ with temperature shows that combination and disproportionation are not the only reactions accounting for ethylene and butane production. Furthermore, if only the reactions (4a), (4b), and (4d) are important, $R_f(C_4H_{10})/(R_f(C_2H_4))$ should decrease with temperature since $C_4H_{10}^*$ becomes more unstable at high temperature. However, it has been found that $R_f(C_4H_{10})/R_f(C_2H_4)$ increased with temperature. In the present study, reactions at high temperature were accompanied by high cadmium

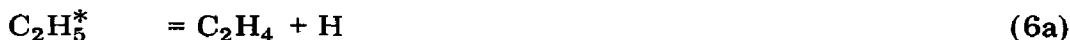
TABLE 4

Ratio of the rate of formation of butane to ethylene as a function of pressure and temperature.

Ethane pressure (Torr)	$R_f(\text{C}_4\text{H}_{10})/R_f(\text{C}_2\text{H}_4)$		
	573 K	553 K	533 K
3	0.930	0.108	—
4	0.969	0.246	—
5	1.047	0.341	—
6	1.468	0.464	0.116
8	2.729	1.206	0.214
12	4.096	1.813	0.404
18	3.478	3.353	1.844
24	4.678	3.880	1.893
30	4.742	4.716	2.432
40	5.632	5.222	2.823

vapor pressures in the reaction vessel, thus a higher ethyl radical concentration resulted from the primary reaction. The real attribution of the variation in $R_f(\text{C}_4\text{H}_{10})/R_f(\text{C}_2\text{H}_4)$ with temperature may be determined by the relative importance of ethyl radical decomposition *vis-à-vis* disproportionation at different concentrations of ethyl radical.

It appears that ethyl radical decomposition is of significance under the experimental conditions. Now the question is whether this decomposition happens only to a hot ethyl radical. If this is the case, it will lead to the reactions:



M may be considered to be ethane. Since the life-time of the hot radical C_2H_5^* is predominantly dependent on the concentration of ethane, the ratio (6a)/(6b) at a definite ethane pressure will not be changed with the concentration of C_2H_5^* . Therefore, although a higher C_2H_5^* concentration resulted in the experimental conditions at high temperature the ratio $R_f(\text{C}_4\text{H}_{10})/R_f(\text{C}_2\text{H}_4)$ should not increase. Furthermore, with the increase of temperature, since reaction (6a) will be favored over reaction (6b), the ratio $R_f(\text{C}_4\text{H}_{10})/R_f(\text{C}_2\text{H}_4)$ should actually be expected to decrease. But the results have been found to be the opposite and reactions (6a) and (6b) appear to be excluded.

However, there is still some doubt about the occurrence of the series of reactions (4a) - (4b) at low pressures of ethane. By assuming that only reactions (4), (5), and (6) are of importance, one obtains the following equations:

$$R_f(\text{C}_2\text{H}_4) = k_5 [\text{C}_2\text{H}_5]^2 + k_6 [\text{C}_2\text{H}_5] \quad (V)$$

