

Enhanced Formation of Ozone by the Addition of Chloropicrin (Trichloronitromethane) to Propene/NO/Air/Photoirradiation Systems

Shiro Hatakeyama,* Takashi Imamura, and Nobuaki Washida

Atmospheric Environment Division, National Institute for Environmental Studies,
16-2 Onogawa, Tsukuba, Ibaraki 305-0053

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The photolysis of chloropicrin in air at 1 atm was performed in a 6-m³ photochemical reaction chamber with a combination of Xe arc lamps and Pyrex filters as a light source. Phosgene was obtained as one of the main products with a yield of unity. No nitrosyl chloride was observed, which supports the C–N scission mechanism for the photolysis. Photochemical ozone formation was enhanced when chloropicrin was added to the propene/NO/air/photoirradiation system after the ozone concentration maximum had been reached. The ozone-formation factor for chloropicrin under the conditions employed was, however, estimated to be 0.25 mole of ozone formed per mole of the decomposed chloropicrin. This implies that the Cl atom, itself, contributes to the destruction of ozone rather than to the formation of ozone under the experimental conditions. NO₂ released from chloropicrin is the source of enhanced ozone. If the amount of chloropicrin as a soil fumigant increases, it can cause an increase of the ozone concentration in suburban and/or rural areas.

Chloropicrin (trichloronitromethane, CCl₃NO₂; hereafter abbreviated as CP) is a pesticide that is widely used in agriculture for soil fumigation prior to cultivation. Its production in Japan amounted to 8300 t in 1995.¹ Although it is usually applied below the soil surface, it can evaporate into the atmosphere. CP has a vapor pressure of about 40 Torr (1 Torr = 133.322 Pa) at 34 °C. Therefore, if it has sufficient photochemical reactivity in air, it can affect the degree of ozone formation in urban and suburban atmospheres. Photochemical ozone formation is currently a very common air-pollution issue.² Because of the very strict regulation of automobile exhaust, the air quality of Tokyo has improved compared with 20 years ago. However, recently, high concentrations of ozone have been reported in rural areas,³ such as the Gunma, Saitama, and Tochigi Prefectures, located in the Kanto Plain surrounding Tokyo. One obvious reason for this is the use of vehicles powered by internal-combustion engines. Another possible cause of high ozone concentrations is the application of soil fumigants.

Chloropicrin has unique characteristics in atmospheric chemistry. Because it is fully chlorinated, it is fairly unreactive with OH radicals. On the other hand, it can form both Cl atoms and NO₂. The reaction of Cl with O₃ is known to be the cause of the stratospheric ozone depletion induced by CFC's.⁴ Recently, we demonstrated the destruction of ozone by Cl atoms or Br atoms released from the photolysis of halocarbons by UV light.⁵ NO₂ can be a source of tropospheric ozone, which is assumed to be one of the greenhouse gases.

Recently, Carter et al.⁶ reported the effect of the presence of CP on photochemical ozone formation in a HC/NO_x/air/photoirradiation system. The photolysis of CP in air by light having a wavelength longer than 300 nm was

found to proceed by a mechanism more likely to be C–N scission (CCl₃NO₂ + *hν* → CCl₃ + NO₂) than the oxygen-assisted simultaneous formation of phosgene and nitrosyl chloride (CCl₃NO₂ + *hν* → Cl₂CO + ClNO), the latter mechanism having been proposed by Moilanen et al.⁷ Carter et al.⁶ also reported that the introduction of CP into a photochemical reaction of a hydrocarbon, or a mixture of hydrocarbons, with NO in air increased the formation of ozone to a large extent. This was regarded as being a clear indication that CP affects photochemical ozone formation in urban areas. However, CP was initially contained in their reaction systems. In most cases, soil fumigant is applied in areas far from big cities, which are sources of precursors of photochemical ozone. This is the situation of Tokyo and its surrounding area. Usually, photochemical ozone is formed before the air mass from big cities reaches such an area. Thus, it remains to be seen what happens when CP is added to the atmosphere after photochemical ozone has formed.

