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FT-IR product study of the gas-phase Br-initiated oxidation of *trans*-2-butene under atmospheric conditions between 246 and 298 K

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ABSTRACT

The products of the Br-atom initiated oxidation of *trans*-2-butene have been studied in a large-volume reaction chamber between 246 and 298 K using in situ FT-IR for the analysis. 3-Bromobutan-2-one, acetaldehyde and acetylbromide were the major products of this oxidation process. Additional products included formaldehyde and hydrogen bromide and evidence was found for the formation of 3-bromobutan-2-hydroperoxide. Decreasing the temperature from 298 K down to 246 K resulted in an increase in the yield of 3-bromobutan-2-one and a decrease in the yields of acetaldehyde, acetylbromide, formaldehyde and hydrogen bromide. Addition of NO to the reaction system resulted in nearly a doubling of the yields of 3-bromobutan-2-one, acetaldehyde and formaldehyde. The reaction mechanism is discussed and possible consequences of the results for the involvement of bromine/alkene chemistry in the springtime depletion of ozone in the Arctic are considered.

1. Introduction

Halogen-containing compounds are ubiquitous components of the atmosphere (Asplund and Grimvall, 1991; Hoekstra and De Leer, 1995; Gribble, 1994a,b; Tokarczyk and Moore, 1994). Over 2400 organohalogen species are produced by biogenic processes involving marine organisms, seaweed, plants, seeds, trees, fungi, lichens, algae, bacteria, microbes and insects. Methyl bromide (CH_3Br) is now believed to be the most important atmospheric organobromine reservoir substance in the atmosphere and has both biogenic and anthropogenic sources (Lobert et al., 1995; Fabian et al., 1995; Manö and Andreae, 1994; Khalil et al., 1993; Singh and Kanakidou, 1993). Its global tropospheric mixing ratio is typically $\geqslant 10$ ppt (Fabian et al., 1994; Khalil et al. 1993; Albritton and Watson, 1993). The estimations of the global emission rates of CH_3Br include large uncertainties with values ranging from ≈ 75 to 400 Gg/yr (Lobert et al., 1995; Platt and Janssen, 1995; Manö and Andreae, 1994; Reeves and Penkett, 1993; Khalil et al., 1993). The anthropogenic contribution is currently estimated to be in the order of 40–50% (Lobert et al., 1995; Reeves and Penkett, 1993).

Tropospheric ozone depletion in Arctic regions during the time period of polar sunrise is now a well established phenomena (McConnell et al., 1992; Bottenheim et al., 1990; Mickle et al. 1989; Oltmans et al., 1989; Barrie et al., 1988, 1989). During these episodes ozone concentrations drop from the normal ≈ 40 ppb down to < 2 ppb within less than one day. In field measurement campaigns an anti-correlation between bromine containing compounds and ozone concentration has been found (Barrie et al., 1994a,b; Leaitch et al., 1994;

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Li et al., 1994; Yokouchi et al., 1994). Recent field measurements carried out at Ny-Ålesund (Spitzbergen-Svalbard) within the European Commission financed project ARCTOC (Arctic Tropospheric Ozone Chemistry) have established beyond reasonable doubt that the cause for the sudden ozone loss is induced by bromine and chlorine catalysed reactions, whereby BrO_x plays a major role and ClO_x probably enhances the efficiency of the O_3 depletion (Platt et al., this journal).

Field measurements on the concentration ratios between C_2–C_6 hydrocarbons measured during the ozone depletion episodes (Jobson et al., 1994; Solberg et al., 1994) support that the OH-radical is not the principal reactive species propagating the photochemistry during the ozone depletion events. The available evidence strongly endorses that during these events the oxidation of the hydrocarbons is being driven by chlorine and bromine chemistry.

The atmospheric degradation of organobromine species via OH radicals or photolysis may release BrO_x radicals which are capable of destroying tropospheric ozone. The BrO-concentrations measured in springtime at the Canadian Arctic at Alert using Long Path Differential Absorption Spectroscopy (Hausmann and Platt, 1994) vary between 4 to 17 ppt. Additionally, it has become clearer that heterogeneous processes on sea-salt aerosols and ice surfaces at low temperatures are of major importance in which halogens are chemically converted and released to the troposphere (Abbatt, 1994; Hanson and Ravishankara, 1992; McConnell et al., 1992; Fan and Jacob, 1992).

The atmospheric chemistry of the reactions of bromine atoms with VOCs (volatile organic compounds) have been not as extensively investigated as the corresponding reactions with OH radicals and Cl atoms. Recently, within the framework of the ARCTOC project, we considerably extended the kinetic data base for the reaction of Br atoms with VOCs (Bierbach et al., 1996) which had previously only consisted of measurements for acetylene and a very limited number of alkanes, alkenes and aldehydes (Barnes et al., 1989; Seakins et al., 1992; Wallington et al., 1989; Yarwood et al., 1992; Niki et al., 1985, and references therein). The reactions of Br atoms with alkanes and simple aldehydes are straightforward H-atom abstraction reactions whereas reactions with acetylene and alkenes are addition reactions the rates of which depend strongly on the oxygen partial pressure (Barnes et al., 1989). Mechanistic investigations on the reactions of Br atoms with unsaturated hydrocarbons are presently only available for acetylene and ethylene at room temperature (Barnes et al., 1989; Yarwood et al., 1992). In a continuation of our investigations of Br-atom reactions with VOCs within the ARCTOC project we present here a product and mechanistic investigation the Br-atom initiated degradation of *trans*-2-butene in the temperature range 246–298 K with and without NO_x *trans*-2-butene was chosen as a model alkene in order to assess potential impacts/influences of Br/alkene interactions on any bromine chemistry which might be occurring during the ozone depletion events in the Arctic. The NO_x concentration was varied over a considerable range in order to establish differences that may occur in the product distribution pattern for different atmospheric conditions, e.g., at mid latitudes where high temperatures and high NO_x levels or under Arctic conditions where low temperature and low NO_x levels dominate.

2. Experimental

The experiments have been carried out in a 0.42 m^3 Duran glass chamber which is surrounded by 24 super actinic fluorescent lamps (Philips TL05/40W, 320 nm $< \lambda <$ 480 nm, $\lambda_{max} = 360$ nm). It has an integrated White mirror system with an optical path length of 50.4 m for in situ monitoring of reactants and products by FT-IR spectroscopy. The reactor temperature is variable between 240 and 320 K and was stable to within ± 1 K. The experiments were performed in the range from 246 to 298 K using the following procedure. The reactants *trans*-2-butene (≈ 25 ppmV) and molecular bromine vapour (≈ 50 ppmV) were added to the evacuated chamber which was then filled with synthetic air up to a total pressure of 1000 ± 2 mbar. The reaction mixture was stirred for 15 min in the dark until the temperature remained constant. An infrared spectrum was then recorded to determine the exact starting concentration of *trans*-2-butene. Control experiments were performed at all of the temperatures investigated in order to check for a possible dark reaction

between molecular bromine and *trans*-2-butene. Within the experimental error limits the *trans*-2-butene concentrations recorded directly after filling up the reactor where always the same over the entire temperature range as those recorded prior to ignition of the lamps 15–30 min later. The reaction mixtures were irradiated for a time period of 30–45 min during which time infrared spectra were recorded at 1 cm^{-1} resolution by co-adding 128 interferograms over a period of 120 s. Typically time-resolved data were obtained in the range 650–4000 cm^{-1} by recording 13–15 spectra successively. Irradiation of the reaction mixtures initiated the oxidation of *trans*-2-butene via bromine atoms formed through the photolysis of bromine vapour:

