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The Gas-phase Nitration of Alkanes

A.P.Ballod and V.Ya.Shtern

The principal chemical and kinetic results obtained for this reaction are reported and discussed critically. A brief description is given of its industrial application to the manufacture of nitroalkanes. The detailed mechanism suggested during recent years for the nitration of alkanes by nitrogen dioxide is discussed in terms of the primary steps. The fundamental similarity of the mechanisms of nitration by nitrogen dioxide and by nitric acid is established on the basis of experimental data. A list of 119 references is included.

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I. LIQUID-PHASE NITRATION OF ALKANES

Towards the end of the nineteenth century Konovalov [1-3] discovered the subsequently famous method of introducing a nitro-group into an alkane or the side-chain of an alkyl-aromatic hydrocarbon by treatment with dilute nitric acid in sealed tubes (acid of specific gravity 1.075 at 120–130°C for 4–6 h). Since that time research on the nitration of the alkyl chain has become traditional for the Russian school of organic chemists.

During the first period, lasting until 1914, the most notable work was undertaken by Konovalov [1-10], Markovnikov [11-19], and Nametkin [20-27]. The attention paid by these eminent chemists to the nitration of saturated hydrocarbons is quite understandable. At the turn of the century the problem of the utilisation of petroleum became acute, not only as fuel but also as raw material for the production of intermediates in industrial organic synthesis. A serious obstacle to the latter use was the considerable chemical stability and hence low reactivity of saturated hydrocarbons, the main components of petroleum. Therefore any possibility of the chemical "revival" of these hydrocarbons was extremely important, and work leading to the discovery and study of chemical reactions of saturated hydrocarbons was fundamentally progressive.

During this first period the liquid-phase nitration of the alkyl chain (in alkanes, naphthenes, and alkylbenzenes) by nitric acid was closely examined by the above workers. They established experimental conditions for the reaction, the formation both of nitration products (nitro-compounds) and of oxidation products (aldehydes, ketones, alcohols, acids, and carbon monoxide and dioxide), and the qualitative and in several cases quantitative composition of the products. At the same time the first mechanisms were suggested in terms of valency-saturated intermediate and final compounds.

The first view on the mechanism of the newly discovered reaction was expressed by Konovalov in the principle that "nitric acid always nitrates initially, whatever its concentration, and oxidation is a secondary, subsequent step". Later, however, when the great stability of nitro-products to oxidation had become clear (for example, the oxidation of xylylnitromethane by nitric acid took place at temperatures 25 deg above those for the original pseudo-cumene), Konovalov concluded that the nitro-product underwent oxidation only at the instant of its formation.

Nametkin adopted a different approach to the mechanism of nitration. His attention was attracted by Konovalov's suggestion that, at the instant of formation by the double decomposition

$$RH + HNO_3 \rightarrow RNO_2 + H_2O$$

the nitro-compound is in an unstable state, and therefore immediately and readily undergoes further oxidation to aldehydes, ketones, alcohols, carbon monoxide and dioxide, etc. However, Nametkin regards this route to oxidation products as inconsistent with the "law of stepwise reaction "stages" formulated by Ostwald [28] as "no process leads immediately to the most stable state: the next or the least stable state of those possible is established initially". Indeed, the acceptance of such a law and of Konovalov's hypothesis leads to the conclusion that in the present case the formation of stable nitro-compounds is quite impossible, since, being in an unstable state at the instant of formation, the nitro-compound undergoes further oxidation.

An escape from the discrepancy was provided by Nametkin's hypothesis that *aci*- or iso-nitro-compounds are formed as an intermediate stage in the action of nitric acid on saturated hydrocarbons:

$$\rangle CH_2 + HONO_2 \rightarrow \rangle C{=}NOOH + H_2O$$

$$-CH_3 + HONO_2 \rightarrow -CH{=}NOOH + H_2O.$$

Under the influence of the acid medium or a high temperature these intermediates either isomerise into stable nitro-compounds or decompose by Nef's reaction into ketones (aldehydes) and nitrous oxide with subsequent oxidation of the ketone (aldehyde) to carboxylic acids.

Thus, whereas Konovalov suggested that the overall nitration involves two consecutive reactions—nitration of the hydrocarbon to the nitro-product followed by oxidation of the latter by nitric acid to oxygenated products—Nametkin postulated two parallel reactions—nitration itself and oxidation.

As we shall see later, Nametkin proved to be correct. In the light of modern views, the overall reaction of nitration actually involves two parallel chemical changes, yielding respectively nitro-products and oxygen-containing compounds. We now know that this is accomplished by

means of free radicals, but the classical investigators of nitration—Konovalov, Markovnikov, and Nametkin—were unaware of this, and had to consider the mechanism of this reaction in terms of valency-saturated compounds. Nevertheless, Nametkin's hypothesis gave a fundamentally correct view of the mechanism of nitration.

On the whole all the vast and high-quality experimental information and the theoretical views developed during the first period of investigation on the reaction mechanism formed the foundation on which the subsequent intense study of the nitration of saturated hydrocarbons has continued. An astonishingly deep insight was obtained by these brilliant investigators, who were able to foresee the great value of nitration processes for the chemistry of petroleum.

II. GAS-PHASE NITRATION OF ALKANES

For two whole decades from the beginning of the First World War hardly any publications appeared on the nitration of saturated hydrocarbons: only in the mid-1930s was study of this chemical reaction resumed, not only in our own but also in other countries. However, considerable development and complication had occurred during 1914 to 1934 in the problems facing the renewed investigation, the experimental equipment in which it was now conducted, and finally theoretical views on the mechanism of complicated chemical reactions, which undoubtedly include nitration. And since the general characteristics of Konovalov nitration, the conditions under which it occurred, and (to a first approximation) its chemistry had already been established during the first period preceding 1914, research workers during the 1930s had two main tasks.

The first problem was to find optimum conditions for conducting nitration in order to secure maximum yields of the required products, which nitroalkanes had then become, having already found application. At the present time (the 1970s) the range of uses of nitroalkanes is quite wide: they are employed both as intermediates for the manufacture of nitro-alcohols, hydroxyalkylamines, and polynitro-compounds and also as solvents, stabilisers, explosives, and fuels for jet and piston engines [29].

The increasing emphasis on practical utilisation of the reaction had its natural consequence in the change in the experimental conditions under which study of the nitration of saturated hydrocarbons—mainly alkanes—was continued. Liquid-phase nitration by Konovalov's procedure, with its relatively low temperatures (120–140°C) and reaction velocities, was of no interest for industrial purposes. All researches after the mid-1930s, therefore, involved study of the nitration of the alkane chain almost exclusively in the gas phase at far higher temperatures (300–550°C). The number of nitrating agents also increased, with the use of nitrogen dioxide as well as nitric acid. This became possible after the appearance during 1934–1935 of papers by Shorygin and Topchiev [30,31], who were the first to nitrate alkanes by means of nitrogen dioxide. As will become clear from the later discussion, their discovery exerted a great influence on the whole subsequent development of research on the nitration of the alkane chain.

The second task was to elucidate the detailed mechanism of the nitration of saturated hydrocarbons. It must be stressed that the transition to the practically oriented study of nitration not only did not diminish but, on the contrary, increased interest in ascertaining the true mechanism of the process. This is quite understandable, since any extension of knowledge on the mechanism of a chemical reaction, in addition to its cognitive interest, at the same time advances the boundaries of the rational rather than the inventor's search for optimum conditions for the practical application of the reaction. But now the true mechanism of the high-temperature gas-phase reaction no longer implied merely the sequence of stable (valency-saturated) compounds. At this time the concepts of the chain theory, with its assertion of the important and decisive role of labile structures (free radicals) in the mechanism of a considerable number of high-temperature gas-phase and liquid-phase reactions, became increasingly widely accepted. Indeed, experimental information was fairly soon accumulated confirming unambiguously the participation of active centres (free radicals) in the nitration of saturated hydrocarbons. From this time elucidation of the mechanism of nitration of the alkane chain in terms of primary steps, i.e. involving free radicals, became the second task, initially sometimes not clearly understood but rather intuitively perceived by investigators.

