Experimental investigation and kinetic modeling of the negative temperature coefficient of the reaction rate in rich propane—oxygen mixtures

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The phenomenon of the negative temperature coefficient (NTC) of the reaction rate of the oxidation of rich propane—oxygen mixtures was experimentally studied. The NTC phenomenon is qualitatively described by a simple kinetic model containing a minimum set of reactions related to the oxidation of the starting hydrocarbon, propane, and the propyl $C_3H_7^{\cdot}$ radical formed.

Key words: oxidation, propane, cool flames, negative temperature coefficient.

The region of the negative temperature coefficient (NTC) and the related phenomenon of cool flames (*CF*) are known for hydrocarbon oxidation.[1—3] To establish the mechanism of these phenomena in detail, one must first of all solve the problem to which extent are they determined by the properties of the starting hydrocarbon itself or by the reactions of products of its oxidation. When propane is oxidized, propylene and acetaldehyde, in particular, are formed in considerable amounts, and the oxidation of the latter is also accompanied by the appearance of *CF*.[4,5]

To solve this problem, the effect of the products formed during the oxidation should be decreased as much as possible. This can be achieved by maximum enrichment of the starting mixture in the hydrocarbon. When, *e.g.*, NTC is observed for the hydrocarbon : oxygen ratio equal to 25 : 1, it is reasonable to assume that there is a series of elementary reactions related to the oxidation of only the starting hydrocarbon (but not of its products), which can lead to the appearance of NTC in the oxidation of this hydrocarbon.

When reactions involving oxidation products are ruled out at least in the first approximation, this simplifies substantially the initial kinetic model and distinguishes more distinctly the elementary reactions that make the maximum contribution to NTC phenomena. This approach does not assume that under some conditions, oxidation products do not participate in the formation of these phenomena, but it allows one to attain a clearer understanding of the role of these or other elementary reactions.

The purpose of this work is to study experimentally the NTC phenomenon in the oxidation of rich propane—oxygen mixtures and develop a minimum kinetic model sufficient for a qualitative explanation of the phenomena observed.

Experimental

Propane was oxidized on a standard static setup with a Pyrex reactor ($V = 400$ cm^3). The pressure was measured by a sensitive membrane manometer. At low temperatures ($T <$ 600 K), CH_2O, CH_3OH, C_3H_6, CH_3CHO, CO, CO_2, and H_2O are the main products. In lower amounts, C_2H_4, C_2H_5OH, C_3H_6O, and traces of CH_3COCH_3 are observed.

The ratio between the main products changed several times as the temperature increased, and no sharp changes in the compositions of the products were observed on going to the NTC region.

The NTC region was determined from the temperature dependence of the maximum reaction rate at a constant pressure and composition of the C_3H_8—O_2 mixture. The maximum rate of pressure change in the system ($[d\Delta p/dt]_{max}$) was taken as a measure of the maximum rate. The kinetic $\Delta p(t)$ curves had pronounced S-like shapes. In the kinetic modeling, the NTC region was determined from the rate of propane consumption. The validity of the comparison of the experimental and calculated NTC regions will be discussed below.

Results and Discussion

The experimentally determined NTC region at p = 200 Torr for the C_3H_8—O_2 mixtures with different compositions is presented in Fig. 1. It can be seen that as the mixture is enriched in propane, the temperature region exhibiting the NTC effect remains almost unchanged, and only its intensity changes. Curve *4* in Fig. 1, corresponding to the composition $C_3H_8 : O_2 =$ 23, agrees satisfactorily with the data[6] for the 95% propane—5% O_2 mixture (it should be noted that in this case, the NTC region was determined[6] from the temperature dependence of the induction period).

In accordance with the purpose of this work, let us consider in detail only curve *4* in Fig. 1. This NTC curve corresponds to a content of ~96% propane in the

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Table 1. Mechanism of propane oxidation

