Production of nitric acid in the atmosphere under different conditions*

HASZPRA L., *Institute for Atmospheric Physics H-1675 Budapest, P. O. Box 39., Hungary and*
TURÁNYI T.*Central Research Institute for Chemistry H-1525 Budapest, P. O. Box 17., Hungary*

A légköri salétromsav keletkezése különböző feltételek között. A légkörben a nitrogén-vegyületek átalakulásait bonyolult, nemlineáris kölcsönhatások szabályozzák. Ezért az emisszió, a koncentráció és az ülepedés közötti kapcsolatot csak komplex matematikai modellek segítségével írhatjuk le. A tanulmány olyan modellt ismertet, amelynek segítségével megvizsgálható, hogyan függ a salétromsav-képződés sebessége és a salétromsav koncentrációja a légkörbe bocsátott szennyeződés kémiai összetételétől. A számítások bizonyítják, hogy a salétromsav képződés és a nitrogén-oxid koncentráció közötti kapcsolat nem lineáris. A salétromsav keletkezés sebességét és légköri koncentrációját a szénhidrogén emisszió/koncentráció befolyásolja.

⁎

Production of nitric acid in the atmosphere under different conditions. In the atmosphere the transformations of the nitrogen compounds are controlled by complicated non-linear interactions. Therefore, the relations between the emission, concentration and deposition can be described only by complex mathematical models. In the paper a model is presented by means of which the dependence of the concentration and the production rate of nitric acid on the chemical composition of the pollution emitted is studied. The calculations prove that there is no linear relation between the rate of the nitric acid production and nitrogen oxide concentration. The production rate and the concentration of nitric acid are influenced by the hydrocarbon emission/concentration.

⁎

Introduction. The acidification of soil and surface waters, the damage to vegetation and building materials cause a growing problem in several countries of the world. These processes are generated by the acidic compounds, first of all by sulfuric and nitric acids being deposited from the atmosphere.

The dominant part of atmospheric sulfuric and nitric acids originates from sulfur dioxide and nitrogen oxides released by human activity. Due to the close control for the sulfur dioxide emission the role of nitrogen compounds in acidic deposition have been growing recently and this tendency is expected to continue in future. Therefore, studies on the formation of nitric acid have an important place in the list of invertigations dealing with acidic deposition and with environmental protection.

1. *Transformations of nitrogen compounds*

Nitrogen oxides, dominantly in the form of nitrogen monoxide. are released into the atmosphere during the use of fossil fuel, for example from the exhaust of the motor vehicles. Nitrogen monoxide catalizing the oxidation

of organic species is quickly transformed into nitrogen dioxide. Nitric acid can be directly produced from nitrogen dioxide through its reaction with hydroxyl radical. Nitric acid can be produced from NO_3 and N_2O_5, as well. These precursors are also formed from nitrogen dioxide. Nitric acid can be considered as a final product. It leaves the atmosphere either directly by wet and dry deposition or transformation into nitrate aerosol.

The amount of nitric acid produced and the rate of its formation are not only controlled by nitrogen oxide emissions. They depend on the intensity of solar radiation, air temperature, humidity and the general composition of the atmosphere. The interactions of atmospheric trace gases are so complicated that they can be investigated only by computer based mathematical models.

