QUALITATIVE ANALYSIS OF THE OXYGEN ATMOSPHERIC MODEL. II. THE SOURCE−SINK PAIRS

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Stationary concentrations of the atomic and molecular oxygen and ozone in the oxygen atmosphere under isothermal conditions are determined for all pairs of source and sink. The values of sink and source for stable states are derived. It is shown that there are no stable states in the oxygen atmosphere with the atomic oxygen sink. The hierarchy of stationary oxygen concentrations changes when the sink of molecular oxygen exceeds the source outcome related to the total number of oxygen particles.

1. INTRODUCTION

The investigation into chemical kinetics of the processes occurring in the atmosphere has made it possible to isolate the Chapman cycle, as the basis, determining the change in concentrations of oxygen components.[1] However, the presence of other substances and compounds in the atmosphere in different states limits the use of this cycle for describing the atmospheric processes. The investigation of the influence of substances of natural and anthropogenic origin on the dynamics of atmospheric oxygen has made the subject of many studies.[2−7] The quantity and chemical composition of substances in the atmosphere are described in detail in Ref. 2−6, and their spatial distribution is represented schematically in Ref. 8. Among those we distinguish the nitric oxide as well as the oxides of hydrogen, chlorine, bromine and sulfur, making primary impact on the ozone behavior.[2,3] The direct relationship between the anthropogenic chlorine and the decrease in the ozone at 15−20 km altitude has been established in Ref. 7. Heterogeneous processes are investigated occurring on the aerosol surface (SO_2 particles of volcanic origin and ice) in the altitude range between 20 and 30 km[9] and in the troposphere.[10]

Wider use of the Chapman cycle takes place in two alternative directions. In the first one the cycle is supplemented with chemical reactions, whose number is sometimes about several tens, and in the second one the additional reactions are parameterized by introducing sinks and sources.

In this paper we present a qualitative analysis of the oxygen atmosphere model with a source and a linear sink. Only few papers dealing with this problem can be found in literature. The influence of the ozone sink and molecular oxygen as well as the molecular oxygen source on the behavior of temperature and oxygen components under exothermic conditions is considered in Ref. 11 where it is shown that this influence may be significant in the transient processes. In Ref. 12 shown is the existence of a small range of values of sinks and sources when only low deviations of stationary concentrations from their unperturbed values can occur. It remains unclear, how the stationary concentrations and relaxation times characterizing the oxygen atmosphere may change under strong variations of the source and sink powers.

The aim of this paper is to analyze the stationary concentrations of the oxygen atmosphere, whose components dynamics is determined by photochemical reactions (Chapman cycle) in the presence of a linear sink and the source of oxygen particles, whose powers vary over a wide range. The models of sinks and sources are described in Ref. 11. In this paper the "sink−source" pairs are selected for the analysis. In this case the problem can be solved analytically and it is more close to actual situations with a great deal of sinks and sources. The variety of chemical composition of substances and their different states determine a wide range of variation of the magnitude of sink rates and source powers.

Taking into consideration the conditionality of the problem under study, associated by now with the lack of a quantitative analysis of the sinks and sources of oxygen in the atmosphere and their classification, we investigate the rates of sinks not exceeding the magnitude of $k_{N_2} NA$, where k_{N_2} is the rate of the reaction $O + O_2 + N_2 \rightarrow O_3 + N_2$ and N is the nitrogen concentration. The values of sources do not exceed the magnitude of $k_{N_2} NA^2$, where A is the concentration of molecular oxygen in the atmosphere. Sources and sinks normalized to these maximum values vary in the range from 10^{-13} to 1.

2. THE BASIC SYSTEM OF EQUATIONS

Let x, y, and z be the concentrations of molecular and atomic oxygen and ozone, respectively. The number of nitrogen molecules is assumed to be constant. Within the framework of the oxygen atmosphere model the set of equations determining the dynamics of variation of oxygen particles in the Chapman approximation is

$$\frac{dx}{dt} = -k_x x + l_x + J_3 z - J_2 x - k_{N_2} Nxy +$$

$$+ 2k_3 yz - k_2^{O_2} x^2 y - k_2^{O_3} xyz \; ;$$

$$\frac{dy}{dt} = -k_y y + l_y + J_3 z + 2J_2 x - k_{N_2} Nxy - k_3 yz -$$

$$- k_2^{O_2} x^2 y - k_2^{O_3} xyz \; ;$$

$$\frac{dz}{dt} = -k_z z + l_z - J_3 z + k_{N_2} Nxy - k_3 yz +$$

$$+ k_2^{O_2} x^2 y + k_2^{O_3} xyz. \tag{1}$$

Here l_i and k_i are the coefficients characterizing sources and sinks, respectively.

