Rate Constant and Products for the Reaction of Cl Atom With *n*-Butyraldehyde

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ABSTRACT: The photooxidations of *n*-butyraldehyde initiated by Cl atom were carried out at room temperature (298 ± 2K) and 1 atm pressure. The rate coefficient for the reactions of Cl atom with *n*-butyraldehyde was determined as $k = (2.04 \pm 0.36) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} by using relative rate techniques. The photooxidation products of *n*-butyraldehyde reaction with Cl atom were also studied by using both gas chromatography-mass spectrometry (GC-MS) and gas chromatography techniques. C_2H_5CHO, CH_3CHO, CO and CO_2 were the major products observed. In the absence of NO, the observed yields of C_2H_5CHO, CH_3CHO, and CO were 60%, 3%, and 9%, respectively. However, when NO was introduced into the reaction chamber and the initial ratios of $[NO]_0/[n\text{-butyraldehyde}]_0$ were between 1 and 8, the yield of C_2H_5CHO decreased to 33%, whereas that of CH_3CHO and CO rose up to 21% and 25%, respectively. On the basis of mechanism data deduced in this study and the fraction molar yields, the approximate branching ratios for Cl atom attack at —C(O)H, α-, β-, and γ-positions in *n*-butyraldehyde could be derived as $\geq$42%, <25%, 21%, and $\leq$12%, respectively. © 2007 Wiley Periodicals, Inc. Int J Chem Kinet 39: 168–174, 2007

INTRODUCTION

Recently, several aliphatic aldehydes (e.g., *n*-butyraldehyde) have been identified and quantified in vehicle emissions [1,2]. *n*-Butyraldehyde and higher aldehydes have been observed in ambient air and in the emissions of various plant species [3,4]. Aldehydes can significantly contribute to secondary aerosol formation through heterogeneous reactions [5]. Photodissociation of aldehydes represents an important source of free radicals such as HO_2, OH, and RO_2 in the lower atmosphere [6]. As sources of free radicals in the atmosphere and precursors in the organic aerosols, aldehydes play a significant role in urban photochemical smog and in the regional ozone layer. In addition, aldehydes are also the precursors of peroxyacyl nitrates, which are phytotoxic and strongly eye-irritating compounds [7].

The atmospheric oxidation of aldehydes is mainly initiated by photolysis and their reaction with OH radicals during daytime, and, to a lesser extent, with NO_3 radicals during nighttime. Previous studies have shown that the rate constants for the reactions of Cl atoms with certain aldehydes can be much larger than those of corresponding molecules with OH radicals [8,9]. Even though the concentration of Cl atoms is lower than that of OH radicals, their faster rates of reactions with aldehydes can make Cl atom reactions competitive with OH

reactions. Ambient measurements of tetrachloroethene and other volatile organic compounds suggested that Cl atom concentrations are less than 10^3 atoms cm^{-3} in the global troposphere but may be significantly higher in the marine boundary layer (in 10^4 atoms cm^{-3} range) [10–12]. Spicer et al. predicted that maximum chlorine atom levels occur shortly after sunrise with a peak concentration of 1.3×10^5 atoms cm^{-3} in both the remote marine boundary layer and coastal urban areas, and suggested that Cl atoms play a potential important role in the atmospheric chemistry of such areas [13].

The reliable data of the rate coefficients and the atmospheric oxidation mechanisms for the reaction of Cl atoms with aldehydes are useful in the estimation of the photochemical ozone creation potential (POCP). To our knowledge, there are still no reports about the kinetic and mechanistic data for the reaction of *n*-butyraldehyde with Cl atoms. Besides kinetic study for the reaction of Cl atoms with *n*-butyraldehyde, the present work also includes product studies of the photooxidation of *n*-butyraldehyde initiated by Cl atoms.

EXPERIMENTAL

The experimental systems used for the present study have been described in detail elsewhere [14], and are only briefly presented here.

