Reactions of Methylene Radicals with Benzene and Toluene in the Gas Phase[1]

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Many investigations have been made of the reactions of methylene radicals with a variety of organic substances, concerning the electronic state of methylene radicals during the course of the reactions,[2,3] the reactivity of the radical,[4,5] and the unimolecular decomposition and isomerization of energetic addition intermediates of the radical and the parent reactants.[6,7]

A benzene solution of diazomathane was photo-irradiated to give C_7H_8, and its chemistry was formulated equally well as cycloheptatriene or norcaradiene.[8] Meerwein et al.[9] reported that cycloheptatriene and norcaradiene were produced under similar conditions. However, they never obtained toluene.

This paper concerns the reactions of methylene radicals resulting from a photolysis of ketene with benzene and with toluene in the gas phase; it is a part of the study of the reactions of methylene radicals.

Experimental

Ketene was prepared by the pyrolysis of acetic anhydride[10] at 500°C in vacuo; it was distilled from a trap at -120°C to a trap at -196°C three times and then stored in a sample tube kept at -196°C. Its gas chromatograms (columns, benzylether and squalane) showed no impurity.

Benzene and toluene (G. R. grade reagents supplied by the Tokyo Kasei Kogyo Co.) were repeatedly degassed to 10^{-4} mmHg at -196°C and stored in sample tubes kept at -78°C. Nitrogen, Oxygen and nitric oxide (purity, 99.99, 99.98 and 99.5% respectively; supplied by the Takachiho Shoji Co.) were used without further purification. Carbon dioxide was obtained by evaporation from dry ice at -78°C. All of the above chemicals were shown by gas chromatography to have no impurity affecting the results.

The light source was a high-pressure mercury arc lamp (type I-9, supplied by the Wako Denki Co.) operated at 2.5 amp. and 200 V. Cylindrical irradiation cells were made of pyrex glass (transparent down to 2900 Å) or of quartz, their diameters and lengths being 50 mm. and 10∼50 mm. respectively. In some experiments a UV-25 filter (supplied by the Mitsubishi Denki Co.) was used, one which was transparent down to 2300 Å. Although all the spectral region of the light emitted from the lamp was used to irradiate the cell, the most effective radiation in the present study, where rather high pressures were adopted, is considered to be the light around 3130 Å, since the quantum yield of carbon monoxide formation in the photolysis of pure ketene

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[1] A part of this paper was read at the 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962.

[2] H. M. Frey, *J. Am. Chem. Soc.*, **82**, 5947 (1960).

[3] K. R. Kopecky, G. S. Hammond and P. A Leermakers, ibid., **83**, 2397 (1961).

[4] J. N. Butler and G. B. Kistiakowsky, ibid., **82**, 759 (1960).

[5] J. N. Bradley and A. Ledwith, *J. Chem. Soc.*, **1961**, 1495.

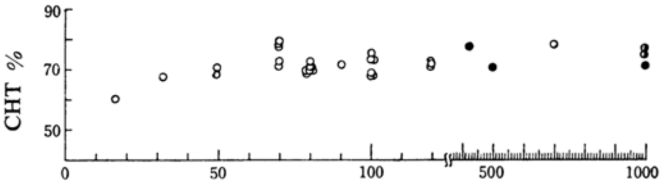
[6] H. M. Frey, *Trans. Faraday Soc.*, **58**, 516 (1961).

[7] B. Grzybowska, J. H. Knox and A. F. Trotman-Dickenson, *J. Chem. Soc.*, **1961**, 4402.

[8] W. von Doering and L. H. Knox, *J. Am. Chem. Soc.*, **72**, 2305 (1950).

[9] H. Meerwein, H. Disselnkötter, F. Rappen, H. V. Rintelen and H. van de Vloed, *Ann.*, **604**, 151 (1957).

[10] G. J. Fisher, A. F. McLean and A. W. Schizer, *J. Org. Chem.*, **18**, 1055 (1953).



Total pressure, mmHg

Fig. 1. Percentage yield of CHT plotted against total pressure.
Pyrex irradiation cell.
Ketene pressure: 4∼60 mmHg,
Benzene pressure: 12∼60 mmHg.
○ : Ketene and benzene, ◑ : CO_2 added, ● : N_2 added.

has been shown by Strachan and Noyes[11] to be 2 and pressure independent at 3130Å or shorter and to be very much smaller and remarkably reduced by raising the pressure at longer wave lengths (around 3660 Å).

