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EIGIL HESSTVEDT
Institute of Geophysics, University of Oslo

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A photochemical model is used to study the chemistry of a mixture of air, NO_x, and C_2H_4. Mixing ratios from 10^{-8} to 10^{-4} are assumed for the two pollutants. It is shown that if the mixture contains more NO_x than C_2H_4, then no formation of oxidants and no conversion of NO_x to HNO_2 or HNO_3 occur. If, on the other hand, there is more C_2H_4 than NO_x, then O_3, H_2O_2, CH_2O, and CO increase to levels markedly above the natural background levels. A major part of the NO_x is converted to HNO_2 and, to a lesser degree, to HNO_3. Maximum production of O_3 is found to occur for a C_2H_4/NO_x ratio of about 20:1.

E. Hesstvedt, Institute of Geophysics, University of Oslo, P.O.Box 1022, Blindern, Oslo 3, Norway

INTRODUCTION

Photochemical models have often been used to simulate smog-formation in air polluted with nitrogen oxides and hydrocarbons. In these models the time variation of pollutants such as NO, NO_2, O_3, and hydrocarbons has been computed, and the results have been compared to laboratory experiments and to observations taken in urban air with similar characteristics. For some of the more recent models the agreement is reasonable. Such models should therefore be considered as most useful means by which to study the photochemistry of smog formation.

The present work is an attempt to simulate the photochemistry in air polluted with various quantities of nitrogen oxides and ethylene. Particular attention is given to mixtures leading to concentrations of O_3, H_2O_2, CO, CH_2O, HNO_2, and HNO_3 well above their normal atmospheric values. As a general result it is found that production of these components depends not only upon the concentrations of the two primary pollutants, but even more strongly upon the ratio of their concentrations. The highest ozone concentrations are expected when there is 10–30 times more ethylene than nitrogen oxides in the mixture. Generally speaking, the production of secondary pollutants is favoured when there is more ethylene than nitrogen oxides in the mixture.

1. THE PHOTOCHEMICAL MODEL

25 chemical components are considered in the model. These are assumed to react with each other in accordance with the reactions listed in Table 1. On this basis we may compute the composition of the air as a function of time. As external conditions we have taken the solar radiation at 60° latitude at equinox, a number density (M) of 2.5×10^{19} cm^{-3} and a surface temperature appropriate for the season ($+17°C$ in summer, $0°C$ in winter). The column density of O_2 is taken as 4.5×10^{24} cm^{-2},

Table 1. Reactions and reaction rate coefficients used in the model. Values given for photodissociations refer to 60° latitude, summer, at noon

R1	$O + O_2 + M \rightarrow O_3 + M$	$1.1 \times 10^{-34} \exp(510/T)$
R2a	$O_3 + h\nu(\lambda > 310 \text{ nm}) \rightarrow O(^3P) + O_2$	1.4×10^{-4}
R2b	$O_3 + h\nu(\lambda < 310 \text{ nm}) \rightarrow O(^1D) + O_2$	7.6×10^{-6}
R3	$O(^1D) + M \rightarrow O(^3P) + M$	5.9×10^{-11}
R4	$O(^1D) + H_2O \rightarrow 2 HO$	3.5×10^{-10}
R5	$H + O_2 + M \rightarrow HO_2 + M$	$2.1 \times 10^{-32} \exp(290/T)$
R6	$HO + H_2O_2 \rightarrow HO_2 + H_2O$	$1.7 \times 10^{-11} \exp(-910/T)$
R7	$HO + CO \rightarrow CO_2 + H$	1.3×10^{-13}
R8	$H_2O_2 + h\nu \rightarrow 2 HO$	1.1×10^{-6}
R9	$O + H_2O_2 \rightarrow HO_2 + HO$	$2.75 \times 10^{-12} \exp(-2125/T)$
R10	$2 HO_2 \rightarrow H_2O_2 + O_2$	$3 \times 10^{-11} \exp(-500/T)$
R11	$HO_2 + O_3 \rightarrow HO + 2 O_2$	$10^{-13} \exp(-1250/T)$
R12	$HO + H_2 \rightarrow H_2O + H$	$10^{-10} \exp(-2950/T)$
R13	$NO + HO_2 \rightarrow NO_2 + HO$	2×10^{-13}
R14	$NO + O_3 \rightarrow NO_2 + O_2$	$9 \times 10^{-13} \exp(-1200/T)$
R15	$NO + NO_3 \rightarrow 2 NO_2$	8.7×10^{-12}
R16	$NO + HO \rightarrow HNO_2$	4×10^{-12}
R17	$NO + NO + O_2 \rightarrow 2 NO_2$	$3.3 \times 10^{-39} \exp(530/T)$
R18	$NO_2 + HO \rightarrow HNO_3$	5×10^{-12}
R19	$NO_2 + h\nu \rightarrow NO + O$	4.6×10^{-3}
R20	$NO_2 + O \rightarrow NO + O_2$	9.1×10^{-12}
R21	$NO_2 + HO_2 \rightarrow HNO_2 + O_2$	2×10^{-14}
R22	$NO_2 + O_3 \rightarrow NO_3 + O_2$	$1.1 \times 10^{-13} \exp(-2450/T)$
R23	$NO_2 + O + M \rightarrow NO_3 + M$	10^{-31}
R24	$NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$	$2.3 \times 10^{-13} \exp(-1000/T)$
R25	$NO_2 + NO_3 \rightarrow N_2O_5$	8.5×10^{-12}
R26	$NO_3 + h\nu \rightarrow NO + O_2$	6.4×10^{-2}
R27	$N_2O_5 + M \rightarrow NO_2 + NO_3 + M$	$2.2 \times 10^{-5} \exp(-9780/T)$
R28	$HNO_2 + HO \rightarrow NO_2 + H_2O$	6.8×10^{-12}
R29	$HNO_2 + h\nu \rightarrow NO + HO$	4.6×10^{-4}
R30	$HNO_3 + h\nu \rightarrow NO_2 + HO$	7.6×10^{-8}
R31	$HNO_3 + HO \rightarrow NO_3 + H_2O$	1.3×10^{-13}
R32	$C_2H_4 + HO \rightarrow CH_2O + CH_3$	3×10^{-12}
R33	$C_2H_4 + O \rightarrow CH_3 + CHO$	5×10^{-13}
R34	$C_2H_4 + O_3 \rightarrow CH_3O_2 + CHO$	$7.8 \times 10^{-15} \exp(-2400/T)$
R35a	$CH_2O + h\nu \rightarrow CHO + H$	1.3×10^{-5}
R35b	$CH_2O + h\nu \rightarrow CO + H_2$	3.7×10^{-5}
R36	$CH_2O + HO \rightarrow HO_2 + \cdots$	1.4×10^{-11}
R37	$CH_3 + O_2 \rightarrow CH_3O_2$	4.3×10^{-13}
R38	$CHO + O_2 \rightarrow CO + HO_2$	1.7×10^{-13}
R39	$CH_3O + O_2 \rightarrow CH_2O + HO_2$	3×10^{-18}
R40	$CH_3O_2 + NO \rightarrow HNO_2 + CH_2O$	$1.4 \times 10^{-12} \exp(-500/T)$
R41	$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	$3.3 \times 10^{-12} \exp(-500/T)$
R42	$2 CH_3O_2 \rightarrow 2 CH_3O + O_2$	6.8×10^{-14}
R43	$2 CH_3O_2 \rightarrow CH_3O_2H + CH_2O_2$	6.8×10^{-14}
R44	$CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2$	6.7×10^{-14}
R45	$CH_3O_2H + h\nu \rightarrow CH_3 + HO$	3.4×10^{-6}
R46	$CH_3O_2H + HO \rightarrow CH_3O_2 + H_2O$	$4 \times 10^{-13} T^{1/2} \exp(-600/T)$

