Rate Constant of the α-Pinene + Atomic Hydrogen Reaction at 295 K

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Abstract

The rate constant of the reaction of α-pinene with atomic hydrogen was determined at 295 K using the fast-flow reactor technique directly coupled to a mass spectrometric detection technique. The value was found to be equal to $(9.8 \pm 3.3) \times 10^{-13}$ cm^3 molecules^{-1} s^{-1} and independent of the helium pressure between 1 and 2 torr. The major reaction product formed is pinane showing that the stabilization of the adduct radical $C_{10}H_{17}^*$, followed by a subsequent hydrogen atom addition step, is the important reaction route. © 1994 John Wiley & Sons, Inc.

Introduction

It is well known that terpenes and in particular α-pinene are very important biogenic hydrocarbons emitted on a global scale [1]. Although the rate constants of the primary destruction reactions of α-pinene under atmospheric conditions involving hydroxyl and nitrate radicals and ozone are relatively well established [2], not much is known of the further kinetics and mechanism of its degradation path [3]. One possible way to clarify this complex reaction mechanism is an investigation of the α-pinene/OH reaction with a fast-flow reactor technique. Since the OH-radicals are produced by the H + NO_2 titration reaction, it was noticed that in the absence of NO_2, a fraction of the α-pinene disappears in a reaction with atomic hydrogen.

$$C_{10}H_{16} + H \longrightarrow \text{products} \tag{1}$$

In order to estimate the possible interference of reaction (1) in the $C_{10}H_{16}$/OH system, the rate constant of reaction (1) has to be determined separately and its relative importance in this fast-flow reactor study established.

From fundamental point of view hydrogen atom addition reactions to double bonds are of interest and especially the kinetic behavior of the energized adduct [4,5] is likewise important. Recent work on the hydrogen atom reactions with cycloalkenes [6] and *trans*-2-butene [7] has to be mentioned here also.

In this contribution a mass spectrometric detection technique directly coupled to a fast-flow reactor will be used to determine for the first time the rate constant k_1. In view of the complexity of mass fragmentation spectra and large number of isotope contributions, a detailed reaction product analysis was impossible. In order to carry out such an analysis a GC-MS technique would be required. It will be shown though that at a pressure of 2 torr stabilization of the adduct $C_{10}H_{17}^*$ is the dominant path relative to its decomposition into other hydrocarbon molecules or fragments.

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Experimental Technique

Fast-Flow Reactor and Detection

Although the use and characteristics of the fast-flow reactor technique is very well known in gas-phase kinetic studies, a brief description will be given here since this particular experimental set-up has not been described elsewhere.

A schematic view of the system is given in Figure 1. It consists of a quartz reactor with an internal diameter of 2.8 cm and a length of 70 cm. By means of an oil rotary pump with a nominal pump capacity of 35 m^3 hr^{-1} a flow velocity v of (10.9 ± 0.2) m s^{-1} is obtained at 295 K with helium as a carrier gas. Reagent flows are maintained by mass flow controllers in the range from 1 to 1000 cm^3 min^{-1}. The addition of α-pinene is realized by flowing a fraction of the carrier gas through a separate pyrex vessel across the α-pinene liquid.

Weight loss measurements of the α-pinene containing vessel allowed a calculation of the α-pinene concentrations in the gas phase in the reactor. While the α-pinene /He flow is introduced through the central quartz probe with an external diameter of 0.6 cm, the hydrogen atoms are generated by a microwave discharge in a 0.1% H_2/He mixture. The reaction time t is determined by the axial position of the α-pinene inlet with respect to the detection point downstream of the fast-flow reactor. At this point a mass spectrometric detection system is directly coupled to the fast-flow reactor for on-line reactant analysis. It is a magnetic instrument of the type Micromass 8–80 from Vacuum Generators with a magnetic field sector of 80° and radius of 8 cm and it is equipped with a "closed" ionization source with both a variable electron energy and electron emission current of respectively 5 to 100 eV and 10 to 400 μA. The detector consist of a 17 Cu/Be dynode ion multiplier operating at 2.5 kV. A fine metering valve with a range from 1×10^{-4} to 2×10^{-2} atm 1 min^{-1} allowed a pressure of 2×10^{-6} torr inside the mass spectrometer to be set which was independent of the reactor pressure. The latter is determined by means of a Barocel absolute pressure gauge. In