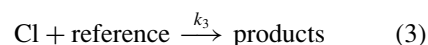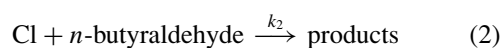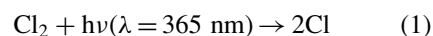### Indoor Teflon Bag Reaction Chamber

All experiments were performed using a Teflon bag of approximately 100 L hung inside a ligneous box of about 1 m^3 volume. The Teflon film of 0.14-mm thickness was adopted here to reduce the interference by penetration of the reactant and product molecules. Four fluorescent tubes (30 W, Academy of Electric Lamp-House in Beijing) were set on the inner wall of the cabinet surrounding the Teflon bag. These four "black lamps" provided UV radiation, with intensity maximum around 365 nm. Aluminum foil covering the inner wall of the cabinet reflected UV light to enhance the light efficiency and to prevent the leakage of UV light.

A mercury-free greaseless vacuum system was used for all experiments. Pressure measurements were done with an MKS Baratron capacitance manometer, MKS 270 B. Measured amounts of the reagents were flushed from Pyrex bulbs into the Teflon reaction chamber by a stream of air, which was purified by passing through desiccant, charcoal, and 5 Å molecular sieve. A mass flow meter (range $= 0$–5000 mL min^{-1}, ShengYe Technology Company, Beijing) controlled the flow rate.

Kinetic Study of the Reaction of Cl atom With *n*-Butyraldehyde

Kinetic experiments of the reaction of Cl atoms with *n*-butyraldehyde were carried out at 298 ± 2 K and 1 atm. The Cl atoms were generated through photodegradation of molecular chlorine using fluorescent lamps.

The rate constant for the gas-phase reaction of Cl atoms with *n*-butyraldehyde was determined using a relative rate method. The decays of *n*-butyraldehyde and of a suitable reference compound, whose rate constant with Cl atoms was reliably known, were monitored in parallel in the presence of Cl atoms.

$$Cl_2 + h\nu(\lambda = 365 \text{ nm}) \rightarrow 2Cl \qquad (1)$$

$$Cl + n\text{-butyraldehyde} \xrightarrow{k_2} \text{products} \qquad (2)$$

$$Cl + \text{reference} \xrightarrow{k_3} \text{products} \qquad (3)$$

Provided that *n*-butyraldehyde and the reference are removed solely by reaction with Cl atoms, then

$$\ln \left\{ \frac{[n - \text{butyraldehyde}]_0}{[n - \text{butyraldehyde}]_t} \right\} = \frac{k_2}{k_3}$$
$$\cdot \ln \left\{ \frac{[\text{reference}]_0}{[\text{reference}]_t} \right\} \qquad (I)$$

where $[n\text{-butyraldehyde}]_0$ and $[\text{reference}]_0$ are the concentrations of the *n*-butyraldehyde and reference compound, respectively, at time t_0; $[n\text{-butyraldehyde}]_t$ and $[\text{reference}]_t$ are the corresponding concentrations at time t; and k_2 and k_3 are the rate constants for reactions (2) and (3), respectively. Kinetic experiments were performed using both propane and isopropanol as reference compounds in order to ensure the accurate rate coefficients for the reaction of *n*-butyraldehyde with Cl atoms. The initial reactant concentrations (in units of molecule cm^{-3}) were as follows: Cl$_2$, 5×10^{14} to 7×10^{14}; *n*-butyraldehyde, 7×10^{14} to 9×10^{14}; propane, $\sim 9 \times 10^{14}$; and isopropanol, $\sim 9 \times 10^{14}$. The concentration–time behaviors of *n*-butyraldehyde and reference compounds were monitored over a 100–120-min irradiation period by using a gas chromatography with flame ionization detector (GC-FID, HP5890, Agilent Technologies). Successful quantitative analyses for both sets of kinetic experiments were achieved on a 2 m × 3-mm Teflon column packed with GDX 103 (60–80 mesh).

Products of the Reaction of Cl Atom With *n*-Butyraldehyde

Product investigations were also carried out in the reaction chamber at room temperature and 1 atm. The

Cl atoms were generated through photodegradation of Cl_2 by fluorescent lamps. Products were identified and quantified by GC-MS and GC-FID, respectively. Determination of n-butyraldehyde, propionaldehyde, and acetaldehyde was done by GC-FID (HP5890, Agilent Technologies), equipped with a 2 m × 3-mm Teflon column packed with GDX 103 (60–80 mesh). CO and CO_2 were measured by GC-FID (GC112A, Shanghai Precision & Scientific Instrument Co., Ltd., Shanghai, China) with a methanizer [15], equipped with a 1.2 m × 3-mm Teflon column packed with TDX-01 (60–80 mesh).

