Computer simulation of thermal decomposition reactions of alkyl nitrates

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An approach to the construction of models for thermal decomposition of organic compounds based on *recombination reaction networks* was developed. Each species (molecule, ion, or radical) is considered as a potential reagent. It was suggested that the newly formed species can react with all other species which are already present in the reaction mixture. The results of reactions are represented as a bipartite graph whose vertices are formed either by species generated or by the descriptions of interactions, while the oriented edges determine the relations between the reagents and the reaction products. Based on analysis of the experimental data on the mechanisms of thermal decomposition, empirical rules were developed for simulating possible thermal decomposition reactions of the major classes of energetic compounds. The proposed approach allows one to describe the complete spectrum of reactions occurring in the course of thermal decomposition. The approach was realized in the CASB computer program and was exemplified by simulation of thermal decomposition of methyl, ethyl, and isopropyl nitrates. All stages of the mechanisms (some of which have been reported in the literature) were reproduced. A number of new decomposition reactions, which have not been studied experimentally, are suggested.

Key words: recombination reaction network, simulation of reaction mechanisms; thermal decomposition, alkyl nitrates.

Although a large number of experimental investigations was performed, pathways of thermal decomposition of organic compounds and, in particular, of energetic compounds, remain unclear. Interest in this problem stems from the necessity of studying the thermal stability of energetic compounds. This problem is also of interest from the viewpoint of assessment of the capabilities of potentially energetic compounds, which have not yet been synthesized. The solution of this problem may also be useful in studying the kinetics of inflammation of energetic compounds and in gaining a deeper insight into the nature of thermal decomposition.

Most of the experimental methods for estimating thermal stability allow one to follow the course of this process only in the first stage of decomposition. When analyzing the experimental data, it is generally assumed that thermal decomposition of nitro compounds involves the cleavage of the $R-NO_2$ bond as the first stage.[1–3] However, every so often there is no direct evidence in favor of this statement.[4–6] The data on the complete set of reactions, which occur at the subsequent stages of thermal decomposition and which strongly affect the type and yields of the final products, are scarce. In the present work, we develop a general approach to computer simulation of the complete spectrum of possible reactions taking place upon thermal decomposition. In addition, this approach is useful in interpreting experimental data and simulating the thermodynamics and kinetics of thermolysis of organic compounds.

The basis for the proposed methodology is a combination of procedures for the computer design of organic synthesis and for expert estimation of experimental data on thermolysis. The major postulates of the suggested approach have been reported previously in detail[7,8] using nitroalkanes and nitramines as examples.[9–11] In the present work, we extended this approach to another class of energetic compounds, *viz.*, to nitre esters.

Polynitro esters are widely used as components of energetic mixtures. In particular, these compounds are used as accelerators of combustion because they can substantially reduce the time of inflammation of air-fuel mixtures. However, it is difficult to control inflammation processes of these systems due to the absence of reliable data on the reaction mechanisms. It was only established with a fair degree of assurance that thermal decomposition of nitric esters proceeds through homolysis of the $O-NO_2$ bond to form NO_2 and the corresponding alkoxyl radical.[1] The subsequent reactions, particularly deep stages of decomposition, which, undoubtedly, play a decisive role in the inflam-

mation mechanism, remain poorly understood. To illustrate the proposed method, we used methyl, ethyl, and isopropyl nitrates as model compounds because sufficiently complete experimental data are available for these compounds (note, in particular, studies of decomposition of the above-mentioned nitrates by shock waves[12,13]).

Methodological fundamentals of simulation of thermal decomposition

The general method for the simulation of complex processes in closed chemical systems, in particular, homolytic thermolysis, involves exhaustive combinatorial search through the possible reaction pathways based on structural formulas of compounds followed by selection of thermochemically most favorable stages. Previously,[8] we have developed schemes describing decomposition processes as expert rules based on the analysis of the experimental data. The proposed method for the computer simulation of thermal decomposition involves certain concepts both of synthetic and retrosynthetic approaches to organic synthesis design.[14,15] This method deals with forward reactions when the direction of simulation coincides with that of real processes and by analogy with the retrosynthetic approach to synthesis design, thereby simplifying a given desired structure.

We consider all reactions as simultaneous and competitive processes. In this case, intermediates can be obtained _via_ several pathways and they, in turn, are potentially able to react with all other species because all these species exist in a single closed chemical system. This consideration gives a complete pattern of processes that occur during thermolysis.[16] In this case, the relations between intermediates cannot be considered as a traditional reaction graph or a synthesis tree. The pattern comprises a more complex directed reaction network represented as a _recombination reaction network_ (RRN).[8] This network can be described by a bipartite oriented graph in which vertices of one type represent the molecular structure and vertices of the second type describe the reaction.[17] According to the definition of bipartite graphs, the edges always join vertices of different types, _viz._, vertices of compounds and vertices of reactions. All vertices are joined by oriented edges, which allows one to distinguish the reagents (incoming edges) and the reaction products (outgoing edges) (Fig. 1).

Vertices denoted by numbers in squares represent chemical compounds and those in ovals represent reactions (the first figure denotes the number of the iteration at which a particular reaction is generated using the CASB program (see below), and the second figure denotes the corresponding ordinal number of the reaction). For example, the vertex (1 : 1) (see Fig. 1) has one edge incoming from vertex 1 (methyl nitrate) and two outgoing edges corresponding to the reaction prod-

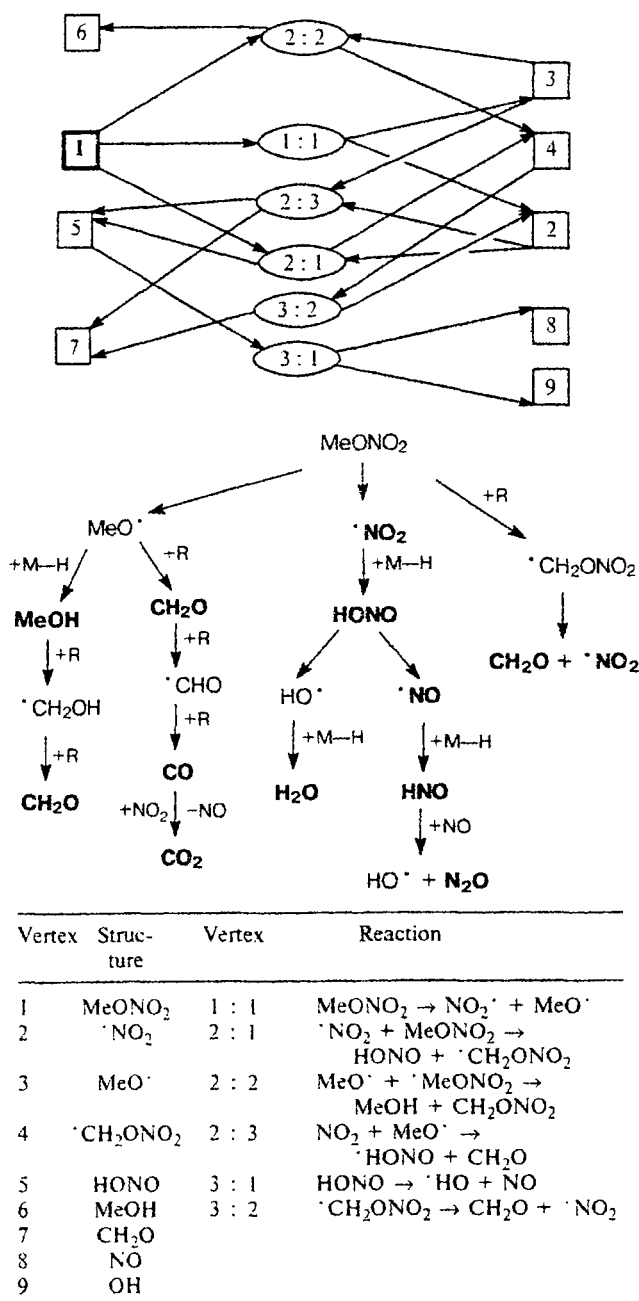| Vertex	Structure	Vertex	Reaction
1	$MeONO_2$	1 : 1	$MeONO_2 \rightarrow NO_2 \cdot + MeO \cdot$
2	$\cdot NO_2$	2 : 1	$\cdot NO_2 + MeONO_2 \rightarrow$ $HONO + \cdot CH_2ONO_2$
3	$MeO \cdot$	2 : 2	$MeO \cdot + \cdot MeONO_2 \rightarrow$ $MeOH + CH_2ONO_2$
4	$\cdot CH_2ONO_2$	2 : 3	$NO_2 + MeO \cdot \rightarrow$ $\cdot HONO + CH_2O$
5	$HONO$	3 : 1	$HONO \rightarrow \cdot HO + NO$
6	$MeOH$	3 : 2	$\cdot CH_2ONO_2 \rightarrow CH_2O + \cdot NO_2$
7	CH_2O		
8	NO		
9	OH		