$*$ El $-$ CHOCH $=$ CHCO$_3$ or its methyl−substituted derivatives
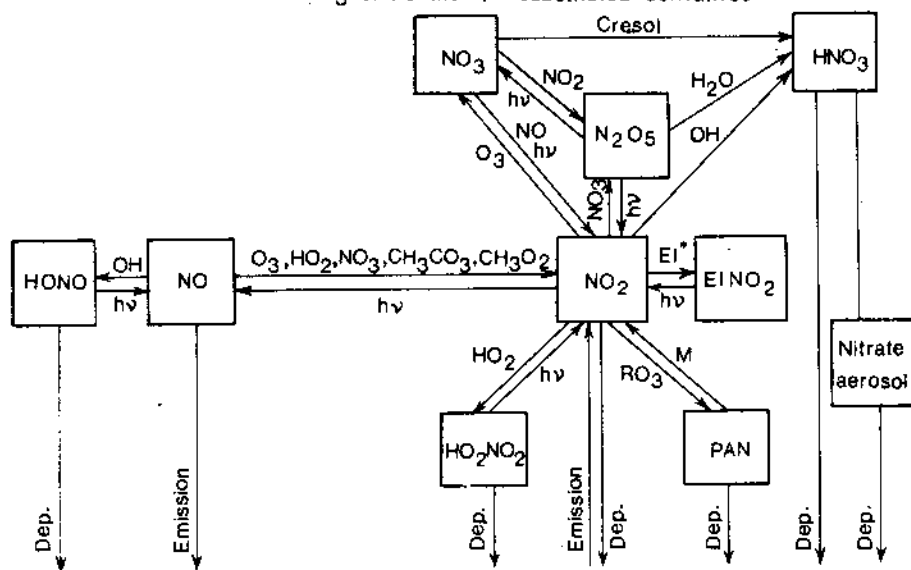
Fig. 1.: The transformation of nitrogen species in the model

To construct such a mathematical model a proper chemical reaction mechanism is necessary. Recently Bérces and his co-workers in the Central Research Institute for Chemistry, Hungarian Academy of Sciences, elaborated a reaction mechanism for the investigation of photochemical smog formation (*Bérces* et al., 1985). That reaction scheme has been considered to be suitable for our purposes. The reaction mechanism is a lumped one in which the hydrocarbons of similar properties are grouped and each group is represented by one species. It is based on the smog mechanism of Atkinson and his co-workers (*Atkinson* et al., 1982) taking into account new findings and data. The mechanism consists of 64 chemical reactions of 41 species. In addition, it has been completed with 24 further steps simulating the emission and deposition of the trace constituents as first order chemical reactions. The scheme of those parts of our reaction mechanism, which relates to the nitrogen species is presented in *Fig. 1*. In the figure only some important agents are

indicated on the reaction paths. The chemical part of the reaction mechanism has been tested against smog chamber measurements of Pitts and his co-workers (*Pitts* et al., 1979) and a good agreement has been obtained.

2. The model

For tracing the dependence of nitric acid production on the composition of the pollution emitted the following model has been constructed: The air corresponding to the background condition travels through a city. The composition of the pollutants emitted from the city and the strength of the

TABLE I

Emission values used in the model calculations (molecule cm^{-2}s^{-1})

	Background (Europe)	Urban (industry + transport) (reference case)
NO$_x$	1.1×10^{11} (a) (b)	2.2×10^{12} (g)
CO	2.9×10^{12} (c)	2.0×10^{13} (g)
SO$_2$	4.7×10^{11} (b) (c) (d)	2.0×10^{12} (g)
Alkane	1.1×10^{11} (c) (e)	2.6×10^{12} (h)
Ethene	2.0×10^{10} (b) (c)	2.1×10^{11} (h)
Propene	1.0×10^{10} (c) (f)	1.6×10^{11} (h)
Butene	8.0×10^{9} (b) (c)	1.6×10^{11} (h)
Toluene	1.8×10^{10} (c)	2.4×10^{11} (h)
Xylene	2.0×10^{10} (b) (c)	4.4×10^{11} (h)
HCHO	2.8×10^{9} (c)	5.0×10^{10} (h)
CH$_3$CHO	4.9×10^{8} (c)	8.6×10^{9} (h)
Me-CO-Et	2.4×10^{9} (c)	7.0×10^{10} (h)

(a) *Bónis*, 1981; (b) *Eliassen* et al., 1982; (c) *Derwent* and *Hov*, 1982; (d) *Várhelyi*, 1982; (e) *Hov* et al., 1978; (f) *Tille* et al., 1985; (g) estimated emission of Budapest based on the data of the Institute for Environmental Protection, Hungary; (h) calculated from the data of *Derwent* and *Hov* (1979)

source can be varied. The effect of different emission composition is traced in the air leaving the city using the complex chemical reaction mechanism. In the model continental background conditions based on typical European data and a city similar to Budapest are assumed *(Table I)*. The physical parameters are: summer, clear sky, the daily variation of the temperature and humidity correspond to the monthly averages in July in Budapest. The air enters the city at 10 a.m. and leaves it two hours later. Beyond the city background emission is supposed.