while the column density of O_3 is assumed to vary with the season. The following values are chosen: summer: 9.3×10^{18} cm^{-2}, autumn: 7.8×10^{18} cm^{-2}, early winter: 8.1×10^{18} cm^{-2}, late winter: 1.0×10^{19} cm^{-2}, and spring: 1.1×10^{19} cm^{-2}. As initial values for the chemical

components (except NO, NO_2, and C_2H_4) we have taken normal atmospheric values. However, the results do not depend critically upon this choice.

For C_2H_4 and NO_x (the sum of NO and NO_2), the initial values are varied over a very wide range. Mixing ratios of 10^{-8}, 10^{-7}, 10^{-6}, 10^{-5}, and 10^{-4} are used, and this gives 25 combinations.

The formation of O_3 is, in most cases, determined by the ratio of NO_2 to NO. The initial value of this ratio is therefore an important parameter, which strongly influences the time scale of oxidant formation (see Fig. 1). We have considered two values of the ratio, 1:3 and 1:1; the former is considered as being more realistic.

Because of absorption of UV-light by O_2 and O_3, only wavelengths above about 290 nm are of interest in a study of the photo-

chemistry at the earth's surface. Solar fluxes as well as absorption cross-sections of O_2 and O_3 are taken from Ackerman (1970). Absorption cross-sections for other components have been compiled and reviewed by Hudson & Kieffer (1974). Reaction rate coefficients have been compiled and reviewed by Garvin & Hampson (1974). Data recommended by these authors are used.

Dissociation rate coefficients are computed every minute following the varying elevation of the sun.

$O(^3P)$, $O(^1D)$, HO, H, N_2O_5, CH_3, CH_3O, and CHO have lifetimes shorter than one second. We may therefore assume these components to be in photochemical equilibrium with their chemical environment. Referring to Table 1, we may describe their production and destruction by the following list:

Production		Destruction
R2b	$O(^1D)$	R3, R4
R2a, R19	$O(^3P)$	R1, R20, R33
R4, R8, R11, R13, R29	HO	R7, R16, R18, R28, R32, R36
R7, R12, R35a	H	R5
R25	N_2O_5	R27
R32, R33	CH_3	R37
R41, R42	CH_3O	R39
R33, R34, R35a	CHO	R38

The chemistry of O_2 and H_2O is so slow in our model that we may ignore it. For these components typical atmospheric values are assumed.

