

# Kinetics of Free Radicals Produced by Infrared Multiphoton-Induced Decompositions. 1. Reactions of Allyl Radicals with Nitrogen Dioxide and Bromine

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**Abstract:** A new versatile technique to study quantitatively the gaseous reactions of polyatomic free radicals is described in detail. Free radicals are generated homogeneously in a tubular reactor by the infrared multiphoton-induced decomposition (MPD) of suitable radical precursors. The concentrations of reactants and products (both stable and labile) are monitored by using photoionization mass spectrometry. Reactions of the allyl radical, generated by the MPD of allyl bromide, with nitrogen dioxide and bromine have been studied at 300 K. The measured rate constants are  $3.9(\pm 0.8) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  for the  $\text{C}_3\text{H}_5 + \text{NO}_2$  reaction and  $9.0(\pm 1.8) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  for the  $\text{C}_3\text{H}_5 + \text{Br}_2$  reaction. The potential of the experimental facility for other kinds of studies is discussed.

## Introduction

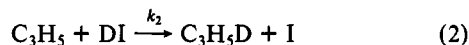
The gaseous reactions of polyatomic organic free radicals are well-known to be important in combustion processes as well as in other gaseous oxidations including the production of photochemical smog.<sup>1-4</sup> Yet most of the basic information which is available today on the reactivity of these labile intermediates is still based on indirect evidence, from studies in which data analysis required knowledge of complex mechanisms and/or from investigations in which these species were not directly detected.<sup>5</sup> We have now developed a new experimental facility with which one can isolate individual elementary reactions of polyatomic free radicals under controlled conditions suitable for their direct and quantitative study. The radicals are generated homogeneously in a tubular reactor by the infrared multiphoton-induced decomposition (MPD) of suitable precursors. Concentration profiles of both labile and stable reactants and products are dynamically monitored by using photoionization mass spectrometry. In this paper we present the experimental method and report on its first application, the generation of allyl radicals and the study of their reactions with  $\text{NO}_2$  and  $\text{Br}_2$  at ambient temperature.

Although allylic free radicals are important intermediates in the pyrolysis of olefins and cycloalkanes and in the combustion of hydrocarbons, little quantitative information is available on their reactivity. The only prior quantitative studies of gaseous allyl radical reactions which involved direct monitoring of the free radical itself were investigations of the recombination reaction (1). van den Bergh and Callear monitored the time dependence



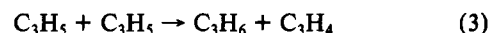
of the UV absorption of  $\text{C}_3\text{H}_5$  by using kinetic-flash-spectroscopy,<sup>6</sup> and MacFadden and Currie used time-of-flight mass spectrometry to observe  $\text{C}_3\text{H}_5$  decay profiles following flash photolysis of divinyl ether.<sup>7</sup>

Reaction 1 as well as reaction 2 has been studied in a semidirect



manner by Golden and co-workers at elevated temperatures by

using the very low-pressure pyrolysis (VLPP) method.<sup>8</sup> The reactant DI was used to "titrate"  $\text{C}_3\text{H}_5$ . Mass spectrometric monitoring of  $\text{C}_3\text{H}_5\text{D}$  under reaction conditions and with DI in great excess yielded a measure of the allyl radical concentration in the system and the ratio of  $k_2$  to readily calculable constants for effusion of reacting species from the pyrolysis cell. The failure to detect products resulting from the disproportionation of allyl radicals



by several investigators,<sup>8-10</sup> as well as the reported failure of toluene to act as an efficient scavenger of allyl radicals even at elevated temperatures,<sup>9</sup> indicates that H-atom abstraction by allyl radicals is far less labile than for alkyl radicals. Estimates of the Arrhenius parameters of the allyl + toluene H-atom-transfer reaction are available from older indirect studies of allyl radical reactivity.<sup>11</sup>

## Experimental Apparatus

Any experimental facility which is to be used for the direct and quantitative study of the kinetics of polyatomic free radicals requires two essential features. The first is a method of generating the radicals homogeneously throughout the reaction zone in a period which is short compared to the half-life of subsequent reactions. This method should preferably not perturb the known state variables of the system (e.g., temperature and pressure). The second essential feature is a selective, versatile, and sensitive method of detecting and dynamically monitoring these reactive intermediates at concentration levels which are so low that the radical recombination processes are slow compared to the rates of the alternative radical reactions which are under study. The way we have been able to obtain these necessary performance features in our new experimental facility is described in this section together with other important details of the apparatus.

**I. Generation of Polyatomic Free Radicals.** It is becoming increasingly apparent that polyatomic molecules which absorb infrared radiation in the 9-11- $\mu\text{m}$  region can decompose to a significant extent by collisionless MPD when subjected to rather mildly concentrated  $\text{CO}_2$  TEA laser pulses (i.e., pulses with fluences  $< 5 \text{ J/cm}^2$ , a practical upper limit for the types of experiments described in this paper) provided that the activation barrier to dissociation is not too large (usually under 50 kcal/mol) and provided that the molecule contains several heavy atoms (a property which can create a virtual continuum of quantum states in the absorbing molecule at and above its average energy under ambient conditions).<sup>12,13</sup> Significant collisionless MPD (5% or greater) during

(1) G. J. Minkoff and C. F. H. Tipper, "Chemistry of Combustion Reactions", Butterworths, London, 1962.

