MATHEMATICAL SIMULATION OF THE SPREAD OF AEROSOL AND GASEOUS POLLUTANTS IN THE GROUND ATMOSPHERIC LAYER

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A model of sulfur, nitrogen, and carbon compounds transport is proposed on the basis of numerical solution of the semiempirical equation of turbulent diffusion. The results of numerical experiments are presented characterizing the spread of pollutants in the southern region of Lake Baykal for typical meteorological situations.

Mathematical models that can be used to estimate possible consequences of one or another impact on the environment are widely used now for describing the spread of atmospheric pollutants and for revealing causal relationships. Reasonably comprehensive reviews of the literature on simulation of the pollutant transport are done in Refs. 1–10.

Models of formation of the acid precipitation have been intensively developed in recent years. Analytical balanced models of transformation disregarding the processes of pollutant transport and diffusion are described in Refs. 4, 6, and 11. The fields of average annual concentration of sulfur and nitrogen compounds were calculated for Central Europe for the Lagrange models.[12] These models[12,13] disregard the phenomena on subregional level, including orographic effects.

The occasional concentration of sulfur and nitrogen oxides and products of their transformation were calculated for Northern America,[3,7] European countries, western part of the territory of our country,[3,14–16] and central part of island Honshu (Japan)[17] using the three-dimensional Euler models based on a solution of the semiempirical equation of turbulent diffusion.

The Euler–Lagrange approach was applied for simulation of long-range transport and transformation of sulfur and nitrogen compounds in the Baltic region.[18] The processes of pollutant transport and diffusion were studied in that paper separately in horizontal and vertical directions, the orographic inhomogeneities were ignored.

A model of transport of sulfur, nitrogen, and carbon compounds is proposed in this paper based on a solution of the semiempirical equation of turbulent diffusion[19] taking into account chemical reactions. The following system of equations is used as an initial one:

$$\frac{\partial S}{\partial t} + \mathbf{V}\ \mathrm{grad}\ S - W_{\mathrm{g}} \frac{\partial S}{\partial x_3} = \sum_{i=1}^{3} \frac{\partial}{\partial x_i} K_i \frac{\partial S}{\partial x_i} - AS + F. \tag{1}$$

Here, t is time; $\mathbf{V} = (u, v, w)$ is the velocity vector; u and v are the horizontal components and w is the vertical component of the velocity of air motion along the axes of the Cartesian rectangular coordinate system (x_1, x_2, x_3); $S = \{S_j\}$ is the tensor of values of mass concentration of the pollutants under study $(j = \overline{1, n})$; K_1, K_2, and K_3 are the coefficients of turbulent diffusion along the axes x_1, x_2, and x_3, respectively; $A(x_i, t) = \{A_{jk}(x_i, t)\}$ is the matrix operator describing the interaction of different substances and their local variations $(i = \overline{1, 3},\ k = \overline{1, (n^3 - n)/6})$; $F(x_i, t)$ is the vector function describing the sources of pollutants; $W_{\mathrm{g}} = \{W_{\mathrm{g}j}\}$ is the tensor of velocities of gravitational sedimentation of the substances; and, n is the number of substances in a multicomponent medium.

Keeping in mind the solution of the problem of the pollutant spread over a region, it is natural to assume the rural distribution of the substance concentrations to be known. Due to the lack of the detailed experimental information, the initial conditions S_j were set as rural distribution and $S_j = 0$ otherwise.

The boundary conditions were set as follows:

$$\begin{aligned} &\partial S_j/\partial x_1 = 0 \quad \text{at} \quad x_1 = 0, X,\\ &\partial S_j/\partial x_2 = 0 \quad \text{at} \quad x_2 = 0, Y,\\ &\partial S_j/\partial x_3 = 0 \quad \text{at} \quad x_3 = 0, H, \end{aligned} \tag{2}$$

where $x_1 = 0$, $x_1 = X$, $x_2 = Y$, and $x_3 = H$ are the boundaries of the calculation domain. The boundary condition that allows for the reflection and absorption of pollutants depending on the properties of the underlying surface was set on the underlying surface at $z = \delta(x_1, x_2)$.

