

ARTICLE

Time-Resolved FTIR Study on the Reaction of CHCl_2 with NO_2 [†]

Kun-hui Liu, Chun-fan Yang, Huan Wang, Wei-qiang Wu, Hong-mei Su*

State Key Laboratory of Molecular Reaction Dynamics, Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

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The environmentally important free radical reaction of chlorinated methyl CHCl_2 with NO_2 was investigated by step-scan time-resolved FTIR (TR-FTIR) emission spectroscopy. Vibrationally excited products of CHClO , NO , CO , and HCl are observed in the high-resolution IR emission spectra and three possible reaction channels are therefore elucidated. In particular, the product CO is newly detected and the product HCl is identified explicitly as a yield from the $\text{CHCl}_2 + \text{NO}_2$ reaction, taking advantage of the sensitive detection of HCl and CO with TR-FTIR. These results are of particular interests to understand the related realistic chemical processes including atmospheric photochemistry, biofuel combustion, waste destruction, and smoking fire.

Key words: TR-FTIR, Dichloromethyl, NO_2 , Reaction product channel

I. INTRODUCTION

The reactions of chlorine-containing radicals are playing key roles in a number of important environmental issues, including stratospheric ozone depletion, and the incineration of chlorine-containing chemical and polymeric wastes [1-5]. Chlorine-substituted small radicals, such as CH_2Cl , CHCl_2 , and CCl_3 , contain additional bonding due to the interaction of the unpaired electron with the lone pairs of the chlorine. Also, these radicals have unusually large out-of-plane mode anharmonicities caused by the unpaired electron [6]. In comparison with non-chlorinated CH_3 radicals, chlorinated methyl radicals exhibit increased kinetic stability in the combustion environment as the number of chlorine increases in methyl. This is due to the weaker C-O bonds in the peroxy adducts formed by the addition of these methyl radicals to molecular oxygen. Therefore, the reactions between chlorinated methyl with O_2 are relatively slow and consequently, the importance of reactions of these radicals with other open-shell species, such as H , O , OH , NO_x ($x=1, 2$), increases. On the other hand, nitrogen oxides are known to be major atmospheric pollutants released by combustion process [7,8].

In order to minimize the harmful effects before their release into the atmosphere, one effective way is to chemically reduce them by the reburning of the combustion products [9-11]. Therefore, the reactions of chlorinated methyl radicals with NO_2 can be expected to

be important during the oxidation of chlorinated compounds, because traces of nitrogen oxides are also often present [12].

Despite of their importance, chlorinated methyl radical reactions with NO_2 have been the subject of few direct studies. For $\text{CHCl}_2 + \text{NO}_2$, the reaction kinetics was investigated by Timonen *et al.* using a tubular flow reactor coupled to a photoionization mass spectrometer [13]. Several important results were reported. The rate constant was found to be pressure-independent but it obeyed the following dependence over the temperature range 220-360 K: $k = (8.90 \pm 0.16) \times 10^{-12} (T/300)^{-1.48 \pm 0.13} \text{ cm}^3 / (\text{molecule} \cdot \text{s})$. In addition, their experiment indicated CHClO and NO to be major products and also measured a weak signal of HCl product.

Very recently, Li *et al.* reported theoretical calculation results on the reaction of CHCl_2 with NO_2 at the B3LYP and MC-QCISD (single-point) levels [14]. Their calculation explored six reaction channels for the title reaction, *i.e.*, P1($\text{CHClO} + \text{ClNO}$), P2($\text{CHClO} + \text{ClON}$), P3($\text{CCl}_2\text{O} + \text{HNO}$), P4($\text{CCl}_2\text{O} + \text{HON}$), P5($\text{CCl}_2 + \text{HONO}$), and P6($\text{CHClO} + \text{Cl} + \text{NO}$). Among these six reaction channels, they determined that P1($\text{CHClO} + \text{ClNO}$) was the most thermodynamically and kinetically accessible channel for the $\text{CHCl}_2 + \text{NO}_2$ reaction which could explain why CHClO and NO were the major products observed by Timonen's experiments. Nevertheless, the theoretical calculations did not explore other product channels such as the channel forming HCl .

Evidently, the knowledge of the products and channels of the highly reactive $\text{CHCl}_2 + \text{NO}_2$ reaction remains uncertain although this information is highly desirable for understanding the reaction mechanism and related combustion and atmospheric processes.

