

Reaction of Methylene with Methyl Isopropyl Ether

Tadashi INOUE and Yoshimasa TAKEZAKI*

(Takezaki Laboratory)

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Vapor phase reaction of methylene produced by ketene photolysis has been studied in the presence of methyl isopropyl ether as the substrate in the temperature range between 0° and 100°.

From the product analysis, the following relative reactivities (per bond) have been determined in the insertion of CH₂ into various kinds of C-H bond:

α primary : β primary = 1 : 0.7,

α primary : α tertiary = 1 : 1.8~3 (varying with temperature),

$E_{\alpha\text{prim}} = E_{\beta\text{prim}} = E_{\alpha\text{tert}} + 1.0\text{Kcal.}$

INTRODUCTION

Extensive investigations have been made in recent years on the complex features of the reaction of methylene produced from ketene or diazomethane by photolysis. From the survey of the papers so far appeared, it seems that at least two factors, *i. e.*, the difference in CH₂ source and the reaction medium (liquid or gas phase), affect the product distribution appreciably. The occurrence of direct insertion of CH₂ into C-H bond, however, seems to be well established as a main reaction in the system containing saturated substrate^{1,11}, and the discriminating character of this insertion among the bonds of different types has been accepted generally at least in the gas phase^{2,3,4,5}. On the other hand, in the gas phase it has been pointed out that some H atom abstraction by CH₂ occurs simultaneously^{1,6}, and the CH₃ thus formed would produce, via usual radical reaction course, the products similar to those by methylene insertion. The reason why and the extent of this side reaction have been discussed and a trial has been made to explain the problem of discrimination on these points⁶, but no definite conclusions have been obtained.

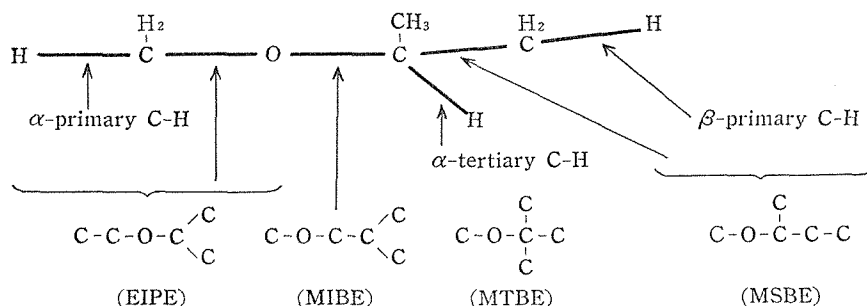
Furthermore, the indications that the insertion of CH₂ into C-C⁷ or C-O⁸ bond cannot take place have been obtained, and, though not decidedly, the possibility of O-H insertion has been suggested in the reaction with methanol conducted in our laboratory⁸.

Following the previous work in the research of the reaction of methylene with oxygen-containing compounds⁹, the vapor phase reaction with methyl isopropyl ether was examined in which methylene was produced photochemically from ketene. From the gas chromatographical analysis of the isomer distribution in the reaction products which is predicted by the scheme shown below, together with the assumption that the observed products have mainly resulted from the

* 井上忠司, 竹崎嘉真

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direct insertion of CH_2 under the present conditions, relative reactivities of some C-H bonds toward insertion in branched chain ether have been obtained.



The arrows denote the sites of the insertion of CH_2 .

EXPERIMENTAL

Reactor. A glass cylinder (45mm ϕ ×170mm, 270cc) with a quartz window was mounted in an electric furnace kept at reaction temperatures within $\pm 2^\circ$ or in an ice water bath having a quartz window for irradiation.

Light source: High pressure mercury lamp (SHLD 500w, d.c. operated, 2537Å reversed). The beam is collimated roughly by a quartz lens and stops. A water-cooled water layer between two UV-27 glass filters cuts off the light shorter than 3130Å and heat radiation. Considering the intensity distribution of the lamp and the absorbance of ketene⁹, the only 3130 and 3346Å light remains effective.

Materials. Ethers (reactant and the authentic samples for the identification of product isomers) were synthesized by the methods given in "Synthetic Organic Chemistry"⁹. Ketene was prepared from acetone by the ketene lamp method¹⁰, and purified by bulb-to-bulb distillation and stored in a polyethylene reservoir at -78° . Under this condition, only 0.8% of the sample polymerized in a week. These reactants were sufficiently pure as examined by gas chromatography.

