

INSERTION OF METHYLENE INTO THE CARBON-HYDROGEN BONDS OF THE C₁ TO C₄ ALKANES*

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SUMMARY

Relative rates of insertion of methylene into all the C-H bonds of methane, ethane, propane, n-butane and isobutane have been measured. These molecules react in the ratios 1:2.52:3.32:4.28:3.89. When combined with the absolute reaction rate of $1.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ for methane, rates of 4.8, 6.3, 8.1 and $7.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ are obtained, respectively, for ethane, propane, n-butane and isobutane. Insertion at secondary carbons in propane and n-butane is favored by a factor of 1.29–1.31 over primary C-H insertion in these compounds; insertion at the tertiary position in isobutane is favored by a factor of 1.33 over that at the primary position. These results can be explained in terms of the ability of methylene to exhibit considerable discrimination in insertion reactions, based on differences in bond energy and steric effects. Both nitric oxide and carbon monoxide are shown to be effective in suppressing reaction products attributed to the reactions of triplet methylene.

INTRODUCTION

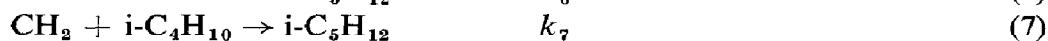
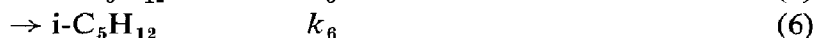
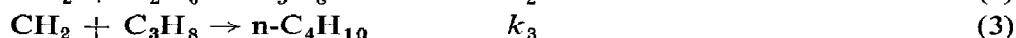
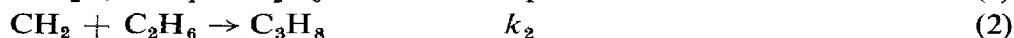
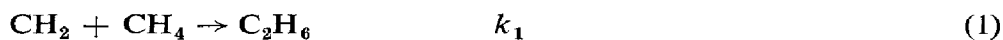
The reaction of methylene with the paraffin gases has been the subject of numerous studies in recent years. Methods for isolating the reactions leading to insertion products, now usually attributed to singlet methylene, include the addition of small quantities of oxygen¹ or nitric oxide^{2,3} to the reaction mixture to scavenge triplet methylene and alkyl radicals. More recently it was also discovered that carbon monoxide is more reactive towards triplet than singlet methylene⁴.

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Under properly chosen conditions⁵ it may be added to the reactant mixture to remove the triplet preferentially, and so allow the study of reactions of the singlet.

The recently reported absolute reaction rate of singlet methylene with methane⁶ has given added import to the measurement of relative reaction rates for this molecule. If a self-consistent set of relative rates is determined, including that of methane, absolute rates can be assigned to all. The present work is a report on the relative insertion rates of methylene into the C-H bonds of methane, ethane, propane, n-butane and isobutane. The hydrocarbon pairs whose relative reaction rates were sought are methane/n-butane, ethane/isobutane, and ethane/n-butane. The set was completed by making use of the previously published results of Halberstadt and McNesby² for the pair methane/propane. In all the above cases a small quantity of nitric oxide (1 to 10%) was added to the reaction mixture to act as a radical scavenger. Redundant information was obtained by studying the hydrocarbon pair propane/n-butane in the presence of nitric oxide as well as in the presence of carbon monoxide acting as a triplet methylene scavenger. The following set of reactions will establish the nomenclature used throughout this paper.



The above equations are meant to represent only those reactions of methylene leading to insertion products. Abstraction reactions will not be discussed since their products are eliminated by the presence of nitric oxide or carbon monoxide in the reactant mixture.

