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The Hydroperoxy-radical (HO_2) in V.V.Voevodskii's Research and at the Present Time. Results and Problems

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The role of HO_2 radicals in the kinetics of the gas-phase oxidation of hydrogen-containing substances is considered. It is shown that at a high concentration of active centres, for example, when the latter are generated under the influence of a fairly powerful radiation source, non-linear reactions of HO_2 radicals, i.e. their interaction with one another and with other active species, become important. These processes play an important role in the following kinetic systems considered: at the second limit in mixtures of hydrogen with oxygen under the conditions of artificial chain initiation; in the region of Earth's ozone layer; in lasers based on the reactions between H_2 and F_2.
The bibliography includes 44 references.

CONTENTS

I. Introduction 496
II. Non-linear reactions of HO_2 radicals associated with the oxidation of hydrogen 497
III. Reactions of HO_2 radicals in Earth's ozonosphere 499
IV. The HO_2 radical in the laser based on the reaction between H_2 and F_2 501

I. INTRODUCTION

The ways of science are strange and unpredictable. Two different and sometimes opposite pathways converge unexpectedly. Similarly human beings following such pathways (if still alive) may meet or their memories may be juxtaposed and it would seem that everything could be predicted if one thought on these lines. This rare gift of prediction was to a large extent typical of Vladislav Vladislavovich Voevodskii.

Returning periodically to the study of HO_2 radicals, mainly after Voevodskii's death, we realised how much Voevodskii foresaw in those cases where others saw only exercises in the solution of kinetic equations. Thirty years ago, at the time when one of the present authors was Voevodskii's Diploma Student, Voevodskii stated: "in this triatomic species (HO_2 radical) are contained half of the future oxidation theories; it is a live radical, which is destroyed on the walls only in narrow tubes, and in all real instances it behaves as a truly reactive substance like hydrogen and oxygen atoms. If we learn to measure HO_2 radicals, we shall obtain a key to oxidation mechanisms".

Thirty years have elapsed and these ideas, confirmed by extensive experimental data, have become generally accepted in the chemistry of the gas-phase oxidation of hydrogen-containing substances. It is now well known that HO_2 radicals are formed in the oxidation of hydrogen, hydrocarbons, aldehydes, alcohols, ketones, ethers, and many other hydrogen-containing organic and inorganic substances.

The first hypothesis of the formation of HO_2 in the gas phase was put forward in 1926 by Marshall[1] and independently by Taylor[2] in order to explain the results obtained in the oxidation of hydrogen photosensitised by mercury. The rate constant for the formation of HO_2 radicals

$$\dot{H} + O_2 + M \rightarrow H\dot{O}_2 + M \qquad (1)$$

was estimated in 1930[3] and at the same time Hinshelwood explained the second self-ignition limit in hydrogen–oxygen mixtures by chain termination in terms of reaction (1).[3,4] The HO_2 radical appeared for the first time in 1937 in hypothetical hydrocarbon oxidation mechanisms when von Elbe and Lewis published a radical-chain mechanism for the oxidation of paraffinic hydrocarbons[5]. At the end of the 1940s, Voevodskii attempted to detect HO_2 radicals on the basis of the gases evolved by frozen products in the study of the oxidation of hydrogen above the second limit. This investigation initiated a series of others, where the rate constant for the chain branching reaction was measured:

$$\dot{H} + O_2 \rightarrow \dot{O}H + \ddot{O} \qquad (2)$$

and the relative efficiency of the water molecules in reaction (1) was estimated[6,7]. The ratio $k_1^{H_2O}/k_1^{H_2} = 5$ obtained[6] still remains virtually unchanged.