(2) R. R. Baldwin and R. W. Walker, *Symp. (Int.) Combust.*, [Proc.], **14**, 241 (1973).

(3) K. L. Demerjian, J. A. Kerr, and J. G. Calvert, *Adv. Environ. Sci. Technol.*, **4** (1974).

(4) A. H. Falls and J. H. Seinfeld, *Environ. Sci. Technol.*, **12**, 1398 (1978), and references therein.

(5) J. A. Kerr, "Free Radicals", Vol. 1, J. K. Kochi, Ed., Wiley, New York, 1973, Chapter 1.

(6) H. E. van den Bergh and A. B. Callear, *Trans. Faraday Soc.*, **66**, 2681 (1970).

(7) K. O. MacFadden and C. L. Currie, *J. Chem. Phys.*, **58**, 1213 (1973).

(8) (a) M. Rossi, K. D. King, and D. M. Golden, *J. Am. Chem. Soc.*, **101**, 1223 (1979); (b) M. Rossi and D. M. Golden, *ibid.*, **101**, 1230 (1979).

(9) W. Tsang, *J. Chem. Phys.*, **46**, 2817 (1967).

(10) Disproportionation of other allylic radicals has also been found to be a minor pathway by D. L. Baulch, P. K. Chown, and D. C. Montague, *Int. J. Chem. Kinet.*, **11**, 1055 (1979).

(11) R. J. Akers and J. J. Throssell, *Chem. Commun.*, 432 (1966), and references cited therein.

(12) Aa. S. Sudbø, D. J. Krajnovich, H. S. Kwok, Y. R. Shen, and Y. T. Lee, *Annu. Rev. Phys. Chem.*, **30** (1979).

each laser pulse at fluences under  $5 \text{ J/cm}^2$  has now been reported for a variety of larger molecules (six atoms or more) including  $\text{CH}_3\text{COO-C}_2\text{H}_5$ ,<sup>14</sup>  $\text{SF}_6$ ,<sup>15</sup>  $\text{SF}_6$ ,<sup>16</sup>  $\text{SF}_2\text{NF}_2$ ,<sup>17</sup>  $\text{S}_2\text{F}_{10}$ ,<sup>18</sup>  $\text{N}_2\text{F}_4$ ,<sup>19</sup>  $\text{C}_2\text{H}_5\text{ONO}_2$ ,<sup>20</sup> and a 44-atom molecule  $\text{UO}_2(\text{hfacac})_2\cdot\text{THF}$ .<sup>13</sup> It seems increasingly evident that MPD can occur under mild conditions in a wide assortment of molecules even if barriers to decomposition are high<sup>15-18</sup> and the molecules are large and complex<sup>13</sup> and that it should soon become a straightforward matter to identify suitable polyatomic molecules as convenient precursors of free radicals of interest for chemical kinetic studies.

In our experiments we use pulsed infrared radiation from a Lumonics 103-2 line-tunable (9.2–10.8  $\mu\text{m}$ )  $\text{CO}_2$  TEA laser. The light is directed axially down a 0.95-cm i.d. Pyrex flow reactor. For assurance of uniform irradiation down the length of the tube (and hence uniform radical generation throughout the tubular reactor), the radiation is not focused but rather is concentrated either with a 3:1 Galilean telescope (constructed with  $\text{BaF}_2$  uncoated lenses of 150- and -50-mm focal lengths) or with a 5-m focal length Cu spherical mirror. (The long waist of the beam is located inside the flow reactor in the region before the sampling orifice.) The concentrated laser light is collimated by a 0.8-cm orifice located in front of the NaCl window which is at one end of the flow reactor. Both light-concentrating methods have yielded the same experimental results. Our location of the spherical mirror produces a very slightly converging beam in the section of the flow reactor which is sampled during an experiment. Since this arrangement essentially eliminates irradiation of the reactor walls with laser light, it has become our preferred method of concentrating the radiation.

The telescope or the spherical mirror is used to concentrate the radiation to the desired fluence for the experiment, up to values near  $5 \text{ J/cm}^2$ . This upper limit is due to the fact that the salt optics and windows degrade rather rapidly during a set of experiments when laser pulses above this fluence are used.

We have chosen allyl bromide as our allyl radical source because it has most of the desired properties of a suitable precursor: a known thermal decomposition route to produce the desired radical,<sup>21</sup> strong absorption at  $10.6 \mu\text{m}$  (due to  $=\text{CH}_2$  motions) and a modest activation barrier to decomposition ( $\sim 55 \text{ kcal/mol}$ ).<sup>21</sup> We have found that near  $5 \text{ J/cm}^2$  less than 1% of the allyl bromide decomposes during each laser pulse. Since this amount of decomposition was adequate for our kinetic studies, we have not yet explored the potential usefulness of other possible allyl radical sources. It is likely that the decomposition efficiency was not higher because of a relatively low density of states of  $\text{C}_3\text{H}_5\text{Br}$  at ambient energies.