The separation technique[20] was used to construct the calculation code for solving the discrete analogues of Eq. (1). The code consisting of two stages was considered for every small interval. The transport and diffusion were considered at the first stage for each substance independently,[19] and mutual adaptation and interaction of all substances were considered at the second stage taking into account the local transformations and the effect of sources

$$\frac{\partial S_j}{\partial t} + \sum_{p=0}^{n} \sum_{q=p}^{n} \sum_{r=q}^{n} a_{jk} S_p S_q S_r = F_j, \tag{3}$$

$$\left\{ \sum_{p=0}^{n} \sum_{q=p}^{n} \sum_{r=q}^{n} a_{jk} S_p S_q S_r \right\} = A_{jk}, \ S_0 = 1,$$

$j = \overline{1, n}$, $k = \overline{1, (n^3 - n)/6}$. Thus, one can consider Eq. (3) at each point of the integration domain as a system of ordinary differential equations with the coefficients being parametrically dependent on the spatial coordinates. Consideration of all processes of pollutant interactions and transformation at each stage makes it possible to perform experiments with different operators $A(x_i, t)$ and vector functions $F(x_i, t)$ $(i = \overline{1, 3})$ without a change of the model structure as a whole.

The system of equations (1) and (2) is numerically integrated in the Cartesian coordinate system using the method of fictitious domains.[21] Temporal approximation of the problem is constructed at the first stage by the technique of bicyclic complete separation.[20] The method of solution is described in detail in Ref. 19. The employed implicit scheme of the variable component separation yields a solution for the second-order non-commutative operators as a function of time and coordinates. A modification of the semi-implicit two-step code with good stabilizing properties[22] is used at the second stage of solution of the system of equations (3).

A number of complex chemical and photochemical reactions proceed in industrial emissions of pollutants such as sulfur dioxide and nitrogen and carbon oxides. As a result, new more toxic substances, for example, acids are produced. This leads to acid rains. Since the atmosphere is the system with oxidizing properties due to the presence of free oxygen in it, practically all reactions in which sulfur and nitrogen compounds take part produce sulfates and nitrates as higher forms of oxidation.[11]

The model under consideration takes into account 156 chemical reactions and 82 reagents borrowed from Refs. 3, 9, and 23–26. Their stoechiometric formulas and rate constants are given in Appendix. Gas-phase oxidation of sulfur dioxide proceeds through reactions R6, R77, R93, R115, R116, R134, R135, R137–141, R143, R147–R152, and R156; nitrogen oxides – through reactions R7–R10, R25, R26, R28–31, R51, R62, R70, R72, R79, R89, R91, R92, R117, R130, R136, and R155. Reactions with radicals OH and CH_3O and with atomic oxygen run most intensively. Photochemical processes play an essential role in the production of radicals. Reactions R1–R4, R22, R27, R33, R34, R40, R41, R43, R46, R48, R49, R55, R56, R59, R60, R88, R97, R128, R138–R141, R143, R147, and other reactions with radical-oxidants cease in the dark.

Thus, gas-phase oxidation of sulfur and nitrogen compounds at night can proceed only through molecular reactions that run much slower than the radical ones.[11] The rates of molecular reactions R24, R29, and R148 with ozone are several orders of magnitude lower than that of radical reactions. Sulfuric acid is produced through the reaction R153.

The characteristic feature of the reactions of gas-phase oxidation of nitrogen oxides is cyclic character of some of then that conceptually does not lead to removal of nitrogen oxides from the atmosphere. The equilibrium state between ozone and nitrogen oxide and dioxide characteristic of the given level of solar illumination is established through reactions R5, R24, R27, R29, and R32–R34. Nitrogen oxide quickly vanishes in the dark through the continuing reactions R24 and R32.

Nitric acid is produced through four reactions: R28, R38, R62, and R89.

Let us present the results of numerical experiments characterizing the spread of atmospheric pollutants from industrial objects of Irkutsk, Angarsk, Usol'e–Sibirskoe, Cheremkhovo, Zima, Shelekhov, Slyudyanka, and Baykal'sk. The domain of integration with an area of 400×250 km 2 km high located above the underlying surface was chosen for simulation of the processes. Temporal and horizontal steps were 300 s and 5 km, respectively, and vertical steps were set as follows:

$$\Delta z = \begin{cases} 50 \text{ m} & \text{for} \quad z \le 150 \text{ m}, \\ 150 \text{ m}, & 150 < z \le 300 \text{ m}, \\ 200 \text{ m}, & 300 < z \le 500 \text{ m}, \\ 500 \text{ m}, & z > 500 \text{ m}. \end{cases}$$

The coefficient of vertical turbulent diffusion was set to be equal to 10 m^2/s, $j_1 = (0.5 + \sqrt{\mathbf{V}^2/2})\, \Delta x_1$, $j_2 = (0.5 + \sqrt{\mathbf{V}^2/2})\, \Delta x_2$, wind at the upper boundary was northwest, its speed was 10 m/s.