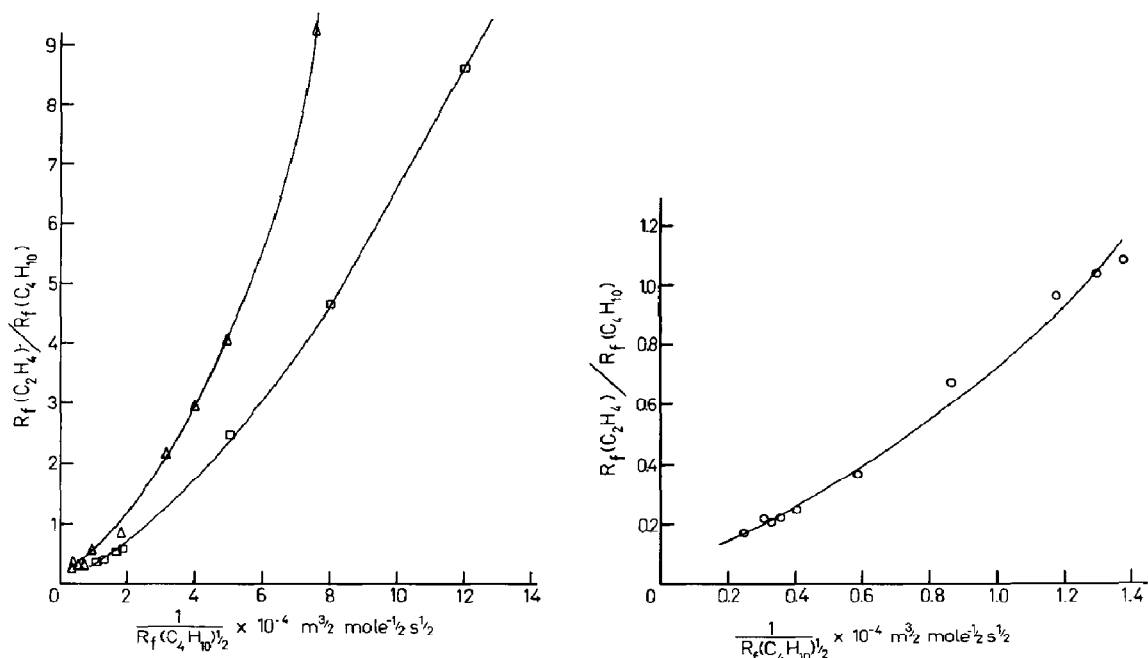


Fig. 3. Rate of formation of ethylene/butane vs. reciprocal of square root of rate of butane formation. (a) Δ , 553 K; \square , 533 K; (b) \circ , 573 K.

$$R_f(C_4H_{10}) = k_4 [C_2H_5]^2 \quad (\text{VI})$$

$$[C_2H_5] = R_f(C_4H_{10})^{1/2} / k_4^{1/2} \quad (\text{VII})$$

$$\begin{aligned} \frac{R_f(C_2H_4)}{R_f(C_4H_{10})} &= \frac{k_5}{k_4} + \frac{k_6}{k_4 [C_2H_5]} \\ &= \frac{k_5}{k_4} + \frac{k_6}{k_4^{1/2}} \frac{1}{R_f(C_4H_{10})^{1/2}} \end{aligned} \quad (\text{VIII})$$

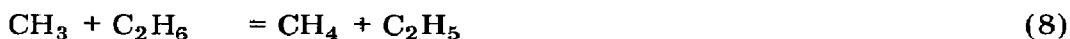
The graph of $R_f(C_2H_4)/R_f(C_4H_{10})$ vs. $1/R_f(C_4H_{10})^{1/2}$ is shown in Figs. 3a and b. It appears that the ratio $R_f(C_2H_4)/R_f(C_4H_{10})$ tends to increase in the region of low values of rate of butane formation *i.e.*, the region of low pressures of ethane. This shows that the third body effect, *i.e.* reactions (4a) - (4d), is significant at low pressures of ethane.

Methane production

On energetic grounds there is a possibility that methane is produced from:



followed by [17, 18]:



By using the steady-state treatment, one obtains the rate of methane formation from reactions (2a) and (8);

$$\begin{aligned} R_f(\text{CH}_4) &= k_8 [\text{CH}_3] [\text{C}_2\text{H}_6] \\ &= 2k_{2a} [\text{Cd}^*(^3\text{P}_1)] [\text{C}_2\text{H}_6] \end{aligned} \quad (\text{IX})$$

and the rate of hydrogen formation from reactions (2) and (3):

$$\begin{aligned} R_f(\text{H}_2) &= k_3 [\text{H}] [\text{C}_2\text{H}_6] \\ &= k_2 [\text{Cd}^*(^3\text{P}_1)] [\text{C}_2\text{H}_6] \end{aligned} \quad (\text{X})$$

the ratio

$$\frac{R_f(\text{CH}_4)}{R_f(\text{H}_2)} = \frac{2k_{2a}}{k_2} \quad (\text{XI})$$

should be constant at a definite temperature and independent of pressure of ethane. From the results listed in Tables 1, 2 and 3 it is clear that the ratio varies with decreasing pressure. Therefore it appears that methane formation is not the result of C-C bond split process (2a).

