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Reaction of Hydrogen Atoms with Acrylaldehyde

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The reaction of hydrogen atoms with acrylaldehyde was investigated in a fast flow reactor equipped with a time-of-flight type mass spectrometer under reduced pressure. Main reaction products were carbon monoxide, ethylene, ethane, methane, and propanal. Consideration of the distributions of the reaction products under various reaction conditions showed that hydrogen atoms attacked the C=C double bond, especially its inner carbon side under reduced pressure. Resulting hot radicals caused subsequent reactions. The relative value of the apparent bimolecular rate constant of the reaction against that of *trans*-2-butene with hydrogen atoms was 1.6±0.2, which supported the above-mentioned initial reaction.

Hydrogen atoms add to C=C double bonds forming vibrationally excited alkyl radicals. These excited radicals can undergo unimolecular dissociation or be collisionally stabilized. On the other hand, the weak aldehydic hydrogen of saturated aldehydes is known to be abstracted by hydrogen atoms. The reaction of hydrogen atoms with simple monoolefins and aldehydes were already well elucidated, and data on respective reaction rates have also been fully reviewed.[1,2] By contrast the reactions of conjugated double bond systems with hydrogen atoms in gas phase seem not to have been fully studied. One known example is H+butadiene.[1,3] The reason for the remarkably high rate constant for this reaction seems to be still uncertain.

Acrylaldehyde is an interesting compound because it contains a conjugated double bond system, as well as a weakly bound aldehydic hydrogen. Though the reaction with oxygen atoms has been studied,[4,5] that with hydrogen atoms has never been investigated.

From the viewpoint of environmental science, acrylaldehyde is a noteworthy compound because of its possible role in photochemical smog and its strong toxicity. Only one study on the potential of smog formation of acrylaldehyde has so far been published.[6] Thus, the investigation of the reaction sequences in the mixture of acrylaldehyde with the simplest species, atomic hydrogen, will contribute to our understanding of the role of acrylaldehyde in photochemical smog.

Experimental

The experimental apparatus is illustrated in Fig. 1, which is almost similar to the apparatus of Arrington *et al.*[7] Hydrogen atoms were produced by a 2450 MHz microwave discharge in a mixture of hydrogen and argon, and were introduced into a Pyrex reaction tube (inner diam, 1.28 cm). Acrylaldehyde was added to the flow *via* an inner tube (outer diam, 0.32 cm) which was movable in order to control the reaction time. A part of the reaction mixture was directly introduced into a time-of-flight type mass spectrometer (Hokushin Denki Co., Ltd., Bendix Model) through a pin-hole (diam, 0.01 cm) positioned at the end of the reaction tube.

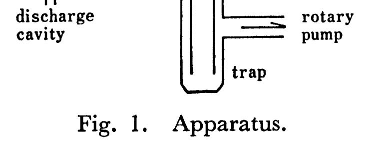

Fig. 1. Apparatus.

The reactions were carried out at room temperature (298±5 °C). The pressure in the reaction tube (around 0.3 Torr) was measured by a McLeod gauge. The pressure drop along the reaction tube between the point of addition of acrylaldehyde and the pin-hole (maximum distance, 10 cm) was found to be negligibly small.

The mass flow velocity of each gas was calculated from the pressure drop with time in a standard volume. The linear flow velocity (about 3 m/s) was calculated from the total volume flow rate, the reactor pressure and the cross-sectional area of the reaction tube. The reaction time was calculated by dividing the length between the point of addition of acrylaldehyde and the pin-hole to the mass spectrometer by the linear flow velocity. The reaction time was varied between 3 and 33 ms by the change of the position of the inner tube.

The concentration of hydrogen atoms was determined through titration with ethylene. A similar method was adopted by Halstead *et al.*[8] The concentration of hydrogen atoms was usually around 3×10^{-7} mol/l, and that of acrylaldehyde was $(1—10)\times10^{-7}$ mol/l. The total concentration of gases was around 1.5×10^{-5} mol/l.

The major products were identified by analysis of the ionization efficiency curves of the respective parent mass peaks. The quantitative analyses were carried out based on the fragmentation patterns and relative sensitivities of standard samples.