For the calculation a reliable, consistent background concentration set is needed. To obtain such a concentration set a model run only with background

TABLE II

Factors for the urban emissions (A* reference case)

Factors	Case							
	A*	B	C	D	E	F	G	H
NO$_x$	1	1.5	1	1	1.5	1.5	1	1.5
Alifatic HC	1	1	1.5	1	1.5	1	1.5	1.5
Aromatic HC	1	1	1	1.5	1	1,5	1.5	1.5

emissions has been made. The calculated concentrations have been compared with the results of the measurements published in the literature and it has been found that the concentrations calculated are within the range of the measurements reported for continental air.

The first model run has served as a reference case in which the emissions presented in Table I are used. In the further calculations these emission values have been changed and the effects in the air leaving the city have been traced. Seven cases have been calculated: increased NO_x emission, increased alifatic hydrocarbon emission, increased aromatic hydrocarbon emission, and all of their combinations. The word "increased" means 50% in all of the cases (see *Table II*). In the calculations the mixed layer over the city is 1200 m high and the emitted substances are distributed homogeneously in that layer. The formation of the concentrations in the air leaving the city has been traced for 18 hours, until 6 o'clock next morning. In Europe the source areas are so close to each other that usually an air parcel spends a much shorter time under background condition.

At first, the changes in the composition of the air leaving the urban area were studied. In *Table III* the typical changes are marked with arrows of

TABLE III

Qualitative changes of the atmospheric concentrations beyond the city relative to the reference case for the cases of Table II. The direction and the size of the arrows denote the direction and the measure of the changes

	B	C	D	E	F	G	H
NO_2	⇑	~	↓	⇑	⇑	↓	⇑
HNO_3	↑	~	~	↑	↑	~	↑
PAN	⇓	↑	⇑	↓	↓	⇑	~
O_3	↓	↑	↑	↓	↓	↑	↓
OH	⇓	~	↑	⇓	↓	↑	↓
Alkane	↑	⇑	~	⇑	↑	⇑	⇑
Propene	⇑	⇑	↓	⇑	↑	⇑	⇑
Toluene	↑	~	⇑	↑	⇑	⇑	⇑
SO_2	↑	~	~	↑	~	~	↑

different sizes. It can be seen that in the case of increased NO_x emission (case B) a significant fall in the concentration of oxidants occurs. They are consumed in the transformation of the increased amount of NO to NO_2. Since less oxidant is available, the oxidation of hydrocarbons and so the production of PAN becomes slower. Because of the depressed concentration of oxidants the rate of sulfuric acid formation in homogeneous gas phase reactions becomes lower, therefore the sulfur dioxide concentration is somewhat higher in comparison with the reference case.
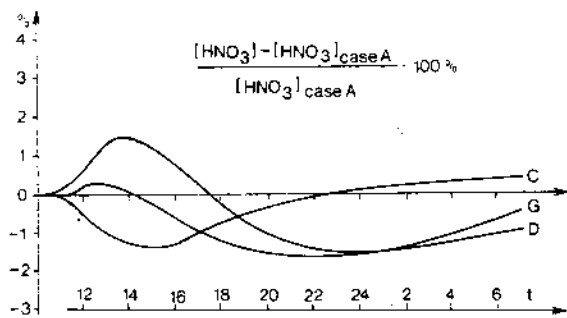

Fig. 2.: The relative changes in the nitric acid concentration for the cases in which the NO_x emission corresponds to the reference case (case A)
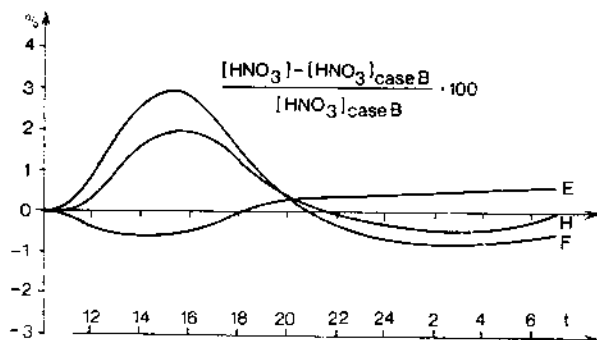