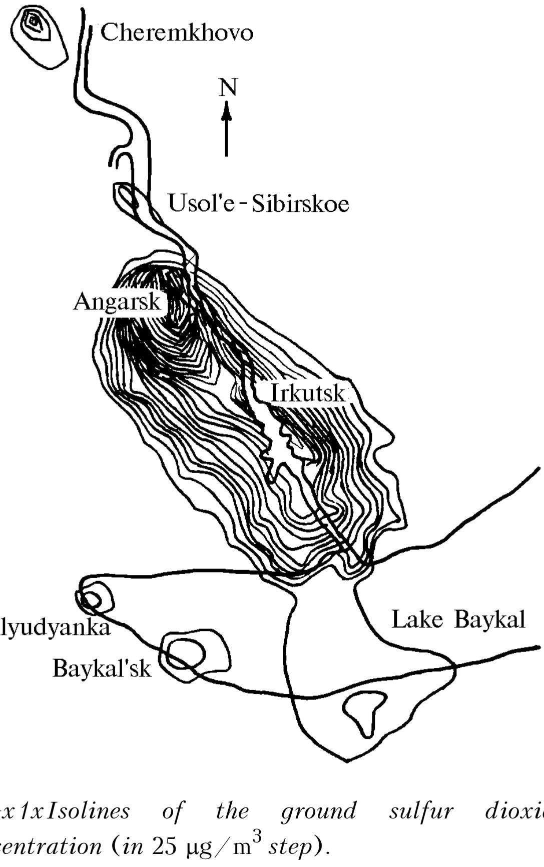
The calculated values of the ground concentrations of sulfur and nitrogen dioxides and carbon oxide are shown in Figs. 1–3 as fractions of average daily maximum permissible concentration given in Table I.

TABLE Ix Maximum permissible concentration of pollutants in the atmospheric air from Refx27x

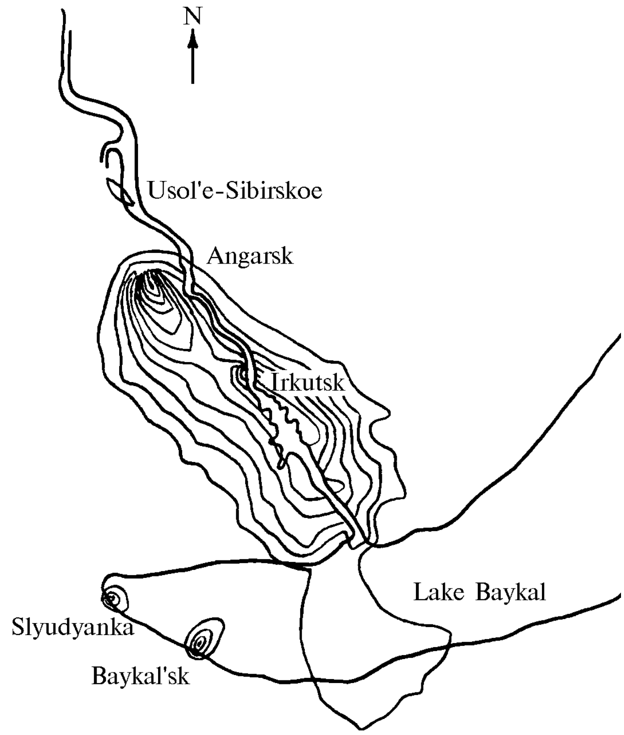
Pollutant	Maximum permissible concentration, mg/m^3	
	Instantaneous	Average daily
Sulfur dioxide	0.5	0.05
Nitrogen dioxide	0.085	0.04
Carbon oxide	5	3

Analysis of the results of numerical experiments under various meteorological conditions shows that the Baykal'sk Integrated Pulp and Paper Mill and the enterprises of Slyudyanka make the greatest contribution to the atmospheric pollution over Southern Baykal that exceeds the maximum instantaneous values of permissible concentration for sulfur and nitrogen oxides.

