Pyrolysis of Acetaldehyde Azine in the Presence of Propene

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The pyrolysis of acetaldehyde azine in the presence of propene has been studied in the temperature range 268—352 °C. The major hydrocarbon products are of composition C_5H_{10} and pathways for their production involving ethylidene are discussed.

THE reactions of photolytically produced ethylidene have been studied by a number of workers using diazoethane,[1-3] methylketen,[4,5] and 3-methyldiazirine [6] as sources. The reaction products are varied and though it is generally observed that both *cis*- and *trans*-but-2-ene are formed it is apparent that the behaviour of ethylidene is dependent upon the precursor and the wavelength employed and, in contrast to methylene, there is little evidence of insertion and addition reactions. We have shown [7] that ethylidene is produced in the pyrolysis of acetaldehyde azine and that there is evidence from product formation to imply that a reaction (or reactions) with propene was taking place. It therefore appeared appropriate to study the pyrolysis of acetaldehyde azine in the presence of added propene in order to obtain more evidence for these reactions.

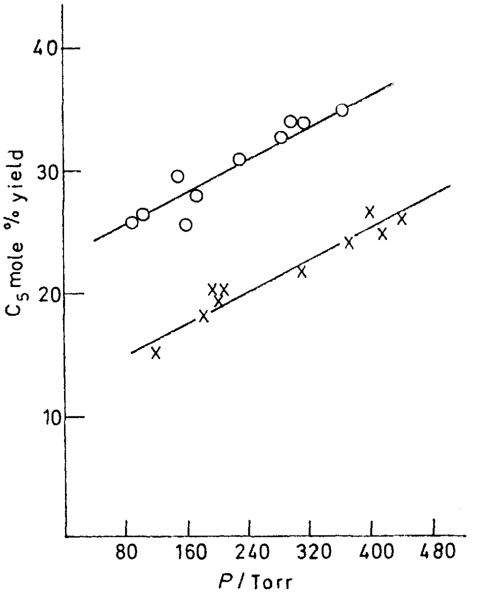

FIGURE 1 Variation of mole percentage yield C_5 hydrocarbons: all CH products with pressure: ○, 300 °C; ×, 345 °C

EXPERIMENTAL

Apparatus and Procedure.—The static apparatus employed was the same as that previously described.[7] Mixtures of acetaldehyde azine and propene of known composition were prepared in a mixing bulb and the compositions of the mixtures were regularly checked by g.l.c. This also served to confirm the absence of any reaction in the mixing bulb. Other operating procedures were as previously described. Ratios of acetaldehyde azine to added gas varied from 1 : 1 to 1 : 11 and total pressures from 20 to 450 Torr. The pyrolysis temperature varied between 268 and 352 °C. All analyses were carried out by g.l.c. and compounds were identified by comparison with samples of pure hydrocarbons. All these were obtained commercially with the exception of *cis*- and *trans*-1,2-dimethylcyclopropane which were kindly provided by Professor H. M. Frey.

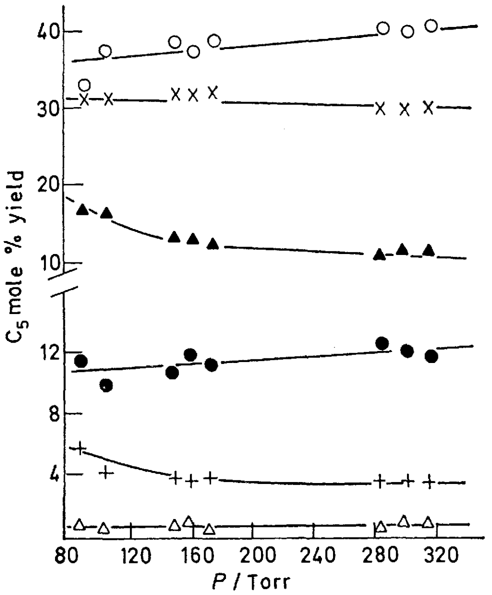

FIGURE 2 Pressure dependence of C_5 products at 300 °C. Propene : azine = 11 : 1. ○, Pent-2-ene + n-pentane; ×, 2-methylbut-1-ene; ▲, pent-1-ene; ●, 2-methylbut-2-ene; +, isopentane; △, 3-methylbut-1-ene

RESULTS

Product Distribution compared with the Absence of Propene.—Nitrogen, hydrogen cyanide, and methyl cyanide were produced, although the yield of methyl cyanide was

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[1] R. K. Brinton and D. H. Volman, *J. Chem. Phys.*, 1951, **19**, 1394.