The remaining 17 components have, at least in some of the 25 alternatives of the model, a lifetime which is more than one second, i.e. more than one tenth of our time step, which is taken to be 10 seconds. For these components we have to integrate simultaneous differential equations of the form

$$\frac{d\,[X]}{d\,t} = P_x - Q_x \cdot [X]$$

where P_x is the production and $Q_x \cdot [X]$ is the destruction term of the component X. P_x and Q_x do not have [X] as a factor, but may in many cases be implicit functions of [X] through the complex chemistry of the system as a whole. If P_x and Q_x vary only in significantly over the time step, our equations are particularly easy to integrate:

$$[X]_{t+\Delta t} = [X]_e + ([X]_t - [X]_e) \cdot \exp(-Q_x \cdot \Delta t)$$

where $[X]_e = P_x/Q_x$, or alternatively

$$[X]_{t+\Delta t} = [X]_t + (P_x - Q_x \cdot [X]) \cdot \Delta t$$

if $P_x \gg Q_x \cdot [X]$. The reactions determining these 14 components are:

Production		Destruction
R19	O_3 (odd oxygen)	R14, R20, R22, R23, R33, R34
R5, R36, R38, R39	HO_2	R10, R11, R13, R21
R10	H_2O_2	R6, R8, R9
R19, R20, R29	NO	R13, R14, R15, R16, R17, R40, R41
R13, R14, R28, R41	NO_2	R19, R20, R21
R22, R23	NO_3	R15, R26
R16, R21, R40	HNO_2	R28, R29
R18	HNO_3	R30, R31
	C_2H_4	R32, R33, R34
R34, R37	CH_3O_2	R40, R41, R42, R43, R44
R32, R39, R40	CH_2O	R35a, R35b, R36
R43	CH_2O_2	
R43, R44	CH_3O_2H	R45, R46
R35b, R38	CO	R7

2. RESULTS

On the basis of the reactions listed in Table 1 we have computed the composition of the 25 gas mixtures as a function of time. Computations are made for five different times of the year: late winter, spring, summer, autumn, and early winter. Some computations cover a period of 24 hours; however, the night-time chemistry does not offer much of interest for our problem. Most of our computations therefore cover a four-hour period around noon, from 10 a.m. to 2 p.m.

It clearly appears from our models that they fall into two classes: if there is initially more ethylene than nitrogen oxides in the mixture, then a production of oxidants (O_3 and/or H_2O_2) takes place. If, on the other hand, there are more nitrogen oxides than ethylene in the mixture, then no such formation takes place. On the contrary, the concentration is in many cases reduced to values well below normal atmospheric values. This division into two classes is independent of the initial value of the ratio NO_2/NO. It does, however, to some extent depend on season: in winter only one of the 25 models gives ozone values above normal.

The lifetime of O_3 varies from a fraction of a second to half an hour. In most cases the lifetime is shorter than three minutes. For a qualitative discussion we may therefore assume

that O_3 is not very far from photochemical equilibrium. The expression

$$[O_3] \approx J_{NO_2} \cdot [NO_2]/(k_{14} \cdot [NO] + k_{34}[C_2H_4])$$

may serve as a good first approximation. The ethylene term in the denominator only becomes significant when the C_2H_4/NO_x ratio is large, above about 100.

It is the aim of this paper to study in particular gas mixtures which lead to formation of oxidants well above normal atmospheric values.
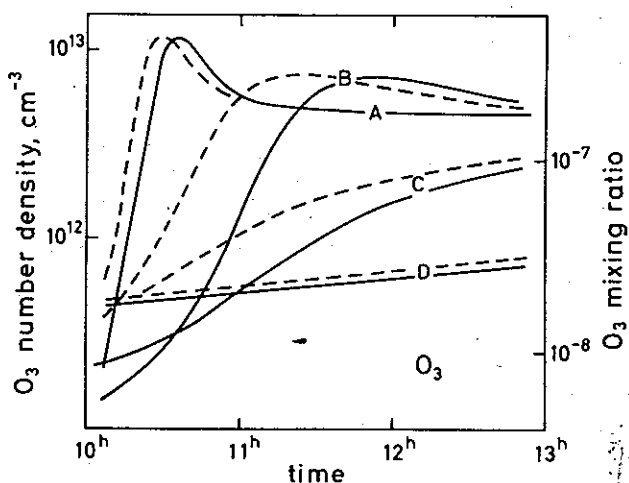

Fig. 1. Formation of O_3 in a C_2H_4-NO_x-air mixture (60° latitude, summer $[C_2H_4]/[NO_x] = 15$). Curves A, B, C, and D refer to 10^{-5}, 10^{-6}, 10^{-7}, and 10^{-8}, respectively for mixing ratio of NO_x. Results for $[NO_2]/[NO_x] = 0.25$ at the beginning of the experiment are shown by solid curves, while dashed curves refer to a value of 0.5 for this ratio.
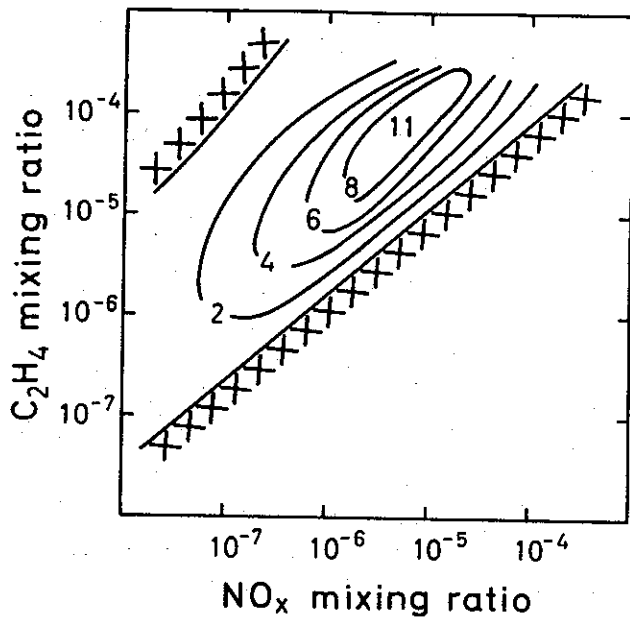
Fig. 2. Maximum values of O_3 (number density $\times 10^{-12} cm^{-3}$) during a four-hour period around noon (summer) for different combinations of mixing ratios of NO_x and C_2H_4.