In the work reported here, we studied the photolysis of CP in air and the effect of introducing CP on photochemical ozone formation in a propene/NO/air/photoirradiation system following the attainment of the maximum ozone concentration. It was examined whether CP contributes to the enhancement of ozone. It was also examined which role the Cl atom plays, net ozone formation or net ozone destruction.

Experimental

A large-volume (6 m³) evacuable and bakable photochemical reaction chamber was used for all of the experiments. Details concerning this chamber were reported previously.⁸ Nineteen 1-kW Xe-arc lamps were used for photoirradiation. The light intensity, determined by the NO₂ photolysis rate (*k*₁), was 0.20 min^{–1}. The concentrations of the reactants and products were monitored by

means of an FT-IR (Fuji Electric, FIRIS-100Z) with 64 repeat scans at 1 cm⁻¹ resolution. Multi-reflection using 128 separate paths provided a 221.5-m path length. Ozone and NO/NO_x were continuously monitored with a chemiluminescent ozone analyzer (Monitor Labs Model 8410) and a chemiluminescent NO_x analyzer (Monitor Labs Model 8440). Since the NO_x analyzer has sensitivity to CP, only NO was monitored by the analyzer after introducing CP to the reaction system.

Chloropicrin (Wako) was used following trap-to-trap distillation. Propene (Takachiho, 99.5%) and NO (Nippon Sanso, ultra-pure grade) were used without further purification.

In CP photolysis experiments, 0.5–2.0 ppm of CP was introduced into the chamber, which contained air at 1 atm pressure. For photochemical ozone-formation experiments, the typical experimental procedure was as follows. After the chamber had been filled with purified air, propene (3.0 ppm) and NO (1.5 ppm), measured volumetrically using a capacitance manometer, were introduced into the chamber in a stream of pure nitrogen. Then, irradiation was initiated; photochemical ozone formed gradually and the maximum concentration was reached within 300 min. When the ozone concentration started to decrease, CP (0.2 to 6 ppm) was added to the reaction mixture.

Results and Discussion

1. Photolysis of Chloropicrin in Air by Xe Arc Radiation. The CP concentration decreased exponentially during irradiation under 1 atm of air. The decomposition rate of CP did not depend on the initial concentration of CP (0.5–2.0 ppm). Therefore, it can be concluded that CP decreases only by photolysis in this reaction system. The photodecomposition rate was determined to be $9.6 \times 10^{-4} \text{ min}^{-1}$. $J_{\text{CP}}/J_{\text{NO}_2}$ was 0.005. Figure 1 shows the IR spectra of the reactants (A), the reactants and products (B), and the products [spectrum was synthesized by subtraction] (C). Figure 1(C) indicates the presence of phosgene (Cl₂CO), ozone (O₃), nitrogen dioxide (NO₂), chlorine nitrate (ClONO₂), and nitryl chloride (ClNO₂). Nitrosyl chloride (ClNO) was not observed at any time. If CP decomposes to ClNO and phosgene, NO should accumulate, because the photolysis of ClNO is fast and neither peroxy radicals nor ozone oxidizing NO to NO₂ exist in the reaction system. The accumulation of NO was not observed. These results are consistent with the findings of Carter et al.,⁶ the mechanism of Molianen et al.⁷ can, therefore, be eliminated. As pointed out by Carter et al.,⁶ the simultaneous production of phosgene and nitrosyl chloride is unlikely using the wavelength range of the light source (> 300 nm) employed in this work.