Reaction		A^a	E^b
$C_3H_8 + O_2 \rightarrow C_3H_7^{\cdot} + HO_2^{\cdot}$	(1)	3.95(15)	47.4
$C_3H_7^{\cdot} + HO_2^{\cdot} \rightarrow C_3H_8 + O_2$	(−1)	1.00(12)	0
$C_3H_7^{\cdot} + O_2 \rightarrow C_3H_7O_2^{\cdot}$	(2)	2.00(12)	0
$C_3H_7O_2^{\cdot} \rightarrow C_3H_7^{\cdot} + O_2$	(−2)	1.00(15)^c	31.5
$C_3H_7^{\cdot} + O_2 \rightarrow C_3H_6 + HO_2^{\cdot}$	(3)	1.00(10)	2.2
$C_3H_7O_2^{\cdot} + C_3H_8 \rightarrow$ $\rightarrow C_3H_7OOH + C_3H_7^{\cdot}$	(4)	5.00(11)	15.0
$C_3H_7OOH \rightarrow C_3H_7O^{\cdot} + OH^{\cdot}$	(5)	4.00(15)^c	43.0
$C_3H_7O^{\cdot} + C_3H_8 \rightarrow$ $\rightarrow C_3H_7OH + C_3H_7^{\cdot}$	(6)	5.00(11)	7.0
$OH^{\cdot} + C_3H_8 \rightarrow H_2O + C_3H_7^{\cdot}$	(7)	1.40(12)	0.9
$HO_2^{\cdot} + C_3H_8 \rightarrow H_2O_2 + C_3H_7^{\cdot}$	(8)	5.00(11)	15.0
$H_2O_2 + M \rightarrow OH^{\cdot} + OH^{\cdot} + M$	(9)	1.20(17)	45.8
$C_3H_7O_2^{\cdot} + C_3H_7O_2^{\cdot} \rightarrow$ $\rightarrow C_3H_7O^{\cdot} + C_3H_7O^{\cdot} + O_2$	(10)	1.00(11)	0
$C_3H_7O_2^{\cdot} + C_3H_7O_2^{\cdot} \rightarrow$ $\rightarrow C_3H_7OH + C_3H_5CHO + O_2$	(11)	4.50(10)	0
$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2$	(12)	1.30(11)	1.23
$HO_2^{\cdot} + C_3H_7O_2^{\cdot} \rightarrow$ $\rightarrow C_3H_7O^{\cdot} + OH^{\cdot} + O_2$	(13)	3.00(11)	0
$C_3H_7^{\cdot} + C_3H_7^{\cdot} \rightarrow C_3H_8 + C_3H_6$	(14)	1.80(13)	0
$C_3H_7^{\cdot} + C_3H_7O_2^{\cdot} \rightarrow$ $\rightarrow C_3H_7O^{\cdot} + C_3H_7O^{\cdot}$	(15)	2.70(13)	0
$C_3H_7O^{\cdot} + O_2 \rightarrow C_2H_5CHO + HO_2^{\cdot}$	(16)	6.00(10)	2.6
$C_3H_7^{\cdot} + HO_2^{\cdot} \rightarrow C_3H_7O^{\cdot} + OH^{\cdot}$	(17)	4.00(13)	0
$C_3H_7O^{\cdot} \rightarrow C_2H_5^{\cdot} + CH_2O$	(18)	8.00(13)^c	21.1
$C_2H_5^{\cdot} + O_2 \rightarrow C_2H_5O_2^{\cdot}$	(19)	2.00(12)	0
$C_2H_5O_2^{\cdot} \rightarrow C_2H_5^{\cdot} + O_2$	(−19)	1.00(15)^c	31.5
$C_2H_5O_2^{\cdot} + C_3H_8 \rightarrow$ $\rightarrow C_2H_5OOH + C_3H_7^{\cdot}$	(20)	5.00(11)	15.0
$C_2H_5OOH \rightarrow C_2H_5O^{\cdot} + OH^{\cdot}$	(21)	4.00(15)^c	43.0
$C_2H_5O^{\cdot} + O_2 \rightarrow CH_3CHO + HO_2^{\cdot}$	(22)	6.00(10)	2.6
$C_2H_5^{\cdot} + O_2 \rightarrow C_2H_4 + HO_2^{\cdot}$	(23)	1.00(10)	2.2
$C_2H_5O^{\cdot} + C_2H_8 \rightarrow C_2H_5OH + C_3H_7^{\cdot}$	(24)	5.00(11)	7.0
$C_2H_5O_2^{\cdot} + C_2H_5O_2^{\cdot} \rightarrow$ $\rightarrow C_2H_5O^{\cdot} + C_2H_5O^{\cdot}$	(25)	1.00(11)	0
$C_2H_5O_2^{\cdot} + C_2H_5O_2^{\cdot} \rightarrow$ $\rightarrow C_2H_5OH + CH_3CHO + O_2$	(26)	4.50(10)	0
$C_2H_5O_2^{\cdot} + HO_2^{\cdot} \rightarrow C_2H_5OOH + O_2$	(27)	4.60(10)	0
$C_2H_5O_2^{\cdot} + C_3H_7O_2^{\cdot} \rightarrow$ $\rightarrow C_2H_5O^{\cdot} + C_3H_7O^{\cdot} + O_2$	(28)	1.00(11)	0