Our attention will therefore be focused on the cases when the C_2H_4/NO_x ratio is greater than 1. Already the results from our 25 models indicate that the highest concentrations of O_3 occur when the C_2H_4/NO_x ratio is between 10 and 100. In order to be more specific about the conditions which lead to the highest densities of O_3, we have computed a series of models with intermediate values of the C_2H_4/NO_x ratio. The results are shown in Fig. 2. The computations refer to 60° latitude, summer, and the diagram shows the highest O_3 number densities (unit 10^{12} cm^{-3}) within a four-hour period around noon. The diagram clearly demonstrates that the O_3 formation primarily depends on the C_2H_4/NO_x ratio. The highest values are found when this ratio is 15:1. For other values of the ratio the O_3 formation is smaller. The requirements seem to be more restrictive on the lower side; values below 2:1 will hardly result in significant increase in O_3. The same seems to be true if the ratio is greater than about 400, but this figure depends to some extent on the absolute densities of the two pollutants.

These results agree qualitatively with ex-

perimental work (for reference, see Schuck, Pitts & Wan 1966). Several investigators have pointed out that maximum oxidant formation or maximum eye irritation occur for a certain value (between 10 and 100, approximately) of the hydrocarbon/NO_x ratio. When this ratio is smaller than about 5 or higher than about 200, oxidant formation and eye irritation become insignificant.

While experiments give us very little information about the various chains of reactions which lead to O_3 formation, our model provides an opportunity to weigh the different reactions against each other. Of primary importance is a comparison of the reactions which convert NO to NO_2. We find that R13, R14, and R41 dominate over the other candidates we have considered. However, the effect of reaction R14 is rapidly counteracted by reactions R19 and R20, through which NO_2 is quickly recycled to NO. The net effect of these reactions is therefore likely to be small
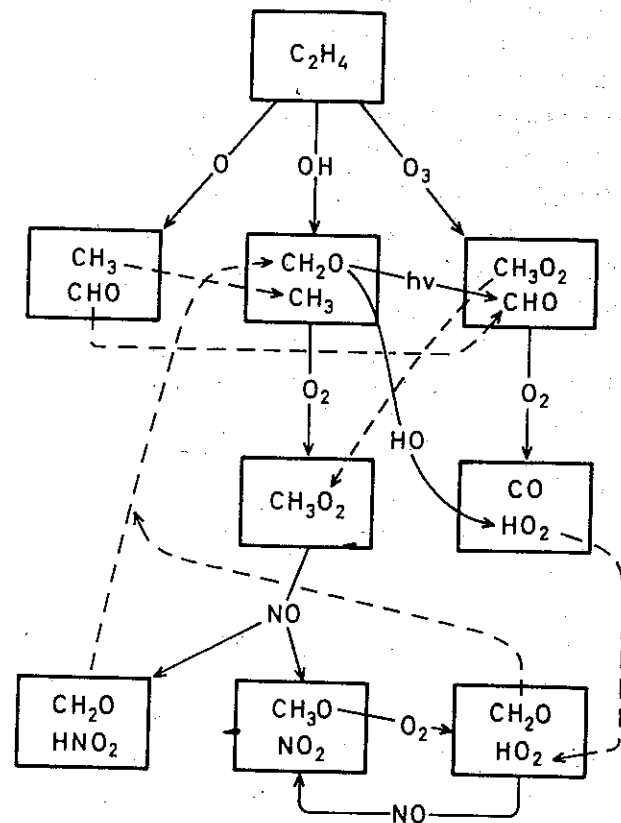

Fig. 3. Flow diagram for photochemical distintegration of C_2H_4, leading to conversion of NO to NO_2.
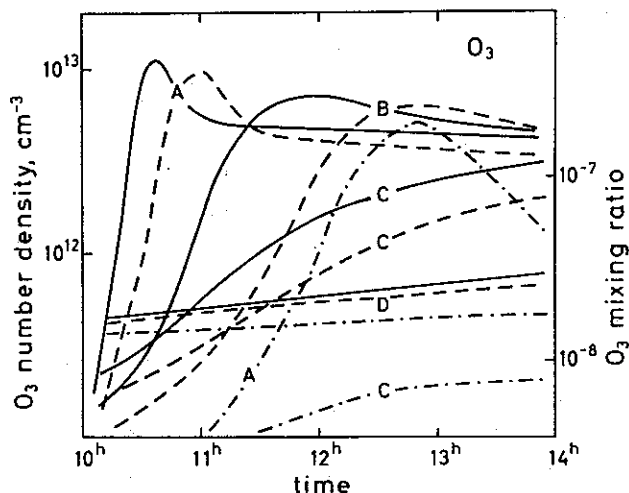
Fig. 4. Formation of O_3 in a C_2H_4-NO_x-air mixture (60° latitude, $[C_2H_4]/[NO_x]=15$). Curves A, B, C, and D refer to 10^{-5}, 10^{-6}, 10^{-7}, and 10^{-8}, respectively, for the mixing ratio of NO_x. Solid curves are for summer, dashed curves for equinox, and dash-dotted curves for winter.

compared to the effect of reactions R13 and R41. The latter reaction is rapidly followed by reaction R39, whereby HO_2 is formed. This adds to the importance of reaction R13.