Fig. 1. Fragment of the recombination reaction network of thermal decomposition of methyl nitrate. The final products corresponding to the experimental data are given in bold type (here and in Figs. 2 and 3).

ucts, _viz._, to the nitro radical (vertex 2) and the methoxy radical (vertex 3).

We name each combination of the potential participants of the reaction a chemical system (CS). Chemical systems are combinations with reiterations, _i.e._, the same intermediate can enter into the equation several times (for example, Me + Me $\rightarrow C_2H_6$).

The numbers of possible combinations are calculated as C_{n+k-1}^{k}, where n is the number of all accessible elements from a set of intermediates and k is the number of reagents in the reaction equation (in our case, $1 \le k \le 3$).

For example, when analyzing a network consisting of 10 intermediates, there is a need to analyze 10 variants of CS in the search for monomolecular reactions, 55 combinations of intermediates in the search for bimolecular reactions, and 220 combinations in the search for trimolecular reactions.

In the case when thermal decomposition involves decay of the initial compounds as the determining direction, special rules for conversions were developed. These rules preclude, in particular, the possibility of formation of structures with increased molecular weight. Rigid conditions for the applicability of this rule decrease the number of molecular structures which correspond to this rule and are present in the network and sharply decrease the number of combinations. In addition, it is known that mono- and bimolecular processes prevail in the course of thermal decomposition and, hence, we did not consider trimolecular processes.

The CASB (Computer-Assisted Structure Building[8]) program was designed to simulate chemical processes based on RRN. In the course of generation of recombination reaction networks, the CASB program prepares chemical systems from intermediates obtained previously (at the first stage, from a given initial compound) using a nonredundant exhaustive search through their combinations. Each chemical system can involve from one to three intermediates. The chemical systems are transformed according to the "if—then" rules (Table 1).[7,8] These rules are classified into three types, *viz.*, into *transformation*, *stabilizing*, and *excluding* rules, in accordance with the way of their application. First, CS are evaluated using the transformation rules and if the CS contains the structural fragment described in the rule, the chemical system is transformed according to this rule. These rules are based on the major criterion for the selection of the reactions generated. The chemical system obtained in the reaction is examined using the stabilizing rules, which describe the ways of converting unstable species into more stable species (for example, multiple bonds are formed instead of vicinal biradicals). Finally, once the CS is divided into constituent structures (reaction products), each structure is tested for the presence of forbidden fragments using the excluding rules (for example, the formation of nonvicinal biradicals can be forbidden). If a forbidden structural fragment is found in at least one product, the reaction is discarded. If all newly generated intermediates do not contain forbidden fragments, the program uses an algorithm for the search for isomorphic embedding of graphs to check whether the obtained structures are present in the RRN. If the structure of the product is already present in the network, only the new reaction is added; otherwise new structures as well as the reaction which affords these

structures are added to the RRN. Finally, the program rejects degenerated reactions in which at least one product acts simultaneously as the reagent.

Each rule is described by the structural formula to which a molecular graph corresponds. A set of conditions, which should be fulfilled, and a set of changes, which should be performed to obtain reaction products, are assigned to each atom and bond. The algorithm for the search for the graph, which is described in the rule, in the chemical system is analogous to the algorithm for the search for the embeddings of subgraphs into the graph. When choosing the following atom (bond) in one of the compounds of the CS, the program compares the true values of its properties with those given for the corresponding vertex (edge) of the graph in the rule. Allowed values are given by a numerical equation associated with one of the following mathematical relations: "=," "≠," ">," "<," "≥." or "≤." If the true value of the property corresponds to the value specified in the rule, the comparison of the properties is continued. When the properties of the selected atom (bond) are in complete agreement with the requirements described in the rule, the atom (bond) is placed into the structural fragment of the CS corresponding to the molecular graph of the rule; otherwise the selected atom (bond) is omitted from consideration and the process of the search is returned to the previous atom to select the next adjacent atom or bond. When describing the rules, there is no need to set values for each vertex of the graph and to specify relations for all the properties described below. The properties whose values are not specified are ignored. In addition, for a number of properties, the manner in which the properties will be changed in the course of conversions of the CS to form reaction products can be described. For example, the multiplicity of the bond, which is initially equal to 1, may become equal to 2 in the course of the reaction.

The program can analyze the following properties of the atoms:

(1) *The atom type* determines the chemical element whose atom should correspond to a particular vertex of the molecular graph described in the rule. There are three ways of specifying this property. First, one can specify a particular chemical element and assign the relation "=." Second, a particular element, for example, carbon, can be excluded. For this purpose, the value "C" should be set and the relation "≠" should be assigned. That is "all atoms except for C" (H atoms have no vertices in structural formulas). Finally, one can give a set of chemical elements, for example, {N,O,F}, to one of which an atom should correspond, which allows one to specify more particularly the notion of the heteroatom. No operations are associated with this property.

(2) *The number of adjacent heteroatoms* specifies the number of heteroatoms directly bound to a given atom. Any one of the above-mentioned mathematical relations used for searching for a given vertex in the real CS may be associated with this numerical property. Since the

Table 1. Basis set of the "if—then" rules in the simulation of thermal decomposition of organic compounds