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*Author to whom correspondence should be addressed. E-mail: hongmei@iccas.ac.cn

In this work, we focus our examination on the multiple reaction products by means of step-scan time-resolved FTIR emission spectroscopy (TR-FTIR). Vibrationally excited products of CHClO , NO , CO , and HCl are observed in the IR emission spectra, among which the product CO is newly detected. Particularly, we aim to identify explicitly the existence of an HCl channel for the title reaction, taking advantage of the sensitive detection of HCl with TR-FTIR because this result is specifically important to identify the source of HCl in many realistic chemical processes, e.g., atmospheric photochemistry, biofuel combustion, waste destruction, and smoking fire [15-17].

II. EXPERIMENTS

The reaction products are monitored by step-scan, time-resolved FTIR emission spectroscopy [18,19]. The step-scan FTIR spectrometer is commercially available but requires significant modification for coupling with pulsed laser and study of photolysis initiated free radical reactions. This newly upgraded machine comprises a Nicolet Nexus 870 step-scan FTIR spectrometer, Lambda Physik (LPX305i) Excimer laser and a pulse generator (Stanford Research DG535) to initiate the laser pulse and achieve synchronization of the laser with data collection, two digitizers (internal 100 kHz 16-bit digitizer and external 100 MHz 14-bit GAGE 8012A digitizer) which offer fast time resolution and a wide dynamic range as needed, and a personal computer to control the whole experiment. The detector used in this experiment is a liquid nitrogen (77 K) cooled InSb detector.

The reaction is initiated in a stainless steel flow reaction chamber. A pair of parallel multi-layer coated mirrors (reflectivity $R > 0.95$ at 248 nm) reflects the UV laser beam multiple times to increase the photolysis zone. CHCl_2 radicals are generated by 248 nm photodissociation (100 mJ/(cm^2 -pulse), 10 Hz repetition rate) of CHCl_2Br (Aldrich, purity $> 98\%$, 20 Pa) [20]. CHCl_2Br and NO_2 (purity $\geq 99.5\%$, 90 Pa) enter the flow chamber 1 cm above the photolysis beam via needle valves. The chamber is pumped by an 8 L/s mechanical pump and the stagnation pressure of the chamber is measured by an MKS capacitance monometer. The constant pressure of sample is maintained by adjusting the pumping speed and the needle valves. Transient infrared emission is collected by a pair of gold-coated Welsh-Cell spherical mirrors and collimated by a CaF_2 lens to the step-scan Fourier spectrometer (Nicolet Nexus 870). The spectrometer and the collimating tube are both flushed with N_2 to prevent environmental CO_2 absorption. The spectral resolution is set at 0.5 cm^{-1} .

III. RESULTS AND DISCUSSION

A. Detection of the reaction products

CHCl_2 radicals are produced via photolysis of CHCl_2Br at 248 nm. Following a $\sigma^* \leftarrow n$ transition with the transition dipole parallel to the C-Br bond, it can be anticipated that the photolysis of CHCl_2Br only gives rise to CHCl_2 radical just like the behavior of the analogous CH_2ClBr molecule [20,21]. Thus, this provides a good source for generating CHCl_2 radicals for the subsequent study of their reaction with NO_2 . On the other hand, due to the small absorption cross section of NO_2 molecules at 248 nm ($3.8 \times 10^{-20} \text{ cm}^2$), the possible interference caused by the photodissociation of NO_2 ($\text{NO}_2 \rightarrow \text{O} + \text{NO}$) can be suppressed effectively by adjusting the laser power intensity. It is estimated that only a negligible amount (approximately 0.5%) of NO_2 molecules underwent dissociation at the laser power of 100 mJ/cm^2 and as a result, no IR emission signals due to the photofragment NO was observed in the reference experiment when pure NO_2 was irradiated at 248 nm.

When the gas mixture of NO_2 and CHCl_2Br was irradiated by 248 nm laser, strong IR emission bands were observed as shown in Fig.1, which shows specific time slices of the TR-FTIR emission spectra from 13 μs to 138 μs with a 0.5 cm^{-1} spectral resolution. Apparently,

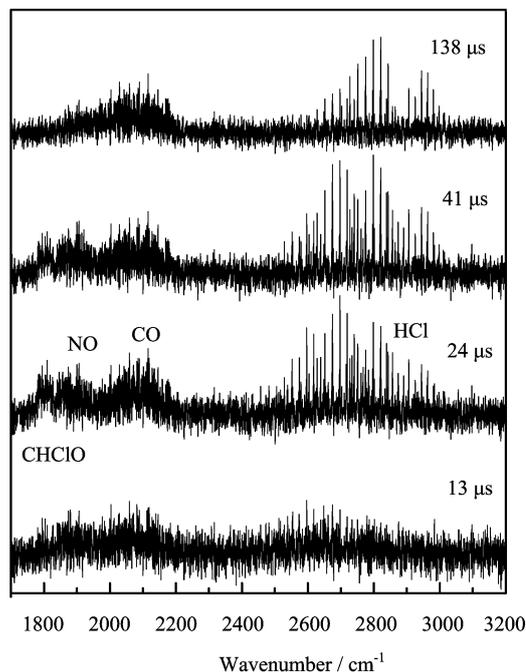


FIG. 1 TR-FTIR emission spectra from the products of the reaction of $\text{CHCl}_2 + \text{NO}_2$ taken at typical delay times after the initiation of the reaction by 248 nm laser photolysis. The spectra were collected using InSb detector at 0.5 cm^{-1} spectral resolution.