The yield of phosgene was almost unity. According to the C–N scission mechanism, the CP-photolysis reaction pathway is as follows:

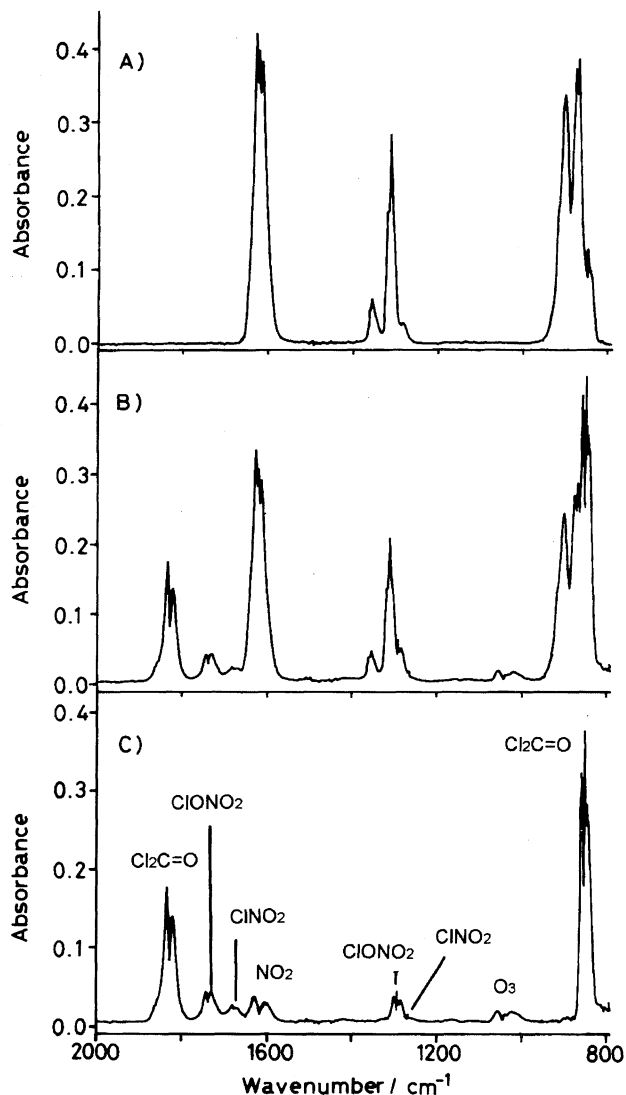
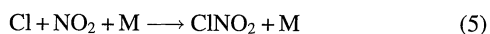
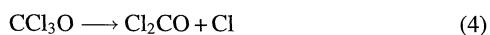
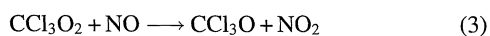
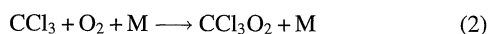
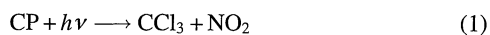
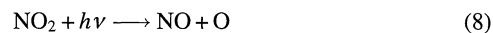


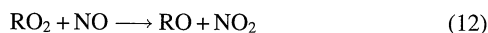
Fig. 1. FT-IR spectra are shown of (A) reactants, (B) mixture of reactants and products, and (C) products [the spectrum was synthesized by subtraction of spectrum (A) from spectrum (B)].



Reaction 6 contributes to ozone depletion, whereas reactions 8 and 9 contribute to ozone formation. Thus, it is not clear which process is more effective in the troposphere.

In the earth's atmosphere, there are many kinds of hydrocarbons. Cl atoms can react with HC's in a way similar to how OH radicals react with HC's, which can form peroxy radicals that enhance ozone formation in air by combination of the following reactions and reaction 8:





This effect should also be taken into account.

2. Additional Formation of Photochemical Ozone by Introducing Chloropicrin Following the Attainment of the Maximum Ozone Concentration. CP was added to the propene/NO/air photoirradiation system after the maximum ozone concentration had been reached following 300 min of irradiation. An ozone increase was observed when more than 3 ppm of CP was introduced. The addition of CP of less than 1 ppm did not show a clear increase, although a delay in the depletion rate of ozone was observed. Figure 2 shows the time profiles of ozone, NO, and $\text{NO}_x\text{-NO}$ in both the absence and presence of CP. A small increase in the ozone concentration can be seen in Fig. 2(B), following the introduction of CP.