In some experiments, a part of the reaction mixture was pumped by a Toepler pump into a gas sampler and was analyzed by means of gas chromatography with columns of Molecular Sieve 5A (for CO), Porapak Q and 3,4-dimethylsulforane (for hydrocarbons), and Polyethylene glycol 1500 (for aldehydes).

Purest hydrogen and argon (both 99.99%) obtained commercially were passed through traps cooled at liquid nitrogen temperature, and then introduced to the discharge region through leaks. Commercially obtained acrylaldehyde was purified gas-chromatographically with a column of Tritolyl phosphate. The resultant purity was at least 99%.

Results

Figure 2 shows the yields of the products estimated by use of mass spectrometry at the reaction time of

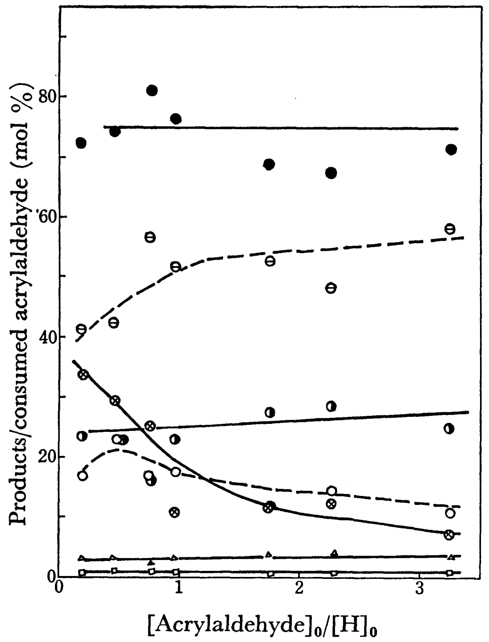

Fig. 2. The distribution of products at various different $[A]_0/[H]_0$.
Reaction conditions: total pressure, 0.38 Torr (Ar, 1.7×10^{-5} mol/l, H_2, 3.9×10^{-6} mol/l); $[H]_0$, 4.0×10^{-7} mol/l; $[A]_0$, 1.0×10^{-7} – 1.3×10^{-6} mol/l; reaction time, 22 ms.
Products: ● CO, ⊖ C_2H_4, ◑ C_2H_5CHO, ⊗ CH_4, ○ C_2H_6, △ CH_3CHO, □ C_3H_8.

TABLE 1. THE RESULTS OF GAS CHROMATOGRAPHIC ANALYSES

Product (mol %)	Initial concn of acrylaldehyde	
	1.1×10^{-6} mol/l	2.2×10^{-7} mol/l
Carbon monoxide	77	77
Ethylene	67	58
Propanal	15	9.8
Ethane	13	16
Methane	14	16
Acetaldehyde	1.7	2.6
Others	trace	5.4 (propane)
		2.4 (propylene)
		0.4 (acetylene)

The figures are the mole percent of the product divided by the consumed acrylaldehyde. Because the amounts of the consumed acrylaldehyde could not be measured, the equivalent concentration of the consumed acrylaldehyde was calculated from mass balance considerations, on the assumption that no products were missed. Reaction conditions: total pressure, 0.50 Torr ([Ar]= 2.6×10^{-5} mol/l, $[H_2]=6.0\times10^{-7}$ mol/l), the initial concentration of hydrogen atoms, 1.75×10^{-7} mol/l.

22 ms. The analytical results are shown in Table 1. These two results agree with each other, though allowance should be made for the different reaction conditions and the very different time for analyses. The relatively low yield of propanal (Table 1) may be attributed to its probable adsorption in the analysis system for gas chromatography.