It is clear from the above discussion that a comprehensive kinetic investigation using all the methods available for the study of this reaction was required in order to solve the second problem, the mechanism of nitration. This was by no means immediately understood—only at the end of the 1950s—some 20–25 years after resumption of investigation of the nitration of the alkane chain. This does not mean, of course, that aspects of the mechanism were completely excluded from the attention of research workers during the whole quarter-century. On the contrary, by the end of the 1930s (see below) Titov had already suggested a mechanism for the nitration of alkanes involving free radicals, which is still relevant at the present time.

The renewed investigation can conveniently be divided into two periods: the second period lasted from the 1930s to the 1960s (the first period had ended in 1914), and the third period began in the 1960s and continues at the present time. During the second period much experimental work was undertaken in establishing the industrial gas-phase nitration of alkanes, and the first investigations were made to determine the reaction mechanism in terms of primary steps, involving free radicals. The third period is characterised mainly by more detailed investigation of the reaction mechanism. The study of kinetic aspects of nitration has become considerably more intense, and the first radical-chain scheme has been suggested for nitration.

1. Development of the Industrial Production of Nitroalkanes

We shall begin our survey of results obtained during the second period with an examination of the most important work aimed at the industrial application of the nitration of alkanes. It involved essentially a search for optimum conditions for the production of nitroalkanes, and comprised two long series of studies undertaken in the U.S.A. The American papers resulted from a cooperative investigation by the Commercial Solvents Corporation and Purdue University. The first series of studies was made by Hass and his coworkers between 1934 and 1953 [32–45], and the second by Bachman et al. from 1952 to 1961. [46–53]

Hass used C_1–C_6 alkanes, and was one of the first to change to high-temperature nitration in the gas phase. The experiments were made in glass or metal laboratory flow-type apparatus. The nitrating agent was either

50–70% nitric acid (at 400–700°C for up to 2 s) or nitrogen dioxide (at 250–600°C from a few seconds up to 14 min). In most cases the reaction was conducted under atmospheric pressure. Hass studied the influence of temperature, contact time, and composition of mixture (ratio of alkane to nitrating agent) on the total yields of nitroalkanes obtained in the nitration of methane [33,38], ethane [33,36], propane [37,44], n-butane and isobutane [33], n-pentane [34], 2,2-dimethylbutane [41], and 2,3-dimethylbutane [40]. At the same time he determined the composition of the resulting mixture of nitroalkanes and analysed other reaction products. The possibility of increasing the yield of nitroalkanes by conducting the reaction under high pressures of methane (7 and 70 atm) [43] and ethane (7 atm),[36] as well as with additions of oxygen, nitrogen, and nitric oxide [44], was also examined.

Table 1. Nitration of alkanes by nitric acid and by nitrogen dioxide (from results obtained by Hass).

Alkane	RH / HNO_3	T, °C	Pressure, atm	Contact, s	Conversion to RNO_2,%	Nitroalkanes RNO_2					Ref.
						CH_3	C_2H_5	C_3H_7 n-	C_3H_7 iso-	C_4H_9	
Methane	9:1	475	1	0.18	13	—	—	—	—	—	38
»	12.7:1	442	1.25	2.01	16.7	—	—	—	—	—	38
»	10.5:1	444	7	0.75	27.1	—	—	—	—	—	43
»	20:1	465	70	0.28	18.8	—	—	—	—	—	43
Ethane	1—2:1	420	1	1	9	10—20	80—90	—	—	—	33
»	8—10:1	450	7	0.3	33	27	73	—	—	—	36
Propane	1—2:1	420	1	1	21	9	26	32	33	—	33
n-Butane	1—2:1	420	1	1	28	6	12	5	27	50	33
	RH:NO_2										
Propane	4:1	248	1	14 min	26	14	3	11	72	—	37
»	4:1	505—510	1	—	—	15	15	15	55	—	37
»	4:1	790—795	1	—	—	23.5	23.5	29.5	23.5	—	37

Some of the results obtained by Hass et al. are listed in Table 1. They show firstly that the rate of the gas-phase nitration of alkanes increases when nitrogen dioxide is replaced as nitrating agent by nitric acid. Hass made no attempt to explain this fact. Table 1 shows also that the ability to replace hydrogen atoms in an alkane by the nitro-group was retained on passing from the liquid-phase to the gas-phase reaction with nitric acid (and with nitrogen dioxide). Moreover, a considerable number of experimental results obtained by Hass (not included in Table 1) indicate increasing ease of substitution of a hydrogen atom in gas-phase nitration on passing from a primary to a secondary and then to a tertiary carbon atom. It is especially noteworthy that, as Hass proved, nitroalkanes are accompanied in both gas-phase and liquid-phase processes by oxygen-containing products (aldehydes, ketones, alcohols, oxides of carbon), i.e. the so called oxidising reaction path.

Naturally, there are also differences. Firstly, in contrast to the liquid-phase process, gas-phase nitration yields isomeric nitroalkanes, which means diminished selectivity of the reaction (Table 1). A second difference is the formation in the gas-phase reaction not only of nitroalkanes corresponding to the initial hydrocarbon but also lower nitroalkanes (Table 1). A third difference is the absence of polynitroalkanes in the gas-phase products, despite attempts by Hass to direct the process towards their formation; yet polynitroalkanes are almost always obtained when the reaction is conducted in the liquid phase. Fourthly and finally, alkenes are found among the products of gas-phase nitration but are absent from the liquid-phase process.

All these features are usually explained by the more severe temperature conditions of gas-phase nitration, with which we can agree. For example, the discovery by Hass that the 1-nitroalkane is formed in addition to the 2-nitroalkane on passing from the liquid phase to the gas phase is a consequence of the greater (by 4–5 kcal $mole^{-1}$) energy of a carbon–hydrogen bond attached to a primary than to a secondary carbon atom [54]: the activation energy of substitution by a nitro-group is therefore higher for a hydrogen atom at a primary than at a secondary carbon atom, so that the relative importance of the reaction leading to formation of the 1-nitroalkane should increase with rise in temperature. Furthermore, the high temperature of the gas-phase nitration of alkanes is probably the reason for the appearance of alkenes, since it is now known that the thermal decomposition of nitroalkanes leads to the formation not only of alkyl radicals and nitrogen dioxide but also of the corresponding alkene and nitrous acid [55,56].

Although Hass put forward several hypotheses [33,34,39,40,45], he was unable to relate the second difference—the formation of nitroalkanes having a smaller carbon skeleton than in the original alkane—with the higher temperature of gas-phase nitration. At the present time (the 1970s), however, it is generally accepted that alkoxy-radicals are present during the gas-phase process, and undergo thermal decomposition into aldehydes (or ketones) and alkyl radicals containing fewer carbon atoms than originally present. Reaction of these alkyl radicals with nitrogen dioxide leads to formation of the lower nitroalkanes.

Hass [44] investigated also the effect of added oxygen on the nitration of methane and propane by nitric acid dioxide at 395 and 410°C, varying the quantity of oxygen from zero to fivefold the molar proportion of the nitrating agent. With methane the conversion of nitric acid into nitromethane passed through a maximum of 24.2% when the molar ratio of oxygen was 2.6, falling to 1.4% when the ratio was 5. With propane, however, increasing the ratio of oxygen to nitrating agent from 0 to 3 produced a continuous increase in conversion of nitric acid from 28% to 62%, and of nitrogen dioxide from 13.7% to 24.7%. Unfortunately, no information was given on the effect of additions of oxygen either on decomposition of the alkane or on the composition of the nitroalkanes obtained.