**II. Detection of Polyatomic Free Radicals.** For several years we have been using a photoionization mass spectrometer (PIMS) which uses intense atomic resonance lamps to provide the ionizing radiation as a selective and sensitive detector of polyatomic free radicals.<sup>22-25</sup> Our PIMS as well as those of others have now been used to detect and monitor free radicals emerging from a variety of reactors including primitive cross-beam reactors,<sup>22-24</sup> flow,<sup>25-29</sup> and stop-flow reactors.<sup>30,31</sup>

(13) A. Kaldor, R. B. Hall, D. M. Cox, J. A. Horsley, P. Rabinowitz, and G. M. Kramer, *J. Am. Chem. Soc.*, **101**, 4465 (1979).

(14) W. C. Danen, W. D. Munslow, and D. W. Setser, *J. Am. Chem. Soc.*, **99**, 6961 (1977).

(15) R. R. Karl and J. L. Lyman, *J. Chem. Phys.*, **69**, 1196 (1978).

(16) P. Kolodner, C. Winterfeld, and E. Yablonovitch, *Opt. Commun.*, **20**, 119 (1977).

(17) J. L. Lyman, W. C. Danen, A. C. Nilsson, and A. V. Nowak, *J. Chem. Phys.*, **71**, 1206 (1979).

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(19) Aa. S. Sudbø, P. A. Schultz, E. R. Grant, Y. R. Shen, and Y. T. Lee, *J. Chem. Phys.*, **70**, 912 (1979).

(20) I. R. Slagle and D. Gutman, unpublished results.

(21) S. W. Benson and H. E. O'Neal, *Natl. Stand. Ref. Data Ser. U.S., Natl. Bur. Stand., NSRDS-NBS 21*, 509 (1970).

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(23) J. R. Kanofsky, D. Lucas, F. Pruss, and D. Gutman, *J. Phys. Chem.*, **78**, 311 (1974).

(24) I. R. Slagle, J. F. Dudich, and D. Gutman, *J. Phys. Chem.*, **83**, 3065 (1979).

(25) I. R. Slagle, F. J. Pruss, Jr., and D. Gutman, *Int. J. Chem. Kinet.*, **6**, 111 (1974).

(26) I. R. Slagle, D. Gutman, and J. R. Gilbert, *Symp. (Int.) Combust., [Proc.]*, **15**, 785 (1974).

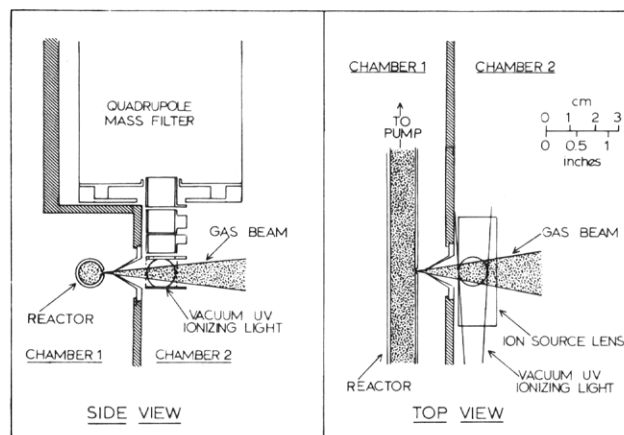
(27) I. T. N. Jones and K. D. Bayes, *J. Am. Chem. Soc.*, **94**, 6869 (1972).

(28) N. Washida, R. I. Martinez, and K. D. Bayes, *Z. Naturforsch., A*, **29A**, 251 (1974).

(29) T. M. Lenhardt, C. E. McDade, and K. D. Bayes, *J. Chem. Phys.*, **72**, 304 (1980).

(30) J. T. Herron and R. E. Huie, *J. Am. Chem. Soc.*, **99**, 5430 (1977).

(31) J. T. Herron and R. E. Huie, *Int. J. Chem. Kinet.*, **10**, 1019 (1978).



**Figure 1.** Drawing of flow reactor and mass spectrometer in two-chamber vacuum system.

We have now modified one of our PIMS apparatuses in order to couple it to the flow reactor used in this study. Special care was given to increasing detection sensitivity by reducing the distance from the sampling orifice in the flow reactor to the center of the PIMS ionizing region.

Detection begins with a gas sample continuously emerging from a 0.044-cm diameter hole in the side of the tubular reactor which is located 32 cm from the salt window. The entire flow tube is 46 cm long. At the end opposite the salt window is a beam energy absorber and a pumping port.

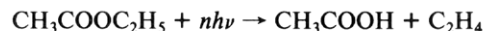
The gas emerging from the sampling hole is immediately collimated into a beam by a conical skimmer and then flows through the open ion source of a quadrupole mass filter (see Figure 1). Ions produced by the photoionization process are accelerated perpendicular to the gas flow, mass selected, and detected by using conventional pulse counting methods. Ion signals are recorded with a signal averager which is synchronized to begin recording ion pulses 20 ms before each laser pulse. Typical signal-averager dwell times for recording ion samples are 0.5 and 1.0 ms.