About 1000-mL gas samples were collected from the chamber onto Tenax-TA solid adsorbent in liquid nitrogen, with subsequent thermal desorption at 180°C into a 100-mL syringe. It was then analyzed by combined GC-MS, using a 0.32 mm × 30 m × 20-μm HP-PLOT Q capillary column, initially held at 85°C or 1 min and then temperature programmed to 250°C at 3° in^{-1}, in a HP6890 GC interfaced to an HP 5973 mass selective detector.

Chemicals

The chemicals used and their stated purities were n-butyraldehyde (99%), propionaldehyde (99%), isopropanol (99%), frpm Aldrich Chemical Co. The chlorine gas was prepared by dropwise addition of HCl to $KMnO_4$ in our laboratory. n-Butyraldehyde, propionaldehyde, isopropanol, and Cl_2 were further purified by repeat freeze, pump, and thaw cycles and fractional distillation before use. Acetaldehyde (1.03 mg/mL in water), propane (1.2% in N_2), CO (5.28 ppm in N_2), CO_2 (511 ppm in N_2), and standard gases were obtained from National Research Center for Certified Reference Materials, China.

RESULTS AND DISCUSSION

Relative Rate Constant for the Reaction of Cl Atom With n-Butyraldehyde

Some tests on n-butyraldehyde/isopropanol or propane/air mixtures in the chamber showed that losses of the compounds to the wall or via photolysis were <3% for all processes over a 2-h period. In comparision to the measured decays for the compounds during the kinetic experiments, the contributions from wall loss and photolysis were negligible. Mixtures of n-butyraldehyde and isopropanol/propane with Cl_2 were stable in the dark for about 2 h in the reaction chamber.

Kinetic investigations were performed by irradiation of n-butyraldehyde/Cl_2/propane or isopropanol/air mixtures. Figure 1 illustrates the
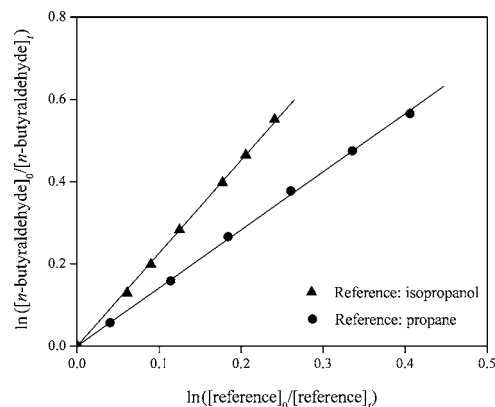
Figure 1 Plots of $\ln([n\text{-butyraldehyde}]_0/[n\text{-butyralde-}$ $\text{hyde}]_t)$ vs. $\ln([\text{reference}]_0/[\text{reference}]_t)$ for Cl atom reactions with n-butyraldehyde.

kinetic data obtained from two experiments plotted according to Eq. (I). Least-squares analysis of these data led to the rate coefficient ratios of $k(\text{Cl}+n\text{-butyraldehyde})/k(\text{Cl}+\text{isopropanol}) = 2.39 \pm 0.15$ and $k(\text{Cl}+n\text{-butyraldehyde})/k(\text{Cl}+\text{propane}) = 1.39 \pm 0.04$, respectively. On the basis of the values of $k(\text{Cl}+\text{isopropanol}) = 8.6 \times 10^{-11}$ cm^3 molecul^{-1} s^{-1} and $k(\text{Cl}+\text{propane}) = 1.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K [16], the rate constant of $k(\text{Cl}+n\text{-}$ butyraldehyde) could be calculated as $(2.06 \pm 0.13) \times 10^{-10}$ and $(1.95 \pm 0.06) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. The quoted errors were twice the standard deviation arising from the least-squares fit of the straight lines but not including the estimate of the errors in the reference rate constants. We estimated that potential systematic errors of $\pm 10\%$ associated with uncertainties in the reference rate constants for $k(\text{Cl}+n\text{-}$ butyraldehyde). Propagating this additional uncertainty gave $k(\text{Cl}+n\text{-butyraldehyde}) = (2.06 \pm 0.34) \times 10^{-10}$ and $(1.95 \pm 0.26) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. The two rate constants based on different references agreed with each other to within 5%. We chose to cite a final value for $k(\text{Cl}+n\text{-butyraldehyde})$, which was the average of those determined using the two different reference compounds together with error limits that encompass the extremes of the individual determinations. Hence, $k(\text{Cl}+n\text{-butyraldehyde}) = (2.04 \pm 0.36) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. This work provided the first rate constant for the reaction of Cl atoms with n-butyraldehyde.