The study of the oxidation of hydrogen at atmospheric pressure near the third limit in reactors treated with acids[7,8] led Voevodskii to the conclusion that at an early stage of the process hydrogen peroxide is the main product, in agreement with Kondrat'ev's preliminary data[9]. This feature of the oxidation of hydrogen in acid-treated reactors indicated the importance of the formation of hydrogen peroxide

$$2H\dot{O}_2 \rightarrow H_2O_2 + O_2 \qquad (3)$$

together with the process

$$H\dot{O}_2 + H_2 \rightarrow H_2O_2 + \dot{H}\,. \qquad (4)$$

(In the subsequent decades this idea was developed by Baldwin[10,11] and others.)

The measurement of the rate constant for reaction (4) is difficult because of the low rate of this process. In the study of the oxidation of hydrogen above the second limit Voevodskii was able to measure k_4,[6,7] which, together with the few available data obtained by other workers, served as a basis for the value recommended by Baulch[12].

Even when he became attracted to many new problems, Voevodskii continued to be interested in the reactions of HO_2 radicals. Seventeen years after the first attempt to detect HO_2, Panfilov, one of Voevodskii's students, successfully applied the EPR method to the determination of frozen HO_2 radicals in hydrogen combustion products[13]. Soon afterwards, Nalbandyan and coworkers[14] converted the radical "freezing out" method with subsequent analysis of the EPR spectra into a quantitative procedure for the

determination of $H\dot{O}_2$ and $R\dot{O}_2$ radicals in gas-phase oxidation and combustion reactions.

The regions corresponding to the combustion and slow oxidation of hydrogen were reinvestigated in order to study the characteristics of the accumulation of $H\dot{O}_2$ radicals. In particular, it was shown[14] that, in the region of the slow reaction between the second and third limits, the $H\dot{O}_2$ concentration is 10^{13} radical cm^{-3} and increases as the third limit is approached[14,15], as predicted by Voevodskii's calculations[7].

Using a modified method involving the freezing out of $H\dot{O}_2$ and $R\dot{O}_2$ radicals (fractionation) and analysing their EPR spectra, Nalbandyan and Mantashyan[14] established that the oxidation of hydrocarbons and lower aldehydes also involve the formation of $H\dot{O}_2$ radicals at a high concentration. The following processes serve as the sources of these active species:

$$\dot{C}_nH_{2n+1} + O_2 \rightarrow [\dot{C}_nH_{2n}O_2H] \rightarrow H\dot{O}_2 + C_nH_{2n},$$

$$\dot{C}_nH_{2n+1} + O_2 \rightarrow H\dot{O}_2 + C_nH_{2n},$$

$$H\dot{C}O \text{ (from aldehydes)} + O_2 \rightarrow H\dot{O}_2 + CO,$$

$$CO + \dot{O}H \rightarrow CO_2 + \dot{H} \xrightarrow{+O_2+M} H\dot{O}_2 .$$

On passing from the low-temperature to the higher-temperature region in the oxidation of hydrocarbons[5], the ratio $[H\dot{O}_2]/[R\dot{O}_2]$ increases appreciably[14]. This finding confirms the earlier hypothesis concerning the change in the mechanism of the oxidation of hydrocarbon on passing through the region corresponding to a negative temperature coefficient of the reaction and the involvement of $H\dot{O}_2$ radicals in chain propagation reactions in the higher-temperature oxidation region[14].

Whereas in the low-temperature oxidation region the formation of $H\dot{O}_2$ radicals leads to chain termination, on raising the temperature chain propagation reactions become important:

$$H\dot{O}_2 + RH \rightarrow H_2O_2 + \dot{R}, \qquad (5)$$

$$H\dot{O}_2 + R'CHO \rightarrow H_2O_2 + R'C\dot{O}, \qquad (6)$$

and the decomposition of the hydrogen peroxide formed leads to degenerate branching. Thus it was found that, in agreement with Voevodskii's views, in the higher-temperature oxidation region the $H\dot{O}_2$ radical is an active intermediate—a chain carrier.

