Bull. Chem. Soc. Jpn., *54*, *678—684 (1981)* [Vol. 54, No. 3

Reaction of Metastable Ar Atoms with Propylene in Flow System

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(Received August 30, 1980)

The reaction of metastable Ar atoms with propylene was studied in a discharge flow system. The major product is ethylene, although ethane, propane and butadiene are also identified as minor products. Within a limited range of propylene concentration the yield of ethylene is proportional to the concentration of propylene. Competitive quenching methods using mixtures of propylene and N_2O or CO_2 provided a rate constant of $(8.4\pm 0.3)\times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for the reaction of metastable Ar atom with propylene to yield ethylene. The assumption of a radical mechanism for the main reaction is consistent with the results of competitive quenching, radical scavenger and spin trapping experiments. Measurements of ion current in the reaction mixtures allow an estimation that ionic species contribute less than 2% to the reaction path leading to the formation of ethylene. The metastable Ar atom reaction was also compared to the direct and mercury-sensitized photolysis of propylene.

Reactions of metastable rare gas atoms have been studied by many workers interested in both the physical and chemical aspects of the reaction.$^{1-5)}$ Various types of ionizations (Penning, associative and dissociative) and the chemiluminescence of atoms and molecules on collision with metastable rare gas atoms have been studied.$^{6-8)}$ Quenching rate constants of the metastables by various atoms and molecules also have been determined in discharge flow systems or pulsed radiolysis systems. However, in contrast to the many studies on mercury-sensitized photolysis of inorganic and organic compounds, studies on the reaction mechanism of excited rare gas atoms by product analysis are quite few in number apart from several papers on the rare gas sensitized photolysis of simple alkanes.$^{9,10)}$ In the rare gas sensitized photolysis, the wavelength for the exciting light is in the far ultraviolet region, and it is usually difficult to differentiate the direct photolysis and the sensitized photolysis, unless the reactant is transparent or has only a weak absorption at the wavelength corresponding to the atomic resonance line of the rare gas atom.

The comparison between direct photolysis, rare gas sensitized photolysis and the metastable rare gas atom reaction would be interesting in order to help to elucidate the reaction modes of molecules electronically excited to high energy states near or above their ionization levels. Here we will report on the reaction of metastable Ar atoms with propylene. Electron impact methods including discharge and radiolysis are required for the generation of metastable rare gas atoms. The discharge flow method may be preferable to the radiolysis method for the product analysis, since the metastable atom source can be separated from the reaction region, and the metastables can be brought together with the reactant downstream from the source of the metastable atom. One difficulty in working with flow methods, in particular if the reactants are volatile compounds, is how to achieve quantitative recovery of the volatile products in the flow system. We succeeded in carrying out the quantitative determination of the product yield by working at a conveniently selected flow rate.

Experimental

Apparatus and Procedures. A schematic diagram of the apparatus is shown in Fig. 1. Metastable Ar atoms are produced by cold discharge in a hollow cathode. A mixture of Ar($^3P_2$) and Ar($^3P_0$) is produced by the discharge, but their differentiation is not possible in the system, and hereafter we will describe the mixture as Ar*. In order to avoid exposing the reactant to UV light from discharge source, the discharge tube is equipped with a rightangle bend and a light trap between the reaction zone and the discharge region. The flow rate is monitored by a rotar meter (Ueshima Brooks tube). Since the rotar meter was calibrated with Ar at 1 atm of pressure, the flow rate at reduced pressure was determined by measuring the decrease in the amount of Ar in a container, keeping the flow conditions same as in the actual discharge experiment. Discharge current was kept at 10—11 mA. Reactant propylene and quenching materials (N_2O, CO_2, and NO) were introduced through a sintered glass disk into the Ar flow. The reaction part of the tube is 20 mm in diameter and 300 mm in length. Pressure in the tube was measured by an oil manometer. Two pairs of electrodes (P_1 and P_2) are furnished in the reaction tube upstream and downstream from the reactant mixing position.