[2] H. M. Frey, *Chem. and Ind.*, 1962, 218; *J. Chem. Soc.*, 1962, 2293.

[3] C. L. Kibby and G. B. Kistiakowsky, *J. Phys. Chem.*, 1966, **70**, 126.

[4] D. P. Chong and G. B. Kistiakowsky, *J. Phys. Chem.*, 1964, **68**, 1793.

[5] G. B. Kistiakowsky and B. H. Mahan, *J. Amer. Chem. Soc.*, 1957, **79**, 2412.

[6] H. M. Frey and I. D. R. Stevens, *J. Chem. Soc.*, 1965, 1700.

[7] B. G. Gowenlock, R. M. Haynes, and C. A. F. Johnson, *J. Chem. Soc.* (*B*), 1971, 1098.

reduced. Almost all the hydrocarbons that were formed in the pyrolysis of the azine alone were still formed, although at changed relative yields. Isobutane was greatly reduced and was of only minor importance whereas n-butane and the butenes were increased. Buta-1,3-diene and acetylene were absent. The relative yields of the C_4 hydrocarbons remained fairly constant over large changes in experimental conditions. The C_5H_{10} hydrocarbons were greatly increased and small almost trace quantities of some higher hydrocarbons were formed and identified (4-methylpent-1-ene, hexa-1,5-diene, hex-1-ene, 3-methylpentane, 2-methylpentane and, probably, 4-methylhex-1-ene). Increase in total pressure of the system caused a decrease in the yield of C_2 hydrocarbons and isobutane, while the C_5 hydrocarbons were increased. An increase in temperature at constant pressure led to an increase in ethane and ethylene and a decrease in the pentenes, although the effect was less marked for pent-1-ene. An increase in the ratio of propene to acetaldehyde azine at the same total pressure led to an increase in C_2 hydrocarbons and in the pentenes, while isobutane, but-2-ene, and isopentane were decreased.

Of the C_6 hydrocarbons, 4-methylpent-1-ene was favoured to a small extent by decrease in pressure and increase in temperature; hexa-1,5-diene showed only a 20% variation under all conditions, whereas hex-1-ene was increased at the higher pressures and the lower temperatures the overall variations being by a factor of *ca.* 600%.

At 285 °C, the C_5 hydrocarbons accounted for almost 40% of the total hydrocarbons formed and this represents the most important variation from the pyrolysis of the azine without additive. The major details of C_5 hydrocarbon production are illustrated in Figures 1—4.

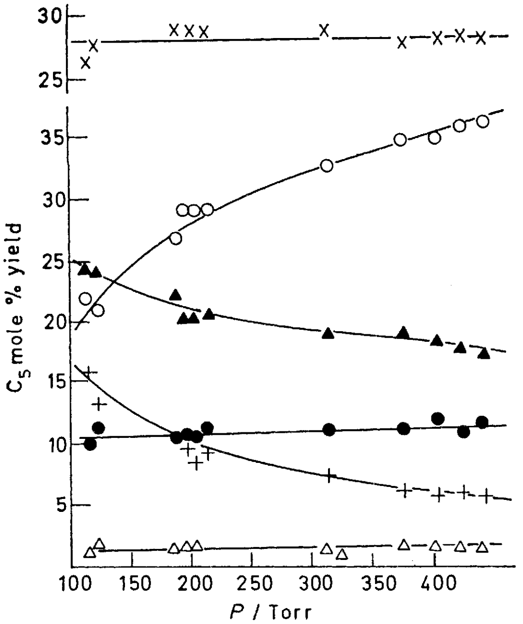


FIGURE 3 Pressure dependence of C_5 products at 345 °C. Propene : azine = 11 : 1. ○, Pent-2-ene + n-pentane; ×, 2-methylbut-1-ene; ▲, pent-1-ene; ●, 2-methylbut-2-ene; +, isopentane; △, 3-methylbut-1-ene