EXPERIMENTAL

A conventional mercury-free glass high vacuum system was used for storage and transfer of gases. That portion of the system that came in contact with gas mixtures was fitted with greaseless stopcocks equipped with polytetrafluoroethylene plugs. The reaction vessel was a quartz cylinder 100 mm in length and 50 mm in diameter. Gases were circulated through the photolysis chamber with a polytetrafluoroethylene-coated magnetic stirring bar contained in a glass chamber adjacent to the quartz reaction cell. The photolysis source was a Hanovia 100 W medium pressure mercury lamp. The region peaking at 313 nm was isolated using a combination of chemical and glass filters⁷. Samples for analysis were removed by expansion into an evacuated gas-tight syringe for transfer and injection into a gas chromato-

graph. Analyses were made as previously described^{2,8}, using a 30 ft × 1/4 in. column of squalane on firebrick.

Matheson research grade methane was used; it contained a trace of ethane, for which corrections were made in the analysis. Ketene and other hydrocarbons were prepared and purified as previously described^{2,8}. Matheson C. P. nitric oxide was purified by five successive distillations from a trap cooled in an isopentane-liquid nitrogen slush bath. Matheson C. P. carbon monoxide was purified by passing it through a trap cooled to liquid nitrogen temperature.

Predetermined pressures of gases were measured in a calibrated portion of the vacuum system, using a Wallace and Tiernan differential manometer that could be read to ± 0.2 Torr. These gases were trapped in a cold finger connected to the reaction vessel, at liquid nitrogen temperature, and thawed at a convenient time with the stirrer in operation. It was determined that, with the present appara-

TABLE 1

PRESSURES OF VARIOUS GASES USED IN THIS STUDY, IN TORR

Run	Ketene	Methane	Ethane	Propane	Isobutane	n-Butane	Nitric oxide	Total
9	10.1	—	174.9	—	175.0	—	4.3	364.3
10	9.9	—	174.9	—	175.1	—	3.9	363.8
11	9.9	—	174.8	—	174.8	—	10.1	369.6
12	9.9	—	45.0	—	44.9	—	1.3	101.1
13	10.1	—	74.8	—	74.9	—	2.1	161.9
14	10.1	—	41.6	—	42.0	—	1.3	95.0
15	10.2	—	75.1	—	74.9	—	2.0	162.2
16	10.1	—	125.0	—	125.0	—	3.0	263.1
17	10.2	—	125.0	—	124.8	—	2.7	262.7
22	20.2	—	250.0	—	250.1	—	7.6	527.9
23	20.0	—	350.0	—	353.6	—	9.9	733.5
24	20.0	—	349.7	—	348.9	—	10.5	729.1
26	20.1	—	180.2	—	—	180.2	11.5	392.0
27	21.2	—	173.3	—	—	174.3	10.9	379.7
28	21.3	88.4	—	—	—	89.5	10.5	209.7
29	23.1	89.3	—	—	—	90.4	10.1	212.9
30	23.1	50.5	—	—	—	49.9	11.0	134.5
31	20.1	50.1	—	—	—	48.7	10.9	129.8
32	20.1	349.1	—	—	—	348.9	10.0	728.1
33	19.9	350.5	—	—	—	350.6	3.7	724.7
34	20.3	233.3	—	—	—	233.7	9.8	497.1
35	20.5	232.9	—	—	—	233.1	9.7	496.2
37	20.3	—	—	135.5	—	135.3	9.8	300.9
38	20.2	—	—	132.9	—	133.4	10.0	296.5
39	20.3	—	—	95.4	—	95.3	197.4 ^a	408.4
40	20.3	—	—	101.1	—	102.2	200.8 ^a	424.4

^a Carbon monoxide added to mixture instead of nitric oxide.

tus, a mixing time of 1.5 h was necessary for the mixture to attain homogeneity if the total pressure was below $\frac{1}{2}$ atm, and 2 h were needed for pressures above this level. Separate experiments certified that no reaction took place during this mixing time so long as the shutter was in place between the reaction vessel and the optical train. Nevertheless a dark sample was always removed for analysis before the shutter was opened for any run to assure that the mixture was uniform, and to allow for corrections necessary due to the presence of trace impurities in some of the hydrocarbons. Usual irradiation time was 1 h, and the extent of reaction was normally less than 0.1% with respect to the hydrocarbons. The reaction vessel was kept at ambient temperature, $31 \pm 1^\circ\text{C}$ during photolysis. The gaseous mixtures studied are listed in detail in Table 1.