Condensable amounts of product and propylene were collected in a helical trap, D, cooled by liquid nitrogen. Quantitative recovery of products of high vapor pressure in the flow system was carefully checked by measuring the

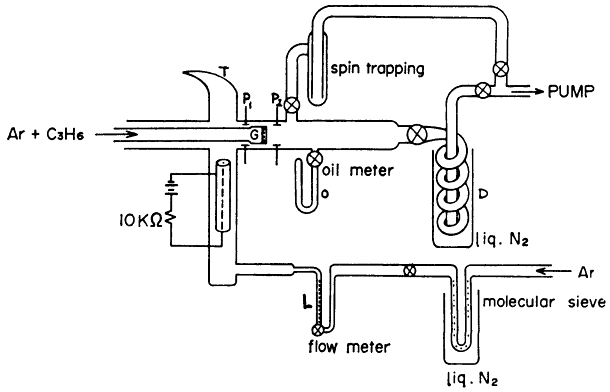

Fig. 1. The schematic diagram of the apparatus.

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amounts of ethylene, ethane and propane contained in the original propylene at three different flow rates from 4.5 to 20.8 μmol s^{-1} of Ar. The quantitative recovery of the impurity hydrocarbons was achieved when the flow rate of Ar was 4.5 μmol s^{-1} (0.2 Torr (1 Torr≈133.3 Pa) and 1.3 m s^{-1} linear flow velocity). With larger flow rates, the recovery of the impurity hydrocarbons was not sufficient. We could not determine the recovery efficiency for the propylene reactant because of its large amount, but we may assume that it is nearly quantitative, considering its low vapor pressure compared with those of ethylene and ethane. All experimental runs described hereafter were carried out with a flow rate of 4.5 μmol s^{-1} at 0.2 Torr.

Product identification and yield determination were performed by GC with a TCD and a FID in train with He carrier. For ethylene, ethane and propane analysis, an activated alumina TR column of 3.75 m was used. The retention times of these compounds at 90 °C are 3 min 30 s for ethane, 6 min 50 s for ethylene, 9 min for propane and 20 min 42 s for propylene. A 3 m long activated charcoal column was used for the analysis of acetylene, propyne, and allene. The retention times for authentic compounds at 190 °C are 3 min 30 s for acetylene, 19 min 20 s for allene, 19 min 40 s for propyne and 27 min 50 s for propylene.

Before each reaction run, the system was cleaned by passing Ar for 30 to 60 min with discharge. Several minutes after the propylene was introduced, the helical trap D was cooled with liquid nitrogen. We assumed that the starting time of the reaction corresponds to the time when the trap was first cooled. The run time for each reaction was usually 10 min. No appreciable change in flow rate was noticed when the trap was cooled with liquid nitrogen. The collected condensates were transferred to a gas sampler and analyzed by GC.

The formation of Ar* in the system was confirmed by observing the well known emission of N_2 ($C^3\Pi_u \rightarrow B^3\Pi_g$) at 337 nm, introducing N_2 into the Ar flow. Since the linear flow velocity was small (1.3 m s^{-1}), the intensity of the emission was very weak, and a photon counting technique was necessary to take the spectrum. A determination of the Ar* concentration was not attempted. When a mixture of N_2 and propylene was introduced into the Ar flow, the emission disappeared.

Materials. Ar was obtained from a cylinder with a stated purity of 99.999% and was used after passage through a molecular sieve column cooled with liquid nitrogen. Propylene, N_2O, CO_2, and NO were obtained from Takachiho Co. The propylene contained 2.1×10^{-3}% ethane, 2.2×10^{-3}% propane, and 2.3×10^{-4}% ethylene, but these amounts were much smaller than those produced by the reaction, so the propylene was used without further purification. For the competitive experiments with propylene and other quenchers, mixtures of propylene and N_2O or CO_2 of three different concentration ratios were prepared, and their exact concentration ratios were determined by GC.

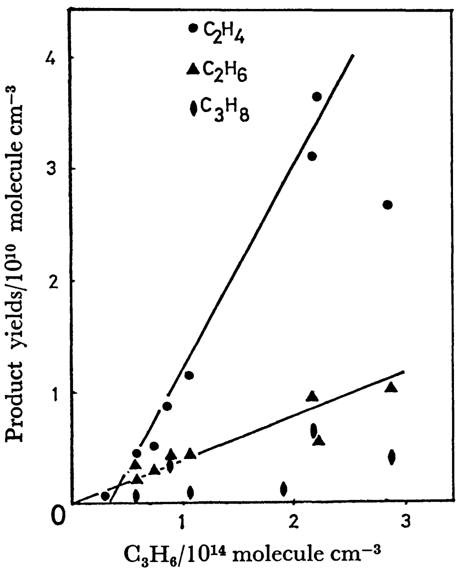

Fig. 2. Product yields *vs.* propylene concentration.

