Insertion of Methylene into Alkanes

M. L. Halberstadt[1] and J. R. McNesby

Contribution from the National Bureau of Standards, Washington, D. C. 20234.
Received March 6, 1967

Abstract: Ketene was photolyzed in the presence of mixtures of pairs of hydrocarbons with NO added to scavenge alkyl radicals. The relative rates of insertion for methane : primary propane : secondary propane are 0.43 : 1.0 : 0.43, and for ethane: primary *n*-butane: secondary *n*-butane they are 1.0: 1.0: 0.88. In the case of isobutane, the relative rates of insertion into primary and tertiary bonds are 1.0: 0.13. When effects of recombination of alkyl radicals formed by abstraction of H by CH_2 are eliminated by the NO scavenger, insertion is seen to be nearly indiscriminate. It is suggested that the singlet CH_2 lies about 2.5 kcal mole^{-1} above the ground-state triplet.

The measurement of the relative rates of insertion of CH_2 into CH bonds in hydrocarbons can, in principle, be accomplished by measuring the relative rates of formation of the stable hydrocarbon products. As an example of such a measurement, consider the reaction of CH_2 with a mixture of methane and propane. The reactions of interest are

$$CH_2 + CH_4 \longrightarrow C_2H_6 \tag{1}$$

$$CH_2 + C_3H_8 \longrightarrow n\text{-}C_4H_{10} \tag{2}$$

$$CH_2 + C_3H_8 \longrightarrow i\text{-}C_4H_{10} \tag{3}$$

If these were the only reactions affecting the products C_2H_6, n-C_4H_{10}, and i-C_4H_{10}, a simple measurement of the products at small conversions would give the relative rate constants directly. There are two well-known complications, however, and these may be delineated.

(1) The products are excited by the exothermicities of the reactions and may, therefore, dissociate into free radicals.

$$C_2H_6^* \longrightarrow 2CH_3 \tag{4}$$

$$n\text{-}C_4H_{10}^* \longrightarrow CH_3 + n\text{-}C_3H_7 \tag{5}$$

$$n\text{-}C_4H_{10}^* \longrightarrow 2C_2H_5 \tag{6}$$

$$i\text{-}C_4H_{10}^* \longrightarrow CH_3 + i\text{-}C_3H_7 \tag{7}$$

The subsequent association reactions of the free radicals so formed may be expected to produce C_2H_6, n-C_4H_{10}, and i-C_4H_{10} in proportions quite different from those resulting from the reactions of interest (eq 1–3).

(2) As shown previously[2] for the case of the reaction of CH_2 with isobutane at high temperature, direct abstraction may also occur, probably by the triplet state of CH_2. For the system presently under consideration, methyl, *n*-propyl, and isopropyl radicals are produced which may, by association with methyl, form the same products resulting from reactions 1–3.

Because of these two complications, the experiments to be described were carried out (a) at increasing pressures in an attempt to stabilize all alkanes formed in reactions 1–3 and (b) in the presence of enough NO to scavenge all alkyl radicals produced by abstraction of hydrogen by CH_2. The source of CH_2 was photolysis of ketene at 3130 A. The pairs of hydrocarbons used were methane + propane and ethane + *n*-butane. Some experiments were also done on the photolysis of ketene in the presence of isobutane.

Experimental Section

Research grade methane was purified by trapping it on molecular sieve 5A at liquid nitrogen temperature and retaining the portion released between −50 and −10° on warm-up. The ethane impurity was negligibly small relative to the amounts of ethane produced in the reaction. Other hydrocarbons were purified by gas chromatography and contained no significant impurity. Ketene was prepared by pyrolysis of acetic anhydride[3] and contained, as the only hydrocarbon impurity, a small amount of allene. Photolysis of this ketene did not produce ethane or butane. Mixtures of ketene, methane, and propane were prepared using a quartz spiral manometer as the pressure gauge. No grease, oil, wax, or other organic material was present in the gas-handling system except for polytetrafluoroethylene seats in the metal vacuum valves. Photolyses were carried out within a quartz reaction cell using a medium-pressure mercury arc from which the 3130-A line was selected by means of an interference filter. During photolysis, mixtures were circulated by means of a magnetically operated pump with a polytetrafluoroethylene piston. Analyses were made by gas chromatography using a squalane-on-firebrick column. Areas under peaks were measured and converted to relative numbers of moles using calibration factors separately determined. All reactions were carried out to less than 1% conversion of the hydrocarbon. The amount of NO added to the mixture was about 5% of that of the ketene. While reaction of free radicals with NO–radical adducts has been proposed as a source of alkanes in pyrolytic systems,[4] it is well known that in room-temperature photolyses the addition of NO or O_2 results in the elimination of free-radical association products.[5,6]