Rule	Graphical representation	Reaction type	Mode of operation	Setting				
				Atom	Property	Relation	Value	Operation
1	1—2 ↓ 1 + 2	Homolysis of the C—C bond	Conversion	1	Atom type	=	C	No
					Unpaired electrons	=	0	Set = 1
					Charge	=	0	No
				2	The same as for atom 1			
2	1—2 ↓ 1 + 2	Homolysis of the X—X bond	Conversion	1	Atom type	≠	C	No
					Unpaired electrons	=	0	Set = 1
					Charge	=	0	No
				2	The same as for atom 1			
3	1 + 2	Chain propagation	Conversion	1	Valence	≤	1	Automatically
					Unpaired electrons	≥	1	Change for −1
					Charge	=	0	No
				2	Heteroatoms	≥	1	Automatically
					H atoms	≥	1	Automatically
					Unpaired electrons	=	0	Set = 1
					Charge	=	0	No
4	(structure) ↓ 1 + 2	Elimination of the nitro group	Conversion	1	Unpaired electrons	=	0	Set = 1
					Charge	=	0	No
				2	Atom type	=	N	No
					Unpaired electrons	=	0	Set = 1
					Charge	=	+1	No
				3	Atom type	=	O	No
					Charge	=	0	No
				4	Atom type	=	O	No
					Charge	=	−1	No
5	1 + 2=3 ↓ 1 + 2≡3	Formation of CO	Conversion	1	Valence	≤	1	Automatically
					Unpaired electrons	≥	1	Change for −1
					Charge	=	0	No
				2	Atom type	=	C	No
					H atoms	=	1	Automatically
					Unpaired electrons	=	1	Set = 0
					Charge	=	0	Set =−1
				3	Atom type	=	O	No
					Charge	=	0	Set = 1
6	4=1 + 2=3 ↓ 4=1 + 2≡3	Formation of CO (involving NO_x)	Conversion	1	Atom type	=	N	No
					Valence	=	2	Automatically
					Unpaired electrons	≥	1	Change for −1
					Charge	=	0	No
				2,3	See rule 5		Atoms	2,3
				4	Atom type	=	O	No
7	1 +·2 ↓ 1—2	Recombination of radicals	Conversion	1	Atom type	=	C	No
					Valence	<	1	Automatically
					Unpaired electrons	≥	1	Change for −1
					Charge	=	0	No
				2	Atom type	≠	C	No
					Heteroatoms	≥	1	Automatically
					Unpaired electrons	≥	1	Change for −1
					Charge	=	0	No
8	1-2=3 + 4≡5 ↓ 2≡3 + 1=4=5	Formation of CO_2	Conversion	1	Atom type	=	O	No
					Unpaired electrons	≥	1	Change for −1
				2	Atom type	=	N	No
					Unpaired electrons	=	0	Set = 1
					Charge	=	0	No
				3	Atom type	=	O	No
				4	Atom type	=	C	No
					Unpaired electrons	=	0	No
					Charge	=	−1	Set = 0
				5	Atom type	=	O	No
					Charge	=	+1	Set = 0

(to be continued)

Table 1 *(continued)*

Rule	Graphical representation	Reaction type	Mode of operation	Setting				
				Atom	Property	Relation	Value	Operation
9	2=1 + 3=4 ↓ 2=1=3 + 4	Formation of nitrous oxide	Conversion	1	Atom type	=	N	No
					Unpaired electrons	=	1	Set = 0
					Charge	=	0	Set = 1
				2	Atom type	=	O	No
				3	Atom type	=	N	No
					H atoms	≥	1	Automatically
					Charge	=	0	Set = −1
				4	Atom type	=	O	No
					Unpaired electrons	=	0	Set = 1
10	2=1—3	Rearrangement of the free nitro radical	Stabilization	1	Atom type	=	N	No
					Unpaired electrons	=	1	Set = 0
					Charge	=	+1	Set = 0
				2	Atom type	=	O	No
				3	Atom type	=	O	No
					Unpaired electrons	=	0	Set = 1
					Charge	=	−1	Set = 0
11	1—2 ↓ 1=2	Closure of vicinal biradicals	Stabilization	1	Unpaired electrons	≥	1	Change for −1
				2	The same as for atom 1			
12	1 + 2	Nonvicinal biradicals	Exclusion	1	Valence	<	2	Automatically
					Unpaired electrons	≥	1	No
				2	The same as for atom 1			
13	1 + 2 + 3	Triradicals	Exclusion	1	Unpaired electrons	≥	1	No
				2	The same as for atom 1			
				3	The same as for atom 1			
14	1	Polyradical at one atom	Exclusion	1	Unpaired electrons	≥	2	No

number of adjacent heteroatoms placed at the atom as a result of the reaction depends on the resulting products. the final value of the property is not specified.

(3) *The number of adjacent H atoms* determines the number of H atoms bound to a particular atom.

(4) *The degree of vertex* characterizes the number of bonds with nonhydrogen atoms. The multiple bonds are calculated as the corresponding numbers of σ-bonds.

(5) *The hybridization* deals with the sp^3, sp^2, or sp values.

(6) *The number of valence electrons* determines the number of electrons on the outer electron shell.

(7) *The number of lone electron pairs* characterizes the number of lone electron pairs on the outer electron shell of the atom.
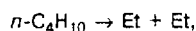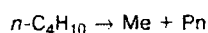
(8) *The number of unpaired electrons* characterizes the presence of the radical center or carbene-like species and can be changed in the reaction. The following three variants are possible: *the previous value is retained; changed for* a particular value, or *is set equal* to a specified new value.

(9) *The charge* specifies the formal negative or positive charge on a given atom. This value can be changed in a manner described previously.

Only one property, *viz.,* the multiplicity, is incorporated into the rules for edges of the graphs (bonds). This
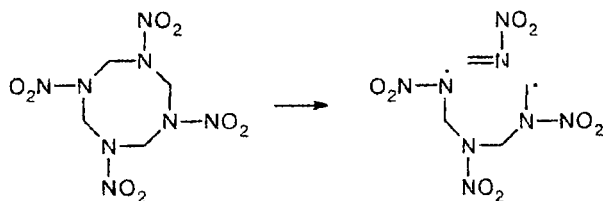
property is also evaluated using all mathematical relations and the required values can be given by analogy with the properties "charge" and "the number of unpaired electrons."

The above-mentioned rules have the following modes of operation: *inactive* and *single, exhaustive,* or *combined application.* This allows one to easily adapt the prepared sets of rules to a particular aim of investigation. For example, if a certain rule is not suited for the problem under consideration, one can change the mode of the rule to inactive. Then this rule will not be in use in the course of generation of the RRN. In the mode of a single use, the rule is applied to the chemical system once for each nonequivalent embedding of the rule to give different reaction products in each case. For example, when the rule of homolytic cleavage of the C—C bond is used in this mode for n-C_4H_{10}, the program gives the following variants:

$$n\text{-}C_4H_{10} \rightarrow Me + Pn$$
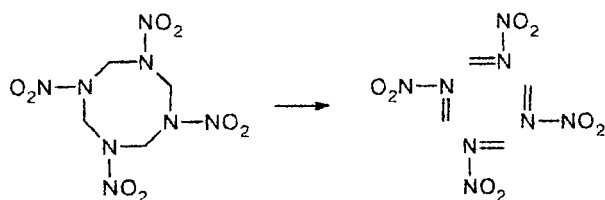
$$n\text{-}C_4H_{10} \rightarrow Et + Et,$$

or in the case of 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (octogen), based on the rule describing elimination of methylnitramine, the following reaction

is generated in the mode of single application of the rule:

This mode of operation of the rule is most commonly used and it is applicable to the majority of chemical reactions.

However, in some instances there is a need to consider simultaneously changes of all reaction centers. For example, concerted ring opening was suggested for the mechanism of thermolysis of octogen in a number of studies[18,21]:

The mode of exhaustive application of the rule is used for describing the above-mentioned process.

If there is a need to consider instances of both single and exhaustive changes of CS, the combined mode of operation of the rule should be used. This mode may be useful, for example, in considering thermal decomposition of 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane to follow possible pathways both of successive elimination of methylenenitramine and of concerted opening of the ring as a whole.