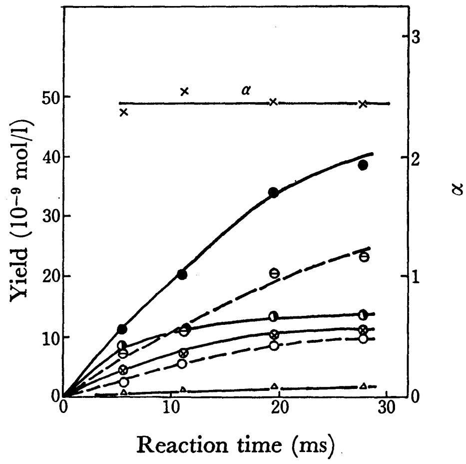

Fig. 3. Product growth curves with reaction time.
Reaction conditions: total pressure, 0.38 Torr (Ar, 1.7 $\times10^{-5}$ mol/l, H_2, 3.9×10^{-6} mol/l); $[H]_0$, 2.3×10^{-7} mol/l; $[A]_0$, 1.0×10^{-7} mol/l.
Products: ● CO, ⊖ C_2H_4, ◑ C_2H_5CHO, ⊗ CH_4, ○ C_2H_6, △ CH_3CHO.
α(×): in this estimation, 1.5 mol of hydrogen atoms was assumed to be consumed for 1 mol production of CO, see text.

Figure 3 shows the growth of each product and the change of the stoichiometric ratio α with reaction time. Here, α is the ratio of the amount of the consumed hydrogen atoms to that of the consumed acrylaldehyde.

$$\alpha = ([H]_0-[H])/([A]_0-[A]) \qquad \text{(i)}$$

$[A]$, $[A]_0$ are the concentrations of acrylaldehyde, and $[H]$, $[H]_0$, those of hydrogen atoms, at the reaction time t and at the initial time, respectively.

The amount of the consumed hydrogen atoms was calculated on the assumption that they were either trapped in the products (such as ethylene, methane, ethane, and propanal), or converted to hydrogen molecules. In the former case, the amount of the trapped hydrogen atoms was estimated from the yields of the products. In the latter case, carbon monoxide was produced simultaneously. The amount of the consumed hydrogen atoms ($-\Delta[H]$) was estimated to be about 1.5 times as large as the amount of the produced carbon monoxide ($\Delta[CO]$) from consideration of the hydrogen mass balance in an experiment where the initial hydrogen atoms were almost completely consumed within 33 ms. The experimental condition of the reaction were: The initial concn of the hydrogen atoms, 4.0×10^{-7} mol/l, $[A]_0/[H]_0$, 0.5. The reaction was found to be completed in about 30 ms. Because the amounts of the hydrogen atoms trapped in the products other than CO could be calculated, the ratio, $-\Delta[H]/\Delta[CO]$ could be easily estimated from the hydrogen mass balance. The ratio might depend on the initial conditions and change with reaction time, but we were obliged to adopt the constant value 1.5 in the estimation of α.

The value α was shown to be roughly constant throughout the reaction (Fig. 3). This fact allows to calculate the apparent bimolecular reaction rate constant of the reaction (ii) by the following simple procedure.

$$\text{acrylaldehyde} + \text{H} \longrightarrow \text{products} \qquad \text{(ii)}$$

The rate equation (iii) is integrated to result in (iv).

$$d[\text{A}]/dt = k_{ap}[\text{A}][\text{H}] \qquad \text{(iii)}$$

$$\begin{aligned} k_{ap}t &= [1/([\text{H}]_0-[\text{A}]_0)] \ln([\text{A}]_0[\text{H}]/[\text{A}][\text{H}]_0) \\ &= [1/([\text{H}]_0-[\text{A}]_0)] \ln[[\text{A}]_0([\text{H}]_0-\alpha([\text{A}]_0-[\text{A}]))/ \\ &\quad [\text{A}][\text{H}]_0] \end{aligned} \qquad \text{(iv)}$$

The right hand side of the above equation could be calculated from the data of $[H]_0$, $[A]_0$, $[A]$, and α. The resultant values are plotted against the reaction time t in Fig. 4. The slope of the straight line gave the bimolecular rate constant.

