Selectivity of Singlet Methylene Reactions with Cycloalkenes[1a]

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The gas phase reactions of singlet methylene with cyclohexene and cyclopentene over a wide pressure range gave the expected products from C–H insertion and C=C addition; no subsequent decomposition or rearrangement was observed. The product ratios gave intramolecular, per bond, relative insertion rates into the vinylic, allylic, and nonallylic C–H bonds which are the same as for acyclic olefins. Competition reactions with isobutene, however, revealed that the absolute magnitude of these rates is about 50–80% higher than that of the previously studied olefins. The C=C addition rate, on the other hand, is in the same range as that observed for straight chain 1-alkenes. A dynamic effect is proposed to account for the selectivity of both the inter- and intramolecular effects in C–H insertion.

The question of selectivity in the reactions of methylene has been a topic of interest ever since 1956 when Doering et al. reported a study of methylene reactions with liquid hydrocarbons and commented that "Methylene must be classified as the most indiscriminate reagent known in organic chemistry."[2] In the work that followed, the importance of phase effects, singlet and triplet methylene reactivity, and methylene precursors were elucidated. In the gas phase, singlet methylene reacts with primary, secondary, and tertiary C–H bonds in the ratio of 1:1.3:1.4. This selectivity is less pronounced in the liquid phase.[3] For acyclic alkenes, the insertion rate into vinylic C–H bonds is about 65% as fast as into allylic and paraffinic bonds.[3,4] The per bond methylene addition to the C=C bond is about eight to ten times as fast as C–H insertion.

Cyclopentene and cyclohexene are ideal systems to measure the selectivity of methylene reactions. They contain three types of C–H bonds as well as the C=C. They are large enough that subsequent reactions of the bicyclic compounds or the methylcycloalkenes formed can be stabilized at easily accessible pressures. Methylene reactions in liquid cyclohexene were studied in Doering's early work[2] and later by Kopecky, Hammond, and Leermakers.[5] This liquid work showed general agreement with the acyclic alkenes for C–H insertion and a slightly reduced (≃50%) reactivity at the C=C. Our work represents the first study in the gas phase of cycloalkene systems.[6] In order to compare the reactivity of the cyclic and acyclic alkenes, competition studies with isobutene were done as well.

The mechanism of addition of methylene to C=C and C–H bonds has received a good deal of attention by theoreticians recently.[8-11] The prediction of both detailed calculations[8,9,11] and MO following[10] is that methylene addition to the C=C bond proceeds by an unsymmetrical pathway which is symmetry allowed. In cycloalkenes where the geometry is more rigid than acyclic hydrocarbons, the effects of this unsymmetrical mechanism might be apparent. The C–H bond insertion reaction should be less sensitive to the structure of the molecule if it involves an end-on approach to the H atom. As will be seen, however, the results from the cycloalkene studies show that the C–H bond reactions are more sensitive to the cyclic structure than is the C=C addition pathway.

Experimental Section

Diazomethane was prepared from *N,N'*-nitrosomethylurea

and stored in a butylphthalate matrix at liquid nitrogen temperature. Cyclopentene (99.9%) and cyclohexene (99.9%) were used as received from Chemical Samples, Inc. Matheson oxygen (99.6%), perfluoropropane (99%), and isobutene (99%) were used directly from the containers.

The sample preparation and irradiation procedures have been described previously.[12] To increase the surface to volume ratio for some of the runs, the pyrex irradiation vessel was packed with 6 mm pyrex tubes into which slits had been cut. Irradiations were done at 436 and 366 nm using a 200-W high-pressure Hg lamp and narrow bandpass filters (±10 nm). All single compound irradiations were done at room temperature and lasted, in general, about 3 h. The competitive reactions were carried out using a 100-W lamp and a 6-h irradiation time.

