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Dissociation of 3-Methylpenta-1,4-diene and the Resonance Energy of the Pentadienyl Radical

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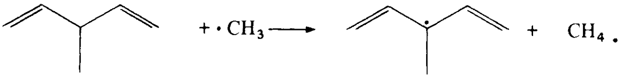
From measurements of the initial rate of formation of methane in the pyrolysis of 3-methylpenta-1,4-diene at temperatures over the range 653-716 K and pressures between 15 and 200 Torr,* methane has been shown to be formed by an homogeneous, first-order process. Examination of the other products of pyrolysis shows the most reasonable mode of formation of primary methane to be

followed by



(ii)

The rate expression for reaction (i) is

$$\log (k_i/\mathrm{s}^{-1}) = (15.36 \pm 0.1) - (65040 \pm 300)/\theta$$

where $\theta = 2.303\,RT/\mathrm{cal\,mol}^{-1}$ (1 cal = 4.18 J) and this leads to $D[\mathrm{H—CH(C_2H_3)_2}] = 76.4\ \mathrm{kcal\,mol}^{-1}$, which by comparison with the value of 95.0 for the secondary C—H bond dissociation energy in alkanes leads to a figure of 18.6 ± 1.5 kcal mol^{-1} for the resonance stabilisation energy of the pentadienyl radical.

In an earlier investigation[1] to determine the resonance stabilisation energy of the pentadienyl radical, the rate of dissociation of hexa-1,3-diene into a methyl radical and a pentadienyl radical was estimated from the rate of formation of the primary product, methane. It was assumed that methyl radicals formed in the initial step reacted at comparable rates with the parent molecule, either by addition to form a resonance stabilised adduct radical or by hydrogen abstraction to form methane and a second resonance stabilised radical. Since these *ad hoc* assumptions detract from the reliability of the estimated resonance energy, it was decided to determine this quantity by a method which did not necessitate these assumptions. 3-methylpenta-1,4-diene must also dissociate on pyrolysis by cleavage of the weakest C—C bond in the molecule to form a methyl radical and the resonance stabilised pentadienyl radical. With this compound, subsequent addition of methyl radicals leads to the formation not of resonance stabilised radicals, but of radicals which may reasonably be expected to redissociate mainly to methyl and either the parent diene or its isomer. Measurement of the methane formed in the pyrolysis of 3-methylpenta-1,4-diene has yielded a less ambiguous value for the resonance stabilisation energy of the pentadienyl radical which is in good agreement with that obtained from the study of the dissociation of hexa-1,3-diene.

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* 1 Torr = (101 325/760) Pa.

EXPERIMENTAL

MATERIALS

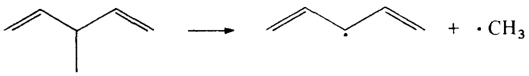
3-methylpenta-1,4-diene (Wiley Organics, > 99% purity), after thorough outgassing and prolonged pumping at −98 °C gave only a single peak when analysed by gas chromatography using a squalane SCOT column (30.5 m).

APPARATUS AND PROCEDURE

This was essentially the same as that described previously.[1] The methane and propene present in the products which were volatile at −126 °C were estimated by gas chromatography using a silica gel column (1 m) at 50 °C. Qualitative and quantitative analyses of products which were liquid at room temperature were performed using a squalane SCOT column (30.5 m) at 30 °C.

