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The Kinetics of the Thermal Decomposition of Isobutene

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The thermal decomposition of isobutene was found to be a homogeneous gas reaction of the first order. The first-order constant is $0.5 \cdot 10^{13} \exp(67,000/RT)$. The products of the decomposition included H_2 , CH_4 , and allene. The experimental results are explained in terms of a chain mechanism, the initiating step being the decomposition of the isobutene molecule into an H atom and a $\cdot CH_2-C=CH_2$



radical. The most probable value of the $D(C-H)$ in isobutene is 76 kcal./mole. This estimate is based on certain assumptions concerning the frequency factors.

THE aim of this work was to supplement that done on the pyrolysis of propylene. We used the same apparatus and technique as described in the preceding paper. The isobutene was kindly supplied by Messrs. I.C.I., Billingham, and contained over 99 percent of C_4H_8 . This product was further purified by a vacuum distillation from a trap at $-80^\circ C$ into one cooled by liquid air. The criterion of purity was that the product recovered from any pyrolysis should give the same rate of decomposition on being pyrolyzed once more. By this standard the distilled isobutene was sufficiently pure (see Table I). The reproducibility of the results was not as good as in the case of propylene, and this was particularly noticeable in experiments performed at lower temperatures (see Table I and Fig. 1).

It was found that the thermal decomposition of isobutene is a homogeneous gas reaction of the first order. Packing of the reaction vessel with silica wool (increasing the surface by factor of 6) caused no change in the rate of decomposition (see Table II and Fig. 1). The reaction was shown to be first order

by changing the pressure of isobutene from about 1 mm of Hg up to 20 mm of Hg, the results being summarized in Table III. The variation of the first-order constant with temperature is shown in graph 1, where $\log k$ is plotted against $1/T$. This graph contains all the experimental results. The "best" straight line corresponds to an energy of activation of 67 kcal./mole and a frequency factor of 5.10^{12} . The experimental error is about ± 4 kcal./mole. Table IV contains all the results not tabulated in the preceding tables.

THE PRODUCTS OF DECOMPOSITION

The decomposition of isobutene produced H_2 and CH_4 in proportions independent of temperature and pressure of C_4H_8 . The results of the analysis of $H_2 + CH_4$ mixture are summarized in Table V. The average composition of this mixture was 1 mole of H_2 to 9 moles of CH_4 .

The analysis of other products of the pyrolysis was very difficult as the percentage of decomposition was kept extremely low (from about 0.01 percent up to 2 percent) in order to avoid side reactions. The distillation on a Podbielmak type still* revealed that allene was another main product of decomposition. Its quantity suggested that the ratio $(H_2 + CH_4)/allene$ was 1:1. The allene fraction was identified by its boiling point (-34° – $-35^\circ C$) and by its reaction with solution of $HgCl_2$ (white precipitate).

TABLE II. Packed reaction vessel.

Run	$T^\circ C$	P mm Hg	$K \cdot 10^3$ sec. ⁻¹	Percent H_2	Percent CH_4
72	725	8.0	14.5	—	—
74	730	8.4	18	—	—
73	732	8.3	22	—	—
75	760	8.5	51	14%	86%
76	793	11.5	155	—	—

TABLE I.

Run	Previous pyrolysis	$T^\circ C$	P mm Hg	$K \cdot 10^3$ sec. ⁻¹	$K_{767} \cdot 10^3$ sec. ⁻¹ *
Temperature round $767^\circ C$					
1	Not pyrolyzed	771	8.8	48.9	45.6
2	Not pyrolyzed	771	8.8	47.4	44.1
3	Once pyrolyzed at $770^\circ C$	768	9.0	45.6	43.8
4	Once pyrolyzed at $770^\circ C$	767	8.7	46.0	46.0
5	Once pyrolyzed at $770^\circ C$	767	8.6	43.7	43.7
41	Once pyrolyzed at $790^\circ C$	767	9.2	41.8	41.8
42	Once pyrolyzed at $790^\circ C$	769	9.0	49.0	44.0
46	Twice pyrolyzed at $790^\circ C$	763	9.5	38.8	43.0
47	Twice pyrolyzed at $790^\circ C$	762	8.9	45.8	60.5
53	Twice pyrolyzed at $740^\circ C$	760	8.5	35.0	43.9
Temperature round $708^\circ C$					
50	Twice pyrolyzed at $740^\circ C$	709	8.9	4.7	4.5
51	Twice pyrolyzed at $740^\circ C$	708	8.7	5.7	5.7
52	Twice pyrolyzed at $740^\circ C$	707	8.6	6.0	6.2
54	3 times pyrolyzed at $740^\circ C$	704	8.9	8.0	9.3
55	4 times pyrolyzed at $740^\circ C$	706	8.4	6.0	6.5
56	4 times pyrolyzed at $740^\circ C$	704	8.5	5.5	6.1
14	3 times pyrolyzed at $770^\circ C$	711	8.5	10.0	8.8
15	3 times pyrolyzed at $770^\circ C$	711	8.7	9.5	8.3

* This column contains the values of K interpolated to a constant temperature for the sake of comparison.