Procedure. Reactants were introduced successively into the reactor up to the desired pressure, and after the exposure of definite duration the products (all in vapor state in the reactor) were withdrawn by means of Toepler pump into a gas burette through a small cold trap cooled at -78°C . Liquid and gaseous products thus obtained were analyzed separately by gas chromatography, the column packings being as follows: for CO , CH_4 , and CO_2 , active carbon at 80° ; for C_2H_6 , C_3H_8 , and C_4H_{10} , Na permutite 2m at 45° ; and for ether isomers, tricresyl phosphate + polyethylene glycol (300) on celite 4m at 50° .

RESULT AND DISCUSSION

At first, variation of reaction products with the change of the charge ratio (Me isopropyl ether/Ketene) was studied at 50° within the range from 0 to 5 (Table 1 and Fig. 1); as is shown by the curves in the Figure, it, seems that,

Table 1. Reaction products.

Ketene charge mmHg	MIPE Charge mmHg	(MIPE) (Ketene)	Time of irradiation (min)	Fraction of Decomposition	(Product)/(CO)								Balance
					C ₂ H ₄	C ₃ H ₆	C ₂ H ₆	C ₃ H ₈	MSBE	EIPE	MTBE	MeOMe	
Reaction at 50°C													
24.9	0	0	6	0.271	0.240	0.048	trace	0	—	—	—		0.62
67.3	70.4	1.05	10	0.138	0.184	0.041	0.051	—	0.158	0.112	0.083		0.95
44.3	66.4	1.50	10	0.186	0.192	0.067	0.055	—	0.158	0.125	0.090		1.07
50.6	91.7	1.81	6	0.147	0.115	0.045	0.043	0.013	0.173	0.121	0.070		0.85
50.0	141.3	2.83	10	0.189	0.114	0.040	0.063	0.011	0.193	—	—		—
44.9	137.3	3.06	9	0.162	0.070	0.060	0.037	0.014	0.210	0.163	0.121		0.93
39.6	160.3	4.05	12	0.187	0.100	0.042	0.061	0.010	0.233	0.160	—		—
43.7	195.5	4.47	10	0.220	0.092	0.033	0.047	trace	—	—	—		—
29.5	145.0	4.92	15	0.379	0.048	0.048	0.044	0.010	0.220	0.151	0.122		0.88
Reaction at 100°C													
31.0	109.0	3.32	12	0.266	0.111	0.044	0.071		0.227	0.168	0.109		1.00
41.3	165.9	4.02	12	0.251	0.087	0.037	0.052		0.224	0.160	0.099		0.87
36.9	158.0	4.28	11	0.226	0.074	0.039	0.050		0.228	0.156	0.093		0.84
Reaction at 0°C													
39.3	161.5	4.11	15	0.289	0.168	0.054	0.100		0.239	0.173	0.176		1.29
35.7	171.0	4.79	15	0.378	0.083	0.048	0.060		0.246	0.175	0.190		1.04
36.3	174.8	4.81	15	0.379	0.085	0.055	0.055		0.249	0.171	0.175		1.04
34.9	174.8	5.00	16	0.354	0.087	0.054	0.061		0.241	0.176	0.171		1.05
19.2	96.2	5.01	15	0.355	0.056	0.060	0.040		0.272	0.180	0.173		1.00
34.7	147.0	4.24	15	(0.35)								0.033	

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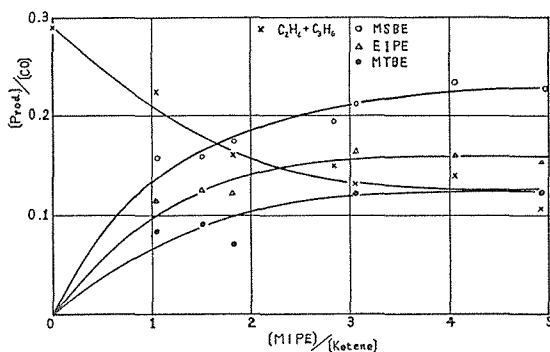


Fig. 1. Reaction product at 50°C.

when ether is present 4 times or more as much as ketene the reaction of CH_2 with ketene is almost negligible in competition with the substrate. Then, runs were made at two reaction temperatures with the charge ratio of 4-5 (Table 1). In the present investigation, no experiment has been conducted on the effect of partial pressure of each component or of the light intensity, and the extents of ketene decomposition in a single run were 20-30% of the initial charge, further, no examination has been made for the trends in product distribution with the degree of photodecomposition. Therefore, we cannot discuss the mechanism in detail and get the relative rates of methylene reactions of different reaction-order by comparing merely the final amounts of products in each run. As for the reactions of the same type, $CH_2 + \text{ether} \rightarrow \text{higher ether}$ (4 isomers), however, these data may be used for the calculation of relative reactivities.

