

## ANALYSIS OF ATMOSPHERIC PHOTOCHEMISTRY AT NORTHERN LATITUDES

J. W. Bottenheim and O. P. Strausz

Hydrocarbon Research Center, Department of Chemistry, University of Alberta,  
Edmonton, Alberta T6G 2G2 (Canada)

Solar irradiation is the source of light for atmospheric photochemistry; since the total hours of sunshine and solar wavelength distribution vary markedly between an average summer and winter day at northern geographical areas a notable seasonal difference in photochemically initiated chemistry might be expected. We have recently undertaken a computer modeling study of the atmospheric chemistry of hypothetical clean and polluted air mixtures at 55°N latitude in order to examine this variation and to gain an insight in the potential for ozone and oxidant formation in these regions. The chemical model used for the calculations has been described in detail elsewhere;<sup>1</sup> in short, it includes the basic NO<sub>x</sub>-O<sub>3</sub> chemistry, the CH<sub>4</sub> + CO<sub>2</sub> cycle for clean air, and propylene and *n*-butane as model hydrocarbons for polluted air modeling. Heterogeneous reactions are not considered. The clean air model assumes constant mixing ratios for CH<sub>4</sub> (1.5 ppm) and CO (0.2 ppm), and the NO<sub>x</sub> (≡ NO + NO<sub>2</sub>) mixing ratio is kept at a daily average value of 6 ppb, balanced by an NO<sub>x</sub> source term and HNO<sub>3</sub> rainout; the polluted air parcel is favoured to yield high ozone levels since the ratio of the initial hydrocarbon level (1 ppm *n*-butane; 0.3 ppm propylene) and the NO<sub>x</sub> level (0.1 ppm NO, 0.05 ppm NO<sub>2</sub>) is ~10, under which conditions high oxidant formation is expected to take place.

Attention is focussed on the 4 photochemical reactions, listed in Table I, which are predominant in determining the atmospheric gas phase chemistry. The absorption rates of these reactions as a function of the time of day and season were estimated by the procedure of Schere and Demerjian,<sup>2</sup> using recent data for absorption cross sections and quantum yields.

For summer conditions the wavelength dependent albedo factors from ref. 2 were used, while during the winter the albedo factor was set at 75% to reflect the presence of snow cover on the ground.

Table I. Important atmospheric photochemical reactions and their specific absorption rates during solar noon at 55°N latitude.

Reaction	Specific absorption rate (min <sup>-1</sup> )	
	Summer	Winter
(1) NO <sub>2</sub> + hν → NO + O( <sup>3</sup> P)	0.47	0.17
(2) O <sub>3</sub> + hν → O <sub>2</sub> + O( <sup>1</sup> D)	1.8 × 10 <sup>-3</sup>	5.3 × 10 <sup>-5</sup>
(3) HONO + hν → NO + HO	0.15	0.051
(4) a. CH <sub>2</sub> O + hν $\xrightarrow{O_2}$ CO + 2HO <sub>2</sub>	2.4 × 10 <sup>-3</sup>	4.1 × 10 <sup>-4</sup>
b. RCHO + hν $\xrightarrow{O_2}$ RCO <sub>3</sub> + HO <sub>2</sub> (R = CH <sub>3</sub> )	3.4 × 10 <sup>-4</sup>	3.9 × 10 <sup>-5</sup>
1. <u>NO<sub>2</sub> + hν → NO + O(<sup>3</sup>P)</u>		

This reaction governs the rate of photochemical ozone formation and is a prominent feature of the so-called photostationary state equation

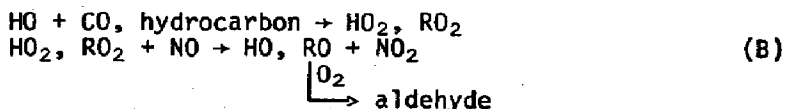
$$[O_3] = \frac{k_1[NO]}{k_5[NO_2]} \quad (A)$$

involving the title reaction and reaction 5:  $NO + O_3 \rightarrow NO_2 + O_2$ . From Table I  $k_1$  (summer)/ $k_1$  (winter)  $\approx 3$ , while  $k_5$  (summer)/ $k_5$  (winter)  $\approx 2$  under representative Alberta conditions. Consequently, the difference between average ozone levels during summer and winter should be relatively small provided relation A is applicable and there are no major variations in the  $(NO_2)/(NO)$  ratio. Our calculations suggest that in clean summer air the  $(NO_2)/(NO)$  ratio is to some extent influenced by the radical chemistry evolving from the  $CH_4$ - $CO_2$  cycle and  $(O_3)_{\text{summer}}/(O_3)_{\text{winter}} \approx 2$ . However, the rise in daytime ozone towards a maximum shortly after solar noon is directly related to the daytime variation in  $k_1$ ; in fact, in clean air when the average  $NO_x$  mixing ratio is of the order of a few ppb, or less, the  $(NO_2)/(NO)$  ratio *decreases* towards a midday *minimum* due to reaction 1. When little or no sunshine is available most of the  $NO_x$  consists of  $NO_2$  since any  $NO$  from natural sources is titrated by  $O_3$  via reaction 5.

Our hypothetical polluted air mixture is much richer in  $NO_x$  which effectively titrates background  $O_3$ . As a result the  $(NO_2)/(NO)$  is the predominant factor in determining  $O_3$  levels; high ozone levels are predicted only after conversion of a major portion of  $NO$  to  $NO_2$ , largely accelerated by free radical chemistry. Our calculations suggest that high ozone levels will be produced during the summer afternoon but not during the winter. The latter result is due to a combination of the slower  $NO \rightarrow NO_2$  conversion rate during the winter<sup>3</sup> and the much smaller amounts of available sunshine.