On the basis of the series of investigations Hass formulated several empirical "rules" of nitration, mostly concerned with technical aspects of the process. His views on the mechanism of the nitration of alkanes, expressed in these rules, can be summarised as follows: (*a*) at moderate temperatures (300–500°C) nitration does not result in rearrangement of the carbon skeleton of the initial hydrocarbon; (*b*) under such conditions, however, oxygen-containing products and nitro-compounds undergo considerable decomposition with the formation of alkenes and degradation products (e.g. the pyrolysis of nitroethane and of 1-nitropropane yields alkanes, aldehydes, carbon monoxide and dioxide, and nitrogen, but no lower nitro-compounds); (*c*) nitration is accompanied by oxidation, with nitric acid oxidising both alkanes and nitroalkanes; and (*d*) he accepts McCleary and Degering's statement [57] (below) that nitric acid forms nitroalkanes by reaction with alkyl radicals

$$\dot{R} + HNO_3 \rightarrow RNO_2 + OH \ .$$

Bachman and his coworkers continued the studies of Hass by investigating the gas-phase nitration of propane and butane with nitric acid and nitrogen dioxide. Like Hass they examined the effects of temperature, ratio of hydrocarbon to nitrating agent, and contact time on the formation of nitroalkanes. Their results showed (Table 2) that optimum conditions for the nitration of butane comprised a ratio to nitric acid of 12.3 at 425°C for 1.6 s, when the yield of nitroalkane reached 50% of the butane consumed and 36% of the acid was converted into this product[47]. Propane could be nitrated by nitrogen dioxide most effectively at a ratio to the latter of 4.2 at 325°C with a time of contact of ~2 min, when the yield reached 51% of the propane consumed and the conversion 14–17% of the nitrogen dioxide consumed[48].

Table 2. Effects of composition of mixture, temperature, and time of contact on yield of nitroalkanes and conversion of nitrating agent into nitroalkanes (Bachman[48,49]).

Alkane	Nitrating agent	RH / Agent	T, °C	Contact	Nitroalkanes, yield, %	Nitroalkanes, conversion of HNO_3, %
C_4H_{10}	HNO_3	15	405	1.6 s	31	15
»	»	12.3	425	»	50	36
»	»	»	435	»	33	22
C_4H_{10}	HNO_3	12	425	1.6 s	38	17.4
»	»	16.2	»	»	44	24
»	»	15.6	»	»	37	15.6
C_3H_8	HNO_3	20	423	1.8 s	27.4	—
»	»	10	»	1.73 s	38.3	—
C_3H_8	NO_2	5.85	248	1.8 min	47	14
»	»	4.17	300	1.93 min	49	14
»	»	4.2	325	1.93 min	51	17

Table 3. Effect of additions of molecular oxygen on the formation of nitroalkanes RNO_2 from butane and propane (Bachman[48,49]).

Alkane	Nitrating agent	RH / Agent	NO_2 / Agent	T, °C	Contact	Yield of RNO_2, % on RH consumed	Conversion of agent into RNO_2, %	Consumption of RH, moles
C_4H_{10}	HNO_3	15	0	425	1.6 s	48	36	0.55
»	»	»	2	»	»	24	43	1.06
»	»	»	3	»	»	10	26	2.0
C_3H_8	NO_2	4—4.2	0	325	1.93 min	51	16.6	—
»	»	»	0.5	»	»	43	19.9	—
»	»	»	1.0	»	»	40	13.6	—
C_3H_8	NO_2	4—4.2	0	300	»	49	16.1	—
»	»	»	0.5	»	»	58	28.1	—
»	»	»	1.0	»	»	50	16.4	—

Having determined the maximum yields of nitroalkanes, Bachman directed his further efforts at improving the results, for which purpose he studied the effect of considerable additions of oxygen on the nitration of butane and propane[46,49]. Table 3 shows that the conversion of the nitrating agent into nitroalkanes passes through a maximum with increase in the quantity of oxygen added, whether nitric acid or nitrogen dioxide is used. He attributed this to simultaneous oxidation of the initial alkane with formation of an alkyl hydroperoxide. Breakdown of this product at the peroxy-bond to give alkoxyl and hydroxyl radicals is a branching step, which was used to explain the increasing conversion of the nitrating agent by the action of oxygen on the nitration.

Bachman's hypothesis that oxidation of the alkane takes place at the same time as its nitration is obviously correct. However, the branched character of the oxidation alone is insufficient to explain the increase in conversion, especially as later additions of oxygen beyond the conversion maximum act in the opposite direction. More detailed examination of the interaction of these two reactions is undoubtedly desirable, but several of the necessary data—primarily the consumption of the initial alkanes and frequently the composition of the resulting nitroalkanes—are lacking from the publications both of Hass and of Bachman.

Bachman studied also the effect of additions of halogens on the nitration of propane by nitric acid and by nitrogen dioxide[49,50]. The quantities of halogens were considerably smaller than those of oxygen added at the same time. Degrees of conversion and nitroalkane yields depended on the halogen concentrations. Optimum additions of chlorine and bromine were found at which maximum conversions and yields were obtained.

Bachman's experiments[47] on the influence of the ratio of the surface area of the reaction vessel to its volume S/V on the nitration of butane by nitric acid are interesting. Change in the ratio from 28 to 300 cm^{-1} at 425°C had no effect on the final results: both the degrees of conversion of butane and of nitric acid and the yield of nitroalkanes remained almost constant. Only the proportion of carbonyl compounds diminished slightly, while the quantity of carbon monoxide increased. These results most probably indicate that the reaction is homogeneous under the given conditions.

In his views on the mechanism of nitration Bachman[46] adopted all the main suggestions made by Titov (below). The only modification introduced by Bachman into Titov's set of concepts concerned the path by which nitrogen dioxide is formed during nitration by nitric acid. In 1952 Bachman was probably the first to suggest that, in the high-temperature nitration of alkanes by nitric acid, nitrogen dioxide is formed by the reaction

$$HNO_3 + M \rightarrow NO_2 + OH + M$$

which by that time had become well known and thoroughly studied.

The results obtained by Hass and by Bachman and their coworkers formed the basis for the initial trial production of nitroalkanes at Sterlington (Louisiana, U.S.A.), which was followed (in 1955) by a works manufacturing many thousands of tons a year. The process involves[58] reaction between 75% nitric acid and excess of propane under 7–9 atm (gauge) at 450°C for 1 s. Nitroalkanes and dilute acid are condensed and separated, while nitric oxide is oxidised to nitric acid and returned to the reaction vessel. Varying the conditions enables the proportions of individual nitroalkanes to be varied over the ranges 10–30% of nitromethane, 20–25% of nitroethane, and 55–65% of nitropropanes.

2. Initial Ideas on the Participation of Free Radicals in the Gas-phase Nitration of Alkanes

Passing now to publications during the second period of investigation that endeavoured to establish the mechanism of nitration, we shall first give the main content of the "theory of the nitration of saturated hydrocarbons and side-chains of arylalkanes", as Titov termed his investigation in his summary paper[69]. Discussing the high-temperature nitration of saturated hydrocarbons

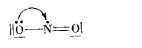
by nitrogen dioxide, he was the first to suggest[59-69] that free hydrocarbon radicals were involved, and attributed their formation to the reaction

$$RH + NO_2 \rightarrow \dot{R} + HNO_2 . \quad (1)$$

However, he regarded the nitro-products as produced by the recombination of free alkyl radicals with nitrogen dioxide, which also possesses the character of a free radical:

$$\dot{R} + NO_2 \rightarrow RNO_2 . \quad (2)$$

The structure of nitrogen dioxide, which can be written



to allow for interaction between the unpaired electron and the mobile p-electrons, enabled Titov to predict that it would react with free alkyl radicals both through the nitrogen atom and through an oxygen atom, i.e. that it would form not only nitro-compounds but also nitrites by the recombination

$$\dot{R} + ONO \rightarrow RONO . \quad (3)$$

Although by the end of the 1930s Hass had shown quite reliably that nitro-compounds containing fewer carbon atoms than in the original hydrocarbon are formed in the high-temperature nitration of alkanes, his attempts to explain this fact were unsuccessful. In 1940 Titov[61] suggested a mechanism for such puzzling degradation of nitro-compounds that was based on the assumption that, under the conditions of high-temperature nitration, an alkyl nitrite undergoes pyrolysis, which according to Rice[70] should give an alkoxy-radical, whose further thermal decomposition yields an aldehyde (or a ketone) and an alkyl radical containing a smaller number of carbon atoms than in the original hydrocarbon. Thus for isobutane as example Titov wrote down the reactions

$$(CH_3)_2CH\dot{C}H_2 + NO_2 \rightarrow (CH_3)_2CHCH_2ONO , \quad (3')$$

$$(CH_3)_2CHCH_2ONO \rightarrow (CH_3)_2CHCH_2\dot{O} + NO , \quad (4)$$

$$(CH_3)_2CHCH_2\dot{O} \rightarrow (CH_3)_2\dot{C}H + HCHO , \quad (5)$$

$$(CH_3)_2\dot{C}H + NO_2 \rightarrow (CH_3)_2CHNO_2 . \quad (2')$$

The mechanism of the gas-phase nitration of alkanes by nitrogen dioxide proposed by Titov in the 1930s comprised a set of primary steps. It must be emphasised that the choice of the actual free radicals and the sequence and nature of the elementary reactions were suggested solely on the basis of results for the chemistry of nitration in terms of stable species. No kinetic study had then been made of nitration, so that information was lacking on the formal kinetics of the reaction (e.g. the effective rate constants in Arrhenius coordinates, the order of the reaction with respect to the initial substances, the kinetics with respect to pressure, etc.) and on the kinetics with respect to stable species. Thus all those data were absent, ignorance of which makes it so difficult to establish the mechanism of chemical reactions involving free radicals. The insight exhibited by Titov in formulating his mechanism is especially surprising. Indeed, as we shall see later, the chemical framework of his scheme was largely adopted by subsequent investigators.