RESULTS

In order to complete the set of reactants to include all the C_1 to C_4 paraffins in conjunction with previous work, it was necessary to study the reactant pairs: methane/n-butane, ethane/n-butane and ethane/isobutane. The pair propane/n-butane was studied in order to provide an internal check on the method. Since all runs were made in the presence of nitric oxide or carbon monoxide, none of the products usually attributed to abstraction by methylene, or insertion followed by decomposition into alkyl radicals and subsequent free radical reactions were observed. This, together with demonstration of complete stabilization of insertion products, greatly facilitated analysis and interpretation of results; product distributions, normalized to equal concentrations of reactants, could be taken as a direct measure of the relative rates of insertion into the respective C-H bonds. The individual reactant pairs will now be discussed separately.

Methane/n-butane

It has previously been shown^{1,2} that insertion of methylene into methane results in the formation of vibrationally excited ethane that is not entirely stabilized at pressures up to one atm. Insertion into propane and larger molecules undoubtedly also gives excited products; however, these are essentially stabilized completely at pressures above a few Torr⁹. The intermediate case of ethane will be considered shortly. In the photolysis of mixtures of methane and n-butane the products are ethane, isopentane and n-pentane. At pressures above 100 Torr we will expect to see a product distribution similar to that observed in the methane/propane case. All of the product pentane will be stabilized but some of the ethane will decompose, the methyl radical so formed being scavenged by the nitric oxide; it will, therefore, not appear as a gaseous product. As the pressure is raised, a successively larger fraction of the ethane is stabilized, and a plot of the ratio of ethane to n-pentane observed in the products as a function of pressure should increase with increasing pressure, tending to a constant value or high-pressure limit. It is, in fact, the uni-

TABLE 2

PRODUCT RATIOS FOR RUNS WITH METHANE AND n-BUTANE, NORMALIZED TO A REACTANT RATIO OF UNITY

Pressure (Torr)	Ethane/ n-Pentane k_1/k_5	Ethane/ Total pentane $k_1/(k_5 + k_6)$	Isopentane/ n-Pentane k_6/k_5
728.1	0.34	0.19	0.87
724.7	0.33	0.18	0.86
497.1	0.29	0.16	0.87
496.2	0.30	0.16	0.87
212.9	0.23	0.12	0.89
209.7	0.22	0.12	0.88
134.5	0.16	0.08	0.87
129.8	0.15	0.08	0.88
	$(0.43 \pm 0.02)^a$	$(0.23 \pm 0.01)^a$	0.87 ± 0.01