Results and Discussion

Ketene–Propane–Methane System. (a) Insertion of CH_2 into Methane and the Primary CH Bond in Propane. In the present context, we consider only the ethane and *n*-butane products whose amounts are controlled by the following mechanism.

$$CH_2 + CH_4 \longrightarrow C_2H_6^*\ (E^*) \quad \Delta H^\circ{}_0 = -93.5\ \text{kcal mole}^{-1}\,{}^{7,8} \tag{1}$$

$$CH_2 + C_3H_8 \longrightarrow n\text{-}C_4H_{10}^*\ (B)^* \tag{2}$$

$$E^* \longrightarrow 2CH_3 \xrightarrow{NO} X \tag{8}$$

---

(1) National Academy of Sciences–National Research Council Postdoctoral Resident Research Associate, 1963–1965.

(2) M. L. Halberstadt and J. R. McNesby, *J. Chem. Phys.*, **45**, 1666 (1966).

(3) G. J. Fischer, A. F. McLean, and A. W. Schnizer, *J. Org. Chem.*, **18**, 1055 (1953).

(4) B. W. Wojciechowski and K. J. Laidler, *Trans. Faraday Soc.*, **59**, 369 (1963).

(5) J. A. Bell and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **84**, 3417 (1962).

(6) (a) S. G. Lias and P. Ausloos, *J. Chem. Phys.*, **43**, 2748 (1965); (b) A. Scala and P. Ausloos, *J. Phys. Chem.*, **70**, 260 (1966).

(7) Using ΔH_f° = 93.0 kcal mole^{-1} for CH_2 based upon the 25° value of 93.9 given in ref 8a (assuming the ground-state triplet CH_2 was the species ionized in that work) and the respective values −16.0 and −16.5 for methane and ethane.[8b]

(8) (a) V. H. Dibeler, M. Krauss, R. M. Reese, and F. N. Harlee, *J. Chem. Phys.*, **42**, 3791 (1965); (b) National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1965.

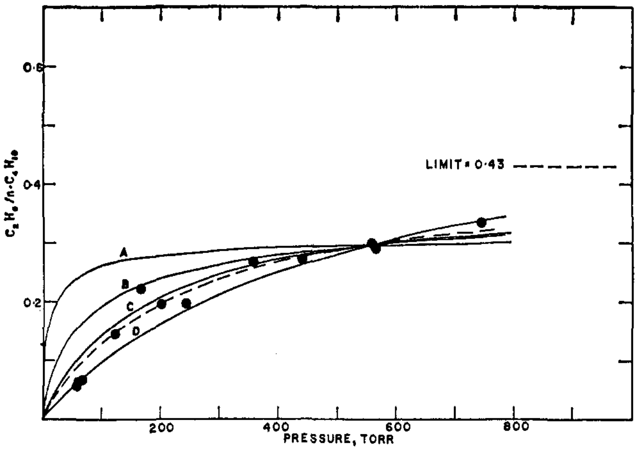

Figure 1. Fitting curves for $\langle\epsilon^\dagger\rangle$ to the data. Photolysis of ketene in the presence of equimolar mixture of methane and propane in the presence of NO. Curves A, B, C, D correspond respectively to $\langle\epsilon^\dagger\rangle$'s of 5.0, 9.5, 12.2, 15.7 kcal. The best fit to experimental points is chosen as the dashed line for which $\langle\epsilon^\dagger\rangle$ = 13.0 kcal.