$$Br_2 + h\nu \rightarrow 2Br.$$

In a number of experiments, NO was also added to the reaction system. The initial concentration of NO was typically 5 ppm with trace impurities of approximately 0.2 ppm NO_2. Of the compounds used in the study *cis/trans*-2,3-epoxybutane, acetaldeyde and acetylbromide were obtained from Aldrich Company and had stated purities of 97, 96, 99 and 99%, respectively. 3-bromobutan-2-one which had a purity of 97% was obtained from Lancaster Company. *Trans*-2-butene and hydrogen bromide were obtained from Messer Griesheim GmbH with a purity of $\geqslant$99% and $\geqslant$99.8%, respectively. 3-bromobutan-2-ol, which is not commercially available, was synthesised using a method described by Iqbal and Owen, 1960 with a purity of >98%. All compounds were used for the generation of calibrated gas-phase reference spectra without any further purification.

3. Results and discussion

3.1. *Identification of products*

In the absence of NO_x. Table 1 lists the products obtained and their formation yields for the different temperatures under which the reaction was investigated. The yields of all the products are associated with a total estimated error of $\pm$10%. The main source of error in the yields is caused by spectral overlapping of absorption bands of similar compounds which makes subtraction of calibrated reference spectra somewhat difficult. Other error sources such as gas phase calibration, optical path length, temperature, pressure etc. were found to be very small in comparison with the error introduced by computer-aided spectra subtraction. In the absence of NO_x the major reaction products are 3-bromobutan-2-one, acetaldehyde, acetylbromide and hydrogen bromide. Formaldehyde was a minor product. Traces of CO and CO_2 and HCOOH were detected but their aggregate yields were $\leqslant$1–2% C. Typical examples of concentration-time profiles of the products and concentration versus *trans*-2-butene consumption plots of the products under NO_x-free conditions are given in Figs. 1 and 2 for 297 K, respectively. In Fig. 2 it can be seen that the yields of 3-bromobutan-2-one, acetaldehyde and acetylbromide are all a linear function of the consumption of *trans*-2-butene indicating that they are direct oxidation products and are not subject to further oxidation. In the case of HCHO, the plot in Fig. 2 is curved and only shows partial linearity at longer reaction times indicating that it is being formed in secondary reactions.

The yields of the individual products are plotted as a function of temperature in Fig. 3. Decreasing the temperature causes the yield of 3-bromobutan-2-one to slightly increase whereas the yields of acetaldehyde, acetylbromide and HBr gradually decrease and are virtually zero at 246 K. The yield of 3-bromobutan-2-one increases from approximately 40% at room temperature up to 50% at 246 K (see Table 1). As can be seen in Table 1 the yields of acetaldehyde and acetylbromide decrease with decreasing temperature from 18% C and 3% C at 298 K down to $\approx$0.9 and $\approx$0.1 at 246 K, respectively. Interestingly, within the experimental error limits, the acetaldehyde/acetylbromide yield ratio remains constant at 6.33$\pm$0.41 over the whole temperature range. The possible reason for this behaviour is discussed below. Over the entire temperature range studied the total carbon balance (exculding the estimated contribution from 3-bromo-2-butylhydroperoxide, see below) varied randomly within the range 56$\pm$8% indicating that (a) major product(s) are still not accounted for.

Fig. 4, trace (a), shows the products formed in the reaction of Br atoms with *trans*-2-butene at 297 K in a NO_x-free system after 30 min irradiation. Absorptions belonging to the major products 3-bromobutan-2-one, acetaldehyde and acetylbromide are indicated, hydrogen bromide

Table 1. *Formation yields of the products observed in the Br-initiated oxidation of trans-2-butene in 1000 mbar synthetic air at 297 K; the errors are estimated total errors and are essentially due to subtraction uncertainties using the FTIR-facility*

T [K]	3-bromo-2-butanone Yield [%C]	3-bromobutyl-2-hydroperoxide Yield [%C]***	Acetaldehyde Yield [%C]	Acetylbromide Yield [%C]	Formaldehyde Yield [%C]	PAN Yield [%C]	HBr Yield [%]**	Total Yield [%C]
298±1	36.8±3.7	31.0±3.1	18.0±1.8	3.1±0.3	≈0.3	–	13.7±1.4	88.9±8.9
298±1*	63.8±6.4	7.1±0.7	40.0±4.0	2.8±0.3	≈0.7	2.1±0.2	8.8±0.9	113.7±11.4
297±1	37.8±3.8	30.0±3.0	19.3±1.9	2.8±0.3	≈0.3	–	12.1±1.2	89.9±9.0
292±1	44.2±4.4	33.0±3.3	17.0±1.7	2.6±0.3	≈0.3	–	10.3±1.0	96.8±9.7
286±1	37.6±3.8	35.1±3.5	13.1±1.3	2.1±0.2	≈0.3	–	7.8±0.8	87.9±8.8
278±1	49.6±5.0	35.8±3.6	8.7±0.9	1.4±0.1	≈0.1	–	3.2±0.3	95.5±9.6
274±1	47.4±4.7	35.4±3.5	8.1±0.8	1.3±0.1	≈0.1	–	1.7±0.2	92.2±9.2
269±1	50.6±5.1	34.8±3.5	5.7±0.6	0.8±0.1	<0.1	–	0.5±0.1	91.9±9.2
263±1	45.8±4.6	33.8±3.4	2.9±0.3	0.5±0.1	–	–	≈0.4	82.9±8.3
258±1	54.0±5.4	32.1±3.2	2.5±0.3	≈0.4	–	–	≈0.2	89.0±8.9
252±1	46.6±4.7	29.7±3.0	1.2±0.1	≈0.2	–	–	–	77.7±7.8
246±1	50.6±5.1	28.7±2.9	0.9±0.1	≈0.1	–	–	–	80.3±8.0

* Addition of ≈5 ppmV NO; ** 100×(ppm HBr/ppm trans-2-butene-consumption); *** Estimated value using an FTIR — extinction coefficient of 1.39×10^{-4} ppm V^{-1} m^{-1} (base 10) at 3600 cm^{-1} from the structurally related 3-bromobutan-2-ol; the quoted errors are those due to spectral subtraction uncertainties.

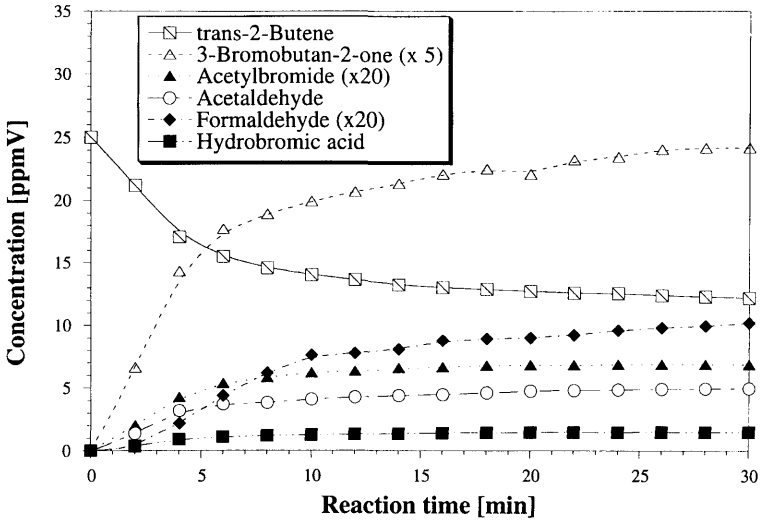

Fig. 1. Concentration–time profiles of the products observed in the Br-atom initiated oxidation of *trans*-2-butene at 297 K in 1000 mbar of synthetic air.