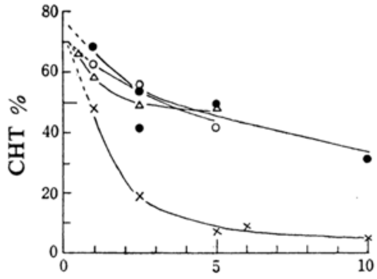
Reactants at suitable pressures were introduced successively into the irradiation cell with a breakable seal and then sealed off. After irradiation the cell was attached to the analysis system, and the breakable seal was broken by a steel breaker. The gasses not condensable at −196°C were analyzed by micro-gas analysis. Hydrocarbons which evaporated at −120°C ($C_2\sim C_4$) were analyzed by gas chromatography under reduced pressure. The columns used were packed with benzylether and squalane. The ethane and ethylene which emerged from the former column at the same retention time were recovered by a trap kept at −196°C and were subjected to the latter column in order to separate them. Substances which did not evaporate at −120°C were analyzed with a gas chromatograph (type GC-lA, supplied by the Shimadzu Seisakusho Co.). The separation columns used were Silicone DC550 for the reaction products with benzene and 7, 8-benzoquinoline for the products with toluene.

Results

The Reaction of Methylene with Benzene.— The products detected were carbon monoxide, ethylene, cycloheptatriene (designated afterwards as CHT), toluene (T) and small amounts of acetylene, ethane, propylene and propane. All the products, except CHT and T, were produced from the photolysis of ketene.

When the pyrex irradiation cell was used, the percentage yield of CHT (CHT%, CHT× 100/(CHT+T)) was found to be 70±7% at any pressure in the cell raised by added nitrogen or carbon dioxide, as Fig. 1 shows.

When the quartz irradiation cell was used, on the other hand, the percentage yield of CHT decreased with an increase in the irradiation period, but it seemed to move to about 70% at no irradiation (see Fig. 2). A small amount of [3.2.0]-bicyclohepta-2, 5-diene (<5% of CHT+T) was also detected. This time dependence of CHT% and the production of the bicycloheptadiene in the quartz cell can be understood in terms of the secondary photochemical isomerization of CHT, which was at first produced by the reaction of methylene with benzene. The photochemical isomerization of CHT in the gas phase has been reported by Srinivasan[12] to yield toluene and a small amount of the bicycloheptadiene.



Irradiation period, min.

Fig. 2. Percentage yield of CHT plotted against irradiation period.
Quartz irradiation cell.
Ketene pressure: 20 mmHg,
Benzene pressure: 60 mmHg.
○ : N_2 500 mmHg, filter, ○ : filter,
△ : CO_2 500 mmHg, filter, × : none.

The material balance, $\{2(C_2H_4+C_2H_2+C_2H_6)+3(C_3H_6+C_3H_8)+(CHT+T)\}/CO$, was 0.67± 0.1, definitely smaller than unity even at the initial stage of the reaction. This poverty in the material balance shows that there existed some products which could not be detected, since the material balance in the photolysis of pure ketene was good at least at the initial stage of the reaction.

The Reaction of Methylene with Toluene.— The results are summarized in Table I. When the pyrex irradiation cell was used, ethylbenzene (EB), *m*- and *p*-xylenes (*m*-Xy, *p*-Xy) and an unidentified compound (X) were the major products other than those resulting from

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[11] A. N. Strachan and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **76**, 3258 (1954).

[12] R. Srinivasan, ibid., **84**, 3432 (1962).

TABLE I. REACTION OF METHYLENE WITH TOLUENE

Ketene	Toluene	O_2	Irradiation period	Product				
				X	o-Xy	m-Xy	p-Xy	EB
	mmHg		min.			µmol. (%)		
10	25	0	30	0.12 (8)	0	0.58 (42)	0.35 (25)	0.34 (25)
10	25	0	40	0.36 (10)	trace	1.42 (39)	0.97 (27)	0.90 (25)
10	20	0	30	0	0		0.78[b]	
10	20	0	45	0.19 (11)	0		1.49[b] (89)	
10	20	0	60	0.40 (18)	trace		1.85[b] (82)	
10	20	0	23	0.05 (6)	0		0.79[b] (94)	
20	18	0	30	0.60 (9)	0.28 (4)	2.42 (37)	1.59 (23)	1.61 (25)
20	18	18	ca. 25	0.11 (7)	trace	0.59 (40)	0.38 (26)	0.40 (27)
10[a]	25	0	5	0.26 (6)	0.69 (17)	1.53 (36)	0.83 (20)	0.98 (23)

a) Reaction in the quartz cell. Others are in the pyrex cell.
b) Amount of m-Xy+p-Xy+EB.