$$B^* \longrightarrow R + R' \xrightarrow{NO} X \qquad (9)$$

$$E^* + M \longrightarrow E + M \qquad (10)$$

$$B^* + M \longrightarrow B + M \qquad (11)$$

Application of the stationary-state principle for the assured[9,10] condition $k_9 \ll k_{11}[M]$, where [M] is the concentration of an "average" quenching gas, M, leads to the following result under the condition that the methane and propane concentrations are equal.

$$[C_2H_6]/[n\text{-}C_4H_{10}] = (k_1/k_2)\{k_{10}[M]/(k_8 + k_{10}[M])\} \qquad (I)$$

The term in the braces signifies the fraction of initially formed $C_2H_6{}^*$ that is stabilized, *i.e.*, the Rabinovitch notation,[11] $S/(S + D) = k_{10}[M]/(k_8 + k_{10}[M])$. Complete stabilization, $S/(S + D) = 1$, is achieved when $k_{10}[M] \gg k_8$. In this circumstance eq I becomes

$$[C_2H_6]/[n\text{-}C_4H_{10}] = k_1/k_2 \qquad (II)$$

When [M] becomes sufficiently large (increasing pressure), the ratio $[C_2H_6]/[n\text{-}C_4H_{10}]$ should become constant and equal to k_1/k_2. The data presented in Figure 1 show that this condition is not reached even at 745 torr. Because the latter pressure approaches the practical upper limit in the present experiments, an alternative treatment of the data is needed to evaluate k_1/k_2. The procedure of Rabinovitch and co-workers has been developed specifically for the case of decomposition of excited ethane[9,10] and is directly applicable to the present results. The RRKM theory[12,13] of unimolecular reactions forms the basis of the procedure in which the rate constant for decomposition of an excited molecule is calculated from a quantum statistical transition-state model as a function of $\langle\epsilon^\dagger\rangle$, the active energy of the complex above $\langle\epsilon_0\rangle$, the critical reaction energy at 0°K. For $C_2H_6{}^*$ decomposition $\langle\epsilon_0\rangle = 85$ kcal. The evaluation of $\langle\epsilon^\dagger\rangle = \langle\epsilon\rangle - \langle\epsilon_0\rangle$ is obtained by identifying $\langle\epsilon\rangle$ with ΔH°_0 plus the thermal energy of about 2.0 kcal mole^{-1}. The value of $\langle\epsilon\rangle$ for reaction of a thermal CH_2 with methane is $-\Delta H^\circ_0 = \langle\epsilon\rangle = 93.5$ kcal mole^{-1}. Thus, $\langle\epsilon^\dagger\rangle = 93.5 + 2.0 - 85.0 = 10.5$ kcal mole^{-1}. For various $\langle\epsilon^\dagger\rangle$, $S/(S + D)$ as a function of pressure has been tabulated[10] and used to obtain the curves shown in Figure 1 according to eq III.

$$[C_2H_6]/[n\text{-}C_4H_{10}] = (k_1/k_2)[S/(S + D)] \qquad (III)$$

In order to present the curves in Figure 1, it was necessary to multiply the calculated $S/(S + D)$ by a number (presumably k_1/k_2) which gives the observed $[C_2H_6]/[n\text{-}C_4H_{10}]$ at 560 torr. Now, with a single point (560 torr) consistent with each of the family of curves in Figure 1, it is only necessary to select the curve which most closely approximates the data. The best fit is $12.2 < \langle\epsilon^\dagger\rangle < 15.7$ kcal mole^{-1}, and a probable value of 13.0 kcal mole^{-1} is selected. This result is to be compared with the value $\langle\epsilon^\dagger\rangle = 10.5$ kcal mole^{-1} just calculated from the thermochemistry. In order for the thermochemical value to agree with the observed $\langle\epsilon^\dagger\rangle = 13.0$ kcal mole^{-1}, CH_2 must carry over some 2.5 kcal mole^{-1} excess energy from the primary photochemical act. Now, the 3130-A photon corresponds to 90.8 kcal mole^{-1}, and the energy required to rupture the ketene molecule at 25°[8b] is about 81.9 kcal mole^{-1}. Evidently, in the act of insertion, CH_2 carries over about 2.5 of the 8.9 kcal mole^{-1} available to CO and CH_2.