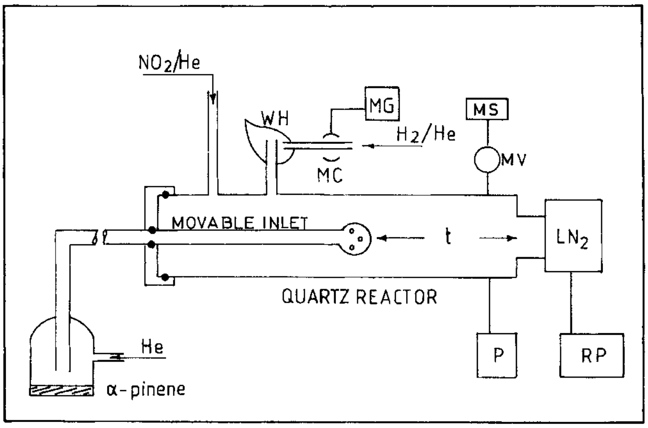

Figure 1. Schematic view of the experimental set up. (MC): Microwave cavity; (MG): Microwave generator; (WH): Wood's horn; (MS): Mass spectrometer; (MV): Metering value; (P): Absolute pressure gauge; (LN2): Liquid nitrogen trap; (RP): Oil rotary pump; and (t): Reaction time.

order to determine the rate constant k_1 the decay of the mass spectrometric signal of the α-pinene fragment at mass 93 was followed as a function of the reaction time in excess of hydrogen atoms. The latter concentration [H] has been determined by means of the H + NO_2 titration with the end point taken at the appearance of the NO_2 signal. Detection limits for most components are in the 0.1 to 2 ppm range.

Flow Characteristics

In order to be able to derive reliable kinetic date from fast flow reactor experiments, a few experimental criteria must be fulfilled [8]. First, it is clear that laminar flow conditions must be established with a Reynolds Number Re of less than 2000. In this case at 2 torr helium pressure and 295 K, one finds $Re = 6.9$. Second, the time for reagent mixing must be sufficiently long to realize a radially flat concentration profile for all reagents added. This is not a problem for both H-atoms and NO_2 since both inlets are located upstream of the mixing point. It may be a problem for α-pinene added through the central probe. One can calculate that the distance z for complete mixing must be larger than $v \times d^2/2\ D$ where d is the radial distance between the mixing point and the reactor wall and D the binary diffusion coefficient of α-pinene in helium. The latter is not well known but can be estimated to be about 80 $cm^2\ s^{-1}$ at 2 torr and 295 K. With a value of $d = 0.9$ cm one arrives at a minimal mixing distance $z > 6$ cm which on the time scale corresponds to 5 ms. Since all the experiments are carried out at $z \geq 15$ cm, poor mixing of the reagents cannot not be a problem.

Finally in order to be allowed to neglect axial diffusion, the dimensionless parameter $D \times k_1 \times [H]/v^2$ must be much smaller than 1 [8]. In view of the rather small value of k_1 (see section on experimental results) leading to pseudo-first-order decay constants never exceeding 40 s^{-1}, the above criterion is easily met.

Reagents

Gases and gas mixtures are from Indugas. Hydrogen is added from a 0.1% H_2/He mixture while nitrogen dioxide is a 0.85% NO_2/He mixture each prepared in helium with a purity of 99.9996%. The α-pinene liquid is from Aldrich and has a purity of 98%.