Figure 3 shows the difference between the ozone concentration with CP ($[\text{O}_3]_{\text{CP}}$) and without CP ($[\text{O}_3]_{\text{ref}}$) as a function of time, following the introduction of CP. As the concentration of added CP increased, the formation of ozone increased. The ozone concentration increased linearly, particularly at the early stage. From the slopes of the plots in Fig. 3, the increase in the ozone concentration per unit time could be calculated (ozone increment rate). The ozone in-

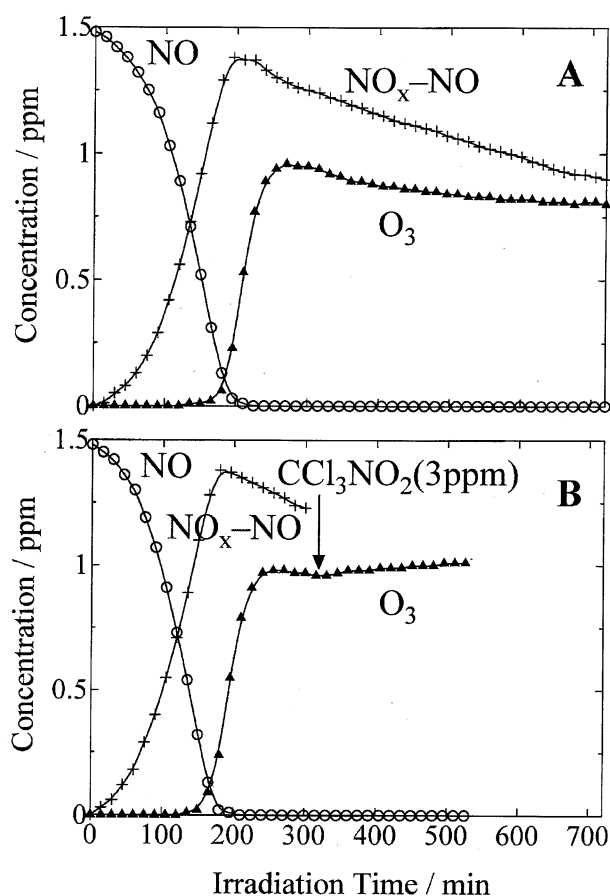


Fig. 2. Time profiles are shown for ozone, NO, and $\text{NO}_x\text{-NO}$ in both the absence (A) and presence (B) of added CP. Since the NO_x analyzer has sensitivity to CP, only NO was monitored by the analyzer after introducing CP.

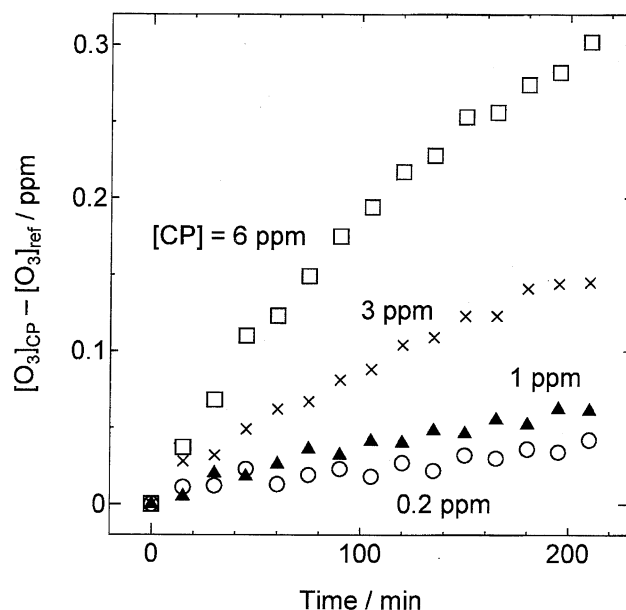


Fig. 3. The difference between the ozone concentration with CP ($[\text{O}_3]_{\text{CP}}$) and without CP ($[\text{O}_3]_{\text{ref}}$) is plotted versus the time following the introduction of CP.

