



# Isotope Effect in the Thermal Cracking of Propane-1C13

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dependent on intensity. Hence it is evident that the formation of "dimer" is a second-order process. The apparent slight dependence of the ratio [CH2O+CO]/[dimer]<sup>1</sup> on intensity is probably due to increased polymerization of the formaldehyde in the long runs at low intensity.

#### **Activation Energies**

The slopes of the plot  $\log(k_{\rm CH_4}/k_{\rm C_2H_6^{\frac{1}{2}}})$  vs. 1/T, given in Fig. 3, correspond to activation energies of 8.8 at 28 mm, and 9.2 at 110 mm. On the basis of the previous discussion this is equal to  $E_5 - \frac{1}{2}E_6$ . Assuming  $E_6$ , the activation energy for recombination of two methyls, to be zero, the activation energy for the reaction of methyl radicals with dimethyl ether  $(E_5)$  is equal to 9.0 kcal. Similarly, from a plot of  $\log[CH_2O+CO]/$ [dimer]<sup>1</sup> vs. 1/T, given in Fig. 4, the activation energy for the unimolecular decomposition of the CH<sub>3</sub>OCH<sub>2</sub> radical is equal to 18.5 and 20.0 kcal. at 28 mm and 110 mm respectively, and if the activation energy for the recombination of two methoxy-methyl radicals is assumed to be zero, then  $E_4$  may be taken as 19 kcal. In plotting the curves in Fig. 4, the runs at the highest temperature have been given little weight, since experimental errors are much larger at the highest temperatures.

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### Isotope Effect in the Thermal Cracking of Propane-1-C<sup>13</sup>

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T was recently found that the dissociation probabilities of the  $C^{12}-C^{12}$  and the  $C^{12}-C^{13}$ bonds of the molecule-ions formed from propane- $1 - C^{13}$  by electron impact differ by *ca*. 20 percent.<sup>1</sup> This observation led us to look for a similar difference in ordinary chemical reactions of propane- $1-C^{13}$ . The pyrolysis of propane was selected for study, since this reaction is one whose mechanism is presumably well understood.<sup>2</sup> Significant differences were found in the reactivities of bonds to terminal C13 and C12 atoms. The magnitude of the effect, 8 percent more frequent rupture of  $C^{12} - C^{12}$  bonds than of  $C^{12} - C^{13}$  bonds,

TABLE I. Composition of feed propane-1-C<sup>13</sup> (53%).

Species	Mole fraction	
C12H,C12H,C12H,	$0.457_5 \pm .0013$	
C12H,C12H,C13H,	$.526_{5} + .0017$	
C12H,C13H,C12H,	$.0048 \pm .0001$	
C12H, C13H, C13H,	$0056 \pm 0001$	
$C^{13}H_{*}C^{12}H_{*}C^{13}H_{*}$	$0056 \pm 0001$	
$C^{13}H_{*}C^{13}H_{*}C^{13}H_{*}$		

<sup>1</sup> Beeck, Otvos, Stevenson, and Wagner, J. Chem. Phys.

16, 255 (1948). <sup>2</sup> E. W. R. Steacie, Atomic and Free Radical Reactions New York 1946). (Reinhold Publishing Corporation, New York, 1946). Particularly pages 103-105. is such that the effect should not be neglected in quantitative tracer experiments with carbon isotopes where reaction rates are involved.

Propane-1 –  $C^{13}$  (53 percent), prepared as previously described and with the isotopic species distribution shown in Table I, was cracked to a depth of approximately 10 percent (three separate experiments) at temperatures between 500 and 550°C. The product was separated into three fractions, hydrogen and methane, ethane, and ethylene, and propylene and propane, by one plate, isothermal distillation at very low pressure (low temperature). The relative concentrations of the isotopic methanes, ethylenes, and ethanes, as well as the total concentrations of hydrogen, methane, ethylene, ethane, propylene, and pro-

TABLE II. Mole fractions of "heavy" products.

· · · · · · · · · · · · · · · · · · ·	Found‡	Calculated, assuming no isotope effect
$C^{13}H_4$ in methane $C^{12}C^{13}H_4$ in ethylene $C^{12}C^{13}H_6$ in ethane	$\begin{array}{r} 0.263 \pm .002 \\ .288 \pm .004 \\ .252 \pm .010 \end{array}$	0.272 .277 .277

<sup>‡</sup> The original data were empirically corrected for mass dependent, ion source discrimination effects. The indicated uncertainties are the mean deviations of analyses in three separate cracking experiments.