As for n-butyraldehye, the rate constant for Cl atom reaction ($k = 2.04 \times 10^{-10}$ molecule cm^{-3} s^{-1}) is almost 1 order of magnitude higher than that for OH radical reaction ($k = 2.4 \times 10^{-11}$ molecule cm^{-3} s^{-1}) [16]. In free troposphere, the concentration of OH radicals is nearly 100 times higher than Cl atoms, so the reaction of Cl atom may be less important than the reaction of

OH radicals. In the marine boundary layer or coastal area, the reaction of Cl atom with *n*-butyraldehyde could compete with OH reactions because of the high Cl atom concentration.

Product Study of the Cl Atom Initiated Oxidation of *n*-Butyraldehyde
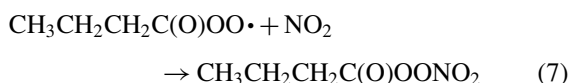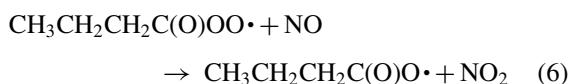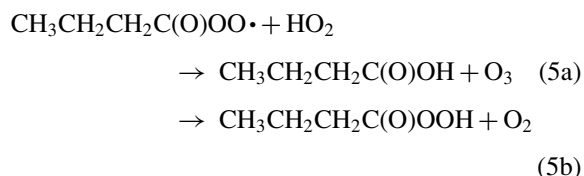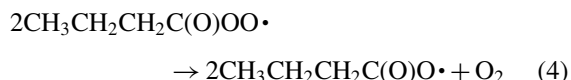
The products of the Cl atom initiated oxidation of *n*-butyraldehyde were studied by the UV irradiation of *n*-butyraldehyde/Cl_2/NO/air and *n*-butyraldehyde/Cl_2/air mixtures. Initial concentrations (in molecule cm^{-3} units) were as follows: *n*-butyraldehyde, 5×10^{14} to 8×10^{14}; Cl_2, 4×10^{14} to 11×10^{14}; NO, 0 to 40×10^{14}. Typical plots of the concentrations of reactant and major products for irradiation of *n*-butyraldehyde/Cl_2/air mixtures over the time period of analysis are illustrated in Fig. 2. The mixtures were irradiated for a period ranging between 100 and 130 min, and the main observed products gave the carbon balance of about 65%, which indicates the presence of other oxidation products that we did not detect.

Acetaldehyde, propionaldehyde, CO, and CO_2 were the main products observed in all experiments. In addi-

Figure 2 Plots of product concentrations for the Cl atom reaction with *n*-C3H7CHO with or without added NO: (A):[*n*-C_3H_7CHO] = 74, [NO] = 0; (B) [*n*-C_3H_7CHO] = 79, [NO] = 330; in units of $\times 10^{13}$ molecule cm^{-3}.