The limiting high-pressure value of k_2/k_1 for $\langle\epsilon^\dagger\rangle = 15.7$ kcal mole^{-1} is equal to 1.67, and for $\langle\epsilon^\dagger\rangle = 12.2$ kcal mole^{-1}, $k_2/k_1 = 2.50$. For the selected value of $\langle\epsilon^\dagger\rangle = 13.0$ kcal mole^{-1}, $k_2/k_1 = 2.33$. For insertion into the six CH bonds in propane relative to the four primary CH bonds in methane, the insertion ratio is somewhat more than the value (1.50) toward which the observed ratio should tend[9] in the absence of discrimination when effects of abstraction are eliminated by scavenging free radicals. For the case of insertion into propane in the presence of O_2, a statistical secondary to primary ratio (0.33) is approached rather closely (experimental value 0.40).[9] In the presence of NO, as will be discussed later, the present study gives a ratio of 0.43.

Our results may be expressed in terms of the rate constant for stabilization of excited ethane *vs.* that for its dissociation. Since the value of $[C_2H_6]/[n\text{-}C_4H_{10}]$ is 0.30 at 560 torr and the limiting high-pressure value is 0.43, $S/(S + D) = 0.70 = k_{10}[M]/(k_{10}[M] + k_4)$. It follows that $k_4/k_{10} = 240$ mm.

Bell and Kistiakowsky[5] investigated the reaction of CH_2 from diazomethane photolysis with CD_4 and obtained a value of $k_{4D}/k_{10D} = 26$ mm. If one includes a deuterium isotope correction suggested by Setser and Rabinovitch,[9,10] this becomes $k_4/k_{10} \sim 65$ mm. The result means that $\langle\epsilon^\dagger\rangle \sim 9$ kcal. While there have been a number of arguments advocating various values of the heat of formation of diazomethane ranging from 49 to 103 kcal,[14-16] no agreement on the magnitude of this quantity has been reached. Further, the active wavelengths in the work of Bell and Kistiakowsky are not given, and it is not possible to compare their rate constant ratios with ours. On the assumption that the stabilization rate constant is 10^{14} mole^{-1} cc sec^{-1},

---

(9) G. Z. Whitten and B. S. Rabinovitch, *J. Phys. Chem.*, **69**, 4348 (1965).

(10) B. S. Rabinovitch and D. W. Setser, *Advan. Photochem.*, **3**, 1 (1964).

(11) D. W. Setser and B. S. Rabinovitch, *J. Chem. Phys.*, **40**, 2427 (1964).

(12) R. A. Marcus, *ibid.*, **20**, 352, 359 (1952); **43**, 2658 (1965).

(13) O. K. Rice, *J. Phys. Chem.*, **65**, 1588 (1961).

(14) G. S. Paulett and R. Ettinger, *J. Chem. Phys.*, **39**, 825, 3534 (1963); **41**, 2557 (1964).

(15) J. A. Bell, *ibid.*, **41**, 2556 (1964).

(16) J. C. Hassler and D. W. Setser, *J. Am. Chem. Soc.*, **87**, 3793 (1965).

$k_4 = 1.4 \times 10^9$ sec^{-1} for the decomposition of $C_2H_6^*$ in the present work.