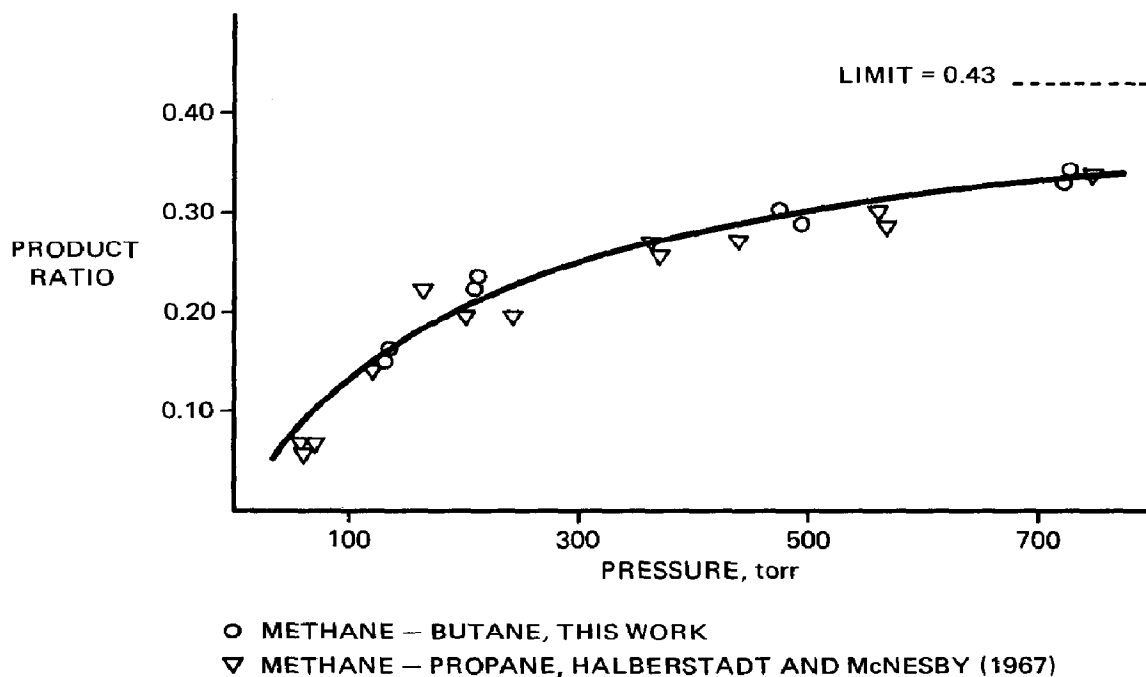
^a High pressure limit.

Fig. 1. Product ratios as a function of pressure for the photolysis of ketene/methane/n-butane/NO and ketene/methane/propane/NO mixtures. ○, Ethane/n-pentane; ▼, ethane/n-butane from ref. 2. The curve is that which corresponds to an excess energy of the methylene of about 2.5 kcal/mole as determined in ref. 2.

molecular decomposition curve for ethane that has been chemically activated by the insertion of methylene into methane.

Table 2 presents the experimental results, and Fig. 1 shows a plot of the ratio of ethane to n-pentane as a function of pressure. It is seen to be identical to the curve for the ethane to n-butane ratio vs. pressure in the reaction of methylene

with methane/propane mixtures in the presence of NO^2 . The assumption that butane and pentane products are fully stabilized at the pressures under study is thereby justified. The implications of the unimolecular dissociation of ethane thus formed, with regard to the energy of the methylene, have been discussed previously². Despite the recent redetermination of the heat of formation of ketene¹⁰ and the re-examination of the theoretical models for ethane decomposition¹¹, the estimate of 2.5 kcal for the energy separation between the first excited singlet and ground state triplet does not require revision. A more definitive statement will have to await the publication of the results of the chemical activation study of ethane by Simons and co-workers¹², but it appears that the estimate will not change by more than a factor of two, putting it far outside the range of the recently published theoretical values of 0.91¹³ and 0.88 eV¹⁴.

The extrapolated high-pressure value (indicated by the subscript ∞) that is obtained for the relative rate of insertion into methane and the primary C-H bond in n-butane is $(k_1/k_5)_\infty = 0.43 \pm 0.02$. An additional datum obtained from Table 2 is the relative rate of insertion into the primary and secondary C-H bonds in n-butane: $k_5/k_6 = 1.14 \pm 0.01$. (Error limits are given as standard deviations when four or more measurements of a quantity are available, and average deviations in other cases; the value ± 0.02 for the high pressure limit is estimated.) It may be noted that the third column in Table 2 provides additional check on the precision of the experiments since it can be derived independently from data in the second and fourth columns, while the numbers listed were computed directly from the product analyses. The high-pressure limit for the ratio $[k_1/(k_5 + k_6)]_\infty$ is calculated to be 0.23 ± 0.01 .