tion, one unidentified products was also observed. The GC peak of the unknown product eluted before but very close to the retention time of *n*-butyraldehyde. This unknown product was identified probably as 3-hydroxy-1-propionaldehyde or its isomers by GC-MS (see the following discussion).
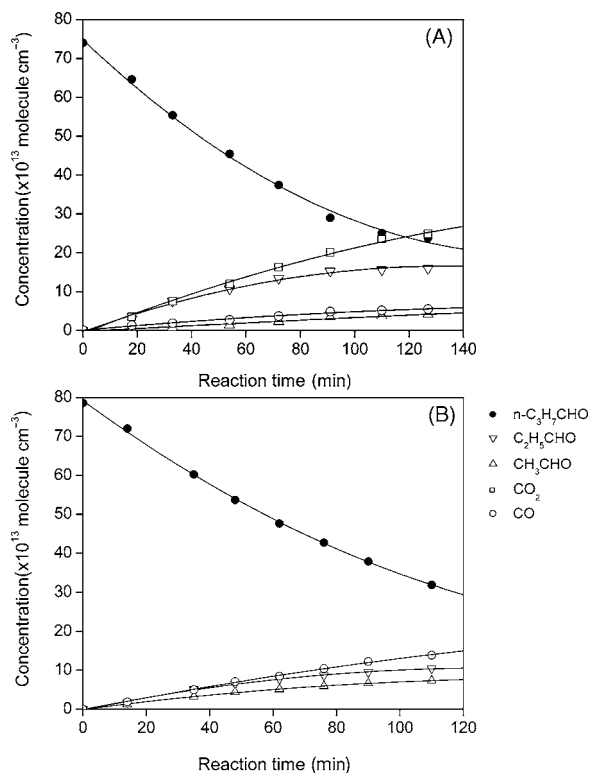
The reaction of Cl atoms with *n*-butyraldehyde proceeded by the oxidation of the radicals formed following H-atom abstraction from the C—H bonds [16]. The alkyl radicals formed after H-atom abstraction at the —C(O)H, i.e., α-, β-, and γ-positions in *n*-butyraldehyde, would add O_2 to give corresponding acylperoxy radicals and alkylperoxy radicals.

CH₃CH₂CH₂C(O)OO• Radical. In the absence of NO_x, the acylperoxy radical reacts with itself (4) and, to a lesser extent, reacts with HO_2 radicals, leading to the formation of organic acids and peroxyacids (5a, 5b). In the presence of NO_x, it also reacts with NO to form $CH_3CH_2CH_2C(O)O•$ radical (6), and react with NO_2 to form $CH_3CH_2CH_2C(O)OONO_2$ (7).
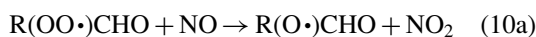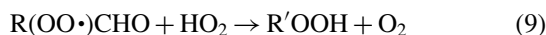
$$2CH_3CH_2CH_2C(O)OO•$$
$$\rightarrow 2CH_3CH_2CH_2C(O)O• + O_2 \quad (4)$$
$$CH_3CH_2CH_2C(O)OO• + HO_2$$
$$\rightarrow CH_3CH_2CH_2C(O)OH + O_3 \quad (5a)$$
$$\rightarrow CH_3CH_2CH_2C(O)OOH + O_2$$
$$(5b)$$

$$CH_3CH_2CH_2C(O)OO• + NO$$
$$\rightarrow CH_3CH_2CH_2C(O)O• + NO_2 \quad (6)$$
$$CH_3CH_2CH_2C(O)OO• + NO_2$$
$$\rightarrow CH_3CH_2CH_2C(O)OONO_2 \quad (7)$$
$$CH_3CH_2CH_2C(O)O• \rightarrow CH_3CH_2CH_2• + CO_2 \quad (8)$$

The alkoxy radical $CH_3CH_2CH_2C(O)O•$ is expected to rapidly decompose to $CH_3CH_2CH_2•$ and CO_2 (8). The alkyl radical of $CH_3CH_2CH_2•$ finally converts to a certain amount of propionaldehyde.

In the absence of NO_x, the alkylperoxy radicals formed after the H-atom abstraction at α-, β-, and γ-positions in *n*-butyraldehyde then predominantly react with acylperoxy radical to form alkoxy radical, or with HO_2 radicals leading to form hydroperoxide species (9), although the self-reaction of these alkylperoxy radicals is less important. When NO is added, these alkylperoxy radicals are expected to easily react with NO (10). The contribution of the channel (10b) forming organic nitrates ($RONO_2$) in these $RO_2 + NO$ reactions is

considered to be small ($\leq 7\%$) [17].

$$R(OO\cdot)CHO + HO_2 \rightarrow R'OOH + O_2 \quad (9)$$

$$R(OO\cdot)CHO + NO \rightarrow R(O\cdot)CHO + NO_2 \quad (10a)$$

$$\rightarrow R(ONO_2)CHO \quad (10b)$$

The alkoxy radical $R(O\cdot)CHO$ then reacts via a number of pathways, involving decomposition, isomerization through a six-membered transition state, and reaction with oxygen [18]. But not all of these reaction pathways are possible for these three alkoxy radicals.