$C_2H_5O_2^{\cdot} + C_3H_7O_2^{\cdot} \rightarrow$ $\rightarrow C_2H_5OH + C_2H_5CHO + O_2$	(29)	4.50(10)	0
$C_2H_5^{\cdot} + C_2H_5O_2^{\cdot} \rightarrow$ $\rightarrow C_2H_5O^{\cdot} + C_2H_5O^{\cdot}$	(30)	2.70(13)	0
$C_2H_5^{\cdot} + C_3H_7O_2^{\cdot} \rightarrow$ $\rightarrow C_2H_5O^{\cdot} + C_3H_7O^{\cdot}$	(31)	2.70(13)	0
$C_2H_5^{\cdot} + HO_2^{\cdot} \rightarrow C_2H_6 + O_2$	(32)	4.00(13)	0
$C_2H_5^{\cdot} + HO_2^{\cdot} \rightarrow C_2H_5O^{\cdot} + OH^{\cdot}$	(33)	4.00(13)	0
$C_2H_5^{\cdot} + C_2H_5^{\cdot} \rightarrow C_2H_4 + C_2H_6$	(34)	1.80(13)	0
$C_2H_5^{\cdot} + C_3H_7^{\cdot} \rightarrow C_2H_6 + C_3H_8$	(35)	1.80(13)	0
$C_2H_5O^{\cdot} \rightarrow CH_3^{\cdot} + CH_2O$	(36)	8.00(13)^c	21.1
$CH_3^{\cdot} + O_2 \rightarrow CH_3O_2^{\cdot}$	(37)	1.32(11)	0
$CH_3O_2^{\cdot} \rightarrow CH_3^{\cdot} + O_2$	(−37)	5.00(13)^c	31.5
$CH_3O_2^{\cdot} + C_3H_8 \rightarrow$ $\rightarrow CH_3OOH + C_3H_7^{\cdot}$	(38)	5.00(11)	15.0
$CH_3OOH \rightarrow CH_3O^{\cdot} + OH^{\cdot}$	(39)	4.00(14)^c	43.0
$CH_3O^{\cdot} + C_3H_8 \rightarrow CH_3OH + C_3H_7^{\cdot}$	(40)	5.00(11)	7.0
$CH_3O^{\cdot} + O_2 \rightarrow CH_2O + HO_2^{\cdot}$	(41)	6.00(10)	2.6
$CH_3O_2^{\cdot} + CH_3O_2^{\cdot} \rightarrow$ $\rightarrow CH_3O^{\cdot} + CH_3O^{\cdot} + O_2$	(42)	1.00(11)	0
$CH_3O_2^{\cdot} + CH_3O_2^{\cdot} \rightarrow$ $\rightarrow CH_3OH + CH_2O + O_2$	(43)	4.45(10)	0
$CH_3O_2^{\cdot} + C_2H_5O_2^{\cdot} \rightarrow$ $\rightarrow CH_3O^{\cdot} + C_2H_5O^{\cdot} + O_2$	(44)	1.00(11)	0
$CH_3O_2^{\cdot} + C_2H_5O_2^{\cdot} \rightarrow$ $\rightarrow CH_3OH + CH_3CHO + O_2$	(45)	4.44(10)	0
$CH_3O_2^{\cdot} + C_3H_7O_2^{\cdot} \rightarrow$ $\rightarrow CH_3O^{\cdot} + C_3H_7O^{\cdot} + O_2$	(46)	1.00(11)	0
$CH_3O_2^{\cdot} + C_3H_7O_2^{\cdot} \rightarrow$ $\rightarrow CH_3OH + C_2H_5CHO + O_2$	(47)	4.40(10)	0
$CH_3^{\cdot} + CH_3^{\cdot} \rightarrow C_2H_6$	(48)	1.80(13)	0
$CH_3^{\cdot} + C_2H_5^{\cdot} \rightarrow C_3H_8$	(49)	1.80(13)	0
$CH_3^{\cdot} + C_3H_7^{\cdot} \rightarrow CH_4 + C_3H_6$	(50)	1.80(13)	0
$HO_2^{\cdot} + CH_3OO^{\cdot} \rightarrow$ $\rightarrow CH_3OOH + O_2$	(51)	4.60(10)	0
$HO_2^{\cdot} + CH_3^{\cdot} \rightarrow CH_3O^{\cdot} + OH^{\cdot}$	(52)	4.00(13)	0
$CH_3OO^{\cdot} + CH_3^{\cdot} \rightarrow$ $\rightarrow CH_3O^{\cdot} + CH_3O^{\cdot}$	(53)	2.70(13)	0
$CH_3O_2^{\cdot} \rightarrow$ Termination	(54)	5.00^c	0
$C_2H_5O_2^{\cdot} \rightarrow$ Termination	(55)	5.00^c	0
$C_3H_7O_2^{\cdot} \rightarrow$ Termination	(56)	5.00^c	0
$CH_3^{\cdot} \rightarrow$ Termination	(57)	5.00^c	0
$C_2H_5^{\cdot} \rightarrow$ Termination	(58)	5.00^c	0
$C_3H_7^{\cdot} \rightarrow$ Termination	(59)	5.00^c	0