Results and Discussion

Loss of Hydrogen Atoms on the Wall

Since the pseudo-first-order decay constant $k_{obs} = k_1$ [H] of reaction (1) will be determined in excess of hydrogen atoms it must be checked how the hydrogen concentration is affected by the reactor wall condition. With a freshly cleaned reactor the H-atom concentration remained constant within 5% in the whole kinetic zone. After about one week the reactor wall condition seemed to deteriorate somewhat leading to a higher H-atom loss. As an example the natural logarithm of the H-atom concentration as a function of time is shown in Figure 2 for the worst case.

A straight line is obtained with as slope $k_w = (13.0 \pm 0.4)\ s^{-1}$. In view of this relatively low value for k_w one knows that the loss of H-atoms is controlled by its

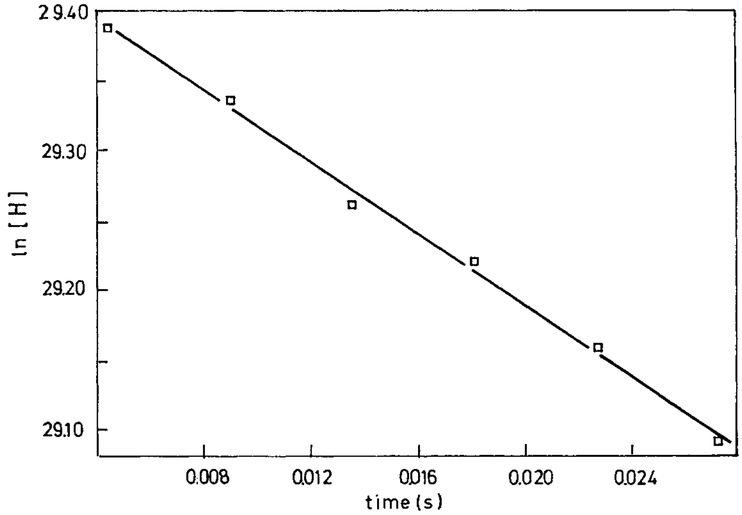

Figure 2. Natural logarithm of H-atom concentration as a function of the time: Reactor pressure P_r and temperature T_r are respectively 2 torr and 295 K.

sticking coefficient and thus k_w is given by [9].

$$k_w = \frac{\gamma_H c}{2r(1 - \gamma_H/2)} \tag{2}$$

with c being the average thermal velocity of the hydrogen atoms, $(8RT/\pi \text{ M})^{0.5}$ and γ_H the sticking coefficient of the H-atoms on the quartz wall, i.e., the fraction of H-atoms which recombines upon collision. Equation 2 allows us to calculate the sticking coefficient γ_H on quartz equal to $(1.6 \pm 0.05) \times 10^{-4}$. This value is almost a factor of 5 larger than found for clean reactor walls [10]. The magnitude of γ_H is important since plug-flow conditions for active species lost on the reactor wall can only be achieved when $\gamma \ll \frac{D}{r}\left(\frac{2\pi M}{RT}\right)^{0.5}$ [8]. This criterion which requires a γ-value smaller than 10^{-3} is largely fulfilled for hydrogen atoms in the reactor geometry used.

Concerning the hydrogen atom concentrations, two corrections had to be applied. Since the concentrations were at the 1×10^{13} atoms cm^{-3} level the hydrogen atom /NO_2 titration reaction will yield too high a concentration. Indeed OH radicals formed in the titration reaction will undergo subsequent reactions consuming additional NO_2. A simple kinetic model using the reaction and rate constant set given by Wayne et al. [11] allows to calculate by numerical integration the concentrations of the various species involved. It was found that depending on the initial hydrogen atom concentration a correction factor of 6 to 22% had to be applied. In addition depending on the reactor wall condition, an average hydrogen atom loss between 5 and 10% over the entire kinetic zone must also be taken into account.