In the program, each rule is named and provision is made to put references to the published data, which served as the basis for the generation of the rule, and to introduce comments of an author of the rule. The formalism of the description of the rules in the CASB program is sufficiently universal to describe both forward synthetic and retrosynthetic conversions. Hence, each iteration of RRN generation involves a nonredundant exhaustive search through combinations of all intermediates obtained at preceding stages of generation (including the initial compounds), which are evaluated and, where possible, are transformed using all the rules employed.
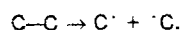
Results of computer simulation

In the present work, a set of rules we developed previously[7,8] was refined and extended to the descrip-

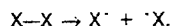tion of decomposition of nitric esters (see Table 1). Below their brief description is given.

Transformation rules.
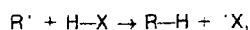*1.* Homolysis of the C—C bond

C—C → C· + ·C.

The rule is used for generating homolytic decomposition of alkyl groups.
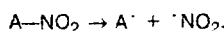*2.* Homolysis of the heteroatom—heteroatom bond

X—X → X· + ·X.

The X atom may be any one heteroatom. The rule is introduced for generating homolysis of functional groups, such as O—O, C(O)O—O(O)C, N—NO$_2$, O—NO$_2$, *etc.*
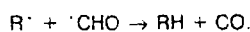*3.* Free-radical chain propagation

R· + H—X → R—H + ·X,

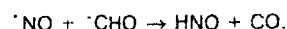where X is a heteroatom.
4. Elimination of the nitro group

A—NO$_2$ → A· + ·NO$_2$.

The A atom can be C (in nitroalkanes), N (in nitramines), or O (in alkyl nitrates).
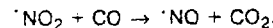*5.* Formation of carbon monoxide

R· + ·CHO → RH + CO.

6. Formation of carbon monoxide (a special case for NO)

·NO + ·CHO → HNO + CO.

7. Radical recombination

R^1· + R^2· → R^1—R^2.

8. Formation of carbon dioxide

·NO$_2$ + CO → ·NO + CO$_2$.

9. Formation of nitrous oxide

2HNO → N$_2$O + H$_2$O.

Stabilizing rules.
10. Rearrangement of the free nitro radical

NO$_2$ → ·ONO.

11. Recombination of vicinal biradicals.

Exclusive rules.
12. Prohibition of nonvicinal biradicals.
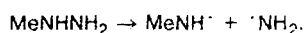*13.* Exclusion of species containing three radical centers.
14. Prohibition of carbene-like species.

Rules *1, 2,* and *4* describe initiation of a chain free-radical reaction. For compounds containing nitro and nitrate groups, such as nitromethane, methyl nitrate,

and ethyl nitrate, the major initiating process is elimination of the nitro group:

$$MeONO_2 \rightarrow MeO^{\cdot} + {}^{\cdot}NO_2.$$

However, two subsequent reactions may be also of importance in thermal decomposition if the compound has a more complex structure and contains other functional groups:

$$MeCHO \rightarrow Me^{\cdot} + {}^{\cdot}CHO,$$

$$MeNHNH_2 \rightarrow MeNH^{\cdot} + {}^{\cdot}NH_2.$$

The radical chain propagation is described both by the general (*3* and *5*) and specific (*6*, *8*, and *9*) rules. Rule *3* describes the formation of new radicals through transfer of the H atom. Since an abundance of "radical—substrate" combinations with the H atom exist in the case of a large number of intermediates, numerous restrictions should be imposed on the applicability of this rule (see Table 1). For example, the reagent should be modest-sized and very reactive (Me or OH), while the substrate should contain at least one heteroatom adjacent to the center of attack, which enhances the stability of the radical formed due to delocalization of the unpaired electron. Rule *5* describes the formation of stable carbon monoxide from the HCO radical, which contains the weak C—H

bond. Rules *6*, *8*, and *9* represent instances which have been described in experimental studies but are not universal.

Rule *7* describes recombination of radicals. Recombination processes, which lead to an increase in the carbon skeleton intermediates are theoretically possible. This is impossible in the case of thermolysis when the general direction of the reaction involves simplification of the structures due to their fragmentation. Hence, we restricted our consideration of recombination reactions to a very narrow spectrum of instances, in particular, to the reactions between the methyl and stable radicals containing the radical center at the heteroatom (NO and NO_2). Rule *10* describes the formal rearrangement of the nitro radical through the transfer of the unpaired electron from nitrogen to oxygen. This rule is based on the experimental data,[1,18] which demonstrate that NO_2 possesses the radical center at the O atom in the $Me^{\cdot} + {}^{\cdot}NO_2 \rightarrow MeONO$ recombination reactions.

Rule *11* converts the vicinal biradical into the multiple bond. This rule as well as the other stabilizing rules serve to represent reactions consisting of several elementary events as a one-stage process. Exclusive rules *12—14* are used for removing reactions which produce undesirable species, in particular, polyradicals, from the RRN.

The above-considered set of rules was used for generating a RRN in the simulation of thermal decomposition of methyl, ethyl, and isopropyl nitrates (see Figs. 2, 3).

Table 2. Possible reactions and their enthalpies during thermal decomposition of methyl nitrate

Iteration, rule		Reaction	ΔH°_{form} /kJ mol^{-1}	Reference	Iteration, rule		Reaction	ΔH°_{form} /kJ mol^{-1}	Reference
(1)	*1*	$MeONO_2 \rightarrow NO_2 + MeO$	84.81	12, 13		*17*	$OH + MeO \rightarrow H_2O + H_2CO$	−334.61	12, 13
(2)	*2*	$NO_2 + MeONO_2 \rightarrow HNO_2 + CH_2ONO_2$	64.75	12, 13		*18*	$CH_2OH + MeO \rightarrow MeOH + H_2CO$	−227.73	13
	3	$MeO + MeONO_2 \rightarrow MeOH + CH_2ONO_2$	−54.67	12, 13		*19*	$OH + HNO_2 \rightarrow H_2O + NO_2$	−180.74	12, 13
	4	$NO_2 + MeO \rightarrow HNO_2 + H_2CO$	−153.87	12, 13		*20*	$CH_2OH + HNO_2 \rightarrow MeOH + NO_2$	−73.86	*
(3)	*5*	$HNO_2 \rightarrow NO + OH$	135.47	12, 13		*21*	$OH + MeOH \rightarrow H_2O + CH_2OH$	−106.88	13
	6	$CH_2ONO_2 \rightarrow H_2CO + NO_2$	−133.80	12, 13		*22*	$OH + H_2CO \rightarrow H_2O + HCO$	−34.78	12, 13
	7	$NO_2 + MeOH \rightarrow HNO_2 + CH_2OH$	75.03	*		*23*	$CH_2OH + H_2CO \rightarrow MeOH + HCO$	−28.51	*
	8	$NO_2 + H_2CO \rightarrow HNO_2 + HCO$	45.35	12, 13		*24*	$NO_2 + HCO \rightarrow HNO_2 + CO$	−94.22	12, 13
	9	$CH_2ONO_2 + MeO \rightarrow MeONO_2 + H_2CO$	−218.61	*		*25*	$MeO + HCO \rightarrow MeOH + CO$	−213.63	13
	10	$MeO + HNO_2 \rightarrow MeOH + NO_2$	−119.42	*		*26*	$CH_2ONO_2 + HCO \rightarrow MeONO_2 + CO$	−158.97	*
	11	$MeO + H_2CO \rightarrow MeOH + HCO$	−74.07	13		*27*	$OH + HCO \rightarrow H_2O + CO$	−274.96	13
	12	$CH_2ONO_2 + HNO_2 \rightarrow MeONO_2 + NO_2$	−64.75	12, 13		*28*	$CH_2OH + HCO \rightarrow MeOH + CO$	−168.08	*
	13	$CH_2ONO_2 + MeOH \rightarrow MeONO_2 + CH_2OH$	9.11	*		*29*	$NO + HCO \rightarrow HNO + CO$	−43.51	13
	14	$CH_2ONO_2 + H_2CO \rightarrow MeONO_2 + HCO$	−19.40	*	(5)	*30*	$NO_2 + HNO \rightarrow HNO_2 + NO$	−50.70	13
(4)	*15*	$OH + MeONO_2 \rightarrow H_2O + CH_2ONO_2$	−115.99	12, 13		*31*	$MeO + HNO \rightarrow MeOH + NO$	−170.13	13
	16	$CH_2OH + MeONO_2 \rightarrow MeOH + CH_2ONO_2$	−9.11	*		*32*	$CH_2ONO_2 + HNO \rightarrow MeONO_2 + NO$	−115.45	*
						33	$OH + HNO \rightarrow H_2O + NO$	−231.45	13
						34	$CH_2OH + HNO \rightarrow MeOH + NO$	−124.56	*
						35	$NO_2 + CO \rightarrow NO + CO_2$	−203.82	13
						36	$NO + HNO \rightarrow N_2O + OH$	−1.09	1