It has been found [5] that methyl radicals can be produced by:



which is then followed by:



to lead to methane formation:

$$\begin{aligned} R_f(\text{CH}_4) &= k_8 [\text{CH}_3] [\text{C}_2\text{H}_6] \\ &= 2k_7 [\text{H}] [\text{C}_2\text{H}_5] \end{aligned} \quad (\text{XII})$$

From eqns. (X) and (XII) one obtains:

$$\frac{R_f(\text{CH}_4)}{R_f(\text{H}_2)} = \frac{2k_7}{k_3} [\text{C}_2\text{H}_5] \quad (\text{XIII})$$

In eqn. (III), if it is assumed that $[\text{C}_2\text{H}_6] \ll k_{4b}/k_{4d}$, the following equations are obtained:

$$R_f(\text{C}_4\text{H}_{10}) \approx \frac{k_{4a}k_{4d}}{k_{4b}} [\text{C}_2\text{H}_6] [\text{C}_2\text{H}_5]^2 \quad (\text{XIV})$$

$$[\text{C}_2\text{H}_5] \approx \left[\frac{k_{4b}}{k_{4a}k_{4d}} \right]^{1/2} \frac{R_f(\text{C}_4\text{H}_{10})^{1/2}}{[\text{C}_2\text{H}_6]^{1/2}} \quad (\text{XV})$$

If the expression for ethyl radical concentration is applied to eqn. (XIII) one obtains:

$$\frac{R_f(\text{CH}_4)}{R_f(\text{H}_2)R_f(\text{C}_4\text{H}_{10})^{1/2}} = \frac{2k_7}{k_3} \left[\frac{k_{4b}}{k_{4a}k_{4d}} \right]^{1/2} \frac{1}{[\text{C}_2\text{H}_6]^{3/2}} \quad (\text{XVI})$$

The linearity of the plot of $R_f(\text{CH}_4)/R_f(\text{H}_2)R_f(\text{C}_4\text{H}_{10})^{1/2}$ vs. $1/[\text{C}_2\text{H}_6]^{3/2}$

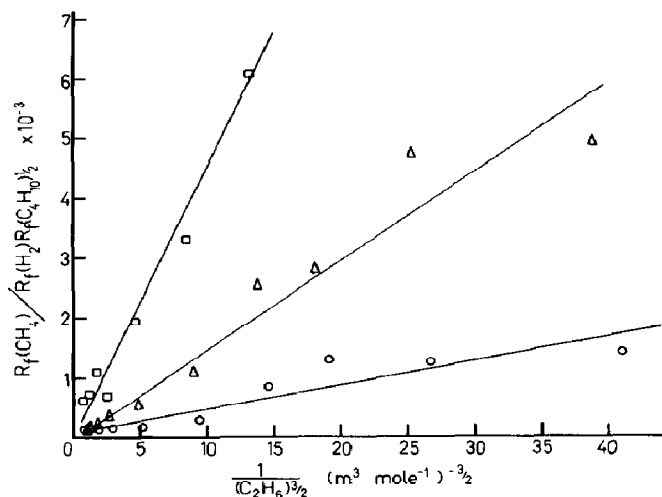


Fig. 4. $R_f[\text{CH}_4]/R_f[\text{H}_2] \cdot R_f[\text{C}_4\text{H}_{10}]^{1/2}$ vs. $1/[\text{C}_2\text{H}_6]^{3/2}$. \square , 533 K; \triangle , 553 K; \circ , 573 K.

shown in Fig. 4 appears to confirm mechanisms (7) and (8) for the formation of methane.