Rate Constant k_1 of the Reaction α-Pinene + H-Atoms

Due to fragmentation in the ionization source the parent ion of α-pinene at $m/e = 136$ is only weak and therefore the α-pinene decay was followed at the major fragment ion $m/e = 93$ [12]. The experiments were carried out at 1 and 2 torr total helium pressure. Initial α-pinene concentrations in the range from 5×10^{10} to 5×10^{11} molecules cm^{-3} are mixed with an excess of atomic hydrogen in a ratio from 10 to 50. Since reaction 1 must yield a radical as reaction product which is in principle either the adduct $C_{10}H_{17}^*$ or in case of hydrogen abstraction $C_{10}H_{15}$, further consecutive reactions might deplete the hydrogen atom concentration. In order to suppress these reactions the well known radical scavenger NO is added in two different concentrations: 9.4×10^{13} and 3.25×10^{15} molecules cm^{-3}. At the highest concentration another correction for H-atom concentration must be applied in view of the termolecular loss process $H + NO + He \rightarrow HNO + He$. Taking a rate constant of 4.3×10^{-32} cm^6 $molecules^{-2}$ s^{-1} for this reaction [13], one arrives at an additional H-atom decay of 9.1 s^{-1}. Depending on the reactor wall conditions an overall H-atom loss in the kinetic zone between 13 and 31 ms of 20 to 35% must be taken into account.

While the uncertainties in reactor pressure, flow velocity, and temperature lead to an uncertainty of 5% at the most, an overall uncertainty of 30% on the average H-atom concentration seems reasonable.

As an example the natural logarithm of the α-pinene concentration as a function of the reaction time is shown at 1 and 2 torr, respectively (Fig. 3 and Fig. 4). The slopes of these straight lines directly yield $k_{obs} = k_1$ [H] (Table I).

When k_{obs} is plotted as a function of the hydrogen atom concentration a reasonably good straight line is obtained (Fig. 5). As can be seen from the 2 torr data, the large excess of NO in Experiment 2 does not have a systematic effect on the observed decay constants k_{obs}. This is a strong indication that secondary reactions leading to an additional depletion of α-pinene are unimportant.

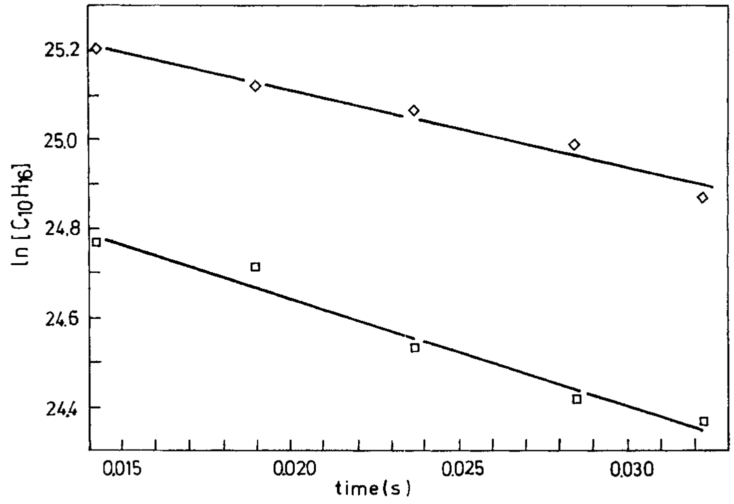

Figure 3. Natural logarithm of the α-pinene concentration as a function of the reaction time. Reactor pressure $P_r = 1$ torr, hydrogen atom concentrations are: (◇) [H] $= 1.59 \times 10^{13}$ atoms cm^{-3} and (□) [H] $= 2.13 \times 10^{13}$ atoms cm^{-3}. The NO concentration is 9.4×10^{13} molecules cm^{-3}.