(b) Insertion of CH_2 into Primary and Secondary CH in Propane. The insertion of CH_2 into the primary and secondary positions of propane results in *n*-butane and isobutane. As shown by Whitten and Rabinovitch, above 10 torr, there is no effect of pressure on the ratio isobutane/*n*-butane. Figure 2 presents these ratios obtained in the presence of NO and compares them with the high-pressure results of Whitten and Rabinovitch. The agreement is reasonably good above 40 torr where all values of the ratio fall within the range 0.41 ± 5%. The statistical value, of course, is 0.33. The consistently higher isobutane/*n*-butane ratio in the absence of NO (0.64 ± 0.01) may be attributed to discrimination in abstraction by CH_2 of secondary and primary hydrogen and an attending relative increase in the concentration of isopropyl radicals with which methyl radicals associate. While Whitten and Rabinovitch find no significant increase in the isobutane/*n*-butane ratio at high pressures in the absence of radical scavenger, they do report other evidence for abstraction reactions, *e.g.*, the appearance of hexanes even at pressures near 1 atm. Some of the results of other workers[17,18] are included in Figure 2, and it can be seen that their isobutane/*n*-butane ratios obtained in the absence of NO are in fair agreement with the present results, the Frey and Kistiakowsky ratios, and ours all falling in the range 0.60 ± 0.04.

Ketene–*n*-Butane–Ethane System. Table I shows the relative amounts of propane, isopentane, and *n*-pentane produced. The processes of interest are as follows.

$$CH_2 + C_2H_6 \longrightarrow C_3H_8 \quad \Delta H^\circ_0 = -98 \text{ kcal mole}^{-1} \qquad (12)$$

$$CH_2 + n\text{-}C_4H_{10} \longrightarrow CH_3CH(CH_3)CH_2CH_3 \qquad (13)$$

$$CH_2 + n\text{-}C_4H_{10} \longrightarrow n\text{-}C_5H_{12} \qquad (14)$$

The value of ϵ_0 is 82.7 kcal mole^{-1} [9,10] for the process

$$C_3H_8^* \longrightarrow CH_3 + C_2H_5 \qquad (15)$$

It follows that $\langle \epsilon^\dagger \rangle = 98 - 82.7 +$ the energy carried over by CH_2. If the latter is about 2.5 kcal mole^{-1} as in the case of reaction of CH_2 with CH_4, $\langle \epsilon^\dagger \rangle$ is about 17.8 kcal mole^{-1}. Under these conditions[10] about 90% of the excited propane is stabilized at 214 mm, the highest pressure recorded in Table I with NO present. It is possible to make only a rough estimate of k_{12}/k_{13}. If 90% of the propane is stabilized at 214 mm, the high-pressure limit for $C_3H_8/n\text{-}C_5H_{12}$ is about unity. Thus $k_{12}/k_{14} \sim 1.0$.

There is no effect of pressure or of ethane on the ratio $i\text{-}C_5H_{12}/n\text{-}C_5H_{12}$ in the presence of NO, and the high-pressure limit is achieved at all pressures giving $k_{13}/k_{14} = 0.88 \pm 0.02$. This result is somewhat higher than the statistical value of 0.67. In the absence of NO, again the $i\text{-}C_5H_{12}/n\text{-}C_5H_{12}$ ratio of 1.21 is substantially greater than in its absence.

Ketene–Isobutane System. Two quantitatively significant experiments were done with this mixture in the presence of about 2% NO. The result of interest is that neopentane/isopentane = 0.13 ± 0.02.

$$CH_2 + i\text{-}C_4H_{10} \longrightarrow (CH_3)_4C \qquad (16)$$

$$CH_2 + i\text{-}C_4H_{10} \longrightarrow CH_3CH_2CH(CH_3)_2 \qquad (17)$$

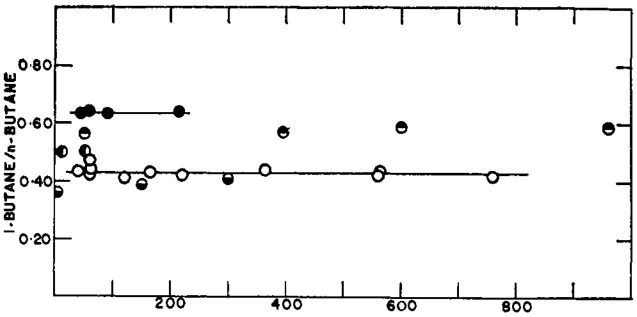

Figure 2. Insertion of CH_2 into the primary and secondary positions in propane.

Thus, $k_{16}/k_{17} = 0.13$, while the statistical value is 0.11. The results of these and other experiments done in the absence of NO are summarized in Table II.