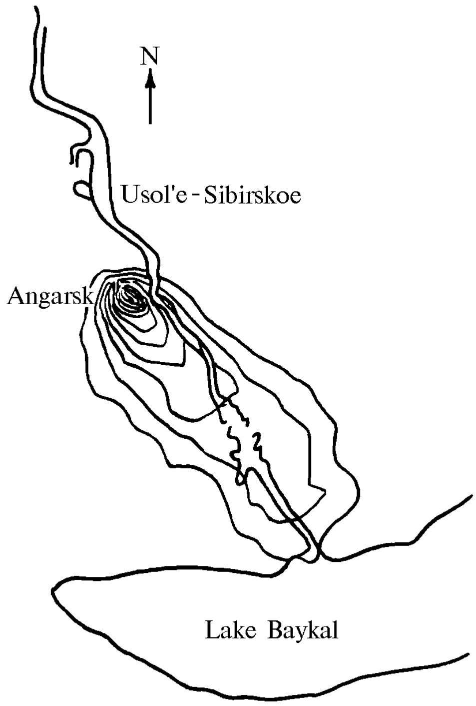
The pollutant spread to greater distances from the BIPPM than from the enterprises of Slyudyanka due to different heights of the sources.



FIGx1xIsolines of the ground sulfur dioxide concentration (in 25 μg/m^3 *step).*



FIGx2xIsolines of the ground nitrogen dioxide concentration (in 20 μg/m^3 *step)x*



FIGx3xIsolines of the ground carbon oxide concentration (in 1500 μg/m^3 *step).*

APPENDIX

No. of reaction	Reaction	Rate constant
1	2	3
R1	$O_3 + h\nu \rightarrow O_2 + O(^1D)$	$5.1\cdot10^{-5a}$
R2	$O(^1D) + M \rightarrow O + M$	$3.2\cdot10^{-11}$
R3	$O(^1D) + H_2O \rightarrow 2OH$	$2.2\cdot10^{-10}$
R4	$O_3 + h\nu \rightarrow O_2 + O(^3P)$	$7.82\cdot10^{-4a}$
R5	$O(^3P) + O_2 + M \rightarrow O_3 + M$	$6.3\cdot10^{-34b}$
R6	$O(^3P) + SO_2 \rightarrow SO_3$	$5.68\cdot10^{-14}$
R7	$O(^3P) + NO \rightarrow NO_2$	$3\cdot10^{-11}$
R8	$O(^3P) + NO_2 \rightarrow NO_3$	$2.25\cdot10^{-11}$
R9	$O(^3P) + NO_2 \rightarrow NO + O_2$	$9.3\cdot10^{-12}$
R10	$O(^3P) + NO_3 \rightarrow NO_2 + O_2$	$1\cdot10^{-11}$
R11	$O(^3P) + O_3 \rightarrow 2O_2$	$7.7\cdot10^{-15}$
R12	$O(^3P) + OH \rightarrow O_2 + H$	$3.3\cdot10^{-11}$
R13	$O(^3P) + HO_2 \rightarrow OH + O_2$	$5.9\cdot10^{-11}$
R14	$OH + O_3 \rightarrow HO_2 + O_2$	$6.8\cdot10^{-14}$
R15	$2OH \rightarrow H_2O_2$	$6\cdot10^{-12}$
R16	$2OH \rightarrow H_2O + O$	$1.4\cdot10^{-12}$
R17	$HO_2 + O_3 \rightarrow OH + 2O_2$	$1.93\cdot10^{-15}$
R18	$HO_2 + OH \rightarrow H_2O + O_2$	$4\cdot10^{-11}$
R19	$2HO_2 \rightarrow H_2O_2 + O_2$	$1.7\cdot10^{-12}$