The product spectrum was analyzed by FID gas chromatography. Separation of the products was accomplished using a ⅛ in. × 40 ft stainless steel column with 10% polypropylene glycol on Anakrom C-22A. 1,1-Dimethylcyclopropane and 3-methylbutene-1 were not separated, but since they both arise from C=C addition to isobutene, their total yield was used. For the cyclopentene system the relative retention volumes of the products to cyclopentene at 25 °C were 1.57 (3-methylcyclopentene), 1.65 (4-methylcyclopentene), 2.42 (1-methylcyclopentene), and 3.06 (bicyclo[3.1.0]hexane). At 60 °C, the relative retention volumes of the C_7H_{12} products to cyclohexene were 1.49, 1.52, 1.96, and 2.62 for 3-, 4-, and 1-methylcyclohexene, and bicyclo[4.1.0]heptane, respectively. The resolution of the 3- and 4-methyl isomers was not complete, but was adequate to determine accurately their yields by electronic integration. Some of the early cyclopentene data were obtained with an ⅛ in. tandem column of 10 ft β,β'-oxydipropionitrile, 10 ft dimethylsulfolane, 5 ft silicone oil, and 6 ft AgNO₃ and yielded results identical with the single polypropylene glycol column.

The products were identified by comparison of their retention volumes with authentic samples and for the cyclopentene products by comparison of their mass spectra with published values[13] or mass spectra of authentic samples measured in our laboratory. The product yields were calculated from the peak areas measured by an electronic integrator. The FID sensitivity was measured for all the products and found to be directly proportional to the number of carbon atoms in the molecules within the precision of the measurements.

TABLE I: Reactions of $^1CH_2$ with Cyclopentene[a]

Total pressure, Torr	O_2/⬠	Products			
		△-⬠	⬠=	⬠(CH3)	⬠=(CH3)
296	0.12	37.0	9.8	35.3	17.9
199	0.12	36.1	8.8	38.6	16.4
201[b]	0.12	39.1	10.3	34.4	16.2
204[c]	0.10	40.1 ± 0.4	9.6 ± 0.2	34.7 ± 0.3	15.5 ± 0.2
96[d]	0.13	38.1	9.3	35.8	16.7
25	0.29	38.7	10.9	33.8	16.5
25	0.13	39.4	10.6	33.7	16.4
25	0.06	39.3	8.3	36.1	16.4
17	0.11	38.4	11.7	33.3	16.7
15	0.13	40.2	12.2	31.7	15.9
10	0.13	39.9	11.8	31.1	17.1
10[b]	0.13	39.6	11.7	30.1	18.5
10[d]	0.12	39.3	12.9	31.2	16.5
Av		38.9 ± 1.2	10.6 ± 1.4	33.8 ± 2.4	16.7 ± 0.8

[a] All reactions run using diazomethane as methylene precursor. Diazomethane:hydrocarbon ratio varied between 1:17 and 1:7. Irradiation times 3 h at 436 nm unless otherwise noted. [b] Packed reaction vessel. Surface to volume ratio increased by a factor of 22 over empty cell. [c] Averages of three samples extracted at 2, 4, and 6 h. [d] Irradiation wavelength 366 nm.

TABLE II: Reactions of $^1CH_2$ with Cyclohexene[a]

Total pressure, Torr	O_2/⬡	Products			
		△-⬡	⬡=	⬡(CH3)	⬡=(CH3)
600	0.10	35.2	10.0	27.6	27.2
603[b]	0.09	34.4	10.8	29.4	25.4
600[d]	0.10	34.0	7.4	32.0	26.6
304	0.10	34.6	8.3	30.1	27.0
84[c]	0.16	32.0 ± 0.8	10.7 ± 0.6	29.1 ± 0.3	28.2 ± 0.7
78	0.14	30.7	9.5	31.2	28.5
60	0.10	31.3	11.4	28.9	28.4
60[b]	0.10	30.9	10.8	29.1	29.2
60 (2 runs)[d]	0.10	37.3 ± 0.6	8.3 ± 3.0	28.8 ± 2.4	25.7 ± 1.3
54	0.05	31.4	9.4	30.8	28.4
25	0.34	32.5	10.9	28.7	27.9
12	0.13	32.8	10.8	27.7	28.7
Av		33.1 ± 2.0	9.9 ± 1.3	29.5 ± 1.3	27.6 ± 1.2

[a,b,c,d] Same footnotes as in Table I.