Table I. Photolysis of Ketene Plus *n*-Butane and Ethane at 3130 A

Pressure, torr						
Ketene	*n*-Butane	Ethane	Methane	NO	$i\text{-}C_5H_{12}/n\text{-}C_5H_{12}$	$C_3H_8/n\text{-}C_5H_{12}$
22	22	0	0	0	1.21	. . .
22	19	19	0	0	1.27	1.26
22	19	19	0	0	1.17	1.04
21	35	35	0	0	1.20	1.26
22	107	107	0	0	1.17	1.10
23	16	0	17	0	1.25	. . .
22	30	0	17	0	1.23	. . .
22	37	0	38	0	1.23	. . .
22	103	0	108	0	1.19	. . .
22	22	0	0	0.9	0.90	. . .
22	20	20	0	0.8	0.89	0.86
21	96	97	0	1.7	0.86	0.97
63[a]	507[a]	0	0	0	0.92	. . .
88[a]	712[a]	0	0	0	0.88	. . .
50[b]	10–50[b]	0	0	0	0.93	. . .

[a] Reference 17. [b] Reference 18.

Table II. Photolysis of Ketene Plus Isobutane at 3130 A

Pressure, torr					
Ketene	Isobutane	Ethane	Methane	NO	$neo\text{-}C_5H_{12}/i\text{-}C_5H_{12}$
22	23	0	0	1.0	0.15
23	110	111	0	1.8	0.11
22	13	0	0	0	0.34
22	22	0	0	0	0.31
22	16	0	15	0	0.42
50	10–50	0	0	0	0.56

Table III shows that when alkyl radicals are removed by NO, insertion into CH bonds is nearly statistical in agreement with the early conclusions of Doering and his

Table III. Relative Rates of Insertion into CH Bonds

	$(k_n/k_1)^a$		
Reactant	Exptl	Statistical	Product ratio
C_3H_8	0.43	0.33	$i\text{-}C_4H_{10}/n\text{-}C_4H_{10}$
$n\text{-}C_4H_{10}$	0.88	0.67	$i\text{-}C_5H_{12}/n\text{-}C_5H_{12}$
$i\text{-}C_4H_{10}$	0.13	0.11	$neo\text{-}C_5H_{12}/i\text{-}C_5H_{12}$

[a] k_1 is the rate constant for insertion into the primary CH bonds, and k_n is that for insertion into the secondary or tertiary bond. The ratios are *not* per bond.

---

[17] H. M. Frey and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, 79, 6373 (1957).

[18] J. H. Knox and A. F. Trotman-Dickenson, *Chem., Ind.* (London), 731 (1957).

co-workers.[19] However, the experiments[17,18] following Doering's early liquid-phase work showed a nonstatistical insertion in the gas phase which was most pronounced in the case of insertion of CH_2 into isobutane.[18] It has been suggested by Frey and Kistiakowsky[17] that the indiscriminacy in the liquid phase is to be attributed to excited CH_2 which inserts before it can lose its energy. They observed a trend away from statistical when inert gas was added to remove the excitation from CH_2 and implied that thermal CH_2 discriminates in its insertion reactions. However, if CH_2 singlet is transformed by collision to the ground-state triplet, discriminate *abstraction* may be expected.[2] As a consequence association of methyl and alkyl radicals may produce the illusion of a more discriminate insertion by CH_2 as pointed out by Richardson and coworkers.[20] The elimination of this factor, of course, constitutes the basic reason for scavenging free radicals by addition of NO in the present work as well as in the recent work of Whitten and Rabinovitch[9] and by the addition of O_2 in the work of Carr.[21]

The present finding that $k_1/k_2 \sim 0.43$ also lends support to the conclusion that insertion is relatively indiscriminate even when two different reactant molecules such as methane and propane are involved.

The present work is, therefore, in essential agreement with the conclusions of Carr[21] who found that the reaction of CH_2 with isopentane involved insertion of CH_2 in a relatively indiscriminate fashion with a slight trend toward favoring insertion at the most highly substituted CH bond.