If one compares the results obtained in this study with the work of Steacie and Potvin [8], it is evident that hydrogen is the principal product in each case and that methane can be shown to arise from secondary processes. However, propane is found as a principal product in their work whereas it is absent here. It is our contention that propane production occurs in secondary processes and would not be observable at the low percentage decompositions studied in this work. Their low ethylene concentrations might be explained in the same manner since ethylene has a quenching cross-section several orders of magnitude larger than ethane and would tend to be consumed at longer reaction times. In comparing these results to those of Loucks and Laidler [15] on the high temperature mercury photosensitized decomposition of ethane, one observes that hydrogen is again the principal product. They can account for the ethylene/butane ratio by including decomposition of the ethyl radical as well as disproportionation and recombination of the radicals. Thus they find no evidence for pressure dependent butane formation. In addition they found no methane production which seems to indicate that this secondary process is not occurring in the mercury photosensitization case.

One way to confirm the pressure dependent rate of formation of butane would be to carry out these same experiments in the presence of added inert gas. However, the results might not be easily interpreted since increased inert gas would act to reduce the ethylene formation from the decomposition reaction.

All three sets of experiments confirm the low reactivity of the alkanes in photosensitized reactions. A quenching cross-section cannot be determined from these experiments since in all probability a number of excited states of Cd are present.

Acknowledgements

The authors gratefully acknowledge the financial support of the National Research Council of Canada and the University Council for Research, St. Francis Xavier University.

References

- 1 H. S. Taylor and D. G. Hill, *Z. Phys. Chem.*, B2 (1929) 499; *J. Am. Chem. Soc.*, 51 (1929) 2922.
- 2 E. W. R. Steacie and N. W. F. Phillips, *J. Chem. Phys.*, 6 (1938) 179.
- 3 E. W. R. Steacie and N. W. F. Phillips, *Can. J. Res.*, B16 (1938) 303.
- 4 E. W. R. Steacie, W. A. Alexander and N. W. F. Phillips, *Can. J. Res.*, B16 (1938) 314.
- 5 E. W. R. Steacie and R. L. Cunningham, *J. Chem. Phys.*, 8 (1940) 800.
- 6 B. deB. Darwent and E. W. R. Steacie, *J. Chem. Phys.*, 16 (1948) 381.
- 7 S. Bywater and E. W. R. Steacie, *J. Chem. Phys.*, 19 (1951) 326.
- 8 E. W. R. Steacie and R. Potvin, *J. Chem. Phys.*, 7 (1939) 782.
- 9 E. W. R. Steacie and D. J. LeRoy, *J. Chem. Phys.*, 11 (1943) 164; 12 (1944) 34.
- 10 B. E. Knox and H. B. Palmer, *Chem. Rev.*, 61 (1961) 247.
- 11 P. Young, G. Greig and O. P. Strausz, *J. Am. Chem. Soc.*, 92 (1970) 413.
- 12 B. C. Roqutte and J. H. Futrell, *J. Chem. Phys.*, 37 (1962) 378.
- 13 B. S. Rabinovitch and D. W. Setser, *Adv. Photochem.*, 3 (1964) 1.
- 14 S. Bywater and E. W. R. Steacie, *J. Chem. Phys.*, 19 (1951) 326.
- 15 L. F. Loucks and K. J. Laidler, *Can. J. Chem.*, 45 (1967) 2795.
- 16 A. Shepp and K. O. Kutsche, *J. Chem. Phys.*, 26 (1957) 1020.
- 17 J. P. Cunningham and H. S. Taylor, *J. Chem. Phys.*, 6 (1938) 359.
- 18 A. F. Trotman-Dickinson and E. W. R. Steacie, *J. Chem. Phys.*, 19 (1951) 329.