Most of the details of the construction and performance of the PIMS, including a description of the resonance lamps used to produce the ions, have been reported previously.<sup>22-26</sup> The main modifications made in the present apparatus involved the reconstruction of our ion source lenses on narrower plates to permit placement of the ionizing region closer to the wall separating the two vacuum chambers, the enclosure of our open ionizing area with high transmission screens to shield the area from the electrical potential of the chamber wall, and the rebuilding of the divider between the chambers to permit locating the center of the ionizing region only 2.4 cm from the sampling orifice in the flow reactor. These changes have increased the sensitivity of our apparatus about fivefold.

Ions emerging from the mass spectrometer are detected with a Daly scintillation detector,<sup>32</sup> which is extremely useful as a mass spectrometer detector because of its chemical inertness. However, this detector is very sensitive to stray light. Careful attention to eliminating much of this stray light and to discrimination of pulses originating from the detection of the remaining light has given us at least another factor of 5 improvement in our effective detection sensitivity. Our measured sensitivity for allyl radicals is  $(1-2) \times 10^8$  ion counts  $\text{s}^{-1}/\text{torr}$  of radicals in the flow reactor.<sup>33</sup> Our background signal was  $\sim 200$  counts/s ( $\sim 150$  counts/s originate from scattered vacuum UV light from the chlorine lamp used to photoionize the allyl radicals).

## Experimental Results

In this section we report the results of three sets of experiments. The first involved the photolysis of ethyl acetate, a molecule which produces two stable products upon MPD (or pyrolysis)<sup>14,34,35</sup>



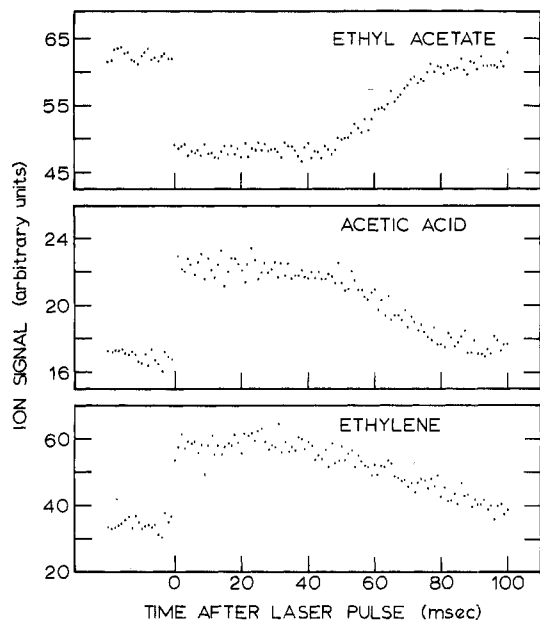
These experiments were performed to test the response time of

(32) N. R. Daly, *Rev. Sci. Instrum.*, **31**, 264 (1960).

(33) Initial allyl radical concentrations for determining sensitivity were calculated from data obtained in the experiments of the  $\text{C}_3\text{H}_5 + \text{NO}_2$  reaction in which the reaction went to completion and in which  $\text{NO}_2$  was not in great excess. The loss of  $\text{NO}_2$  was monitored and equated to the initial  $\text{C}_3\text{H}_5$  concentration.

(34) D. Gutman, W. Braun, and W. Tsang, *J. Chem. Phys.*, **67**, 4291 (1977).

(35) Reference 21, p 158.



**Figure 2.** Ion signal profiles of reactants and products resulting from the multiphoton-induced decomposition of ethyl acetate. See text for conditions of experiment.

the apparatus and the uniformity of the laser irradiation along the tubular reactor (uniform illumination would produce uniform reactant and product concentrations along the length of the reactor). The second involved a study of the mechanism of the reaction of allyl radicals with  $\text{NO}_2$ . In these experiments the potential product ion signals were monitored to determine their presence or absence. And the final set of experiments involved the photolysis of allyl bromide with and without the presence of a molecule ( $\text{NO}_2$  or  $\text{Br}_2$ ) which reacts with the allyl radical. These latter experiments have yielded the rate constants for the allyl radical reactions with these molecules at ambient temperature.

In all the experiments reported here gas mixtures flowed through the reactor at 4 m/s to assure nearly ideal plug-flow conditions. The flowing gas mixture consisted primarily of an inert carrier gas (>99% He) to prevent heating of the bulk gas and was kept at a total pressure of 1.0 torr. The pressure in the reactor drops less than 5% between the measuring point near the salt window and the sampling point. Pressure was measured with  $\pm 2\%$  accuracy with a capacitance manometer. Total gas flows were measured at the output of the flow-reactor pump with a rising soap bubble in a burette, and flows of reactants were measured by directing them into a known volume and monitoring the pressure rise with the same capacitance manometer. The glass flow tube was cleaned with a 5%  $\text{NH}_4\text{F}\cdot\text{HF}$  solution, rinsed with a 0.5% boric acid solution, then dried to leave a film of dry acid on the walls.