Ethane/isobutane

Previous work with ethane² indicated that the excited propane formed upon methylene insertion was not completely stabilized at pressures below 200 Torr, though the high pressure limit for its stabilization was below 1 atm. This is also suggested by the work of Rabinovitch and Setser⁹, and Growcock *et al.*¹² from which we can calculate that the unimolecular rate constant for propane decomposition has reached $>98\%$ of its high pressure value at 100 Torr and 600 K. A series of runs with pressures ranging from 95 Torr to 1 atm was therefore made with the ethane/isobutane mixture. Results are presented in Table 3. While the scatter in these results is somewhat greater than desirable, there is no obvious trend with pressure as was found with methane as the reactant. A linear least squares analysis of the propane/iso pentane ratio as a function of pressure yields a line parallel to the abscissa with an intercept at a value for the ratio of 0.72. The average value obtained from the Table is 0.74 ± 0.04 ; this value is more consistent with the other results in this study and is the one used in calculations involving this quantity. Once again an intramolecular ratio can be obtained, that for the relative rate of insertion at the primary and tertiary positions in isobutane: $k_7/k_8 = 6.70 \pm 0.36$. The rate constants for reaction with ethane and isobutane are in the ratio $k_2/(k_7 + k_8) = 0.65 \pm 0.03$.

TABLE 3

PRODUCT RATIO FOR RUNS WITH ETHANE AND ISOBUTANE, NORMALIZED TO A REACTANT RATIO OF UNITY

Pressure (Torr)	Propane/ Isopentane k_2/k_7	Propane/ Total pentane $k_2/(k_7 + k_8)$	Neopentane/ Isopentane k_8/k_7
733.5	0.71	0.63	0.15
729.1	0.80	0.69	0.14
527.9	0.75	0.67	0.14
369.6	0.76	0.65	0.17
364.3	0.76	0.67	0.15
363.8	0.79	0.68	0.15
263.1	0.72	0.63	0.15
262.7	0.73	0.63	0.14
162.2	0.69	0.61	0.14
161.9	0.72	0.63	0.15
101.1	0.75	0.64	0.16
95.0	0.71	0.63	0.15
	0.74 ± 0.04	0.65 ± 0.03	0.15 ± 0.01

Ethane/n-butane

Having established that essentially all the propane formed by methylene insertion into ethane is stabilized above 100 Torr, it was deemed unnecessary to make a complete pressure-dependent study in this case. Instead, only two runs

TABLE 4

PRODUCT RATIOS FOR RUNS WITH ETHANE/n-BUTANE AND PROPANE/n-BUTANE MIXTURES, NORMALIZED TO A REACTANT RATIO OF UNITY

A. Ethane and n-butane

Pressure	Propane/ n-Pentane k_2/k_5	Propane/ Total pentane $k_2/(k_5 + k_6)$	Isopentane/ n-Pentane k_6/k_5
392.0	1.07	0.57	0.87
379.7	1.09	0.58	0.88
	1.08 ± 0.01	0.58 ± 0.01	0.88 ± 0.01

B. Propane and n-butane

Pressure	Isobutane/ n-Pentane k_4/k_5	Isobutane/ Total pentane $k_4/(k_5 + k_6)$	Isopentane/ n-Pentane k_6/k_5
300.9	0.44	0.23	0.88
296.5	0.45	0.24	0.88
424.4 ^a	0.44	0.24	0.88
408.4 ^a	0.43	0.23	0.87
	0.44 ± 0.01	0.24 ± 0.01	0.88 ± 0.01

^a Carbon monoxide added to mixture instead of nitric oxide.

were made at a pressure of $\frac{1}{2}$ atm, which is within 99% of the high-pressure limit¹². Results are presented in Table 4. The relative rate of insertion into the primary bonds of ethane and n-butane is seen to be 1.08 ± 0.01 . This is slightly greater than the value of 1.00 estimated previously² from two runs at pressures that were below the high-pressure limit for propane stabilization. Ethane and n-butane react in the ratio $k_2/(k_5 + k_6) = 0.58 \pm 0.01$.