For a quantitative description of the oxidation of hydrocarbons at a high temperature, it is necessary to know the rate constants for reactions (5) and (6), the few available values for which are listed in Table 1. The rate constants for the interaction of $H\dot{O}_2$ radicals with paraffinic hydrocarbons, presented in Lloyd's review[3], were measured by Baldwin and coworkers at a single temperature (500°C). Assuming that the activation energy for C_2H_6 is 14 kcal $mole^{-1}$ and that the difference between the enthalpies of reaction (5) enters into the activation energy with a coefficient of unity (according to the Semenov–Polanyi rule, with a coefficient of 0.75 for endothermic reactions[17]), Lloyd[3] obtained the Arrhenius parameters of reactions (5) listed in Table 1.

The products of the interaction of $H\dot{O}_2$ radicals with olefins are unknown[3,18]. The rate constants have been estimated[18].

We examined the pathways followed in the "linear" reactions of $H\dot{O}_2$ in the oxidation of hydrogen and hydrocarbons, i.e. the reactions of $H\dot{O}_2$ radicals with stable substances. These processes are important, because they lead to the third chain limit in the oxidation of hydrogen[7] and to the characteristics of the higher-temperature oxidation of hydrocarbons mentioned above.

However, nowadays non-linear reactions of $H\dot{O}_2$ radicals and their reactions with active species are attracting the attention of investigators to an increasing extent. We shall demonstrate three examples of the importance of non-linear processes involving $H\dot{O}_2$ radicals. We shall consider only situations in which the initial reactions where the species are generated are associated with the effect of radiation on reactive gaseous mixtures: (1) the influence of modern sources of ionising radiation (isotopes, nuclear reactors, accelerators) on the ignition limits associated with a branched chain mechanism; (2) the reactions of $H\dot{O}_2$ radicals in Earth's ozonosphere; (3) the reactions of $H\dot{O}_2$ radicals in common chemical lasers. As classical examples, we shall consider a mixture of hydrogen and oxygen for the first case and the working mixture in the laser whose operation is based on the reaction between H_2 and F_2 (the mechanism of this reaction was discovered at the Institute of Chemical Physics[19,20] and the most important chemical lasers in existence at the present time are based on it) for the third case.

Table 1. The rate constants for reactions (5) and (6) [$k = A\exp(-E/RT)$].

RH	C_2H_6	C_3H_8	n-C_4H_{10}	iso-C_4H_{10}	CH_4O*
ΔH_i, kcal $mole^{-1}$	8.36	4.84	4.97	1.27	−0.9
E, kcal $mole^{-1}$	14.0	10.5	10.5	7.0	10.4
$\lg A$ (cm^3 $mole^{-1}$ s^{-1})	12.0	11.3	11.7	11.0	13.0

*k was measured in the temperature range 773–793 K [16]; for the remaining RH, estimates taken from Ref. 3 are quoted.

II. NON-LINEAR REACTIONS OF $H\dot{O}_2$ RADICALS ASSOCIATED WITH THE OXIDATION OF HYDROGEN

The problem of the influence of radiation and of other physical methods for the generation of active species on the reaction of hydrogen with oxygen is the problem of the positive interaction of chains. The idea, logic, and initial method are due to Semenov[17] and the first postwar experiments, on the basis of which Semenov derived the mechanism, were carried out by Dubovitskii and Nalbandyan[21]. According to Semenov's calculation[17], when one begins with the rate of generation of oxygen atoms in Nalbandyan's photochemical experiments and one assumes that $H\dot{O}_2$ radicals are destroyed on the reactor wall and the chains interact solely via the reaction

$$\dot{H} + H\dot{O}_2 \rightarrow 2\dot{O}H,$$

then a rate constant of 10^{-11} cm^2 $molecule^{-1}$ s^{-1} must be attributed to the latter reaction in order to account for the observed limiting increase of pressure. Since that time

the reaction between $\dot{H}$ and $H\dot{O}_2$, which was found to proceed via the three channels

$$\dot{H} + H\dot{O}_2 \begin{cases} \longrightarrow 2\dot{O}H, & (7) \\ \longrightarrow H_2 + O_2, & (8) \\ \longrightarrow H_2O + \ddot{O}, & (9) \end{cases}$$

has been the subject of numerous investigations. Table 2 presents the experimental data accumulated hitherto. If Westenberg's results (which are probably erroneous [22,31]) are rejected, then, despite the quantitative discrepancy, all these data confirm a single main idea: the reaction between $\dot{H}$ and $H\dot{O}_2$ involves chain branching and not chain termination, in agreement with Semenov's hypothesis, because $k_8 < k_7 + k_9$.