* For the distillation we could only use samples of isobutene pyrolyzed twice or three times at higher temperatures.

TABLE III.

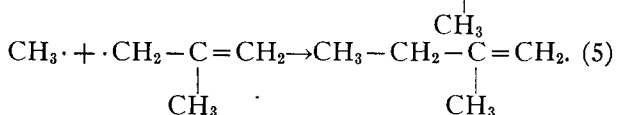
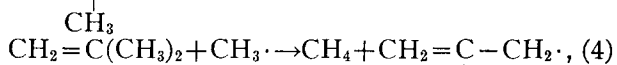
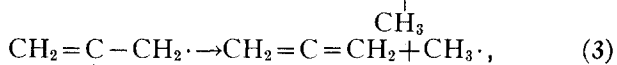
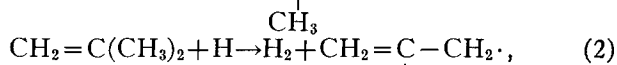
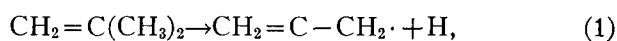
Run	T°C	P mm Hg	Time of contact sec.	Percent of decomp.	$K \cdot 10^3 \cdot \text{sec.}^{-1}$	$K_{660} \cdot 10^3 \text{ sec.}^{-1}^*$
59	660	19.5	0.180	0.023	1.3	1.3
60	660	8.5	0.195	0.033	1.7	1.7
62	657	4.6	0.200	0.036	0.8	0.9
$K_{688} \cdot 10^3 \text{ sec.}^{-1}^*$						
31	689	15.2	0.170	0.075	4.4	4.2
29	687	8.7	0.195	0.082	4.2	4.4
30	687	8.8	0.195	0.062	3.2	3.3
32	688	2.9	0.220	0.064	2.9	2.9
33	688	2.8	0.220	0.073	3.3	3.3
$K_{768} \cdot 10^3 \text{ sec.}^{-1}^*$						
8	768	13.2	0.160	0.86	54	54
4	767	8.7	0.180	0.83	46	48
5	767	8.6	0.180	0.79	44	46
6	768	2.9	0.210	0.80	38	38
7	769	2.9	0.205	0.78	38	37
$K_{808} \cdot 10^3 \text{ sec.}^{-1}^*$						
64	806	8.9	0.185	4.25	230	250
65	808	4.7	0.195	4.30	220	220
68	809	2.8	0.200	3.20	160	155
67	809	1.3	0.215	5.38	250	240

* This column contains the values of K interpolated to a constant temperature for the sake of comparison.

DISCUSSION

The reported facts are against any mechanism of unimolecular type, i.e., based on the assumption that the rate-determining step is the breaking of some bond in the molecule of isobutene, followed by a sequence of rapid reactions between the radicals so created and the undecomposed C_4H_8 . The decisive argument is that the observed energy of activation of 67 kcal./mole is too low to be regarded as a dissociation energy of any bond existing in the molecule of isobutene. In addition, the fact that the percentage of CH_4 was so high is by itself a powerful argument against the unimolecular mechanism of the type proposed for the decomposition of propylene. According to this mechanism more H_2 should be produced in the decomposition of isobutene than was observed in the case of propylene. The chance of reaction between H atoms and the H's of the CH_3 groups doubles, while that of addition to the central C decreases as a result of shielding of this atom by the two CH_3 groups. Thus the ambiguity which we encountered in the case of propylene does not exist in the case of isobutene. We can, therefore, safely assume that the pyrolysis of isobutene proceeds according to the following chain mechanism, corresponding to that previously proposed to account for

the decomposition of propylene.



The reactions (1) and (2) are the chain initiation, the reactions (3) and (4) are the chain propagation and the reaction (5) is the chain termination.**

At this point it should be mentioned that the pyrolysis of isobutene was investigated recently by Rice and Haynes.¹ The experimental results of these authors support in some respect the present findings.