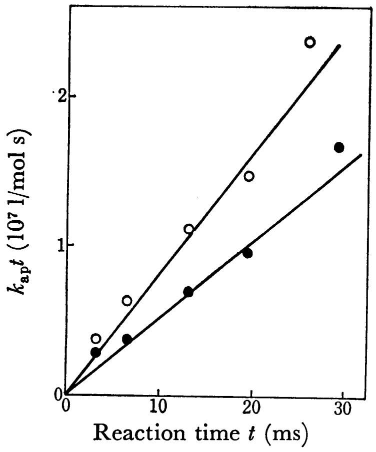

Fig. 4. The relationship between $k_{ap}t$ *vs.* reaction time. Reaction conditions: total pressure, 0.29 Torr (Ar, 1.4 $\times 10^{-6}$ mol/l, H_2, 1.4×10^{-5} mol/l); $[H]_0$, 2.84×10^{-7} mol/l, $[A]_0$ and [*trans*-2-butene]$_0$, 1.60×10^{-7} mol/l.
-●-: For reaction of *trans*-2-butene (α=2.8),
-○-: for reaction of acrylaldehyde (α=2.4).

$$k_{ap} \text{ for acrylaldehyde} = (8.1\pm0.8)\times10^8 \text{ l/mol s}$$

The reaction of *trans*-2-butene with hydrogen atoms was studied in the same apparatus as a reference. The apparent bimolecular rate constant was obtained similarly (Fig. 4) to be,

$$k_{ap} \text{ for } trans\text{-2-butene} = (5.1\pm0.5)\times10^8 \text{ l/mol s.}$$

Thus the relative rate constant of the reaction of acrylaldehyde, k_{ap}(for acrylaldehyde)/k_{ap}(for *trans*-2-butene), was calculated from the above absolute rate constants to be 1.6±0.2. The possible incomplete mixing of the reactants and the diffusion of hydrogen atoms along the reaction tube make the exact estimation of the reaction time difficult. Thus the relative value might be more reliable than the absolute one, though it is worth nothing that the absolute constant for *trans*-2-butene agrees well with the value reported by Daby *et al.*[9]

Discussion

Reaction Mechanism. In the experiments where the initial rate $[A]_0/[H]_0$ is less than 1, the low yield of ethylene is compensated by the relatively high yields of ethane and methane, as shown in Fig. 2. This should be due to the occurrence of the secondary reactions of the product ethylene with hydrogen atoms to some extent to yield methane and ethane. The apparent reaction rate constant of ethylene with hydrogen atoms was reported by Michael *et al.* to be 0.9×10^8 l/mol s in 0.96 Torr Ar,[10] whereas our value in a similar apparatus is 0.4×10^8 l/mol s in 0.5 Torr Ar,[11] and is much smaller than that of acrylaldehyde, 8.1×10^8 l/mol s as described previously; thus the consumption of the primary product ethylene is expected to occur to any appreciable extent only when hydrogen atoms still remain after acrylaldehyde is almost completely consumed.

On the other hand, in the experiments where the ratio $[A]_0/[H]_0$ is kept larger than 1, the yield of each product is relatively constant and does not depend on that ratio. The observed product distribution should then reflect the primary reaction sequences of acrylaldehyde with hydrogen atoms.

Addition of hydrogen atoms to aldehydic CO bond has not been observed to proceed to any appreciable extent.[1] Hydrogen atoms may then either add to the C=C double bond or abstract the aldehydic hydrogen from acrylaldehyde. The rate of the reaction of saturated aldehydes with hydrogen atoms is known to be smaller than the addition to simple monoolefins by a factor of around 10. Then the abstraction of the aldehydic hydrogen is not expected to be the main reaction in the case of acrylaldehyde. This idea is supported by the experimental observation that acetylene was produced only in a negligibly small yield. Acetylene should have been produced in a relatively high yield through subsequent reactions, if the abstraction was the main primary process. The following reaction sequence is expected to follow the abstraction:

$$\text{CH}_2\text{=CHCHO} + \text{H} \longrightarrow \text{CH}_2\text{=CH}\dot{\text{C}}\text{O} + \text{H}_2$$
$$\text{CH}_2\text{=CH}\dot{\text{C}}\text{O} + \text{H} \longrightarrow$$
$$\text{CH}\equiv\text{CH} + \text{CO} + \text{H}_2,\ \text{CH}_2\text{=}\dot{\text{C}}\text{H} + \text{CHO}$$
$$\text{CH}_2\text{=}\dot{\text{C}}\text{H} + \text{H} \longrightarrow \text{CH}\equiv\text{CH} + \text{H}_2.^{12-14)}$$

of course, we cannot deny the following possibility completely, based on the absence of acetylene among the reaction products.