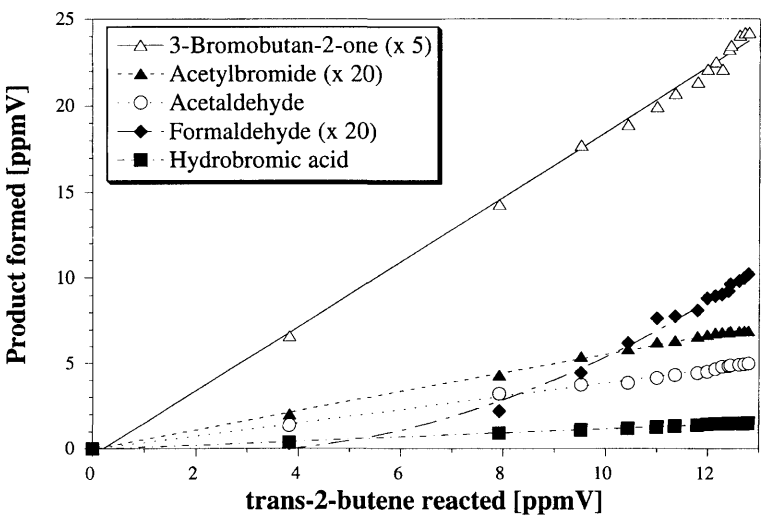

Fig. 2. Plot of the product concentrations observed in the Br + *trans*-2-butene reaction at 297 K in 1000 mbar of synthetic air as a function of the consumption of *trans*-2-butene.

has already been subtracted in order to show more clearly the aldehydic C—H stretching vibrations in the 3000–2600 cm^{-1} region. Fig. 4, trace (b), is the same spectrum after further subtraction of 3-bromobutan-2-one, acetaldehyde and acetylbromide. The residual infrared spectrum shows strong absorptions at $\approx$3597 cm^{-1} and in the CH-stretching vibration region 3000–2600 cm^{-1} along with numerous bands in the fingerprint region. The strong band at 3597 cm^{-1} is indicative of the presence of the —OH group. Formic and acetic acids and methyl hydroperoxide are possible products which could give rise to an —OH absorption, however, tests for these compounds were negative. 3-bromo-2-butylhydroperoxide (CH_3—$CH_2(OOH)$—CH_2Br—CH_3) and 3-bromo-

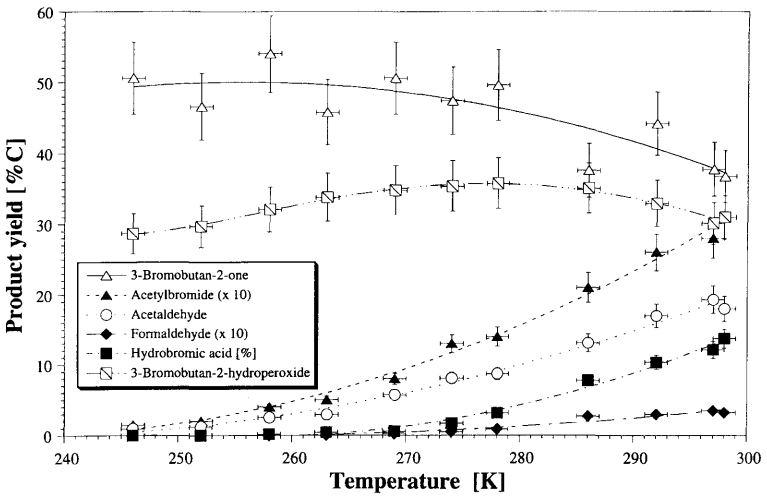

Fig. 3. Formation yields of the products measured in the Br-atom initiated oxidation of *trans*-2-butene in 1000 mbar of synthetic air as a function of temperature.

2-butanol ($CH_3-CH_2(OH)-CH_2Br-CH_3$) are also possible oxidation products which are expected to have strong $-OH$ absorptions. As will be discussed later in the text, the spectrum in trace (b) is believed to be mainly due to 3-bromo-2-butylhydroperoxide ($CH_3-CH_2(OOH)-CH_2Br-CH_3$) rather than 3-bromo-2-butanol ($CH_3-CH_2(OH)-CH_2Br-CH_3$). A search was made for *cis*- and *trans*-2,3-epoxybutane which could be formed by elimination of BrO from 3-bromo-2-butylperoxyl radicals or addition of BrO radicals to the double bond under elimination of Br. No evidence was found for formation of *cis*- or *trans*-2,3-epoxybutane.

In the presence of NO_x. Experiments in the presence of NO were only performed at 297 K. In the presence of NO the yields of 3-bromobutan-2-one and acetaldehyde are both approximately a factor of 2 higher than in the corresponding NO_x-free case. The yields given in Table 1 are those calculated after 4 min irradiation when NO was still present in considerable excess over NO_2. In these experiments the NO was rapidly oxidised by the different peroxyl radicals produced in the system within the first few minutes of the photolysis forming NO_2 which was consequently also quickly removed from the reaction system via the formation of stable peroxy nitrates. After approximately 8–10 min irradiation time the system was virtually NO_x-free and the subsequent chemistry was essentially the same as that of the NO_x-free experiments.

Obviously in the NO_x-containing system OH radicals can also be formed from reactions of NO with HO_2 radicals formed during the oxidation process:

$$HO_2 + NO \rightarrow OH + NO_2 .$$

No indication was found for OH radical formation in the NO_x-free system, its formation would have lead to the formation of 3-hydroxybutan-2-one which was searched for but not found. The contribution from OH radicals in the NO_x-containing system is probably $\leqslant 10\%$. There are a number of factors which support this. The Br-atom concentration in the system is known to be of the order 10^9 molecules cm^{-3} under the present experimental conditions and similarly the OH-radical concentration is typically 2×10^7 molecules cm^{-3} when NO_x/alkene systems are irradiated. Since the rate coefficients for the reaction of OH and Br with *trans*-2-butene are 6.4×10^{-11} and 9.3×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 297 K, loss rates of *trans*-2-butene of 1.3×10^{-3} and 9.3×10^{-3} s^{-1} are expected for reaction with OH and Br, respectively, i.e., a contribution of around 8% from OH radicals is calculated for the initial phase of the photolysis. Further, as indicated above the acetaldehyde/acetylbromide ratio for the NO_x-free systems has been observed to remain