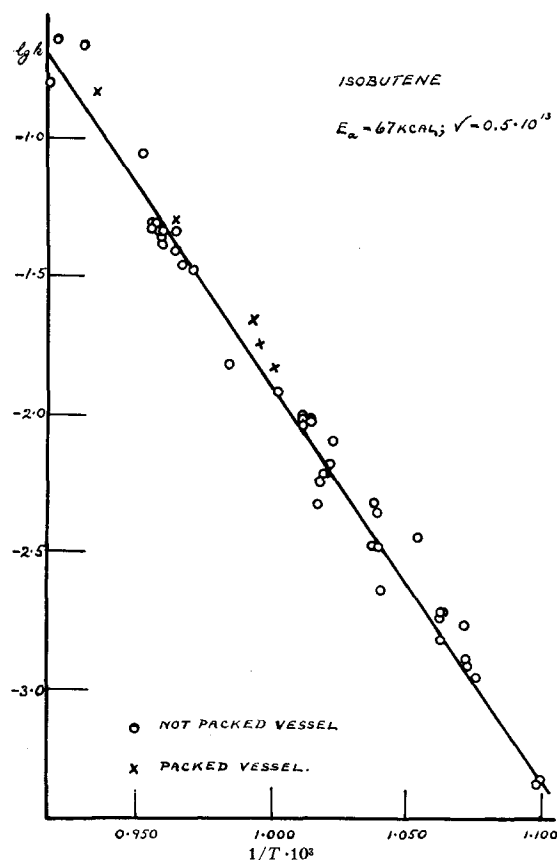


FIG. 1.

** The two other chain terminations can be ruled out in the same way as mentioned in the preceding paper.

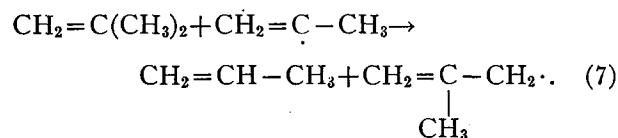
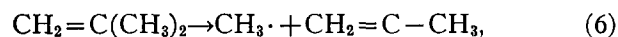
¹ F. O. Rice and W. S. Haynes, J. Am. Chem. Soc. **70**, 964 (1948).

TABLE IV.

Run	T°C	P mm Hg	Time of contact sec.	Percent decomp.	$K \cdot 10^3 \text{ sec.}^{-1}$
25	636	8.6	0.185	0.009	0.48
26	638	8.5	0.190	0.009	0.46
22	656	8.6	0.170	0.019	1.1
23	659	8.5	0.195	0.025	1.3
24	659	8.4	0.160	0.019	1.2
10	667	8.9	0.185	0.035	1.9
11	668	8.8	0.180	0.034	1.9
12	668	8.6	0.185	0.033	1.8
13	668	8.8	0.180	0.027	1.5
69	675	8.7	0.205	0.082	4.0
20	687	8.8	0.190	0.068	3.6
21	687	8.5	0.195	0.070	3.6
16	711	8.8	0.175	0.160	9.4
17	714	8.6	0.180	0.175	9.7
18	714	8.7	0.165	0.155	9.5
19	714	8.4	0.170	0.155	9.1
28	723	8.6	0.160	0.19	12
27	754	8.7	0.165	0.56	34

Thus H_2 , CH_4 , and allene were reported as the products of decomposition, and the ratio of H_2/CH_4 was very close to that found in the present work. From their data we calculated the first-order constant at 790°C as $190 \cdot 10^{-3} \text{ sec.}^{-1}$,*** while our value at this temperature (interpolated) was $120 \cdot 10^{-3} \text{ sec.}^{-1}$

In conclusion Rice and Haynes postulated a chain mechanism which differs from that given above only in the initiation steps. The initiation proposed by these authors was



It should be noticed, however, that Rice's mechanism does not account for the formation of H_2 , which was found as a product of reaction by Rice and Haynes and in the present investigation.****

