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## PHYSICAL AND INORGANIC CHEMISTRY

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### Reactions of Methylene. IV. Propylene and Cyclopropane

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Photochemical reactions of ketene and diazomethane with cyclopropane and with propylene, each present in large excess, were studied using radiation of different wave lengths and the products were analyzed by gas chromatography. The products were attributed mainly to the reactions of methylene formed in the primary photochemical processes. The initial product of reaction of methylene with cyclopropane is energy-rich methyl cyclopropane which isomerizes unimolecularly into a mixture of butene isomers unless stabilized by collisions. The reaction of methylene with propylene involves two competitive initial processes: a reaction with the carbon-carbon double bond, forming energy-rich methylcyclopropane and reactions with the C-H bonds which give a mixture of isomeric butenes. Methylcyclopropane formed also rearranges into butenes unless stabilized by collisions. The lifetimes of the energy-rich methylcyclopropane molecules depend greatly on the source of methylene and also on the choice between cyclopropane and propylene. On the other hand, the composition of the mixture of butenes is the same in all cases studied, except for a possibly significant trend observed in the reaction with cyclopropane when the source of methylene is varied. These data are considered from the point of view of a classical model of unimolecular reactions and the trends in lifetimes are attributed to varying amounts of excess energy of methyl cyclopropane. The finding that the composition of the butene fraction does not depend on whether methylene reacts with cyclopropane or with propylene is interpreted to mean that the energy of the "hot" molecules migrates freely among the normal modes of vibration of methylcyclopropane molecules, within the time between their formation and rearrangement. It is also noted that the selectivity in the rate of attack by methylene on carbon-carbon double bonds and carbon-hydrogen bonds decreases in general as the excess energy of photochemically generated methylene is increased.

#### Introduction

In the first paper of this series<sup>2</sup> the reactions of methylene with ethylene, propane, cyclopropane, and *n*-butane were described. It was shown that when methylene formed by photolysis of ketene reacts with the double bond of ethylene, cyclopropane is formed having energy in excess of that required for its isomerization to propylene. These "hot" cyclopropane molecules can be stabilized by collisions. Other work on the reaction of methylene with olefins<sup>3-6</sup> confirmed this basic mechanism. In brief preliminary investigations<sup>2,7</sup> it was shown that in the reactions of methylene with cyclopropane and with propylene "hot" methyl cyclopro-

pane molecules are formed, which isomerize into a mixture of butene isomers unless stabilized by collisions.

The transition states through which these two reactions of methylene proceed to the same "hot" intermediate are quite different and hence different normal modes of vibration in methyl cyclopropane should be initially excited. The problem as to whether this has an effect on the relative rates of isomerization of the "hot" molecules into various butene isomers is of considerable interest for the general theory of unimolecular reactions and is one of the main subjects of this investigation. The other and related one is the effect of the total energy content of "hot" methyl cyclopropane molecules on the rate and course of their isomerization into butenes.

#### Experimental Details

Experiments were conducted in a good vacuum system. The desired quantities of those gases which were to be used for an experiment were introduced one by one into a vessel of known volume, the pressure of each was measured, and they were condensed into a small side tube attached to the reaction vessel. The contents of the tube were then rapidly evaporated into a cylindrical fused-quartz reaction vessel

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(2) H. M. Frey and G. B. Kistiakowsky, *THIS JOURNAL*, **79**, 6373 (1957).

(3) B. S. Rabinovitch, E. Tschuikow-Roux and E. W. Schlag, *ibid.*, **81**, 1081 (1959).

(4) J. H. Knox, A. F. Trotman-Dickenson and C. H. J. Wells, *J. Chem. Soc.*, 2897 (1958).

(5) H. M. Frey, *Proc. Roy. Soc. (London)*, **A250**, 409 (1959).

(6) H. M. Frey, *ibid.*, **A250**, 575 (1959).

(7) J. H. Knox and A. F. Trotman-Dickenson, *Chemistry & Industry (London)*, 1039 (1957).

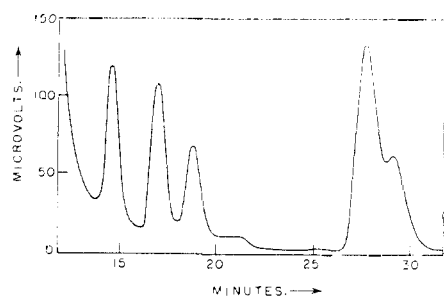


Fig. 1.—Gas chromatogram from a typical run. Note the tail of the large peak due to cyclopropane on the left. Following are peaks due to methyl cyclopropane, *trans*-2-butene, isobutene, 1-butene and *cis*-2-butene.

of 3.5 cm. diameter and 120 cc. volume. A manometer attached to the reaction vessel allowed the total pressure to be measured during the course of the reaction. A sealed-in-quartz magnetic stirrer in the vessel was kept running throughout the photolysis to ensure good mixing. The reaction vessel was surrounded by three concentric annular quartz optical filter cells, two of 0.65 cm. thickness which allowed the filter solutions to circulate and one of 0.35 cm. thickness which did not.