This leads us to a closer examination of the production and destruction of HO_2 and CH_3O_2. We find that these components are produced by daughter products of ethylene: HO_2 is primarily formed through reactions R5, R36, R38, and R39, while CH_3O_2 is formed through reactions R34 and R37. None of these reactions involve nitrogen. On the other hand, HO_2 is primarily destroyed through reactions R13 and R21, while the destruction of CH_3O_2 mainly proceeds through reactions R40 and R41. These four reactions involve nitrogen oxides. Thus conversion of NO to NO_2 is favoured by a high ethylene content, while a high NO_x content has the opposite effect. A critical value of the ratio C_2H_4/NO_x exists, such that O_3 reaches high levels when the ratio is above this critical value, while the opposite is true when the ratio is smaller. We have determined this critical value to be approximately 1 or perhaps a little higher, say 5.

When the ratio C_2H_4/NO_x reaches very high values, larger than several hundred, our reasoning no longer holds. The main reason for this

is that O_3 is no longer proportional (approximately) to the ratio NO_2/NO, since reaction R34 gradually takes over as the most important loss reaction for O_3. In addition, NO_2 formed from NO is rapidly converted to HNO_2 through reaction R21. As a logical consequence of this decrease in O_3 with very low and very high values of the ratio C_2H_4/NO_x, there must exist a value for this ratio which gives a maximum O_3 content. We have determined this value of the ratio to be 15:1.

The complex chemistry through which CH_3O_2 and HO_2 are formed as daughter products of C_2H_4 is shown schematically in Fig. 3. The two important reactions which convert NO to NO_2 are also included.

We have already mentioned that the formation of O_3 depends to some extent on the season. Under winter conditions ozone is reduced well below background levels for al-
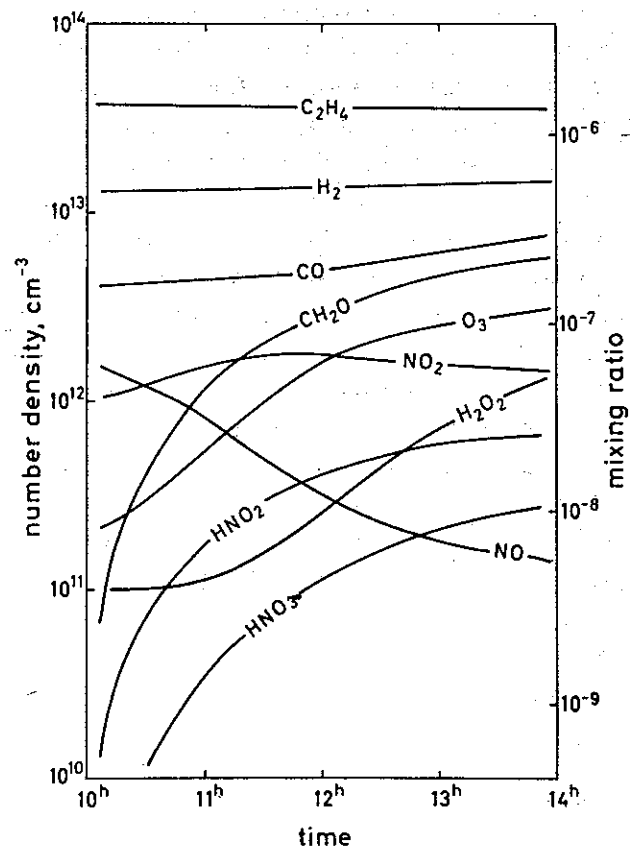

Fig. 5. Composition of a C_2H_4-NO_x-air mixture exposed to solar radiation (60° latitude, summer $[C_2H_4]/[M]=1.5\times10^{-6}$, $[NO_x]/[M]=10^{-7}$ at the beginning of the experiment).
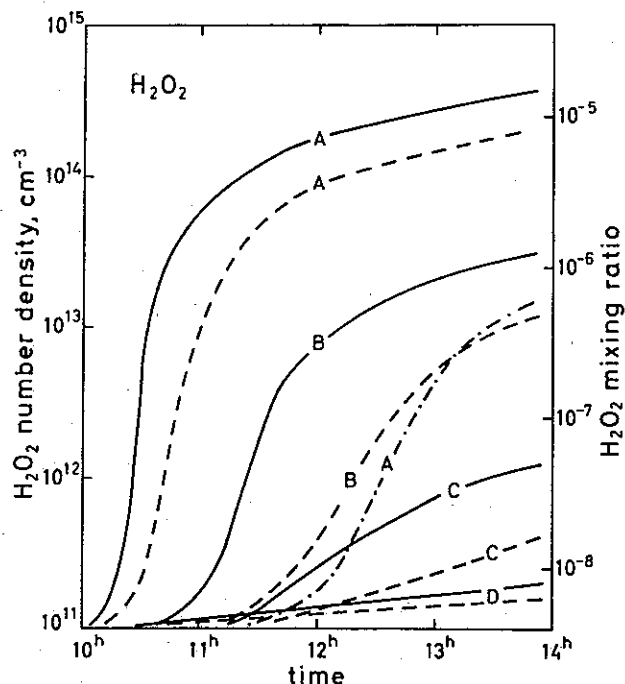
Fig. 6. Formation of H_2O_2 in a C_2H_4-NO_x-air mixture (60° latitude, $[C_2H_4]/[NO_x]=15$). Notations as in Fig. 4.

most all our gas mixtures. The obvious reason for this is the lack of ultraviolet radiation due to low sun. This results in a slow photodissociation of NO_2, which is the source of odd oxygen. On the other hand, computations for summer and equinox give, for certain C_2H_4/NO_x ratios, high ozone values. This is illustrated in Fig. 4, which shows the results of four hours' integration around local noon for 60° latitude and for a C_2H_4/NO_x ratio of 15:1.