Starting material C3H8	Mole percent of total 100	Millimoles 0.445	Milligram-atoms of carbon 1.34
Product			
$H_2$	2.79	0.0133	
CH₄	3.50	.0167	0.0167
C <sub>2</sub> H <sub>4</sub>	3.41	.0163	.0326
C <sub>2</sub> H <sub>6</sub>	0.27	.0013	.0026
C <sub>2</sub> H <sub>6</sub>	2.94	.0141	.0423
C <sub>3</sub> H <sub>8</sub>	87.1	.415	1.245
Total	100.0	0.476	1.34

TABLE III. Material balance in the cracking of propane-1-C<sup>13</sup>.

pane, were determined mass spectrometrically. The mole fractions of "heavy" methane, ethylene, and ethane in the product methane, ethylene, and ethane, computed from the analytical data, are shown in Table II, where these mole fractions are compared with those computed from the isotopic composition of the original propane- $1 - C^{13}$  on the assumption of no isotope effects.

The concentration of total ethane relative to that of total ethylene plus propylene in the reaction product indicates an effective chain length of about 20. Thus to the extent that the Rice-Herzfeld mechanism applies to the pyrolysis of propane, the methane is primarily a product of the chain carrying reaction,

$$n - C_3 H_7 \rightarrow C_2 H_4 + C H_3, \tag{1}$$

as is all of the ethylene. Thus it would be expected that any isotope effects observed in ethylene formation would be complementary in methane formation, as is observed (Table II). Interpreting the "low" methane- $C^{13}$  and the "high" ethylene- $C^{13}$  in terms of the Rice-Herzfeld mechanism, one concludes hydrogen atoms to be preferentially removed from the  $C^{13}$  methyl group in the chain carrying step,

$$C_{3}H_{8} + R \rightarrow n - C_{3}H_{7} + RH.$$
 (2)

Such greater reactivity of C<sup>13</sup>-H bonds is con-

trary to expectations based on the known effect of mass on zero point energy, which should affect the difference in activation energies and thus the relative reactivities of  $C^{12}$ —H and  $C^{13}$ —H bonds. Whatever the origin of the effect may be, the data indicate for the over-all reaction an 8 percent greater frequency of rupture of  $C^{12}$ — $C^{12}$ than of  $C^{12}$ — $C^{13}$  bonds.

The ethane presumably arises primarily from the chain initiating reaction,

$$C_{3}H_{8} \rightarrow C_{2}H_{5} + CH_{3}; \qquad (3)$$

thus the "low" concentration of ethane- $C^{13}$  in the product indicates a preferential breaking of the  $C^{12}-C^{13}$  bond of propane- $1-C^{13}$  in the chain initiating reaction. The relatively poorer reproducibility of the mole fraction of heavy ethane indicates a need for further study of the chain initiating step, with particular reference to possible wall effects.

 $\cdot$ A material balance for one of the cracking experiments, as shown in Table III, is in complete agreement with earlier studies of the reaction.<sup>2</sup>

Neglecting chain terminating reactions between radicals, the following relationships should hold among quantities of products formed:  $CH_4 = C_2H_6 + C_2H_4$ ;  $H_2 = C_3H_6$ . To the extent that methyl radicals and hydrogen atoms participate in chain breaking steps, the quantities on the left of the above equations should be smaller than those on the right. This was found to be the case by 5 and 6 percent, respectively. The ratio  $(C_2H_4+C_3H_6)/C_2H_6$  is a measure of chain length, which in this experiment was about 23. The ratio  $6 \times C_{3}H_{6}/2 \times C_{2}H_{4}$  gives the relative reactivity of a secondary hydrogen to that of a primary in the reaction  $R+C_3H_8 \rightarrow RH+C_3H_7$ . This value is 2.6, which may be compared with the value 3.5 corresponding to a 2.0 kcal./mole difference in the activation energies for removal of secondary and primary hydrogen atoms at 525°C.3

<sup>3</sup> Reference 2, pages 318-319.