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Reaction of Metastable Ar Atoms with *cis*- and *trans*- 2-Butene in Flow System[#]

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The chemical behavior of *cis*- and *trans*-2-butene has been investigated in a flow system with metastable Ar atoms . In the case of *cis*-2-butene, split of the C-C single bond between CH_3 and CH=CH was observed, while in the case of *trans*-2-butene no reaction was observed. Geometrical isomerization of neither *cis*- nor *trans*-2-butene was observed.

Previously, we reported results of a study on the reaction of propene with metastable Ar (a mixture of Ar($^3P_2$) and Ar($^3P_0$), described as Ar*, hereafter). We observed the split of the C-C single bond between CH_3 and CH=CH, confirming the formation of methane, ethane and ethylene as the final products.[1)] Here, we studied the reaction of Ar* with *cis*- and *trans*-2-butene to see their chemical behaviors.

Quite a number of papers have been published on geometrical isomerization with various sensitizers (mainly produced by photochemical processes). We considered that Ar* produced by microwave discharge is a possible candidate as a sensitizer for the *cis-trans* isomerization. Although this was our initial motivation of the present study, our experimental findings were different, and the splitting of a C-C single bond between CH_3 and CH=CH is observed, in parallel with our previous finding in the study of the reaction of propene with Ar*.

A schematic diagram of the experimental arrangement is shown in Fig. 1. Reaction chamber was evacuated by Kiney type pump (pumping speed 1500 l/min). To generate Ar*, a microwave generator (2450 MHz) was used. Ar was introduced through inlet tube, and its flow rate was controlled by a fine needle valve, monitoring the flow rate with a purgemeter (carboroy float). The flow rate of Ar was 2.9×10^{-5} mol/s at a purgemeter reading of 40, 4.4×10^{-5} mol/s at 60, and 4.9×10^{-5} mol/s at 80, respectively. Linear velocity of Ar flow was 28 m/s at a flow rate of 2.4×10^{-5} mol/s. To confirm the generation of Ar*, we observed emission of second positive band from excited nitrogen molecule by introducing N_2 through the reactant inlet. Intensity of emission at 337 nm increased almost linearly with increase of flow rate of N_2 from 10 to 60 of the purgemeter reading (sapphire float), and it was saturated at 90 of the reading, reaching to a

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[#] Dedicated to Professor Emeritus Osamu Simamura, The University of Tokyo, for felicitous occasion of his 80th birthday.

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maximum concentration of Ar*. Reactants *cis*- and *trans*-2-butene were commercially obtained. They contained a small amount of ethane, propane, butane, 1-butene, and the geometrical isomer of 2-butene. *Trans*-2-butene contained, in addition, a trace of propene, but *cis*-2-butene did not, as will be seen in blank experiments later in Table 1. We used 2-butenes without further purification. They were introduced through the reactant inlet. The period of flow reaction (between opening time of reactant cock and shutdown time of MW power) was usually 2 minutes Condensable products (mainly propene) and intact 2-butene(s) were collected on liquid nitrogen trap T installed downstream. After two minutes reaction period, metal valve V was closed to switch Ar flow from the main pumping line to GC sampling line, and glass cock G was opened to connect the auxiliary pump. Condensable products and intact 2-butene(s) were transferred from warmed up trap T to GC sampler (capacity 0.4 ml) cooled by liquid nitrogen. For GC analysis of products and the intact reactant, a sebaconitrile column of 9 m in length was used with FID, and the carrier gas was N_2. For the quantitative GC analysis with FID, sensitivities for propene, *cis*- and *trans*-2-butene were determined in advance.

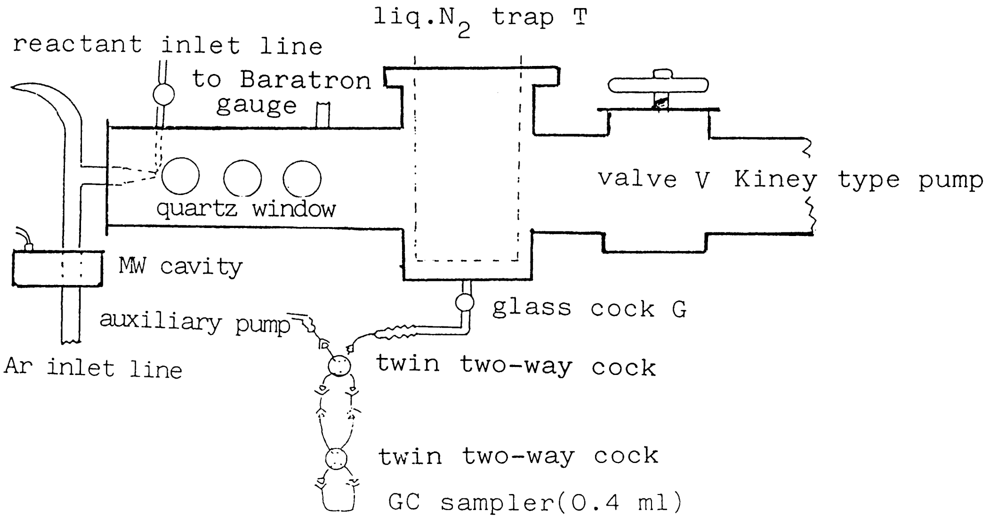

Fig.1. Schematic diagram of the apparatus.