Titov, of course, was interested in the nitration of saturated hydrocarbons not only by nitrogen dioxide but also (perhaps still more strongly) by nitric acid. He formulated the fundamental principles of this process, too. He boldly postulated that nitric acid molecules do not exert an independent nitrating action on the alkane chain but are merely the "source of the progressive regeneration" of oxides of nitrogen. Even with nitric acid, however, the true nitrating agent is still the nitrogen dioxide molecule. Nitration thus takes place, of course, by the above set of reactions (1)–(5).

In order to prove the chemical inertness of nitric acid towards the alkane chain Titov undertook special experiments on the action of the acid on various hydrocarbons[61,62,67] both in the presence of oxides of nitrogen and in their absence (achieved by the addition of urea nitrate). At temperatures up to 150°C nitric acid (specific gravity < 1.4) hardly reacted with alkanes or with the side-chain of alkylbenzenes.

This result raised the question of the route by which nitric acid became the source of nitrogen dioxide. Titov suggested that nitric acid could react readily with nitrous acid and with nitric oxide, not only at high but even at low temperatures, with formation of nitrogen dioxide in both cases:

$$HNO_3 + HNO_2 \rightleftarrows 2NO_2 + H_2O , \quad (6)$$

$$2HNO_3 + NO \rightleftarrows 3NO_2 + H_2O . \quad (7)$$

It was emphasised that nitrous acid already appears in the first stage as a result of reaction (1), that nitric oxide is formed by secondary oxidation processes, and that both reactions (6) and (7) lead to a progressive increase in the concentration of nitrogen dioxide, even in liquid-phase nitration at low temperatures.

Somewhat later, after the publication of Hass's results showing that replacement of nitrogen dioxide by nitric acid increased the rate of the high-temperature nitration of alkanes, Titov[69] suggested that at high temperatures the formation of nitrate radicals from nitric acid was also possible:

$$\begin{aligned} 2HNO_3 &\rightarrow N_2O_5 + H_2O \\ N_2O_5 &\rightarrow \dot{N}O_3 + NO_2 . \end{aligned} \quad (8)$$

By analogy with the dioxide Titov represents the very rapid reaction of the above radical with the alkane chain by the equation

$$RH + \dot{N}O_3 \rightarrow \dot{R} + HNO_3 . \quad (9)$$

The great activity of the nitrate radical in this reaction is attributed by Titov to purely energetic considerations and the fact that it is more strongly electrophilic than nitrogen dioxide: the former are based on the greater heat of formation of nitric than of nitrous acid; and the electrophilicity of the two species will be proportional to a first approximation to the strengths of the corresponding acids—nitric and nitrous.

Objections to certain aspects of Titov's mechanism appeared in the literature. The first was his assertion that nitrogen dioxide is formed from nitric acid by reactions (6)–(8). Bachman et al. were probably the first to reject in 1952 [46] such reaction paths in high-temperatur nitration by nitric acid, and the second were Geiseler and

Reinhardt [71] in 1957. Both papers replaced reactions (6)–(8) by the thermal decomposition of nitric acid†:

$$HNO_3 + M \rightarrow OH + NO_2 + M \quad . \qquad (10)$$

This gas-phase decomposition has now been thoroughly studied [72-74], and has the rate constant

$$k = 1.6 \cdot 10^{15} \exp(-30\,000/RT) \ \text{cm}^3 \ \text{mole}^{-1} \ \text{s}^{-1} \quad .$$

Elementary calculation shows that with this rate coefficient reaction (10) is fully able to supply the quantities of nitrogen dioxide corresponding to the quantities of nitroalkanes actually obtained at 300–400°C. Indeed, the subsequent discussion will show that the Reviewers have obtained experimental evidence of the occurrence of reaction (10) as primary stage in the high-temperature nitration of the alkane chain by nitric acid.

A different situation is found with nitration by nitric acid at low temperatures (in both liquid and gaseous phases). Calculation shows that under these conditions the necessary quantities of nitrogen dioxide cannot be formed from nitric acid by reaction (10), so that a different route must be assumed. Perhaps reactions (6) to (8) occur at low temperatures, as assumed by Titov also for high temperatures. It is noteworthy that he did not study in greater detail the conditions for and the possibility of obtaining nitrogen dioxide from nitric acid at a sufficient rate at low temperatures.

The second aspect of Titov's mechanism to be refuted was the assumption that the actual nitrating agent was nitrogen dioxide even when nitric acid was used. In opposition to this several authors suggested the reaction

$$\dot{R} + HNO_3 \rightarrow RNO_2 + \dot{O}H \ , \qquad (11)$$

which was first considered in 1938 by McCleary and Degering [57], who detected nitroethane and ethyl nitrate among the products of the action of nitric acid on tetraethyl-lead at 150°C. They suggested the scheme

$$Pb(C_2H_5)_4 \rightarrow Pb + 4\dot{C}_2H_5$$
$$\dot{C}_2H_5 + HNO_3 \rightarrow C_2H_5NO_2 + \dot{O}H$$
$$\dot{C}_2H_5 + \dot{O}H \rightarrow C_2H_5OH$$
$$C_2H_5OH + HNO_3 \rightarrow C_2H_5ONO_2 + H_2O \ .$$

There is no doubt that the ethyl radical is present. The thermal decomposition of tetraethyl-lead has been well studied and is widely used for the production of ethyl radicals. It can thus be accepted that one of Titov's fundamental assumptions—that free alkyl radicals are involved in the formation of nitro-compounds from alkanes—found direct experimental confirmation in the above work.

However, we cannot accept that nitroalkanes are formed by reaction (11). Since at high temperatures nitric acid undergoes thermal decomposition into nitrogen dioxide and a hydroxyl radical (Eqn. 10), the competition between reactions (2) and (11) must be considered in order to choose between them. In 1967 the Reviewers [75] found experimentally that reaction (2) has zero activation energy and the rate constant $k = 2.9 \times 10^{12}$ cm^3 mole^{-1} s^{-1}. Reaction (11) takes place with incomparably greater difficulty. The few numerical data available on reactions involving abstraction by an alkyl radical not of a hydrogen atom but of a group of atoms (e.g. $\cdot CH_3 + CH_3CHO \rightarrow CH_3COCH_3 + H\cdot$ [76]) suggest that the activation energy is greater and the pre-exponential factor smaller than for abstraction of a hydrogen atom. Therefore it can reasonably be assumed that at high temperatures (300–500°C), when decomposition of nitric acid is intense, the rate of reaction (2) will be considerably higher than that of reaction (11). Indeed, if we accept that $E_{11} = 10$ kcal mole^{-1} and $A_{11} \simeq 2 \times 10^{11}$ cm^3 mole^{-1} s^{-1}, we find that at 300°C

$$\frac{W_2}{W_{11}} = \frac{k_2[R] \cdot [NO_2]}{k_{11}[R] \cdot [HNO_3]} = \frac{2.9 \cdot 10^{12}[NO_2]}{2 \cdot 10^{11} \cdot e^{-10000/R \cdot 573} \cdot [HNO_3]} = 0.6 \cdot 10^5 \frac{[NO_2]}{[HNO_3]} \quad .$$

Thus even if the concentration of nitrogen dioxide is only 1% of that of nitric acid, W_2 still exceeds W_{11} almost hundredfold. We therefore regard as justified Titov's assertion that nitrogen dioxide is the immediate nitrating agent in the action of nitric acid on alkanes at high temperatures.

