

1229. *The Pyrolysis of But-1-ene, and the Resonance Energy of the Allyl Radical*

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MUCH discussion has taken place on the resonance energy of the allyl radical. Benson and his co-workers¹ put forward good experimental evidence, from the iodine-catalysed isomerisation of but-1-ene, to suggest that the resonance energy of the allyl radical is 12.6 ± 1 kcal. In addition they deduced values, which are in excellent agreement with this result, from the pyrolysis of vinylcyclopropane and vinylcyclobutanes, although Ellis and Frey² had cast doubt on the reliability of the estimates of the allyl resonance energy calculated from the isomerisation of cyclopropanes. The largest obstacle in the way of accepting the results of Benson and his colleagues is that a much higher allylic resonance energy can be deduced from the pyrolysis of but-1-ene studied by Sehon and

¹ K. W. Egger, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, 1964, **86**, 5420.

² R. J. Ellis and H. M. Frey, *J.*, 1964, 959.

Szwarc by the toluene-carrier technique.^{3,4} Since, however, many of Szwarc's original results from pyrolysis experiments have been revised by the application of an aniline-carrier technique,^{5,6} and improved analytical equipment, a re-investigation of the pyrolysis of but-1-ene seemed desirable.

Results of the pyrolysis of but-1-ene by the aniline-carrier technique are recorded in

TABLE 1

The pyrolysis of but-1-ene at constant pressure

Temp. (°K)	Total pressure (mm.)	Contact time (sec.)	But-1-ene (10 ⁵ mole)	CH ₄ (10 ⁵ mole)	10 ² k ₁ (sec. ⁻¹)
900	11.2	1.76	106	2.8	1.56
927	11.6	1.60	66.7	4.4	4.24
936	11.4	1.90	29.1	2.8	5.39
953	11.1	1.62	86.8	12.3	9.45
955	11.7	1.60	32.5	5.1	10.8
968	10.7	1.90	20.4	5.2	14.6
971	11.5	1.75	24.6	6.5	17.5
989	11.5	1.65	21.5	8.4	30.2
990	11.5	1.63	31.9	12.7	32.1

TABLE 2

The effect of pressure on the decomposition of but-1-ene

Temp. (°K)	Total pressure (mm.)	Contact time (sec.)	But-1-ene (10 ⁵ mole)	CH ₄ (10 ⁵ mole)	10 ² k ₁ (sec. ⁻¹)
952	4.0	2.93	26.3	3.45	4.80
952	6.8	2.15	28.5	4.04	7.43
952	11.7	1.60	32.5	5.13	10.3
952	17.5	1.33	50.3	8.20	13.4
952	21.3	1.48	24.5	4.40	13.4 *
970	5.5	2.58	25.5	5.56	9.53
970	11.5	1.75	24.6	6.51	16.7
970	17.8	1.49	25.1	6.78	21.1
970	22.2	1.49	27.4	7.28	20.8 *
970	22.4	1.46	28.0	7.68	22.0 *

* These results are less reliable owing to the difficulty of maintaining a high pressure of aniline vapour.

Tables 1 and 2. First-order rate constants (k_1) for the decomposition were derived from the yields of methane in accordance with the scheme:



This is the basis of the mechanism proposed by Szwarc and Sehon,³ and, since they established that the first-order rate constants, based on the methane formation, were independent of surface-to-volume ratio, partial pressure of butene, and contact time, these aspects were not investigated further. Small amounts of hydrogen (5—15% of the methane) were also found in the products of the aniline-carrier experiments.

³ M. Szwarc and A. H. Sehon, *J. Chem. Phys.*, 1950, **18**, 237.

⁴ A. H. Sehon and M. Szwarc, *Proc. Roy. Soc.*, 1950, *A*, **202**, 263.

⁵ G. L. Esteban, J. A. Kerr, and A. F. Trotman-Dickenson, *J.*, 1963, 3873.

⁶ J. A. Kerr, A. F. Trotman-Dickenson, and M. Wolter, *J.*, 1964, 3584.

A least-mean-squares treatment of the rate constants for the decomposition at a constant total pressure of about 11.5 mm. of mercury gives:

$$\log k_1 (\text{sec.}^{-1}) = 12.71 - (59,100/2.3RT).$$

The activation energy is in satisfactory agreement with the value of 61.5 kcal. mole⁻¹ deduced by Szwarc and Sehon³ from their results at about the same total pressure. As seen from Table 2, however, the present results show that the rate constant is considerably pressure-dependent. Plots of $\log k$ against $\log p$ from the results in Table 2 at 952 and 970°K yield approximate straight lines with slopes of about 0.7. Sehon and Szwarc found a much smaller pressure effect on their rate constants from the toluene experiments. It appears that the activation energies found in both studies of the decomposition of but-1-ene do not correspond to the high-pressure activation energy which is required in thermochemical calculations. Unfortunately, aniline- or toluene-carrier experiments cannot be adapted to work at high pressures.

Benson¹ defines the resonance energy of the methylallyl radical as the difference between the dissociation energies of the secondary C-H bonds in n-butane and but-1-ene. Assuming that the resonance energies of the methylallyl and allyl radical will be the same, it follows that the resonance energy of the allyl radical is defined as the difference between the dissociation energies of the primary C-H bonds in propane and propene. Taking the resonance energy of allyl as 13 kcal. and $D(\text{C}_3\text{H}_7^{\text{a}}-\text{H}) = 98$ kcal. mole⁻¹, this gives $D(\text{C}_3\text{H}_5-\text{H}) = 85$ kcal. mole⁻¹. On this basis, the heat of formation of the allyl radical is 37.9 kcal. mole⁻¹ and $D(\text{CH}_3\text{-CH}_2\text{-CH}\cdot\text{CH}_2) = 71.5$ kcal. mole⁻¹.

The maximum difference between the limiting high-pressure activation (E_∞) energy of a unimolecular reaction and the experimental value determined at lower pressures is $\frac{1}{2}n'RT$, where n' is the number of effective oscillators in the molecule. The value of n' for but-1-ene is not known but it must be close to that for isomerisation of methylcyclopropane to butenes where $n' = 19$.⁷ At about 1000°K, then, it follows that the activation energy (60 kcal. mole⁻¹) found here for the decomposition of but-1-ene at 10 mm. pressure is not incompatible with a limiting high-pressure value of 71.5 kcal. mole⁻¹. The exact correction will depend on how far into the second-order region the pressure fall-off curve has gone at 10 mm. pressure. Unfortunately, the data obtained here are too limited to permit a quantitative calculation of this effect from the slope of the $\log k_1$ versus $\log p$ plot.

It is interesting to note that, if one assumes a value for the high-pressure rate constant for the decomposition at 970°K of 1 sec.⁻¹, then the limiting high-pressure A -factor has a value of about 10^{16} sec.⁻¹.

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⁷ J. P. Chesick, *J. Amer. Chem. Soc.*, 1960, **82**, 3277.