these IR emission bands originate from the vibrationally excited products of the $\text{CHCl}_2+\text{NO}_2$ reaction.

IR emission spectra record the infrared fluorescence emitted from vibrationally excited species due to a set of vibrational transitions $v \rightarrow v-1$ and thus the band is generally much broader than normal static IR absorption spectra and the peak center exhibits somewhat of a red shift relative to the fundamental frequency position ($1 \rightarrow 0$). As shown in Fig.1, these IR emission bands appear in a few microseconds and reach their maximum intensity at 24 μs . Four emission bands are observed and three of them due to diatomic molecules are rotationally resolved. The rotationally resolved emission band spanning from 2500-3100 cm^{-1} can be easily assigned to the rovibrational transitions of HCl. The other two rotationally resolved emission bands 1950-2200 and 1840-1950 cm^{-1} are ascribed to rovibrational transitions of CO and NO, respectively. The resolved rovibrational lines of NO are partially superimposed on top of an irresolvable emission band which is most likely due to the polyatomic molecule CHClO judging from its spectral position [22,23]. Because the detector InSb cuts off at 1840 cm^{-1} , only part of the emission bands of CHClO and NO is detected in the spectra. Among the four reaction products, the polyatomic product CHClO decays faster than diatomic molecules NO, CO, and HCl because the former undergoes faster vibrational relaxation. By the time 138 μs as compared to 24 μs , the emission bands of CHClO can hardly be discerned underneath the spectra of NO because of its complete vibrational relaxation.

B. Vibrational energy disposal of HCl

Due to the advantage of the broad band and the nature of IR emission, TR-FTIR emission spectra can provide the information of an almost complete vibrational state distribution. The vibrational state distribution is usually acquired by spectral fitting to experimental IR spectra using nonlinear least-squares fitting procedures which has been described in detail in Ref.[24]. Figure 2 shows the representative spectral fitting results for the IR emission bands of the products HCl from the $\text{CHCl}_2+\text{NO}_2$ reaction. The rotational line positions and intensities fit well with the experimental spectra, demonstrating further the unambiguous assignment of the spectra to HCl. The spectral fitting yields the vibrational populations and rotational temperature. The rotational temperature of 300 K generates the best fitting results, indicating that the rotational excitation has been thermalized. This is reasonable because these spectra are acquired as early as 13 μs after photolysis, corresponding to roughly 130 collisions (with total pressure of 110 Pa), sufficient to equilibrate rotational distribution. By spectral fitting, the vibrational populations of HCl are derived to be 1.00 ± 0.05 , 0.90 ± 0.11 , 0.11 ± 0.01 , 0.090 ± 0.005 for the vibrational

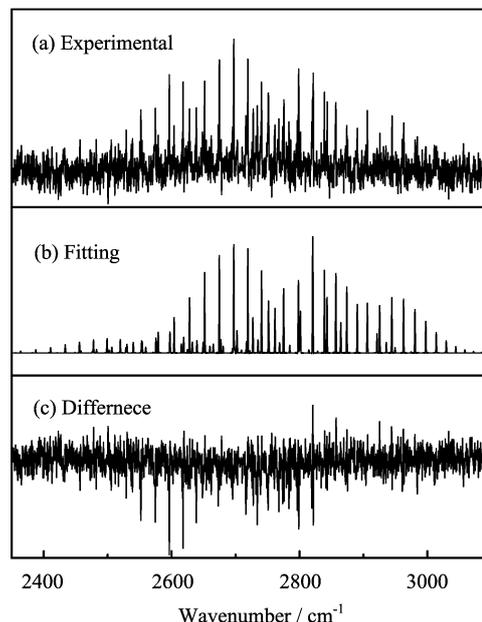


FIG. 2 Representative spectral fitting results for the IR emission bands of the product HCl at the reaction time of 24 μs . (a) Experimental spectrum; (b) Fitting spectrum; (c) Difference, i.e., the residual of the subtraction of the fitting spectrum from experimental spectrum.