Summation of stationary equations of the system (1) with the corresponding weights gives the equation determining the linear relations between sources and sinks and the stationary concentrations (x_s, y_s, z_s),

$$2(-k_x x_s + l_x) - k_y y_s + l_y + 3(-k_z z_s + l_z) = 0 \; . \tag{2}$$

The relationship (2) determines the linear relations between stationary states of the oxygen components.

For a convenience of operating with the magnitudes of different order we introduce a dimensionless time

$$t' = t \, k_{N_2} N_{30} A_{30} \; ,$$

$$(A_{30} = 2x_{30} + y_{30} + 3z_{30}) \; ,$$

$$(k_{N_2} NA = 47.5 \text{ Hz}) \tag{3}$$

and the coordinates

$$x = A_{30} X \; , \qquad y = A_{30} Y \; , \qquad z = A_{30} Z \; , \tag{4}$$

where x_{30}, y_{30}, and z_{30} are the stationary states of the oxygen atmosphere in the absence of sources and sinks, selected, for certainty, to be the parameters at 30 km altitude.

In the coordinates (X, Y, Z) the basic system of equations (1) takes the form

$$\frac{dX}{dt} = -K_x X + L_x + K_3 Z - K_2 X - XY +$$

$$+ 2K_3 YZ - K_8 X^2 Y - K_9 XYZ \; ;$$

$$\frac{dY}{dt} = -K_y Y + L_y + K_3 Z + 2K_2 X - XY -$$

$$- K_1 YZ - K_8 X^2 Y - K_9 XYZ \; ;$$

$$\frac{dZ}{dt} = -K_z Z + L_z - K_3 Z + XY - K_1 YZ +$$

$$+ K_8 X^2 Y + K_9 XYZ \; . \tag{5}$$

The set of equations (5) is the basis for subsequent qualitative analysis of the oxygen atmosphere. The coefficients in Eq. (5) are determined in Refs. 12 and 13.

Let us give the values of some quantities used below. In the absence of sinks and sources the stationary concentrations of oxygen components, calculated for 30 km altitude, are as follows

$$\cdot_{30} = 7.32 \cdot 10^{16} \text{ cm}^3 \; ,$$

$$y_{30} = 3.59 \cdot 10^8 \text{ cm}^3 \; ,$$

$$z_{30} = 1.96 \cdot 10^{13} \text{ cm}^3 \; . \tag{6}$$

The roots of the characteristic equation of the linearized, in the vicinity of (x_{30}, y_{30}, z_{30}), set of equations (5) are

$$a_1 = 1 / \tau_1 = 1 / 0.03 \text{ s}^{-1} \; ,$$

$$a_2 = 1 / \tau_2 = 1 / (0.9 \cdot 10^6) \text{ s}^{-1} \; . \tag{7}$$

At small deviations from stationary values the variation of concentrations of atomic oxygen and ozone are determined by the relationships

$$y(t) = y_{30} + \exp\left[-\frac{t - t_0}{\tau_1}\right] y_0 + 0.000\,02 \exp\left[-\frac{t - t_0}{\tau_2}\right] z_0 \; ,$$
$$\tag{8}$$
$$z(t) = z_{30} + \exp\left[-\frac{t - t_0}{\tau_2}\right] z_0 \; ,$$

where y_0 and z_0 are the deviations at the initial time t_0. In the method of quasistationary concentrations[14] the inverse value of the root of the characteristic equation is related to the time of relaxation to a stationary state. It is this sense in which we use it, when considering the set with three active components. It should be noted that the peculiarity of equations in the Chapman cycle is in the fact that along with the hierarchy of normalized reaction rates[5] there exists the hierarchy of stationary concentrations of oxygen components (see Eq. (6)). In the case of zero deviation of the ozone concentration it follows from Eq. (6) that atomic oxygen relaxes to stationary concentration in a time τ_1 whereas at small ozone concentration deviations, exceeding essentially the atomic oxygen concentration, the time of O relaxation increases up to τ_2. Thus, the relaxation time obeys the hierarchy of concentrations and depends on the values of small deviations of components standing higher in the hierarchy. As one can see from Eq. (7), the relaxation times also form their own hierarchy.