crement rate was plotted versus the CP decrement rate; the resulting straight line is shown in Fig. 4. The slope is 0.25, which means that one molecule of ozone is formed for every four molecules of CP which react. Therefore, the formation of ozone from the photolysis of NO_2 , produced by the photolysis of CP, competes with the depletion of ozone by Cl atoms produced through reaction 4. If Cl contributes to the net formation of ozone, as discussed in the previous section (reactions 10–12 and reactions 8 and 9), the slope should be much larger than 0.25. Thus, chlorine produced from the photolysis of CP acts primarily as a destroyer of ozone. Reactions contributing to the formation and depletion of ozone in this system are as follows:

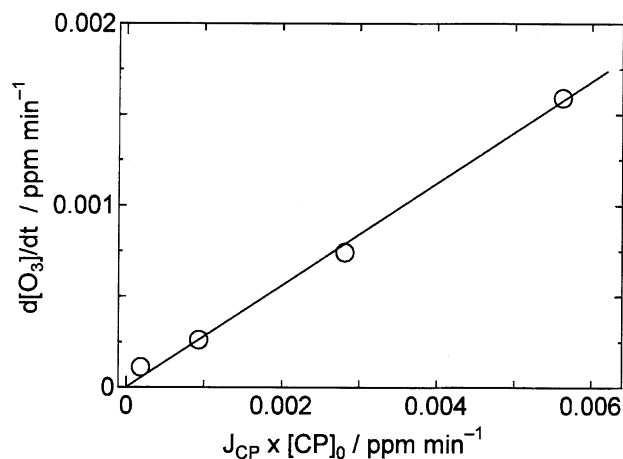


Fig. 4. The ozone increment rate is plotted versus the CP decrement rate.

Rate constant / cm³ molecule⁻¹ s⁻¹ ⁹

Here, formaldehyde (HCHO) is taken as a representative organic compound that can react with Cl atoms. CP is introduced into the reaction system at the point where most of the NO has already been converted to NO_x species. Because the concentration of NO is kept low (< 1 ppb), reaction 15 most likely does not contribute significantly to ozone production. Therefore, it can be concluded that the injection of CP at a later time in the photochemical reaction enhances the ozone formation totally, although chlorine atoms contribute to net destruction of ozone. NO₂ formed by the photolysis of CP in the reaction system is the main source of ozone enhancement observed after the introduction of CP. However, it is not clear yet if Cl atoms contribute to the net formation of ozone in the real atmosphere where NO is present at a significant concentration level.

3. Atmospheric Implications. The formation of photochemical oxidants and their long-range transport into the Kanto Plain during the summer season was investigated extensively by Ueda and co-workers.^{10,11} A highly polluted air mass, emitted in Tokyo in the morning, is transported north-westward by a sea breeze to the central and then northern part of the Kanto Plain, where it finally encounters the mountains surrounding the plain. On its way, the air mass passes Urawa (Saitama Prefecture, 25 km north-northwest of Tokyo) and Takasaki (Gunma Prefecture, 100 km northwest of Tokyo). The maximum daily ozone concentrations are observed at approximately 13:00 in Urawa, 18:00 in Takasaki, and much later in the mountainous area.¹¹ High concentrations of ozone are observed in Takasaki and the area close to the mountains, rather than in Tokyo. This occurs because photochemical

ozone forms during the transport process. These observations are consistent with our previous laboratory findings.

Because the number density of fields and paddies increases along the way from Tokyo to the areas beyond Urawa, the addition of CP, released from fumigated soil, to polluted air can increase the ozone concentration beyond an existing maximum. Therefore, if the amount of CP emanating from cultivated soil becomes larger, the degree of photochemical smog pollution can be increased.

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