DISCUSSION

We focus attention on the C_5 hydrocarbon products because their probable origin lies in an overall reaction of type (A), there being far more C_5H_{10} produced than C_5H_{12}. Such a suggestion implies some insertion or

$$CH_3CH\!: + C_3H_6 \longrightarrow C_5H_{10} \qquad (A)$$

addition reaction of ethylidene with the propene and indicates that disproportionation of C_5H_{11} radicals cannot be a major pathway. Previous studies[1,6] with photolytically produced ethylidene show that when the carbene is highly vibrationally excited[6] no reaction occurs with propene and that in other cases the isomerisation to ethylene and decomposition to acetylene and hydrogen predominate over reaction with propene or the initial substrate. Production of pentenes in these systems is a minor reaction[2,4] the product being primarily *cis*- and *trans*-1,2-dimethylcyclopropane. It should be noted, however, that the literature provides very little evidence for the reactions of thermally equilibrated ethylidene produced from pyrolysis. It is also apparent that ethylidene is much less reactive in addition, abstraction, and insertion than is methylene and that reactivity towards alkenes diminishes from ethylene to propene to but-2-ene.

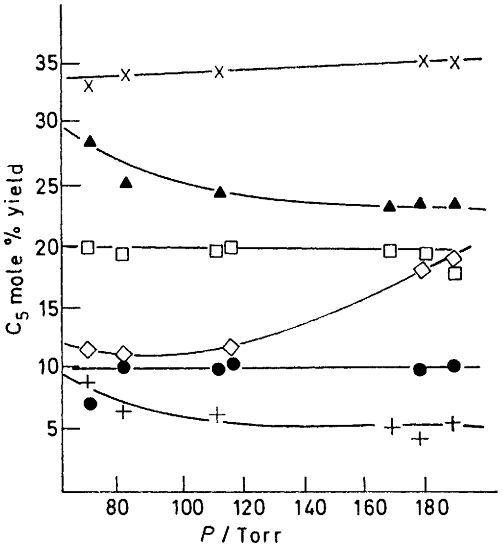
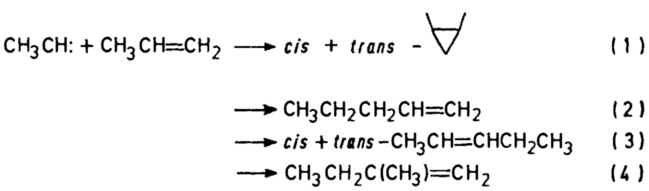


FIGURE 4 Pressure dependence of C_5 products at 300 °C. Propene : azine = 6.3 : 1. ×, 2-methylbut-1-ene; ▲, pent-1-ene (values plotted are 10% high); □, pent-2-ene; ◇, n-pentane; ●, 2-methylbut-2-ene; +, isopentane

Propene is not decomposed under our reaction conditions and thus we consider that the main function of propene is to scavenge radicals and carbenes produced in the thermal decomposition of acetaldehyde azine. A reaction scheme expansion of (A) is (1)—(4) corresponding to addition across the C=C double bond, insertion into



$$CH_3CH\!: + CH_3CH{=}CH_2 \longrightarrow \textit{cis} + \textit{trans}\text{ -} \qquad (1)$$

$$\longrightarrow CH_3CH_2CH_2CH{=}CH_2 \qquad (2)$$

$$\longrightarrow \textit{cis} + \textit{trans}\text{-}CH_3CH{=}CHCH_2CH_3 \qquad (3)$$

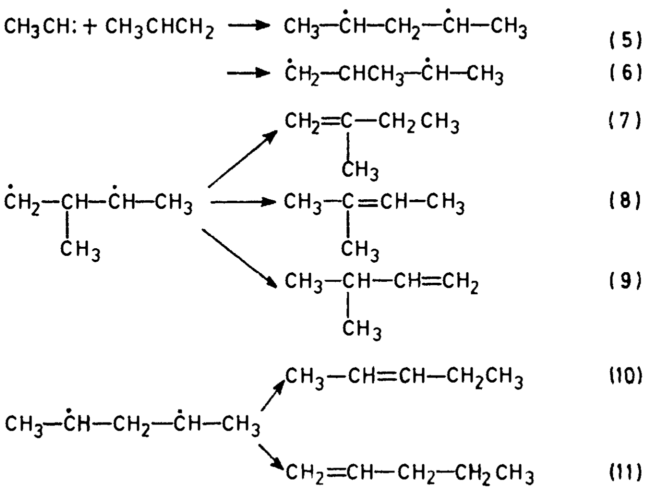
$$\longrightarrow CH_3CH_2C(CH_3){=}CH_2 \qquad (4)$$