* This work.

At the first stage, all the above-considered nitrates decompose to form NO_2 and the corresponding alkoxyl radical. However, the cleavage of the C—C bond at the α position with respect to the C—O bond as an alternative pathway of decomposition becomes possible as the size of the alkyl radical increases. At the first stage, this

pathway requires a higher energy: 255.61 kJ mol^{-1} compared to 75.03 kJ mol^{-1} in the case of $EtONO_2$ and 237.13 kJ mol^{-1} compared to 81.17 kJ mol^{-1} in the case of Pr^iONO_2.

However, in the case of subsequent formation of carbonyl compounds, which are detected among de-

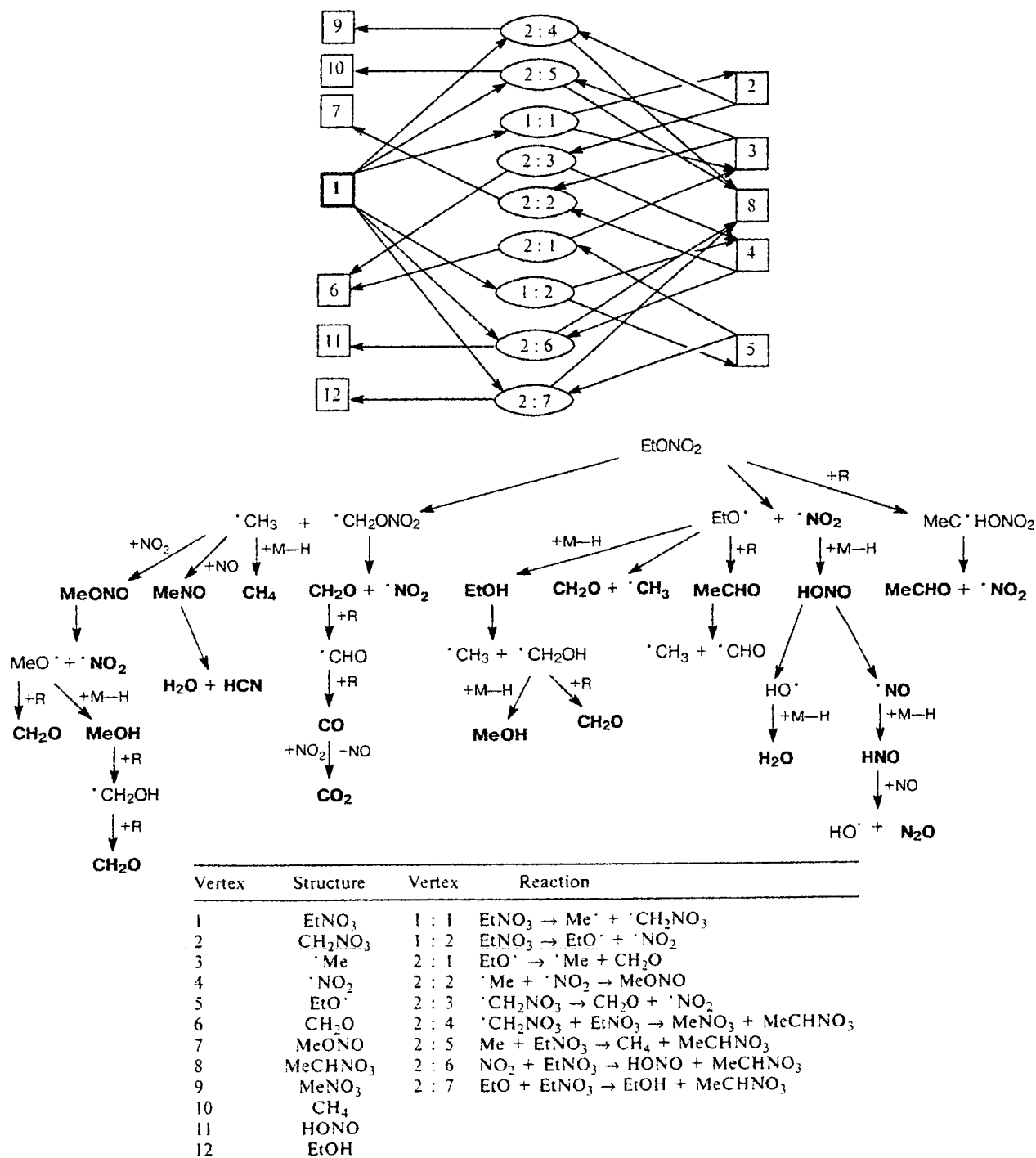| Vertex	Structure	Vertex	Reaction
1	$EtNO_3$	1 : 1	$EtNO_3 \rightarrow Me^{\cdot} + {}^{\cdot}CH_2NO_3$
2	CH_2NO_3	1 : 2	$EtNO_3 \rightarrow EtO^{\cdot} + {}^{\cdot}NO_2$
3	${}^{\cdot}Me$	2 : 1	$EtO^{\cdot} \rightarrow {}^{\cdot}Me + CH_2O$
4	${}^{\cdot}NO_2$	2 : 2	${}^{\cdot}Me + {}^{\cdot}NO_2 \rightarrow MeONO$
5	$EtO^{\cdot}$	2 : 3	${}^{\cdot}CH_2NO_3 \rightarrow CH_2O + {}^{\cdot}NO_2$
6	CH_2O	2 : 4	${}^{\cdot}CH_2NO_3 + EtNO_3 \rightarrow MeNO_3 + MeCHNO_3$
7	$MeONO$	2 : 5	$Me + EtNO_3 \rightarrow CH_4 + MeCHNO_3$
8	$MeCHNO_3$	2 : 6	$NO_2 + EtNO_3 \rightarrow HONO + MeCHNO_3$
9	$MeNO_3$	2 : 7	$EtO + EtNO_3 \rightarrow EtOH + MeCHNO_3$
10	CH_4		
11	$HONO$		
12	$EtOH$		

Fig. 2. Fragment of the recombination reaction network of thermal decomposition of ethyl nitrate.

composition products, the overall process with the participation of these radicals becomes energetically more favorable compared to the corresponding pathways of formation of carbonyl compounds *via* alkoxyl radicals: -133.80 kJ mol^{-1} (Table 2, rule *6*) and -146.63 kJ mol^{-1} (Table 3, rule *15*) compared to 43.81 kJ mol^{-1} (Table 3, rule *3*) and 9.32 kJ mol^{-1}

(Table 4, rule *3*), respectively. Consideration of the overall decomposition reaction of the compounds under study allowed the conclusion that these processes are very similar for all nitric esters. Thus, the final decomposition products are identical and new intermediates appear only due to an increase in the lengths of the alkyl radical.