Returning to the chain mechanism proposed in the present work, it should be observed that this mechanism accounts for the formation of H_2 as well as for that of CH_4 and allene. The CH_4/H_2 ratio gives the length of the chain. Using the stationary state method we obtain the following expressions:

$$d(\text{H}_2 + \text{CH}_4)/dt \sim [k_1 + (k_1 \cdot k_3 \cdot k_4/k_5)^{\frac{1}{2}}] \cdot (\text{C}_4\text{H}_8)$$

$$\sim (k_1 \cdot k_3 \cdot k_4/k_5)^{\frac{1}{2}} \cdot (\text{C}_4\text{H}_8);$$

chain length

$$\sim (k_3 \cdot k_4/k_1 \cdot k_5)^{\frac{1}{2}}.$$

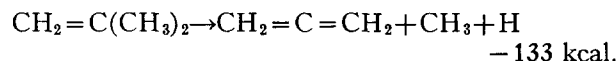
*** We use for this calculation the result obtained in the experiment performed at 790°C , pressure of 9 mm of Hg and time of contact 0.3 sec., as these conditions are similar to those at which we worked.

**** However, see C. D. Hurd and L. K. Eilers, Ind. Eng. Chem. 26, 776 (1934) and C. D. Hurd and F. H. Blunck, J. Am. Chem. Soc. 59, 1869 (1937).

TABLE V.

Run	Previous treatment of sample	T°C	P mm of Hg	Percent H_2	Percent CH_4
35	Once pyrolyzed at 690°C	690	8.8	10	90
38	3 times pyrolyzed at 690°C	690	8.9	8	92
39	5 times pyrolyzed at 690°C	690	8.8	10	90
54	3 times pyrolyzed at 740°C	704	8.9	9.5	90.5
55	4 times pyrolyzed at 740°C	706	8.4	11	89
51	2 times pyrolyzed at 740°C	708	8.7	10	90
49	Once pyrolyzed at 740°C	740	8.7	9.5	90.5
53	2 times pyrolyzed at 740°C	760	8.5	10.5	89.5
46	2 times pyrolyzed at 790°C	763	9.5	10	90
41	Once pyrolyzed at 790°C	767	9.2	8	92
3	Once pyrolyzed at 770°C	768	9.0	11	89
8	2 times pyrolyzed at 770°C	768	13.2	12	88
63	4 times pyrolyzed at 740°C	774	8.6	12	88
64	5 times pyrolyzed at 740°C	806	8.9	11	89
68	2 times pyrolyzed at 800°C	809	2.8	13	87

The approximate expression follows from the assumption that k_1 is much smaller than k_3 , k_4 , or k_5 . The expression for $d(\text{H}_2 + \text{CH}_4)/dt$ leads to the energy of activation of $\frac{1}{2}(E_1 + E_3 + E_4) \sim 69 \text{ kcal./mole}$, as $E_1 + E_3$ is equal to or slightly greater than 133 kcal. , the endothermicity of the reaction:



and E_4 is probably about $4 \text{ kcal./mole.}^\dagger$

The reactions (4) and (5) are bimolecular reactions which should correspond to about the same collision frequency, while the reactions (1) and (3) are unimolecular decompositions and on theoretical grounds² should have frequency factors of the order 10^{13} . Thus the frequency factor for the over-all reaction should be also of the order 10^{13} . In such a way the discussed mechanism accounts for the observed energy of activation and frequency factor.

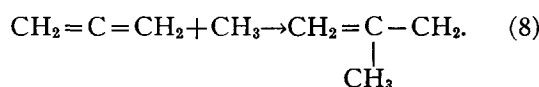
From the expression for the chain length we obtain $\ln. (\text{chain length}) = (1/2RT)(E_1 - E_3 - E_4) - \frac{1}{2} \ln. 6$. The last term arises from the statistical factor of 6 existing in the frequency factor of reaction (1) but not in that of reaction (3). Now, putting for the chain length $\text{CH}_4/\text{H}_2 = 9$ and for E_4 a value of 4 kcal. (see the previous footnote), we obtain

$$E_1 - E_3 \sim 17 \text{ kcal.},$$

while

$$E_1 + E_3 = 133 \text{ kcal.} + x,$$

where x is the energy of activation for the reaction (8).



[†] For analogy with the energy of activation for $\text{CH}_3 + \text{CH}_3 \cdot \text{CH}=\text{CH}_2 \rightarrow \text{CH}_4 + \text{CH}_2=\text{CH}=\text{CH}_2$ see H. S. Taylor and J. O. Smith, J. Chem. Phys. 8, 543 (1940).

² M. Polanyi and E. Wigner, Zeits. f. physik Chemie A139, 439 (1928).