TABLE II. EFFECTS OF OXYGEN AND NITRIC OXIDE ON CHT% (IN THE PYREX CELL)

Ketene	Benzene	O_2, NO	Irradiation period	Product		CHT %
				T	CHT	
	mmHg		min.	µmol.		%
20	60	O_2 20	30	0.93	1.60	63
20	60	O_2 1	30	0.91	2.17	70
20	60	0	30	1.02	2.45	71
20	60	O_2 1	30	0.91	1.99	69
20	60	0	30	0.78	2.11	73
20	60	O_2 10	30	0.61	1.15	66
20	30	NO 15	15	0.82	1.89	70
20	60	0	15	1.01	2.14	68

the photolysis of ketene. The amount of o-xylene (o-Xy) was too small to be measured quantitatively. When the quartz irradiation cell was used, however, there was much more o-xylene. About a five-fold increase in the yield of ethane was observed over that from the photolysis of ketene or that in the reaction of methylene with benzene.

The Effects of Oxygen and Nitric Oxide.—The results are summarized in Tables I and II. The addition of oxygen or nitric oxide did not affect the relative yield among the products which were produced by the reaction of methylene with benzene or toluene.

Discussion

The Reaction of Methylene with Benzene.—The most striking difference between our results and those of Doering and Knox[8] and of Meerwein and his co-workers[9] lies in the fact that we have obtained a considerable amount of toluene, while they did not. This difference must have been caused not by the difference in the source of methylene radicals, *i.e.*, of the photolysis of diazomethane employed by them and that of ketene used by us, but by the difference in the phase of the system, the liquid phase in their experiments and the gas phase in ours; there should be no essential difference in the mode of the reactions of methylene radicals whether they are produced by the photolysis of diazomethane or by that of ketene.[6,7,13]

It is almost certain that the methylene produced by the photolysis of diazomethane is at first in a singlet state and that, in the presence of a large amount of inert gas, the singlet-state methylene is collisionally deactivated to a triplet state.[6,14] Although there is no such positive evidence for the methylene produced by the photolysis of ketene, it would also be in a singlet state if the spin conservation rule is applied. Triplet methylene may

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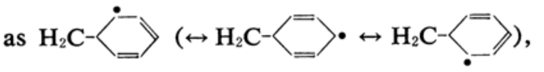
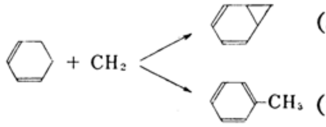
[13] H. M. Frey, *Trans. Faraday Soc.*, **57**, 951 (1961).
[14] G. Herzberg, *Proc. Royal Soc.*, **A262**, 291 (1961).

be added to benzene to give a biradical such as



which may be easily scavenged by oxygen or nitric oxide. The fact that the addition of oxygen or nitric oxide did not alter the CHT%, together with the above discussion, seems to indicate that CHT and T are produced by the singlet methylene and benzene.

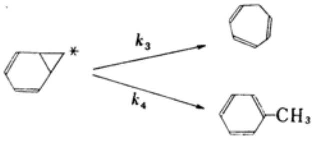
As is suggested by the reactions of methylene with olefins, the reaction with benzene may be expected to occur in two parallel ways, namely, the addition to a carbon-carbon double bond and the insertion into a carbon-hydrogen single bond, giving norcaradiene and toluene:



(addition) (1)

(insertion). (2)

The fact that the photolysis of a benzene solution of diazomethane did not give toluene,[8,9] however, seems to obviate the possibility of inserting methylene into the carbon-hydrogen bond in benzene, and the toluene obtained in the gas phase may be produced not by reaction 2 but by the isomerization of the norcaradiene produced in reaction 1. Unsubstituted norcaradiene has not yet been synthesized,[15] and it must be extremely unstable. The norcaradiene formed in reaction 1 would easily isomerize into CHT and T almost instantaneously.