R20	$2HO_2 + M \rightarrow H_2O_2 + O_2 + M$	$5.2\cdot10^{-32b}$
R21	$2HO_2 + H_2O \rightarrow H_2O_2 + O_2 + H_2O$	$7.84\cdot10^{-30b}$
R22	$H_2O_2 + h\nu \rightarrow 2OH$	$1\cdot10^{-5a}$
R23	$H_2O_2 + OH \rightarrow HO_2 + H_2O$	$1.63\cdot10^{-12}$
R24	$NO + O_3 \rightarrow NO_2 + O_2$	$1.8\cdot10^{-14}$
R25	$NO + OH \rightarrow HNO_2$	$5.5\cdot10^{-11}$
R26	$NO + HO_2 \rightarrow OH + NO_2$	$8.1\cdot10^{-12}$
R27	$NO_2 + h\nu \rightarrow NO + O$	$7.8\cdot10^{-3a}$
R28	$NO_2 + OH \rightarrow HNO_3$	$2.4\cdot10^{-11}$
R29	$NO_2 + O_3 \rightarrow NO_3 + O_2$	$2.9\cdot10^{-17}$
R30	$NO_2 + HO_2 \rightarrow HNO_2 + O_2$	$3\cdot10^{-14}$
R31	$NO_2 + HO_2 \rightarrow HNO_4$	$1.08\cdot10^{-12}$
R32	$NO_3 + NO \rightarrow 2NO_2$	$1.9\cdot10^{-11}$
R33	$NO_3 + h\nu \rightarrow NO_2 + O$	$2.1\cdot10^{-1a}$
R34	$NO_3 + h\nu \rightarrow NO + O_2$	$2.2\cdot10^{-2a}$
R35	$NO_3 + NO_2 \rightarrow N_2O_5$	$9.6\cdot10^{-13}$
R36	$NO_3 + NO_2 \rightarrow NO_2 + NO + O_2$	$7.5\cdot10^{-15}$
R37	$2NO_3 \rightarrow 2NO_2 + O_2$	$2.16\cdot10^{-15}$
R38	$N_2O_5 + H_2O \rightarrow 2HNO_3$	$3.38\cdot10^{-21}$
R39	$N_2O_5 \rightarrow NO_3 + NO_2$	$1.44\cdot10^{-1a}$
R40	$N_2O_5 + h\nu \rightarrow NO_2 + NO_3$	$2.4\cdot10^{-5a}$
R41	$HNO_2 + h\nu \rightarrow OH + NO$	$1.7\cdot10^{-3a}$
R42	$HNO_2 + OH \rightarrow H_2O + NO_2$	$6.6\cdot10^{-12}$
R43	$HNO_3 + h\nu \rightarrow OH + NO_2$	$7.8\cdot10^{-7a}$
R44	$HNO_3 + OH \rightarrow NO_3 + H_2O$	$8.5\cdot10^{-14}$
R45	$HNO_4 \rightarrow NO_2 + HO_2$	$1\cdot10^{-1a}$
R46	$HNO_4 + h\nu \rightarrow NO_2 + HO_2$	$5.8\cdot10^{-6a}$