In the atmosphere small deviations from the ozone stationary concentrations, exceeding the atomic oxygen stationary concentrations under conditions of polar day, occur in the ozone holes. Therefore, the above atomic oxygen stationary concentrations must differ from the stationary concentration by several orders of magnitude during some weeks. Unfortunately, it is impossible to make a comparison with the measured atomic oxygen concentrations since no measurements of atomic oxygen in the atmosphere and in the ozone holes, in particular, are available.

Thus, in the nonturbulent oxygen atmosphere there exist hierarchies of stationary concentrations (O, O_3, and O_2) and of relaxation times ($\tau_1 = 0.03$ s and $\tau_2 = 0.9 \cdot 10^6$ s). Below we consider what happens with these hierarchies at atmospheric disturbance by the mechanism of sink and source.

3. STATIONARY CONCENTRATIONS

The only solution of the set of equations (5) in the absence of sources and sinks, derived for the values of reaction rates corresponding to 30 km altitude, is designated as a "reference" solution for x_{30}, y_{30}, and z_{30}. It will be used below as a standard for stationary concentrations found for different values of sink and source. Selection of the above altitude is not caused by any facts, and a selection of another standard within the limits of stratospheric altitudes does not change the qualitative conclusions.

Analysis of the stationary concentrations taking account of the source (L_j) and the sink (K_i) will be conducted for a simple case allowing the analytical solution for nine pairs. Note that the relationship (2) is fulfilled provided that at least one source and a sink are not equal to zero simultaneously. The applicability of equations of atmospheric photochemistry set imposes a restriction on the permissible values of stationary concentrations both from above (no more than 10^{23}) and from below (no less than 10^4) what gives for the logarithms of normalized concentrations the relationships:

$$-4 < \log(Y) < 16 ,$$
$$-14 < \log(X) < 8 , \tag{9}$$
$$-9 < \log(Z) < 10 .$$

Figure 1 shows the general picture of the stationary concentration distributions in the concentration space for six pairs of sinks and sources. The pairs are chosen for which the stable states exist. Logarithms of concentration of atomic (Y) and molecular oxygen (X) and of ozone (Z) are shown on the axes. The shapes of surfaces, involving these concentrations, are indicative of different versions of the O, O_2, and O_3 behaviors at variations of sinks and sources. Note that the plots for the pairs (K_x, L_x) and (K_z, L_z) have close shapes. What all the plots have in common is that the outflow and inflow take place for one and the same component.

The point A on the plot corresponds to the state of oxygen atmosphere with stationary concentrations of O, O_2, and O_3 at $K_x = 0$ and $L_x = 0$ that corresponds to the reference case.

The use of the model with one source and a sink imposes tough restrictions on the oxygen component for which the sink takes place. Its stationary concentration is determined by the ratio of the source power to the sink rate and it does not depend on the rates of the Chapman cycle chemical reactions.

As an example, we refer to the molecular oxygen sink and source (pairs K_x and L_x) and show the manner in which the O, O_2, and O_3 stationary concentrations vary. Stationary concentrations of molecular and atomic oxygen and ozone are determined by the expressions

$$X_s = \frac{L_x}{K_x} ;$$

$$Y_s = \frac{1}{\dfrac{K_9 X_s - K_1}{2K_3} + \sqrt{\dfrac{K_1(1+K_8)}{K_4 K_3} + \dfrac{(K_1 - K_9 X_s)^2}{2K_3^2}}} ;$$

$$Z_s = \frac{K_4 X_s (K_9 X_s - K_1)}{2K_1 K_3} +$$

$$+ X_s \sqrt{\frac{K_4(1 + K_8 X_s)}{K_1 K_3} + \frac{K_4^2 (K_1 - K_9 X_s)^2}{(2K_1 K_3)^2}} . \tag{10}$$

Let us now look at the diagram in Fig. 1 where the dependence of O, O_2, and O_3 concentrations is presented at selected values of K_x and L_x. From the surface type it follows that there are two mutually exclusive scenarios of deviation from the reference state: 1) increase of O and decrease of O_2 and O_3 , and 2) decrease of O and increase of O_2 and O_3.