[a] A/cm^3 mol^{-1} s^{-1}. [b] E/kcal mol^{-1}. [c] A/s^{-1}.

mixture. The overall content of the oxidation products cannot be greater than 8% (no more than 50% oxygen is usually consumed up to the moment of achieving the maximum rate), *i.e.*, it can be considered in the first approximation that the reactions of radicals formed in the system with the propane molecule make the main contribution to the oxidation mechanism rather than the reactions with the products of its oxidation.

Kinetic modeling. Only the reactions of the C_3 radicals genetically related to the structure of the starting propane molecule are taken into account in the first and, perhaps, most interesting approximation of the development of a model of oxidation of "superrich" propane—oxygen mixtures. Let us examine whether this minimum set of reactions is enough for the appearance of NTC.

This set is presented in Table 1 by reactions (1)—(17). We shall call it the M1 model. This model contains no hypothetical reactions. All reactions are known, and the only question that arises concerns the correct choice of the rate constant values for these reactions. Explanations on the choice of the rate constant values are given in the Appendix. Some remarks should be given only for reaction (3). The position of the NTC region and the appearance of the phenomenon itself are substantially determined by this reaction. However, it is doubtful that

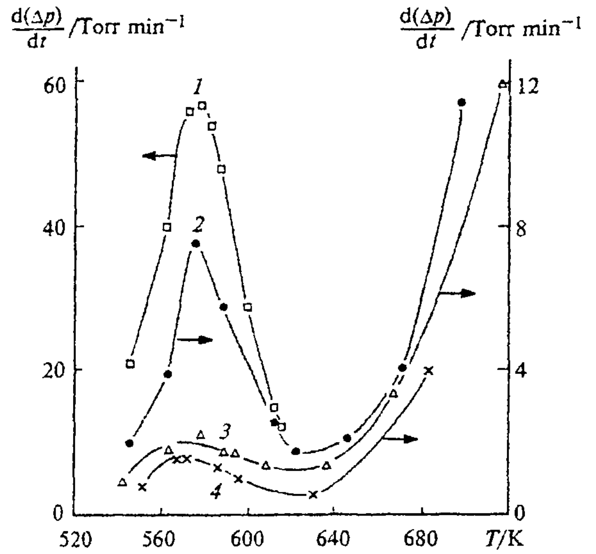

Fig. 1. Experimental temperature dependence of the maximum rate of the pressure increase $d(\Delta p)/dt$ for the oxidation of propane—oxygen mixtures with the composition $[C_3H_8] : [O_2]$ = 1 (*1*), 7.5 (*2*), 18 (*3*), and 23 (*4*). Initial pressure p_0 = 200 Torr.