Appendix continued

1	2	3
R47	$CH_4 + OH \rightarrow CH_3 + H_2O$	$6.6 \cdot 10^{-15}$
R48	$CH_4 + O(^1D) \rightarrow CH_3 + OH$	$1.3 \cdot 10^{-10}$
R49	$CH_4 + O(^1D) \rightarrow CH_2O + H_2$	$1.4 \cdot 10^{-11}$
R50	$CH_3 + O_2 \rightarrow CH_3O_2$	$8.25 \cdot 10^{-12}$
R51	$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	$7 \cdot 10^{-12}$
R52	$2CH_3O_2 \rightarrow 2CH_3O + O_2$	$1.6 \cdot 10^{-13}$
R53	$2CH_3O_2 \rightarrow CH_2O + CH_3OH + O_2$	$2.1 \cdot 10^{-13}$
R54	$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$	$1.5 \cdot 10^{-12}$
R55	$CH_3OOH + h\nu \rightarrow CH_3O + OH$	$5.3 \cdot 10^{-6a}$
R56	$CH_3OOH + h\nu \rightarrow H + CH_3 + O_2$	$6.8 \cdot 10^{-8a}$
R57	$CH_3OOH + OH \rightarrow CH_3O_2 + H_2O$	$1.3 \cdot 10^{-12}$
R58	$CH_3O + O_2 \rightarrow CH_2O + HO_2$	$5.42 \cdot 10^{-12}$
R59	$CH_2O + h\nu \rightarrow H + HCO$	$2.8 \cdot 10^{-5a}$
R60	$CH_2O + h\nu \rightarrow H_2 + CO$	$5.1 \cdot 10^{-5a}$
R61	$CH_2O + OH \rightarrow HCO + H_2O$	$1.42 \cdot 10^{-11}$
R62	$CH_2O + NO_3 \rightarrow HNO_3 + HCO$	$6 \cdot 10^{-16}$
R63	$CH_2O \rightarrow$ heterogeneous loss	$1 \cdot 10^{-6a}$
R64	$HCO + O_2 \rightarrow CO + HO_2$	$5 \cdot 10^{-12}$
R65	$CO + OH \rightarrow CO_2 + H$	$2.2 \cdot 10^{-13}$
R66	$H + O_2 + M \rightarrow HO_2 + M$	$2.3 \cdot 10^{-32b}$
R67	$O + CH_3 \rightarrow CH_2O + H$	$1.4 \cdot 10^{-10}$
R68	$O + H_2O_2 \rightarrow HO_2 + OH$	$1.7 \cdot 10^{-15}$
R69	$\text{н}-C_3H_7O_2 + CH_3COCH_2O_2 \rightarrow$ $\text{н}-C_3H_7O + CH_3COCH_2O + O_2$	$2.3 \cdot 10^{-14}$
R70	$C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2$	$8.8 \cdot 10^{-12}$
R71	$C_2H_6 + OH \rightarrow C_2H_5 + H_2O$	$2.7 \cdot 10^{-13}$
R72	$\text{н}-C_3H_7O_2 + NO \rightarrow \text{н}-C_3H_7O + NO_2$	$8.7 \cdot 10^{-12}$
R73	$C_2H_5O_2 + HO_2 \rightarrow C_2H_5OOH + O_2$	$6.5 \cdot 10^{-12}$
R74	$C_2H_5OOH + OH \rightarrow H_2O + C_2H_5O_2$	$1.5 \cdot 10^{-11}$
R75	$C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2$	$1.2 \cdot 10^{-15}$
R76	$HO_2NO_2 + M \rightarrow HO_2 + NO_2 + M$	$1.3 \cdot 10^{-20}$
R77	$C_2H_5O + SO_2 \rightarrow C_2H_5OSO_2$	$1 \cdot 10^{-14}$
R78	$C_2H_5O + O_2 \rightarrow CH_2O_2CH_2OH$	$8.4 \cdot 10^{-12}$
R79	$C_2H_4 + NO_3 \rightarrow C_2H_4ONO_2$	$1.1 \cdot 10^{-16}$
R80	$C_2H_4 + O_3 \rightarrow CH_2O_2 + CH_2O$	$5.07 \cdot 10^{-18}$
R81	$2CH_3COCH_2O \rightarrow 2CH_2COCH_3 + O_2$	$9.94 \cdot 10^{-14}$
R82	$HOCH_2CHO + OH \rightarrow H_2O +$ $+ HOCH_2CO$	$8 \cdot 10^{-12}$
R83	$C_3H_8 + OH \rightarrow H_2O + C_3H_7$	$1.1 \cdot 10^{-12}$
R84	$2CH_3CO_3 \rightarrow 2CH_3CO_2 + O_2$	$1.6 \cdot 10^{-11}$
R85	$\text{н}-C_3H_7O + O_2 \rightarrow C_2H_5CHO + mO_2$	$8 \cdot 10^{-15}$
R86	$CH_3SCH_3 + O \rightarrow CH_3SO + CH_3$	$5 \cdot 10^{-11}$
R87	$CH_3CHO + OH \rightarrow CH_3CO + H_2O$	$1.49 \cdot 10^{-11}$
R88	$CH_3CHO + h\nu \rightarrow CH_3 + HCO$	$6.8 \cdot 10^{-5a}$
R89	$CH_3CHO + NO_3 \rightarrow HNO_3 + CH_3CO$	$2.7 \cdot 10^{-15}$
R90	$CH_3CHO \rightarrow$ heterogeneous loss	$1 \cdot 10^{-6a}$
R91	$CH_3CO_3 + NO \rightarrow CH_3CO_2 + NO_2$	$1.4 \cdot 10^{-12}$