Propane/n-butane

The relative value of all the rate constants k_1 to k_8 can be determined from the results presented above, in conjunction with the work of Halberstadt and McNesby². The data obtained with the present mixture of gases provide an independent check on the results, since they allow the direct comparison of insertion into propane and n-butane without invoking the high pressure limit of the runs with methane. In this instance, isobutane is the only product resulting from reaction with propane that is measured, since the trace of product n-butane is lost in the very much larger quantity of n-butane reactant. The relative rate of insertion into the primary and secondary positions in propane is well known², however, so that measurement of the isobutane peak alone is sufficient. Results are shown in Table 4 for two runs in which nitric oxide was added as the radical scavenger. Two additional runs were made, with this hydrocarbon mixture, in which a relatively large quantity of carbon monoxide replaced the nitric oxide. The results are shown as the last two entries in Table 4, and are seen to be identical to those in which nitric oxide was present. Averaging all four values gives 0.44 ± 0.01 for the relative rate of insertion into the secondary C-H bond in propane and the primary bond in n-butane. The value of 1.14 ± 0.02 for insertion at the primary and secondary positions in n-butane is identical to that measured earlier. Using the value of $k_4/k_3 = 0.43^2$ we calculate the relative rates of reaction of propane and butane, $(k_3 + k_4)/(k_5 + k_6) = 0.80 \pm 0.02$. We have thus shown by direct comparison that, although the mode of action of nitric oxide and carbon monoxide in mixtures containing singlet and triplet methylene may be quite different,^{4,5,15,16} their presence can lead to identical results under properly chosen conditions.

DISCUSSION

Sufficient data are now available to establish the relative reaction rates for methylene insertion into the C-H bonds of all the C_1 to C_4 paraffins. It is informative to consider these reactions on a "per molecule" basis as well as "per bond". As shown in Table 5, the relative rates of reaction of these compounds do not differ greatly from one another. However, the deviation from the statistical ratio must be noted. Methylene formed by ketene photolysis at 313 nm in the gas phase does not insert indiscriminately into all C-H bonds. It is quite capable of distinguishing between the primary bonds of methane and ethane, which have bond

TABLE 5

RATE CONSTANTS FOR INSERTION OF METHYLENE INTO THE C₁ TO C₄ PARAFFINS, PER MOLECULE

Molecule	Relative rate			Absolute rate (cm ³ molecule ⁻¹ sec ⁻¹)	
	This work	Ref. 20 ^a	Statistical	This work	Ref. 5
Methane	1.0	1.0	1	1.9×10^{-12b}	
Ethane	2.52	2.2	1.5	4.8×10^{-12}	
Propane	3.32	3.3	2	6.3×10^{-12}	4.4×10^{-12}
n-Butane	4.28	4.1	2.5	8.1×10^{-12}	8.0×10^{-12}
Isobutane	3.89	3.5	2.5	7.4×10^{-12}	

^a Based in part on the results of Halberstadt and McNesby².^b Braun *et al.*⁶.

energies of 104 and 98 kcal respectively¹⁷. It also favors insertion at the more highly substituted positions and may even be influenced somewhat by steric considerations, as will be discussed shortly. Using the value of Braun *et al.*⁶ for the absolute rate of insertion of methylene into methane, we can assign absolute rates for insertion into the other compounds; these are also listed in Table 5. While they do not represent the overall reaction rates of methylene with these hydrocarbons, since the products resulting from the reaction of the triplet have been specifically excluded, they probably represent the initial reaction rates quite well because of the considerably slower reaction of the triplet with hydrocarbons^{6,18}.

One of the more interesting results of this study concerns the differences in insertion rate of methylene into various individual C-H bonds. The quantities have been computed and are tabulated in Table 6, where they are also compared with recently published values. Extraction of information from this Table can be illustrated for the case of relative insertion rates in ethane and the primary position in isobutane. The number of primary C-H bonds in these molecules is in the ratio of 6/9, but the measured value of k_2/k_7 is 0.74. This means that the primary bond in ethane is $0.74 \times 9/6 = 1.11$ times as reactive as that in isobutane.