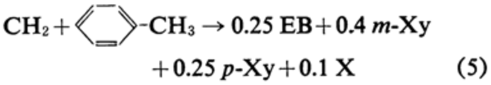
(3)

(4)

The almost constant value of CHT% (70%) indicates that the rate constant ratio, k_3/k_4, is about 7/3 in the gas phase.

The relative yield of ethane to ethylene did not vary in the photolysis of pure ketene and in the reaction of methylene with benzene. This fact may indicate that the hydrogen atom abstraction from benzene by methylene does not play any important role in the reaction.

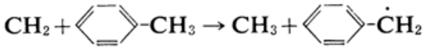
The Reaction of Methylene with Toluene.—The overall reaction can be written as follows:



(5)

By an argument similar to that on the reaction of methylene with benzene, the constancy of the relative yield among products in the presence and in the absence of oxygen may be taken as indicating that they are also produced by singlet methylene and toluene. Ethylbenzene can be produced by the insertion of methylene into a carbon-hydrogen single bond of methyl on the benzene ring. The scarcity of *o*-xylene among the products indicates that the steric hindrance caused by the substituted methyl acts strongly in this case.

The approximate five-fold increase in the yield of ethane can be explained by the abstraction of a hydrogen atom by methylene from the substituted methyl in toluene,



(6)

followed by a recombination of the methyl radicals thus formed to give ethane. The complete elimination of ethane by oxygen suggests that ethane is formed by such a radical mechanism.

The formation of *o*-xylene in the quartz cell may be due to the secondary photoisomerization of methylcycloheptatrienes, which might have possibly been produced.

The Reactivity of Methylene Radicals.—The photolysis of pure ketene is accepted as taking place in the following way:

$$CH_2CO + h\nu \rightarrow CH_2 + CO \tag{7}$$

$$CH_2 + CH_2CO \xrightarrow{k_8} C_2H_4 + CO \tag{8}$$

$$\searrow\xrightarrow{k_9} \text{other products.} \tag{9}$$

In the presence of another reactant, R, the methylene produced in reaction 7 reacts with R to give products, P_i's, as follows:

$$CH_2 + R \xrightarrow{k_{10R}} \sum c_i P_i \tag{10}$$

The steady state treatment requires the following relation:

$$\frac{R_{CO}}{R_{C_2H_4}} = 2 + \frac{k_9}{k_8} + \frac{k_{10R}}{k_8}\frac{[R]}{[K]} \tag{I}$$

where [K] refers to the concentration of ketene and k_{10R}, to the rate constant of reaction 10 for a particular reactant, R. The value of k_9/k_8 can be estimated as 0.2 by applying Equation (I) to the photolysis of pure ketene, in which $[R]=0$ and $R_{CO}/R_{C_2H_4}$ is about 2.2.[11] Plotting CO/C_2H_4 against [R]/[K], one can obtain k_{10R}/k_8, the value of which shows the reactivity of methylene with reactant R relative to that with ketene to give ethylene and carbon monoxide.

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[15] It is highly probable that the product in the liquid-phase reaction of methylene with benzene, which was identified by Meerwein et al.[9] as norcaradiene from the fact that it absorbed two molecules of hydrogen per molecule, was actually [3. 2. 0]-bicyclohepta-2, 5-diene, which is the major product of the photoisomerization of CHT in the liquid phase.[16]

[16] W. G. Dauben and R. L. Cargil, *Tetrahedron*, 12, 186 (1961).

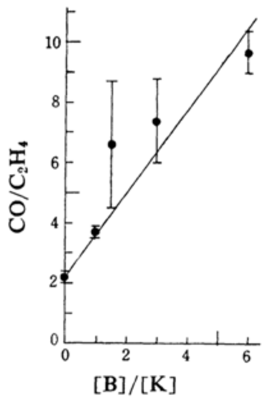

Fig. 3. CO/C_2H_4 plotted against benzene to ketene ratio.

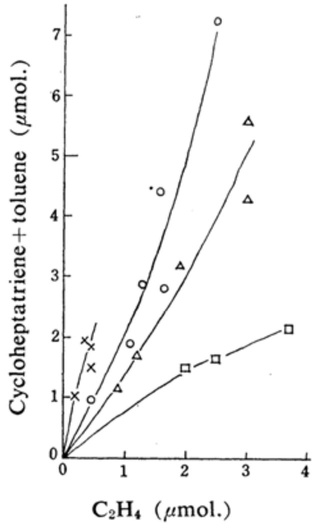

Fig. 4. Amount of cycloheptatriene+toluene plotted against ethylene. Benzene to ketene ratio,
□: 1, △: 1.5, ○: 3, ×: 6.