Results

The results for the reactions of methylene with cyclopentene are given in Table I and with cyclohexene in Table II. Experiments were run over a pressure range of 10–300 Torr for cyclopentene and 10–600 Torr for cyclohexene. Perfluoropropane was added as an inert gas for experiments run at pressures above the vapor pressures of the hydrocarbon. The products observed are the three methylcycloalkene isomers expected from C–H insertion and the bicyclic hydrocarbon resulting from C=C addition. Methylenecyclopentane was sought but was not observed at our limits of detectability (0.5%). Methylenecyclohexane would appear under the 4-methylcyclohexene peak. However, from the absence of methylenecyclopentane in the cyclopentene system and the nearly equivalent yields of 3- and 4-methylcyclohexene, the methylene isomer yield is assumed to be very small. A small yield of cyclohexene (<1%) was observed in the cyclopentene system. For both systems there is no change outside the experimental error in the product ratios over the entire pressure range measured. The yields are also insensitive to the surface to volume ratio of the reaction vessel, to the irradiation wavelength, and to oxygen concentrations in the range of 5–20%. This invariance of the yields with a fourfold change in oxygen concentration shows that above 5% O_2 the triplet methylene produced is effectively scavenged.[14]

These results indicate that we are measuring the initial product distribution resulting from the reactions of singlet methylene with cyclopentene and cyclohexene. The failure to observe any trends in the yields with change in pressure or wavelength means that the initial adducts formed are collisionally stabilized before any isomerization occurs. This result might be expected by comparing the Arrhenius parameters for isomerization of bicyclo[3.1.0]hexane[15] and bicyclo[4.1.0]heptane[16] with those for chemically activated[12] or pyrolyzed[15] bicyclo[3.1.0]hex-2-ene. The ratios of the methyl isomers are also very far from the expected equilibrium values based on the work of Gil-Av[17] and show no change with time over a period of 6 h.

In Table III the relative reactivities of C=C and the three types of C–H bonds are listed. The numbers are obtained from the averages of the values in Tables I and II. Also included are the results of the liquid phase reactions with cyclohexene reported by Doering[2] which show remarkably good agreement with our gas phase results.

TABLE III: Relative Yields/Bond for $^1CH_2$ Addition and Insertion in Cyclohexene and Cyclopentene

Reactant	C=C addition	C–H (vinylic)	C–H (allylic)	C–H (nonallylic)
Cyclopentene	38.9 ± 1.2	5.3 ± 0.7	8.5 ± 0.6	8.3 ± 0.4
Cyclohexene (25 °C, gas)	33.1 ± 2.0	5.0 ± 0.7	7.4 ± 0.3	6.9 ± 0.3
Cyclohexene (15 °C, liquid)[a]	37	5.5	6.5	6.5
Cyclohexene (−75 °C, liquid)[a]	40	5.0	6.3	6.3

[a] Reference 2.

TABLE IV: Relative Reactivities of $^1CH_2$ with Isobutene and Cyclopentene and Cyclohexene[a]

	C–H (vinylic)	C–H (allylic)	C=C addition
Cyclopentene/ isobutene	0.72 ± 0.10	1.5 ± 0.1	0.94 ± 0.08
Cyclohexene/ isobutene[b]	1.0 ± 0.1	1.8 ± 0.2	0.74 ± 0.08

[a] Irradiations of equimolar mixtures of isobutene and the cycloalkene for 6 h using a 100-W Hg lamp. 10% O_2 present. [b] Average of only two determinations.