Taking for α a reasonable value of 2 kcal. we obtain

$$D(C-H) = E_1 = 76 \text{ kcal./mole.}$$

This value corresponds to 5.10^{13} as the frequency factor of the unimolecular constant for the first step of the decomposition of isobutene. It would be expected that this factor should be twice as high as

that for propylene (from statistical reason), and thus the good agreement between the frequency factors found for toluene, the xylenes,³ propylene, and isobutene provides some justification for the applied approximations.

³ M. Szwarc, *Nature* **160**, 403 (1947); *J. Chem. Phys.* **16**, 128 (1948).

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Vibrational Analysis of the 3400A Triplet-Singlet Emission of Benzene*

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The triplet-singlet emission of benzene at 3400A in a rigid glass-solution has been obtained and measured more accurately than in previous work. An assignment is proposed accounting for all the important bands observed. The analysis of the vibrational structure indicates the presence of the $703 \text{ cm}^{-1} b_{2g}$ fundamental, showing that in the triplet-singlet transition, the triplet level combines in the same manner as a ${}^1B_{1u}$ state for electric dipole radiation. This will lead to a definite assignment of the symmetry of this triplet level when the theoretical rules for intercombinations in polyatomic molecules are derived. The analysis supports a hexagonally symmetric planar model for this triplet state.

INTRODUCTION

THAT the phosphorescence emission observed from many organic molecules was a transition from a triplet to the ground singlet state of the molecule was suggested by Lewis and Kasha.^{1,2} Sklar³ reported finding a weak absorption in the 3400A region (spectrum shown by Lewis and Kasha²) which he attributed to one of the triplet levels predicted in his theoretical calculations. It was suggested that this absorption represented the symmetry allowed transition ${}^1A_{1g} \rightarrow {}^3E_u$ which was predicted at 2120A. Theory, however, predicted an additional transition ${}^1A_{1g} \rightarrow {}^3B_{1u}$ at 4750A. Inability to find this transition was ascribed to the double forbiddenness of the transition (both spin and symmetry forbidden), whereas the transition ${}^1A_{1g} \rightarrow {}^3E_u$ is spin forbidden only.

A further calculation of the triplet level was made by Goepfert-Mayer and Sklar⁴ using the method of anti-symmetrized products of molecular orbitals. Their calculations showed ${}^3B_{1u}$ as the lowest triplet level, followed in turn at higher energies by

3E_u and ${}^3B_{2u}$. The calculated transition ${}^1A_{1g} \rightarrow {}^3B_{1u}$ was at 8300A. London⁵ recalculated these levels including a number of integrals neglected by Goepfert-Mayer and Sklar. The new calculated transition ${}^1A_{1g} \rightarrow {}^3B_{1u}$ is at 2760A. It should be noted in this recalculation, the singlet levels are in poor agreement with observation, and the relatively good agreement with the lowest triplet level must be regarded as fortuitous.

It is very unlikely that there is a lower triplet level than that involved in this 3400A transition, since the lowest frequency band of the absorption agrees almost exactly with the highest frequency band of the phosphorescence emission.¹ In general emission in polyatomic molecules in condensed media has been observed only from the lowest level above the ground state of a given multiplicity, even though excitation occurs exclusively in higher levels.⁶ It is, therefore, more likely that the singlet-triplet absorption at 3400A and its corresponding emission are to be correlated with the lowest triplet level (${}^3B_{1u}$) predicted by theory. Absorption to the higher triplet levels (3E_u and ${}^3B_{2u}$) is expected to be hidden by the much more intense singlet-singlet bands.

Roothaan and Mulliken⁷ have indicated, however, that previously calculated integrals may be sufficiently in error to reverse the position of the

* From the dissertation submitted in partial fulfillment of the requirements for the Degree of Doctor of Philosophy at the University of California at Berkeley.

** Shell Research Fellow in Chemistry 1946-1947. Abraham Rosenberg Fellow in Chemistry 1947-1948. Present address: Department of Physics, University of Chicago, Chicago, Illinois.

¹ G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.* **66**, 2100 (1944).

² G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.* **67**, 994 (1945).

³ A. L. Sklar, *J. Chem. Phys.* **5**, 669 (1937).

⁴ M. Goepfert-Mayer and A. L. Sklar, *J. Chem. Phys.* **6**, 645 (1938).

⁵ A. London, *J. Chem. Phys.* **13**, 396 (1943).

⁶ Data on this point are not too convincing in the literature. Further evidence to be published soon has been obtained by Dr. M. Kasha of this laboratory.

⁷ C. C. J. Roothaan and R. S. Mulliken, *J. Chem. Phys.* **16**, 118 (1948).