It was shown above that the peak value of O_3 is almost independent of the degree of pollution, as long as the C_2H_4/NO_x ratio remains the same. However, this does not mean that the degree of pollution is unimportant for smog formation in the atmosphere. According to Fig. 4, it takes 22 minutes to reach an O_3 level of 2×10^{12} molecules/cm³, when the mixing ratios of C_2H_4 and NO_x are 1.5×10^{-4} and 10^{-5}, respectively, while it takes 66 minutes to reach the same level when the mixing ratios are 1.5×10^{-5} and 10^{-6}, and 150 minutes when the mixing ratios are 1.5×10^{-6} and 10^{-7}. The time required to reach high O_3

levels goes up by a factor of 2.5–3 when the degree of pollution is reduced by a factor of 10. This is important to have in mind when results from box models are applied to the real atmosphere. If the pollutants are emitted from a single source, high concentrations will persist only for a short time. A realistic simulation of a real case must also include dilution of the pollutants due to turbulent motion of the air.

Up to now we have primarily discussed the formation of O_3 in our models. However, also the other chemical components undergo developments which are quite interesting. Fig. 5 is presented as an example of the development in a mixture which leads to high O_3. The mixing ratios of C_2H_4 and NO_x are 1.5×10^{-6} and 10^{-7}, respectively. Generally speaking, most of the free carbon goes to CO and CH_2O, while HNO_3 and, in particular, HNO_2 gradually takes over a considerable fraction of the odd nitrogen. However, rather than discussing the complex development of each model, we shall consider the chemical components one by one:

a) *Hydrogen peroxide, H_2O_2*
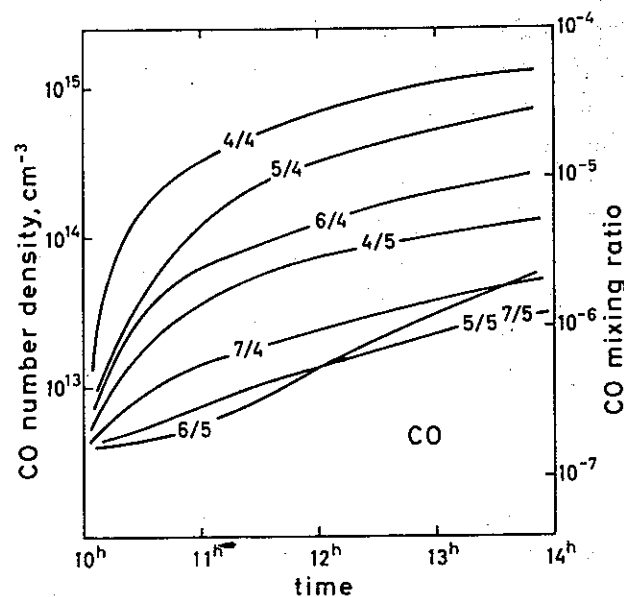
H_2O_2 is formed through reaction R10. High

Fig. 7. Formation of CO in a C_2H_4-NO_x-air mixture (60° latitude, summer. The notation m/n means the mixing ratios of NO_x and C_2H_4 are 10^{-m} and 10^{-n}, respectively).
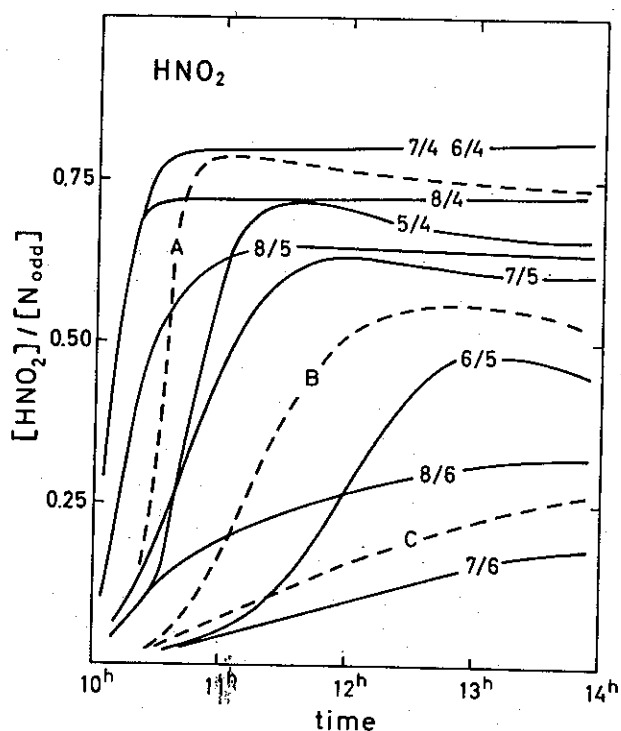
Fig. 8. Formation of HNO_2 in a C_2H_4-NO_x-air mixture, given as fraction of total add N. (60° latitude, summer). The significance of the notations m/n, A, B, and C is explained in Figs. 1 and 7.