$$\text{CH}_2\text{=CHCHO} + \text{H} \longrightarrow \text{CH}_2\text{=CHCO} + \text{H}_2$$
$$\text{CH}_2\text{=CHCO} + \text{H} \longrightarrow \text{CH}_2\text{=CH}_2 + \text{CO}$$

Thus the primary processes are considered to be the additions (1a) and (1b).

$$\begin{aligned} \text{CH}_2\text{=CHCHO} + \text{H} &\rightleftharpoons \dot{\text{C}}\text{H}_2\text{CH}_2\text{CHO}^*\ (\text{I}_a^*) \quad (1\text{a}, -1\text{a}) \\ &\rightleftharpoons \text{CH}_3\dot{\text{C}}\text{HCHO}^*\ (\text{I}_b^*) \quad (1\text{b}, -1\text{b}) \end{aligned}$$

Here, the asterisk means that the species possesses some excess energy.

The resulting hot alkyl-like radicals $I_a{}^*$ and $I_b{}^*$ may either decompose unimolecularly or be stabilized.

$$\text{I}_a{}^* \longrightarrow \text{CH}_2\text{=CH}_2 + \text{CHO} \qquad (2)$$
$$\text{I}_a{}^* + \text{M} \longrightarrow \text{I}_a + \text{M} \qquad (3\text{a})$$
$$\text{I}_b{}^* + \text{M} \longrightarrow \text{I}_b + \text{M} \qquad (3\text{b})$$

Though no thermochemical or structural data on the radicals I_a and I_b are known, we expect that $I_a{}^*$ may behave like the hot *n*-propyl radical and $I_b{}^*$ like the hot isopropyl radical produced in the reaction of propylene with hydrogen atoms.[15,16] I_b* is assumed not to decompose because it does not seem to lead to any favorable dissociation reactions. By the analogy to the hydrogen atom-propylene system, the possible subsequent reactions are summarized as follows:

$$I_a, I_b + H \longrightarrow CH_3CH_2CHO^* \qquad (4)$$

$$CH_3CH_2CHO^* + M \longrightarrow CH_3CH_2CHO + M \qquad (5)$$

$$CH_3CH_2CHO^* \longrightarrow CH_3CH_2 + CHO \qquad (6)$$

$$CH_3CH_2 + H \longrightarrow C_2H_6,\ 2CH_3 \qquad (7)$$

$$CH_3 + H + M \longrightarrow CH_4 + M \qquad (8)$$

$$CHO + H \longrightarrow CO + H_2 \qquad (9)$$

Considerations of the fact that relatively complex radicals react with hydrogen atoms very rapidly† and of the fact that the concentration of hydrogen atoms is much higher than the possible concentrations of these radicals in the present study guarantee the neglect of any reactions other than those described above for the radicals, I_a, I_b, and C_2H_5. But for the radicals, CH_3 and CHO, radical-radical reactions may be as important as radical-atomic hydrogen reactions, because the latter reactions are not expected to be rapid enough under reduced pressure. The rate constant of Reaction 9 seems to be still uncertain,[18,19] but if a probable value of around 1×10^9 l/mol s is adopted, the reactions such as 10 and 11[19,20] cannot be neglected.

$$CHO + CHO \longrightarrow H_2 + 2CO \qquad (10)$$

$$CHO + CH_3 \longrightarrow CH_4 + CO \qquad (11)$$

The Reaction 12 may not be neglected, similarly.

$$CH_3 + CH_3 \longrightarrow C_2H_6 \qquad (12)$$

The occurrence of Reactions 10 and 11 is expected to result in lowering the ratio, $-\Delta[H]/\Delta[CO]$, below 2. If the Reactions are limited to (1)—(9), the ratio should be 2. In fact, we have found the ratio 1.5, as described before.

According to the preceding discussions, we propose the reactions (1a, −1a) and (1b, −1b) followed by (2) through (12) as the main reaction sequence of the system of acrylaldehyde with hydrogen atoms under the reaction conditions of reduced pressure and also of $[A]_0/[H]_0\approx1$.

