Rate Constants for the Reactions of O(^{3}P) with Selected Monoterpenes

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ABSTRACT

Rate constants for the gas phase reactions of O(^{3}P) atom with a series of monoterpenes have been determined at ambient temperature (~302-309K) and atmospheric pressure using a relative rate technique. Using the literature rate constants for O(^{3}P) + isobutene, cis and trans-2-butene, 3-methyl-1-butene, 2-methyl-2-butene and 2,3-dimethyl-2-butene as the standards, the O(^{3}P) rate constants derived for the terpenes (in units of 10^{-11} cm^{3}molecule^{-1}s^{-1}) are 2.8±0.4 for α-pinene, 2.8±0.5 for β-pinene, 3.1±0.5 for Δ^3-carene, 3.5±0.5 for 2-carene, 2.6±0.5 for camphene, 7.6±1.2 for d-limonene, 9.0±1.6 for γ-terpinene and 10.7±1.6 for terpinolene. The relative rate constants in this work agreed with literature values to within ±10% for the standard alkenes, and to within ±~35% for the terpenes.

Compound Index: O(^{3}P), α-pinene, β-pinene, Δ^3-carene, 2-carene, camphene, d-limonene, γ-terpinene, terpinolene, 2-methyl-2-butene, isobutene, cis-2-butene, trans-2-butene, 3-methyl-1-butene, 2,3-dimethyl-2-butene

Subject Index: O(^{3}P) rate constants, monoterpenes

INTRODUCTION

Monoterpene hydrocarbons are emitted from certain species of vegetation [1,2] and play a role in the formation of carbon monoxide, ozone, and aerosols in urban and rural areas [3-7]. As with other unsaturated compounds, they can react in the atmosphere with OH radical, O_3, NO_3 radical and $O(^3P)$ atom, with their relative importance depending on atmospheric conditions [8-10]. The reactions with OH radical and O_3 are usually the most important removal processes in the daytime, though the NO_3 reaction can be a major sink at night [10]. Although reactions of alkenes with $O(^3P)$ are generally not important under most urban or rural conditions, and are generally neglected in condensed chemical mechanism used in airshed models [11,12], they might be non-negligible under high NO_2 conditions in source areas. Since the major source of $O(^3P)$ is the photolysis of NO_2 [8-12], the importance of $O(^3P)$ reactions increases with the absolute NO_2 concentration. Environmental chamber experiments, which are necessary to the development and testing of atmospheric reaction mechanisms for organic compounds, generally employ higher NO_x concentrations than are typical in the atmosphere [13]. Model simulations indicate that $O(^3P)$ + alkene reactions can affect results of environmental chamber experiments carried out in our laboratory for developing and testing mechanisms for terpenes [14]. Therefore, a knowledge of the $O(^3P)$ + terpene rate constants is necessary to the development and evaluation of atmospheric reaction mechanisms for these compounds.

Although rate constants have been measured for the reactions of most of the terpenes with OH radical [9,15], O_3 [9,16], and NO_3 radical [9,10], only limited data are available concerning their reactions with $O(^3P)$. $O(^3P)$ rate constants have been reported for α-pinene [17-19], β-pinene [17,18], Δ^3-carene [19], and d-limonene [17,18]. There is no information available concerning the $O(^3P)$ rate constants for any other terpenes.

In this work, as part of our experimental studies in support of the development of chemical mechanisms for the atmospheric reactions of terpenes [14], we have determined the rate constants at ambient temperature and atmospheric pressure for the reactions of $O(^3P)$ with a series of representative monoterpenes, whose structures are shown in Figure 1. To verify the relative rate method employed, we measured rate constants for a number of other alkenes for which such data have been reported in the literature [18].

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EXPERIMENTAL

The relative rate method employed involves monitoring relative rates of decays of ~0.1-0.2 ppm of various test and standard compounds when $O(^3P)$ is generated by the photolysis of ~50 ppm of NO_2 in N_2, with ~50 ppm of NO also present to suppress O_3 or NO_3 radicals. (One ppm is ~2.5 x 10^{13} molec cm^{-3} at ambient temperature and pressure.) 2-Methyl-2-butene was used as the reference compound in all experiments in this work.