Appendix continued

1	2	3
R92	$CH_3CO_3 + NO_2 \rightarrow CH_3CO_3NO_2$	$2.5{\cdot}10^{-12}$
R93	$CH_3CO_3 + SO_2 \rightarrow CH_3CO_2 + SO_3$	$2{\cdot}10^{-17}$
R94	$CH_3CO_3 + HO_2 \rightarrow CH_3COO_2H + O_2$	$1.5{\cdot}10^{-12}$
R95	$CH_3CO_3NO_2 \rightarrow$ heterogeneous loss	$1{\cdot}10^{-6a}$
R96	$CH_3CO_3NO_2 \rightarrow CH_3CO_3 + NO_2$	$1.9{\cdot}10^{-4a}$
R97	$O(^1D) + H_2 \rightarrow OH + H$	$1.1{\cdot}10^{-10}$
R98	$CH_3CO + O_2 \rightarrow CH_3CO_3$	$6{\cdot}10^{-12}$
R99	$CH_3COO_2H + OH \rightarrow H_2O + CH_3CO_3$	$1{\cdot}10^{-11}$
R100	$CH_3SSCH_3 + O \rightarrow CH_3SO + CH_3S$	$1.3{\cdot}10^{-10}$
R101	$CH_3OH + OH \rightarrow CH_3O + H_2O$	$9{\cdot}10^{-13}$
R102	$C_3H_6 + O_3 \rightarrow CH_2O_2^* + CH_3CHO$	$5{\cdot}10^{-18}$
R103	$C_3H_6 + O_3 \rightarrow CH_3CHO_2^* + CH_2O$	$5{\cdot}10^{-18}$
R104	$CH_3SCH_3 + OH \rightarrow CH_2SCH_3 + H_2O$	$4.4{\cdot}10^{-12}$
R105	$CH_3SCH_3 + OH \rightarrow CH_3S(OH)CH_3$	$1.7{\cdot}10^{-12}$
R106	$H{-}C_3H_7O_2 + HOCH_2CHO_2CH_3 \rightarrow$ $\rightarrow$ н$-C_3H_7O$ + н$-C_3H_7O_2 + O_2$	$1.35{\cdot}10^{-15}$
R107	$CH_2O_2^* + M \rightarrow CH_2O_2 + M$	$1.72{\cdot}10^{-10}$
R108	$CH_2O + mO_2 \rightarrow mOCH_2O_2$	$7.9{\cdot}10^{-14}$
R109	$CH_3CO_3 + CH_3O_2 \rightarrow$ $\rightarrow CH_3O + CH_3CO_2 + O_2$	$5.5{\cdot}10^{-12}$
R110	$CH_3CO_3 + CH_3O_2 \rightarrow$ $\rightarrow CH_3COOH + CH_2O + O_2$	$5.5{\cdot}10^{-12}$
R111	$CH_3CHO_2^* + M \rightarrow CH_3CHO_2 + M$	$1.72{\cdot}10^{-10}$
R112	$2C_2H_5O_2 \rightarrow C_2H_5OH + CH_3CHO + O_2$	$8.6{\cdot}10^{-14}$
R113	$2C_2H_5O_2 \rightarrow 2C_2H_5O + O_2$	$8.6{\cdot}10^{-14}$
R114	$2C_2H_5O_2 \rightarrow C_2H_5O_2C_2H_5 + O_2$	$8.6{\cdot}10^{-14}$
R115	$CH_2O_2 + SO_2 \rightarrow SO_3 + CH_2O$	$1.75{\cdot}10^{-14}$
R116	$CH_3CHO_2 + SO_2 \rightarrow SO_3 + CH_3CHO$	$1.75{\cdot}10^{-14}$
R117	$CH_2O_2 + NO \rightarrow NO_2 + CH_2O$	$1.75{\cdot}10^{-14}$
R118	$CH_3CHO_2 + H_2O \rightarrow CH_3COOH + H_2O$	$1{\cdot}10^{-18}$
R119	2н$-C_3H_7O_2 \rightarrow$ 2н$-C_3H_7O + O_2$	$1.35{\cdot}10^{-15}$
R120	$H + HO_2 \rightarrow H_2 + O_2$	$5.6{\cdot}10^{-12}$
R121	$CH_2O + CH_2O_2 \rightarrow HCO_2CH_2OH$	$4.38{\cdot}10^{-15}$
R122	$CH_2O_2 + CH_3CHO \rightarrow$ $\rightarrow CH_3CO_2CH_2OH$	$4.38{\cdot}10^{-15}$
R123	$CH_3CHO_2 + CH_2O \rightarrow$ $\rightarrow CH_3CO_2CH_2OH$	$4.38{\cdot}10^{-15}$
R124	$CH_3CHO_2 + CH_3CHO \rightarrow$ $\rightarrow CH_3CO_2CHCH_3OH$	$4.38{\cdot}10^{-15}$
R125	$C_3H_6 + OH + M \rightarrow$ н$-C_3H_7O + M$	$8{\cdot}10^{-27b}$
R126	$HOCH_2CHO_2CH_3 + NO \rightarrow$ $\rightarrow NO_2 + H{-}C_3H_7O$	$8.1{\cdot}10^{-12}$
R127	$H + HO_2 \rightarrow 2OH$	$7.2{\cdot}10^{-11}$
R128	$CH_3COCH_3 + h\nu \rightarrow C_2H_5 + HCO$	$3{\cdot}10^{-5a}$
R129	$CH_3COCH_3 + OH \rightarrow H_2O +$ $+ CH_2COCH_3$	$2.3{\cdot}10^{-13}$
R130	$CH_3COCH_2O_2 + NO \rightarrow NO_2 +$ $+ CH_3COCH_2O$	$8.1{\cdot}10^{-12}$