The light source consisted of two medium-pressure mercury arc lamps (General Electric UA-3) with aluminum reflectors. To prevent side reactions due to mercury atoms excited by the 2536 Å. resonance radiation, air saturated with mercury vapor at 75° was passed through one of the 0.65 cm. thick filter cells. Even under the conditions of maximum exposure used in the experiments, no hydrogenation of ethylene could be detected in ethylene-hydrogen mixtures, indicating that the concentration of excited mercury atoms in the reaction vessel was negligible. To isolate the 2600 Å. group of lines the 0.35 cm. filter cell was filled with a 500 g./l. aqueous solution of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  and an 0.25 g./l. aqueous solution of  $\text{KMnO}_4$  was passed through the other 0.65 cm. cell and discarded, thus also serving to keep the reaction vessel at room temperature. Using this combination of filter solutions, 64% of the total radiation absorbed by ketene was between 2475 and 2820 Å. To isolate the 3100 Å. group of lines, the permanganate filter was replaced by an 0.5 g./l. aqueous solution of  $\text{CdI}_2$ , which was also used as the coolant. Using this filter, 62% of the total radiation absorbed by ketene was between 2950 and 3220 Å.

Ketene was prepared by the pyrolysis of acetic anhydride.<sup>2,8,9</sup> Diazomethane was prepared in milligram quantities immediately prior to each experiment by treating *N*-methylnitroso urea with strong aqueous KOH, passing the gas evolved through a Dry Ice trap to remove water vapor and into a liquid nitrogen trap to collect the diazomethane. Propylene and cyclopropane were Matheson C.P. grade and were further purified by bulb-to-bulb distillation.

After irradiation of ketene, the contents of the reaction vessel were passed through a tube containing magnesium perchlorate and Ascarite, which removed unreacted ketene, and then through a liquid nitrogen trap, the non-condensable gases (principally CO) being discarded. The photolyses involving diazomethane were carried nearly to completion so that removal of excess diazomethane was not necessary.

The condensable gases were analyzed by a gas chromatograph<sup>8</sup> capable of detecting  $10^{-9}$  mole. A Liston-Becker D. C. breaker amplifier (r.m.s. noise 0.005  $\mu\text{v}$ .) and a Varian G-10 recorder amplified and recorded the signal from a hot-wire thermal conductivity detector. Helium, purified by passing it through a liquid nitrogen trap, was used as a carrier gas, flowing at about 50 ml./min. Provision was made for collecting fractionated gases coming off the columns. The columns were calibrated with known mixtures, the areas of the peaks (obtained by a square-counting method) being used for quantitative analyses.

Ketene-propylene and ketene-cyclopropane mixtures in a ratio of about 1:10 were photolyzed with 2600 and 3100 Å.

(8) G. B. Kistiakowsky and Kenneth Sauer, *THIS JOURNAL*, **80**, 1066 (1958).

(9) A. D. Jenkins, *J. Chem. Soc.*, 2563 (1952).

radiation until approximately 10% of the ketene was decomposed. Exposure times varied from 30 minutes to 4 hr. Diazomethane-propylene and diazomethane-cyclopropane mixtures in a ratio of about 1:50 were photolyzed by polychromatic radiation consisting of wave lengths longer than 3100 Å. until nearly all the diazomethane was decomposed. Exposure times varied from ten to forty-five minutes. In each case less than 2% of the reaction mixture consisted of  $\text{C}_4$  products, so that the products of reaction of methylene with these  $\text{C}_4$  hydrocarbons were less than 0.05% of the reaction mixture and produced negligible interference in the analyses.

A 25 foot column, packed with Johns-Mansville Chromosorb which has been treated with a saturated solution of silver nitrate in Carbitol (diethylene glycol monoethyl ether), maintained at 0° by an ice-bath, separated the  $\text{C}_4$  products from the propylene or cyclopropane, whichever was the main constituent of the reaction mixture and further separated all the  $\text{C}_4$  hydrocarbons except 1-butene and *cis* 2-butene. The fraction containing these two compounds was collected and cleanly separated on a Carbitol column.

The principal error in the analyses lay in the extrapolation of the base line, since most of the peaks were not completely separated (see Fig. 1). The large propylene or cyclopropane peak tailed somewhat and the methyl cyclopropane, *trans* 2-butene and isobutene peaks occurred on the tail of the large peak. The exact value of the areas depended on which french curve was chosen to extrapolate the tail of the large peak; this error was ten to twenty times greater than the error (0.3%) in measuring an area once a base line had been drawn. To obtain better estimates of the errors involved, several portions of each sample were chromatographed separately when it was large enough.

## Results

The relative yields of  $\text{C}_4$  hydrocarbons as a function of total pressure for the reaction of methylene from three sources (ketene and 2600 Å. radiation, ketene and 3100 Å. radiation, diazomethane and polychromatic radiation) with cyclopropane are given in Table I; for the reaction with propylene in Table II. The butene composition in each case is presented in the form most convenient for evaluating relative rate constants. The effect involved in changing the exposure time within the limits used was small compared to the errors in analysis as can be seen from Table III, which also shows the degree of reproducibility of chromatographic analysis.

In addition to the  $\text{C}_4$  hydrocarbons, the products also found in the reaction mixture were:

Ethylene, from reaction of methylene with ketene or diazomethane.

Cyclopropane (when propylene was the principal reactant) or propylene (when cyclopropane was the principal reactant) from the reaction of methylene with ethylene.

Ethane and propane (butane was hidden by the propylene and cyclopropane peaks) from alkyl radicals formed by H abstraction by methylene.<sup>2</sup>

Six pentene isomers, three dimethyl cyclopropane isomers and ethyl cyclopropane from the reactions of methylene with  $\text{C}_4$  hydrocarbons. Only the dimethyl cyclopropane isomers could possibly interfere with the analysis for  $\text{C}_4$  hydrocarbons.