Almost twenty years later (in 1957) Geiseler and Reinhardt [71] studied the nitration of ethane by nitric acid under atmospheric pressure at 380–460°C. They determined the effective rate constant [$k_{eff} = 4.49 \times 10^{15} \exp(-47\,500/RT)$ s^{-1}], established optimum temperatures of formation of the nitroalkanes, and studied the thermal decomposition of nitroethane. Besides obtaining important experimental data, they concluded that both Titov's reaction (2) and McCleary and Degering's reaction (11) occurred as direct acts of nitration of ethane. No evidence, either experimental or theoretical, was given that reaction (11) occurred to an appreciable extent. Therefore the Reviewers' calculation indicating the non-competitiveness of reaction (11) with (2) is still valid. This provides no support for the direct combination [71] of the mechanisms of Titov and of McCleary and Degering‡.

The assertion that nitroalkanes are formed by reaction (11) (when alkanes are nitrated by nitric acid) again appeared in the literature in 1965. Ingold and his coworkers [77] reached this conclusion from a study of the reaction between methane and nitric acid at 349.5°C, the variation in the acid concentration being followed by the infrared spectrum. These investigators discovered several interesting features: (i) the rate of decomposition of nitric acid is increased by the presence of methane; (ii) consumption of nitric acid is of the first order with respect to the acid, but only slightly dependent on methane; (iii) although nitrogen dioxide is formed during the process, it does not inhibit decomposition of the acid; and (iv) the reaction velocity is $W = 2.8k_a[HNO_3]$, where k_a is the rate constant of the decomposition of nitric acid.

In order to ascertain a mechanism of reaction between methane and nitric acid consistent with these features the authors examined the series of known elementary reactions

$$HNO_3 \xrightarrow{a} \dot{O}H + NO_2$$
$$\dot{O}H + HNO_3 \xrightarrow{b} H_2O + \dot{N}O_3$$
$$\dot{O}H + CH_4 \xrightarrow{c} H_2O + \dot{C}H_3$$
$$\dot{C}H_3 + HNO_3 \xrightarrow{d} CH_3NO_2 + \dot{O}H$$
$$\dot{C}H_3 + NO_2 \xrightarrow{e} CH_3NO_2$$
$$\dot{C}H_3 + HNO_3 \xrightarrow{f} CH_3OH + NO_2 \quad .$$

Firstly they considered non-chain mechanisms, e.g. the set of reactions a, c, and e or a, c, e, and f, etc., but formulae for the reaction velocity derived from these mechanisms did not satisfy the experimental data. Closest

†Here and subsequently M represents any molecule of the reaction mixture.

‡We considered it necessary to emphasise this point, since Geiseler and Reinhardt's paper gained some publicity, and is widely quoted in the literature on the nitration of hydrocarbons.

agreement with the above experimental features was provided by the chain mechanism comprising the fundamental reactions

$$HNO_3 \xrightarrow{a} \dot{O}H + NO_2$$
$$\dot{O}H + CH_4 \xrightarrow{c} H_2O + \dot{C}H_3$$
$$\dot{C}H_3 + HNO_3 \begin{cases} \xrightarrow{d} CH_3NO_2 + \dot{O}H \\ \xrightarrow{f} CH_3OH + NO_2 \end{cases}.$$

It should be noted that Ingold et al. use CH_3NO_2 to represent the sum of nitromethane and methyl nitrite. They do not deny that reactions *b* and *f* may also occur to a slight extent. Thus the limiting stage in their mechanism is the breakdown of nitric acid into a hydroxyl radical and nitrogen dioxide. However, the main reaction yielding nitromethane and methyl nitrite is assumed to be interaction of the alkyl radical with the acid (*d*).

There can be no doubt about the first conclusion (concerning reaction *a*), at least at and above 350°C. The second conclusion—that nitromethane is formed by reaction *d*—has a quite different status. It is strange that these workers did not think of comparing, even to a first approximation, the quantitative kinetics of the two possible competing reactions *d* and *e* yielding nitromethane. The Reviewers have made such a comparison when discussing McCleary and Degering's work (above), and have concluded that the probability of the formation of nitroalkanes and alkyl nitrites by reaction *d* is very small.

It must be added that Ingold regards formation of the alcohol by reaction *f* as confirming the suggested mechanism. However, his mechanism is terminated, it may be said "compulsorily", at the stage of formation of nitromethane, and does not even involve either methyl nitrite or the alkoxy-radical (the latter is necessarily formed by the reaction $\cdot CH_3 + NO_2 \rightarrow CH_3O\cdot + NO$). Yet such an ordinary reaction as that of methoxyl with the initial alkane would undoubtedly have yielded the alcohol even without the inclusion of reaction *f* in the mechanism.

Titov's third principle—thermal decomposition into alkoxyl and nitric oxide of the alkyl nitrites formed—was refined by Gray[78]. On the basis of known thermochemical data he emphasised that the energy of the carbon–oxygen bond in an alkyl nitrite is ~57 kcal mole^{-1}, so that, when the molecule is formed by recombination of an alkyl radical with nitrogen dioxide, it possesses this energy of excitation. Gray assumes that in the liquid phase, although the energy of the adjacent oxygen–nitrogen bond is only ~37 kcal mole^{-1}, the excited alkyl nitrite can nevertheless be deactivated by collisions. The resulting stable alkyl nitrite, having lost the excess energy, must be regarded as of primary origin, formed by the single elementary reaction between the alkyl radical and nitrogen dioxide. A different situation obtains in gas-phase nitration. Here, according to Gray, the lifetime of the excited nitrite is so brief that decomposition into alkoxyl and nitric oxide takes place considerably sooner than the excess energy can be released in collisions. The analytically determinable alkyl nitrite is then formed by subsequent reaction between the alkoxy-radical and nitric oxide with formation of an oxygen–nitrogen bond, which is the weakest bond in the molecule. Such an alkyl nitrite must be regarded as of secondary origin, since its formation involves two successive elementary steps. Thus Gray's work gave rise to the problem of determining experimentally the primary or secondary origin of the alkyl nitrite (in the above senses of these terms) in the nitration of alkanes.

III. KINETICS AND MECHANISM OF THE GAS-PHASE NITRATION OF ALKANES. RADICAL-CHAIN MECHANISM OF THE NITRATION OF METHANE AND PROPANE

The above critiques[57,71,77,78] of certain aspects of the mechanism suggested by Titov completed the second period of investigation. The third period, beginning in the mid-1950s and continuing at the present time, has been characterised by steadily growing interest in the kinetics of the high-temperature nitration of the alkane chain. Such emphasis is not, of course, accidental. Only the most general idea of the mechanism of nitration had been formulated from all the preceding research. The scientific foundations of this chemical change, i.e. its detailed mechanism in terms of the quantitative kinetics of primary steps, had not been established. A more profound kinetic study of nitration therefore became necessary.

One of the first was Yoffe's study[79] of the action of nitrogen dioxide on alkanes (C_1–C_5) under static conditions at subatmospheric pressures. He discovered that nitration may take place either as a slow reaction without visible emission, as a slow reaction accompanied by light blue luminescence, or as an explosive reaction.

In the case of pentane the slow reaction takes place at 200–300°C. The products included primary and secondary nitroalkanes, nitric oxide, and carbon monoxide and dioxide, as well as alkyl nitrites. This worker assumed that the primary stage was detachment of a hydrogen atom from the alkane by the nitrogen dioxide. The resulting alkyl radicals react with nitrogen dioxide to yield nitroalkanes and alkyl nitrites.