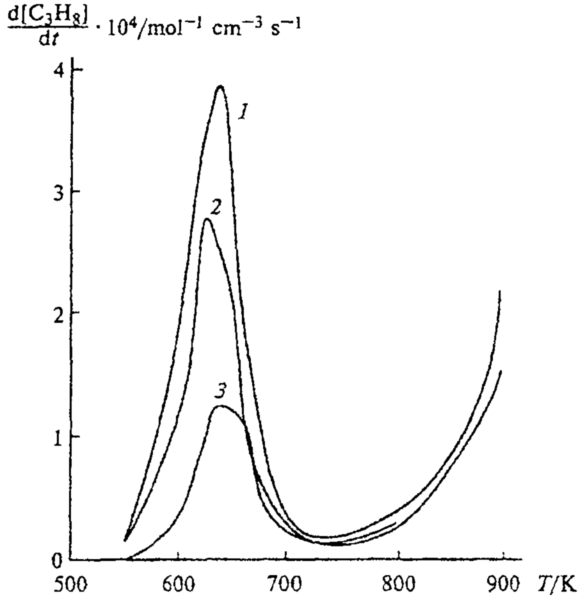

Fig. 2. Temperature dependences of the maximum rate of propane conversion calculated by the M1 (*1*), M2 (*2*), and M3 (*3*) models for the oxidation of propane—oxygen mixtures. Initial pressure p_0 = 200 Torr. Composition of the mixture: $[C_3H_8] : [O_2]$ = 23.

reaction (3) is in fact elementary rather than effective,[7] since it can be replaced with the sequence of reactions

$$C_3H_7 + O_2 \rightarrow C_3H_7OO \rightarrow C_3H_6OOH \rightarrow C_3H_6 + HO_2, \quad (3')$$

in which the elementary character of each of the stages is doubtless. Presently, it is impossible to introduce the sequence of reactions (3′) into the model, because reliable data on the rate constants of the second and third reactions of sequence (3′) are unavailable. Since, however, the rate constant value for (3) is available[8,9] (without discussing its character), it is included in the model.

Curve *1* in Fig. 2 demonstrates the NTC region calculated by the M1 model. It can be seen that at least for saturated hydrocarbon, the NTC phenomenon appears when the oxidation of only one alkyl radical genetically related to the structure of the starting molecule is taken into account. Under this approximation, the differences between *n*- and isopropyl radicals are not taken into account.

The following reactions are[10] the stages that make the maximum contribution to the appearance of the NTC: (2), (−2), (3), (4), (5), (8), and (9). The remaining stages in M1 (reactions of radical propagation and termination) cannot lead to the NTC of the reaction. A comparison between curve *1* in Fig. 2 and curve *4* in Fig. 1 shows that the calculated NTC curve is shifted to the high-temperature region.

The account for reaction (18) is the next evident step of refinement of the model. This reaction occurs rapidly even at low temperatures and is independent of the presence of oxidation products. An ethyl radical is formed in reaction (18) and, hence, all reactions related to its oxidation, except the reactions of the C_2 radicals with the oxidation products, should be taken into account. In this case, reactions (18)—(35) should be included in the model. The series of reactions (1)—(35) will be called the M2 model. The results of the calculations based on this model are presented in Fig. 2 (curve *2*).

The account for reaction (36) and the additional inclusion of reactions (36)—(53) in the model are a further refinement of the model. The overall model including 53 reactions will be designated as M3. Curve *3* in Fig. 2 is the result of the calculations based on M3. The refinement of the model due to the reactions initiated by elementary acts (18) and (36) almost does not result in shifting of the NTC region, although according to the experiment, the calculated maximum rates approach the experimental rates in value. The divergence between the calculated NTC region on the temperature scale and the position of the experimentally determined NTC region is not greater than 90 K. This divergence would have been considered as great if the development of a quantitative model had been the purpose of the work.

Discussion of the results of modeling. First, let us consider the problem on the correctness of the comparison between the NTC regions obtained from the determination of the maximum rate of pressure change (experiment) and the maximum rate of propane consumption (calculation). The program of the kinetic calculations admitted the possibility of calculating the rate of pressure increase. Since the model suggested can be

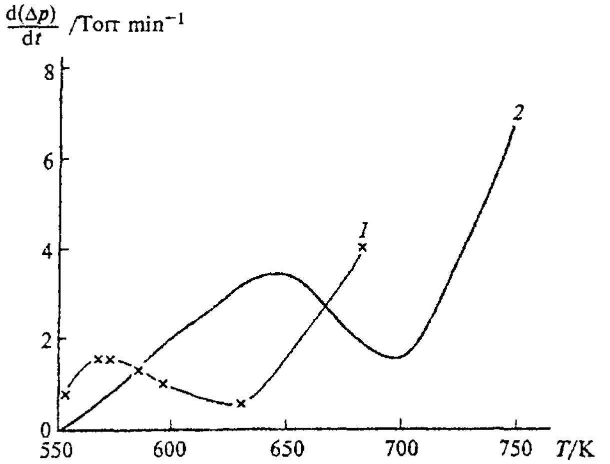

Fig. 3. Experimental (*1*) and calculated (*2*) temperature dependences of the maximum rate of the pressure increase $d(\Delta p)/dt$ for the oxidation of propane—oxygen mixtures. Initial pressure p_0 = 200 Torr. Composition of the mixture: $[C_3H_8] : [O_2]$ = 23.