Quantitative characteristics of the X, Y, and Z dependence on the sink and source are given in Fig. 2 where the logarithms of stationary concentrations of O, O_2, and O_3 normalized to the corresponding reference concentrations are presented. Let us consider the upper pair of curves. The increase of stationary concentration is indicated by the positive values of vertical axis and the decrease of stationary concentration as compared with the reference one is indicated by the negative values of vertical axis. On the surface, characterizing the atomic oxygen variation, the horizontal axes are logarithms of a source $\log(L_x)$ and a sink $\log(K_x)$. In this case at zero point their maximum is attained, the value (-10) corresponds to the decrease of normalized values of a sink and a source by ten orders of magnitude as compared with the maximum value.
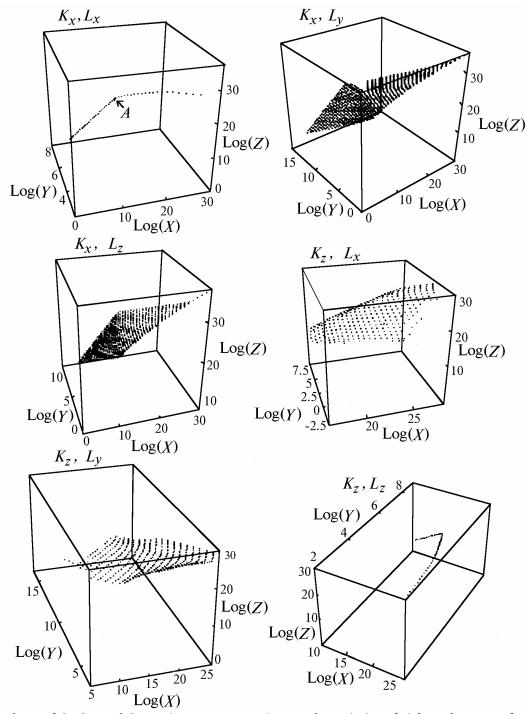
FIG. 1. Dependence of O, O_2, and O_3 stationary concentrations on the variation of sinks and sources of molecular oxygen. The reference concentration corresponds to the point A.

As can be seen from Fig. 2, in the region of weak sinks and strong sources we can observe a decrease of stationary concentration of atomic oxygen and an increase in concentrations of the molecular oxygen and ozone. In the region of weak sources and strong sinks the stationary concentration of atomic oxygen varies slightly but the values of concentration of molecular oxygen and ozone decrease sharply (by 15 orders of magnitude). Breaking of hierarchy of stationary concentrations occurs when the value of sink exceeds the value of source by more than five orders of magnitude.

On the contour diagram corresponding to the surface of steady states of atomic oxygen the point is indicated by boldface where the stationary concentration of atomic oxygen is equal to the reference one, and the transition from one isoline to another one corresponds to the variation of the relevant stationary concentration by one order of magnitude. In this case,

on the contour diagram the crowding of isolines denotes the steeper slope on the surface diagram. Thus, on the contour diagram of atomic oxygen at $K_x > L_x$ (strong sink and weak source) the ratio of the stationary concentration to the reference one is no less than 0.1, and in the region where $K_x < L_x$ (strong source and weak sink) this ratio decreases down to 10^{-10}.

Having combined the contour diagrams for oxygen components on one diagram (Fig. 3) and having set the values of sink and source, we obtain the values of stationary concentrations for each of the components simultaneously.
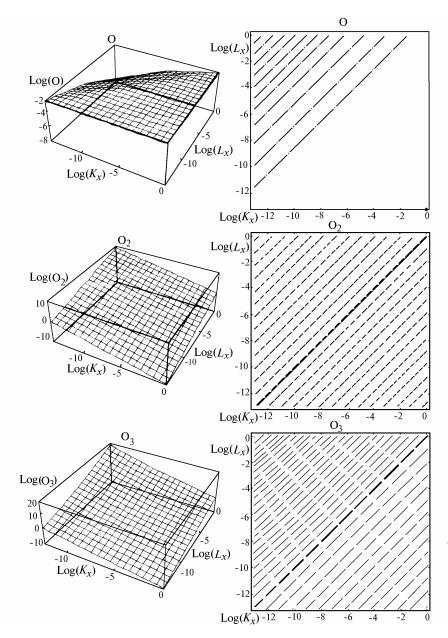

FIG. 2. Variation of O, O_2, and O_3 stationary concentrations depending on the sink and source of molecular oxygen. All values in the left–hand column are given in a logarithmic scale. Contour diagrams of corresponding surfaces from the left–hand column are given in the right–hand column. The concentration variation by one order of magnitude corresponds to the transition from one isoline to the other.