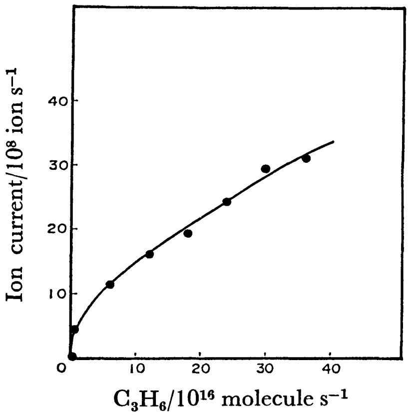

Fig. 3. Dependence of ion current on propylene concentration.

Results and Discussion

Product Identification, and the Relationship between Product Yields and Propylene Concentration. The major product was ethylene, with ethane and propane as minor products. Although usually H_2 and CH_4 were not collected in the present sampling method using a liquid nitrogen trap, occasionally some amount of CH_4 was detected. Butadiene was identified by a MS analysis of the products, but a quantitative determination of its amount was not attempted. Acetylene, propyne, and allene were carefully searched for, but not found in the product. Figure 2 shows the relationship between the yields of ethylene, ethane and propane and the propylene concentration. The concentration of the products is defined as the final concentration at the end of the reaction path, and it is calculated from the yield of the product per unit time and the linear flow velocity (1.3 m s^{-1}). It is the yield of the product integrated over a given residence time (0.3 s) in the flow system (see Eqs. 12 and 13). Over a limited range the yield of ethylene is proportional to the concentration of propylene; however, the yield decreases at higher concentrations of propylene. The yields of ethane and propane also appear to increase with an increase of propylene concentration, but their proportionalities are not conclusive due to their low yields. The plot of ethylene yield *vs.* propylene concentration appears not to pass through origin, but we consider this to be due to the experimental error. Although we could not determine the initial concentration of Ar*, the yield of ethylene, *ca.* 3×10^{10} molecule cm^{-3}, may indicate a lower limit for the Ar* con-

TABLE 1. RATIO OF ION YIELD TO ETHYLENE YIELD

Flow rate of propylene molecule s^{-1}	Ion yield per unit time ion s^{-1}	Ethylene yield per unit time molecule s^{-1}	Ratio of ion yield to ethylene yield
1.2×10^{17}	1.6×10^{11}	8.5×10^{12}	1.9×10^{-2}
2.5×10^{17}	2.5×10^{11}	1.3×10^{13}	1.9×10^{-2}

centration, if we assume one atom of Ar* produces one molecule of ethylene.

Ion Current Measurement. Ion current was measured at electrodes P_1 and P_2. Ion current upstream from the reactant inlet position is less than 1.0×10^{-11} A (6×10^7 ion s^{-1}), indicating that the participation of charged particles (possibly Ar^+) as reactants is negligible compared with Ar* ($\approx 3\times10^{10}$ atom s^{-1}). In Fig. 3 the relationship between ion current at P_2 and propylene concentration is shown. The ion current increases with increasing propylene concentration, but not exactly linear. Since the measured ion current corresponds approximately to the amount of ions produced in the volume defined by the two electrodes P_2, we would need parallel electrodes 300 mm long in order to know the total ion yield in the flow system. Here we calculated an upper limit of the yield in the total volume of the reaction region by multiplying the measured ion current a factor of 100 (the ratio of the total volume of the reaction region to the volume defined by the two electrodes). Table 1 gives the ion yield (calculated upper limit), ethylene yield under the same conditions, and ratio of ion yield to ethylene yield. From these results we may conclude that the formation of ionic species is less than 2% of the ethylene yield.

In the present experimental setup the identification of ionic products was not possible, but we may assume that the measured ions are propylene parent ions or associated ions[11] (possibly $Ar(C_3H_6)^+$) and not fragment ions. Since the ionization potential of propylene is 9.73 eV, and the energy of Ar* is 11.5 eV for $Ar(^3P_2)$ and 11.7 eV for $Ar(^3P_0)$, the formation of propylene parent ion is possible. However, the formation of fragment ions is less likely, since the appearance potentials for allyl and vinyl ions from propylene are 12.1 eV and 13.8 eV respectively.[12]

The competitive quenching method for determining the rate constant for the Ar+propylene reaction.* If we assume ethylene is formed through the propylene quenching of Ar*, the following two processes compete when a mixture of propylene and another quencher is mixed with Ar*:

$$Ar^* + C_3H_6 \xrightarrow{k_1} Ar + C_3H_6^* \longrightarrow \text{ethylene and other product(s)}, \tag{1}$$

$$Ar^* + Q\,(\text{another quencher}) \xrightarrow{k_q} Ar + Q^*(\text{or product(s) from } Q^*). \tag{2}$$

