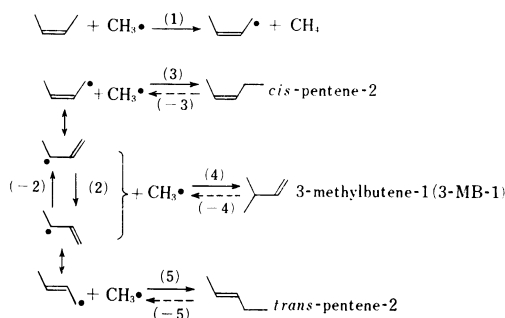


The Isomer Ratio of the Pentenes Formed by $\text{CH}_3\cdot$ -Butenyl CombinationNobuo YOKOYAMA^{*1}

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(Received January 31, 1970)

Yokoyama and Brinton¹⁾ studied the gas phase reaction of *cis*-butene-2 with $\text{CH}_3\cdot$ which was generated by pyrolysis of di-*t*-butylperoxide. Allylic hydrogen abstraction by $\text{CH}_3\cdot$ caused the formation of butenyl radical which gave three pentene isomers when combined with $\text{CH}_3\cdot$. The process is illustrated by the scheme shown below, which includes allylic resonance and *cis-trans* rotation about the center bond.



(3) and (5) are the only mechanisms leading to the pentene-2 formation in this system, but 3-MB-1 is also formed by disproportionation of the pentyl radical which is present in the system. However, the quantity of 3-MB-1 formed *via* each route could be distinguished, and the present discussion is limited to 3-MB-1 formed *via* (4) only.

The average ratios of the quantities of pentene isomers were found to be nearly constant at a certain temperature. Their values are shown in Table 1, together with the equilibrium ratios of these pentenes calculated from the generally accepted data.²⁾

It should be noted that *trans/cis* ratio exceeded that of the equilibrium in spite of the fact that the reaction was started with *cis*-butene-2. This ratio should have been equal to the equilibrium ratio if there had been the reverse reactions (−3), (−4),

and (−5) taking place at sufficient rates. Or it should have been smaller than the equilibrium ratio if (2) had not been sufficiently faster than (3). In fact, the internal rotation (± 2) must be much faster than (3), (4), and (5), for the same values were obtained for the isomer ratios when the reaction was started with *trans*-butene-2.

trans/cis equilibrium ratio *b* may be expressed as

$$b = \frac{k_2}{k_{-2}} \cdot \frac{k_3}{k_4} \cdot \frac{k_5}{k_{-5}} \quad (6)$$

However, since (−3) and (−5) must be eventually non-existent and (± 2) were proved to be sufficiently faster than (3) and (5), the following equation should hold for the observed *trans/cis* ratio

$$a = \frac{k_2}{k_{-2}} \cdot \frac{k_5}{k_3} \quad (7)$$

The following relation should then be valid

$$a/b = k_{-5}/k_{-3} \quad (8)$$

This is the ratio of the rates of bond cleavage to produce butenyl and methyl radicals from *trans*- and *cis*-pentene-2, which could not be directly measured in such temperature range. It is interesting to note that there seems to be a slight difference in the rates of this bond cleavage, *trans* form having a slightly faster rate than *cis*, and that it is not due to the difference in the bond energy. The present data show no evidence for non-zero difference in the activation energy which should be approximately equal to the bond energy itself, because its reverse reaction (radical-radical combination) should have zero or near-zero activation energy.

Exactly the same discussion is applicable to 3-MB-1/*trans*-pentene-2 ratio. In this case the electron density ratio of $\cdot\text{CH}_2\text{CH}=\text{CH}_2 \leftrightarrow \text{CH}_2=\text{CH}\cdot$ has a similar role to k_2/k_{-2} in the previous case, and the final result is

$$c/d = k_{-4}/k_{-5} \quad (9)$$

As is seen in Table 1, *c/d* shows a large divergency from unity, and again no non-zero activation energy difference can be detected. Thus, through this kinetic observation, the bond cleavages of the three pentene isomers (−3), (−4), and (−5) were found to have different rates, (−5) slightly faster than (−3), and (−4) appreciably faster than (−5), not due to the differences in the bond

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1) N. Yokoyama and R. K. Brinton, *Can. J. Chem.*, **47**, 2987 (1969).

2) F. D. Rossini, "Selected values of Physical and Thermodynamic properties of Hydrocarbons and Related Compounds" (API), Carnegie Press, Pittsburgh, Pa. (1953).

TABLE I. PENTENE RATIOS

Temp. °C	<i>trans</i> -pentene-2/ <i>cis</i> -pentene-2			3-MB-1/ <i>trans</i> -pentene-2		
	<i>a</i>	<i>b</i>	<i>a/b</i>	<i>c</i>	<i>d</i>	<i>c/d</i>
	observed	equilibrium calculated		observed	equilibrium calculated	
163.0	1.28	1.19	1.1	0.63	0.24	2.6
150.2	1.28	1.22	1.1	0.59	0.24	2.5
136.8	1.35	1.26	1.1	0.59	0.23	2.6
125.8	1.31	1.28	1.0	0.56	0.22	2.5

energies.

It was concluded that the *cis/trans* internal rotation of the butenyl radical was fast enough to maintain the equilibrium under the employed conditions, compared with the rates of the competitive chemical reactions. In contrast to this finding, Walling and Thaler³⁾ reported the complete retention of *cis-trans* configuration of the butenyl radical at 40°C. Although the reaction conditions were entirely different (liquid phase, Cl abstraction as the competitive chemical reaction in their case), this extreme difference between

126—163°C and 40°C is quite interesting. Somewhere between these two temperature regions there might be a certain region in which the internal rotation and the competitive chemical reaction have comparative rates, which would enable one to determine the rate of *cis-trans* rotation of the butenyl radical by comparison with the rate of the competitive reaction, for which no other means of measurement is available at present.

3) C. Walling and W. Thaler, *J. Amer. Chem. Soc.*, **83**, 3877 (1961).