

INDICATIONS OF A PUZZLING MECHANISM IN THE PYROLYSIS OF
1,3-BUTADIENE

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Abstract: The pyrolysis of $[1-^{14}\text{C}]$ -1,3-butadiene gives insights into unconventional reaction steps by means of the distribution of radioactivity in the main products.

1,3-butadiene (1) is an important intermediate in the discussion of an alternative mechanism to form aromatics via (4 + 2)-cycloaddition from acyclic hydrocarbons at high temperatures^{1,2}). From the mechanistic point of view the phenomenon of aromatization in the gas phase is, however, still unsolved. Therefore some non-classic reaction pathways like hydrogen transfers³) and/or the cycloaddition of 1 with unsaturated radicals⁴) were proposed.

Although the pyrolysis of pure 1 has been studied under various reaction conditions many times before⁵⁻⁹) no details of the reaction mechanism could be deduced from these experiments. Even from studies with labelled 1,3-butadiene¹⁰⁻¹²) only little experimental evidence has been obtained on the nature of the starting step¹³), on the mechanism of methane formation^{6,9}), and on the origin of the aromatics¹⁻⁴).

In connection with studies of constructive reactions under conditions of the pyrolysis of hydrocarbons we examined, among other things, the thermal conversion of ordinary 1,3-butadiene¹⁴) and in selected runs also of $1-^{14}\text{C}$ -1,3-butadiene ($[1-^{14}\text{C}]-\underline{1}$)^{15,16}). The surprising results observed during the pyrolysis of isotopically labelled 1 induce us to publish these results in advance.

Corresponding to ¹⁴) 1 was pyrolyzed in a 10:1 mixture with $[1-^{14}\text{C}]-\underline{1}$ at 740 to 780°C and a resulting contact time of 0.2 to 0.4 sec. The gross activity of the feed was about 10 MBq mol⁻¹, the conversion of 1 was 10 to 30%.

Though the reaction conditions were adjusted carefully the reproducibility of the results was comparatively unsatisfactory. This corresponds to other observations^{9,14)} and means that the reaction system is a very thermolabile one. Therefore we assume a complex reaction system whose competing reaction paths depend significantly but in various ways on the complex parameter set. Based on this statement we give information about the average values of the selectivity S_1 of all main products ($S_1 \geq 2\%$) which are formed in the pyrolysis of $\underline{1}$ (Table 1). Information is also

Table 1: Selectivity (S_1) and relative number of labelled C-atoms (n_1) of the main products from $[1-^{14}\text{C}]\underline{1}$

product	S_1 a)	n_1 b)
methane	15	1.0
acetylene	3	1.1
ethylene	23	1.1
propylene	4	2.1
1,3-pentadienes	5	2.5
cyclopentadiene	13	2.5
methylocyclopentadienes	2	3.1
benzene	19	2.2
1,3-cyclohexadiene	2	3.0
toluene	4	2.9

a) Moles per 100 moles cracked

b) Calculated values refer to: $* \text{CH}_2=\text{CH}^* = 2.0$

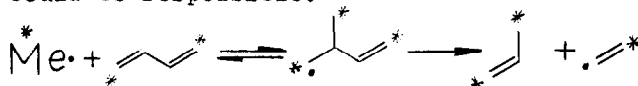
given on the number of labelled C-atoms (n_1) for these products. Because of the identity of the terminal C-atoms in $\underline{1}$ the listed n_1 -values were calculated for $\underline{1}$ hypothetically labelled symmetrically in positions 1 and 4 on the basis of the measured values for $[1-^{14}\text{C}]\underline{1}$.

The sum of activities of all products listed in Table 1 corresponds to more than 85% of the activity of converted $[1-^{14}\text{C}]\underline{1}$. The consistency criterion for the used rgc analysis

$\sum S_1 m_i / \sum S_1 n_i = 2.0$ (m_i - number of C-atoms for each compound) is in good agreement with the experimentally determined value of 2.06.