According to the conventional treatment of competitive reactions, we may obtain the following equation:

$$[C_2H_4]_0/[C_2H_4]_q = 1 + (k_q[Q]/k_1[C_3H_6]), \tag{3}$$

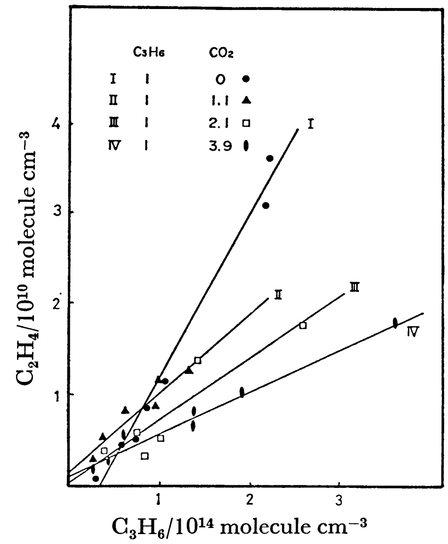

Fig. 4. Ethylene yields *vs.* propylene concentration in the absence and in the presence of CO_2.

where $[C_2H_4]_0$ and $[C_2H_4]_q$ are the yields of ethylene in the absence and in the presence of another quencher Q but with the same concentration of propylene. In the present flow system we need a more detailed consideration to derive Eq. 3 which is different from the case of batch photolysis. This will be given later. If Eq. 3 holds, we may expect that a plot of ($[C_2H_4]_0/[C_2H_4]_q$) *vs.* concentration ratio of Q to propylene should give an intercept of unity and a slope of k_q/k_1.

This seems to be the case for this system as is shown in Fig. 4, which presents ethylene yield as a function of propylene to CO_2 ratio for three different concentration ratios. It is seen that the slope decreases with an increase in the $[CO_2]/[C_3H_6]$ ratio, indicating the decrease of ethylene yield with increase of CO_2 concentration. In order to see if Eq. 3 holds or not, we plot the value of $[C_2H_4]_0/[C_2H_4]_q$ against $[CO_2]/[C_3H_6]$ and $[N_2O]/[C_3H_6]$ at a normalized propylene concentration as Fig. 5 shows. The intercepts of the plots for CO_2 and N_2O are both 1.1 ± 0.1, and the slope is 0.67 ± 0.04 for CO_2 and 0.51 ± 0.03 for N_2O. Combining these values with the quenching rate constants determined by Setser et al.[12] for $Ar(^3P_2)$ (5.3×10^{-10} cm^3 $molecule^{-1}$ s^{-1} for k_{CO_2} and 4.4×10^{-10} cm^3 $molecule^{-1}$ s^{-1} for k_{N_2O}) we obtain $(7.9\pm0.5)\times10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} from the CO_2 experiment and $(8.6\pm0.5)\times10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} from the N_2O experiment for the value of k_1. We consider these two values of k_1 determined from two different series of experiments to be identical within the range of experimental error. Unfortunately the rate constant for propylene quenching of Ar* as determined by

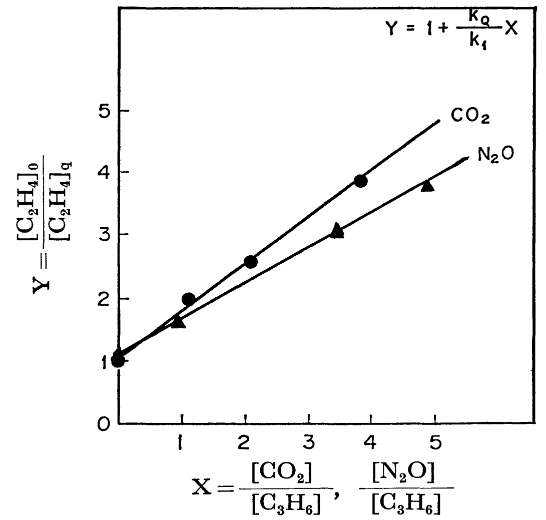

Fig. 5. Plots of $[C_2H_4]_0/[C_2H_4]_q$ *vs.* $[CO_2]/[C_3H_6]$ and $[N_2O]/[C_3H_6]$