Ethyl acetate (Eastman), allyl bromide (Aldrich), and bromine (Mallinckrodt) were purified by the freeze-pump-thaw method at liquid nitrogen temperature.  $\text{NO}_2$  (Matheson) was condensed at dry ice temperature and fractionally distilled. He (Linde high purity grade) was used without additional purification.

The  $\text{CO}_2$  TEA laser was pulsed at 0.5 Hz, and data were accumulated for 500–2000 laser pulses.

The lamps (and ionizing energies) used to detect each species were Ar (11.6 eV) for ethylene and acetic acid, H (10.2 eV) for ethyl acetate, nitric oxide, nitrogen dioxide, allyl bromide, and acrolein, and Cl (8.9–9.2 eV) for allene, allyl, and allyloxy radicals.

**I. MPD of Ethyl Acetate.** Ethyl acetate (0.10% in He at a total pressure of 1.0 torr) was irradiated with the P(18) line of the  $9.6\text{-}\mu\text{m}$  band at  $9.536\text{ }\mu\text{m}$ . The fluence was near  $5\text{ J}/\text{cm}^2$ . The ion profiles recorded for reactants and products are shown in Figure 2.

From the constant ion signals for reactants and products which were recorded as the gas is swept past the sampling point it can be concluded that the laser photolysis was uniform along the

tubular reactor. The mixing zone between the irradiated sample and the incoming fresh gas mixture is apparent in all three traces. The time between laser photolysis and the detectable onset of the mixing zone is about 50 ms which constitutes the available testing time under the same flow conditions (4 m/s) in those experiments in which allyl radical reactions were studied.

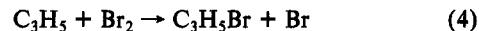
We have measured the ion signal rise time in experiments by using detection dwell times of  $100\text{ }\mu\text{s}$ . We find the rise time to be between 100 and  $200\text{ }\mu\text{s}$ . Such a rise time would be expected simply from the distribution of molecular velocities of the gas molecules being sampled from the flow reactor.<sup>36</sup> In our studies of free radical kinetics, initial reaction conditions are controlled to yield radical decay half-lives greater than 2 ms so that the thermal spread in arrival times of the free radicals at the ion source does not distort the desired measured representation of the free radical concentration profile inside the flow reactor.<sup>36</sup>

Tests were also conducted to determine whether the multiphoton absorption process produced significant subsequent heating of the gas sample following vibrational relaxation of the absorbing molecule. Gas samples containing 0.01% NO in addition to 0.1% ethyl acetate (balance He) were irradiated, and the ion signal of NO was monitored as a function of time. The signal of this nonabsorbing and nonreacting species was unperturbed by the photolysis process, indicating that no significant density changes occurred in the flow reactor following pulsed irradiation by the  $\text{CO}_2$  TEA laser (and hence there were no major temperature fluctuations).

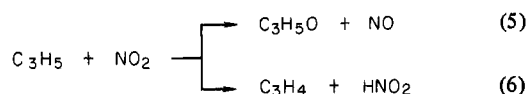
In each of the sets of experiments involving allyl radical reactions, which are discussed in the following sections, two groups of experiments were always performed in which the radical precursor concentration ( $[\text{C}_3\text{H}_5\text{Br}]_0$ ) was different by a factor of 3–4. This change not only altered the initial radical concentration by a large amount but also changed the amount of energy absorbed by the gas mixture by this same large factor. In none of these studies did the change in precursor concentration alter the shape or the half-life of the radical decay profiles in any significant manner, indicating that laser-induced physical heating of the reactive mixtures was of a negligible magnitude. At the higher allyl bromide mole fractions ( $\sim 1.4 \times 10^{-3}$ ) very slightly accelerated radical profiles were observable during the first millisecond following irradiation. Since this behavior could have been due to increased reactivity caused by a mild heating effect (the half-life for cooling of the test gas following pulsed heating would be around 1 ms), experimental conditions were usually arranged to produce radical decay times which were 4 ms or greater.

The ethyl acetate experiments demonstrate that pulsed  $\text{CO}_2$  laser photolysis can be used to instantly and homogeneously alter the concentrations of a gas mixture in an easily characterized manner and that time resolved measurements of gaseous species in these systems can be accomplished quantitatively by using photoionization mass spectrometry.

**II. Mechanism of the  $\text{C}_3\text{H}_5 + \text{NO}_2$  Reaction.** Of the two allyl radical reactions studied, the one with  $\text{Br}_2$  has but one possible route



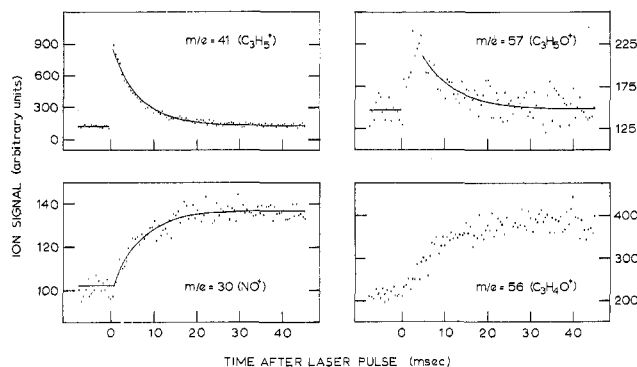
while the fast reaction with  $\text{NO}_2$ , at the low densities of our study, could proceed by two



Both reactions 5 and 6 are exothermic and both types of mechanisms are observed in reactions involving  $\text{NO}_2$ .