**Evaluation of Rate Constants. Cyclopropane.**—The mechanism suggested by previous work for the reaction of methylene with cyclopropane<sup>2,7</sup> is

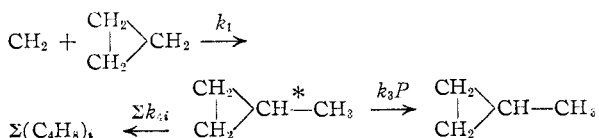


TABLE I<sup>a</sup>

<i>P</i> (total), mm.	Butene (total) Methylcy- clopropane	Fraction of total butene				<i>cis</i> -2- Butene <i>trans</i> -2- Butene
		1- Butene	<i>cis</i> -2- Butene	<i>trans</i> -2- Butene	Iso- butene	
A. Ketene: 2600 Å. radiation						
17.3	9.66	0.345	0.262	0.237	0.156	1.11
20.0	7.30	.350	.240	.296	.114	0.81
21.5	5.56	.372	.225	.252	.150	0.89
37.6	4.76	.410	.222	.215	.150	1.03
40.0	4.90	.389	.245	.230	.136	1.06
107.5	1.43	.347	.277	.250	.127	1.11
107.5	1.47		.255	.241		1.06
112	1.65		.276	.228		1.21
114	1.55	.336	.213	.301	.151	0.71
114	1.43		.303	.252		1.20
170.5	0.75	.485	.222			
170.5	.81					
242	.70					
328	.44					
328	.50	.358	.229	.265	.147	0.86
368	.33	.425	.262	.191	.122	1.37
368	.35	.465	.285	.127	.106	2.24
368	.30	.392	.258	.248	.105	1.05
498	.20					
622	.27			.219	.090	
622	.37					
1180	.12			.207	.126	
B. Ketene: 3100 Å. radiation						
22.6	10.04	0.283	0.298	0.275	0.142	1.08
39.8	6.23	.364	.257	.246	.133	1.05
65.8	2.71	.398	.275	.207	.121	1.13
65.8	2.46	.400	.265	.202	.133	1.31
440	0.31	.507	.274	.115	.104	2.38
440	0.30	.485	.234	.167	.114	1.40
C. Diazomethane: polychromatic radiation						
25	10.01	0.557	0.122	0.189	0.132	0.65
46	5.50	.438	.211	.207	.144	1.02
106	2.70	.476	.186	.209	.129	0.89
106	2.77	.515	.153	.199	.132	.77
134	2.92	.463	.194	.203	.140	.96
134	2.66	.467	.196	.205	.132	.96
151	2.44	.491	.188	.187	.134	1.00
206	1.67	.463	.214	.196	.127	1.09
206	1.65	.466	.210	.195	.130	1.08
402		.470	.221			
540	0.795	.470	.216	.185	.128	1.17
540		.480	.204	.188	.127	1.08
963	.440	.466	.247	.174	.113	1.42
963	.363		.248	.172		1.44
963		.455	.224	.194	.126	1.16

<sup>a</sup> In some early analyses peaks were not completely separated, hence the individual butenes were not all reported.

where  $P$  is the total pressure,  $i = 1$  refers to 1-butene,  $i = 2$  to 2-butenes and  $i = 3$  refers to isobutene. The rate constant for the formation of total butenes is  $k_4 = k_{41} + k_{42} + k_{43}$ . This mechanism yields the steady state relations

$$\frac{(\text{total butene})}{(\text{methyl cyclopropane})} = \frac{k_4}{k_3 P} \quad (1)$$

$$\frac{(C_2H_5)_i}{(\text{total butene})} = \frac{k_{4i}}{k_4} \quad (2)$$

Figure 2 is a plot of the ratio of total butene to methyl cyclopropane in the products of photolysis

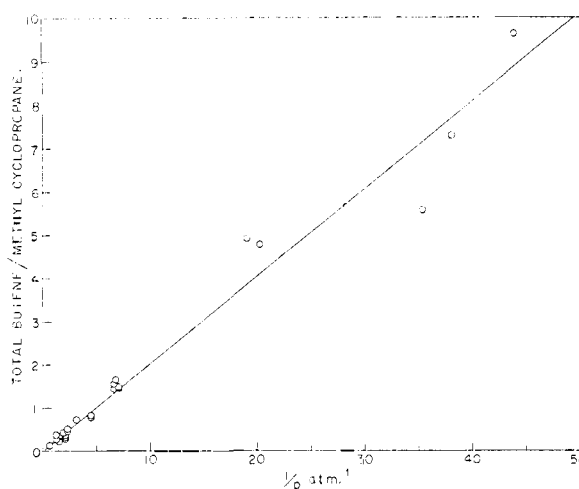


Fig. 2.—A plot of the ratio of the total yield of butenes to methyl cyclopropane against inverse total pressure in the reaction of ketene with cyclopropane, using 2600 Å. radiation.

of cyclopropane–ketene mixtures with 2600 Å. radiation as a function of the reciprocal of the total pressure. The plot for 3100 Å. radiation is similar. The data for the photolysis of cyclopropane–diazomethane mixtures fit a straight line at high pressures, but at low pressures a downward curvature becomes noticeable (see Fig. 3). We shall attempt to explain this later. Only points for pressures above 75 mm. were used to obtain the ratio  $k_4/k_3$  for this set of data.