The conditions and reactants in the kinetic experiments in this study are listed in Table 1. The experiments were carried out in ca. 500-L all-Teflon (2 mil FEP) reaction chambers at ambient temperature and atmospheric pressure, with dry nitrogen usually being used as the diluent gas. In a few experiments medical air or AADCO purified dry air was used to investigate how increasing O_2 affected the results. NO and NO_2 were both introduced with all-glass gas-tight 100 cm^3 syringes, the NO_2 being prepared by allowing an excess of pure oxygen (ca. 75 cm^3) to mix with a measured amount of NO (ca. 25 cm^3) prior to injection. As such, the effective concentration of O_2 in the chamber for these experiments was at the most 150 ppm. The reference compounds (if liquid), the monoterpenes, and m-xylene were added to a glass bulb using a 10μl syringe and injected into the chamber using a combination of heating and a flow of dry nitrogen through the bulb. Camphene, which is solid at ambient temperature, was prepared for injection using vacuum techniques. The amount injected is determined by the pressure of the vapor measured by an MKS Baratron gauge in a calibrated bulb. In the case where the reference compounds were gases at room temperature and atmospheric pressure, a measured amount would be placed into a 2 L flask for dilution and subsequently an appropriate amount would be removed with a syringe and injected into the chamber. Mixing was achieved by manually flexing the sides of the reaction chamber. A minimum of one hour would pass before irradiation began to achieve adequate mixing, and, more importantly, to assess the extent of any dark reactions. Initial concentrations were typically: monoterpenes, ca. 100 ppb each; reference alkenes, 140-150 ppb; and, NO and NO_2, 50 ppm each, with the concentrations determined during the course of the experiment by a chemiluminescence monitor after dilution with dry nitrogen. In addition, m-xylene, which is not expected to react with $O(^3P)$, was also added to the reaction mixture at a concentration of ~0.12 ppm to test for formation of OH radicals.

The organic reactant concentrations were monitored prior to and during the course of the experiments by gas chromatography with flame ionization detection (GC-FID). For the analyses, samples were collected from the chamber in 100 cm^3 all-glass, gas-tight syringes, transferred via a 2.5 cm^3 gas sampling

loop onto a 15 m DB-5 megabore column held at -50°C or -30°C for 3.5 min, and then the GC oven was temperature programmed at 35°C min^{-1} to 10°C, then 15°C min^{-1} to 35°C, and finally 40°C min^{-1} to 200°C.

NO and NO$_2$ were flushed into the reaction bag which was previously purged by filling and emptying it a few times with dilution gas. Sunlight was used as the light source to generate O(^{3}P) from NO$_2$. This was accomplished by exposing the bag to sunlight for periods of time not less than 15 seconds per irradiation, with the irradiation terminated for ~15 minutes for each GC analysis of the reactants. The total irradiation time, not counting periods where the GC analyses were conducted, was typically 2-5 minutes. Depending on the number of GC analyses for each experiment, the total experimental time varied from 180 to 375 minutes.

If it is assumed that reaction with O(^{3}P) is the only significant process consuming the reactant monoterpenes and the reference compound, then, as discussed by Atkinson et al. [20], their O(^{3}P) rate constant ratios for the conditions of the experiment can be derived as:

$$\ln\frac{[monoterpene]_{t_0}}{[monoterpene]_t} = \frac{k_1}{k_2}\ln\frac{[reference]_{t_0}}{[reference]_t} \qquad (1)$$

where [monoterpene]$_0$ and [reference]$_0$ are the concentrations of the monoterpene and reference compound, respectively, at time t_0, and [monoterpene]$_t$ and [reference]$_t$ are the corresponding concentrations at time t, and k_1 and k_2 are the rate constants for the reaction of monoterpene and reference compound with O(^{3}P) atom, respectively. Hence, plots of ln([monoterpene]$_{t_0}$/[monoterpene]$_t$) against ln([reference]$_{t_0}$/[reference]$_t$) should give a slope of k_1/k_2 with zero intercept. The reference compound employed in all our experiments was 2-methyl-2-butene.

The reactants and their stated purity levels were as follows: 2-methyl-2-butene (99%), 3-methyl-1-butene (unknown), 2,3-dimethyl-2-butene (99+%), m-xylene (99%), α-pinene (99%), β-pinene (99%), Δ^3-carene (95%), 2-carene (97%), camphene (85%), d-limonene (97%), γ-terpinene (98%), Aldrich Chemical Company; terpinolene (93.1%), American Tokyo Kasei; isobutene (99.3%), t-2-butene (99.3%), cis-2-butene (99%), Liquid Carbonic Specialty Gas Corp; NO (99.0%), Matheson Gas Company; nitrogen and medical air (the latter used only in Run 13), Liquid Air Company. The camphene was further purified by the vacuum injection method discussed above, which removed nonvolatile impurities. (Note however that impurities would not affect the results unless they co-eluted with the compounds of interest.) The

purified dry air used in runs 15 and 16 was provided by an ADDCO air purification system described elsewhere [21].