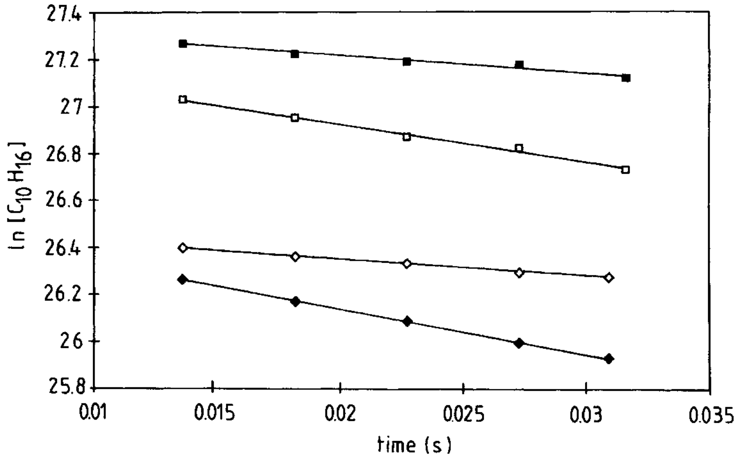

Figure 4. Natural logarithm of the α-pinene concentration as a function of the reaction time. Reactor pressure P_r = 2 torr, hydrogen concentrations are: (■) [H] = 0.60×10^{13} atoms cm^{-3}; (□) [H] = 1.65×10^{13} atoms cm^{-3}; (◇) [H] = 0.51×10^{13} atoms cm^{-3}; and (◆) [H] = 1.81×10^{13} atoms cm^{-3}.

NO-concentrations are: (■, □) 3.25×10^{15} molecules cm^{-3} and (◇, ◆) 9.4×10^{13} molecules cm^{-3}.

A weighted linear regression on both the 1 and 2 torr data using SAS statistical [14] package yields the slope $k_1 = (9.8 \pm 3.3) \times 10^{-13}$ cm^3 $molecules^{-1}$ s^{-1}. The intercept is equal to (0.4 ± 0.8) s^{-1} which indicates that heterogeneous wall reactions are unimportant. In addition since no pressure effect on the value of k_1 was observed, the rate constant has already reached its high pressure limit.

While this is the first determination of the rate constant of the α-pinene with atomic hydrogen, its value can only be compared though with the rate constants of other olefins/hydrogen atom addition reactions [7,15–17]. Olefins with a number of carbon atoms ≥ 3 with one double bond have a rate constant for hydrogen atom addition in the range of 0.6 to 1.5×10^{-12} cm^3 $molecules^{-1}$ s^{-1}. One sees that k_1 falls neatly within this range.

Formation of Pinane $C_{10}H_{18}$

As said in the introduction, a detailed product analysis was not carried out in view of the complexity of the fragmentation spectra. Only the presence of pinane has been checked. With an initial concentration of $[\alpha - C_{10}H_{16}] = 7 \times 10^{12}$ molecules cm^{-3}, $[H] = 8.4 \times 10^{13}$ atoms cm^{-3} and a reaction time of about 30 ms, pinane could be identified beyond doubt. It shows two major ion fragments at m/e = 55 and 95. If the same sensitivity for pinane is assumed as for α-pinene and the ion intensities at the various fragments are summed up, one can estimate that the conversion yield of α-pinene to pinane was at least 50%. In view of the complex reaction mechanism involving a competition between stabilization and decomposition processes, it is known that the product distribution is a function of initial [Hydrocarbon]/[H] ratio [6,7]. The relatively high yield of pinane observed is in agreement with the results obtained for the cyclohexene and cyclopentene / atomic hydrogen reaction where the respective

TABLE I. The pseudo-first-order decay constants $k_{\mathrm{obs}} = k_1$ [H] of the α-pinene + H reaction as a function of the hydrogen atom concentration at 1 and 2 torr total pressure. The carrier gas is helium. The NO-concentrations are as follows: Experiments 1 and 3: 9.4×10^{13} molecules cm^{-3} and Experiment 2: 3.25×10^{15} molecules cm^{-3}.