valid only for the oxidation of very rich mixtures, these calculations were performed for curve *3* in Fig. 2 and compared to the experimental data in Fig. 1, curve *4*. The results of the comparison are presented in Fig. 3. Three conclusions follow from the consideration of Figs. 2 and 3:

1. The NTC regions calculated on the basis of $(d[C_3H_8]/dt)_{max}$ and from $(d(\Delta p)/dt)_{max}$ almost coincide.

2. The absolute calculated and experimental $(d(\Delta p)/dt)_{max}$ values are close, which testifies to the fact that the M3 model is a good first approximation of the model of the low-temperature oxidation of rich propane—oxygen mixtures.

3. The calculated NTC region is shifted by ~90 K to high temperatures as compared to that determined experimentally.

The M3 model of the oxidation of rich propane mixtures suggested in this work is rigidly appropriate only to infinitely rich mixtures, since it does not take into account any reactions involving oxidation products.

The calculations based on the M3 model, as applied to the C_3H_8—O_2 (96 : 4) mixture (see Fig. 3), showed that in the region of maximum oxidation rate, according to the experimental data, formaldehyde is formed in small amounts from aldehydes. The calculations by the M3 model included the degenerate branching reactions

$$C_3H_7OO^{\cdot} + CH_2O \rightarrow C_3H_7OOH + CHO^{\cdot},$$
$$C_2H_5OO^{\cdot} + CH_2O \rightarrow C_2H_5OOH + CHO^{\cdot},$$
$$CH_3OO^{\cdot} + CH_2O \rightarrow CH_3OOH + CHO^{\cdot},$$

and showed that the calculated NTC region was somewhat shifted to low temperatures.

Appendix

Let us consider in detail the reactions of the (2), (−2), (3), (4), and (5) types, which affect most strongly the formation of the NTC region. The rate constants were taken mainly from Ref. 8. In cases where reliable data are unavailable, the values of the Arrhenius parameters of the rate constants were estimated by analogy to the reactions accepted in the model of methane oxidation developed previously.[11,12]

Let us consider first the key reactions.

1. Reactions (37), (2), and (19). At high pressures, the values of the rate constants (usually designed by the "infinity" index ∞) of the addition of alkyl radicals to oxygen are close and equal[8,10] to $\sim 2 \cdot 10^{12}$. For polyatomic radicals with the number of carbon atoms ≥2, this limit is achieved already at pressures equal to several tens of Torr. Therefore, $K_2 = K_{19} = 2 \cdot 10^{12}$ was accepted. For the $CH_3^{\cdot}$ radical, the high-pressure limit is achieved at hundreds of Torr. The pressure dependence of K_{37} was taken into account, and the value of $1.3 \cdot 10^{11}$ at p = 200 Torr was accepted.[12] The following dimensions of the *A* pre-exponential factors of the rate constants are used hereinafter: first-order reactions, s^{-1}; second-order reactions, cm^3 mol^{-1} s^{-1}; and third-order reactions, cm^6 mol^{-2} s^{-1}. The activation energies (*E*) and energies of bond cleavage (*D*) are expressed in kcal mol^{-1}.

2. Reactions (−2), (−19), and (−37). The Arrhenius parameters of these reactions were calculated using the corresponding equilibrium constants.

3. Reactions (3) and (21). For reaction (21), the *A* and *E* values have been determined previously.[8] The $C_3H_7^{\cdot}$ and $C_2H_5^{\cdot}$ radicals differ slightly; therefore, $K_3 = K_{21}$ was accepted.

4. Reactions (4), (8), (22), and (38). Reliable experimental data on the rate constants of these reactions are unavailable. It is usually assumed that *D*(ROO—H) is almost independent of R. Therefore, it is reasonable to accept the same value of the rate constant for all reactions of ROO$^{\cdot}$ and $HO_2^{\cdot}$ with some alkane.[13]

In the methane oxidation model,[11,12] for the reaction

$$CH_3OO^{\cdot} + CH_4 \rightarrow CH_3OOH + CH_3^{\cdot} \qquad (60)$$

$A = 6 \cdot 10^{11}$ and E = 21.5 were accepted.