The net fraction of the hydrogen atom addition to the inner side of the C=C double bond is defined by Eq. v.

$$p=\frac{k_{1a}\times\dfrac{k_2+k_{3a}[M]}{k_{-1a}+k_2+k_{3a}[M]}}{k_{1a}\times\dfrac{k_2+k_{3a}[M]}{k_{-1a}+k_2+k_{3a}[M]}+k_{1b}\times\dfrac{k_{3b}[M]}{k_{-1b}+k_{3b}[M]}} \qquad (v)$$

On the other hand, the following relation can be derived through a simple mass balance treatment.

$$([C_2H_5CHO]+[C_2H_6]+0.5[CH_4])/[C_2H_4] \quad (\text{defined as } R)$$
$$=\frac{k_{1a}k_{3a}[M]/(k_{-1a}+k_2+k_{3a}[M])+k_{1b}k_{3b}[M]/(k_{-1b}+k_{3b}[M])}{k_{1a}k_2/(k_{-1a}+k_2+k_{3a}[M])} \qquad (vi)$$

We can expect $k_2\gg k_{-1a}$, assuming that the hot radical I_a* is similar to usual hot alkyl radicals, which undergo the C–C bond cleavage predominantly.[21] Moreover, the relatively low pressure of the present work allows to assume $k_2>k_{3a}[M]$. Then the following approximations results:

$$p\approx k_{1a}/(k_{1a}+k_{1b}k_{3b}[M]/(k_{-1b}+k_{3b}[M])) \qquad (vii)$$

$$R\approx k_{1b}k_{3b}[M]/k_{1a}(k_{-1b}+k_{3b}[M]) \qquad (viii)$$

Thus the net fraction p is related to the value R by the following equation.

$$p\approx 1/(1+R) \qquad (ix)$$

We have got the value of R as 0.7 from the data shown in Fig. 2. The net fraction of the hydrogen addition to the inner side of the C=C double bond was then estimated to be about 0.60 $(=1/(1+0.7))$ under the present conditions.

Relative Reaction Rate. We wish to find out a quantum-chemical measure with which the reaction rate of the addition of the hydrogen atoms to each carbon atom among various C=C double bonds can be predicted and to know whether the addition of the atoms to acrylaldehyde is similar to the addition to simple olefins, or not.

Yang[22] showed that the activation energy of the addition to olefins were related to the corresponding localization energy. But this measure cannot be used to show the reactivity of individual carbon atom. Daby *et al.*[9] related the relative rate to the free valence. Though they got some success, they had to classify monoolefins into two groups; inner olefins and α-olefins. Thus we suspected if the atomic population might be an adequate measure for our present purpose, considering that atomic hydrogen seems to behave as an electrophilic reagent to some extent.[23]

In fact, we could find a good linear relationship between the atomic population of each carbon atom of C=C double bond of simple olefins and the logarithm of the relative rate constant (data are taken from Cvetanović *et al.*[1,24]) as shown in Fig. 5. The atomic populations were calculated by CNDO/2 for stable configurations (Table 2). In the case of symmetric olefins (*trans-* and *cis-*2-butenes and ethylene), the experimentally obtained rate constants were divided by 2; these olefins are considered to possess two equivalent reaction centers. In the case of propylene, 1-butene and 2-methylpropene, the experimental relative rate constants were plotted against the higher values of atomic population; those of terminal sides. This is reasonable because of the large difference in the atomic populations between the terminal and inner carbons. It is known that the percentage of the addition to the inner side is very small.[25]

The apparent reaction rate constant of acrylaldehyde is described by Eq. x according to the previously given reaction sequence.

$$k_{ap}=k_{1a}(k_2+k_{3a}[M])/(k_{-1a}+k_2+k_{3a}[M])$$
$$+\,k_{1b}k_{3b}[M]/(k_{-1b}+k_{3b}[M]) \qquad (x)$$

By adopting the previous assumption, $k_2\gg k_{-1a}$, we get

$$k_{ap}\approx k_{1a}+k_{1b}k_{3b}[M]/(k_{-1b}+k_{3b}[M])$$
$$\approx k_{1a}(1+R) \qquad (xi)$$

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† For example, the values, 3.6×10^{10} l/mol s by Kurylo *et al.*[17] and 2×10^{10} l/mol s by Michael *et al.*[10] were reported as the rate constant of the reaction, $H+C_2H_5$, under reduced pressure.