Table 2. The ratios of the rate constants for the chain termination and propagation channels in the reaction between $\dot{H}$ and $H\dot{O}_2$.

T, K	$\frac{k_8}{k_7+k_9}$	Method	Refs.
773	0.17	Computer calculation, IInd limit in $H_2 + O_2$ reaction	22
900	0.15	Rate of $H_2 + O_2 + N_2$ flame propagation, computer calculation	23—25
293	0.50	Extrapolation of high-temperature data	23—25
291	0.51 ± 0.2	Discharge flow, measurement of H and H_2O concentrations; $p = 2$ mmHg	26
291	0.75 ± 0.25	Discharge flow, EPR; $p = 50$–250 mmHg	27
291	0.76	Diffusion cloud, mass spectrometry; $p = 20$ mmHg	28
291	1.6	Discharge flow, EPR; $p \leq 2.5$ mmHg	29
293	0.41	Discharge flow, EPR; $p = 10$ mmHg	30

As a result of the studies by Baldwin [11] and other investigators [32], it is known that the mechanism of the oxidation of hydrogen at the second ignition limit depends to a large extent on the treatment of the reaction vessel walls. In vessels treated with oxides and certain metal chlorides the active centres are destroyed at a higher rate on the reactor surface. The principal characteristics observed at the first and second ignition limits can then be accounted for in terms of a reaction mechanism involving only linear reaction processes:

$$H_2 + O_2 \rightarrow 2\dot{O}H, \quad (10)$$

$$\dot{O}H + H_2 \rightarrow H_2O + \dot{H}, \quad (11)$$

$$\dot{H} + O_2 \rightarrow \dot{O}H + \ddot{O}, \quad (2)$$

$$\ddot{O} + H_2 \rightarrow \dot{O}H + \dot{H}, \quad (12)$$

$$\dot{H} \xrightarrow{\text{wall}} (H)_w,$$

$$\ddot{O} \xrightarrow{\text{wall}} (O)_w,$$

$$\dot{O}H \xrightarrow{\text{wall}} (OH)_w,$$

$$\dot{H} + O_2 + M \rightarrow H\dot{O}_2 + M, \quad (1)$$

$$H\dot{O}_2 \xrightarrow{\text{wall}} (HO_2)_w.$$

The opposite case of the "fully reflecting" surface is that of the surface of reactors treated with acids [32] and primarily with boric acid [10,11]. Here the probability of the destruction of $H\dot{O}_2$ radicals on the wall is low ($\leq 10^{-4}$) [33] and the non-linear processes (7)–(9) and (3) make a considerable contribution to the mechanism of the oxidation of hydrogen near the second limit. Experiments show that in acid-treated vessels the second limit occurs at a higher pressure, which also indicates the dominance of the positive chain interaction processes (7) and (9).

The problem of the possible influence of ionising radiation on the ignition region has been examined [34]. After the essential features of the interaction of ions with molecules were established a quarter of a century ago and the corresponding rate constants were estimated, it became possible to convert the fluxed and doses of ionising radiation into the absolute rates of initiation of chemical reactions by such radiation [35]. The *EFDC* plot of the logarithm of the radiation dose rate against the reciprocal of temperature in Fig. 1, taken from Tal'roze [34], shows the dose rates for which the effect of radiation is significant. The region of an appreciable effect by the radiation is limited by plots corresponding to the following four criteria proposed for the analysis of the problem of the radiation-induced initiation of chain processes [34].

