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Free Radicals in Pyrolysis of Propionaldehyde[1,2]

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Study of pyrolysis of propionaldehyde by mercury-mirror technique in the range 850–950° indicates production of a mixture of free methyl and ethyl radicals with the latter predominating. Increase of the ratio CH_3/C_2H_5 with increase of temperature cannot be explained on the basis of competing primary processes but is attributed instead to secondary reactions involving ethyl radical, notably a reaction with free hydrogen atom. Detection of ethyl radical despite its apparent thermal instability is attributed to its important role as chain propagator in this pyrolysis.

In a study of the photolysis of propionaldehyde, Garrison and Burton[3] showed the ethyl radical to be the only alkyl free radical present in measurable amount. This result was explained on the basis of localized electronic excitation at the carbonyl group followed by an internal conversion involving excitation of an adjacent bond in decided preference to a more remote bond. In pyrolysis no such special localization of energy is to be expected. In view of the estimated activation energies of the possible competing processes

E_a,[4] kcal. mole^{-1}

$$CH_3CH_2CHO \longrightarrow CH_3 + CH_2CHO \qquad 78 \qquad (1)$$

$$CH_3CH_2CHO \longrightarrow CH_3CH_2 + CHO \qquad 82 \qquad (2)$$

it was of interest to determine whether a statistical distribution of thermal energy would result in a mixture of alkyl free radicals.

Following Garrison and Burton a mercury-mirror technique[5] was employed in this work.

Experimental

Eastman Kodak Co., white label, propionaldehyde was fractionated under nitrogen in a 50-theoretical-plate column. A constant boiling middle third was retained; $n^{20}D$ 1.3630, (lit.) 1.36356.

Eimer and Amend C.P. mercuric bromide was purified by crystallization from a hot saturated alcoholic solution. After drying, the mercuric bromide was kept at 100° for several hours under vacuum.

This fractionated propionaldehyde was placed over Drierite and hydroquinone. Distillation into a storage vessel in the high-vacuum system was from the temperature of a chlorobenzene mush (−45°). Prior to each pyrolysis, the propionaldehyde was degassed by repeated cycles of freezing, pumping, and melting.

Well-established high-vacuum techniques were employed throughout this investigation. The vacuum system used was capable of maintaining a vacuum of lower than 10^{-6} mm. The apparatus used for identification of free radicals by combination with mercury is essentially as described by Rice and Rice.[4] Temperature of the furnace was maintained constant within a two-degree range by use of a Brown electric pyrometer control. Flow pressure of the propionaldehyde through the furnace was measured by means of a Dubrovin gage attached upstream from the furnace. No greased joints were present in the flow system between the mercury mirror apparatus and the cold trap for retention of products of pyrolysis. A resistance heater was placed around that portion of the mercury-mirror apparatus that held the mercury reservoir; a temperature of about 200° was maintained roughly constant by means of a variac.

The dialkyl mercury resulting from reaction of free radicals with mercury was converted to alkyl mercuric bromide by the method developed by Rice and Rodowskas.[6] This method involves reaction of the dialkyl mercury with an alcoholic solution of mercuric bromide. The alkyl mercuric bromide was separated from excess mercuric bromide by steam distillation. Chemical analyses of the alkyl mercuric bromide samples for carbon, hydrogen and bromide were performed by Clark Microanalytical Laboratory. The H:C:Br ratios were calculated and the $(CH_3)/(C_2H_5)$ ratio was based on the carbon to bromine analysis, since these two were the more accurate.

Investigations were carried out in the temperature range 850–950°. The useful lower limit was set by the low yield of 30 mg. of alkyl mercuric bromide after pyrolysis at that temperature over a period of 24 hours. The flow pressure of propionaldehyde maintained for all pyrolyses was 0.05 mm. at the gage.

Results

All samples of alkyl mercuric bromide obtained in this investigation had a C:Br ratio corresponding to a mixture of methyl and ethyl mercuric bromides. Table I gives some typical analyses and Table II gives the temperature dependence of the $(CH_3)/(C_2H_5)$ ratio in the mixture of compounds. If we assume that no free radicals can pass the mirror, the $(CH_3)/(C_2H_5)$ ratio is the ratio of partial pressures of methyl and of ethyl radicals in its neighborhood. Table II shows the ethyl radical to predominate in the temperature range of 850–950° with the $(CH_3)/(C_2H_5)$ ratio increasing with increasing temperature.

TABLE I

ANALYSES OF ALKYL MERCURIC BROMIDE SAMPLES

Sample	Temp., °C.	Analyses, % H	C	Br	Ratio H	C	Br
5	950	1.25	5.56	27.76	0.225	1	4.99
8	900	1.50	6.46	27.18	.232	1	4.21
9	850	1.65	7.23	26.55	.228	1	3.67
C_2H_5HgBr (theor.)		1.61	7.76	25.8	.281	1	3.32
CH_3HgBr (theor.)		1.02	4.06	27.1	.255	1	6.67

TABLE II

TEMPERATURE DEPENDENCE OF $(CH_3)/(C_2H_5)$ RATIO

Temperature, °C.	C_2H_5, %	$(CH_3)/(C_2H_5)$
850	91	0.10
900	76	.32
950	56	.80

Discussion

Winkler, Fletcher and Hinshelwood[7] investigated the pyrolysis of propionaldehyde at 549° as a function of pressure. They report the principal products to consist of methane, ethane, ethylene,

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[2] This paper is an abstract from a thesis submitted by Thomas J. Sworski to the Department of Chemistry of the University of Notre Dame in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] W. M. Garrison and M. Burton, *J. Chem. Phys.*, **10**, 730 (1942).