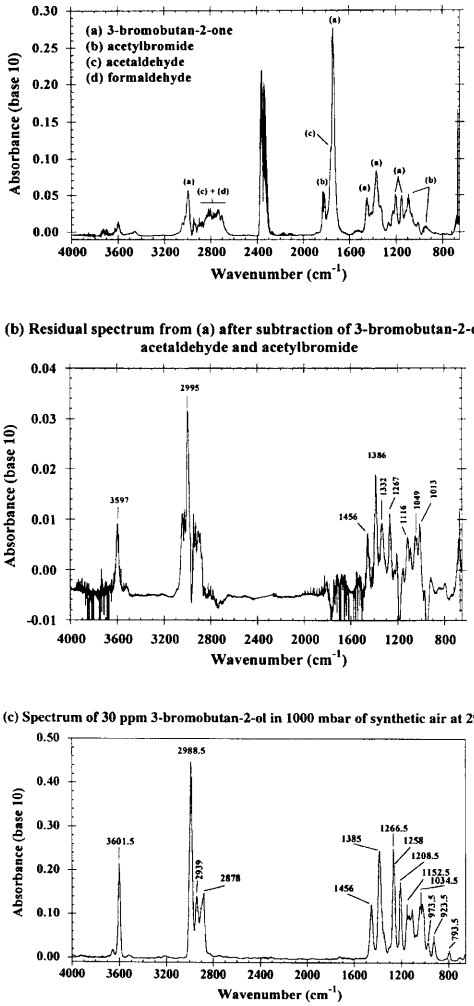

Fig. 4. Infrared spectra in the range 650–4000 cm^{-1} for *trans*-2-butene/bromine/air photolysis systems at 298 K. Trace (a) is the product spectrum recorded after 20 min irradiation of NO_x-free system and trace (b) is the residual spectrum from (a) after subtraction of 3-bromobutan-2-one and acetylbromide. Trace (c) is an infrared spectrum of 30 ppm 3-bromobutan-2-ol recorded in 1000 mbar of synthetic air at 298 K.

constant at 6.33. In the presence of NO_x the yield of acetylbromide is virtually identical with that in the NO_x-free case whereas the yield of acetaldehyde is almost a factor of 2 higher. Making the assumption that the additional acetaldehyde results from reaction of *trans*-2-butene with OH radicals, i.e., approximately 20% C, and that each reaction results in 2 molecules of acetaldehyde, would give a contribution from OH radicals to the *trans*-2-butene decay of approximately 10%. This is an upper limit since the reaction of OH radicals with *trans*-2-butene is known to result in the formation of β-hydroxyalkoxyl radicals which primarily decompose to give an aldehyde and shorter-chain α-hydroxyalkyl radicals (CH_3CHOH) which further react with O_2 also to give an aldehyde (Atkinson, 1994, 1995). In the case of *trans*-2-butene, because of its symmetry, both aldehydes will be acetaldehyde.

In the room temperature experiment with NO_x peroxyacetylnitrate PAN has been observed to be an additional product with an observed yield of 2% C. It is obviously formed via an H-atom abstraction from acetaldehyde followed by subsequent consecutive addition of O_2 and NO_2. The reaction of Br atoms with CH_3CHO is an H-atom abstraction reaction and is relatively fast ($k = 3.7 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K; Niki et al., 1985) and could account for the formation of PAN.

$$CH_3CHO + Br \rightarrow CH_3CO + HBr$$

$$CH_3CO + O_2 \rightarrow CH_3CO(O_2)$$

$$CH_3CO(O_2) + NO_2 + M \rightarrow CH_3CO(O_2)NO_2 + M$$

However, as mentioned earlier in the presence of NO_x OH radicals will be formed in the system and could also oxidise CH_3CHO and contribute to the formation of PAN.

Fig. 5 is the residual product spectrum obtained from the Br-atom initiated oxidation of *trans*-2-butene in the presence of 5 ppm NO at 297 K after 30 min irradiation and subtraction of the products 3-bromobutan-2-one, acetylaldehyde, acetylbromide, HBr and peroxyacetyl nitrate (PAN). The residual spectrum shows the formation of the absorptions which in the NO_x-free system have been tentatively assigned to 3-bromo-2-butylhydroperoxide. In the NO_x-containing system these bands appear after the NO_x has been exhausted in the system. Apart from absorptions at 1660 and 791 cm^{-1} which can be assigned to $BrNO_2$ (Barnes et al., 1991) a number of sharp absorptions are visible at $\approx$2995, 1843, 1662, 1306 and 849 cm^{-1}. Absorptions from BrNO, $BrONO_2$ and HOBr were searched for but could not be

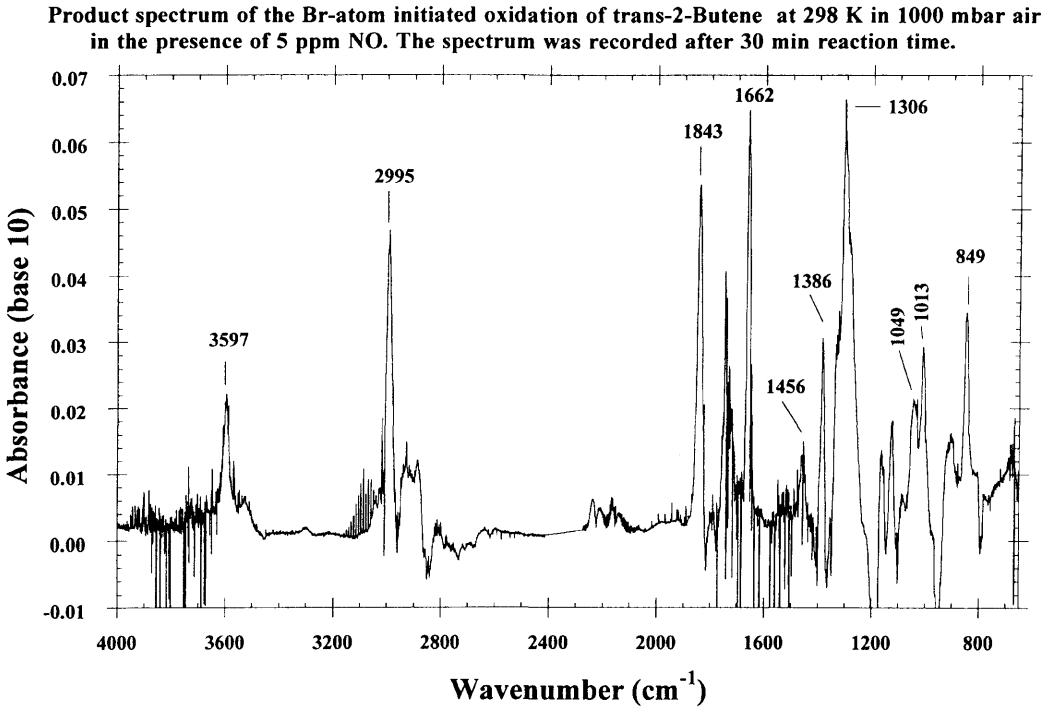

Fig. 5. Residual infrared product spectrum obtained from a *trans*-2-butene/Br_2/air photolysis system containing initially 5 ppm NO and 0.2 pmm NO_2.

detected. Absorptions at 1662, 1306 and 849 cm^{-1} typical for alkyl nitrates (Roberts, 1990) and it is probable that these bands can be assigned to 2-nitrooxy-3-bromobutane formed via the nitrate forming channel in the reactions of the bromobutylperoxyl radicals with NO:

$$CH_3-CH(Br)-CH(O_2)-CH_3+NO$$
$$\rightarrow CH_3-CH(Br)-CH(O)-CH_3+NO_2$$
$$\rightarrow CH_3-CH(Br)-CH(ONO_2)-CH_3\,.$$

The yield of the nitrate can not be determined at present due to the lack of authentic samples. However, reactions of NO with secondary peroxyl radicals such as are produced in the Br/*trans*-2-butene reaction are known to produce nitrates with yields between 4 and 14% (Atkinson, 1994). The absorption at 1843 cm^{-1} is in the carbonyl stretching region, at present the identity of the carbonyl compound giving rise to this absorption is not known.