In Tables 1-a and 1-b, the results of GC analysis of the main recovered substances (propene and 2-butene) are shown. As our reaction system is the flow method, the mol ratios (in percent) are shown, taking the moles of the dominant reactant 2-butene as the denominator. In the upper part of each table, the results of the experiments in the presence of Ar* are shown. And in the lower part of each table, the results of the blank experiments in the absence of Ar* (MW power off) are shown. When the results of *cis*-2-butene (Table 1-a) are compared with those of *trans*-2-butene (Table 1-b), the reaction of *cis*-2-butene with Ar* shows convincingly the formation of propene. In contrast, *trans*-2-butene shows no appreciable augmentation of propene, even if the purchased *trans*-2-butene contains a small amount of propene as contaminant. These tables also show no change in mole ratio of geometrical isomer of 2-butene between the results in the presence of Ar* and those of blank experiments.

Table 1. Results of GC Analysis of Main Recovered Substances in 2 Minutes Flow of Mixture of Ar and *cis*- or *trans*-2-Butene

Table 1-a. Reactant : *cis*-2-Butene

In the presence of Ar* (MW power on)

Run No.	Propene	*trans*-2-Butene
1	0.32 mol%	0.63 mol%
2	0.34	0.79
3	0.13	0.60
4	0.31	0.56
5	0.36	0.69
6	0.23	0.61
7	0.25	0.61
8	0.14	0.59
9	0.14	0.59
10	0.14	0.59
11	0.24	0.61
average	0.24 mol%	0.62 mol%
standard deviation	0.08	0.06

In the absence of Ar* (MW power off)

Run No.	Propene	*trans*-2-Butene
1	not detected	0.70 mol%
2	not detected	0.59
3	not detected	0.61
4	not detected	0.51
average	<0.01 mol%	0.60 mol%
standard deviation		0.07

Table 1-b. Reactant : *trans*-2-Butene

In the presence of Ar* (MW power on)

Run No.	Propene	*cis*-2-Butene
1	0.08 mol%	0.18 mol %
2	0.04	0.12
3	0.05	0.25
4	0.06	0.21
5	0.17	0.25
6	0.12	0.25
average	0.09 mol%	0.21 mol%
standard deviation	0.05	0.05

In the absence of Ar* (MW power off)

Run No.	Propene	*cis*-2-Butene
1	0.08 mol%	0.52 mol%
2	0.03	0.10
3	0.10	0.15
average	0.07 mol%	0.26 mol%
standard deviation	0.03	0.16

It is interesting and rather puzzling that the split of a C-C single bond between methyl and alkenyl group takes place in the reaction of Ar* with *cis*-2-butene and propene, but not with *trans*-2-butene. From energetic point of view, Ar* has sufficient energy ($Ar(^3P_2)$ 11.55 eV and $Ar(^3P_0)$ 11.75 eV) to split the C-C single bond of these alkenes . At the same time, Ar* also can ionize these alkenes (first ionization energy of propene 10.01 eV, *cis*-2-butene 9.32 eV and *trans*-2-butene 9.35 eV, respectively).2) In this sense, homolytic and ionic processes are both possible. However, our previous study1) indicates that the ratio of ionization of propene by Ar* is less than 2 % to the split of the C-C single bond. From the results, we propose that the major process in the present reaction is the electronic energy transfer from Ar* to alkene, rather than ionization. Following the electronic energy transfer, the energized alkene (probably in a triplet state) decomposes to methyl and alkenyl radicals *via* unimolecular process, as shown below:

$$\mathrm{Ar^* + alkene\ (C_nH_{2n}) \longrightarrow Ar + alkene^*\ (triplet)} \qquad (1)$$

$$\mathrm{alkene^* \longrightarrow CH_3\bullet + alkenyl\bullet\ (C_{n-1}H_{2n-3}\bullet)} \qquad (2)$$

Similar reaction schemes have been found in many photosensitized reactions.

Now, question is raised why *cis*-2-butene and propene are reactive, while *trans*-2-butene is not. It is unlikely that *trans*-2-butene is specifically indifferent to Ar* in process (1). Quenching cross sections of *cis*- and *trans*-2-butene to Ar* are not known, but it is difficult to imagine that the quenching cross section of *trans*-2-butene is exceptionally small as compared with that of *cis*-2-butene and propene.3,4) So we assume tentatively that process (1) proceeds equally in both *cis*- and *trans*-2-butenes. Since the decomposition process (2) is that of the electronic excited species, but not of the thermal one, the excited species must be sensitive to the character of their electronic energy levels. If the formed triplet levels of propene and *cis*-2-butene are of the anti-bonding character, but that of *trans*-2-butene is of the bonding, the formers are expected to be reactive. On this point, we need reliable quantum chemical calculations of the bonding character of the MO levels of triplet alkenes, and such calculations are in progress. At the same time, it will be worthwhile to extend the experimental investigations to related alkenes such as 1-butene, 2-methylpropene, and pentene series.

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