the methyl group C–H, insertion into terminal sp^2 C–H, and insertion into central sp^2 C–H. If the insertion reactions (2)—(4) are statistical then the product ratios would be 3 : 2 : 1 in contrast to our high pressure limiting values of 0.6 : 1.32 : 1 (345 °C) and 0.4 : 1.4 : 1 (300 °C). These values may be compared with the analogous reactions of methylene where gas-phase insertions are much nearer to the statistical values than ours. It appears also that the rate of attack on the primary sp^3 C–H bond (2) relative to attack on the sp^2 C–H (4) is temperature dependent, the appropriate values being $E_2 - E_4 = 29 \pm$ kJ mol^{-1} and $\log A_2/A_4 = 2 \pm 0.3$.

Compared with the methylene–but-2-ene system,[8] the yield of 1,2-dimethylcyclopropanes is very low and it is difficult to ascribe this to the isomerisation of the cyclopropanes to pentenes due to excess energy because in the methylene–but-2-ene system the cyclopropanes : total C_5H_{10} ratio falls rapidly from *ca.* 0.5 on lowering the total pressure from 200 to below 50 Torr due to isomerisation reactions, whereas in our studies this ratio is much lower at *ca.* 0.03 and is virtually unaffected by pressure changes. The temperature of the reaction vessel is too low for thermal isomerisation of the substituted cyclopropanes to occur.

The production of 3-methylbut-1-ene and 2-methylbut-2-ene requires comment because neither is the product of a simple insertion or addition step such as (1)—(4). If, we assume, however, that the ethylidene is in the triplet state and that it adds to propene to give biradicals [reactions (5) and (6)] then the products can be rationalised in terms of isomerisations of the biradicals produced. Thus isomerisations of the biradical produced in (6) yield three products [reactions (7)—(9)], including 3-methylbut-1-ene (9) arising from a 1,4-hydrogen shift and 2-methylbut-2-ene (8) arising from one of the two possible 1,2-hydrogen shifts. The small quantities of 3-methylbut-1-ene suggest that the 1,4-shift is less likely and the ratio 2-methylbut-1-ene : 2-methylbut-2-ene of 2.5—3 suggests that the hydrogen migration is not completely random. Isomerisations of the biradical produced in (5) by the 1,2- and 1,4-hydrogen shifts (10) and (11) yield *cis*- and *trans*-pent-2-ene and pent-1-ene. It is necessary to point out that at 327 °C the *trans* : *cis* ratio is always greater than 2 with the value being 2.5 at higher values of the propene : acetaldazine ratio, these values being higher than the equilibrium ratio of 1.66.

The formation of 1,2-dimethylcyclopropanes can also be rationalised from ring closure of the biradical intermediates produced in (5) and (6). Although there is some scatter in the analytical results due to errors in the measurement of the small peak areas, the ratio *cis*- : *trans*-1,2-dimethylcyclopropane falls within the range 0.65—1.26 (*cf.* 1.4 and an equilibrium ratio of 0.34—0.38 [2]) and may suggest random ring closure.



It is suggested that the thermal decomposition of acetaldazine produces triplet ethylidene in contrast to the photolytic systems,[1-6] where singlet ethylidene is formed. Menendez and Figuera [9] have also suggested that the two electronic states could present completely different reactivity. It would be helpful to carry out direct studies of the thermal decompositions of diazoethane and 3-methyldiazirine in the presence of added alkanes to provide further confirmation of our suggestion.

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[8] H. M. Frey, *Proc. Roy. Soc.*, 1959, **A250**, 409; 1959, **A251**, 575.

[9] V. Menendez and J. M. Figuera, *Chem. Phys. Letters*, 1973, **18**, 426.