As we examine individual values, the one that is the most arresting is the large degree of discrimination shown for the primary bond in methane relative to the other primary bonds. Methylene insertion is 68% faster, per bond, for ethane than for methane, probably reflecting the difference in their bond energies as noted earlier. It appears further that the maximum rate is achieved with ethane and that the primary bonds in the larger molecules react at the same rate within experimental error. The reactivity ratios for ethane relative to n-butane and isobutane definitely seem to be larger than unity, outside the range of experimental error. These results are supported by those of Growcock *et al.*¹² who studied the reaction of methylene with ethane and butane, and those of Herzog and Carr¹⁹ who studied the rate of methylene insertion at the primary, secondary and tertiary positions in isopentane. In each case, that primary C-H bond that is more accessible is favored over the more hindered one. The same observation has been made previously by Hase and

TABLE 6
RELATIVE RATE CONSTANTS FOR METHYLENE INSERTION, PER BOND

Reactants	Number ratio	Observed ratio	Reactivity ratio	Other workers
A. Insertion at primary C-H				
Ethane	1.50	$\frac{k_2}{k_1} = 2.52$	1.68	
Methane				
Ethane	1	$\frac{k_2}{k_5} = 1.08$	1.08	1.12 ± 0.09 ^a
n-Butane				
Ethane	0.667	$\frac{k_2}{k_7} = 0.74$	1.11	
Isobutane				
Propane	1	$\frac{k_3}{k_5} = 1.02$	—	
n-Butane				
Isopentane C ₁	—	—	—	1.06 ± 0.02 ^b
Isopentane C ₄				
B. Secondary vs. primary C-H insertion				
Propane	0.333	$\frac{k_4}{k_3} = 0.43^e$	1.29	1.26 ± 0.03 ^d 1.17–1.20 ^e
n-Butane	0.667	$\frac{k_6}{k_5} = 0.88$	1.31	1.35 ^f
Isopentane	—	—	—	1.22 ± 0.03 ^b
C. Tertiary vs. primary C-H insertion				
Isobutane	0.111	$\frac{k_8}{k_7} = 0.15$	1.33	1.37–1.38 ^e
Isopentane	—	—	—	1.42 ± 0.07 ^b

^a Growcock *et al.*¹².

^b Herzog and Carr¹⁹.

^c Halberstadt and McNesby².

^d Bell²⁸.

^e Johnson *et al.*²⁹.

^f Simons *et al.*³⁰; Dees and Setser⁵.

Simons²⁴ who noted that neopentane and n-butane have essentially the same reactivity towards methylene insertion, in spite of the fact that the former has a larger number of active sites. Still further evidence for effect of steric hindrance comes from a comparison of the reactivity ratios in Table 6 (B and C). While hydrogen abstraction at a tertiary carbon proceeds with considerably more facility than at a secondary carbon^{21, 22}, insertion at the tertiary position in isobutane takes place at the same rate, relative to primary insertion, as at the secondary position in butane and propane. This observation would tend to argue against the proposed mechanism of DeMore and Benson²³ in which insertion and abstraction reactions of methylene both begin with an incipient abstraction. Rather, it favors direct attack on the C-H bond itself as suggested by Doering and Prinzbach²⁴, or a combination of the two mechanisms as suggested by the theoretical study of Dobson *et al.*²⁵. This mechanism also has gained support recently from the liquid

phase work of Roth²⁶. For the slightly more open structure of isopentane (C–C is 1.54 Å while C–H is 1.10 Å)²⁷, Herzog and Carr¹⁹ find insertion at the tertiary carbon a little faster relative to primary insertion at C₁. We are led to conclude that methylene insertion does not take place as indiscriminately as has been believed. Nor are the differences in reaction attributable solely to differences in the bond energy of various C–H bonds; energetic and steric considerations are both important. In the case of isobutane the favorable difference of 3.5 kcal/mole²² is counterbalanced by the greater hindrance in the accessibility of the bond. As a result, insertion at the tertiary bond proceeds at about the same rate as that into the secondary bonds of propane and n-butane.

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