With all the alkanes studied other than methane, at temperatures above 300°C and pressures above a certain limit, the reaction is accompanied by luminescence preceded by an induction period. During the latter alkyl nitrites were assumed to be formed, which decomposed into the alkoxyl and nitric oxide. The luminescence, however, may be due to reactions of the alkoxy-radical[80]. On raising the pressure (with the mixture $C_5H_{12} + 4NO_2$), Yoffe discovered a second pressure limit, above which explosion occurred accompanied by a bright white flash. This was preceded by an induction period, which could be eliminated by the addition of ethyl nitrite or shortened by acetaldehyde. With the same mixture at 400°C "composite" flames were observed, which were attributed to the dissociation $2NO_2 \rightarrow 2NO + O_2$. Analysis of the gaseous products showed in this case the presence of carbon monoxide and dioxide, nitric and nitrous oxides, and hydrogen.

Thus this work revealed several interesting features of the nitration of alkanes by nitrogen dioxide—the appearance of blue luminescence and white flames, the occurrence of an induction period, and its dependence on additions of an alkyl nitrite and of an aldehyde. The detection of an alkyl nitrite among the reaction products is significant.

Experimental results were treated differently by Myerson et al.[81], who investigated the action of nitrogen dioxide on propane at 400 and 503°C, confining their attention to the reaction accompanied by a flame. These workers observed that the colour of the flame varied from orange-red to pale blue and white depending on the pressure and the composition of the mixture. They distinguished two types of flames: (i) single-stage flames were weakly actinic; (ii) two-stage flames comprised a flame of the first type followed (after an induction period of ~9 ms) by a hot bright flame. The first flame was attributed to the formation of alkyl nitrites, but the second was regarded as due to the interaction of nitrogen dioxide

with ethylene formed in the first flame. Analysis of the products showed that the first flame, when followed by the second, was accompanied by considerable reaction with the consumption of up to 20% of the propane. The main products were ethylene, methane, carbon monoxide and dioxide, nitric oxide, hydrogen cyanide, and acetylene.

The main argument used by these workers against Titov's mechanism was the absence of propene from the reaction products, which according to this mechanism they believed should have been formed in the flame by the decomposition of 2-nitropropane. The presence of a considerable quantity of ethylene instead of the expected propene and the impossibility with Titov's mechanism that it could be formed from isopropyl at subsequent stages gave these authors grounds for adopting a different mechanism of nitration, involving the formation of intermediate complexes:

$$C_3H_8 + NO_2 \begin{cases} \rightarrow CH_3CH_2(NO_2)CH_3 \begin{cases} \rightarrow \text{Products} \\ \rightarrow \dot{C}H_3 + CH_3CH_2NO_2 \xrightarrow{\text{decomp.}} C_2H_4 + HNO_2 \end{cases} \\ \rightarrow CH_3CH_2(ONO)CH_3 \begin{cases} \rightarrow \text{Products} \\ \rightarrow \dot{C}H_3 + CH_3CH_2ONO \end{cases} \end{cases}.$$

Subsequent reactions of the complexes with nitrogen dioxide and (or) their decomposition yield various products, in particular nitro-compounds and alkyl nitrites having a smaller carbon skeleton than in the original alkane. Thermal decomposition of nitroethane leads to the formation of ethylene.

This mechanism with intermediate complexes is unconvincing. Immediately it was advanced Yoffe[82] made the entirely correct remark that complex formation was hardly feasible at such high temperatures (400 to 500°C). It is also hardly possible to accept the authors' statement that ethylene cannot be formed by Titov's mechanism. Actually the propoxy-radical decomposes to form the ethyl radical ($n\text{-}C_3H_7O\cdot \rightarrow C_2H_5\cdot + HCHO$), which reacts with nitrogen dioxide to give nitroethane, whose thermal decomposition yields mainly ethylene.

In spite of the doubt attaching to a mechanism involving formation of intermediate complexes, this work was important for the development of research on nitration. It continued Yoffe's study[79] of nitration accompanied by weakly actinic emission. As Myerson et al.[81] showed, such luminescence remains in the chain process, when it precedes the hot flame. We shall show below that this glow consists of slowly spreading "cool" flames, revelation of whose nature was an important turning point in establishing the kinetic mechanism of nitration.

In 1957 [sic] Gagarina and Emanuel' reported[83,84] a kinetic investigation of the reaction of methane with nitrogen dioxide under static conditions at pressures below atmospheric and at temperatures of 360–420°C. This was one of the first investigations of the gas-phase nitration of alkanes which laid stress on a kinetic study. The order of the reaction with respect to the starting materials were determined: the first order was observed with respect to methane throughout the temperature range examined; the order with respect to nitrogen dioxide varied from unity at 360 and 380 to 0.5 at 400 and 0.3 at 420°C. Determination of the order in the latter case was complicated by the fact that change in the initial pressure of nitrogen dioxide was accompanied by changes in those of nitric oxide and oxygen in conformity with the equilibrium constant (methane was introduced into the reaction vessel after the nitrogen dioxide, following establishment of the equilibrium $2NO_2 \rightleftharpoons 2NO + O_2$).

In order to ascertain whether nitric oxide and oxygen took part in the reaction, a series of experiments was made at 400°C in which the initial pressures of methane and nitrogen dioxide remained constant and only those of the test gases were varied. Increasing the concentration of nitric oxide increased the rate of reaction (measured from the increase in the total pressure), whereas addition of oxygen produced a sharp decrease. Since the effects of these gases on the reaction were not determined at all temperatures at which its order with respect to nitrogen dioxide had been determined, the authors themselves regarded their values for the order of reaction as not entirely accurate.

The effective activation energy of nitration was determined[83,84] as $E_{eff} = 42$ kcal mole^{-1}. The rate of reaction of methane with nitrogen dioxide was independent of the total pressure, and zero order was maintained during the reaction. This was attributed to the coupling of many elementary stages, involving not only intermediate species but also nitrogen dioxide and oxygen. The constant rate during the reaction is described by the empirical equation $w = k[CH_4][NO_2]/[O_2]$, where k is the effective rate constant and the square brackets indicate instantaneous concentrations of the gases.

The kinetics with respect to products showed[83,84] that the action of nitrogen dioxide on methane yields nitromethane, carbon monoxide and dioxide, nitric oxide, and small quantities of formaldehyde and hydrogen cyanide. Nitromethane was an intermediate product, but not the only one, which was confirmed by comparing its rate of consumption with the rate of increase of the total pressure at various times during the reaction. Calculation showed that around 50% of the products of intensive oxidation of methane (carbon monoxide and dioxide) is produced without intermediate formation of nitromethane.

These workers regard the step $RH + NO_2 \rightarrow R + HNO_2$ as the first stage of initiation of the reaction of alkanes with nitrogen dioxide. They consider that methane can undergo two independent reactions — nitration to nitromethane and intensive oxidation by oxygen in the nitrogen dioxide (oxidation by combined oxygen).

A study of the kinetics of the action of nitrogen dioxide on n-butane was published by Ermakova et al.[85] in 1961. Experiments were made under static conditions with subatmospheric pressures over the temperature range 250–450°C. The order of the reaction at 300°C was 0.7 and 1.4 with respect to butane and nitrogen dioxide respectively. The effective activation energy determined over the above temperature range was 30 kcal mole^{-1}. Either a slow reaction or a reaction with a hot flame was observed depending on the conditions. The temperature dependence of the explosion limit was determined for the mixture $C_5H_{10} + 6.5NO_2$ on the assumption that the explosion was thermal in nature. The primary step in the reaction was regarded as

$$n\text{-}C_4H_{10} + NO_2 \rightarrow n\text{-}\dot{C}_4H_9 + HNO_2,$$

which was followed by formation either of the nitro-compound

$$\dot{C}_4H_9 + NO_2 \rightarrow C_4H_9NO_2$$

or of the alkyl nitrite

$$\dot{C}_4H_9 + NO_2 \rightarrow C_4H_9ONO.$$

From the late 1950s to the early 1960s a comprehensive kinetic investigation of the gas-phase nitration of methane and propane was started at the Institute of Petrochemical Synthesis of the USSR Academy of Sciences[86-100]. This

was directed towards establishing the mechanism of these reactions. The latter phrase applied to a gas-phase reaction involving free radicals has a quite definite and general meaning. It includes as first stage determination of the kinetic mechanism, i.e. elucidation of whether a free-radical, unbranched-chain, ordinary branched-chain, or degenerately branched-chain reaction is involved. This entails the establishment of several kinetic laws — determination of the dependence of the reaction velocity on such factors as time, pressure, temperature, diameter of reaction vessel and the ratio of its surface to its volume, addition of inert gases and intermediate products, composition of initial mixtures, etc.