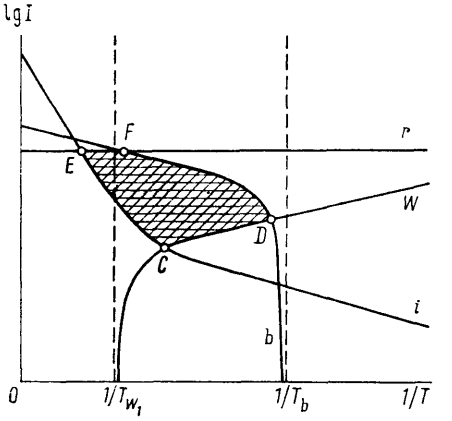


Figure 1. Plots of the b-, i-, r-, and W-criteria.

1. The initiation criterion or the i-criterion, according to which the rate of the radiation-induced initiation must exceed the rate of the thermal generation of active centres; the set of values of the dose rate and temperature satisfying this criterion is located above curve i in Fig. 1.

2. The branching criterion or b-criterion, requiring that the reaction should be self-accelerating under isothermal conditions. This characteristic of the process should be observed to the left of curve b.

3. The absolute rate or W-criterion, according to which it is necessary that the overall reaction rates should exceed a value selected on the grounds of practical considerations. This criterion is satisfied to the right of curve W.

4. The criterion concerning the presence of a source of sufficient intensity or the r-criterion. It is satisfied below the horizontal straight line r corresponding to the maximum dose rate which may be established in the reaction mixture using a particular type of ionising radiation source.

On the basis of the plots in Fig. 1, one may expect that radiation affects the ignition limits for a hydrogen–oxygen mixture only in the range of dose rates corresponding to

the region *EFDC*. The calculations of Poroikova et al.[36] do indeed show that the ionising radiation from the available sources can alter the position of the second ignition limit in hydrogen–oxygen mixtures.

Fig. 2 presents the results of calculations in terms of plots of the dimensionless pressure at the second limit against the logarithm of the ratio of the rate of artificial initiation and the rate of thermal chain generation [the calculation was performed for the following conditions: stoichiometric mixture, 723 K, cylindrical vessel with a radius of 2 cm, and the ratio $k_8/(k_7 + k_9) = 0.15$]. The limit is appreciably displaced when the rate of artificial initiation corresponds to a dose rate of 10^{14}–10^{17} eV cm^{-3} s^{-1}, which requires the use of powerful radiation sources.

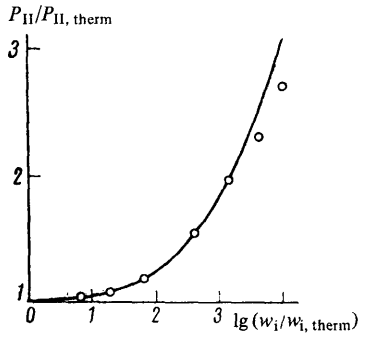


Figure 2. Dependence of the pressure at the second limit on the rate of artificial initiation; p_{II}—pressure at the limit; $p_{II,\,therm}$—pressure at the limit corresponding to thermal chain initiation; W_i—rate of artificial initiation; $W_{i,\,therm}$—rate of thermal generation of active centres.

The circles in Fig. 2 present the results of the calculation by the equation obtained for the second limit taking into account reactions (1)–(4) and (7)–(12), while the continuous line represents the results of the calculation of the second limit on a computer taking into account a more complex mechanism, including the consumption of the initial substances, the self-heating of the reacting mixture, the formation and consumption of hydrogen peroxide, and a number of other non-linear processes[33,36].

Evidently the results of the two calculations agree over a wide range of artificial initiation rates. The limit is controlled by processes (1) and (2) (as for a linear mechanism) and by the quadratic reactions (3) and (7) to (9). At higher rates of initiation there is an additional displacement of the limit (the continuous line passes above the circles) owing to the self-heating of the mixture[33,36].