In this paper the amounts of each product are expressed by the ratio to the CO produced in the same run. This, not only eliminates the complexity due to the variation of the absolute amount of light absorption from run to run, but also gives the quantum yield of each product in the case where sufficient amount of the substrate is present and the reaction $CH_2 + CH_3CO \rightarrow C_2H_4 + CO$ becomes negligible and the process to produce CO is the only primary photodecomposition. The decomposed fraction given in Table 1. is defined by (amount of CO produced)/(amount of ketene charged), so this figure will denote the fraction of ketene used to produce CH_2 photolytically only when the ether is present in large excess.

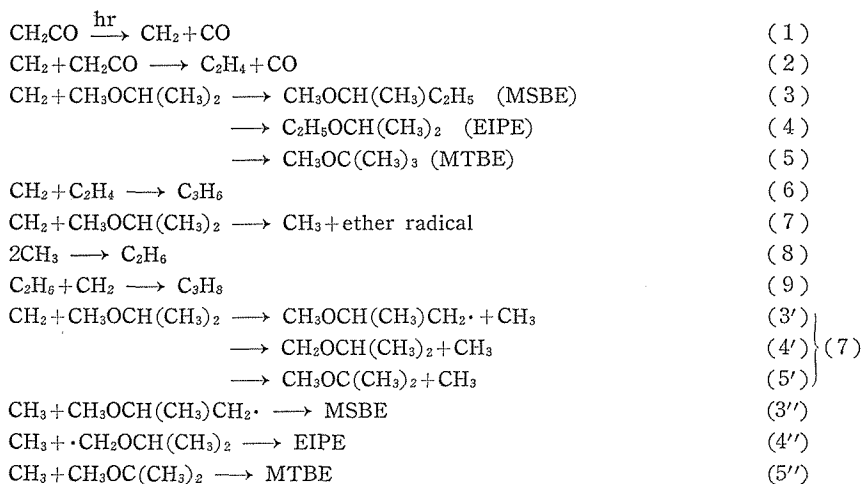
Besides CO, the main products in the presence of the substrate are methyl sec-butyl ether (MSBE), ethyl isopropyl ether (EIPE), and methyl tert-butyl ether (MTBE), and some ethylene and propylene and, as minor products, ethane and propane have been observed. In addition, traces of methane and butane were detected and an unidentified peak was observed in the gas chromatogram of ether analysis (the retention time was a little longer than that of MSBE and the peak area was 0.3 times that of MSBE), but any trace of methyl isobutyl ether (MIBE) could not be found. The presence of a small amount of dimethyl ether was proved in one run (the last line in Table 1). This must be generally so in the other runs although no experiments for the detection were made there; this seems to indicate a slight occurrence of the splitting of C-O bond by methylene, *i. e.*, $CH_2 + CH_3OCH(CH_3)_2 \rightarrow CH_3OCH_3 + CH_2=CH-CH_3$, as was found by Franzen¹¹⁾.

Now, concerning the main reactions, the absence of MIBE rules out the C-O bond insertion in accord with the conclusion by Doering⁷, hence EIPE must have been resulted solely from the insertion into α primary C-H bond; MTBE should be the insertion product of α tertiary C-H bond, and among the two possibilities of the formation of MSBE, *i.e.*, insertion into C-C bond or β primary C-H bond, we assume that the latter is the case here according to Doering⁷.

The existence of ethane suggests the formation of CH_3 radical during the run. The absence of methane would not conflict with this supposition because the reaction tempratur are not so high in this study. Therefore we have to consider the possibility of the formation of the produts observed through the radical processes proposed by Richardson⁶ and also checked by Doering¹¹, *viz.*, $\text{CH}_2 + \text{ROR}'\text{-H} \rightarrow \text{CH}_3 + \text{ROR}'\cdot$, $\text{ROR}'\cdot + \text{CH}_3 \rightarrow \text{ROR}'\text{-CH}_3$. Unfortunately we have no means to discriminate this process from the direct insertion in this study. The material balance of CH_2 given in Table 1. is

$$\text{Balance} = \{2(\text{C}_2\text{H}_4) + 2(\text{C}_2\text{H}_6) + 3(\text{C}_3\text{H}_6) + 3(\text{C}_3\text{H}_8) + (\text{MTBE}) + (\text{EIPE}) + (\text{MSBE})\} / (\text{CO}),$$

and is based on the scheme assumed below, (1)~(9), as the most probable ones. If this is correct and there are no missing products, the balance should be unity. This appears to be satisfied fairly well except the case of decomposition of ketene alone. The scheme involving radical processes (3')~(5''), however, leads to the same balance on CH_2 also.