The second stage is to specify the chemistry of the kinetic mechanism, i.e. to construct a set of primary chemical steps representing in totality the true course of the chemical change. Besides the above kinetic laws great importance attaches here to determining the kinetics with respect to stable species (initial compounds, intermediates, and final products).

Finally, the concluding stage is to compare the overall reaction velocity, calculated from the proposed mechanism by a quasi-stationary method, with the observed rate. During recent years this stage has often included also a comparison of the kinetics with respect to stable reaction products, determined from the suggested mechanism by calculation on an electronic computer, with experimental results for the accumulation of products.

The nitration of methane and propane by nitrogen dioxide was studied[89,91-95,99] under static conditions in glass vacuum apparatus both at 400–600°C and 10–630 mmHg and at 200–500°C and 20–500 mmHg. The variation in the concentration of nitrogen dioxide during the reaction was recorded. The reaction products were analysed polarographically, spectroscopically, and chromatographically. Three types of reaction between alkanes and nitrogen dioxide were established (Fig. 1).[86]

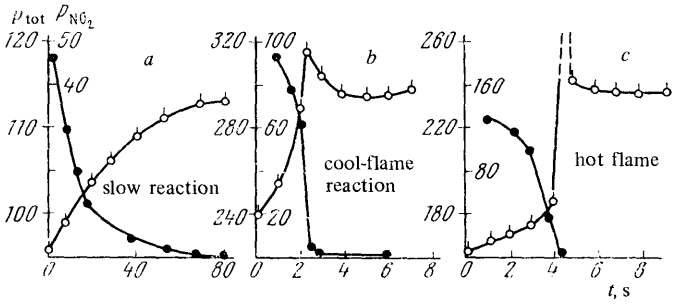


Figure 1. Kinetic curves for three types of reaction in the nitration of propane by nitrogen dioxide at 350°C: *a*) mixture of C_3H_8 + NO_2 (p_{init} = 96 mmHg); *b*) 1.5 C_3H_8 + NO_2 (237); *c*) C_3H_8 + 4NO_2 (162.5): 1) total pressure; 2) pressure of nitrogen dioxide.

1. Slow reaction. Kinetic curves based on the change in pressure Δp and the consumption of nitrogen dioxide are typical of unbranched-chain reactions. The reaction velocity is constant up to 30–50% consumption.

2. Cool-flame reaction. An autocatalytic process terminates in a jump in pressure, which is accompanied by passage through the mixture of a weakly actinic flame, termed "cool" by the authors and visible only in a darkened room. The rate of propagation of such flames is 10–20 cm s^{-1}, and the temperature in them is raised by about 100–150 deg. The nitrogen dioxide has been almost completely exhausted when the pressure peak is reached. The spectra of these cool flames indicates that their emission is due to electronically excited formaldehyde[90].

3. Reaction with a hot flame. This also begins with an autocatalytic process followed by an abrupt rise in pressure and then a rapid fall. At the instant of the jump in pressure the reaction is accompanied by a bright flame, in which it goes to completion.

Special experiments on hot flames appearing at the pressure limit and near the limit within the region of thermal ignition have confirmed that such ignition is a two-stage process[98]: the first stage involves passage of the cool flame, and is followed, in the mixture modified by the accompanying reaction, by the hot flame as the second stage. Transitions from the first to the second and then to the third type of nitration can be achieved either by increasing the pressure or by raising the temperature, and have definite limits with respect to these factors.

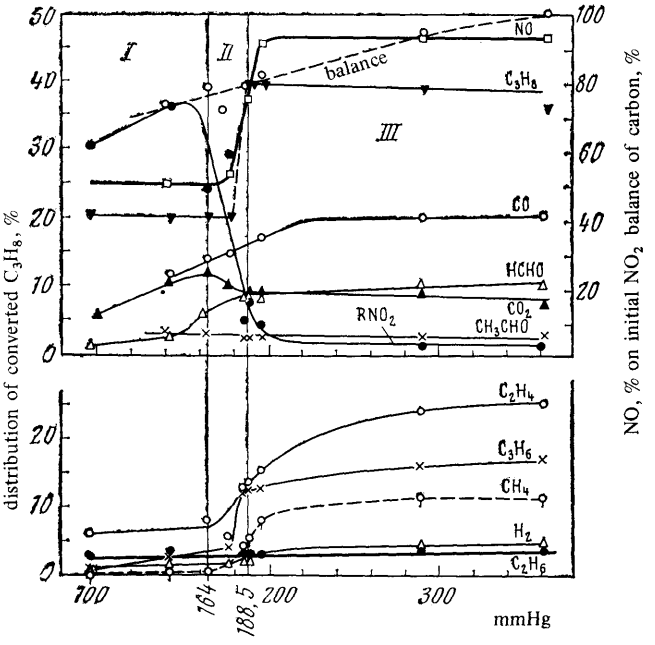


Figure 2. Composition of products at ends of slow and cool-flame reactions in the nitration of propane as function of initial pressure (C_3H_8 + NO_2 at 350°C): I) slow reaction; II) reaction "with a peak" on the pressure-time curve; III) reaction with a cool flame.

Fig. 2 shows marked differences in the composition of the products on termination of the slow and of the cool-flame reactions in the action of nitrogen dioxide on propane at 350°C. The main products of the slow reaction are

nitroalkanes, carbon monoxide, and carbon dioxide, while the quantities of alkenes, carbonyl compounds, methane, and hydrogen are small. At the end of the cool-flame reaction only a minor quantity of nitroalkanes is recorded, whereas the main products are alkenes (ethylene and propene), carbon monoxide and dioxide, formaldehyde, and methane. Only carbon monoxide, carbon dioxide, and nitrogen are found at the end of the hot-flame stages[91].

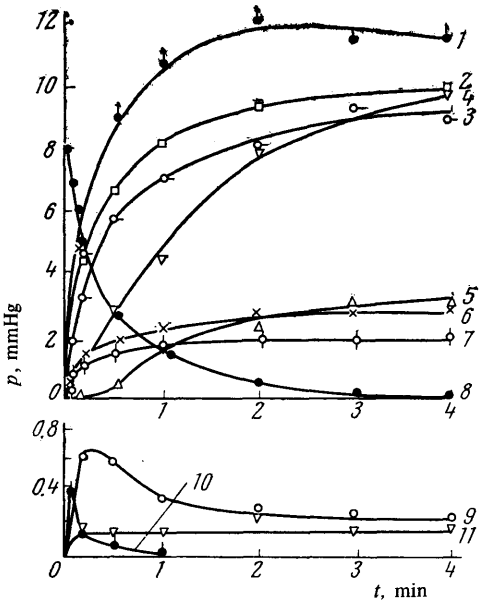


Figure 3. Rates of consumption of nitrogen dioxide and accumulation of products of the slow nitration of propane ($C_3H_8 + NO_2$ at 300°C and initially 320 mmHg): 1) 2-$C_3H_7NO_2$; 2) CO_2 (×0.5); 3) CH_3NO_2; 4) CO (×0.5); 5) $(CH_3)_2CO$; 6) 1-$C_3H_7NO_2$; 7) $C_2H_5NO_2$; 8) NO_2 (×0.1); 9) CH_3ONO; 10) iso-C_3H_7OH; 11) CH_3CHO.

Fig. 3 illustrates the accumulation of products throughout the slow reaction in the nitration of propane. Analysis of the products at the end of the cool-flame induction period§ gave the important result that the composition of the mixture was closely similar to that during the slow reaction. Indeed, nitroalkanes and oxides of carbon predominate at the end of this induction period, whereas methane and alkenes are almost completely absent. This suggests that the autocatalytic reaction leading to the cool flame is identical in mechanism with the slow reaction, and that the difference in composition between the products on termination of the slow and of the cool-flame reactions is due to reactions occurring in the cool flame itself as a consequence of the rise in temperature.

§The cool-flame induction period is the time that elapses from admission of the mixture to the reaction vessel until cool-flame ignition occurs.