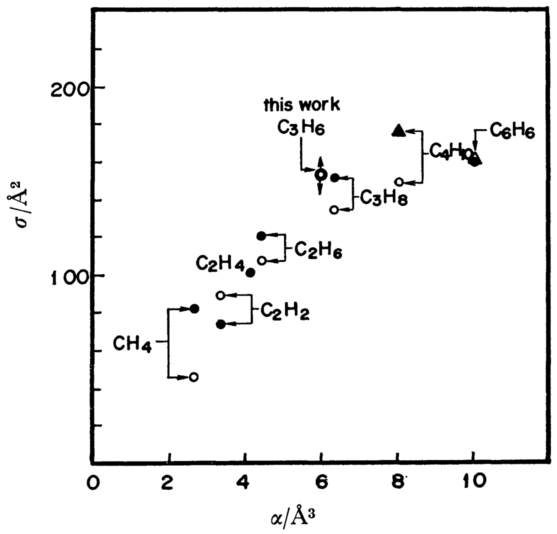

Fig. 6. Ar* quenching cross section by propylene and its polarizability in Bourène's plot.

the atomic absorption method has not been reported yet, and we cannot compare our value with what may be called a physical quenching rate constant or the total quenching rate constant including all quenching processes of Ar*.

Several authors have claimed a good correlation between the quenching cross sections of Ar* and several physical parameters such as polarizability,[13] van der Waals dispersion parameter,[14] and molecular diameter.[15] We would not judge which parameter is the best, but we tentatively plot our value for propylene against polarizability according to Bourène and Le Calvé in Fig. 6. It is seen that our value fits Bourène's plot.

When we used a mixture of propylene and NO for the reaction with Ar*, we observed a more remarkable decrease of ethylene yield than would be expected from a simple competing quenching of Ar* by NO which has an observed quenching rate constant for $Ar(^3P_2)$ of 2.2×10^{-10} cm^3 molecule^{-1} s^{-1}.[12] This decrease may be ascribed to NO scavenging of the intermediate vinyl radical.

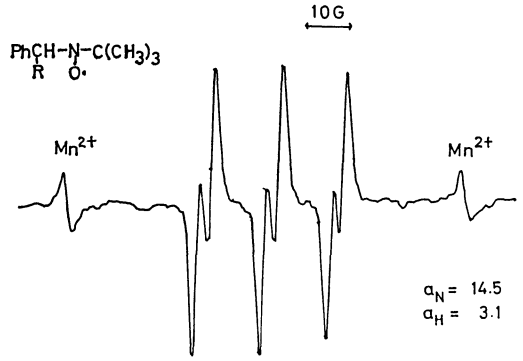

Fig. 7. ESR spectrum of a spin adduct of BPN produced in the reaction of Ar* with propylene.

Spin Trapping Experiment. Presuming that the reaction proceeds through a radical mechanism, we applied spin trapping technique to the present system to identify the intermediate radical(s), (vinyl, methyl, allyl radicals, and H atom might be considered possible). *N*-*t*-Butyl-α-phenylnitrone (*N*-benzylidene-*t*-butylamine *N*-oxide, BPN),[16] 2-methyl-2-nitrosopropane and nitrosobenzene were tested as spin trapping materials. BPN was used by sprinkling powder BPN over glass fibers and placing it in a straight trap instead of the helical trap D. After passing the reaction mixture for several hours with discharge under reaction conditions similar to those in the usual experiment, the powder was dissolved in cyclohexane. The ESR spectrum of the deaerated cyclohexane solution (JRS-PF-3X ESR spectrometer) is shown in Fig. 7. The coupling constants of the spin adduct are 14.5 G (1 G$=10^{-4}$ T) for a_N and 3.1 G for a_H. On comparing the spin coupling constants with the reported values of several spin adducts,[17] this spectrum is interpreted as that of an alkyl radical. Since the coupling constant of the BPN spin adducts is not very sensitive to the structure of the alkyl radical, we are not able to identify its structure uniquely, but methyl radical adduct may be the most probable.