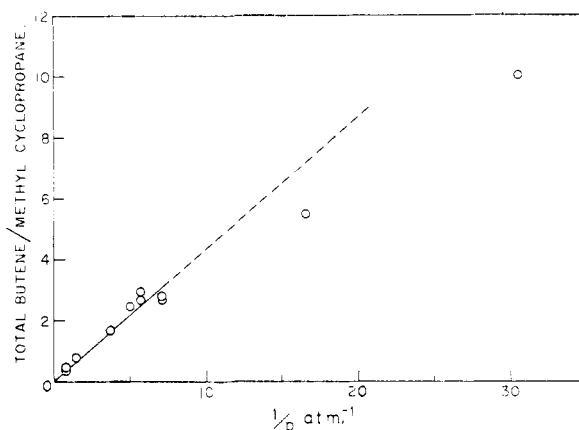


Fig. 3.—A plot of the ratio of the total yield of butenes to methyl cyclopropane against inverse total pressure in the reaction of diazomethane with cyclopropane, using polychromatic radiation.

The rate constant ratios  $k_4/k_3$  and  $k_{4i}/k_4$  were obtained from the data of these three sets of experiments and were used to calculate the quantities given in Table IV, which will be explained in the discussion. The errors quoted in Table IV are 90% confidence limits (90% of the measured values can be expected to fall within these limits): for  $k_4/k_3$  they were obtained by fitting a least-squares straight line to the data; for  $k_{4i}/k_4$  they were obtained from the mean-square deviation from the average of the ratio of each of the butenes to total butene.

TABLE II<sup>a</sup>  
THE REACTION WITH PROPYLENE  
Ratio of butene to methyl cyclopropane

<i>P</i> (total), mm.	$1/P$ , atm. <sup>-1</sup>	Total	1- Butene	<i>cis</i> -2- Butene	<i>trans</i> - 2- Butene	Iso- butene	<i>cis</i> / <i>trans</i>
Ketene: 2600 Å. radiation							
16.6	45.8	3.28			0.627	0.429	
24.0	31.6	2.30		0.436	.405		1.08
24.1	31.5						1.39
24.1	31.5						1.14
35.0	21.6	2.00	1.060	.366	.304	.272	1.20
68.9	11.0	1.42	0.713	.340			
98.0	7.75	0.72	.364	.110	.132	.110	0.83
156.3	4.85	.70	.409	.111	.077	.097	1.43
156.3	4.85	.78	.406	.121	.138	.110	0.88
156.3	4.85	1.00	.554	.189	.125	.133	1.52
600	1.27	0.50	.272	.050	.100	.073	0.50
600	1.27	.60	.350	.087	.076	.087	1.14
1490	0.51	.51	.294	.074	.075	.070	1.01
1490	.51	.49	.331	.056	.045	.056	1.25
1490	.51	.44	.224	.075	.070	.066	1.07
Ketene: 3100 Å. radiation							
16.2	47.0	4.51	2.30	0.705	0.871	0.653	0.81
23.6	32.2	2.49			.451	.368	
23.6	32.2	3.16			.571	.466	
33.4	22.7	2.13	1.08	.434	.346	.271	1.25
33.4	22.7	2.06	1.05	.411	.330	.269	1.24
73.8	10.3	1.22	0.628	.264	.179	.155	1.47
101.0	7.52	0.87	.439	.150	.152	.124	0.95
101.0	7.52	.88	.474	.158	.138	.110	1.15
101.5	7.49	.79	.434	.139	.111	.099	1.25
101.5	7.49	.81	.513	.166	.100	.100	1.66
101.5	7.49	.93	.518	.171	.123	.116	1.39
1970	0.39	.38	.233	.051	.049	.041	1.05
1970	.39	.42	.260	.056	.056	.053	0.99
1970	.39	.43	.262	.062	.053	.051	1.18
1970	.39		.248	.060			
Diazomethane: Polychromatic radiation							
8.3	91.6	11.29	4.36	2.04	2.96	1.93	0.70
22.7	33.5	5.29	2.28	0.980	1.10	0.950	.89
46.4	16.4	3.70	1.702	.655	0.747	.599	.88
46.4	16.4	3.53	1.624	.674	.688	.544	.98
102	7.45	1.99	0.948	.367	.375	.305	.98
102	7.45	1.98	.939	.366	.362	.308	1.01
102	7.45	1.93	.909	.354	.362	.309	0.98
271	2.80	1.326	.640	.220	.215	.251	1.02
271	2.80	1.141	.581	.200	.192	.169	1.04
271	2.80	1.301	.658	.226	.220	.196	1.03
271	2.80	1.040	.597	.223	.229	.220	0.97
271	2.80	1.103	.453	.190	.247	.213	0.77
636	1.20	0.698	.394	.138	.098	.098	1.41
636	1.20	.694	.381	.134	.106	.102	1.27
636	1.20	.659	.365	.127	.104	.096	1.23
2270	0.34	.560	.318	.073	.088	.082	0.83
2270	.34	.694	.400	.092	.107	.096	.86
2270	.34	.532	.309	.071	.074	.077	.95

<sup>a</sup> In some early analyses peaks were not completely separated, hence the individual butenes were not all reported.