RESULTS AND DISCUSSION

Before any experiments were carried out, model simulations were conducted to determine the optimum reaction conditions so that reaction with $O(^3P)$ was the only significant consumption process for the test alkenes. Since alkenes can also react with OH radicals, O_3, NO_3 radicals and NO_2 [8-10,22], it is important that conditions be adjusted to minimize these competing processes. Reactions with O_3 and NO_3 are minimized by suppressing O_3 and NO_3 with relatively high concentrations of NO, which they react rapidly. Reactions with OH radicals are minimized by using high concentrations of NO_2, which reacts with OH. However, the concentration of NO_2 could not be increased too much or consumption of the alkene by reaction with NO_2 may begin to become non-negligible [22]. The importance of $O(^3P)$ reactions is also enhanced, and interferences by O_3 reactions is further reduced, by using N_2 rather than O_2 as the diluent gas, because $O(^3P)$ is consumed by reaction with O_2 to form O_3. Model calculations using the detailed atmospheric mechanism developed by Carter [23,24] predicted that use of ~50 ppm each of NO and NO_2 and ~0.1 - 0.2 ppm of test and reference alkenes resulted in conditions where the only significant alkene consumption process was reaction with $O(^3P)$, at least for the alkenes studied here. However, this method was not expected to work for alkenes with conjugated double bonds, such as isoprene, since their reaction with NO_2 is rapid enough for that reaction to be non-negligible [25]. Indeed, attempt to use this method for isoprene was not successful because significant consumption of this species in the dark was observed after the NO_2 was injected.

Table 1 lists the kinetic experiments which were carried out, the compounds which were studied, the reaction times, and indicates those experiments where air rather than N_2 was used as the diluent gas. In order to avoid GC Interferences, only three to seven compounds were employed in each individual experiment. Note that 2-methyl-2-butene was present in all the experiments, since it served as the reference compound against which all other rate constants were compared. Typical concentration-time plots for a representative experiment are shown on Figure 2, and plots of Equation (1) are shown on Figure 3. Except for the terpinolene runs with air diluent (which are discussed later), the plots on Figure 3 are linear and have essentially zero intercept, and that there was good agreement in relative rates of decay among different experiments.

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A concern in performing these experiments was the possible dark reaction of NO_2 with the alkenes and monoterpenes. However, no dark decay of the monoterpenes was observed over periods of time of up to about one hour. Figure 2 shows that in a representative run (no. 12) with 3-carene there is no indication for a dark reaction between NO_2 and 3-carene before the lights are turned on. Note also that there is no measureable consumption of m-xylene even after the lights are turned on, indicating that OH radical levels are very low in these experiments.

As discussed above, model simulations indicate that the reactions of the alkenes or monoterpenes with species other than the $O(^3P)$ atom should be of negligible importance in our experiments. However, for some of the compounds reactions with O_3 and OH radicals might become non-negligible if the O_2 concentration were increased. Since there is always some O_2 present in our experiments, if these interferences are non-negligible, the results may be sensitive to changing O_2 levels. To check this, three experiments (nos. 13, 15 and 16) were conducted using air rather than N_2 as the diluent gas. The results showed no difference in consumption rates, relative to 2-methyl-2-butene, for α- and β-pinene, d-limonene, and Δ^3-carene. This indicates no O_2 sensitivity, and thus insignificant interference by O_3 reactions, for these rate constant ratios. On the other hand, the relative rates of decay of terpinolene were found to be significantly higher in the experiments with air compared to that with N_2, and also to vary from run to run. This is shown on the upper three curves in Figure 3 (a), where it can be seen that terpoinolene decay rates relative to 2-methyl-2-butene was not only greater in the two experiments using air instead of N_2 as the diluent gas, but also differed from each other. This result can be attributed to the O_3 + terpinolene reaction becoming non-negligible in the experiments with air; the O_3 + terpinolene rate constant is approximately three times higher than that for 2-methyl-2-butene, and approximately an order of magnitude higher than those for the other terpenes used in the runs with O_2. The relative decay rates differed in the two air experiments presumably because the relative levels of O_3 and $O(^3P)$ would be expected to be sensitive to differences in experimental conditions; the initial NO and NO_2 (which was measured only approximately) tended to vary somewhat from run to run. [The air sources in the two runs also differed (see Table 1) though this is not expected to affect the results.] The data from the runs with air were not used in deriving the reported rate constant ratio for terpinolene. However, they were used for the other terpenes for which the results were not significantly different.