$CH_3CH_2CH(O\cdot)CHO$ Radical. This alkoxy radical either decomposes or reacts with O_2. On the basis of the reactions of $CH_3C(O)CH(O\cdot)CH_2CH_3$ radicals of similar structure formed from 2-pentanone, for which the decomposition dominated over its reaction with O_2 [19], $CH_3CH_2CH(O\cdot)CHO$ radical would mainly decompose to propionaldehyde plus one $\cdot CHO$ radical (11). One $\cdot CHO$ radical reacts with O_2 to give a molecule of CO. No $CH_3CH_2C(O)CHO$ was detected during our experiments, which also indicated that the reaction of $CH_3CH_2CH(O\cdot)CHO$ with O_2 (12) could be neglected.

$$CH_3CH_2CH(O\cdot)CHO$$

$$\rightarrow CH_3CH_2CHO + \cdot CHO \quad (11)$$

$$CH_3CH_2CH(O\cdot)CHO + O_2$$

$$\rightarrow CH_3CH_2C(O)CHO + HO_2 \quad (12)$$
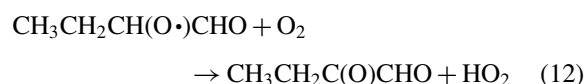
$CH_3CH(O\cdot)CH_2CHO$ Radical. The alkoxy radical either decomposes or reacts with O_2. On the basis of the reaction of $CH_3C(O)CH_2CH(O\cdot)CH_3$ radicals of similar structure formed from 2-pentanone [19], the decomposition of $CH_3CH(O\cdot)CH_2CHO$ radical mainly leads to acetaldehyde plus $\cdot CH_2CHO$ radical (13).

$$CH_3CH(O\cdot)CH_2CHO \rightarrow CH_3CHO + \cdot CH_2CHO \quad (13)$$
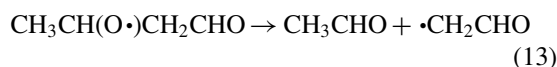
The decomposition pathway followed by the reactions of $\cdot CH_2CHO$ radical under tropospheric conditions results in the formation of CHOCHO or HCHO plus CO. However, CHOCHO was not detected in our experiment, which was probably because the flame ionization detector is not a proper detector for the analysis of glyoxal.
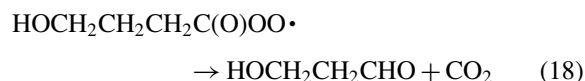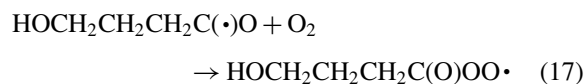
$$CH_3CH(O\cdot)CH_2CHO + O_2$$

$$\rightarrow CH_3C(O)CH_2CHO + HO_2 \quad (14)$$
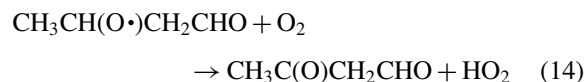
The reaction of O_2 with $CH_3CH(O\cdot)CH_2CHO$ would lead to the product acetyl acetaldehyde (14). However, acetyl acetaldehyde was not observed in our experiments, which was probably due to its concentration below the detection limit. So the O_2 reaction of $CH_3CH(O\cdot)CH_2CHO$ could be negligible.

$CH_2(O\cdot)CH_2CH_2CHO$ Radical. Previous studies indicated that the reactions of n-butoxy radicals were dominated by the reaction with O_2 and 1,5-H shift isomerization ($k_{O_2} = 1.4 \times 10^{-14}$ cm^3 molecule^{-1}s^{-1} [20], taking $[O_2] = 4.9 \times 10^{18}$ molecule cm^{-3}, $k_{O_2} \cdot [O_2] = 6.9 \times 10^4$ s^{-1}; $k_{decompostion} = 3.93 \times 10^{-1}$ s^{-1} [21], $k_{isomerization} = 1.8 \times 10^5$ s^{-1} [22].). On the basis of reactions of n-butoxy radical, the reactions of $CH_2(O\cdot)CH_2CH_2CHO$ radicals might be also dominated by reaction with O_2 or isomerization, with the decomposition being negligible. The reaction of $CH_2(O\cdot)CH_2CH_2CHO$ with O_2 will lead to 1,4-butanedial (15). However, 1,4-butanedial was not observed by GC-MS, probably because 1,4-butanedial does not appear elute from the GC columns [23].