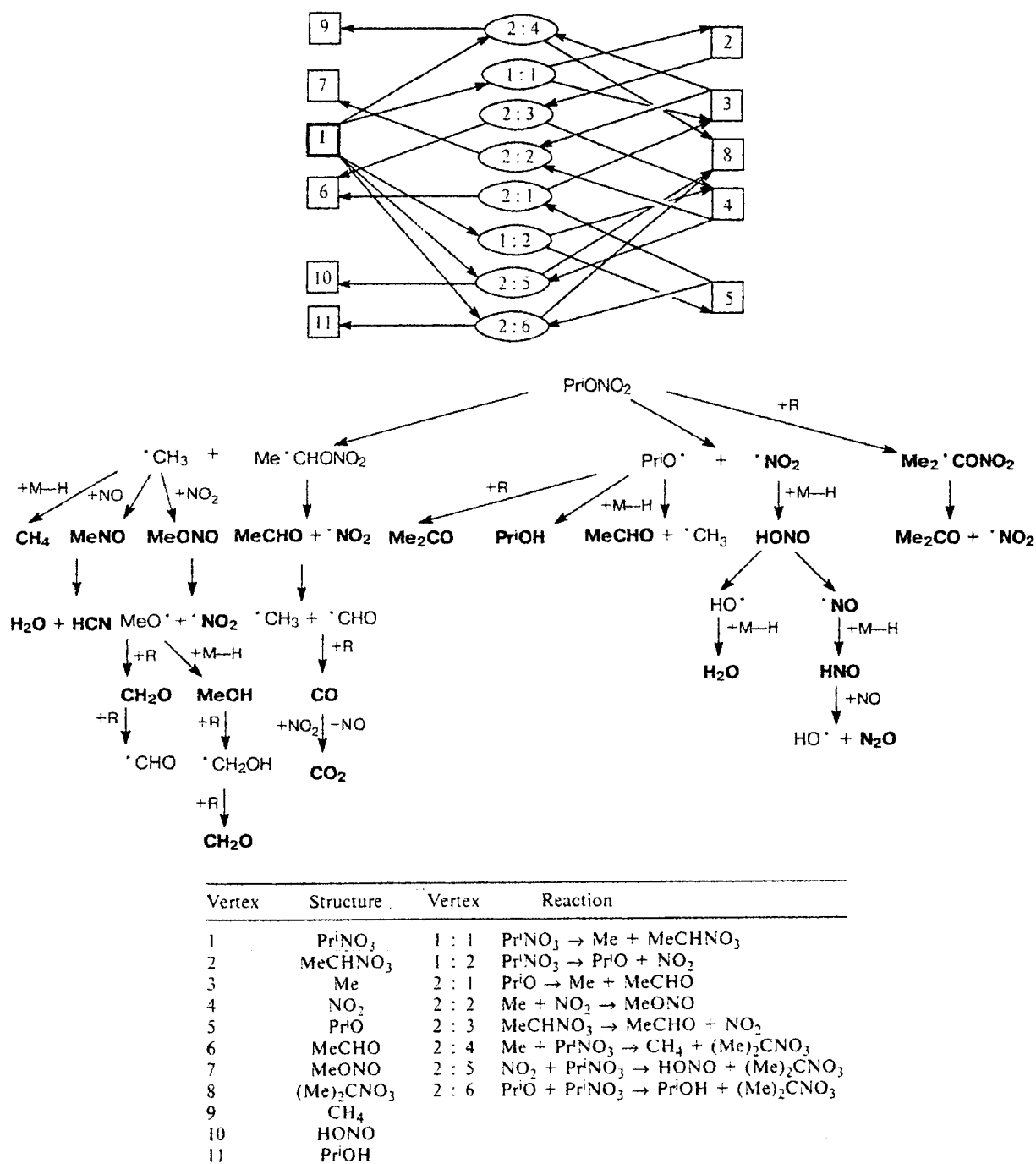| Vertex	Structure	Vertex	Reaction
1	Pr^{i}NO$_3$	1 : 1	Pr^{i}NO$_3$ → Me + MeCHNO$_3$
2	MeCHNO$_3$	1 : 2	Pr^{i}NO$_3$ → Pr^{i}O + NO$_2$
3	Me	2 : 1	Pr^{i}O → Me + MeCHO
4	NO$_2$	2 : 2	Me + NO$_2$ → MeONO
5	Pr^{i}O	2 : 3	MeCHNO$_3$ → MeCHO + NO$_2$
6	MeCHO	2 : 4	Me + Pr^{i}NO$_3$ → CH$_4$ + (Me)$_2$CNO$_3$
7	MeONO	2 : 5	NO$_2$ + Pr^{i}NO$_3$ → HONO + (Me)$_2$CNO$_3$
8	(Me)$_2$CNO$_3$	2 : 6	Pr^{i}O + Pr^{i}NO$_3$ → Pr^{i}OH + (Me)$_2$CNO$_3$
9	CH$_4$		
10	HONO		
11	Pr^{i}OH		

Fig. 3. Fragment of the recombination reaction network of thermal decomposition of isopropyl nitrate.

The iteration procedure used in the computer simulation of thermal decomposition was continued until new compounds and reactions ceased to erise. For all compounds under study, no new intermediates were

Table 3. Possible reactions and their enthalpies during thermal decomposition of ethyl nitrate (except for reactions that coincide with thermal decomposition of methyl nitrate)