The averages of the rate constant ratios, relative to 2-methyl-2-butene (2M2B), are summarized on Table 2. The "Ave. T" shown is the average temperature for the experiments used to derive the ratio; this temperature was used for calculating the "Literature" rate constant from the published temperature-

dependent expressions. Note that the 2,3-dimethyl-2-butene/2M2B ratio is given twice, one for the experiments using only the standard alkenes, and one for the terpene experiments where both these compounds were also present. The rate constant ratio for these two compounds is essentially the same for both sets of runs, indicating that the conditions of the added terpene experiments are comparable to those containing only the standard alkenes.

The rate constants on Table 2 were placed on an absolute basis by using the recommendations of Cvetanović [18] for the absolute rate constants for isobutene, cis- and trans-2-butene, 3-methyl-1-butene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene for the average temperatures of the experiments using these compounds. This was done by deriving an absolute 2M2B rate constant which minimized the least-squares relative difference between the absolute rate constants derived from the data in this work and that 2M2B rate constant, and the absolute rate constants recommended by Cvetanović [18]. The relative difference between our results and the recommendations of Cvetanović [18] are given in parentheses next to the literature values. Note that the relative differences are in all cases within ±6%, indicating that our rate constant ratios are in good agreement with the recommendations of Cvetanović [18]. Although Cvetanović's recommendations had estimated uncertainties of ~20% [18], in view of the good consistency of these data with our relative results, we assume an uncertainty of ~15% for the reference rate constant when estimating uncertainties for our absolute rate constants on Table 2.

The only previous determinations of $O(^3P)$+terpene rate constants which can be compared with this work are relative measurements for α- and β-pinene and d-limonene reported by Gaffney et al [17], which were placed on an absolute basis in the review of Cvetanović [18], and absolute measurements for α-pinene and Δ^3-carene recently reported by Paulson et al. [19]. Our results agree with these values to within ±25% except that the value for d-limonene is ~35% lower than the value recommended by Cvetanović [18] based on the data of Gaffney et al [17]. With the possible exception of d-limonene, the agreement can probably can be considered to be within the uncertainty ranges of the determinations.

Atkinson [26] noted that there was a good correlation between $O(^3P)$ and OH radical rate constants for the alkenes which had been studied up to that time. To show how these new data affect this correlation, Figure 4 shows a log-log plot of the $O(^3P)$ vs OH rate constants for these terpenes and other alkenes. The OH rate constants used were those recommended by Atkinson [9], and the $O(^3P)$ rate constants were either from this work, Cvetanović's review [18], or (for isoprene) from Paulson et al. [19]. Separate symbols are shown for conjugated dialkenes because terpenes with conjugated double bonds could not be

studied using the methods discussed here, and it is of interest to see if their rate constants fit the same correlation. It can be seen that a good correlation can be seen with all these alkenes, with the $O(^3P)$ rate constant being predicted, to within a factor of 2 for most compounds, by the equation

$$k[O(^3P)] = e^{15.14 + 1.69 \ln k[OH]}$$

except for 1-methyl cyclohexene, where the discrepancy is a factor of 2.3. Since this relationship seems to work for isoprene [19] and the other 1,3-dialkenes for which $O(^3P)$ rate constants are available [18], it will probably satisfactorily predict the rate constants for the terpenes whose $O(^3P)$ rate constants could not be measured in this study.

ACKNOWLEDGMENT

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Table 1. List of experiments, reactants and reactant conditions.