Formation of inorganic bromine containing compounds. Hydrogen bromide is formed in substantial yields in the Br-initiated oxidation of *trans*-2-butene at the higher temperatures. The yield of HBr decreases from nearly 14% at room temperature down to less than 1% at 268 K. At temperatures lower than 258 K formation of HBr was not observable in the product infrared spectra. It is difficult to tell from the concentration-time profiles of HBr whether it is formed directly or in secondary reactions. The most obvious source would be H-atom abstraction reactions from acetaldehyde. The parallel decrease of the yields of HBr and that of CH_3CHO with decreasing temperature would be in accord with this process being a major source of HBr. However, the abstraction reaction would produce corresponding quantities of CO and CO_2 from further reactions of the CH_3CO radicals. The yields of both CO and CO_2 are very low in the system which rules out $Br+CH_3CHO$ as a major source of HBr in the system. The observation of HCHO and the shape of its concentration-time profile show that some secondary oxidation of CH_3CHO is occurring in the system.

Other possible sources of HBr are reaction of Br with HO_2 radicals (Laverdet et al., 1990), however, since the reaction mechanism produces copious levels of HO_2 radicals even at low temperatures, a decrease with temperature would not be expected unless rapid loss of HBr to the walls is occurring with decreasing temperature. At presence the behaviour of HBr formation/loss in the reaction system is highly uncertain.

3.2. *Mechanistic interpretation of the results*

Initial reaction steps. Tentative reaction pathways for the formation of the products observed in the Br-atom initiated oxidation of *trans*-2-butene with and without NO_x, are given in figures 6 and 7 respectively. The reaction of Br atoms with *trans*-2-butene can proceed either via addition to the carbon double bond or hydrogen abstraction from one of the methyl groups. The room temperature rate coefficient for the reaction of Br atoms with n-butane at 298 K, where H-atom abstraction is the only possible pathway, is $(7.0 \pm 2.2) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} (derived from the Arrhenius parameters given by Seakins et al., 1992) and is 5 orders of magnitudes lower than the rate coefficient for reaction with *trans*-2-butene at 300 K of $(9.3 \pm 1.9)\ 10^{-12}$ cm^3 molecule^{-1} s^{-1} as measured by Bierbach et al., 1996. From these kinetic data it is obvious that over the temperature range of the present study the abstraction pathway will be negligible. Croton aldehyde, $CH_3-CH=CH-CHO$, the expected major product of the abstraction pathway was searched for but no indication has been found for its formation which supports the assertion.

The measurements clearly show that 3-bromobutan-2-one is the main degradation product and that the presence of NO increases its formation yield. As discussed above, addition of Br atoms to *trans*-2-butene is essentially the only reaction pathway under the present experimental conditions.

Fate of 3-bromobutyl-2-peroxyl radicals. The sole fate of the bromoalkyl radicals formed in the addition of Br atoms to *trans*-2-butene is expected to be reaction with O_2 to form β-bromoalkylperoxyl radicals (3-bromobutyl-2-peroxy), reactions (1) and (2), respectively:

$$H_3C-CH=CH-CH_3 + Br \rightarrow H_3C-CH-CH(Br)-CH_3, \quad (1)$$

$$H_3C-CH-CH(Br)-CH_3 + O_2 \rightarrow H_3C-CHO_2-CH(Br)-CH_3. \quad (2)$$

In the absence of NO the peroxyl radicals can either undergo self reaction or reaction with other peroxyl radicals in the system, most likely HO_2 (Lightfoot et al., 1992; Wallington et al., 1992; LACTOZ Report, 1995). There are two main channels for the self reaction (3a and 3b):

$$2H_3C-CHO_2-CBr(H)-CH_3 \rightarrow H_3C-CH(OH)-CH(Br)-CH_3 + H_3C-CO-CH(Br)-CH_3 + O_2 \quad (3a)$$

$$\rightarrow 2\ H_3C-CHO-CH(Br)-CH_3 + O_2. \quad (3b)$$

From studies on the reaction of HO_2 with other alkylperoxyl radicals the reaction of the β-bromoalkylperoxyl radicals with HO_2 is expected to result primarily in the formation of 3-bromobutyl-2 hydroperoxide, reaction (3c):

$$H_3C-CHO_2-CH(Br)-CH_3 + HO_2 \rightarrow H_3C-CH(OOH)-CH(Br)-CH_3 + O_2 \quad (3c)$$

The other possible channel, reaction (3d),

$$H_3C-CHO_2-CH(Br)-CH_3 + HO_2 \rightarrow H_3C-CO-CH(Br)-CH_3 + H_2O + O_2, \quad (3d)$$

would result in formation of 3-bromobutan-2-one.

In reaction (3a) 3-bromobutan-2-one can be formed directly along with 3-bromobutan-2-ol. In the alternative reaction channel (3b) β-bromobutoxyl radicals are formed which can react further with O_2 to form 3-bromobutan-2-one and HO_2 radicals (4a) or thermally decompose to form acetaldehyde and acetylbromide (4b):

$$H_3C-CHO-CH(Br)-CH_3 + O_2 \rightarrow H_3C-CO-CH(Br)-CH_3 + HO_2, \quad (4a)$$

$$H_3C-CHO-CH(Br)-CH_3 + \Delta + O_2 \rightarrow H_3C-CHO + CH_3CBrO. \quad (4b)$$

From the above mechanistic considerations, under NO_x-free conditions, 3-bromobutan-2-one, 3-bromobutan2-ol, acetylaldehyde, acetylbromide and possibly 3-bromobutyl-2-hydroperoxide are expected products. With the exception of 3-bromo-

butan2-ol and 3-bromobutyl-2-hydroperoxide these products have been positively identified in the Br/*trans*-2-butene oxidation system. 3-bromobutan-2-ol has been synthesised and its infrared reference spectrum is shown in Fig. 4, trace (c). The spectrum has many similarities with the residual product spectrum from the reaction system shown in Fig. 4, trace (b), however, several of the peaks are slightly offset, e.g. the peak of the —OH group situated at 3597 cm^{-1} is offset from that of the —OH group in the residual spectrum in Fig. 1, trace (b) by 4 cm^{-1}. This mismatch is presently being taken as evidence that the compound giving rise to the —OH absorption is probably not 3-bromobutan-2-ol or a mixture of 3-bromobutan-2-ol/3-bromobutyl-2-hydroperoxide but rather is due nearly entirely to 3-bromobutyl-2-hydroperoxide since, to the best of our knowledge, all other possible candidates containing the —OH entity which come into question have been eliminated.

The yields of 3-bromobutyl-2-hydroperoxide given in Table 1 have been estimated using an infrared extinction coefficient of 1.39×10^{-4} ppm V^{-1} m^{-1} (base 10) for the absorption at 3600 cm^{-1}. This is the extinction coefficient from the gas-phase calibration of the structurally related 3-bromobutan-2-ol measured in this laboratory and is also similar in value to the absorption coefficients reported for simple alkyl hydroperoxides. Using this coefficient formation yields of about 30 [%C] (Table 1 and Fig. 1) are obtained for hydroperoxide formation.