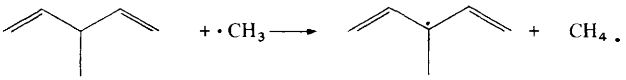
RESULTS AND DISCUSSION

Any primary methane formed in the pyrolysis of 3-methylpenta-1,4-diene may reasonably be expected to result from the reactions



(i)

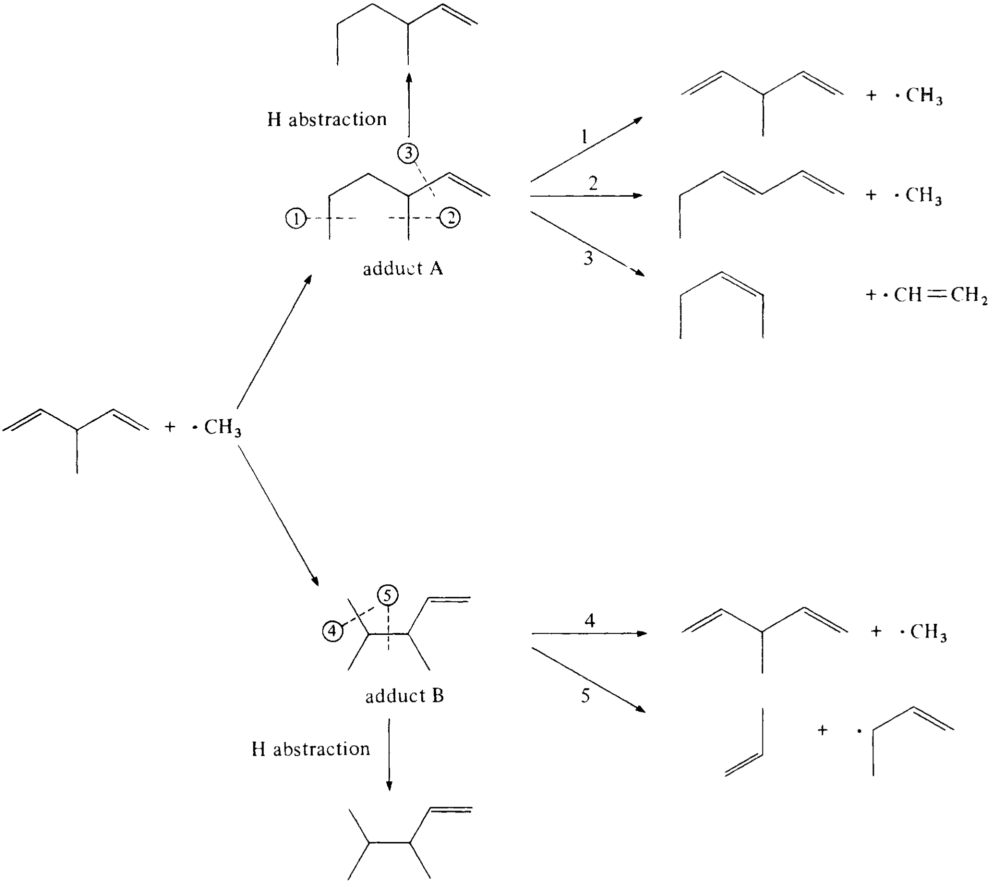
and



(ii)

Reaction (i) involves the rupture of the weakest bond in the molecule and, provided all the methyl radicals formed in this reaction participate subsequently in reaction (ii), the rate of formation of methane may be taken as corresponding to the rate of the dissociation reaction. A complication is that in addition to abstracting hydrogen from the parent molecule, methyl radicals can add to it, and if the adduct is comparatively stable, as would certainly be the case if it were a resonance stabilised adduct, the rate of formation of methane will be some fraction of the rate of the initial dissociation step. In a number of earlier investigations[1-5] this fraction was assumed to be one-half and to be independent of temperature. More recent calculations[6] have shown the assumption to be unreasonable for but-1-ene where, over the temperature and pressure range studied, the rate of the reverse of the addition reaction will greatly exceed that of hydrogen abstraction by the adduct radical. This has recently been confirmed experimentally by measuring yields of methane and n-pentane from pyrolysis of but-1-ene under experimental conditions similar to those employed previously. In all cases the pentane yields were found to be no more than 2-4% of the methane formed, so that methyl addition to but-1-ene must lead to negligible loss of methane. Consequently the reported *A* factor for the dissociation of but-1-ene will be too large by 0.3 logarithmic units, although the activation energy and hence also the resonance energy are unchanged.