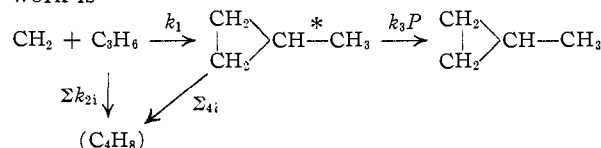
The average ratios of *cis*-2-butene to *trans*-2-butene are also given in Table IV together with their 90% confidence limits. 1.00 is within the confidence limits in each case, but there seems to be a tendency to favor *cis*. Table I shows that there is a slight but definite tendency for the *cis/trans* ratio to increase as the pressure increases in the diazomethane experiments. Since this is the most energetic system studied (see below), it is possible that this effect is due to isomerization of "hot" 2-butene from *cis* into the more stable *trans* form at low pressures. The data are not precise enough, however, to estimate the rate constant for this isomerization.

**Propylene.**—The mechanism for the reaction of methylene with propylene suggested by previous

TABLE III  
EFFECT OF EXTENT OF REACTION ON YIELDS OF PRODUCTS  
USING KETENE. TOTAL PRESSURE 100 MM.

Ex- posure time, min.	% De- comp.	Total butene Methyl cyclo- propane	Fraction of total butene			Isobutene
			1- Butene	<i>cis</i> -2- Butene	<i>trans</i> -2- Butene	
A. Reaction with cyclopropane: 2600 Å. radiation						
157	6	1.55	0.336	0.213	0.301	0.151
		1.43		.303	.252	
240	9	1.65		.276	.228	
531	20	1.43	0.347	.277	.250	0.127
		1.47		.255	.241	
B. Reaction with propylene: 3100 Å. radiation						
15	10	0.785	0.434	0.139	0.111	0.099
		.806	.513	.166	.100	.100
		.929	.518	.171	.123	.116
60	40	.866	.439	.150	.152	.124
		.882	.474	.158	.138	.110

work is



and yields the steady state relations

$$\frac{(\text{C}_4\text{H}_8)}{(\text{methyl cyclopropane})} = \frac{k_2}{k_1} + \frac{k_4}{k_3 P} \left(1 + \frac{k_2}{k_1}\right) \quad (3)$$

$$\frac{(\text{C}_4\text{H}_8)_i}{(\text{methyl cyclopropane})} = \frac{k_{2i}}{k_1} + \frac{k_4}{k_3 P} \left(\frac{k_{4i}}{k_4} + \frac{k_{2i}}{k_1}\right) \quad (4)$$

The plots of the ratio of total butene and the individual butenes to methyl cyclopropane as a function of the reciprocal of the total pressure, are similar to Fig. 2, except that the line intercepts the ordinate. As was observed with cyclopropane, the diazomethane data fit a straight line only at high pressures and hence only points for pressures above 46 mm. were used to obtain the ratios of rate constants. For each of the twelve sets of data a least-squares straight line was fitted and the mean-square deviations used to calculate 90% confidence limits. The intercept gives  $k_2/k_1$  or  $k_{2i}/k_1$  directly. From the plot of total butene yield,  $k_4/k_3$  is obtained by dividing the slope by one plus the intercept. From the plots of individual butene yields,  $k_{4i}/k_4$  are obtained by dividing the slope by  $k_4/k_3$  and subtracting the intercept. The rate constant ratios obtained were used to calculate the quantities given in Tables IV and V, which will be explained in the discussion. It will be noted (Table IV) that the sum of  $k_{4i}/k_4$  is not exactly unity, as would be expected from the definition of  $k_4$ . (The same is true of the sum of  $k_{2i}/k_1$  as compared with  $k_2/k_1$ .) This reflects the experimental errors, since each ratio was determined from a separate plot. In each case, however, unity lies well within the 90% confidence limits of the sum. The average *cis/trans* ratio is also given in Table IV together with its 90% confidence limit. It will be noted that in each case 1.00 falls within the limits but that there appears to be a slight tendency to favor *cis* when ketene is used as a source of methylene.

**Curvature in Diazomethane Plots.**—Frey<sup>5</sup> observed strong curvature at high pressures in the

TABLE IV  
 ENERGIES OF ACTIVATED MOLECULES AND RELATIVE PROBABILITIES OF HYDROGEN TRANSFER

Source of activated molecules	$\frac{k_4}{k_3}$ atm.	Lifetime $1/k_4$ sec.	$E_a$ kcal./ mole	$\alpha_{ba}$	$\alpha_{bb}$	$\alpha_{ab}$	$\frac{k_{41} + k_{42} + k_{43}}{k_4}$	$\frac{Cis}{Trans}$
Diazomethane + cyclopropane	$0.437 \pm 0.040$	$2.3 \times 10^{-10}$	122	$1.19 \pm 0.04$	$0.98 \pm 0.04$	$0.65 \pm 0.02$	1.00	$1.05 \pm 0.21$
Ketene + cyclopropane, 3100 Å.	$.284 \pm .051$	$3.6 \times 10^{-10}$	119	$1.01 \pm .20$	$1.17 \pm .16$	$.625 \pm .06$	1.0	$1.43 \pm .45$
Ketene + cyclopropane, 2600 Å.	$.202 \pm .011$	$4.9 \times 10^{-10}$	117	$0.95 \pm .05$	$1.21 \pm .05$	$.665 \pm .045$	1.00	$1.22 \pm .35$
Diazomethane + propylene	$.120 \pm .008$	$8.3 \times 10^{-10}$	115	$0.90 \pm .18$	$1.10 \pm .12$	$.75 \pm .15$	0.95	$0.99 \pm .17$
Ketene + propylene, 3100 Å.	$.060 \pm .007$	$1.7 \times 10^{-9}$	111	$1.32 \pm .25$	$1.13 \pm .18$	$.90 \pm .20$	1.16	$1.20 \pm .22$
Ketene + propylene, 2600 Å.	$.041 \pm .004$	$2.4 \times 10^{-9}$	109	$1.53 \pm .50$	$1.10 \pm .20$	$.65 \pm .15$	1.18	$1.11 \pm .26$
Thermal (ref. 13)	.00012	$8.3 \times 10^{-7}$	90	1.00	0.91	0.76		
Weighted average of photolytic data				1.08	1.10	0.675		