Exp. No.	Cond.	Compounds [a]						Temp. (K)	Times (min) Init.	Irriad.	Tot.
8		APIN	BPIN	DLIM	TERP	3CAR		303.6	210	3.25	285
9		APIN	DLIM					304.7	225	4.00	285
10		3CAR	TERP					301.3	210	2.75	285
11		BPIN	DLIM					300.0	150	3.75	285
12		3CAR	TERP	MXYL				299.2	[b]	[b]	[b]
13	[c]	DLIM	TERP	MXYL				302.2	60	2.42	180
14		APIN	BPIN	MXYL				301.6	180	3.50	270
15	[d]	APIN	BPIN	MXYL				300.7	180	4.75	300
16	[d]	TERP	3CAR	MXYL				302.0	240	1.75	330
17		GTER	2CAR	MXYL	DM2B			302.5	285	2.17	330
18		2CAR	MXYL	DM2B				301.4	180	4.33	300
19		CAMP	GTER	MXYL	DM2B			306.9	210	2.50	330
20		CAMP	2CAR	MXYL	DM2B			307.8	225	5.00	330
21		GTER	2CAR	MXYL	DM2B			309.1	180	2.25	330
22		3CAR	TERP	CAMP	MXYL	DM2B		307.2	180	3.00	345
23		ISOB	TBUT	CBUT	3MBU	DM2B	MXYL	309.2	150	5.00	330
24		ISOB	TBUT	CBUT	3MBU	DM2B	MXYL	308.8	210	5.00	375

[a] NO, NO_2, and 2-methyl-2-butene present in all experiments. Codes for other reactants: ISOB = isobutene; TBUT = trans-2-butene; CBUT = cis-2-butene; 3MBU = 3-methyl-1-butene; DM2B = 2,3-dimethyl-2-butene; APIN = α-pinene; BPIN = β-pinene; 3CAR = Δ^3-carene; 2CAR = 2-carene; CAMP = camphene; DLIM = d-limonene; GTER = γ-terpinene; TERP = terpinolene.
[b] Not recorded.
[c] Medical air was used as dilution gas instead of N_2.
[d] Purified air was used as dilution gas instead of N_2.

Table 2. Alkene + O(^{3}P) rate constant ratios and rate constants measured in this work and comparison with literature values.

| Compounds | Exp. No. | Ave. T. | k / k(2M2B) | Rate constant (10^{11}x cm^{3}molec^{-1}s^{-1}) | | |
				This Work[1]	Literature	Diff.[2]
Standard Alkenes						
isobutene	23,24	309.0	0.33 ± 0.03	1.78 ± 0.3	1.72[3]	(3%)
cis-2-butene	23,24	309.0	0.340 ± 0.014	1.82 ± 0.3	1.79[3]	(2%)
trans-2-butene	23,24	309.0	0.41 ± 0.02	2.18 ± 0.3	2.31[3]	(-6%)
3-me-1-butene	23,24	309.0	0.081 ± 0.02	0.43 ± 0.1	0.44[3]	(-1%)
2,3-dimetyl-2-Butene	23,24[4]	309.0	1.48 ± 0.06	7.9 ± 1.2	7.5[3]	(6%)
	17-22[4]	305.8	1.47 ± 0.08			
2-methyl-2-butene (2M2B)	-all-	304.0	1.0	5.26	5.56[3]	(-4%)
Monoterpenes						
α-pinene	8,9,14,15	302.6	0.52 ± 0.002	2.79 ± 0.4	3.02[5]	(8%)
					3.7[6]	(25%)
β-pinene	8,11,14,15	301.5	0.52 ± 0.04	2.8 ± 0.5	2.7[5]	(-3%)
Δ^3-carene	8,10,12,16,22	302.7	0.58 ± 0.03	3.12 ± 0.5	3.4[6]	(8%)
2-carene	17,18,20,21	305.2	0.66 ± 0.02	3.54 ± 0.5		
camphene	19,20,22	307.3	0.49 ± 0.05	2.6 ± 0.5		
d-limonene	8,9,11,13	302.6	1.41 ± 0.09	7.6 ± 1.2	12.[5]	(37%)
γ-terpinene	17,19,21	306.2	1.68 ± 0.15	9.0 ± 1.6		
terpinolene	8,10,12,22	302.8	2.00 ± 0.04	10.7 ± 1.6		

[1] Uncertainties in absolute rate constants derived using an estimated ~15% uncertainty in the reference rate constant for 2-methyl-2-butene, combined with the experimental uncertainty in the k/k(2M2B) ratio..

[2] Relative difference between rate constant measured in this work and literature value.

[3] As recommended by Cvetanović [18]

[4] Results are given separately for experiments with only the standard alkenes and experiments with the terpenes to show that the same results are obtained in both cases.

[5] Relative data of Gaffney et al. [17], placed on an absolute basis as recommended by Cvetanović [18].

[6] Absolute rate constant measured by Paulson et al. [19].