[4] F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The John Hopkins Press, Baltimore, Md., 1935.

[5] F. O. Rice, W. R. Johnston and B. L. Evering, THIS JOURNAL, **54**, 3529 (1932).

[6] F. O. Rice and E. L. Rodowskas, THIS JOURNAL, **57**, 350 (1935).

[7] C. A. Winkler, C. J. M. Fletcher and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A146**, 345 (1934).

hydrogen and carbon monoxide and indicate that the formation of hydrogen and ethylene takes place by some simultaneous process.

It is not possible from the data of this investigation to make a quantitative determination of activation energies of competing primary processes. The work of Rice and co-workers[5,8] has shown the importance of secondary reactions. It is evident that in our set-up, in a flow system, some of these reactions can take place before the furnace and the mirror system in a region of both undetermined and variable temperature. Furthermore, the conditions of these experiments have not permitted determination of rate constants but only of general effect of temperature on relative amounts of free radicals produced.

The results of this investigation particularly at 900 and 950° apparently contradict the failure of Rice and Evering[8] to detect ethyl radicals in pyrolysis of propane and butane. From the latter work it may be concluded that ethyl radicals are practically entirely decomposed in the temperature range 900–1100°. Another explanation that must be considered for the latter work is that because of the chain involved the ethyl radicals are present in a negligible concentration when compared to the concentration of methyl radicals. Such a situation can be expected from a scheme for the thermal decomposition of propane in which methyl radical is the chain propagating radical. Significant steps of such a chain are

$$CH_3CH_2CH_3 \longrightarrow CH_3CH_2 + CH_3 \qquad (3)$$

$$R + CH_3CH_2CH_3 \longrightarrow RH + CH_3CH_2CH_2 \qquad (4)$$

$$CH_3CH_2CH_2 \longrightarrow CH_2{=}CH_2 + CH_3 \qquad (5)$$

An apparent chain length of 10.1 has been reported[9] for 550° and a pressure of 23 mm.

We must conclude, however, that in thermal decomposition of butane, where both methyl and ethyl radicals are chain propagators, appreciable decomposition of ethyl radicals takes place most probably by the method suggested by Rice.[10]

$$CH_3CH_2 \longrightarrow CH_2{=}CH_2 + H \qquad (6)$$

If a free radical mechanism existed wherein the ethyl radical was the predominant chain propagator, then the mercury mirror technique should be able to detect it. It is the indication of this experimental study that pyrolysis of propionaldehyde follows such a free radical mechanism. The results of this investigation are consistent with what we know about the mechanism of the decomposition of propionaldehyde.

If the Rice and Rice[4] estimates of the energies of activation of the primary processes (1) and (2) are in correct relation, we might expect a preponderance of methyl radicals to result from the primary processes, and a temperature dependence of the $(CH_3)/(C_2H_5)$ ratio opposite to what we have observed. Independently of the relationship of bond strengths, the preponderance of ethyl radicals observed can be satisfactorily explained on the basis of the chain mechanism

E_a, kcal. mole^{-1}

$$R + CH_3CH_2CHO \longrightarrow RH + CH_3CH_2CO \quad 6.5^{11} \qquad (7)$$

$$CH_3CH_2CO \longrightarrow CH_3CH_2 + CO \quad 17^{12} \qquad (8)$$

It is this chain mechanism which provides sufficient free ethyl radical concentration for detection by the mercury mirror technique.

The temperature dependence of the $(CH_3$ (C_2H_5) ratio is in agreement with the known thermal instability of the ethyl radical. If we assume reaction (6) to be operative, it offers no solution in itself since the H atom produced may, by acting as chain propagator, yield another ethyl radical by reactions (7) and (8). Another decomposition mechanism may be in operation

E_a, kcal. mole^{-1}

$$R + CH_3CH_2CHO \longrightarrow RH + CH_2CH_2CHO \quad 6.5 \qquad (9)$$

$$CH_2CH_2CHO \longrightarrow CH_2{=}CH_2 + CHO \quad 26^{4} \qquad (10)$$

$$CHO \longrightarrow H + CO \qquad (11)$$

The activation energy of reaction (9) is estimated from a comparison with (7). The estimated activation energies for reactions (9) and (10) are higher than the corresponding values for reactions (7) and (8). The effect of temperature increase may then make this decomposition path correspondingly more important and result in a smaller observed ethyl radical percentage with increased temperature.

Another reaction which may be important in the high temperature disappearance of the ethyl radical is

$$H + C_2H_5 \longrightarrow 2CH_3 \qquad (12)$$

The significance of this reaction was pointed out on theoretical grounds by Gorin, Kauzman, Walter and Eyring.[13] Reaction (6) plus reaction (12) would also explain the observed temperature dependence. Paneth and Loleit,[14] for the thermal decomposition of tetraethyl lead, report appreciable decomposition of ethyl radicals at about 600° and complete decomposition of ethyl radicals at 900° with formation of methyl radicals. This observation is in agreement with reactions (6) and (12). A chain including reaction (6) and the sequence of reactions (9) and (10) yielding (in part *via* reaction (11)) H atoms necessary for reaction (12) is consonant with the products of decomposition.

Conclusion

The relative activation energies of the primary processes cannot be determined in this study due to the importance of secondary reactions. Detection of free ethyl radical is made possible by a chain mechanism wherein the ethyl radical is the predominant chain propagator. The temperature dependence of the $(CH_3)/(C_2H_5)$ ratio cannot be quantitatively explained on the basis of the limited available data but it is qualitatively consistent both with a scheme involving reaction between H and C_2H_5 and with experimental observations of Paneth and Loleit on the thermal instability of ethyl radical.

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