In the competitive runs with isobutene and cyclopentene the relative yields of the C_5H_{10} isomers, 1,1-dimethylcyclopropane + 3-methylbutene-1,2-methylbutene-1, and 2-methylbutene-2, were 52.5 ± 2.3, 35.8 ± 1.4, and 11.7 ± 1.2%, respectively, in good agreement with previous work in oxygen scavenged systems.[18] For the longer irradiation times and lower intensity lamp used for these runs, however, the relative product yields from cyclopentene differed slightly from those averages given in Table I. The bicyclic compound yield was higher by about 20% and the 1- and 4-methylcyclopentene isomer yields were lower by about the same amount. The yield of the product from allylic insertion, 3-methylcyclopentene, was smaller but not outside the error limit of the average given in Table I. These changes are thought to arise from a dark reaction between the cycloalkene and diazomethane.[12]

Table IV lists the relative insertion ratios for C=C addition and the comparable C–H positions for isobutene and the two cycloalkenes. The results given for cyclohexene are from only two determinations and thus less certain than for the cyclopentene system. It is clear, however, that for both cycloalkenes the C=C addition mode is slightly less favorable and that the allylic position is more reactive. The vinyl position appears

to be slightly less reactive; however, the vinylic position in isobutene has an abnormally high reactivity, and the vinyl yields in the competitive studies were low from the cycloalkenes. If the vinylic ratio is based on the relative yields in Table III, this C–H position is also more reactive in the cycloalkenes than the comparable position in butene-1 (see Table V).

In order to compare the reactivity of the cycloalkenes with a number of other hydrocarbon systems, a search of the literature was made for those studies giving relative reactivity of $^1CH_2$ produced from diazomethane photolysis using 436-nm light in oxygen scavenged systems. Table V summarizes the available data, most of which have been normalized through use of isobutene in competitive studies or neopentane as an internal standard. Only the value for C=C addition in butene-1 has utilized ketene data, in this case from photolysis at 250–270 nm.[4] The value was measured from isobutene competitive studies and has been corrected assuming a 10% contribution from $^3CH_2$, a reasonable value for the amount of $^3CH_2$ produced at the wavelength used.[19] The C–H insertion positions in the alkenes have been subdivided into categories of primary, secondary, and tertiary as well as vinylic and allylic. For the cycloalkenes, the ratios for C–H insertion were determined from the measured ratio at the allylic position in the isobutene–cycloalkene competition experiments and the relative ratios of the methylcycloalkene product yields given in Table III.

Discussion

The reactivity of methylene with the C=C bond in all the alkenes, including the cycloalkenes, appears to be nearly independent of the structure of the molecule. That isobutene has the highest reactivity probably reflects the importance of the methyl stabilization of valence structures involved along the reaction pathway.[8c] The low reactivity of cis-butene-2

TABLE V: Comparison of Relative $^1CH_2$ Insertion and Addition Rates for Alkanes and Monolefins[a]

Alkanes	C–H insertion						C=C addition	Ref
	Primary		Secondary		Tertiary			
Propane	0.09		0.12					b,c
Butane	0.12		0.16					b
Isobutane	0.11				0.17			b,c
Isopentane	0.11		0.14		0.16			24
Neopentane	0.14							b

Olefins	Nonallylic	Allylic	Nonallylic	Allylic	Vinylic	Vinylic		
Butene-1	0.10			0.11	0.07	0.07	0.93[d]	e
Isobutene		0.11			0.11		1.00[a]	This work, 18
cis-Butene-2		0.08					0.61	f
Cyclopentene			0.17	0.17		0.11	0.94	This work
Cyclohexene			0.19	0.20		0.14	0.74	This work

[a] All results are normalized to addition to C=C of isobutene = 1.0. Unless otherwise noted results are from diazomethane photolysis at 436 nm in oxygen scavenged systems. [b] W. L. Hase, R. L. Johnson, and J. W. Simons, Int. J. Chem. Kinet., 4, 1 (1972). [c] R. L. Johnson, W. L. Hase, and J. W. Simons, J. Chem. Phys., 52, 3911 (1970). [d] Reference 4. C=C addition values used to normalize to isobutene. Photolysis of ketene at 250–270 nm in unscavenged system. 10% correction made for contribution from $^3CH_2$. [e] F. H. Dorer and B. S. Rabinovitch, J. Phys. Chem., 69, 1952 (1965). [f] G. W. Taylor and J. W. Simons, J. Phys. Chem., 74, 464 (1970); 73, 1274 (1969).