α-pinene   β-pinene   camphene   Δ³-carene

2-carene   d-limonene   γ-terpinene   terpinolene
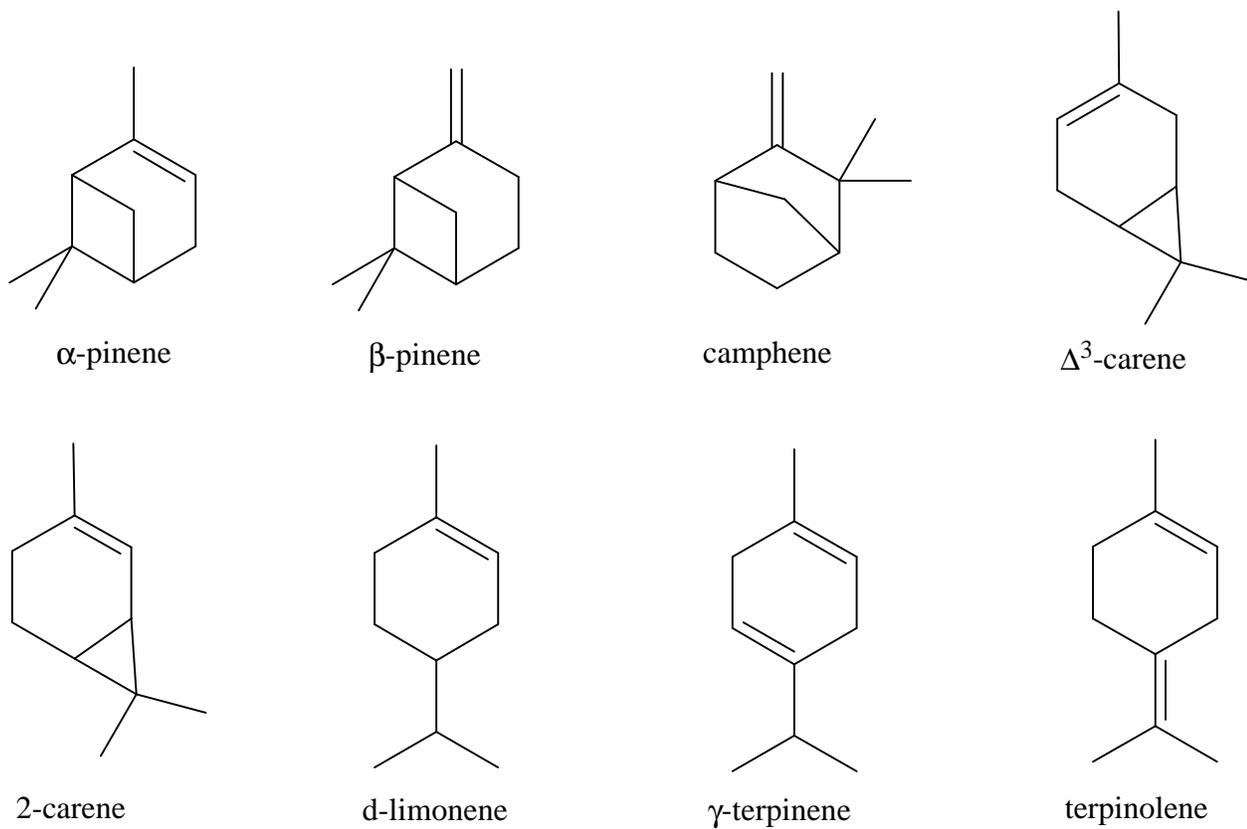
Figure 1. Structures of the terpenes studied in this work.
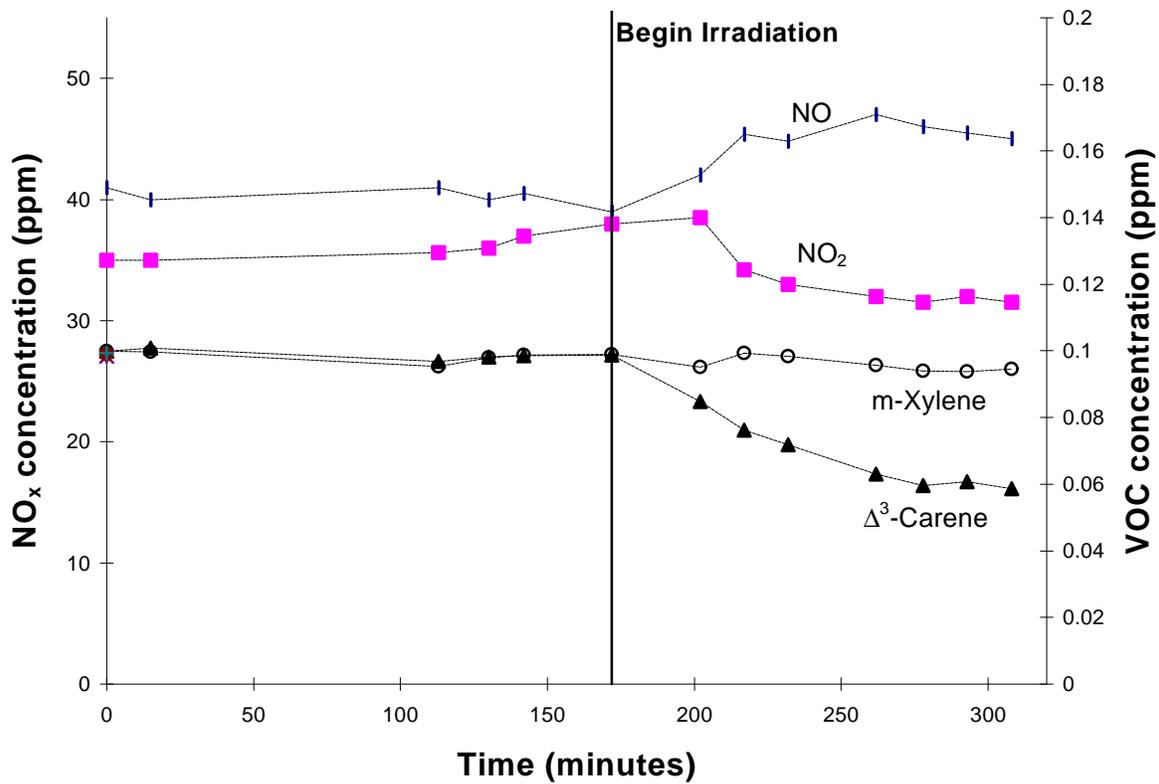