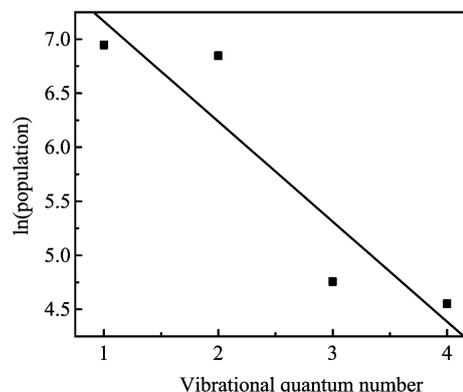


FIG. 3 Representative Boltzmann plot of the vibrational distribution of HCl from the $\text{CHCl}_2+\text{NO}_2$ reaction at the reaction time of 24 μs . The straight line is the best fit of the data to a Boltzmann distribution.

levels of $v=1-4$, respectively. The populations of HCl can be roughly fitted by the Boltzmann distribution with a vibrational temperature of $T_v=4641 \pm 705$ K as shown in Fig.3. The corresponding average vibrational energy is thus calculated to be about 13.4 ± 2.0 kJ/mol.

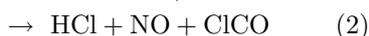
C. Identification of reaction channels

From the detected products CHClO , NO, CO, and HCl, the following possible reaction channels can be elu-

culated which are all thermodynamically feasible [25]:



$$\Delta H^\circ = -192.7 \text{ kJ/mol}$$



$$\Delta H^\circ = -191.2 \text{ kJ/mol}$$



$$\Delta H^\circ = -277.5 \text{ kJ/mol}$$

These channels are all exothermic and thus give rise to vibrationally excited products. Among the three reaction channels, channel (1) $\text{CHClO} + \text{ClNO}$ is indicated by both previous experimental [13] and previous theoretical studies [14]. In Timonen's experiment, they observed the products CHClO and NO which should be ascribed to the $\text{CHClO} + \text{ClNO}$ channel and the facile subsequent dissociation of ClNO [13]. As calculated by Li *et al.*, this is the most favorable channel [14]. Here, we also observed the formation of the products CHClO and NO , confirming further the existence of this channel. Also interestingly, two other species HCl and CO can be identified as primary reaction products from $\text{CHCl}_2 + \text{NO}_2$ due to the fact that the formation kinetics of HCl and CO are identical to the other two established primary products CHClO and NO as shown in Fig.1. The signal rise time is 24 μs for all the four products, indicating the same formation rate and thus the same origin. If HCl and CO are produced from secondary reactions, they should be formed with slower rates.

The explicit identification of HCl in the IR emission spectra confirms the previous experimental observation of HCl with a small amount. Two reaction channels (2) and (3) can both possibly yield HCl and this might be the reason why the vibrational state distribution of HCl is found not to obey Boltzmann distribution perfectly as shown in Fig.3. The finding of HCl as a reaction product of $\text{CHCl}_2 + \text{NO}_2$ indicates that the chlorinated hydrocarbon radical reactions should be important sources emitting the highly toxic and corrosive pollutants HCl in the related chemical processes such as atmospheric photochemistry, biofuel combustion, waste destruction, and smoking fire [15-17].

Here, CO is a newly detected product from which the possible reaction channel (3) can be deduced. CO was not detected neither experimentally nor predicted theoretically by previous studies. The reason why Timonen *et al.* did not detect the product CO is probably due to the fact that the sensitivity of their experimental system is not known for all possible reaction products, just as they claimed. Fortunately with the broad band technique TR-FTIR, some previously uncertain products HCl and CO can be identified, providing an effective method in detection of elementary reaction products complementary to mass spectrometry.

Concerning the reaction mechanism, it has been shown by Li's calculation that the major reaction channel (1) proceeds via a simple three-step addition elimi-

nation path, i.e., the initial association of CHCl_2 radical to NO_2 forming the nitro-adduct $\text{HCl}_2\text{C-NO}_2$ with no barrier, followed by isomerization to the nitrite-adduct $\text{H}_2\text{ClC-ONO}$, and the subsequent ClNO elimination from the nitrite adduct forming eventually $\text{CHClO} + \text{ClNO}$. Because the intermediates and transition states involved all lie below the reactants, the $\text{CHClO} + \text{ClNO}$ channel is suggested to be both thermodynamically and kinetically favorable. However, for the formation mechanisms of other products HCl and CO observed in our experiment, Li's calculation did not provide any information. We anticipate that these smaller fragment products HCl and CO should proceed with more complicated reaction mechanism differing from CHClO . Further theoretical investigations are being undertaken to address these issues.