Fig. 3.: The changes in the nitric acid concentration for the cases of increased NO_x emission relative to the case in which only the NO_x emission is increased (case B)

The increase in the emission of alifatic hydrocarbons (case C) causes little changes in the concentration of the trace constituents other than hydrocarbons. Only the PAN concentration increases by a few percent because its formation is promoted by hydrocarbons.

The increased aromatic hydrocarbon emission (case D) also increases PAN concentration and it also causes some increases in the concentration of oxidants. For the remaining cases essentially combinations of the previous ones have been obtained. Of course, it does not mean that the combination of effect is linear.

The changes in the concentration of nitric acid are presented in separate figures. In *Fig. 2* those cases arre collected in which the NO_x emission corresponds to the reference case (case A). In the figure the changes of the nitric acid concentration relative to the reference case are shown. Remarkable changes can be observed in the nitric acid concentration, although the emission of nitrogen oxides is not modified. *Fig. 3* shows the effect of the increase in the

hydrocarbon emission when the NO_x emission is higher by 50% than in reference case. Here the dependence of the nitric acid concentration on the emission of hydrocarbons can also be realized. The reason is that the variations in the hydrocarbon emission modify the general composition of the atmosphere and so influence the rate of nitric acid production.

In *Fig. 4* the relative changes in the rate of nitric acid production are presented for the cases in which the NO_x emission corresponds to the reference case (case A). The rates of nitric acid production differ remarkably from that
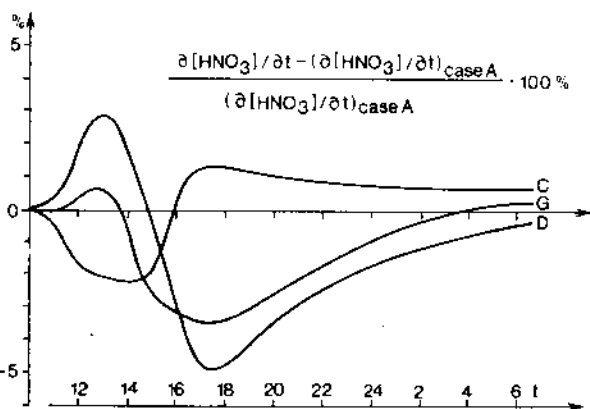

Fig. 4. : The relative changes in the rate of nitric acid production for the cases in which the NO_x emission corresponds to the reference case (case A)
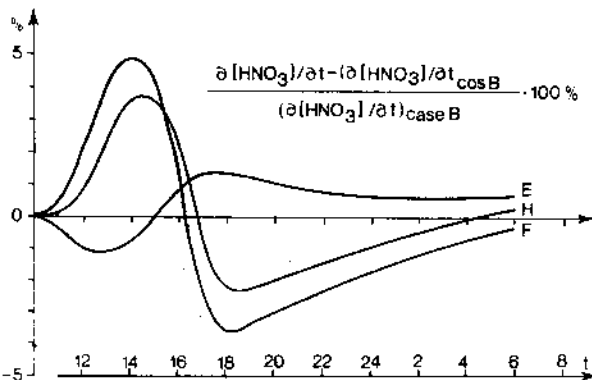

Fig. 5. : The changes in the rate of nitric acid production for the cases of increased NO_x emission relative to the case in which only the NO_x emission is increased (case B)

in the reference case. Similar results are obtained when the cases with increased NO_x and hydrocarbon emissions are compared with the case in which only the emission of nitrogen oxides is increased (case B) *(Fig. 5)*.