Figure 2. Concentrations of NO, NO_2, Δ^3–Carene and m-xylene as a function of time in experiment number 12.
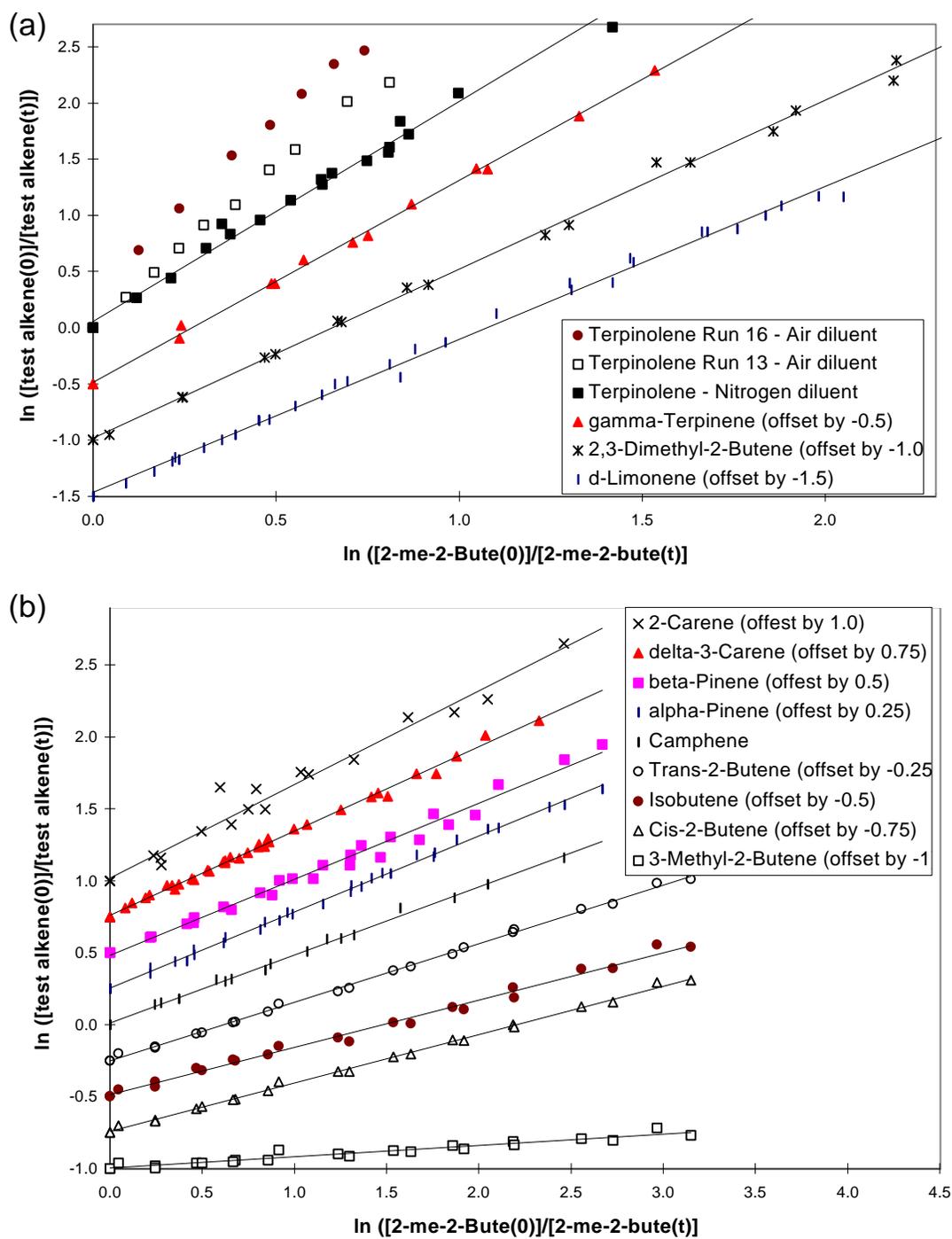
Figure 3. Plots of equation (1) for all the kinetic experiments. The effects of diluent gas on the terpinoline runs is also shown.