We could not find any evidence of a vinyl radical adduct in the spectrum. Although the values of the spin coupling constants of vinyl radical adduct have not been reported in the literature, we would expect the value of a_H for vinyl radical adduct to be much smaller than those of an alkyl radical, considering that the a_H value of phenyl radical adduct is 2.08—2.14 G. It is, however, to be noted that the absence of ESR signals from a vinyl radical adduct in the spectrum does not necessarily mean that vinyl radical is not formed as a reaction intermediate, since the lifetime of some spin adducts is too short to be detected. Generally spin adducts of 2-methyl-2-nitrosopropane and nitrosobenzene show ESR spectra more sensitive to the radical structure. Although we obtained spin adduct ESR spectra with 2-methyl-2-nitrosopropane as the spin trap, we could not obtain an ESR spectrum of the adduct, when nitrosobenzene was used as the spin trap. The 2-methyl-2-nitrosopropane was too volatile to use as a powder, so the

Ar and propylene mixture was bubbled through a dibutyl phthalate solution of the trapping compound. Although the spin adduct spectrum could be observed, the adduct concentration was so low, and we could determine only a_N (14.5 G) but not a_H.

Reaction Mechanism and Rate Equations. The experimental results may be summarized as follows:
(1) Ethylene is the major product, with ethane, propane and butadiene identified as minor products. Hydrogen and methane may be products also, but they could not be confirmed due to sampling difficulties. Acetylene, propyne, and allene were not found in the product.
(2) Within a limited range of propylene concentration, the ethylene yield is proportional to the concentration of propylene.
(3) The remarkable decrease of ethylene yield from a mixture of propylene and NO suggests that ethylene is formed through a radical mechanism.
(4) The spin trapping experiments indicate the formation of an alkyl radical as an intermediate.
(5) The competitive quenching experiments with CO_2 and N_2O show that ethylene formation is directly related to the quenching of Ar* by propylene, and allow the determination of a reasonable rate constant for the propylene quenching of Ar*.
(6) The yield of ionic species as primary product is estimated to be less than 2% of the ethylene yield.

In consideration of these results, the following reaction mechanism is proposed:

$$\text{Ar}^* \longrightarrow \text{Ar (including quenching by wall collision, two and three body collisions with Ar)} \quad (4)$$

$$\text{Ar}^* + \text{C}_3\text{H}_6 \xrightarrow{k_1} \text{Ar} + \text{C}_3\text{H}_6^* \quad (1)$$

$$\text{Ar}^* + \text{Q} \xrightarrow{k_q} \text{Ar} + \text{Q}^* \text{ (or products from Q*)} \quad (2)$$

$$\text{C}_3\text{H}_6^* \xrightarrow{k_5} \text{C}_2\text{H}_3 \text{ (vinyl radical)} + \text{CH}_3 \quad (5)$$

$$\text{C}_3\text{H}_6^* + \text{C}_3\text{H}_6 \xrightarrow{k_6} 2\text{C}_3\text{H}_6 \quad (6)$$

$$\text{C}_2\text{H}_3 + \text{C}_3\text{H}_6 \xrightarrow{k_7} \text{C}_2\text{H}_4 + \text{C}_3\text{H}_5 \text{ (allyl radical)} \quad (7)$$

$$2\text{C}_2\text{H}_3 \xrightarrow{k_8} \text{C}_4\text{H}_6 \text{ (butadiene)} \quad (8)$$

$$2\text{C}_2\text{H}_3 \xrightarrow{k_9} \text{C}_2\text{H}_4 + \text{C}_2\text{H}_2. \quad (9)$$

In order to assess accurately the contribution of these elementary processes, we would need a more complete product analysis and determination of intermediate radical. Here, however, we concentrate our concern on the mechanism of ethylene formation. We consider Reaction 1, 2, and 7 as essentially important in the ethylene formation, but we will briefly discuss the contribution of Reactions 6 and 9. Deactivation of Ar* by wall collision, two and three body quenching with Ar have been studied and discussed by several workers. Wall collision is in the diffusion regime, and the values for two body and three body quenching rate constants are not consistent but depending on the authors. Here in order to estimate the magnitude of these quenching processes under the present conditions, we calculated the sum of the rates of these three terms at 0.2 Torr of Ar (expressed as K),

$$K = (D/\Lambda^2 P) + k'[\text{Ar}] + k''[\text{Ar}]^2 = 1.5\times 10^3\ \text{s}^{-1}, \quad (10)$$

where D is the diffusion rate of Ar at 1 Torr of Ar (54 Torr cm^2 s^{-1}), P is the pressure of Ar in Torr, Λ is the characteristic diffusion length given as $1/\Lambda^2 = (\pi/l)^2 + (2.4/R)^2$ (l: length of the reaction tube, R: radius of the reaction tube, both in mm).[18] For the values of k' and k'', we used the large ones from the reported values, that is, 6×10^{-15} cm^3 molecule^{-1} s^{-1} for k'[19] and 8.6×10^{-31} cm^6 molecule^{-2} s^{-1} for k''.[20] The concentration of Ar* decreases exponentially with travel time or travel length along the reaction tube:

$$[\text{Ar}^*] = [\text{Ar}^*]_0 \exp(-(K + k_1[\text{C}_3\text{H}_6] + k_q[\text{Q}])t), \quad (11)$$

where $[\text{Ar}^*]_0$ is the concentration of [Ar*] at $t=0$.