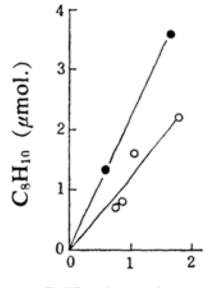

Fig. 5. Amount of C_8H_{10} products plotted against ethylene.
Toluene to ketene ratio,
○: 2, ●: 2.5.

By comparing Reactions (8) and (10), k_{10R}/k_8 can also be obtained from the following equation:

$$\frac{R_{\sum c_i P_i}}{R_{C_2H_4}} = \frac{k_{10R}}{k_8} \frac{[R]}{[K]} \qquad \text{(II)}$$

For benzene, relations I ard II are shown in Figs. 3 and 4, giving 1.4 and 0.7 respectively, for the value of k_{10B}/k_8 where B stands for benzene. The disagreement between the values thus obtained by the two methods implies that, along with CHT and T, some other products which could not be detected are present, possibly a polymer. The poverty of the material balance in the reaction of methylene with benzene supports this idea.

TABLE III. RATE CONSTANT RATIOS OF REACTIONS OF METHYLENE WITH VARIOUS SUBSTANCES

$$CH_2 + CH_2CO \xrightarrow{k_8} C_2H_4 + CO$$

$$CH_2 + R \xrightarrow{k_{10R}} \sum c_i P_i$$

R	k_{10R}/k_8	Reference
C_6H_6	1.4, >0.7[a]	Present result[b]
$C_6H_5CH_3$	>0.75[a]	Present result
C_2H_2	1.1	Reference 18.
C_2H_4	~1[c]	Reference 17.
CO	2.7, 1.25	Reference 19.[b]
CO_2	~0.02[c]	Reference 20.

a) The sign > means the minimum value.
b) Two different values have been obtained.
c) The sign ~ means the approximate value.

For toluene, relation II is shown in Fig. 5, the initial slopes of which give 0.75 for the value of k_{10T}/k_8. Since we may not have detected all the products for toluene, this value should be considered as the lower limit of k_{10T}/k_8.

The values of k_{10R}/k_8 for various reactants are summarized in Table III. The value of k_8 was estimated by Kistiakowsky and Rosenberg[17] to be 10^{-16} cc./molec./sec., and reaction 8 is generally accepted to be a very fast one. From the table one can see that the reactivity of methylene radicals is very high with ethylene, acetylene and aromatics also, not only confined with ketene.

Summary

The reactions of methylene radicals produced by the photolysis of ketene with benzene and with toluene in the gas phase have been

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[17] G. B. Kistiakowsky and N. W. Rosenberg, *J. Am. Chem. Soc.*, **72**, 321 (1950).
[18] T. Terao, N. Sakai and S. Shida, ibid., **85**, 3919 (1963).
[19] T. B. Wilson and G. B. Kistiakowsky, ibid., **80**, 2934 (1958).
[20] G. B. Kistiakowsky and K. Sauer, ibid., **80**, 1066 (1958).

studied. The reaction of methylene with benzene gave cycloheptatriene and toluene in a ratio 7 to 3. The ratio varied neither with the pressure raised by the added nitrogen or carbon dioxide nor with the wave lengths of the incident radiation.

The products obtained in the reaction of methylene with toluene were ethylbenzene, *m*-xylene, *p*-xylene and an unidentified product, their percentages being 25, 40, 25 and 10% respectively. About a five-fold increase in the amount of ethane has been observed over that observed in the reaction with benzene or in the photolysis of pure ketene. This fact indicates that the abstraction of the hydrogen atom by methylene from the methyl in toluene does occur, but that that from the benzene ring does not. Oxygen did not alter the relative yield among the products in the reactions of methylene with either benzene or with toluene. This suggests that the products are formed by the reactions of singlet methylene with benzene and toluene via norcaradiene-type intermediates.

It has quantitatively been shown that the reactivity of methylene redicals is very high with aromatics, ethylene and acetylene, as with ketene.

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