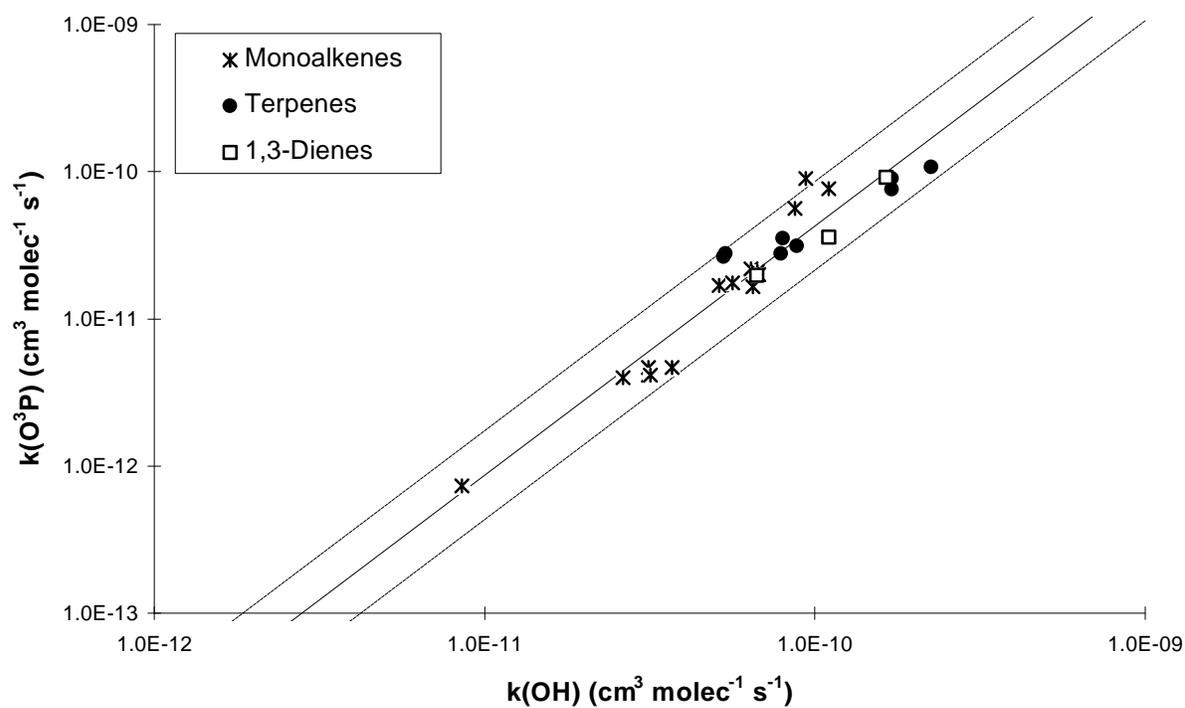
Figure 4. Plots of O(^{3}P) vs OH radical rate constants for various alkenes. Solid line shows best fit to the data; dotted lines show factor of 2 uncertainty range.