 TABLE V  
 RELATIVE RATES OF ATTACK ON C-H AND C=C BONDS

Hydrocarbon	Source of CH <sub>2</sub>	Rate of attack relative to type c C-H bond		
		C=C	Type a C-H	Type b C-H
Ethylene	CH <sub>2</sub> CO 3100 Å.	8.9		
Ethylene-D <sub>2</sub> (ref. 3)	CH <sub>2</sub> CO 3100 Å.	28.5		
	CH <sub>2</sub> CO 3650 Å.	26.5		
Propylene	CH <sub>2</sub> N <sub>2</sub>	$11 \pm 1$	$1.2 \pm 0.4$	$1.0 \pm 0.2$
	CH <sub>2</sub> CO 2600 Å.	$16.5 \pm 5$	$1.5 \pm .5$	$1.1 \pm .3$
	CH <sub>2</sub> CO 3100 Å.	$28.5 \pm 7$	$1.7 \pm .25$	$0.7 \pm .2$
Isobutene (ref. 5) (ref. 10) (ref. 4) (ref. 5)	CH <sub>2</sub> N <sub>2</sub>	10.5	1.1	
	CH <sub>2</sub> CO 3100 Å.	16	0.85	
	CH <sub>2</sub> CO 3100 + 3650 Å.	18	.92	
	CH <sub>3</sub> N <sub>2</sub> with inert gas	17	.87	

plots of his data on the reaction of isobutene with diazomethane. On our plots, however, the region of this curvature would be  $1/P < 0.5$  (due to the fewer degrees of freedom in methyl cyclopropane) *i.e.*, at a much higher pressure than suggested by Fig. 3. In Fig. 3 only two points do not fit well on the straight line. Appreciable amounts of C<sub>5</sub> hydrocarbons were found in these samples, which means that an equivalent amount of C<sub>4</sub> hydrocarbons reacted with methylene. Since C=C bonds are attacked more than ten times as fast as C-H bonds (see Table V), the butenes would be depleted much faster than methyl cyclopropane, resulting in too low a value for the butene/methyl cyclopropane ratio. We can almost certainly conclude, therefore, that the low pressure points in our data are in error, and there is no curvature in this pressure region.

**Lifetimes and Energies of Activated Methyl Cyclopropane.**—Since  $k_3$  is proportional to the collision rate, the lifetimes  $1/k_4$  of the activated methyl cyclopropane molecules can be estimated by assuming that the collisional deactivation efficiency of propylene and cyclopropane is unity. This is a questionable assumption because the methyl cyclopropane molecules produced under different conditions contain different amounts of energy and we choose it for simplicity only. Assuming a collision diameter of 5 Å. and a reduced mass of 56 atomic mass units,  $k_3$  is then approximately  $10^{10}$  atm.<sup>-1</sup> sec.<sup>-1</sup>.

Assuming the same collisional deactivation efficiency, the lifetimes of "hot" cyclopropane and its homologs are found to increase rapidly with increasing number of internal degrees of freedom.

Thus, using 3100 Å. radiation, the ratio  $k_4/k_3$  was found to be equal to 1.19 atm. in the reaction of ketene with ethylene<sup>2,3</sup>; in the reaction with propylene it is 0.060 and in the reaction with isobutene, yielding 1,1-dimethyl cyclopropane,<sup>10</sup> it is only 0.0032. Frey and Kistiakowsky<sup>2</sup> failed to note this trend in their preliminary experiments with cyclopropane, which undoubtedly is due to imperfections of the analytical method which did not resolve the butenes.

Knowing the lifetimes of the activated molecules, the Slater theory of unimolecular reactions<sup>11</sup> provides a self-consistent classical model for estimating the energies of the activated molecules. The Marcus-Rice treatment of the problem<sup>3,12</sup> may give more refined results, but the uncertainty about the relative collisional deactivation efficiency of the various "hot" methyl cyclopropane molecules is such as to make these more elaborate calculations hardly worth while. According to the Slater theory, the rate of isomerization of activated molecules of energy  $E$  is

$$k_4 = \nu (1 - E_0/E)^{n-1} \quad (7)$$

where  $E_0$  is the minimum energy for isomerization to occur,  $\nu$  is an energy-independent frequency factor and  $n$  is an adjustable parameter. These constants can be estimated from the thermal isomerization rate:  $E_0$  is the activation energy,  $\nu$  is the pre-exponential factor of the high pressure limiting

(10) Unpublished data, see Ph.D. thesis of J. N. Butler, Harvard 1959.

(11) N. B. Slater, *Phil. Trans.*, **246A**, 57 (1953); *Proc. Roy. Soc. (London)*, **A194**, 112 (1948); *Proc. Camb. Phil. Soc.*, **35**, 56 (1939).