Thus the four non-linear processes (3) and (7)–(9) involving HO_2 radicals determine the position of the thermal limit in acid-treated vessels and the displacement of the limit following artificial chain initiation. In order to calculate the limit, it is necessary to know both the overall rate constant for the reaction between H and HO_2 and the ratio of the rate constants for the chain propagation and termination channels and their temperature dependence. Values of the above ratio obtained by various workers are listed in Table 2. All the low-temperature results refer to the system where H atoms were obtained from a discharge and the overall pressure in the reaction vessel was several mmHg. In his analysis of causes of the discrepancies between the results, Lloyd[3] points to the possible contribution of excited HO_2^* species to the reaction with H atoms [the heat of reaction (1) is 47 kcal mole^{-1}]. It has been shown[37] that an even more important source of errors is the formation in the discharge of excited hydrogen molecules whose interaction with OH radicals takes place with a low activation energy. The corresponding increase in the concentration of H atoms and the decrease in the concentration of OH radicals may lead[37] to unduly low values of k_7 and of the overall rate constant for the reaction between H and HO_2 (in the available data[22–30], the values of the overall rate constant vary by a factor of 3).

The high temperature results, quoted by Baldwin et al.[22] and by Dixon-Lewis and coworkers[23–25] for only one temperature, were obtained by comparing the experimental position of the second limit and the rate of propagation of the hydrogen-oxygen flame with a very complex oxidation mechanism. The values obtained are thus based on certain numerical rate constants for a whole series of other processes. The rate constants for reactions (7)–(9) and the corresponding activation energies quoted by Hampson and Garvin[38] must therefore be regarded as estimates.

The rate constant for reaction (3) has been measured by many investigators[12]. The activation energy for this process is unknown but is probably small[3]. According to Lloyd's estimates[3], k_3 at 700–800 K is known within the limits of a factor of 2.

It follows from the foregoing data that reliable measurements of the rates of reactions (3) and (7)–(9) are necessary over a wide temperature range.

III. REACTIONS OF HO_2 RADICALS IN EARTH'S OZONOSPHERE

Earth's ozonosphere is a giant photochemical reactor in the ultraviolet part of the spectrum. Until recently it was believed that the photochemistry of the ozone layer is limited to Chapman's oxygen cycle[38]:

$$O_2 + h\nu \rightarrow 2O, \tag{13}$$

$$O + O_2 + M \rightarrow O_3 + M, \tag{14}$$

$$O_3 + h\nu \rightarrow O + O_2, \tag{15}$$

$$O + O_3 \rightarrow 2O_2, \tag{16}$$

in which reactions (14) and (15) are rapid. Reaction (13) involves the generation of active substances comprising the so called odd oxygen (oxygen atoms and ozone molecules), while reaction (16) involves their destruction.

At least three more groups of chain reactions opposing the tendency of sunlight to generate odd oxygen are known at the present time. These groups are the hydrogen, nitrogen, and chlorine ozone decomposition cycles. The reactions in these cycles, together with processes (13) and (16) control the steady-state concentration of ozone (in the ozone layer the concentration of oxygen atoms is much smaller than the concentration of ozone).

The active species in the hydrogen cycle, the so called odd hydrogen (H atoms, OH and HO_2 radicals, and H_2O_2 molecules), are formed from the H_2O, H_2, and CH_4

molecules arriving from Earth's surface. The most important processes in the hydrogen cycle are the following reactions in which the $\dot{O}H$ and $H\dot{O}_2$ radicals behave as catalysts of the decomposition of odd oxygen:

$$O_3 + \dot{O}H \rightarrow H\dot{O}_2 + O_2 ,$$
$$H\dot{O}_2 + \ddot{O} \rightarrow \dot{O}H + O_2 ,$$
$$O_3 + H\dot{O}_2 \rightarrow \dot{O}H + 2O_2 ,$$
$$\dot{O}H + \ddot{O} \rightarrow \dot{H} + O_2 ,$$
$$\dot{H} + O_2 + M \rightarrow H\dot{O}_2 + M .$$

These processes involve the termination of odd oxygen chains, while in relation to the substances constituting odd hydrogen they are chain propagation reactions (the interaction of the hydrogen and oxygen cycles).