A search was conducted for the possible products of the  $\text{C}_3\text{H}_5 + \text{NO}_2$  reaction under conditions where radical-radical reactions would have a negligible rate ( $[\text{C}_3\text{H}_5]_0 < 1 \times 10^{11}\text{ cm}^{-3}$ ). The products  $\text{C}_3\text{H}_5\text{O}$  and NO were detected and their ion signal profiles were measured. No  $\text{C}_3\text{H}_4$  ion signal was detected even

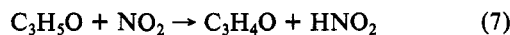
(36) S. B. Moore and R. W. Carr, *Int. J. Mass Spectrom. Ion Phys.*, **24**, 161 (1977).



**Figure 3.** Reactant and product ion signal profiles in  $C_3H_5 + NO_2$  reaction. In all experiments  $P = 1$  torr,  $F = 3\text{--}4$  J/cm<sup>2</sup>. Initial concentrations were  $[NO_2] = 3.3 \times 10^{12}$  cm<sup>-3</sup>,  $[C_3H_5Br] = 5 \times 10^{13}$  cm<sup>-3</sup>, and  $[C_3H_5]_0 \leq 1 \times 10^{11}$  cm<sup>-3</sup>. The balance of the gas mixture was helium ( $\sim 99\%$ ).

in special experiments performed to detect minor amounts of this possible product. Detection problems prevented determination of the presence or absence of  $HNO_2$ . The measured reactant and product ion signal profiles from this set of experiments is shown in Figure 3.

The growth of the  $NO^+$  ion signal exactly mirrors the decay of the  $C_3H_5^+$  ion signal. The pseudo-first-order reaction conditions produce the exponential behavior of both concentration profiles. The exponential decay constant for  $C_3H_5$  ( $157 \pm 4$  s<sup>-1</sup>) agrees with the growth constant for  $NO$  production ( $149 \pm 13$  s<sup>-1</sup>). The lines through the  $C_3H_5^+$  and  $NO^+$  data points in Figure 3 are the exponential functions with these growth and decay constants. The ion signal from the second product of reaction 5 grew rapidly but also subsequently decayed, indicating that  $C_3H_5O$  undergoes a rapid secondary reaction in this system. This secondary reaction most likely involves one of the reactants, possible the reaction



The ion signal profile of  $C_3H_4O^+$ , the ion of one of the products of reaction 7, was also measured (see Figure 3) by using the hydrogen resonance lamp in order to detect acrolein ( $C_3H_4O$ ) if it was present in this system. A delayed appearance of  $C_3H_4O^+$  is observed, indicating that  $C_3H_4O$  is a secondary product. The relatively high ionizing energy needed to detect acrolein could also possibly have fragmented  $C_3H_5O$  to yield an additional  $C_3H_4O^+$  ion signal during the time that this transitory intermediate is present in the system. Since  $C_3H_5O$  was essentially consumed 30 ms after the overall reaction began, the later  $C_3H_4O^+$  ion signal is definitely a measure of  $C_3H_4O$  produced by secondary processes.

The late decay of  $C_3H_5O$  has been fit to an exponential function (see the line through the latter  $C_3H_5O^+$  data points). The decay constant is  $132 \pm 18$  s<sup>-1</sup>. If the loss of  $C_3H_5O$  is due exclusively to reaction 7, then from the known  $NO_2$  concentration one can estimate that the rate constant for this reaction is near  $4 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>.

The ability to dynamically monitor stable and labile species under conditions where radical-radical reactions are suppressed creates the opportunity to directly identify the mechanisms of free radical reactions and also to study secondary processes in some detail. In this study we have determined that the  $C_3H_5 + NO_2$  reaction proceeds only by O atom transfer to produce a labile intermediate, probably the allyloxy radical. In future studies if more than one reactive route is identified for an elementary reaction, the measurements of product production can be conducted quantitatively to yield the macroscopic branching ratios for the reaction under study.

**III. Rate Constants of the  $C_3H_5 + NO_2$  and  $C_3H_5 + Br_2$  Reactions.** Experiments were performed in which allyl radicals were produced by the MPD of allyl bromide in the presence of a second reactant ( $NO_2$  or  $Br_2$ ). In all of these experiments irradiation was with the P(32) line of the 10.6- $\mu$ m band (10.718  $\mu$ m); the fluence used was near 4 J/cm<sup>2</sup>. Less than 0.5% of the allyl bromide decomposed.