Ionization processes of propylene and molecular formation of ethylene from propylene are disregarded. The reaction of propylene with Ar excimer is also neglected considering the excimer concentration is supposed to be much smaller than the Ar* concentration. Although the electronic state of the $C_3H_6^*$ formed through excitation transfer is not known, it may be a superexcited state locating above the first ionization level of propylene. The excited propylene may decompose either through a direct process or through a vibrationally excited ground state. Since the concentration of propylene is low, the rate of the deactivation process 6 may be slower than Reaction 5 and can be neglected. The disproportionation Reaction 9 is also neglected in consideration of the small magnitude of k_9 (5×10^{-12} cm^3 molecule^{-1} s^{-1}) at room temperature.[21] Our experimental finding that acetylene is not found as a product is consistent with this assumption.

According to the proposed reaction mechanism the derivation of the rate equations for $C_3H_6^*$, C_2H_3, and C_2H_4 are straight-forward, assuming the local steady states for the concentrations of the intermediates. In order to solve the rate equations, the additional approximation of discarding the term $k_8[C_2H_3]^2$ is also introduced for mathematical convenience. Although k_8 must be larger than k_9, we believe that neglecting this term does not lead to any serious change in the present analysis of the kinetics.

In the flow system we need an expression for the integrated yield of ethylene as a function of residence time ($\tau = l/v$) which can be expressed as follows:

$$[\text{C}_2\text{H}_4]_q = \int_0^\tau k_7[\text{C}_2\text{H}_3][\text{C}_3\text{H}_6]\,\mathrm{d}t$$
$$= \frac{k_1[\text{Ar}^*]_0[\text{C}_3\text{H}_6]}{(k_1[\text{C}_3\text{H}_6] + k_q[\text{Q}] + K)}(1 - \exp(-k_7[\text{C}_3\text{H}_6]\tau)). \quad (12)$$

When we take a value of τ as 0.3 s, $[C_3H_6]$ as 10^{14} molecule cm^{-3}, and 10^{-14} cm^3 molecule^{-1} s^{-1} for the tentative value of k_7, the following approximation is possible:

$$[\text{C}_2\text{H}_4]_q \doteqdot \frac{k_1[\text{Ar}^*]_0[\text{C}_3\text{H}_6]}{(k_1[\text{C}_3\text{H}_6] + k_q[\text{Q}] + K)} k_7[\text{C}_3\text{H}_6]\tau. \quad (13)$$

This is consistent with our finding that the ethylene yield is nearly proportional to the propylene concentration in a limited low concentration range.

Bearing in mind that $K(\approx 10^3\ \text{s}^{-1})$ is much smaller

Table 2. Product distribution in the reaction of Ar* with propylene, the direct photolysis, and the mercury-sensitized photolysis of propylene

Products	Present work	Direct photolysis			Hg-sensitized photolysis
	$Ar(^3P_2)$ + $Ar(^3P_0)$ (11.5 eV) (11.7 eV)	123.6 nm[a] (10.0 eV)	147.0 nm[b] (8.4 eV)	184.9 nm[c] (6.7 eV)	$Hg(^3P_1)$[d] (4.9 eV)
Hydrogen	not det.	0.8	0.6	0.8	66.5
Methane	not det.	0.2	0.3	0.7	3.4
Acetylene	not found	1.9	3.1	1.1	9.2
Ethylene	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)
Ethane	0.3	0.2	0.6	0.6	1.1
Propyne + allene	not found	0.4	1.2	0.6	54.8
Propane	0.1		0.6	1.1	2.1
Butadiene	found		0.3		0.3
Butenes	not found	0.5	1.0	1.4	5.2
Isobutane	not found	0.5	1.0	0.8	0.4

a) Ref. 22, b) Ref. 22, c) Ref. 24, d) Ref. 27.

than $k_1[C_3H_6]+k_q[Q]$, when we take the ratio $[C_2H_4]_0/[C_2H_4]_q$ for a given propylene concentration, we obtain Eq. 3 as presented before.