## 2. $O_3 + hv \rightarrow O(^1D) + O_2$

The remaining 3 reactions indirectly influence atmospheric ozone levels since they are primary sources of the free radicals that can increase the  $(NO_2)/(NO)$  ratio in equation A via the following chain:



The photolysis of  $O_3$  to yield  $O(^1D)$  atoms, a major primary source of  $HO$  radicals via the ensuing reaction  $O(^1D) + H_2O \xrightarrow{k_6} 2HO$ , is now known to occur only for  $\lambda \leq 3150 \text{ \AA}$ . During the winter at  $55^\circ N$  latitude solar radiation at this wavelength region is virtually nil and hence  $k_2(\text{summer})/k_2(\text{winter})$  is very large (Table I). Since reaction 2 is the only important primary radical source in clean air (photolysis of aldehydes being minor, *vide infra*) a large difference between summer and winter radical concentrations is predicted, see Figure 1. However, the chain length of  $HO$  radicals remains unchanged at 2 steps. Hence the influence of the free radicals on the  $(NO_2)/(NO)$  ratio becomes negligible during the winter. In polluted air reaction 2 is probably a less important primary source for  $HO$  radicals compared to reaction 3, and the drop in  $HO$  levels during the winter is less dramatic.

## 3. $HONO + hv \rightarrow HO + NO$

In principle this reaction is an important source of  $HO$  radicals, provided a route for  $HONO$  formation other than the radical recombination of  $HO + NO$  (reaction 7) is present. However, it is now well established that the homogeneous reaction  $NO + NO_2 + H_2O \rightarrow 2HONO$  (8) is extremely inefficient, and hence  $HONO$  functions mainly as a temporary sink and not as a source of  $HO$  radicals in clean air. As a result the  $HONO$  concentration is predicted to increase during summer days as long as the  $HO$  concentration increases. However, during the winter  $HO$  formation initiated by reaction 2 is so slow

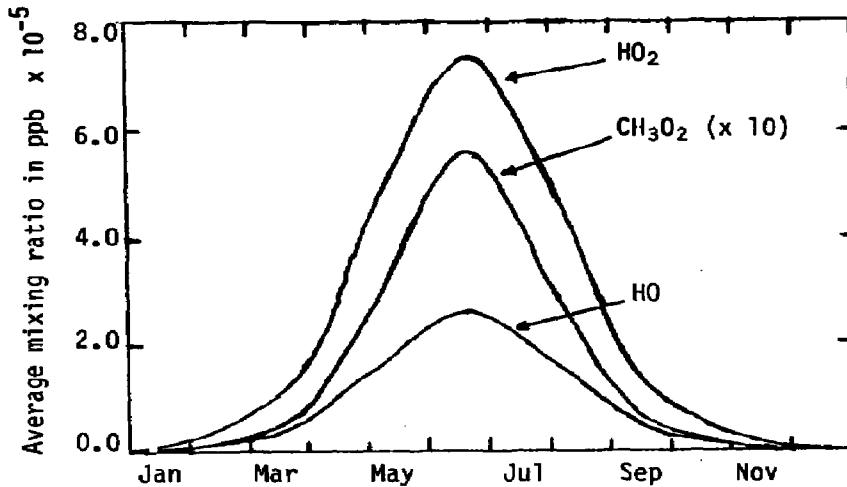
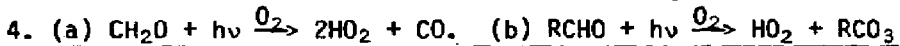


Figure 1.  
Theoretical annual variation in average free radical mixing ratio at 55°N latitude.

that the rate of reaction 7 becomes comparable with that of reaction 3 and our calculations show that during dawn and dusk reaction 3 is a true source of the few HO radicals that are produced. In polluted air reaction 3 is probably an important source of HO radicals at all times since the rate of reaction 8 is likely to be enhanced by heterogeneous effects.



This final set of important photochemical reactions in atmospheric chemistry is mainly important in polluted air. Reaction 4a is formally a primary source of  $\text{HO}_2$  radicals in clean air; since there are no obvious natural sources of  $\text{CH}_2\text{O}$ , its formation has to be attributed to oxidation reactions involving the  $\text{CH}_3\text{O}_2$  radical which is very low in concentration (Figure 1). Hence the predicted levels of  $\text{CH}_2\text{O}$  are very low and  $\text{CH}_2\text{O}$  can be more properly considered as a transfer station between  $\text{CH}_3\text{O}_2$  and  $\text{HO}_2$  radicals. In polluted air aldehydes are usually present from polluting sources (e.g. automobile exhaust) and reactions 4 are essential primary sources of peroxy radicals. These radicals not only influence the  $(\text{NO}_2)/(\text{NO})$  ratio via scheme B and hence the ozone concentration, but are also precursors of the peroxy nitrates (PAN, PNA), other obnoxious oxidants. The more than five-fold decrease in the efficiency of reactions 4 in the winter is due to the fact that insufficient amounts of high energy solar radiation are available. While the lower HO concentration during the winter appears to be compensated for to a certain extent by a large increase in the radical chain length, the peroxy radical chain length is much less affected and hence we conclude that the slower rate of  $\text{NO} \rightarrow \text{NO}_2$  conversion in polluted air during the winter is mainly related to the decrease in the rates of reaction 4.

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