**Table I.** Initial Conditions and Experimental Results of Allyl Radical Rate Constant Measurements

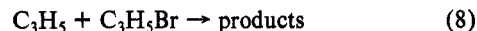
$C_3H_5 + NO_2$ Reaction			
$10^{-12} \times [NO_2], \text{cm}^{-3}$	$10^{-13} \times [C_3H_5Br], \text{cm}^{-3}$	approx $10^{-10} \times [C_3H_5]_0, \text{cm}^{-3}$	$k_{\text{exptl}}, \text{s}^{-1}$
0.0	1.4	2.8	$4 \pm 1^a$
1.1	1.4	2.8	$41 \pm 3$
2.1	1.4	2.8	$77 \pm 4$
2.7	1.4	2.8	$117 \pm 8$
3.4	1.4	2.8	$115 \pm 7$
4.2	1.4	2.8	$154 \pm 9$
5.1	1.4	2.8	$195 \pm 15$
1.0	5.4	11	$45 \pm 2$
1.8	5.4	11	$71 \pm 3$
2.6	5.4	11	$113 \pm 3$
3.1	5.4	11	$121 \pm 6$
4.0	5.4	11	$167 \pm 5$
4.4	5.4	11	$168 \pm 5$
5.0	5.4	11	$207 \pm 7$
5.3	5.4	11	$216 \pm 12$
$C_3H_5 + Br_2$ Reaction			
$10^{-12} \times [Br_2], \text{cm}^{-3}$	$10^{-13} \times [C_3H_5Br], \text{cm}^{-3}$	approx $10^{-10} \times [C_3H_5]_0, \text{cm}^{-3}$	$k_{\text{exptl}}, \text{s}^{-1}$
0.0	1.2	2.4	$5 \pm 1$
4.4	1.2	2.4	$54 \pm 3$
8.4	1.2	2.4	$80 \pm 4$
13	1.2	2.4	$122 \pm 8$
19	1.2	2.4	$187 \pm 18$
0.0	4.7	9.4	$13 \pm 1$
4.2	4.7	9.4	$49 \pm 2$
7.7	4.7	9.4	$68 \pm 4$
11	4.7	9.4	$115 \pm 5$
15	4.7	9.4	$152 \pm 6$
16	4.7	9.4	$150 \pm 8$
18	4.7	9.4	$184 \pm 6$
19	4.7	9.4	$168 \pm 9$

<sup>a</sup> Standard error.

In both the study of reactions 4 and 5 two sets of experiments were performed in which the initial  $C_3H_5Br$  concentrations were different by about a factor of 4 ( $\approx 5 \times 10^{13}$  and  $\approx 1.2 \times 10^{13}$  cm<sup>-3</sup>). The respective initial  $C_3H_5$  concentrations were close to  $1 \times 10^{11}$  and  $3 \times 10^{10}$  cm<sup>-3</sup>. The second-order allyl radical half-life due to radical recombination is greater than 1 s under these conditions,<sup>37</sup> making recombination a negligible sink for allyl radicals under all of our experimental conditions. All radical ion signal profiles were exponential, indicating the pseudo-first-order nature of all experiments (see Figure 3).  $NO_2$  or  $Br_2$  was always in great excess over  $C_3H_5$ .

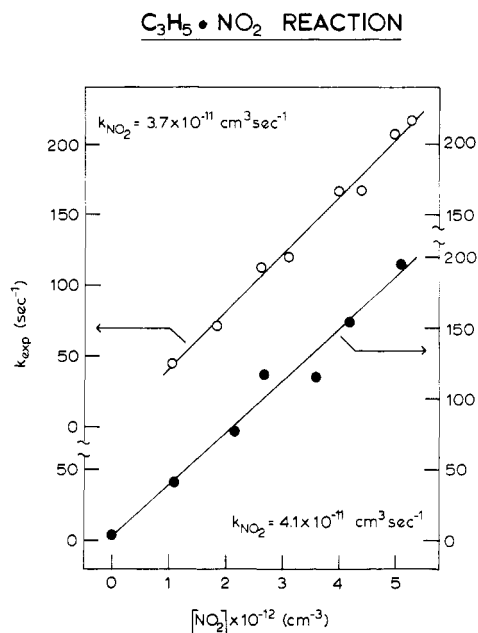
In the set of experiments in which  $[C_3H_5Br]$  was lowest, the  $C_3H_5$  ion signal profile was essentially flat during the testing period (50 ms) when no second reactant was present, indicating that wall recombination was also negligibly slow ( $k_{\text{wall}} < 2$  s<sup>-1</sup>). At the higher  $C_3H_5Br$  initial concentration the first-order decay of  $C_3H_5$  was apparent in the absence of  $NO_2$  or  $Br_2$ . We attribute this decay to reaction with the parent compound  $C_3H_5Br$ .