(and *trans*-butene-2[4]) can be attributed to unfavorable steric hindrance of the methyl groups offsetting their stabilizing effect. With the alkyl groups held back in the cycloalkene structures, some of this repulsion is removed and the C=C reactivity increases slightly. In any case, the differences in reactivity are small, if even outside of the experimental precision, and show little definite trend.

The *intra*molecular ratios for C–H insertion in the cycloalkenes are similar to those of the acyclic alkenes. The allylic position has essentially the same reactivity as a nonallylic position even though the allylic C–H bond dissociation energy is lower by about 10 kcal/mol. The vinylic reactivity is reduced about 40% compared to the other C–H positions. While this is the strongest C–H bond, the lack of any bond energy effect at the allylic position tends to negate that explanation. Rather we attribute the reduced reactivity of the vinylic position to competition for the methylene by the double bond, a suggestion supported by the proposed mechanism of C=C addition.[8,10]

The results in Table V show that for *inter*molecular comparison the absolute reactivity of the C–H bonds in the cycloalkenes at all positions is 50–80% more reactive than acyclic olefin systems. This difference is admittedly small. At the temperature of our experiment (300 K) the selectivity could be accounted for by a difference in the activation energy of about 250 cal/mol, or if the activation energies are the same, a ratio in the preexponential factors of only $10^{0.2}$. These values are so small that it would be extremely difficult experimentally to determine which factor is causing the difference in the rates by a kinetic study of the temperature dependence. Nevertheless, the enhancement for the larger cyclic molecules is real and is also reflected in the increasing absolute rates observed with increasing chain length for the alkanes (see Table V).[20]

There are presently two theories to describe the C–H insertion mechanism.[19] The first, initially proposed by Doering and Skell, involves a one-step insertion into the bond through a triangular transition state. Arguments justifying reactivity differences due to steric hindrance and bond energies have supported this mechanism. The second mechanism, that of DeMore and Benson, is an end-on attack by an abstraction-like process. This mechanism was supported by the recent theoretical analyses of the minimum energy reaction pathway.

It is difficult to reconcile the equal reactivities of the allylic and nonallylic secondary C–H positions in the cycloalkenes with the triangular transition state mechanism. Since the geometries of the two positions are nearly identical, especially for cyclohexene, the large C–H dissociation energy difference would be expected to result in a larger effect than observed for primary to tertiary insertion in alkanes where the bond energy differences are smaller. This expectation is not realized. Theoretical calculations for the end-on attack, however, have not shown any activation energy for the insertion process and thus bond energy effects would play a smaller role for this mechanism. On the basis of the cycloalkene work, therefore, we favor the end-on mechanism.

Since for the reactions reported in Table V complete stabilization of the primary insertion products occurs, the increased reactivity of the cycloalkenes cannot be attributed to decreased decomposition of these larger systems. Instead we suggest that the enhanced reactivity is due to a dynamic effect different from the steric and energetic effects proposed so far.[19] This effect will be important in the incoming channel of the reaction, before the system passes into the exit channel of the reaction pathway.

The exact nature of this effect is obviously not known,[21] but we propose that it depends on the ability of the molecular system to retain a favorable geometry for the abstraction-like reaction throughout the entire time of the collision. Calculations of the minimum energy reaction pathway do not consider the movement of the hydrocarbon entity during the collision. The dynamic study by Wang and Karplus of the $CH_2 + H_2$ reaction, however, has clearly shown the effect of rotation of H_2 during the collision and emphasized the importance of the dynamics of the colliding partners on the result of the reaction.[22] The translational–rotational energy transfer effects will be less important in our larger systems than for hydrogen, but can reasonably account for the small intra- and intermolecular selectivity effects observed in methylene gas phase reactions. The tertiary position will be more rigidly held than the secondary and the primary least stationary of all. The methylene groups in the cycloalkenes are more rigid in the ring structure than the secondary groups of an acyclic paraffin. From the data in Table V, it seems that the cyclic secondary positions have about the same reactivity as the tertiary positions in the acyclic hydrocarbons.