$$CH_2(O\cdot)CH_2CH_2CHO + O_2$$

$$\rightarrow HC(O)CH_2CH_2CHO + HO_2 \quad (15)$$
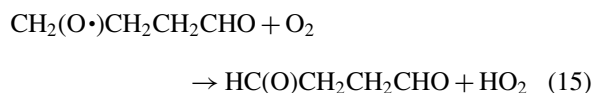
The radical $CH_2(O\cdot)CH_2CH_2CHO$ is isomerized to form $HOCH_2CH_2CH_2C(\cdot)O$ radical (16), which would lead to the formation of 3-hydroxy-1-propionaldehyde after reaction with O_2 (17) and subsequent decomposition (18). Hence, the unidentified product eluted before the retention time of n-butyraldehyde was expected to be 3-hydroxy-1-propionaldehyde. The concentration of 3-hydroxy-1-propionaldehyde was roughly estimated by comparing to the propionaldehyde standard, and finally the production yield is found to be about 2%.

$$CH_2(O\cdot)CH_2CH_2CHO$$

$$\rightarrow HOCH_2CH_2CH_2C(\cdot)O \quad (16)$$

$$HOCH_2CH_2CH_2C(\cdot)O + O_2$$

$$\rightarrow HOCH_2CH_2CH_2C(O)OO\cdot \quad (17)$$

$$HOCH_2CH_2CH_2C(O)OO\cdot$$

$$\rightarrow HOCH_2CH_2CHO + CO_2 \quad (18)$$

The products were investigated by gas chromatography using the mixture containing seven different concentrations of NO between 0 and 40×10^{14} (all in units of molecules cm^{-3}). Product formation yield of propionaldehyde was corrected for its secondary reaction

Table I Yields of C_2H_5HO, CH_3CHO, and CO from the Cl-initiated Photooxidation of *n*-C_3H_7CHO

Initial Concentration ($\times 10^{13}$ molecule cm^{-3})					Product Yield		
C_3H_7CHO	Cl_2	NO	NO_2	$[NO]_0/[C_3H_7CHO]_0$	C_2H_5CHO	CH_3CHO	CO
52	36	0.0	0	0	0.61	0.03	0.09
62	87	0.0	0	0	0.59	0.02	0.09
74	79	0.0	0	0	0.60	0.03	0.07
73	110	34	0	0.5	0.36	0.13	0.13
72	64	69	0	1	0.32	0.22	0.23
73	87	138	0	1.9	0.32	0.20	0.27
59	52	145	0	2.5	0.33	0.19	0.25
79	75	330	0	4.2	0.32	0.20	0.26
48	46	386	62	8	0.33	0.20	0.26

with Cl atoms [24], while the formation yields of acetaldehyde, CO_2, and CO were derived in the early stages of the reaction (about 20% *n*-butyraldehyde was consumed). Product formation yields of CO, actaldehyde, and propionaldehyde are listed in Table 1 and also plotted against $[NO]_0/[n\text{-butyraldehyde}]_0$ (the subscript "0" means the initial concentrations), which are illustrated in Fig. 3. When there was no NO present in the mixture, the observed yields of C_2H_5CHO, CH_3CHO, and CO were 60%, 3%, and 9%, respectively. However, the yields of CO and acetaldehyde rose, whereas that of propionaldehyde decreased as the ratio of $[NO]_0/[n\text{-butyraldehyde}]_0$ increased. In addition, the formation yields of the three compounds were nearly constant for the ratios of $[NO]_0/[n\text{-butyraldehyde}]_0$, between 1 and 8 (the production yields for CO and acetaldehyde and propionaldehyde were 25%, 21%, and 33%, respectively). The decrease in propionaldehyde production yield might be due to

Figure 3 Plots of the product formation yields against the ratio of $[NO]_0/[n\text{-}C_3H_7CHO]_0$ in Cl atom reactions with *n*-C_3H_7CHO.

the formation of peroxy-*n*-butyrylnitrate. The NO is rapidly decreased after the initiation of the reaction and NO_2 is formed, so the main fate of the acylperoxy radicals will be the formation of corresponding stable acyl peroxynitrate and not lower aldehyde [17,25].