In the case of 3-methylpenta-1,4-diene two different adducts (A and B) may be obtained from addition of methyl radicals to the parent molecule, and their various possible subsequent reactions are as follows:



Of the two possible modes of addition, that leading to the formation of the adduct A by addition to a terminal =CH$_2$ group would be expected to be the more likely.[7] The absence of both 3-methylhex-1-ene and 3,4-dimethylpent-1-ene from among the products of pyrolysis at 705 K of 50 Torr samples of 3-methylpenta-1,4-diene for reaction times up to $[CH_4] = 0.5\% \ [C_6H_{10}]_0$ clearly indicates that under these conditions hydrogen abstraction by the adduct can be disregarded. Of the adduct decomposition reactions, only reaction (3) for adduct A and reaction (5) for adduct B do not regenerate methyl radicals. Reaction (3) would appear unlikely on thermochemical grounds, being the most endothermic of all five processes, and indeed only trace amounts of pent-2-ene were found among the products of pyrolysis obtained as described above. Consequently loss of methyl radicals through addition followed by reaction (3) must be negligible. Reaction (5) of adduct B also leads to loss of methyl radicals, and both propene and but-1-ene are fairly important products, being formed in roughly equal amounts. At 705 K a value of 3.7 was found for the ratio $R(CH_4)/R(C_3H_6)$ and a very similar value of 3.4 was found for this ratio at 653 K. Thus even in the unlikely event that the observed propene results only from reaction (5), the error introduced by taking $R(CH_4)$ as being equal to that of the dissociation of 3-methylpenta-1,4-diene will be negligible. Note that on thermochemical grounds the formation of adduct A and its subsequent dissociation by reaction (2) would appear to be the most likely of the processes shown. Consistent with this is the observation that hexa-1,3-diene is formed in amounts comparable to the yields of methane.

The products of pyrolysis of 3-methylpenta-1,4-diene at 705 K were found to include at least six other isomers of the reactant. Although a detailed examination of these isomers was considered unnecessary, it was noted that for short reaction times their total yield was roughly an order of magnitude greater than that of the methane formed. Other low-molecular-weight products formed included penta-1,3-diene in amounts similar to those of the methane formed, and also smaller and roughly equal amounts of ethene and buta-1,3-diene. The former must result from hydrogen abstraction by the pentadienyl radical formed in reaction (i), whilst the two latter compounds may conceivably arise from a four-centre elimination reaction. Small amounts of the saturated products ethane and propane were also observed, but the variation with time of the yields of these products indicated that they were essentially of a secondary character.

TABLE 1.—INITIAL RATES OF FORMATION OF METHANE AND RATE CONSTANTS FOR THE DISSOCIATION OF 3-METHYLPENTA-1,4-DIENE

T/K	$(\mathrm{d}[CH_4]/\mathrm{d}t)_0/10^{-6}$ Torr s^{-1}	$[C_6H_{10}]_0$/Torr	$k_i/10^{-6}$ s^{-1}
653	18.13	50.7	0.358
664	46.24	51.3	0.902
675	102.3	48.8	2.10
684[a]	208.3	50.2	4.15
684.5	209.1	49.8	4.20
694.5	397.9	49.5	8.03
705	802.2	50.7	15.8
715.5	—	—	31.2[b]

[a] Data from experiment using the packed reaction vessel. [b] From least-squares estimate of intercept of plot of log $(\mathrm{d}[CH_4]/\mathrm{d}t)_0$ against log p_0.