As can be seen from Fig. 3, the equation of the curve, where the stationary O_2 and O_3 concentrations coincide with the reference ones, is determined by the ratio $K_x = L_x$. The distance between the line of zero level and a selected isoline gives the value of one order of magnitude, i.e., the value of variation of the sink–to–source ratio, whereas the concentration variation of two orders of magnitude corresponds to the transition from one isoline to the other.

In this manner one can analyze the remaining eight "sink–source" pairs. The normalized stationary concentrations for atomic, molecular oxygen and

ozone for six "sink–source" pairs are presented at superposed contour diagrams on a logarithmic scale in Fig. 3. At all the contour diagrams the transition from one isoline to another corresponds to the change of normalized concentration by two orders of magnitude. The arrows on the plots are connected with curves where the concentration coincides with the reference one, and the arrows point to the direction of the concentration decrease. Isolines are given in the regions where the stationary concentrations are stable. There are no steady states in the atmospheric model with the atomic oxygen

sink. In all pairs (K, L), except for the pair (K_x, L_y) the variation of atomic oxygen concentration is small as compared with the variation when day gives way to night. Loss of hierarchy of stationary concentrations is possible only in the atmosphere with the sink of molecular oxygen at the sink power being much larger than that of the source. The boundary between steady and unsteady states are shown by the dotted curve, the values of K and L are denoted by a solid narrow curve. In this case the ozone concentration is 10^4.
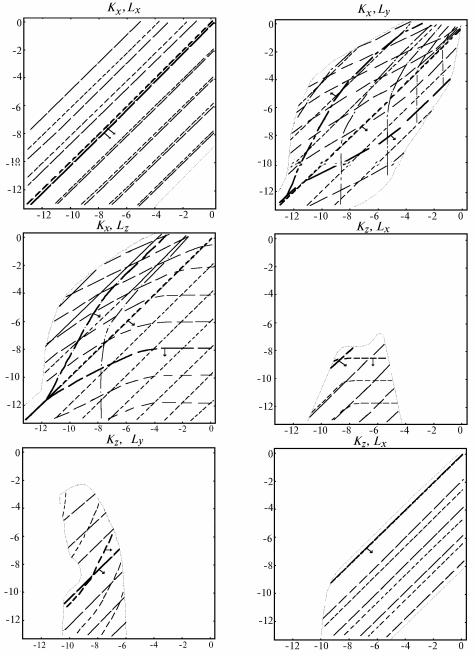

FIG. y. Combined contour diagrams of stable stationary concentrations of oxygen components for different "sink–source" pairs. The bold curves show the concentrations being equal to the reference one. The concentration variation by two orders of magnitude corresponds to the transition from one isoline to another. The designations of curves are: $-\cdot-\cdot-$ (O), $----$ (O$_3$), and $-----$ (O$_2$).

4. HIERARCHY OF RELAXATION TIMES

From the analysis of the stability of stationary concentrations (10) it follows that the instability occurs when the source power exceeds the sink one by no less than five orders of magnitude. All stationary concentrations of a singular point type are the nodes. Our analysis is not expanded to the region of weak sources where the ozone concentration is less than 10^4 cm^{-3}.