It is becoming increasingly clear[22-28] that both triplet and singlet CH_2 are formed in the photolysis of ketene. A very convincing demonstration that this is also true of the photolysis of diazomethane has recently been made by Bader and Generosa.[29] Carr[26] has deduced that about 15% of the CH_2 is triplet in the 3130-A photolysis of ketene.

It may be said that it is the singlet species of CH_2 that inserts indiscriminately.[30] Our observation that CH_2 appears to carry over about 2.5 kcal mole^{-1} in the insertion reaction suggests that the singlet CH_2 lies not more than about 2.5 kcal mole^{-1} above the ground-state triplet assuming that the singlet CH_2 suffers many collisions before inserting and that these collisions result in a fully relaxed singlet CH_2.

Acknowledgment. One of us (M. L. H.) gratefully acknowledges a summer (1966) research fellowship granted by the University of Missouri at Saint Louis.

---

[19] W. von E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, *J. Am. Chem. Soc.*, **78**, 3224 (1956).

[20] D. B. Richardson, M. C. Simmons, and I. Dvoretzky, *ibid.*, **83**, 1934 (1961).

[21] R. W. Carr, Jr., *J. Phys. Chem.*, **70**, 1970 (1966).

[22] J. W. Simons and B. S. Rabinovitch, *ibid.*, **68**, 1322 (1964).

[23] F. H. Dorer and B. S. Rabinovitch, *ibid.*, **69**, 1964 (1965).

[24] S. Ho, I. Unger, and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **87**, 2297 (1965).

[25] H. M. Frey, *Chem. Commun.*, 260 (1965).

[26] R. W. Carr, Jr., and G. B. Kistiakowsky, *J. Phys. Chem.*, **70**, 118 (1966).

[27] C. McKnight and F. S. Rowland, *J. Am. Chem. Soc.*, **88**, 3179 (1966).

[28] C. McKnight and F. S. Rowland, *ibid.*, **89**, 469 (1967).

[29] R. F. W. Bader and J. I. Generosa, *Can. J. Chem.*, **43**, 1631 (1965).

[30] D. F. Ring and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **88**, 4285 (1966).

Homogeneous Catalysis in the Reactions of Olefinic Substances.[1a] VIII. Isomerization of 1,5-Cyclooctadiene with Dichlorobis(triphenylphosphine)platinum(II)[1b]

Hassan A. Tayim and John C. Bailar, Jr.

Contribution from the William Albert Noyes Laboratory of Chemistry, University of Illinois, Urbana, Illinois.

Received January 27, 1967

Abstract: Homogeneous catalytic isomerization of 1,5-cyclooctadiene has been effected by $[PtCl_2(PPh_3)_2]$ in the presence of $SnCl_2 \cdot 2H_2O$, under nitrogen or hydrogen gas. Isomerization occurs by stepwise migration of the double bonds. The effective reaction intermediate may be a hydridoplatinum-olefin complex which has been isolated from the reaction medium and characterized. The synthesis of such a tin-platinum-olefin hydride complex is reported for the first time. The kinetics of the reaction suggest that isomerization occurs in two consecutive reversible first-order reactions. The source of hydrogen for the formation of the metal hydride complex is investigated. Tin(II) chloride has been found essential for the isomerization process. Its role is investigated in detail, and it is suggested that it activates the platinum catalyst by being coordinated to it through the ligand $SnCl_3^-$ which is a strong π acceptor and a weak σ donor.

The catalytic isomerization of monoolefins has formed the subject of many recent publications.[2] Only a few reports, however, have been devoted to the catalytic isomerization of polyolefins.[3] The isomerization of dienes was observed in the synthesis of some

---

[1] (a) Part VII: H. Itatani and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **89**, 1600 (1967). (b) This report is partly based on a portion of the Ph.D. Thesis by H. A. Tayim, University of Illinois, Feb 1967.

[2] For a recent review of homogeneous catalysis, see J. Halpern, *Ann. Rev. Phys. Chem.*, **16**, 103 (1965).

[3] R. Pettit, G. Emerson, and J. Mahler, *J. Chem. Educ.*, **40**, 175 (1963).