A series of runs was performed at 716 K for a range of initial pressure of 3-methylpenta-1,4-diene between 15 and 200 Torr. A double logarithmic plot of initial rate of methane formation (determined as already described[1]) against pressure of reactant gave a straight line of slope 0.99 ± 0.02, indicating a first-order process for methane formation under the experimental conditions. Runs were subsequently performed at seven temperatures over the range 653-716 K, at each temperature a fixed pressure (50 Torr) of 3-methylpenta-1,4-diene being pyrolysed for various times and the products analysed for methane. Reaction times were kept short so that the percentage conversion of 3-methylpenta-1,4-diene to methane was never more than 0.5% and any secondary methane formation was thus kept to a minimum. At all temperatures, methane against time graphs showed that the rate of methane formation fell with time. The results of the experiments are given in table 1. Experiments performed under similar conditions using packed and unpacked reaction vessels yielded similar rates of formation of methane despite a sevenfold change in S/V, so that methane formation in this system is entirely homogeneous.

An Arrhenius plot of the data given in table 1 yielded the rate expression

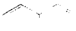
$$\log(k_i/\mathrm{s}^{-1}) = 15.36 \pm 0.1 - (65040 \pm 330)/\theta$$

where $\theta = 2.303\ \boldsymbol{R}T$/cal mol^{-1} and the quoted error limits correspond to the standard deviation.

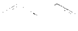
From the experimental activation energy and taking the activation energy for radical recombination to be zero, the enthalpy change for reaction (i) is given by $\Delta H^{\ominus}_{298} = 66.0 \pm 0.3$ kcal mol^{-1}, specific heats were calculated from group additivity data,[8] $C^{\ominus}_p$ for the group [C—(Cd)$_2$(C) (H)] being evaluated by assuming it to be given by $C^{\ominus}_p$ of {[C—(Cd)(C)$_2$(H)]+[C—(Cd)$_2$(H)$_2$]−[C—(Cd)(C)(H)$_2$]}. Hence we have

$$\Delta H^{\ominus}_{\mathrm{f}}(\mathrm{CH_3}) + \Delta H^{\ominus}_{\mathrm{f}}(\text{pentadienyl}) - \Delta H^{\ominus}_{\mathrm{f}}($$  $$) = 66.0$$

and

$$D[\mathrm{H{-}CH(C_2H_3)_2}] = 66.0 + \Delta H^{\ominus}_{\mathrm{f}}($$  $$) - \Delta H^{\ominus}_{\mathrm{f}}(\mathrm{CH_3}) + \Delta H^{\ominus}_{\mathrm{f}}(\mathrm{H}) - \Delta H^{\ominus}_{\mathrm{f}}($$  $$).$$

Taking $\Delta H^{\ominus}_{\mathrm{f}}(\mathrm{CH_3})$ and $\Delta H^{\ominus}_{\mathrm{f}}(\mathrm{H})$ as 34.8 and 52.1 kcal mol^{-1}, respectively,

$$D[\mathrm{H{-}CH(C_2H_3)_2}] = 83.3 + \Delta H^{\ominus}_{\mathrm{f}}($$  $$) - \Delta H^{\ominus}_{\mathrm{f}}($$  $$).$$

The bond dissociation energy of interest has been formulated in this way since enthalpy data for 3-methylpenta-1,4-diene are not available, neither is there a group additivity value for $\Delta H^{\ominus}_{\mathrm{f}}$ of the central group in this molecule, *i.e.* [C—(Cd)$_2$(C)(H)]. The difference between the heats of formation of the two molecules of interest is given by

$$\Delta H^{\ominus}_{\mathrm{f}}[\mathrm{C{-}(C)(H)_3}] + \{\Delta H^{\ominus}_{\mathrm{f}}[\mathrm{C{-}(Cd)_2(C)(H)}] - \Delta H^{\ominus}_{\mathrm{f}}[\mathrm{C{-}(Cd)_2(H)_2}]\}$$

and the difference between the two quantities in the braces may be approximated either to the difference

$$\{\Delta H^{\ominus}_{\mathrm{f}}[\mathrm{C{-}(C)_3H}] - \Delta H^{\ominus}_{\mathrm{f}}[\mathrm{C{-}(C)_2(H)_2}]\} = 3.05\ \text{kcal mol}^{-1}$$

or

$$\{\Delta H^{\ominus}_{\mathrm{f}}[\mathrm{C{-}(Cd)(C)_2(H)}] - \Delta H^{\ominus}_{\mathrm{f}}[\mathrm{C{-}(Cd)(C)(H)_2}]\} = 3.28\ \text{kcal mol}^{-1}.$$