Experiment 1		Experiment 2	
k_{obs} (1 torr) (s^{-1})	[H] (10^{13} atoms cm^{-3})	k_{obs} (2 torr) (s^{-1})	[H] (10^{13} atoms cm^{-3})
8.4 ± 0.8	0.65	5.3 ± 0.4	0.44
9.2 ± 1.1	0.86	6.7 ± 0.9	0.60
11.8 ± 1.9	1.05	8.8 ± 1.4	0.94
14.2 ± 1.2	1.40	15.0 ± 1.1	1.30
17.2 ± 1.9	1.59	15.7 ± 1.1	1.65
22.6 ± 1.4	1.77	23.0 ± 1.7	1.85
23.3 ± 1.3	1.98		
24.4 ± 2.3	2.13		

Experiment 3	
k_{obs} (2 torr) (s^{-1})	[H] (10^{13} atoms cm^{-3})
7.0 ± 0.1	0.51
10.5 ± 0.1	1.1
12.6 ± 0.09	1.5
17.2 ± 0.4	1.6
19.4 ± 0.2	1.8
21.1 ± 0.5	2.1
21.1 ± 0.6	2.3
25.6 ± 0.5	2.6
27.7 ± 0.7	3.1
33.1 ± 0.1	3.2
34.4 ± 0.6	3.8

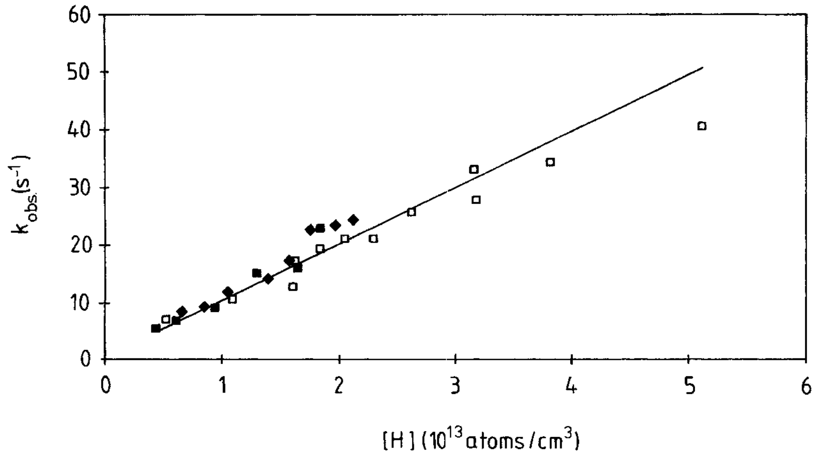

Figure 5. The observed first-order rate constant $k_{\mathrm{obs}} = k_1$ [H] of the α-pinene + H reaction as a function of the hydrogen atom concentration: (◆) P_r = 1 torr, [NO] = 9.4×10^{13} molecules cm^{-3}; (□) P_r = 2 torr, [NO] = 9.4×10^{13} molecules cm^{-3}; and (■) P_r = 2 torr, [NO] = 3.2×10^{15} molecules cm^{-3}.

products cyclohexane and cyclopentane were found to be by far the major reaction products [6]. Stabilization of the $C_{10}H_{17}^{*}$-adduct formed is more important than its decomposition. Addition of nitric oxide in a concentration of 1.1×10^{15} molecules cm^{-3} completely suppressed the pinane formation. Taking into account that the [NO]/[H] ratio is then of the order of 14, one can estimate that the rate constant for the NO-addition to the $C_{10}H_{17}$ radical is at least a factor of 0.1 times the rate constant of the hydrogen atom addition reaction.

When the magnitude of k_1 is compared with the rate constant of the α-pinene + OH reaction [18] which is of the order of 5×10^{-11} cm^3 $molecules^{-1}$ s^{-1} one sees the latter being a factor of about 50 larger than k_1. Possible interferences of hydrogen atom reactions on the primary removal of α-pinene with OH-radicals in flow tube studies may indeed completely be neglected taking into account that the initial [OH]/[H] ratio is at least ≥ 10.

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