concentrations of H_2O_2 therefore depend on high concentrations of HO_2. Since this is also true for O_3, the two oxidants H_2O_2 and O_3 will develop in the same models: also for H_2O_2 the highest concentrations will occur for $[C_2H_4]/[NO_x]=15:1$. As shown in Fig. 5, the amounts of H_2O_2 depend very strongly on the degree of pollution. For an ethylene mixing ratio of 1.5×10^{-4}, H_2O_2 will pass 1 ppm after about 35 minutes, and 10 ppm after 2.5–3 hours. However, such a high concentration will hardly persist for such long times in the real atmosphere, where turbulent diffusion will tend to dilute the pollutants before high concentrations are built up.

b) *Carbon monoxide, CO*

In gas mixtures with high C_2H_4 content, CO will grow well above background level. Fig. 7 shows that the C_2H_4 mixing ratio has to be 10^{-5} or higher for this to occur. And since such high concentrations are unlikely to exist for a sufficiently long time, CO formation is

believed to be unimportant under atmospheric conditions.

c) *Nitrous and nitric acids, HNO_2 and HNO_3*
These two components, and notably HNO_2, are formed from NO_x in models which contain more C_2H_4 than NO_x. For high degrees of pollution ($[C_2H_4]/[M]>10^{-5}$) the formation of HNO_2 proceeds quite rapidly, in approximately half an hour (see Figs. 8–9). But as already mentioned, such high concentrations will hardly exist very long. Under atmospheric conditions one must therefore expect a slower conversion of NO_x to HNO_2 and HNO_3.

d) *Formaldehyde, CH_2O*
Like CO, CH_2O is produced in considerable amounts when the C_2H_4 mixing ratio is high, $\geq 10^{-5}$. However, for reasons already mentioned, the high values indicated in Fig. 10 will hardly occur under atmospheric conditions.

3. APPLICATION TO ATMOSPHERIC CONDITIONS

The models presented here are attempts to simulate the chemical development in an atmosphere with given and fixed degrees of pollution. But if the pollutants are emitted from a single source, polluted air will be diluted with cleaner air during its transport
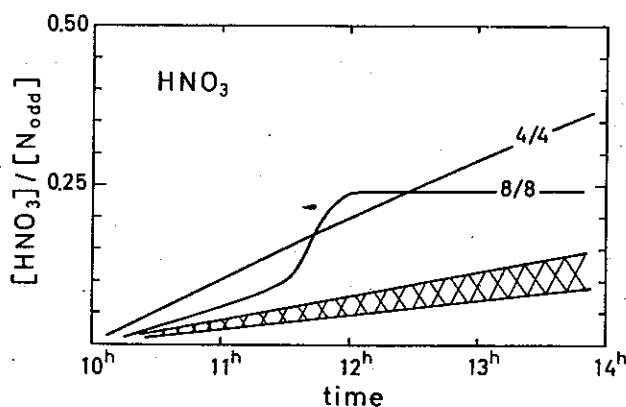

Fig. 9. Formation of HNO_3 in a C_2H_4-NO_x-air mixture, given as fraction of total odd N. (60° latitude, summer). Hatched area covers the cases 5/4, 5/5, 6/5, 7/6, 8/7, A, B, C, and D. For explanations, see Figs. 1 and 7.
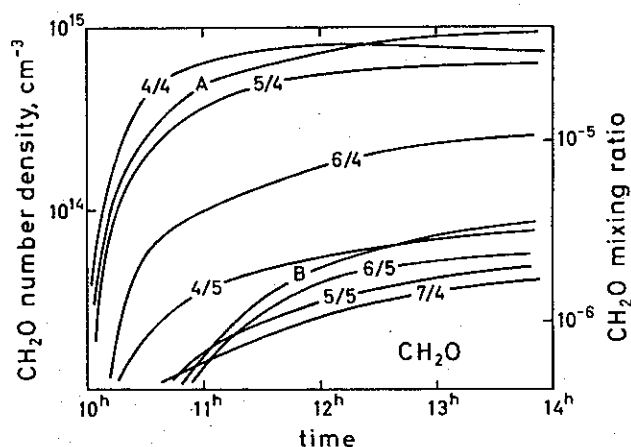
Fig. 10. Formation of CH_2O in a C_2H_4-NO_x-air mixture, (60° latitude, summer). For explanations, see Figs. 1 and 7.

downwind from the source. A complete simulation of such a "real case" must include the effect of turbulent diffusion and mean wind transport.

It is beyond the scope of this paper to treat such a general problem, where the results will depend strongly upon meteorological parameters, such as stability and wind speed. However, as an attempt to evaluate to some extent the effect of dilution, we shall consider a hypothetical model experiment, designed as follows: We shall start with a mixing ratio of 10^{-5} for NO_x and a C_2H_4/NO_x ratio of 15:1. This mixture shall then be diluted with clean air at such a rate that the mixing ratios of odd nitrogen and carbon are reduced exponentially and by a factor of ten in one hour. All chemical components in the model are diluted every third minute according to the formula

$$x_2 = x_1 \cdot f + x_b (1-f)$$

where x_1 and x_2 are the concentrations before and after the dilution, x_b is the background value. In this particular example $f = 10^{-0.05}$. We have also computed a similar experiment with a doubled rate of dilution, i.e., by a factor of ten in half an hour ($f = 10^{-0.1}$). In both experiments the dilution is stopped when the NO_x mixing ratio has decreased to 10^{-8}. The results of these computations are given in Figs. 11 and 12. If the results for O_3 are

compared to the curves in Figure 4, we find great similarities.