Taking the average of these two values (3.16 kcal mol^{-1}) leads to

$$\Delta H^{\ominus}_{\mathrm{f}}($$  $$) - \Delta H^{\ominus}_{\mathrm{f}}($$  $$) = -6.92\ \text{kcal mol}^{-1}$$

and

$$D[\mathrm{H{-}CH(C_2H_3)_2}] = 76.4\ \text{kcal mol}^{-1}.$$

{By comparison, use of Laidler parameters[9] for calculating $\Delta H^{\ominus}_{\mathrm{f}}$ values gives

$$\Delta H^{\ominus}_{\mathrm{f}}($$  $$) - \Delta H^{\ominus}_{\mathrm{f}}($$  $$) = [(\mathrm{C{-}H})_{\mathrm{t}} + 3(\mathrm{C{-}H})_{\mathrm{p}} + (\mathrm{C{-}C}) - 2(\mathrm{C{-}H})_{\mathrm{s}}]$$

$$= -6.96\ \text{kcal mol}^{-1}$$

in close agreement with the value derived from group additivity data.} By comparison with the value of 95.0 ± 1 kcal mol^{-1} for the secondary (C—H) bond dissociation energy, we arrive at a resonance stabilisation energy of 18.6 ± 1.5 kcal mol^{-1} for the pentadienyl radical. This figure is gratifyingly close to the value obtained from the pyrolysis of hexa-1,3-diene and suggests that the assumptions made in deducing this value are reasonable.

The secondary (C—H) bond dissociation energy of 76.4 kcal mol^{-1} in penta-1,4-diene leads to $\Delta H^{\ominus}_{\mathrm{f}}$(pentadienyl) = 49.7 kcal mol^{-1}. At first sight this does not compare favourably with the earlier estimate[1] of 45.9 kcal mol^{-1}. This difference must arise inevitably because of the extra 4 kcal mol^{-1} stabilisation energy of the penta-1,3-diene molecule[9] which does not arise in penta-1,4-diene. As shown above, bond dissociation energies and resonance stabilisation energies are not influenced by these molar resonance stabilisation energies being derived from differences between enthalpies of formation of two molecules where molecule resonance energies cancel out.

Using group additivity data for 3-methylpenta-1,4-diene and the pentadienyl radical, the overall entropy change for reaction (i) is given by $\Delta S^{\ominus}_{\mathrm{c}} = 26.9$ cal K^{-1} mol^{-1}

at 700 K and a standard state of 1 mol dm^{-3}, so that taking the values used previously[1] for the rates of recombination of pentadienyl radicals [log (k_r/dm^3 mol^{-1} s^{-1}) = 9.4] and of methyl radicals [log (k_r/dm^3 mol^{-1} s^{-1}) = 10.42] we have, by the geometric mean rule, log (k_{-1}/dm^3 mol^{-1} s^{-1}) = 10.2 and assuming $E_{-1} = 0$, the entropy of activation for the recombination reaction is $\Delta S_c^\ddagger = -17.5$ cal K^{-1} mol^{-1}. Thus, for the forward reaction $\Delta S_c^\ddagger = 9.4$ cal K^{-1} mol^{-1} at 700 K and hence $A = 10^{15.6}$ s^{-1}. Though slightly higher than the experimental value, the discrepancy between measured and calculated A factors corresponds to a possible error of 1.5 cal K^{-1} mol^{-1} in the overall entropy change, which under the circumstances is reasonable.

The author thanks Professor B. S. Rabinovitch for suggesting this particular investigation.

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