Appendix continued

1	2	3
R131	$CH_3COCH_2O + O_2 \rightarrow HO_2 + CH_3COCHO$	$1.66\cdot10^{-15}$
R132	$H + HO_2 \rightarrow H_2O + O$	$2.4\cdot10^{-12}$
R133	$H + O_3 \rightarrow OH + O_2$	$2.8\cdot10^{-11}$
R134	н$-C_3H_7O_2 + SO_2 \rightarrow SO_3 +$ н$-C_3H_7O$	$1\cdot10^{-16}$
R135	$CH_3COCH_2O_2 + SO_2 \rightarrow SO_3 + CH_2COCH_2O$	$1\cdot10^{-16}$
R136	$O_2C_2H_4ONO_2 + NO \rightarrow 2NO_2 + 2CH_2O$	$7.6\cdot10^{-12}$
R137	$SO_2 + h\nu \rightarrow SO_2^*$	$1.4\cdot10^{-5a}$
R138	$SO_2^* + M \rightarrow SO_2 + M$	$1.5\cdot10^{-13}$
R139	$SO_2^* + O_2 \rightarrow SO_3 + O$	$2.6\cdot10^{-15}$
R140	$SO_2^* + O_3 \rightarrow SO_3 + O_2$	$1.7\cdot10^{-12}$
R141	$SO_2^* + CO \rightarrow SO + CO_2$	$4.3\cdot10^{-15}$
R142	$OH + HNO_4 \rightarrow H_2O + NO_2 + O_2$	$3\cdot10^{-12}$
R143	$SO_2^* + C_3H_6 \rightarrow C_3H_5SO_2H$	$2.8\cdot10^{-11}$
R144	$SO + O_3 \rightarrow SO_2 + O_2$	$6.7\cdot10^{-14}$
R145	$SO + NO_2 \rightarrow SO_2 + NO$	$1.4\cdot10^{-11}$
R146	$SO + O_2 \rightarrow SO_2 + O$	$8.4\cdot10^{-17}$
R147	$SO_2 + SO_2^* \rightarrow SO_3 + SO$	$6.3\cdot10^{-14}$
R148	$SO_2 + O_3 \rightarrow SO_3 + O_2$	$1\cdot10^{-22}$
R149	$SO_2 + OH \rightarrow HSO_3$	$1.5\cdot10^{-12}$
R150	$SO_2 + HO_2 \rightarrow SO_3 + OH$	$1\cdot10^{-18}$
R151	$SO_2 + NO_3 \rightarrow SO_3 + NO_2$	$1\cdot10^{-20}$
R152	$SO_2 + CH_3O_2 \rightarrow CH_3O + SO_3$	$1\cdot10^{-17}$
R153	$SO_3 + H_2O \rightarrow H_2SO_4$	$9\cdot10^{-13}$
R154	$HSO_3 + O_2 \rightarrow HO_2 + SO_3$	$4\cdot10^{-13}$
R155	$HO_2+NO_3 \rightarrow OH + NO_2 + O_2$	$4.3\cdot10^{-12}$
R156	$SO_2 + CH_3O \rightarrow CH_3OSO_2$	$5\cdot10^{-13}$

Here, *a* denotes the first-order rate constant of the reaction (s^{-1}), *b* denotes the third-order rate constant of the reaction ($cm^6\ s^{-1}$/number of molecules), and the rest are the second-order rate constants of the reactions ($cm^3\ s^{-1}$/number of molecules). Rate constants are given under standard conditions.

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