The data were interpreted by using a mechanism which includes only reaction 4 or 6 and reaction 8, presuming that the formation



of  $C_3H_5$  is instantaneous and assuming that  $NO_2$  (or  $Br_2$ ) and  $C_3H_5Br$  are in constant concentration during the experiment. Under these conditions the decay of  $C_3H_5$  is pseudo-first-order with an observed first-order decay constant  $k_{\text{exptl}} = k_5[NO_2] + k_8[C_3H_5Br]$  (or  $k_{\text{exptl}} = k_4[Br_2] + k_8[C_3H_5Br]$ ). Decay constants were measured for  $C_3H_5$  in both sets of experiments as a function of  $NO_2$  or  $Br_2$  concentration. The results are given in Table I. The measured decay constants,  $k_{\text{exptl}}$ , were obtained from the data

(37) These half-lives were calculated by using the estimated  $C_3H_5$  initial concentrations and the room-temperature value of the recombination rate constant  $k_1$  reported in ref 6.



**Figure 4.** Plot of  $k_{\text{exp}}$  vs.  $[\text{NO}_2]$  for experiments done at different  $\text{NO}_2$  concentrations. Open circles indicate experiments with  $[\text{C}_3\text{H}_5\text{Br}] = 5.4 \times 10^{13} \text{ cm}^{-3}$ ; closed circles indicate experiments done with  $[\text{C}_3\text{H}_5\text{Br}] = 1.4 \times 10^{13} \text{ cm}^{-3}$ .  $k_{\text{NO}_2}$  ( $k_6$ ) values determined from slopes of lines fitted through the two sets of experiments.

points by fitting the ion signal profiles to an exponential function by a nonlinear least-squares procedure. The line through the allyl radical data points in Figure 3 is an example of the results of such a fitting procedure.

The various sets of experimental values of  $k_{\text{exp}}$  are plotted in Figures 4 and 5 vs. the concentration of the second reactant  $[\text{NO}_2]$  or  $[\text{Br}_2]$ . The rate constants for reactions 4 and 5 shown in these figures were obtained from the slopes of the lines through sets of values of  $k_{\text{exp}}$  obtained from experiments in which only the concentration of  $\text{NO}_2$  or  $\text{Br}_2$  was changed.

The measured values of  $k_4$  and  $k_5$  are essentially independent of the concentration of the free radical precursor (and also therefore independent of the initial free radical concentration). The virtual identity of two calculated rate constants for each reaction studied indicates the precision of the method and the probable veracity of the data interpretation. The average of the two determinations for each rate constant is

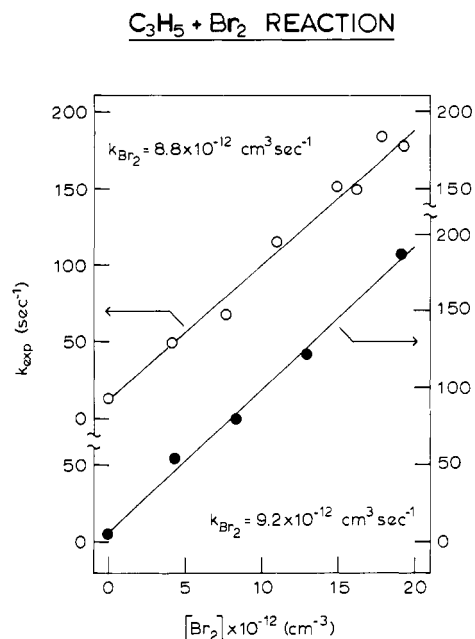
$$k_4 = 9.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$$

$$k_5 = 3.9 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$

We estimate the accuracy of these values to be  $\pm 20\%$ . The temperatures of the experiments were in the range  $300 \pm 3 \text{ K}$ .

## Summary

**I. The Experimental Method.** A versatile method for producing polyatomic free radicals under controlled conditions has been combined with a sensitive and equally versatile method of detecting them to create an instrument well suited for the quantitative study of their reaction. The facility is not complex and is easy to use



**Figure 5.** Plot of  $k_{\text{exp}}$  vs.  $[\text{Br}_2]$  for experiments done at different bromine concentrations. Open circles indicate experiments with  $[\text{C}_3\text{H}_5\text{Br}] = 4.7 \times 10^{13} \text{ cm}^{-3}$ ; closed circles indicate experiments done with  $[\text{C}_3\text{H}_5\text{Br}] = 1.2 \times 10^{13} \text{ cm}^{-3}$ .  $k_{\text{Br}_2}$  ( $k_4$ ) determined from slopes of lines fitted through the two sets of experiments.

and maintain. The experimental approach we have described here should be applicable to studies of any large polyatomic free radical.

We have begun a survey of potential sources of other kinds of free radicals. Each precursor tested has yielded interesting results. Sometimes the anticipated products are detected on the basis of the assumption of the analogous mechanisms to those reported for the pyrolysis of the same compound, and sometimes entirely different products are observed. These latter results suggest that this same experimental facility can also become a valuable tool for searching for nonthermal laser-induced decomposition reactions and for studying pyrolysis mechanisms under more ideal conditions where the initial step is fast and secondary reactions are slower instead of the reverse which is usual in heated systems.

**II. Allyl Radical Reactions.** The two allyl radical reactions we have studied to date have yielded precise results for their rate constants which are also quite accurate by our estimation ( $\pm 20\%$ ). There are no literature values to which we can compare our results.

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