The empirical formula for calculating the activation energies of radical substitution reactions from the values of heats of the reaction was suggested.[14] The electronegativity of radicals, in our case, the ROO$^{\cdot}$ radicals, is an indefinite parameter in this formula. This value of electronegativity was calculated using E = 21.5 for reaction (60). The values of 17 and 14 kcal mol^{-1} were obtained for the reactions of ROO$^{\cdot}$ with ethane and propane, respectively. The value of 18.6 kcal mol^{-1} is recommended for the activation energy of reaction (60) by the large set of data on rate constants of elementary reactions.[15] The same work recommends E = 15 kcal mol^{-1} for the reaction

$$CH_3OO^{\cdot} + C_2H_6 \rightarrow CH_3OOH + C_2H_5^{\cdot}. \qquad (61)$$

It can be easily shown that these two values, 15 and 18.6 kcal mol^{-1}, contradict one another. The *D*(C—H) values in methane and ethane are equal to 105 and 98 kcal mol^{-1}, respectively. The *D*(ROO—H) value is[16] 88 kcal mol^{-1}. Reactions (60) and (61) are endothermic, ΔH° = 17 and 10 kcal mol^{-1}, respectively. Since ΔH° of the reaction is a component of the activation energy, the *E* values for reactions (60) and (61) cannot differ by less than 7 kcal mol^{-1}. The value $E = 21.5$ kcal mol^{-1} accepted by us for reaction (60) agrees well with $E = 15$ kcal mol^{-1} for reaction (61).[15] On the other hand, $E = 15$ kcal mol^{-1} estimated for reaction (38) agrees well with the E value recommended previously[15] for the reaction of $CH_3OO^{\cdot}$ with ethane. All the aforesaid allows $E = 15$ kcal mol^{-1} to be accepted for reactions (4), (8), (22), and (38).

5. Reactions (5), (23), and (39). Using the RRKM theory, K_{∞} of reaction (39) as $4 \cdot 10^{15}\exp(-43{,}000/RT)$ and the pressure dependence of K_{39} were calculated.[17] Based on the published data,[17] $K_{39} = 4 \cdot 10^{14}\exp(-43{,}000/RT)$ was determined[12] for $p \approx 0.5-1$ atm.

For the C_2H_5OOH and C_3H_7OOH molecules, which have a greater number of atoms, the pressure of 200 Torr, under which experiments were performed, and calculations in this work are almost infinite and, hence, the value of $4 \cdot 10^{15}\exp(-43{,}000/RT)$ can be accepted for K_5 and K_{23}. This value has been previously recommended for reaction (23).[8]

6. Reactions (6), (24), and (40). Available data on the reactions of the $RO^{\cdot}$ radicals with alkanes are few and unreliable. In the methane oxidation model,[11] for the reaction

$$CH_3O^{\cdot} + CH_4 \rightarrow CH_3OH + CH_3^{\cdot}$$

$E = 11$ kcal mol^{-1} was accepted. Since the RO—H bond strengths are approximately equivalent in all ROH compounds and equal to 101—103 kcal mol^{-1}, the procedure described in item 4 for the reactions of the $ROO^{\cdot}$ radicals was used to estimate the activation energy of the reaction of $RO^{\cdot}$ with propane. The activation energy of the reactions of $RO^{\cdot}$ with propane was estimated as $E = 7$ kcal mol^{-1}.

7. It is known for a relatively large group of recombination reactions of the $ROO^{\cdot} + ROO^{\cdot}$, $R^{\cdot} + ROO^{\cdot}$, and $R^{\cdot} + R^{\cdot}$ types included in the model that their activation energies are almost equal to zero, and published data contain no substantial contradictions for the values of the rate constants of these reactions.[9,18] Note that they do not define the NTC phenomenon itself. Therefore, to simplify the consideration and analysis of the model, the rate constants of these group reactions were accepted to be equal to similar values for the reactions of $CH_3^{\cdot}$ and $CH_3OO^{\cdot}$.[11,12]

8. In the radical exchange reactions involving the $ROO^{\cdot}$, $HO_2^{\cdot}$, and $RO^{\cdot}$ radicals considered above, the pre-exponential factors are accepted to be the same and equal to $5 \cdot 10^{11}$, when no reference to available data is presented. This approach is well substantiated theoretically.[19]

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