In condensed phases, this dynamic effect should be almost negligible. It is not surprising, therefore, that essentially statistical insertion ratios are observed for the paraffins in the liquid phase.[2,23,24] According to our model, the absolute reactivity of the cycloalkane positions should be *higher than the* paraffins in the gas phase but not in the liquid phase. In addition, the extent of the molecule which is involved in this dynamic effect can be tested by measuring the relative reactivity of insertion into the methyl group of methylcycloalkenes. We are presently carrying out experiments in our laboratory relevant to these questions.

References and Notes

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Effect of Thermal Activation on the Reactions of Chemically Activated sec-Butyl Radicals

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The reactions of trans-2-butene and 1-butene with atomic hydrogen were studied over the temperature range 300–670 K under pressures of 6–10 Torr using a discharge-flow reactor. In the vicinity of room temperature, the main product was n-butane for both reactants, and, as the temperature increases, this is taken over by the formation of propylene and ethane, becoming the main products above 500 K. The experimentally determined decomposition rate constant k_{expt} was compared with that obtained by the Marcus–Rice (RRKM) unimolecular rate theory, $\langle k_a \rangle$. It is found that the temperature dependence of both rate constants is in good agreement, confirming the general validity of the view that the effect of temperature in a chemical activation system is interpretable within the framework of the RRKM theory.

Introduction

The behavior of chemical activation systems has been widely studied in connection with the experimental tests of the Marcus–Rice (RRKM) unimolecular rate theory. The chemically activated alkyl radicals produced by addition of a hydrogen atom to a double bond of an olefin either decompose to a fragment radical and an olefin, or stabilize into corresponding alkyl radicals which normally undergo disproportionation or association, the fate of the activated radicals being a function of temperature and pressure of the reaction system. It can be generally stated that the change of pressure causes a greater change in the stabilization rate than in the decomposition rate, whereas the opposite is the case for the effect of a change in temperature.

Therefore, it should be equally possible to test the RRKM theory by studying the effect of temperature as well as of pressure on the reactions of the chemically activated alkyl radicals provided that the main reaction products can be separated from those arising in the side reactions. However, most tests have been directed toward the investigation of the change of product selectivity with pressure, and very few investigations concerning the effect of temperature have been reported.[1-4]

In previous studies on the system toluene–hydrogen atoms,[5,6] we have shown that the change in the product pattern with temperature is interpretable in the framework of the RRKM theory, and that H–CH$_3$ substitution step is the predominant reaction at elevated temperatures, verifying the validity of the radical chain mechanism proposed for the thermal hydrogenolysis of toluene.[7] However, there were some uncertainties in the heat of formation of the methylcyclo-

hexadienyl radical, and in defining vibrational models in the case of the toluene–H system. Therefore, a further study on a well-defined reaction system was considered necessary in order to confirm the above conclusions. Also, extension to high temperature condition was of some interest with respect to the efficiency of collisional deactivation at elevated temperatures.

The butene–H reaction system was chosen for this purpose on the grounds that (a) this is the simplest system which clearly differentiates between the products arising from decomposition (D) and stabilization (S), and (b) detailed studies by Rabinovitch and co-workers on the effect of pressure on this system have been done[8-10] to be compared. Although the effect of temperature has also been studied in one of the butene isomers,[1] the tested range was from 168 to 298 K, where the energization of the butyl radicals was essentially monoenergetic. Therefore, it was considered meaningful to extend this study to high temperature conditions where broadening of the energy distribution due to the presence of reactants having higher thermal energy would be significant. Thus, this should be reflected in the unimolecular decomposition rate as the effect of temperature.

Experimental Section

trans-2-Butene and 1-butene were chosen in the experimental study. The reactions were studied in a conventional discharge-flow quartz reactor having the heated length of about 300 mm and an i.d. of 27 mm, between 300 and 670 K. The inner wall of the reactor was coated with H$_3$BO$_3$ to minimize heterogeneous loss of atomic hydrogen introduced. The axial temperature variation in the reactor zone, defined as the