Regarding the increase in product yields of CH_3CHO and CO, a similar trend for acetaldehyde was reported by Cheema and coworkers [26] when they studied the mechanisms of Cl atom reaction with propanol. In this work, the reason might be that the degradation of alkylperoxy radicals to alkoxy radicals is the key process for both formation of CH_3CHO and CO. In absence of NO_x, the reaction of $CH_3CH(OO\cdot)CH_2CHO$ with other peroxy radicals including acylperoxy radicals and HO_2 will be the dominant degradation process. Since the reaction of $CH_3CH(OO\cdot)CH_2CHO$ with HO_2 radicals could lead to formation of hydroperoxide species without generating $CH_3CH(O\cdot)CH_2CHO$ radicals, a relatively small amount of $CH_3CH(O\cdot)CH_2CHO$ was formed, and therefore the product yield of CH_3CHO was low. When sufficient NO was added into the mixture, the reaction of $CH_3CH(OO\cdot)CH_2CHO$ with NO would dominate over the other reactions of $CH_3CH(OO\cdot)CH_2CHO$. Then almost all $CH_3CH(OO\cdot)CH_2CHO$ radicals were transformed to $CH_3CH(O\cdot)CH_2CHO$, which led to a high product yield. We thought that the steady yields of acetaldehyde at high $[NO]_0/[propanol]_0$ ratios were appropriate to determine the branching ratios for Cl attack on *n*-butyraldhyde. Hence, the branching ratios of Cl attack at α- and β-positions in *n*-butyraldehyde were derived by considering the formation yields for CO and acetaldehyde as 25% and 21%, respectively. Considering that CO might partly come from the degradation of $\cdot CH_2CHO$ (formed after Cl attack at β-position), the branching ratio of Cl attack at α-position should be the high limit.
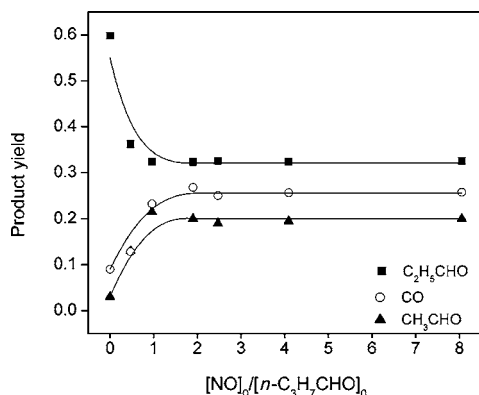
The product yield of CO_2 (44% in the absence of NO) may be taken to estimate an approximate branching ratio of Cl attack at $-C(O)H$ function group in n-butyraldehyde. In the absence of NO, the radical of $CH_3CH_2CH_2C(O)OO\bullet$ may predominantly undergo self-reactions and cross-reactions with other alkylperoxy radicals to produce CO_2, and, to a certain extent, with HO_2 radicals to generate acids and peracids. Considering that about 2% CO_2 is contributed by reaction (18), it might be suggested that at least 42% reaction occurs at $-C(O)H$ in n-butyraldehyde. So the branching ratios for Cl atoms attack at $-C(O)H$, α-, β-, and γ-positions in n-butyraldehyde are $\geq$42%, $\leq$25%, 21%, and $\leq$12%, respectively.

According to the branching ratios of Cl atom attack at $-C(O)H$, α-, β-, and γ-positions and $k(Cl + n$-butyraldhyde$) = 2.04 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, the partial rate coefficients for the groups of n-butyraldhyde can be obtained approximately as following: $k(-C(O)H) = 8.6 \times 10^{-11}$, $k(\alpha-CH_2-) = 5.1 \times 10^{-11}$, $k(\beta-CH_2-) = 4.3 \times 10^{-11}$, and $k(\gamma-CH_3) = 2.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively. The partial rate constant for Cl attack at $-C(O)H$ obtained by this study is close to the upper limit of $(7.5 \pm 0.8) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} reported by Kegley-Owen et al. [27]. Coincidently, our derived values of $k(-C(O)H)$, $k(\beta-CH_2-)$, and $k(\gamma-CH_3)$ agree well with $k(\alpha-CH_2OH) = 8.7 \times 10^{-11}$, $k(\beta-CH_2-) = 4.7 \times 10^{-11}$, and $k(\gamma-CH_3) = 2.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} obtained by Cheema et al. [26] from the analysis of the Cl-initiated oxidation of 1-propanol.

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