(12) R. A. Marcus and O. K. Rice, *J. Phys. Coll. Chem.*, **55**, 894 (1951).

rate and  $n$  is the number of effective oscillators obtained from the fall-off of rate at low pressures. Chesick<sup>13</sup> studied the rate of thermal isomerization of methyl cyclopropane and obtained  $E_0 = 63.5$  kcal./mole and  $\nu = 10^{15.1}$ . Since  $n$  is 13 for cyclopropane, which has 21 vibrational degrees of freedom, we shall take  $n$  for methyl cyclopropane to be 13/21 of the 30 vibrational degrees of freedom, or 18.5.

An independent method of estimating  $\nu$  is available from our data. For each type of methylene produced  $k_4$  was measured for methyl cyclopropane produced by reaction with cyclopropane and with propylene, whose energy difference is known to be  $7.86 \pm 0.11$  kcal./mole.<sup>14</sup> Slater's expression then gives two simultaneous equations for  $E$  and  $\nu$ . Assuming that  $E_0 = 63.5$  kcal./mole and  $n = 18.5$ , the values obtained for  $\nu$  are

Diazomethane	$1.37 \times 10^{15}$ sec. <sup>-1</sup>
Ketene, 3100 Å.	$1.62 \times 10^{15}$ sec. <sup>-1</sup>
Ketene, 2600 Å.	$1.96 \times 10^{15}$ sec. <sup>-1</sup>

The average of these three values is  $\nu = 10^{15.2}$ , which agrees very well with  $\nu = 10^{15.1}$  obtained from the thermal data. It might be noted here that a choice  $n = 17$  gives an average  $\nu = 10^{15.1}$  which suggests that the value  $n = 18.5$  is accurate probably to  $\pm 3$ . The lifetimes and energies of the activated methyl cyclopropane molecules are summarized in Table IV. Also included in the table is the lifetime of thermally activated molecules, estimated from the pressure where the rate of thermal isomerization is half of its high pressure limiting value.<sup>13</sup> The energy of thermally activated molecules, calculated also by eq. 7, is seen to be much less than energy of the activated molecules produced by methylene.

The energies shown in Table IV are unrealistically high because of the classical model selected for the calculation. Thus for the thermally activated molecules the energy shown is 91.5 kcal., whereas it should be 63.5 plus the average thermal energy of methyl cyclopropane at 500°; that is, about 70–75 kcal. total. More realistic estimates of the total energy content of the photochemically formed methyl cyclopropane molecules might be obtained by deducting from the values in Table IV the above difference in the estimates for the thermally activated molecules, *i.e.* ca. 20 kcal.

Of more significance and interest are the relative values: the lifetime of "hot" methyl cyclopropane molecules can be changed by a factor of 3600 on going from the thermal reaction to the most energetic photochemically produced methylene! Differences which are observed in the products of reaction of different types of methylene with the same hydrocarbon prove conclusively that, depending on the conditions of the photolysis, methylene with varying amounts of excess energy can be produced. Since both the translational and the vibrational energy of methylene is incorporated in the "hot" methyl cyclopropane, no positive identification of

which is involved can be made. The high absolute reactivity of methylene<sup>15</sup> and Frey's<sup>5</sup> measurement of the relative deactivating efficiency of inert gases suggest that at least some of the energy of methylene from diazomethane is translational. On the other hand the experiments of Mahan<sup>16</sup> indicated that ethylidene from methyl ketene has excess vibrational energy and this may also be the case for methylene from ketene. Rather surprisingly the total energy content of methylene formed from ketene by radiation of longer wave length (3100 Å.) is slightly larger than of that formed by more energetic photons (2600 Å.), a finding which is very unlikely to be due to experimental errors. Evidently the additional energy imparted to ketene by higher frequency radiation goes into increased vibrational energy of CO molecules.

**Isomerization Mechanism of Methyl Cyclopropane.**—Rabinovitch, Schlag and Wiberg<sup>17</sup> suggested that cyclopropane isomerizes *via* primary formation of a trimethylene radical, but Smith<sup>18</sup> interpreted their results in terms of the hydrogen transfer mechanism of Slater,<sup>19</sup> suggesting that the transition state involves a CH<sub>2</sub> group which is rotated until it lies in the plane of the ring.

The present data cannot distinguish between the two mechanisms, although they favor slightly the hydrogen transfer as the primary step.

Whether it is assumed that a hydrogen atom is transferred first and then the cyclopropane ring breaks (hydrogen transfer mechanism), or it is assumed that the ring breaks to form a trimethylene-type free radical and then the hydrogen is transferred (trimethylene mechanism) the butene isomer which is obtained will depend on the carbons between which the hydrogen is transferred.