Examples of other important chain propagation reactions are presented below:

$$\begin{aligned} 2H\dot{O}_2 &\rightarrow H_2O_2 + O_2, \\ H_2O_2 + h\nu &\rightarrow 2\dot{O}H, \\ H\dot{O}_2 + NO &\rightarrow \dot{O}H + NO_2, \\ H\dot{O}_2 + CH_3\dot{O}_2 &\rightarrow CH_3O_2H + O_2, \\ CH_3O_2H + h\nu &\rightarrow CH_3\dot{O} + \dot{O}H. \end{aligned} \qquad (17)$$

Here Eqn. (17) represents the interaction of the hydrogen and nitrogen cycles (the substances constituting odd nitrogen are NO, NO_2, NO_3, N_2O_5, HNO_3, and HNO_2). The last two processes are associated with the oxidation of natural methane.

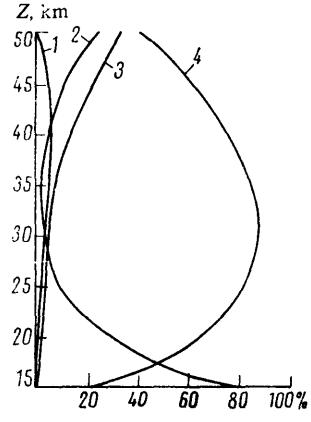


Figure 3. Contribution of the cycles to the rate of decomposition of ozone (%): 1) ClO_X; 2) HO_X; 3) O_X; 4) NO_X.

The relative contribution of the hydrogen cycle to the decomposition of ozone and the relative roles of other ozone decomposition cycles, which we recently calculated [39], are presented in Fig. 3. Evidently the chain reaction involving $H\dot{O}_2$ makes different contributions to the decomposition of ozone and in the lower ozonosphere this contribution may reach 2/3. We chose the chain length ν, equal to the number of odd oxygen molecules decomposed by one molecule of the cycle catalyst, as a measure of the efficiency of cycles in the decomposition of odd oxygen. The ozone decomposition chain length in each cycle, calculated by Tal'roze et al. [39], is presented in Fig. 4. Evidently the chain length in the hydrogen cycle has the smallest dependence on the height above sea level (Z) and amounts on average to several hundreds of units.

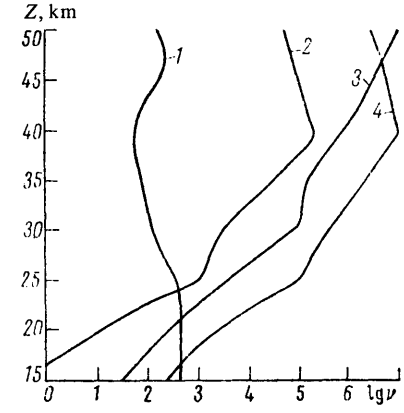


Figure 4. Odd oxygen chain lengths in different cycles: 1) HO_X; 2) ClO_X; 3) NO_X; 4) BrO_X.

Thus the key position of $H\dot{O}_2$ in the chemistry of the ozonosphere is determined to a large extent by its involvement in the "mixing" of different groups of chemical reactions, i.e. in non-linear interactions with active species of other cycles. Apart from the chain propagation reactions described above, the following interactions between the cycles are important:

$H\dot{O}_2 + \dot{O}H \rightarrow O_2 + H_2O$	(chain termination in the HO_X cycle)
$H\dot{O}_2 + NO_2 \rightarrow O_2 + HNO_2$	transfer, washing out by rain →
$H\dot{O}_2 + NO + M \rightarrow M + HNO_3$	→ termination in both cycles
$H\dot{O}_2 + \dot{C}l \rightarrow O_2 + HCl$	$\xrightarrow{+\dot{O}H}$ $H_2O + NO_x, ClO_x$ (partial termination in HO_X cycle)
$H\dot{O}_2 + CH_3\dot{O} \rightarrow O_2 + CH_3OH$	$\xrightarrow{+h\nu}$ regeneration of cycles

These processes largely lead to chain termination, but there also exists a chain propagation channel (photochemical decomposition).