In *Fig. 6* the overall relative reaction rate for nitrogen oxide → nitric acid transformation is presented for three special cases as a function of time. The cases are the reference one, the case B in which only the nitrogen oxide emission is increased, and a case corresponding to the background condition supposed in the model calculations. All of the relative transformation rates vary significantly during the day. Their absolute maxima are at about noon when the NO_2 + OH reaction dominates. A local maximum can be seen at about 6 o'clock p.m. when the reaction of N_2O_5 with water vapour takes over the main role in the nitric acid formation. The transformation rates in the three cases

differ from each other significantly during the time period studied. This fact proves that there is no linear relation between the absolute transformation rate and the nitrogen oxide concentration.

3. Summary

The calculations prove that the overall relative rate of nitric acid production varies in a wide range depending on the general composition of the
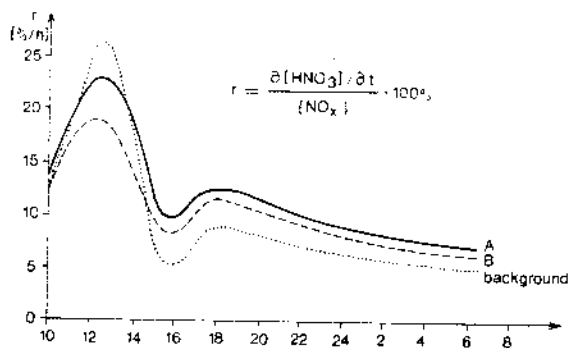

$$r = \frac{\partial [HNO_3]/\partial t}{[NO_x]} \cdot 100\%$$

Fig. 6. : The overall relative reactio rate of the $NO_x \rightarrow HNO^3$ transformation for three specialcases

atmosphere. It means that there is no linear relation between the rate of the nitric acid production and the nitrogen oxide concentration. The time dependence of the relative transformation rate is also significant. We have shown that the production rate and the concentration of nitric acid are influenced by hydrocarbon emissions. Therefore, we suggest that one cannot recommend an overall relative transformation rate for general use in the transport models of nitrogen compounds, at least for the case studies.

REFERENCES

Atkinson, R., Lloyd, A. C. and Winges, L., 1982: An updated chemical mechanism for hydrocarbon (NO_x)SO_2 photooxidations suitable for inclusion in atmospheric simulation models. *Atmospheric Environment 16*, 1341–1355.

Bérces, T., Haszpra, L., Mészáros, E. and Turányi, T., 1985: Légszennyező anyagok terjedésének és kémiai átalakulásának együttes tanulmányozása: primer szennyezőanyagok hatásának vizsgálata a levegő minőségére. KKK1–KLF1 Kutatási jelentés a Környezetvédelmi Intézet számára.

Bónis, K., 1981: A nitrogénvegyületek légköri mérlege Magyarország fölött. *Időjárás 85*, 149–156.

Derwent, R. B. and Hov, Ø., 1979: Computer modelling studies of photochemical air pollution formation in North West Europe. *AERE-Report 9434*.

Derwent, R. G. and Hov, Ø., 1982: The potential for secondary pollutant formation in the atmospheric boundary layer in a high pressure situation over England. *Atmospheric Environment 16*, 655–665.

Eliassen, A., Hov, Ø., Isaksen, I. S. A., Saltbones, J. and Stordai, F., 1982: A Lagrangian long-range transport model with atmospheric boundary layer chemistry. *J. Applied Meteorology 21*, 1645–1661.

Hov, Ø., Isaksen, I. S. A. and Hesstvedt, E., 1978: Diurnal variations of ozone and other pollutants in an urban area. *Atmospheric Environment 12*, 2468–2479.

Pitts, J. N., Darnal, K., Carter, W. P. L., Winer, A. M. and Atkinson, R., 1979: Mechanism of photochemical reactions in urban air. *U. S. EPA-Report*, EPA-600/3–79–110.

Tille, K. J. W., Savelsberg, M. and Bächmann, K., 1985: Airborn measurements of nonmethane hydrocarbons over western Europe: vertical distributions, seasonal cycles of mixing ratios and source strengths. *Atmospheric Environment 19*, 1751–1760.

Várhelyi, G., 1982: On the atmospheric sulfur budget over Hungary. *Időjárás 86*, 333–337.