The reason for the "non-formation" of the alcohol in the oxidation system is presently not clear. There are a number of reasons which may explain our failure to detect the compound in the reaction system. The branching ratios for the radical and carbonyl/alcohol channels in the self-reaction of organic peroxyl radicals has not been established for a wide range of peroxyl radicals (Lightfoot et al., 1992; Wallington et al., 1992; LACTOZ Report, 1995); however, in reaction studies with a C—H bond in an α-position relative to the radical centre, the carbonyl/alcohol channel is usually quite substantial. In the study of Yarwood et al. (1992) on the reactions of Cl and Br atoms with ethene, for example, the fractional branching ratios for the carbonyl/alcohol channel in the self reaction of β-chloro- and β-bromoethylperoxyl radicals have been estimated to be 0.43 in both cases which is not substantially different from that reported for the analogous ethylperoxyl radical. The study of Yarwood et al. suggests that the presence of an halogen substituent adjacent to the peroxyl radical does not adversely affect the peroxyl radical branching ratio, therefore, it is reasonable to assume that the carbonyl/alcohol channel will also be operative and significant in the present case. Since in the present experiments we appear to be generating high levels of HO_2 radicals which result in high yields of β-bromobutyl hydroperoxide it may be that the yield of 3-bromobutan-2-ol is below the detection limit of the experiments. Ongoing work in this laboratory has shown that Br-radical reaction or photolysis would only have a very minor influence on the yield of 3-bromobutan-2-ol if formed. If this is the case, then based on the detection limit for 3-bromobutan-2-ol of $\sim$500 ppbV, a limit can be put on the branching ratio for the radical producing channel of $\approx$2.8% C.

There is an alternative and more probable explanation which may account for the observations. The reactions of Br atoms with peroxyl radicals are reasonably fast. For example, the reaction of Br atoms with HO_2 has a rate coefficient of 2.0×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 298 K and is thought to result exclusively in the formation of HBr and O_2 (Laverdet et al., 1990). An upper limit of $k < 8.3 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} has been measured for the reaction of Br atoms with CH_3O_2 (Kondo and Benson, 1984) and fast reactions have been inferred between bromomethylperoxyl (Orlando et al., 1996) and 2-bromoethylperoxyl and 2-bromo-1-methylpropylperoxyl radicals (Crowley and Moortgat, 1992) to explain experimental observations. Similarly, the reaction of Cl atoms with CH_3OO and C_2H_5OO radicals are known to be fast ($\sim 7 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}; DeMore et al., 1994; Maricq et al., 1994). Two channels have been reported for the Cl reactions with a branching ratio of approximately $\alpha = 0.5$, e.g., for the ethylperoxyl radical:

$$C_2H_5OO + Cl \rightarrow C_2H_5O + ClO,$$

$$C_2H_5OO + Cl \rightarrow C_2H_4OO + HCl.$$

The second channel results in the formation of a Criegee biradical the further reactions of which are currently not well established. If such reaction

pathways are also occurring in the Br-atom initiated oxidation of *trans*-2-butene they could result in significant deviations from the product distributions generally expected in such systems and would probably result in a considerably reduced yield in the 3-bromobutan-2-ol yield because of the competing reaction sequence (the rate coefficients are typical values for halogen-substituted peroxyl radicals, Villenave and Lesclaux, 1995):

$RO_2 + RO_2 \rightarrow$ products (RO, ROH, R'CO)

($k \approx 4. \times 10^{-12}$ cm^3 molecule^{-1} s^{-1})

$RO_2 + HO_2 \rightarrow ROOH + O_2$

($k \approx 6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1})

$RO_2 + Br \rightarrow BrO + RO$

($k \approx 2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1})

$RO + O_2 \rightarrow R'CO + HO_2$

($k \approx 6. \times 10^{-14}$ cm^3 molecule^{-1} s^{-1})

$HO_2 + Br \rightarrow HBr + O_2$

($k \approx 2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1})

In the present experiments, the Br-atom levels were typically 10^9 molecules cm^{-3}. Simulations of the reaction system using the this Br-atom level and the above reaction sequence show that the fate of the 3-bromo-2-butylperoxyl radicals in NO_x free systems is critically dependent on the levels of HO_2, RO_2 and Br atoms in the system.

Fate of 3-bromo-2-butoxy radicals. As discussed above the β-bromobutoxy radicals can react with molecular oxygen or thermally decompose. The product analysis (Table 1) shows quite emphatically that reaction with O_2 forming 3-bromobutan-2-one is the dominant channel. The thermal decomposition channel leads to the formation of acetaldehyde and acetylbromide the yields of which decrease, in a constant ratio (6.33), with decreasing temperature from 18% C and 3% C at 298 K down to $\approx$0.9 and $\approx$0.1 at 246 K, respectively. Assuming that 3-bromobutan2-one, 3-bromobutyl-2-hydroperoxide, acetaldehyde and acetylbromide account, within the experimental error limits, for all the products the results in Table 1 support that the branching ratio of the 3-bromobutan-2-one forming channel in the reaction of the β-bromobutoxyl radicals accounts for approximately 60% of the reaction at 298 K and increases gradually to near unity at 246 K.

Acetaldehyde is formed directly in the thermal decomposition channel. Formation of acetylbromide can only result from further reactions of the bromoethyl radical, $CH_3CH(Br)$, radical the major initial fate of which will be addition of O_2 to form 1-bromoethylperoxyl radicals, reaction (5a):

$CH_3-CH(Br) + O_2 \rightarrow CH_3CHBr(O_2)$

As discussed above for 3-bromobutyl-2-peroxyl radicals a number of reaction channels are possible for the 1-bromoethylperoxyl radicals ((5b) to (5h)) and also the $CH_3CHBr(O)$ radical product from these reactions ((6a) to (6d)):

Possible peroxyl radical reactions

$2CH_3CHBr(O_2) \rightarrow CH_3CHBr(O) + CH_3CHBr(O) + O_2$ (5b)

$\rightarrow CH_3CHO + CH_3CHBrOH + O_2$ (5c)

$CH_3CHBr(O_2) + HO_2 \rightarrow CH_3CHBr(O_2H) + O_2$ (5d)

$\rightarrow CH_3CBrO + H_2O + O_2$ (5e)

$\rightarrow CH_3CHO + HOBr + O_2$ (5f)

$CH_3CHBr(O_2) + Br \rightarrow CH_3CHBr(O) + BrO$ (5g)

$CH_3CHBr(O_2) + M \rightarrow CH_3CHO + BrO + M$ (5h)

Possible reactions of the $CH_3CHBr(O)$ radical

Reaction with O_2

$CH_3-CHBr(O) + O_2 \rightarrow CH_3CBrO + HO_2 + M$ (6a)

Br atom/CH_3 group/HBr elimination

$CH_3-CHBr(O) + M \rightarrow CH_3CHO + Br + M$ (6b)

$CH_3-CHBr(O) + M \rightarrow CH_3CO + HBr + M$ (6c)

$CH_3-CHBr(O) + O_2 + M \rightarrow HCBrO + CH_3OO + M$ (6d)

Because of the high level of Br atoms in the reaction system it is thought that the dominant fate of the 1-bromoethylperoxyl radical will be

reaction with Br atoms to form 1-bromoethoxy radicals, $CH_3CHBr(O)$, although a contribution from the formation of 1-bromoethyl-1-hyroperoxide can not be excluded. 1-bromoethanol which can be formed in the self reaction of 1-bromoethyl-1-peroxyl radicals is not expected to be stable and, if formed, will probably decompose to acetaldehyde and HBr.