In Table 2. are summerized the average values of the observed distribution

Table 2. Relative reactivities.

Site of insertion	Rate const.	Product	Ratio of (prod)/(CO) (A)			Number of relevant bond (B)	Selectivity A/B		
			0°	50°	100°		0°	50°	100°
α primary C-H	k_4	EIPE	1.0	1.0	1.0	3	1.0	1.0	1.0
α tertiary C-H	k_5	MTBE	1.0	0.75	0.61	1	3.0	2.9	1.8
β primary C-H	k_3	MSBE	1.40	1.33	1.39	6	0.70	0.66	0.69

of ether isomers in Table 1. together with the selectivity, *i.e.*, relative reactivity per bond. If we assume the direct insertion mechanism as prevailing, we can take these relative amounts of the product directly as the ratios of the rate constants of CH_2 insertion into different bonding, *i.e.*, k_5/k_4 and k_3/k_4 , and, as the selectivities we get

α primary: β primary = 1 : 0.7,

α primary: α tertiary = 1 : 1.8~3 (varying with temperature),

From the Arrhenius plot (Fig. 2) we can determine the difference of activation heats, *viz.*,

$$E_{\alpha\text{prim}} = E_{\beta\text{prim}} = E_{\alpha\text{tert}} + 1.0\text{kcal.}$$

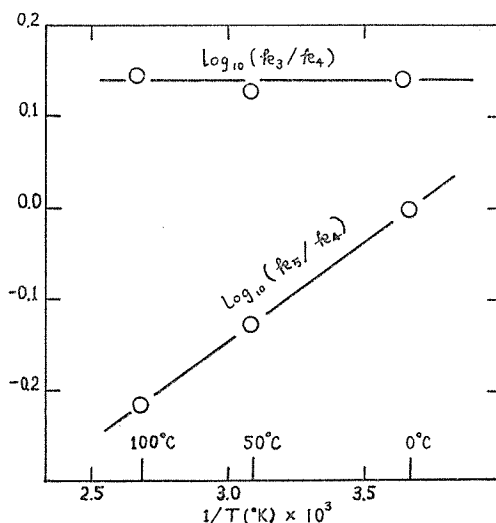


Fig. 2. Arrhenius plot.

These values may be compared with those obtained under various conditions, *e.g.*, α secondary: β secondary = 1 : 0.77 for tetrahydrofuran (liquid, CH_2N_2 , Doering)⁴, and primary: tertiary = 1 : 1.2 (liquid, CH_2N_2 , Doering)⁷, 1 : 1.5 (gas, CH_2N_2 Frey)⁸, or 1 : 1.5 (gas, CH_2CO , Knox, recalculated for 300°K by the present authors)⁵, and $E_{\text{prim}} - E_{\text{tert}} = -190\text{cal}$ (Knox)⁵.

The agreement with other authors' seems to be fairly well except with the value by Knox. It is remarkable that the sign of our value for $E_{\text{prim}} - E_{\text{tert}}$ is just the reverse of that given by Knox. On the other hand, in another extreme case where the product ether isomers are solely resulted through a radical mechanism, if we assume that the mutual recombination of radicals derived from the substrate by the abstraction does not occur (this assumption, *i.e.*, only the combination of CH_3 with CH_3 or with ether radical is allowed, seems quite improbable although no conceivable di-ether could be detected in our analyses), the rate equation becomes a simple form and the following relations are obtained:

$$\frac{(\text{MTBE})}{(\text{EIPE})} = \frac{k_5'}{k_4'} \quad \frac{(\text{MSBE})}{(\text{EIPE})} = \frac{k_3'}{k_4'}$$

Thus, in this extreme case, the ratio of the amounts of products and accordingly the difference of activation heats are to be related to the rate of H atom abstraction from ether by CH_2 , but since we do not know the extent of this course taking part in the whole mechanism (it must be a small portion as pointed out by Doering¹¹), it is difficult to go further into the detailed discussion of our results.

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