IV. CONCLUSION

Step-scan TR-FTIR emission spectroscopy was used to characterize the products, channels and vibrational energy disposal of the multichannel free radical reaction of CHCl_2 with NO_2 . Vibrationally excited products of CHClO , NO , CO , and HCl are observed in the IR emission spectra and three possible reaction channels forming respectively $\text{CHClO} + \text{ClNO}$, $\text{HCl} + \text{NO} + \text{ClCO}$, and $\text{HCl} + \text{ClNO} + \text{CO}$ are therefore elucidated. In particular, the product CO is newly detected and the product HCl is identified explicitly to come from the $\text{CHCl}_2 + \text{NO}_2$ reaction, taking advantage of the sensitive detection of HCl and CO with TR-FTIR.

V. ACKNOWLEDGMENTS

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- [1] WMO Global Ozone Research and Monitoring Project, Report No.20, (1989).
- [2] W. Tsang, *Combust. Sci. Technol.* **74**, 99 (1990).
- [3] A. Violi, A. D'Anna, and A. D'Alessio, *Chemosphere* **42**, 463 (2001).
- [4] N. M. Donahue, *Chem. Rev.* **103**, 4593 (2003).
- [5] W. D. Chang and S. M. Senkan, *Environ. Sci. Technol.* **23**, 442 (1989).
- [6] V. D. Knyazev and I. R. Slagle, *J. Phys. Chem. A* **102**, 1770 (1998).
- [7] T. Faravelli, A. Frassoldati, and E. Ranzi, *Combust. Flame* **132**, 188 (2003).
- [8] P. J. Crutzen, *Annu. Rev. Earth Pl. Sc.* **7**, 443 (1979).
- [9] R. E. Baren, M. A. Erickson, and J. F. Hershberger, *Int. J. Chem. Kinet.* **34**, 12 (2002).

- [10] K. T. Rim and J. F. Hershberger, *J. Phys. Chem. A* **102**, 4592 (1998).
- [11] C. Y. Shi, F. Dong, S. Sun, H. Zhang, L. Guo, J. K. Feng, and F. A. Kong, *Chin. J. Chem. Phys.* **20**, 31 (2007).
- [12] J. X. Zhang, Z. S. Li, J. Y. Liu, and C. C. Sun, *Theor. Chem. Acc.* **117**, 579 (2007).
- [13] A. J. Eskola, W. D. Geppert, M. P. Rissanen, R. S. Timonen, and L. Halonen, *J. Phys. Chem. A* **109**, 5376 (2005).
- [14] J. X. Zhang, Z. S. Li, J. Y. Liu, and C. C. Sun, *J. Comput. Chem.* **27**, 661 (2006).
- [15] Y. B. Huang, Y. A. Yang, G. X. He, S. Hashimoto, and R. J. Gordon, *J. Chem. Phys.* **103**, 5476 (1995).
- [16] S. Kim, P. Klimecky, J. B. Jeffries, F. L. Terry, and R. K. Hanson, *Meas. Sci. Technol.* **14**, 1662 (2003).
- [17] A. A. Stec, T. R. Hull, K. Lebek, J. A. Purser, and D. A. Purser, *Fire Mater.* **32**, 49 (2008).
- [18] Q. H. Zhu, S. L. Huang, X. B. Wang, Z. Hao, Q. F. Zhang, J. R. Cao, X. J. Wu, N. Lv, S. X. Yao, and F. A. Kong, *Chin. J. Chem. Phys.* **6**, 87 (1993).
- [19] K. H. Liu, T. X. Xiang, W. Q. Wu, S. L. Zhao, and H. M. Su, *J. Phys. Chem. A* **112**, 10807 (2008).
- [20] M. Bilde, T. J. Wallington, C. Ferronato, J. J. Orlando, G. S. Tyndall, E. Estupinan, and S. Haberkorn, *J. Phys. Chem. A* **102**, 1976 (1998).
- [21] W. B. Tzeng, Y. R. Lee, and S. M. Lin, *Chem. Phys. Lett.* **227**, 467 (1994).
- [22] M. L. Ragains and B. J. Finlayson-Pitts, *J. Phys. Chem. A* **101**, 1509 (1997).
- [23] H. Niki, P. D. Maker, L. P. Breitenbach, and C. M. Savage, *Chem. Phys. Lett.* **57**, 596 (1978).
- [24] T. C. Xiang, K. H. Liu, S. L. Zhao, H. M. Su, F. A. Kong, and B. S. Wang, *J. Phys. Chem. A* **111**, 9606 (2007).
- [25] NIST webbook, <http://webbook.nist.gov/chemistry/>.