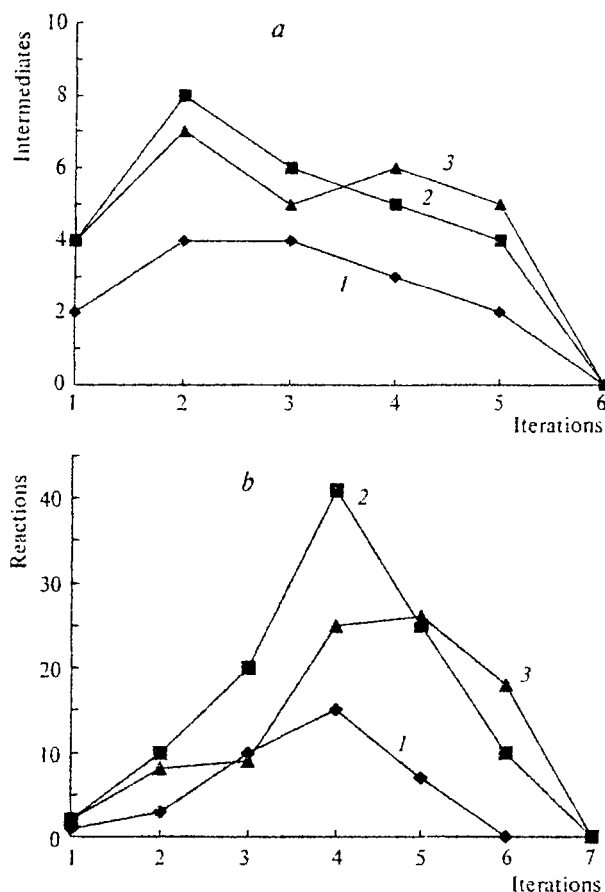| Iteration, rule		Reaction	ΔH°_{form} /kJ mol^{-1}	Reference
(1)	1	$EtONO_2 \to Me + CH_2ONO_2$	255.61	13
	2	$EtONO_2 \to EtO + NO_2$	75.03	13
(2)	3	$EtO \to Me + H_2CO$	43.81	13
	4	$Me + NO_2 \to MeONO$	−147.22	13
	5	$CH_2ONO_2 + EtONO_2 \to$ $MeONO_2 + MeCHONO_2$	−25.83	*
	6	$Me + EtONO_2 \to$ $CH_4 + MeCHONO_2$	−74.95	13
	7	$NO_2 + EtONO_2 \to$ $HNO_2 + MeCHONO_2$	41.88	13
	8	$EtO + EtONO_2 \to$ $EtOH + MeCHONO_2$	−71.94	*
	9	$CH_2ONO_2 + EtO \to$ $MeONO_2 + MeCHO$	−247.50	*
	10	$Me + EtO \to CH_4 + MeCHO$	−296.61	*
	11	$NO_2 + EtO \to HNO_2 + MeCHO$	−179.78	*
(3)	12	$EtOH \to Me + CH_2OH$	265.93	*
	13	$MeCHO \to Me + HCO$	268.94	13
	14	$MeONO \to MeO + NO$	56.51	13
	15	$MeCHONO_2 \to MeCHO + NO_2$	−146.30	13
	16	$CH_2ONO_2 + MeONO \to$ $MeONO_2 + CH_2ONO$	14.29	*
	17	$Me + H_2CO \to CH_4 + HCO$	−71.47	13
	18	$Me + MeONO \to CH_4 + CH_2ONO$	−34.82	*
	19	$Me + MeONO_2 \to$ $CH_4 + CH_2ONO_2$	−49.12	*
	20	$Me + HNO_2 \to CH_4 + NO_2$	−116.83	*
	21	$NO_2 + MeONO \to$ $HNO_2 + CH_2ONO$	82.01	*
	22	$EtO + H_2CO \to EtOH + HCO$	−68.47	*
	23	$EtO + MeONO \to$ $EtOH + CH_2ONO$	−31.81	*
	24	$EtO + MeONO_2 \to$ $EtOH + CH_2ONO_2$	−46.11	*
	25	$EtO + HNO_2 \to EtOH + NO_2$	−113.82	*
(4)	26	$CH_2ONO \to H_2CO + NO$	−179.36	*
	27	$Me + NO \to MeNO$	−145.05	1
	28	$CH_2OH + EtONO_2 \to$ $MeOH + MeCHONO_2$	−31.98	*
	29	$MeO + EtONO_2 \to$ $MeOH + MeCHONO_2$	−77.54	*
	30	$OH + EtONO_2 \to$ $H_2O + MeCHONO_2$	−138.86	13
	31	$CH_2ONO + EtONO_2 \to$ $MeONO + MeCHONO_2$	−40.13	*
	32	$Me + MeO \to CH_4 + H_2CO$	−270.70	13
	33	$EtO + CH_2OH \to$ $MeCHO + MeOH$	−253.64	*
	34	$EtO + MeO \to EtOH + H_2CO$	−267.69	*
	35	$EtO + MeO \to MeCHO + MeOH$	−299.20	*
	36	$EtO + OH \to MeCHO + H_2O$	−360.53	*
	37	$EtO + CH_2ONO \to$ $MeCHO + MeONO$	−261.79	*
	38	$CH_2ONO + H_2CO \to$ $MeONO + HCO$	−36.66	*
(4)	39	$CH_2OH + MeONO \to$ $MeOH + CH_2ONO$	8.15	*
	40	$MeO + MeONO \to$ $MeOH + CH_2ONO$	−37.41	*
	41	$OH + MeONO \to$ $H_2O + CH_2ONO$	−98.73	*
	42	$CH_2ONO + MeONO_2 \to$ $MeONO + CH_2ONO_2$	−14.30	*
	43	$CH_2ONO + HNO_2 \to$ $MeONO + NO_2$	−82.01	*
	44	$CH_2ONO + MeO \to$ $MeONO + H_2CO$	−235.88	*
	45	$Me + HCO \to CH_4 + CO$	−211.05	13
	46	$EtO + HCO \to EtOH + CO$	−375.87	*
	47	$CH_2ONO + HCO \to$ $MeONO + CO$	−176.23	*
(5)	48	$CH_2ONO_2 + MeNO \to$ $MeONO_2 + CH_2NO$	0.04	*
	49	$Me + MeNO \to CH_4 + CH_2NO$	−49.07	*
	50	$Me + MeOH \to CH_4 + CH_2OH$	−42.97	*
	51	$Me + HNO \to CH_4 + NO$	−167.53	13
	52	$NO_2 + MeNO \to HNO_2 + CH_2NO$	67.76	*
	53	$EtO + MeNO \to EtOH + CH_2NO$	−46.06	*
	54	$EtO + MeOH \to EtOH + CH_2OH$	−39.96	*
	55	$EtO + HNO \to EtOH + NO$	−164.52	*
	56	$CH_2OH + MeNO \to$ $MeOH + CH_2NO$	−6.10	*
	57	$MeO + MeNO \to$ $MeOH + CH_2NO$	−51.66	*
	58	$OH + MeNO \to H_2O + CH_2NO$	−112.99	*
	59	$CH_2ONO + MeNO \to$ $MeONO + CH_2NO$	−14.25	*
	60	$CH_2ONO + MeOH \to$ $MeONO + CH_2OH$	−8.15	*
	61	$CH_2ONO + HNO \to$ $MeONO + NO$	−132.72	*
	62	$MeNO \to HCN + H_2O$	−118.75	1, 15
(5)	63	$CH_2NO + EtONO_2 \to$ $MeNO + MeCHONO_2$	−25.87	*
	64	$CH_2NO + EtO \to$ $MeNO + MeCHO$	−247.54	*
	65	$CH_2NO + H_2CO \to$ $MeNO + HCO$	−22.40	*
	66	$CH_2NO + MeONO \to$ $MeNO + CH_2ONO$	14.25	*
	67	$CH_2NO + MeONO_2 \to$ $MeNO + CH_2ONO_2$	−0.04	*
	68	$CH_2NO + HNO_2 \to$ $MeNO + NO_2$	−67.76	*
	69	$CH_2NO + MeO \to$ $MeNO + H_2CO$	−221.62	*
	70	$CH_2NO + MeOH \to$ $MeNO + CH_2OH$	6.10	*
	71	$CH_2NO + HNO \to MeNO + NO$	−118.46	*
	72	$CH_2NO + HCO \to MeNO + CO$	−161.98	*

* This work.

Fig. 4. Distributions of the numbers of structures (*a*) and reactions (*b*) generated over iterations: *1*, methyl nitrate; *2*, ethyl nitrate; *3*, isopropyl nitrate.

found after the fifth iteration and no new reactions were observed after the sixth iteration. A total of 15, 27, and 27 intermediates were generated in the cases of methyl, ethyl, and isopropyl nitrates, respectively. The distributions of the numbers of new structures and reactions over iterations are shown in Fig. 4.