The two dilution experiments give an indication as to how and how much the results from box models are modified when the polluted air is subject to turbulent mixing with clean air. A comparison with Figure 4 shows that the time required to reach a peak value of O_3 remains almost unchanged, but the peak value itself is reduced. The reduction depends strongly upon the rate of dilution. This is also true, and even more pronounced, for H_2O_2. Formaldehyde will probably reach a peak value of a few ppm after 20–30 minutes. The conversion of NO_x to HNO_2 is not likely to be very much different from what we can deduce from box models.
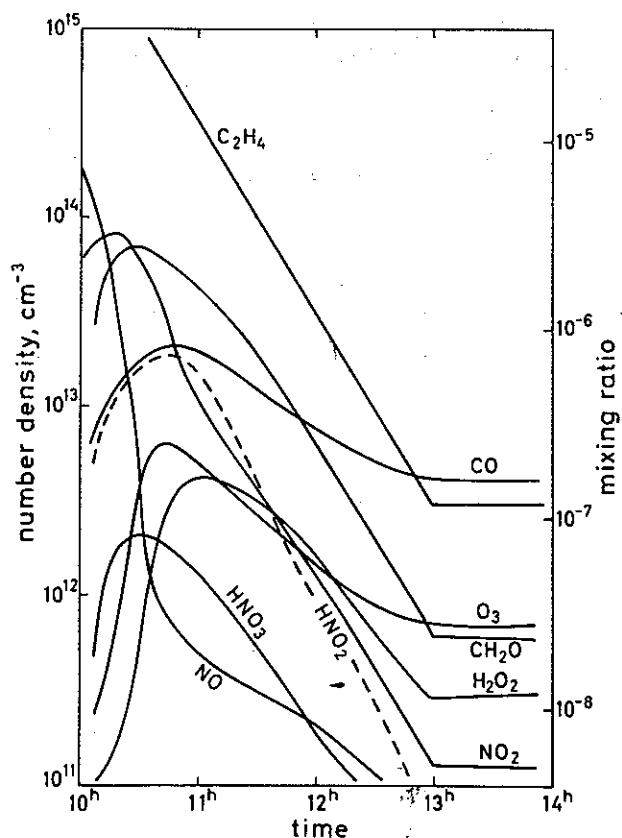
However, although our dilution experiments

Fig. 11. Model experiment with decreasing degree of pollution. The mixing ratios of C_2H_4 and NO_x at the beginning of the experiment are 1.5×10^{-4} and 10^{-5}, respectively. The gas mixture is continuously mixed with clean air at an exponential rate corresponding to a dilution of one order of magnitude in one hour.
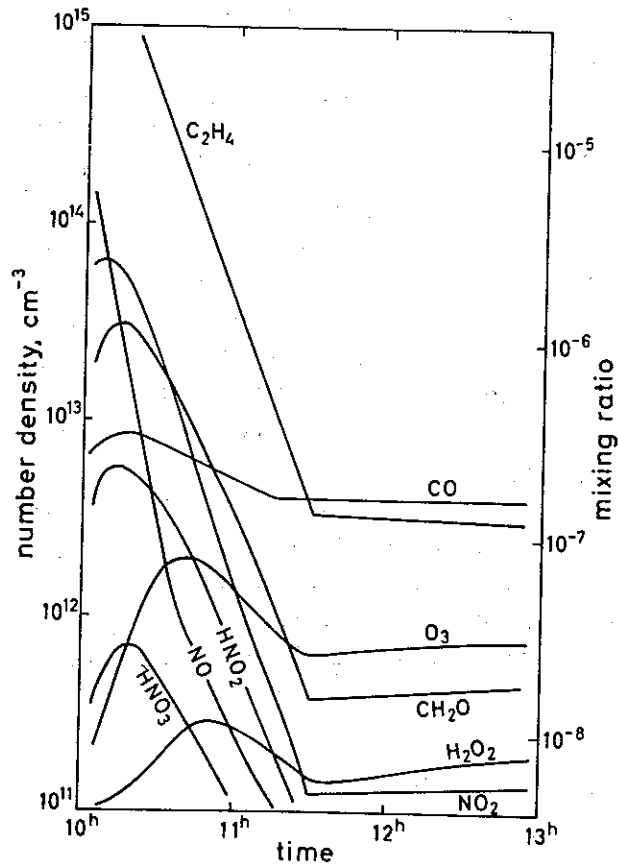
Fig. 12. Same as Fig. 11, but for a rate of dilution of one order of magnitude in half an hour.

the surrounding cleaner air, they do not permit us to draw definite conclusions about oxidant formation in a given place and under specific conditions. Such problems call for comprehensive diffusion models.

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give us useful information about the chemistry in polluted air which is subject to mixing with

REFERENCES

Ackerman, M. 1971. P. 149 in *Mesospheric Models and Related Experiments* (ed. by G. Fiocco). D. Reidel Publishing Company, Dordrecht, Holland.

Garvin, D. & Hampson, R. F. 1974. The Natural Stratosphere of 1974. CIAP Monograph 1. Department of Transportation, Climatic Impact Assessment Program.

Hudson, R. D. & Kieffer. 1974. The Natural Stratosphere of 1974. CIAP Monograph 1. Department of Transportation, Climatic Impact Assessment Program.

Schuck, E. A., Pitts, J. N., Jr. & Wan, J. K. S. 1966. *Air and Wat. Pollut. 10*, 689–711. Pergamon Press.

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