Finally we have to admit that the proposed reaction mechanism does not cover all the reaction products. Ethane may be formed through the recombination of two methyl radicals, but the mechanism for propane formation is not certain. In the proposed mechanism the formation of allyl radical is assumed to take place by the abstraction of H atom from propylene, but we do not know the final destiny of the allyl radical. Further, we discarded the addition reaction of vinyl radical to propylene, although usually radical addition is faster than abstraction. In order to elucidate answers to these still unresolved problems we will need a more thorough product analysis in the future.

Reaction of Ar with Propylene in Comparison with the Direct and Mercury-sensitized Photolysis.* The comparison between the reaction of Ar* with propylene and the direct photolysis[22–25] and mercury-sensitized photolysis[26–28] would be interesting in order to see how the exciting energy and the exciting mode affect the reaction behavior of the excited molecule. In order to compare the reactions in detail we would need to know the electronic state of the excited molecule and the quantum yields of the primary processes or branching ratios. Our experimental results for the product analysis itself is incomplete, and most works on the far ultraviolet photolysis of propylene lack any estimation of the quantum yields of the primary processes. Furthermore, the results reported by the authors in two laboratories are not completely consistent. Bearing these points in mind, we give in Table 2 the relative yields of the final products normalizing the yields to ethylene yield, and discuss the reaction characteristics qualitatively. In the mercury-sensitized photolysis the yield of allene is distinct. Allene is probably formed through H atom abstraction by a $Hg(^3P_0)$ atom. The photolysis of propylene with 184.9 nm radiation was reported by Arai *et al.*[24] Acetylene, propane, allene, propyne and various C_4- and C_5- hydrocarbons are identified in addition to ethylene. Borrel *et al.*[25] also investigated the same photolysis. Their results are not completely consistent with the previous results, and they estimated the quantum yields of the primary processes as follows:

$$C_3H_6^* + h\nu \longrightarrow CH_2{=}CHCH_2 + H \qquad \phi=0.41$$
$$\longrightarrow C_2H_3 + CH_3 \qquad \phi=0.36.$$

They found that the quantum yields of the products decrease with the addition of an inert gases and ascribed this pressure effect to the participation of a Rydberg state as well as the valence bond excited state.

Becker *et al.*[22] studied the photolysis of propylene with 147.0 nm and 123.6 nm radiations and determined the relative yields of the products. Tsuikow-Roux[23] reinvestigated the photolysis at 147.0 nm and compared his results with the previous ones. In all these photolysis the formation of acetylene is confirmed, and with 147.0 and 123.6 nm radiations its yields exceed those of ethylene. Some portions of acetylene may be formed through a disproportionation reaction between two vinyl radicals. However, in order to explain acetylene yields that are twice or three times larger than ethylene yield in the direct photolysis at 147.0 and 123.6 nm, we must call for the direct formation of acetylene from excited propylene or of the decomposition of vibrationally excited ethylene as is assumed in the various reaction systems.[29] In view of the high excitation energy available in Ar*, it is rather unexpected that acetylene is not found in the products of Ar* reaction.

As a whole, the complete reaction system of Ar* with propylene appears to be simpler than that in the direct photolysis in spite of the comparable amounts of energy. One possible explanation for this simple reaction features may be due to the flow technique used in these experiments and the suppression of successive radical reactions by the rapid cooling of the reactant mixture to liquid nitrogen temperature. However, we would like to suggest that in the energy transfer reaction between metastable atoms and acceptor molecules only electron in the outer valence orbital may be subject to excitation,[30] while in the direct photolysis electrons both in outer and inner shells may be excited resulting in more violent or complicated reaction pathways even if the amounts of the excitation energies are comparable. However, at present this suggestion remains speculative one and requires theoretical and experimental evidence.

The authors would like to express sincere thanks to Prof. Soji Tsuchiya and Dr. Seiichiro Koda of The University of Tokyo for their valuable discussions, and to Dr. Shiegeo Tsujimura for his kindness to give facilities for one of the authors (A.S.) to carry out a part of this study at Japan Atomic Energy Research Institute. The authors are also indebted to Prof. Yasuo Itoh and Prof. Rei Hirasawa of The University of Tokyo in the measurement and interpretation of the spin trapping ESR spectra, and to Prof. R. A. Loeliger of International Christian University for careful reading and revision of the manuscript.

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