In the following discussion, the carbon of the cyclopropane ring to which the methyl group is attached will be referred to as the a-carbon, and the other two carbons of the ring will be referred to as b-carbons. Hydrogen atoms attached to these carbons will be referred to by the same letters. Then  $b \rightarrow a$  gives 1-butene, statistical weight 2 ( $k_{41}$ ),  $b \rightarrow b$  gives 2-butene, statistical weight 2 ( $k_{42}$ ),  $a \rightarrow b$  gives isobutene, statistical weight 1 ( $k_{43}$ ). The different statistical weights arise as follows: there are four b-hydrogens, half of which will be transferred randomly to a b-carbon and half to an a-carbon. There is one a-hydrogen, which can be transferred only to a b-carbon. Thus if there were completely random hydrogen transfer,  $k_{41}/k_4$  and  $k_{42}/k_4$  would be  $2/5$  and  $k_{43}/k_4$  would be  $1/5$ . The probability of transfer,  $\alpha$ , will be defined as the ratio of the measured  $k_{4i}/k_4$  to the value for random transfer

$$\begin{aligned}\alpha_{ba} &= 2.5 k_{41}/k_4 \\ \alpha_{bb} &= 2.5 k_{42}/k_4 \\ \alpha_{ab} &= 5 k_{43}/k_4\end{aligned}$$

(If the transfer is random, these coefficients are unity.) The values obtained from the data in Ta-

(13) J. Chesick, private communication. The authors have been informed since writing this paper that more accurate values are  $E_0 = 65.0$  kcal./mole,  $\nu = 10^{15.46}$  and  $n = 18$ . These changes do not affect our conclusions.

(14) J. W. Knowlton and F. D. Rossini, *J. Research Natl. Bur. Standards*, **43**, 113 (1949).

(15) G. B. Kistiakowsky and K. Sauer, *This Journal*, **78**, 5699 (1956); G. B. Kistiakowsky and P. H. Kydd, *ibid.*, **79**, 4825 (1957).

(16) G. B. Kistiakowsky and B. H. Mahan, *ibid.*, **79**, 2412 (1957).

(17) B. S. Rabinovitch, E. W. Schlag and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958).

(18) F. T. Smith, *ibid.*, **29**, 235 (1958).

(19) N. B. Slater, *Proc. Roy. Soc. (London)*, **A218**, 224 (1953).

bles I and II with their 90% confidence limits are shown in Table IV. The values of  $\alpha$  have been weighted by the reciprocals of their confidence limits to obtain the weighted averages shown. From these averages the probability of a  $\rightarrow$  b transfer can be seen to be considerably smaller than b  $\rightarrow$  a or b  $\rightarrow$  b transfer. The values obtained from the propylene data are considerably less precise than those obtained from the cyclopropane data because of the more complex reaction mechanism. As was mentioned before, the three  $k_{ii}/k_4$  ratios being determined from different plots, their sum is not exactly unity. This sum gives an idea of the direction in which the errors are: it is most likely that  $\alpha_{ba}$  is too low for diazomethane-propylene and too high for the two ketene-propylene values.

The isomer distribution in the thermal isomerization of methyl cyclopropane<sup>13</sup> gives values for  $\alpha$  which are similar to ours (Table IV). Further, the activation energy for the formation of isobutene (a  $\rightarrow$  b transfer) was found to be about 3 kcal./mole higher than the activation energy for the formation of the other butenes.

On the basis of the Smith hydrogen transfer mechanism the lower probability of the a  $\rightarrow$  b transfer mechanism is understood readily because here a group with a large moment of inertia,  $C_{CH_3}^H$ , must be rotated instead of  $CH_2$ . No such straightforward explanation is possible for the trimethylene-type intermediate mechanism.

The most significant aspect of Table IV is that the average yields of the three butenes obtained from the reactions with cyclopropane, within the confidence limits of the data, are the same as those from propylene and are, except for the already noted lower probability of a  $\rightarrow$  b transfer, very nearly random. This is most difficult to reconcile with the concept used by Slater in his theory of unimolecular reactions that the energy does not migrate between the normal modes of vibration, since undoubtedly different modes are excited when methylene is inserted between a carbon and hydrogen of cyclopropane or when it opens the double bond of propylene. Thus we are led to conclude that energy does migrate, as in the Rice-Kassel theory, between the normal modes, which migration is readily understandable because of the anharmonicity of molecular vibrations.

Table IV shows seemingly significant trends of  $\alpha_{ba}$  and  $\alpha_{bb}$  values with energy content in the reactions of methylene with cyclopropane, but the trend is reversed when we go to the thermal reaction, which involves molecules of lowest energy. It is possible that these apparent trends are due to experiment errors.

#### Primary Reaction of Methylene with Propylene.

—The high-pressure limiting yields of the butenes give the constants  $k_{21}/k_1$  which may be interpreted in terms of the relative rates of attack of methylene on various types of C-H and C=C bonds. In Table V are listed the rates of attack on C=C bonds, C-H bonds in a methyl group (type a) and the central C-H bond in propylene (type b) as compared to the rate of attack on C-H bonds adjacent to a C=C bond (type c). 90% confidence limits are given for our data. The values of other investigators were obtained by plotting their data as a function of  $1/P$  and extrapolating to  $1/P = 0$ . (See eq. 3 and 4.)

In spite of the large uncertainties in the values, there appear to be regular trends: the high energy systems (diazomethane) provide less differentiation in the rate of attack than low energy systems (ketene). This is in agreement with the results of reaction of methylene with saturated hydrocarbons where methylene from diazomethane was found to react 1.2 times as fast with secondary C-H bonds as with primary,<sup>20</sup> and methylene from ketene was found to react 1.7 times as fast.<sup>2</sup>

It is rather interesting to note from the data of Table V that methylene formed from ketene by the 3100 Å. radiation is more selective, *i.e.* less reactive, than that formed by the 2600 Å. radiation, while the data of Table IV show that its total energy is greater. Unfortunately the uncertainties of the data are such that this trend in Table V is by no means proven and its interpretation will be delayed pending further experimental work.

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(20) H. M. Frey, *THIS JOURNAL*, **80**, 5005 (1958).