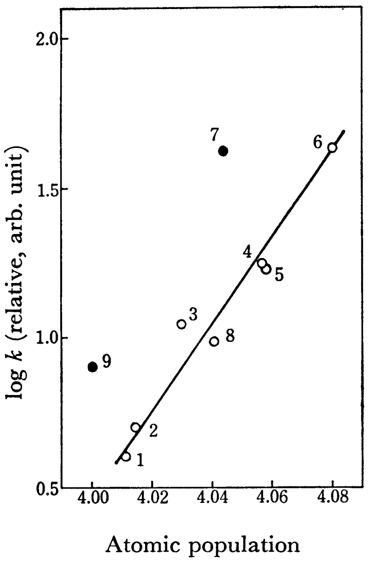

Fig. 5. The relationship between log (relative rate constant) and the atomic population.
1: *cis*-2-Butene, 2: *trans*-2-butene, 3: ethylene, 4: 1-butene, 5: propylene, 6: 2-methylpropene, 7: butadiene, 8: the inner carbon of acrylaldehyde (*vs.* k_{1a}), 9: the terminal carbon of acrylaldehyde (*vs.* $k_{1b}k_{3b}[M]/(k_{-1b}+k_{3b}[M])$).

Table 2. Atomic populations by CNDO/2

Substrate	C_1	C_2
$C_1=C_1$	4.0296	—
$C_1=C_2-C$	4.0573	3.9764
$C_1=C_2-C-C$	4.0568	3.9804
$C_1=C_2-C$ \C	4.0794	3.9389
cis-$C-C_1=C_1-C$	4.0112	—
trans-$C-C_1=C_1-C$	4.0144	—
$C_1=C_2-C_2=C_1$	4.0434	3.9839
$C_1=C_2-C=O$	4.0000	4.0405

The calculations are for stable configurations. The computation program was taken from Ref. 26.

The relative rate constant, k_{ap} (for acrylaldehyde)/k_{ap}(for *trans*-2-butene) was 1.6 as described before. By adoptating 0.7 for R in Eq. xi, we estimated the value of k_{1a}(for acrylaldehyde)/k_{ap}(for *trans*-2-butene) to be 0.94. The apparent rate constant k_{ap} for *trans*-2-butene does not change over a wide pressure range, and should be equal to the primary addition rate constant, which was adopted in Ref. 24.[9] By use of this rate constant for *trans*-2-butene as a common reference, the constant k_{1a}(for acrylaldehyde) was compared with the rate constant for olefins in Fig. 5 (point 8). This point is on the line derived from the data of monoolefins. Thus the atomic population is a good quantum-chemical measure in the case of the addition to the inner carbon side of acrylaldehyde as well as in the case of monoolefins.

In spite of the reasonable relationship between the relative rate constant and the corresponding atomic population for monoolefins, the rate constant of butadiene is much higher than is predicted from its atomic population. Similarly, the rate constant k_{1b} in the case of acrylaldehyde seems to be much higher than expected. The point 9 in Fig. 5 is the lower limit of the relative value of k_{1b} against the atomic population of the terminal carbon of the C=C bond. The point indicates the relative value of $k_{1b}k_{3b}[M]/(k_{-1b}+k_{3b}[M])$ ($=k_{ap}-k_{1a}$) and should be the lower limit of k_{1b}. In these cases, the addition of atomic hydrogen results in production of stable π-allyl type radicals, and their stability should be the cause of the rapidness of the addition. It is expected that the individual atomic population can not be a good measure in this case.

Conclusion

1) Hydrogen atoms add mainly to the C=C double bond of acrylaldehyde, though some other possibilities are not completely eliminated.

2) Under reduced pressure, the net attacking position of hydrogen atoms is mainly (about 60% under the pressure of the present work, 0.3 Torr) the inner carbon side of the C=C double bond. Under higher pressures, the fraction of the addition to the terminal carbon may increase.

3) The rate of the addition to the inner carbon side can be explained by its atomic population as a quantum-chemical measure in a similar fashion as in monoolefins.

4) The subsequent reactions are regarded as unimolecular decompositions and collisional stabilizations of the resulting hot radicals in a similar fashion as in olefin-atomic hydrogen systems.

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