In comparison with other investigations^{5-9,16)} we observed no new reaction products but we found for the first time references to uncommon reaction pathways for the formation of various hydrocarbons. The more interesting mechanistic aspects derived from the results presented in Table 1 are as follows:

- (1) Methane and ethylene have nearly the same number of labelled carbon atoms n_1 . That means (without consideration of details)
 - methane will be formed nearly completely from the terminal C-atoms of 1 and
 - in the formation of ethylene (as well as acetylene) a mechanism involving a vinyl fragment seems to be followed.
- (2) The n_1 -value of propylene is higher than expected. For this a nonterminal addition of a methyl radical to 1,3-butadiene followed by the cleavage of the adduct radical to a manifold labelled propylene and a vinyl radical could be responsible.



- (3) An important irregularity is evident. In accordance with the mentioned concept of aromatization¹⁻³⁾ benzene and 1,3-cyclohexadiene should have the same n_1 -value because in this concept benzene is the immediate product of the dehydrogenation of 1,3-cyclohexadiene. The experimentally determined values are divergent (2.2 against 3.0).

The unusual results reported show that during the pyrolysis of 1 unknown reactions take place which do not correspond to conventional ideas. We are continuing our studies on the pyrolysis of 1,3-dienes hoping to clarify missing mechanistic details.

References and Notes

- 1 E.N.Hague and R.N.Wheeler, *J.Chem.Soc.* 1929, 378; P.Bredael, *Ann.Mines Belg.* 1975, 1045.
- 2 C.D.Hurd, A.R.Macon, J.Simon, and R.Levetan, *J.Am.Chem.Soc.* 84, 4509(1962).
- 3 E.Gil-Av, J.Shabtai, and F.Steckel, *J.Chem.Eng.Data* 5, 98(1960).
- 4 T.Sakai, K.Soma, Y.Sasaki, H.Tominaga, and T.Kunigi, *Adv.Chem.Ser.* 97, 68(1970).
- 5 R.Cypres and C.Braekman-Danheux, *Ann.Mines Belg.* 1974, 1109.
- 6 G.M.Badger and T.M.Spotswood, *J.Chem.Soc.* 1960, 4431.
- 7 S.W.Benson and G.R.Haugen, *J.Phys.Chem.* 71, 1735(1967).
- 8 A.D.Stepuchovitch and G.I.Kats, *Zh.Fiz.Khim.* 28, 1174 (1954).
- 9 L.V.Shevelkova, L.M.Vedeneeva, R.A.Kalinenko, and K.P.Lavrovskij, *Neftekhim.* 12, 693(1972).
- 10 (1,4-²H₂)-1: I.M.Stephenson, R.V.Gemmer, and J.I.Brauman, *J.Am.Chem.Soc.* 94, 8620(1972).
- 11 (1,1,4,4-²H₄)-1: I.Haller and R.Srinivasan, *ibid.* 88, 3694(1966).
- 12 Nonpositional ¹⁴C-labelled 1: L.V.Shevelkova, L.M.Dedeneeva, R.A.Kalinenko, and K.P.Lavrovskij, *Kinet.Kat.* 14, 834(1973).
- 13 G.Gee, *Trans.Faraday Soc.* 34, 712(1938); J.Collin and F.P.Lossing, *Canad.J.Chem.* 35, 778(1957); R.D.Doepker, *J.Phys.Chem.* 72, 4037(1968); G.Richard and R.Martin, *Int.J.Chem.Kinet.* 12, 1021(1980).
- 14 The pyrolysis was performed in a conventional flow system with a reactor made from quartz (V_r ca. 15 ml). The separation of the reaction products for rgc analysis was accomplished by means of an efficient condenser system. A flow proportional counter served as detector.
- 15 [1-¹⁴C]-1 was prepared from acrolein and ¹⁴C-methylmagnesium iodide followed by dehydration.
- 16 B.Ondruschka, unpublished results, Leipzig 1981.

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