The further reactions of the 1-bromoethoxy radical include reaction with O_2, HBr elimination, Br-atom elimination and possibly CH_3-group elimination. Reaction with O_2 will produce acetylbromide which is observed in the system. The elimination of HCl has recently been observed to be the dominant atmospheric fate of 1-chloroethoxy radicals, $CH_3-CHCl(O)$ (Kaiser and Wallington, 1995; Shi et al., 1993; Wallington et al., 1995). However, HBr elimination would give CH_3CO radicals the further reactions of which would eventually yield products such as CO, CO_2, HCHO and CH_3OH. Since the yields of these compounds are very minor this channel is probably of negligible importance for $CH_3CHBr(O)$ radicals. On similar grounds the elimination of CH_3 radicals is also unlikely, also the other expected product of this reaction, formylbromide was not observed. Bromine-atom elimination has recently been shown to be the dominant fate of bromomethoxy radicals under atmospheric conditions (Chen et al., 1995, 1996; Orlando et al., 1995, 1996) accounting for over 80% of the reaction, the other channel being reaction with molecular oxygen.

As shown in Fig. 8 the acetaldehyde/acetylbromide product yield ratio remains constant at 6.33 over the whole temperature range investigated. At present the only plausible explanation which we can think of for this behaviour is that Br-atom elimination must be an important pathway for the 1-bromoethoxy radical. However, in order that the branching remains relatively constant over the temperature range investigated requires that the reactions of the $CH_3CHBr(O)$ radical, i.e., reaction with O_2 and Br-elimination,

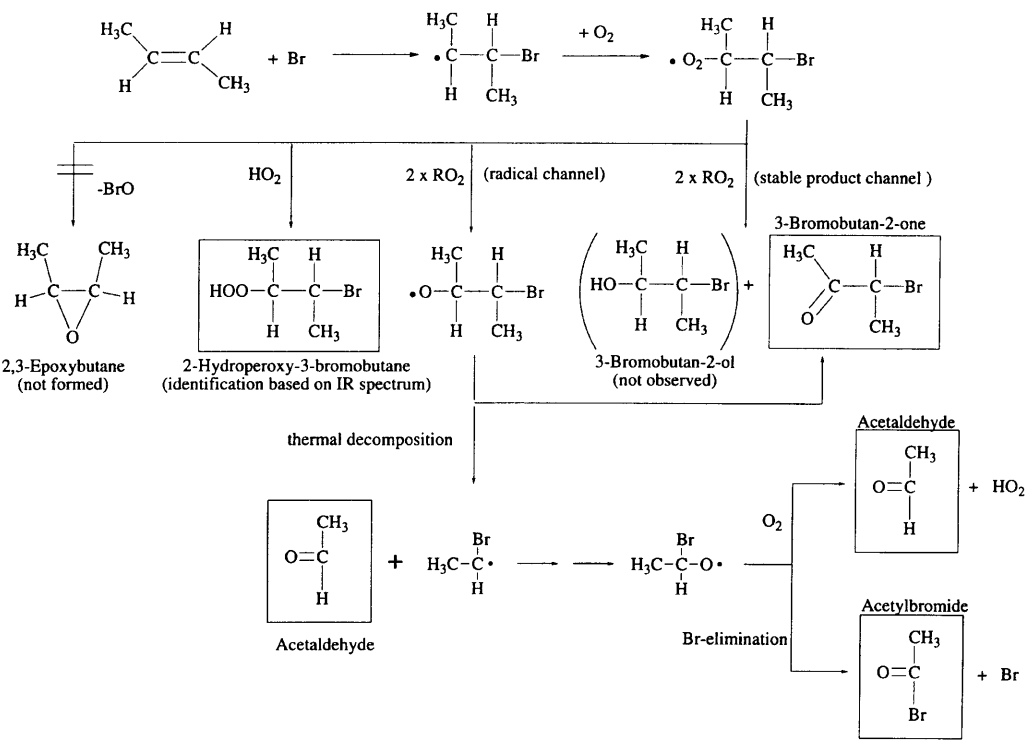

Fig. 6. Tentative mechanism for the Br-atom initiated oxidation of *trans*-2-butene in synthetic air in the *absence* of NO_x.

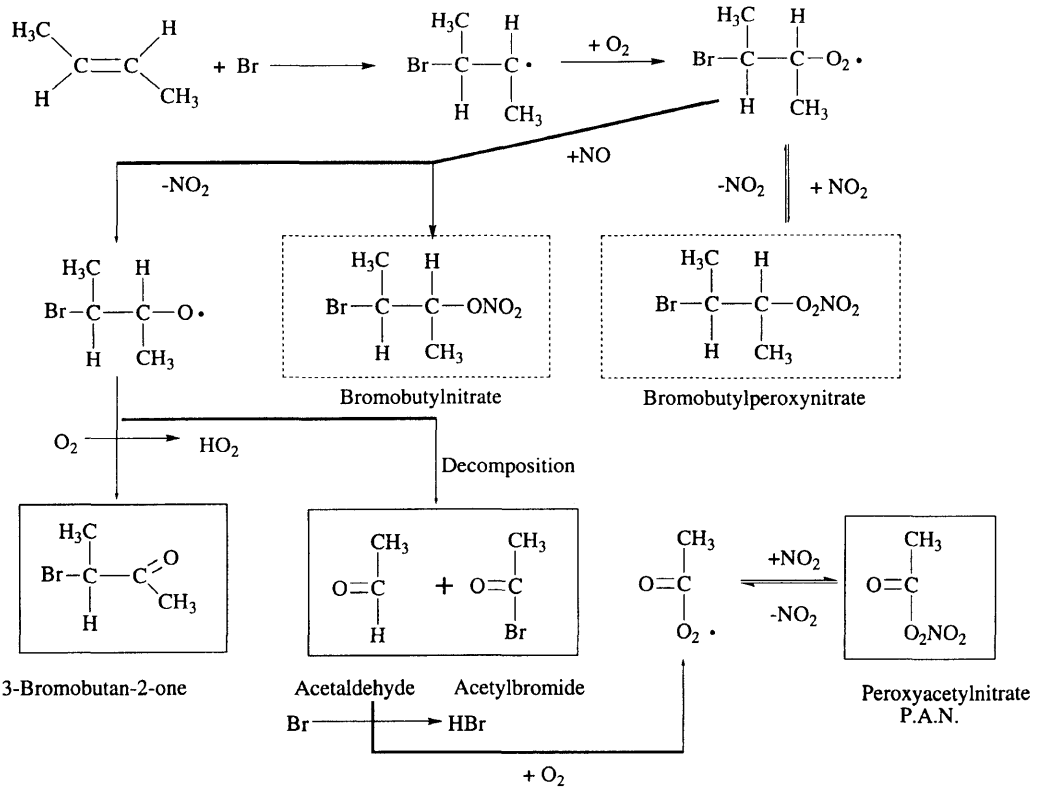

Fig. 7. Tentative mechanism for the Br-atom initiated oxidation of *trans*-2-butene in synthetic air in the *presence* of NO_x.