Figure 4 gives the contour diagrams of the dependence of the relaxation time logarithms on the logarithms of a sink and a source. It should be noted that the value, inverse to the root of characteristic equation of the set of equations (5) linearized in the vicinity of a stationary concentration, is connected with the relaxation time. The arrows on the diagrams indicate the direction of the relaxation time decrease in moving from one isoline to another, and figures show the values of the relaxation time (in seconds). When passing from an isoline to the adjacent one the relaxation time changes by one order of magnitude (the time scale is one year being approximately equal to $3 \cdot 10^7$ s). At any variations of a sink and a source the hierarchy of relaxation times is not violated, although quantitative variations are significant.
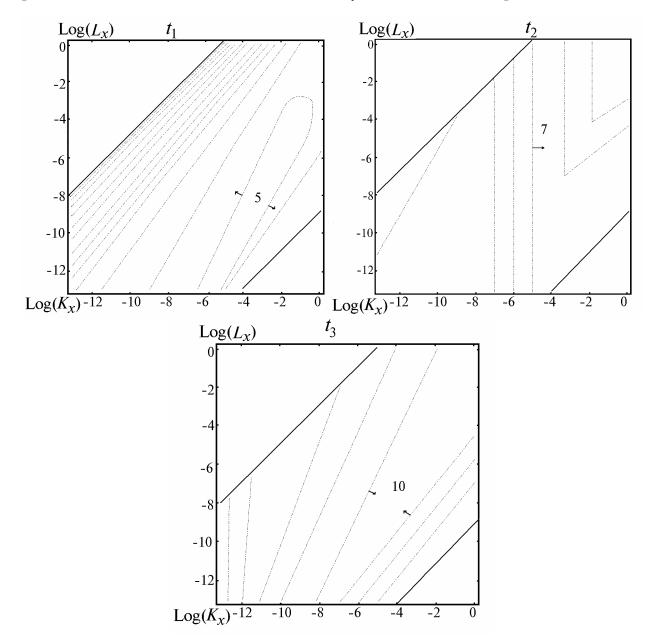

FIG. 4. Dependence of the relaxation times on sink and source of molecular oxygen. All values in the plots are given in the logarithmic scale. Each isoline corresponds to the variation of a relevant value by one order of magnitude.

Of particular interest is the consideration of hierarchy of relaxation times for coincident values of a sink and a source $K_x = L_x$, since at these values stationary concentrations differ slightly from the reference ones. With the increase of the sink and source powers the minimum relaxation time increases while the two large relaxation times decrease sharply. The measurements of relaxation times would allow the determination of the power of natural sink and source. (The O_2 source, as is known, is the processes of photosynthesis).

5. CONCLUSION

Analysis of stationary concentrations of the components of the oxygen atmosphere has been performed. The behavior of the oxygen atmosphere is assumed to be determined by chemical reactions of Chapman cycle taking into account all kinds of the "sink–source" pairs. It is shown that in the systems with sink of atomic oxygen the oxygen atmosphere is unstable. In the systems without this sink the stationary concentration of atomic oxygen varies slightly as compared with its variation when day gives way to night (the case $K_3 = K_4 = 0$) except when the sink is for the molecular oxygen while the source (K_x, L_y) generates atomic oxygen.

In the systems with the molecular oxygen sink the range of values of sink and source, at which the stationary concentrations of O, O_2, and O_3 occur, is sufficiently wide. In this case the molecular oxygen concentration is determined by the ratio $X = jL_j/(2K_x)$ $(j = 1(y),\ 2(x),\ 3(z))$. The ozone concentration is larger than the reference one by several orders of magnitude at $L_x > K_x$ while at inverse inequality only in small range of values of sink and source the ozone stationary concentration is less than the reference one. In the systems with ozone sink the range of values of sink and source, at which the stationary concentrations of O, O_2, and O_3 are achieved, is much less. In this case the ozone concentration is determined by the ratio $Z = jL_j/(3L_z)$ $(j = 1(y),\ 2(x),\ 3(z))$ and the molecular oxygen concentration is less than the reference one.

The sole exception is the case with the atomic oxygen source when the inequality $K_z < L_y$ holds.

The hierarchy of stable stationary concentrations can vary only in the atmosphere with the sink for molecular oxygen under condition of multiple excess of sink over the source (the concentrations of O and O_3 become comparable). For the sink and source of molecular oxygen it is shown that the hierarchy of relaxation times does not vary in the entire range of values of sink and source where the steady states exist.

In the atmosphere with sink and source the third relaxation time occurs exceeding the corresponding times for unperturbed atmosphere. In the atmosphere with sink and source of O_2 under condition of the proximity of the sink values to the source ones, the O_2 and O_3 concentrations differ slightly from the reference ones while the hierarchy of relaxation times experiences significant quantitative variations, i.e., with the increase of K_x and L_x the minimum time grows and the two largest times sharply decrease.

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