For the mechanisms of thermal decomposition under study, some general regularities of thermolysis can be mentioned. Thus, the largest number of intermediates is generated in the second and third iterations, while the maximum number of new reactions is observed in the fourth iteration. This is attributable to the fact that it is the first stage of decomposition of the initial compounds after which the greatest diversity of intermediates is observed, when these products are rather large and reactive species. Due to this diversity of intermediates, the largest number of their possible interactions falls on the following iteration. In the subsequent iterations, low-molecular-weight stable compounds that do not exhibit high reactivity are formed, which leads to a sharp decrease in the total number of interactions. The com-

Table 4. Possible reactions and their enthalpies during thermal decomposition of isopropyl nitrate (except for reactions that coincide with thermal decomposition of methyl nitrate and ethyl nitrate)

Iteration, rule		Reaction	ΔH°_{form} /kJ mol^{-1}	Refer- ence
(1)	*1*	$Pr^iONO_2 \rightarrow Me + MeCHONO_2$	237.13	*
	2	$Pr^iONO_2 \rightarrow Pr^iO + NO_2$	81.18	13
(2)	*3*	$Pr^iO \rightarrow Me + MeCHO$	9.32	13
	4	$Me + Pr^iONO_2 \rightarrow CH_4 + Me_2CONO_2$	−84.65	*
	5	$NO_2 + Pr^iONO_2 \rightarrow HNO_2 + Me_2CONO_2$	32.19	*
	6	$Pr^iO + Pr^iONO_2 \rightarrow Pr^iOH + Me_2CONO_2$	−93.46	*
	7	$Me + Pr^iO \rightarrow CH_4 + Me_2CO$	−306.90	13
	8	$NO_2 + Pr^iO \rightarrow HNO_2 + Me_2CO$	−190.06	13
(3)	*9*	$Me_2CONO_2 \rightarrow NO_2 + Me_2CO$	−141.08	*
	10	$Pr^iO + MeONO \rightarrow Pr^iOH + CH_2ONO$	−43.64	*
	11	$Pr^iO + HNO_2 \rightarrow Pr^iOH + NO_2$	−125.65	*
(4)	*12*	$MeO + Pr^iONO_2 \rightarrow MeOH + Me_2CONO_2$	−87.24	*
	13	$OH + Pr^iONO_2 \rightarrow H_2O + Me_2CONO_2$	−124.98	*
	14	$CH_2ONO + Pr^iONO_2 \rightarrow MeONO + Me_2CONO_2$	−49.83	*
	15	$Pr^iO + MeO \rightarrow Pr^iOH + H_2CO$	−279.52	*
	16	$MeO + Pr^iO \rightarrow MeOH + Me_2CO$	−309.49	13
	17	$OH + Pr^iO \rightarrow H_2O + Me_2CO$	−370.81	13
	18	$CH_2ONO + Pr^iO \rightarrow MeONO + Me_2CO$	−272.08	13
	19	$Pr^iO + HCO \rightarrow Pr^iOH + CO$	−219.87	*
(5)	*20*	$Pr^iO + H_2CO \rightarrow Pr^iOH + HCO$	−80.30	*
	21	$Pr^iO + MeNO \rightarrow Pr^iOH + CH_2NO$	−57.89	*
	22	$Pr^iO + MeOH \rightarrow Pr^iOH + CH_2OH$	−51.79	*
	23	$Pr^iO + HNO \rightarrow Pr^iOH + NO$	−176.35	*
(6)	*24*	$CH_2NO + Pr^iONO_2 \rightarrow MeNO + Me_2CONO_2$	−35.57	*
	25	$CH_2OH + Pr^iONO_2 \rightarrow MeOH + Me_2CONO_2$	−41.67	*
	26	$CH_2NO + Pr^iO \rightarrow MeNO + Me_2CO$	−257.82	13
	27	$CH_2OH + Pr^iO \rightarrow MeOH + Me_2CO$	−263.93	13

* This work.

plete list of the known reactions as well as of new reactions obtained in the course of simulation is given in Tables 2—4.
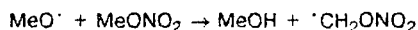
Results and Discussion

In some cases, the monomolecular character of decomposition persists over the course of the process, and the reaction rate is independent of the pressure. The radical decomposition becomes completely monomo-

lecular either if the resulting radicals are inactive or if efficient inhibitors of chain reactions (NO or NO_2) are formed as the products.[1,20] However, secondary reactions very often proceed with the involvement of the initial compound, which leads to a chain radical reaction. Thus, CH_2ONO_2 is formed due to interaction of the initial $MeONO_2$ with active radicals (see Table 2, rules *2, 3, 15,* and *16*). The CASB program generated yet another pathway of formation of CH_2ONO_2 through the cleavage of the C—C bond in $EtONO_2$ (see Table 3, rule *1*). Taking into account all pathways of formation of CH_2ONO_2, it can be suggested that this radical assists in continuing the chain free-radical reaction (see Table 2, rules *12—14* and *32*; Table 3, rules *5, 16,* and *48*) as well as undergoes subsequent conversions (see Table 2, rule *6*). MeNO is obtained by recombination of the Me and NO radicals (see Table 3, rule *27*). This reaction has not been demonstrated previously[12,13] but it has been mentioned in Ref. 18. The program generated a series of reactions (see Table 3, rules *48, 49, 52, 53, 56—59,* and *67*; Table 4, rule *21*) in which the molecule acts as a substrate for the radical attack. This molecule can also undergo subsequent decomposition to give HCN and H_2O as the final products (see Table 3, rule *62*).

In addition to the experimental data,[12,13] which provide an incomplete insight into the chemistry of the $\cdot CH_2OH$ (MeO$\cdot$ isomer) and EtO$\cdot$ radicals, we found the complete set of possible reactions using the CASB program (see Table 2, rules *16, 18, 20, 23, 28,* and *34*; Table 3, rules *28, 33, 39,* and *56* and *3, 8—11, 22—25, 33—37, 46, 53—55,* and *64*). All these intermediates are very active radicals, which can sustain the chain character of the reaction.
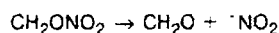
A series of the reactions generated by the CASB program (see Table 2, rules *2, 3, 6, 12, 15,* and *35*; Table 3, rules *1, 3, 6, 7, 15,* and *30*) have not been described previously as individual stages.[12,13] However, these reactions can be considered as constituents of more complex processes. For example, the reaction observed by us

$$MeO\cdot + MeONO_2 \rightarrow MeOH + \cdot CH_2ONO_2$$

is the first elementary act of the complex reaction suggested previously[12,13]

$$MeONO_2 + MeO \rightarrow MeOH + CH_2O + NO_2,$$

where the second stage can be represented as

$$CH_2ONO_2 \rightarrow CH_2O + \cdot NO_2$$

and was also generated by the CASB program. In the case of isopropyl nitrate, a very diversified spectrum of reactions with the Pr^{i}O radical was obtained. We supplemented the pathway of formation of $(Me)_2CO$ reported in the literature[12,13] with several new pathways (see Table 4, rules *7, 8, 9, 16—18, 26,* and *27*).

We determined the enthalpies of the chemical reactions generated using the AMPAC and HyperChem

program packages. The calculations were performed using the semiempirical quantum-chemical PM3 method as the most suitable procedure for the calculations of the structures and properties of nitrogen-containing compounds.[19] When analyzing our results of quantum-chemical calculations (see Tables 2—4), one can see that beginning with the fourth iteration, the reactions of all intermediates are exclusively exothermic. Apparently, it is these reactions that determine the process of thermal decomposition of nitric esters as a process accompanied by liberation of a large quantity of energy. Highly exothermic reactions are associated primarily with the formation of low-molecular-weight stable compounds, such as CO, CO_2, H_2CO, MeCHO, CH_4, NO, H_2O, and HCN. In the case of $EtONO_2$ and Pr^iONO_2, decomposition of alkyl radicals requires additional energy compared to that in the case of $MeONO_2$.

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