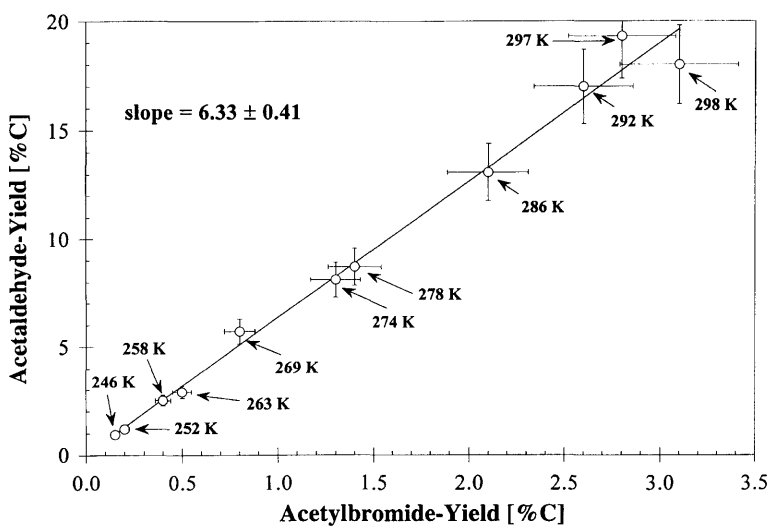

Fig. 8. Plot of the yields of acetaldehyde aganist the yields of acetylbromide obtained in the Br-atom initiated oxidation of *trans*-2-butene in 1000 mbar of synthetic air at various temperatures.

have very similar temperature dependencies or that the changes with temperature are small and do not adversely affect the branching ratio. From the kinetic data available for the reactions of alkoxy radicals with O_2 (Atkinson et al., 1992) it is to be expected that in the case of the secondary 3-bromo-2-butoxy radical that the temperature dependence of the O_2 reaction will be relatively small (0.5–2 kcal/mol) over the temperature range investigated. However, from thermodynamical considerations performed by Orlando et al. (1996) activation energies of the order of 9–12 kcal/mol can be expected for the thermal decomposition of brominated alkoxy radicals which would result in a significant change in the rate over the temperature range of the present study. Obviously more work is still required to elucidate the mechanism resulting in the disproportion between the acetaldehyde and acetylbromide product yields in the Br/*trans*-2-butene reaction observed in the present study.

If we assume that losses of acetaldehyde and acetylbromide in the reaction system are negligible and that reaction with O_2 and Br-atom elimination are the only significant channels for the 1-bromoethoxy radical then the acetaldehyde/acetylbromide product yield ratio can be used to estimate a branching ratio for the $CH_3CHBr(O)$ reaction channels. The results support that Br-elimination will account for approximately 73% of the fate of $CH_3CHBr(O)$ radicals at atmospheric pressure and that the branching ratio is independent of temperature. This value is similar to that reported for bromomethoxy radicals where the Br-atom elimination channel accounts for over 80% of the reaction (Chen et al., 1995, 1996). Using a value of 6×10^{-14} cm^3 molecule^{-1} s^{-1} (recommended value for $O_2 + CH_2BrO$; DeMore et al., 1994) for the reaction of O_2 with $CH_3CHBr(O)$ in combination with the branching ratio for the reactions of $CH_3CHBr(O)$ one can write for atmospheric pressure and 298 K:

$$\frac{k_{\text{Br-elimination}}}{k_{\text{Br-elimination}} + k_{O_2}[O_2]} = \frac{k_{\text{Br-elimination}}}{k_{\text{Br-elimination}} + 6 \times 10^{-14}[4.9 \times 10^{18}]} = 0.73$$

From this expression, a value of

$$k_{\text{Br-elimination}} = 8.0 \times 10^5 \text{ s}^{-1}$$

can be estimated for the rate of elimination of the Br atom. The rate for the Br-atom elimination for $CH_3CHBr(O)$ is similar in magnitude to that estimated for CH_2BrO and $CHBr_2O$ radicals (Orlando et al., 1995, 1996).

Product branching ratios under atmospheric conditions. The yield of 3-bromobutan-2-one in the presence of NO has been determined to be approximately 64% C at 298 K. However as discussed above about 10% of the decay of trans-2-butene can be attributed to reaction with OH radicals which will not result in the formation of 3-bromobutan-2-one. Taking this into consideration along with the yield of 3-bromobutyl-2-hydroperoxide (which stops the further oxidation) results in a value of ~76% for the 3-bromobutan-2-one producing channel from the 3-bromo-2-butoxy radicals in the Br/*trans*-2-butene reaction. Similarly, from the results obtained under NO_x free systems values ranging from ~78% at 298 K down to nearly 100% at 246 K can be estimated for the 3-bromobutan-2-one producing channel.

4. Conclusions

Reactions of Br atoms with alkenes involve addition of Br atoms to the double bond. The work presented here on *trans*-2-butene and also work on other alkenes in this laboratory shows that the major fate of the Br-alkene adduct is formation of brominated carbonyls which retain the original chain length. In the case of *trans*-2-butene and also the other alkenes the yields of these carbonyls will be of the order of 70–80% under atmospheric conditions at 298 K when reaction with NO determines the fate of the RO_2 radicals. The other products will be bond cleavage products, aldehyde and brominated carbonyls. The results from *trans*-2-butene indicate that there will be disproportion between the yields of aldehydes and brominated aldehydes which lies heavily on the side of the aldehydes. At present the most feasible explanation for the phenomena is that Br-elimination occurs during the further oxidation of the β-bromoalkyl radicals formed in the bond cleavage step.

It has been shown for *trans*-2-butene that the yields of the bond cleavage products quickly approaches zero with decreasing temperature and

that the dominant product is the brominated carbonyl, 3-bromo-2-butanone. This pattern is to be expected for other alkenes in the atmosphere. Under conditions of low temperature and when sufficient levels of NO_x are present, brominated carbonyl compounds are probably the sole products from Br/alkene reactions. However, in situations where the levels of NO_x are extremely low as in the Arctic, formation of brominated alcohols and thermally stable brominated hydroperoxides may also occur. The fate of the hydroperoxides is presently uncertain, photolysis and reaction with OH radicals are the normal fates of hydroperoxides in the atmosphere.

Preliminary studies indicate that the photolytic lifetime of 3-bromo-2-butanone will be only of the order of a few hours and that bromine atoms are released during the photolysis. This may be the case for other β-brominated aldehydes/ketones formed in Br/alkene interactions, however, this needs to be established by investigations on other compounds.

In summary, in the first instance the reaction of Br atoms with unsaturated hydrocarbons will act as a sink for bromine at both mid and high latitudes principally through the formation of brominated carbonyls. There is some evidence that in some cases the brominate carbonyl will be photolabile and re-release the bromine within a time scale of hours; however, this effect will be greatest at mid-latitudes where the light intensity is highest. For a full evaluation of the role that Br/alkene interactions may play in the atmosphere, in addition to the gas phase reactions presented here, heterogeneous reactions on ice or aerosol surfaces need to be considered since these may have a different influence on the fate of bromine than that observed in the gas phase reactions.

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