Chain termination in the nitrogen and chlorine cycles takes place via the diffusion of acid species (HNO_X and HCl) to the troposphere and their subsequent washing out by rain. The rate of this process may be calculated with the aid of vertical turbulent diffusion coefficients, which have been estimated by many workers [39-41]. Compared with the rate of transfer, the chemical chain termination reaction

$$H\dot{O}_2 + \dot{O}H \rightarrow O_2 + H_2O \qquad (18)$$

takes place at a high rate in the stratosphere. This explains the relatively small length of the ozone decomposition chain in the hydrogen cycle. Thus reaction (18) is one of the key elementary processes influencing ozone in the lower stratosphere. Many investigators have been

devoted to the measurement of the rate constant for reaction (17). Its reliable measurements are difficult in view of the complexity of the systems in which ȮH and $H\dot{O}_2$ radicals may be obtained simultaneously. Hampson and Garvin[38] recommend values of k_{17} in the range from 2×10^{-11} to 2×10^{-10} cm^{-3} $mol.^{-1}$ s^{-1}, but the scatter of the literature data exceeds this range.

IV. THE $H\dot{O}_2$ RADICAL IN THE LASER BASED ON THE REACTION BETWEEN H_2 AND F_2†

The emission from these lasers is in the infrared because the elementary reactions

$$\dot{H}+F_2\rightarrow HF+\dot{F},$$
$$\dot{F}+H_2\rightarrow HF+\dot{H}$$

lead to the generation of inverted populations of vibrationally excited HF molecules. Despite the outward simplicity of the system, it is difficult to control the active process in the chemical laser. In the first place, when one is dealing with pulsed lasers, it is necessary to mix the initial substances under a considerable pressure. Shilov, Chaikin, and coworkers[19,20] found a simple solution to this problem: oxygen is added and the stabilisation process, which produces a second ignition limit in the fluorine–hydrogen mixture under the conditions of vigorous branching, is

$$\dot{H}+O_2+M\rightarrow H\dot{O}_2+M. \qquad (1)$$

The question arises of the subsequent fate of the $H\dot{O}_2$ radicals and whether or not it is important. This problem has been inadequately analysed and we shall point to only one of its aspects.

A pulsed chemical laser operates effectively under the conditions of intense initiation of the chain reaction. The initiation is achieved by some kind of influence on the fluorine–hydrogen mixture which leads to the appearance of fluorine atoms. The intensity of the initiation is usually such that, after a short period, the concentration of fluorine atoms reaches 0.1–1% of the initial concentration of molecules. It is noteworthy that, in a mixture having a nearly stoichiometric composition, the "slow" active centre is the hydrogen atom and the number of hydrogen atoms is virtually equal to the number of generated fluorine atoms. This factor distinguishes significantly the conditions in the pulsed reaction between fluorine and hydrogen from those in the thermal reaction and also from the reaction between hydrogen and oxygen in the initial stages of self-ignition. Indeed the $H\dot{O}_2$ radicals formed can no longer be regarded as relatively inactive, because the mixture contains a substance (hydrogen atoms) the concentration of which is sufficient to react rapidly with $H\dot{O}_2$ radicals. The hydroxy-radicals formed in this process can react with molecular hydrogen to generate hydrogen atoms. The rate constant for this reaction can be in principle very large and close to the collision number, since the ȮH radicals formed have an average excitation energy of 20 kcal $mole^{-1}$. Thus the situation of "an infinite chain length" is created.

Such are the three kinetic systems, outwardly so different and yet identical as regards the important role of $H\dot{O}_2$ radicals, to the understanding of which Voevodskii's fundamental ideas have made a significant contribution.

†For the description of chemical lasers employing the reaction between H_2 and F_2, see Refs. 42–44.

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