Determination of the order of reaction with respect to the starting materials and of the activation energy yielded formulae for the initial rates of the slow nitration of methane and propane by nitrogen dioxide [89,92]:

$$w_{CH_4+NO_2} = (7.3 \pm 0.6) \cdot 10^{14} \exp[(-33.6 \pm 0.9)/RT] \cdot [CH_4] \cdot [NO_2] \text{ mole cm}^{-3}\text{ s}^{-1}$$
(for 400—500 °C)

$$w_{C_3H_8+NO_2} = (1.0 \pm 0.1) \cdot 10^{15} \exp[(-30.0 \pm 0.5)/RT] \cdot [C_3H_8] \cdot [NO_2] \text{ mole cm}^{-3}\text{ s}^{-1}$$
(for 200—250 °C)

$$w_{C_3H_8+NO_2} = (8.5 \pm 2.5) \cdot 10^{8} \exp[(-30.0 \pm 0.5)/RT] \cdot [C_3H_8]^{0,75} \cdot [NO_2]^{1,6} \text{ mole cm}^{-3}\text{ s}^{-1}$$
(for 300—350 °C)

Studies were made [89,93] of the influence on the kinetics of nitration of varying the ratio of surface to volume S/V and the diameter of the reaction vessel and also of adding inert gases—nitrogen, carbon dioxide, helium—to the mixtures. Increasing the S/V ratio and decreasing the diameter had hardly any effect on the initial rate of the slow reaction but raised the pressure limit of cool-flame ignition. Additions of inert gases left the initial rate of the slow nitration of methane and propane almost unchanged, lowered the pressure limit for the cool-flame ignition of methane, and, rather unexpectedly, raised the pressure limit in the case of propane.

The addition of intermediate products (aldehydes and alkyl nitrites) had hardly any effect on the rate of the slow nitration of methane and propane, but shortened the induction period and lowered the pressure limit of cool-flame ignition [89,93].

The experimental results obtained made it possible to establish the kinetic mechanisms of the cool-flame and the slow nitration of methane and propane by nitrogen dioxide. With the former reaction the task was facilitated by comparison with the cool-flame oxidation of alkanes by free oxygen. Thorough investigation of this latter reaction, known for more than fifty years, indicated a chain process with degenerate branching. These two reactions were closely similar: in both cases the process began, after an induction period, with an autocatalytic reaction leading to a sharp jump in pressure accompanied by passage of a weakly actinic cool flame through the mixture; the jump was followed by a rapid drop in pressure, coinciding with extinction of the cool flame. In both cases the rate of propagation of the cool flame was 10–20 cm s^{-1}, and the temperature 100–150 deg above that of the walls of the reaction vessel. Finally, the source of the emission by the cool flame is electronically excited formaldehyde in both nitration and oxidation [90,100].

There are also differences: (*a*) only one cool flame appears in nitration, but in oxidation the number of successive cool flames may reach seven, as e.g. with propane; (*b*) all the initial reactants are consumed in the single cool flame of nitration, but only 10–20% in each of the cool flames of oxidation. However, these differences were shown [98] to be due to the negative temperature coefficient of reaction velocity characteristic of the oxidation but not of the nitration of alkanes. Therefore the differences do not disprove the similar nature of cool-flame nitration and oxidation of alkanes, and did not prevent the authors from assuming, initially by analogy, a kinetic mechanism of degenerate branching also for the cool-flame nitration of alkanes.

This conclusion is supported by several of the experimental results [89,93] for the nitration of methane and propane by nitrogen dioxide: (i) the induction period is shortened and the pressure limit of cool-flame ignition is lowered by the addition of active intermediate products (aldehydes, alkyl nitrites) to the initial mixture; (ii) increasing the S/V ratio and diminishing the diameter of the reaction

vessel raise the pressure limit of cool-flame ignition; and (iii) dilution of the initial mixture with nitrogen lowers the pressure limit of cool-flame ignition in the nitration of methane. The last two effects find a reasonable explanation in the termination of chains at the walls.

A degenerate-branching mechanism of cool-flame nitration appears at first glance to be inconsistent with the above rise in the pressure limit of cool-flame ignition of propane on addition of an inert gas. An explanation for the difference from methane was obtained from a consideration of paths leading to branching during nitration. Indeed, if it were possible to show that the rate of branching in the nitration of propane diminishes on addition of an inert gas, this would explain the unexpected rise of the limit. Interaction between nitrogen dioxide and aldehydes formed by the thermal breakdown of alkoxy-radicals has been regarded[95,99,100] as the branching step in nitration. It is therefore necessary to determine possible routes by which alkoxy-radicals themselves can be formed.

The first possible path is disproportionation:

$$\dot{R} + NO_2 \rightarrow R\dot{O} + NO \ .$$

Analytically determinable alkyl nitrite is then formed in a secondary stage:

$$R\dot{O} + NO \rightarrow RONO$$

i.e. is of secondary origin. A second path is formation, from the same alkyl radical and nitrogen dioxide, of excited RONO*, which is either converted by loss of excess energy in deactivating collisions into a stable nitrite of primary origin or, because of its short lifetime, breaks down into an alkoxy-radical and nitric oxide. A stable nitrite will then be formed, as in the case of disproportionation, by the reaction RO· + NO: i.e. it will be of secondary origin.

The stable methyl nitrite obtained in a study of the primary reaction between a methyl radical and nitrogen dioxide was shown[75] to be of secondary origin. Additions of an inert gas, of course, cannot influence disproportionation but may promote deactivation of an alkyl nitrite, thereby lowering the alkoxyl concentration and hence also the concentration of aldehydes, which in turn will diminish the rate of branching.

Calculations by means of Kassel's formula yield for excited methyl and propyl nitrites the relatively long lifetimes of 10^{-6} and 10^{-2} s respectively, so that they can be stabilised even at pressures below 1 atm. In this case a primary nitrite should be formed.

During recent years, however, the view has been expressed that not all bonds in a molecule are equally involved in the redistribution of energy[101,102]. In an alkyl nitrite, for example, decomposition involves rupture of the oxygen–nitrogen bond, i.e. a bond between [relatively] heavy atoms, whose vibration frequencies are considerably lower than (33–50% of) those of a carbon–hydrogen bond. Because of the absence of resonance between the frequencies of slow vibrations of the oxygen–nitrogen bond and the rapid vibrations of the carbon–hydrogen bonds, therefore, the transfer of energy to these latter bonds can be ignored. In the Kassel formula for methyl nitrite the number of effective degrees of freedom among which the energy is distributed will then decrease to 6 from 15, and hence the lifetime will be 10^{-11} s. This implies almost instantaneous breakdown into methoxyl and nitric oxide. It is impossible to stabilise such a nitrite at pressures of ~1 atm. Application of this method of calculation to propyl nitrite gives a lifetime of $\sim 10^{-8}$ s. Addition of an inert gas will then increase significantly the probability of deactivation, which will naturally lead to a decrease in the rate of branching, i.e. to a raising of the limit of cool-flame ignition.

Establishment of degenerate branching for cool-flame nitration was an important factor in solving the kinetic mechanism of the slow reaction. The form of the rate curves for the latter (Fig. 1*a*), the lack of effect of additions of aldehydes, alkyl nitrites, and inert gases and of variation in the S/V ratio all appeared to suggest that the slow reaction was an unbranched-chain reaction with homogeneous chain, initiation and termination. However, the Reviewers regard such a view as incorrect.

Indeed, it is impossible to reconcile a change in kinetic mechanism from degenerately branched to unbranched (which supposedly occurs on passing from cool-flame to slow nitration) with the absence[93] of any chemical differences between the slow reaction and the autocatalytic reaction leading to cool-flame ignition. The same intermediate and final products are formed in the two cases, even in the same proportions. Thus the aldehydes responsible for branching in the cool-flame reaction are formed also in the slow reaction, and it is difficult, since transition from the first to the second reaction and *vice versa* have limits with respect to both temperature and pressure, to suppose that slight variation in these parameters at the pressure limit of cool-flame ignition would be able either completely to suppress the branching power of aldehydes or to confer on them this power. It may be recalled here that the oxidation of alkanes by free oxygen also involves a limiting transition between cool-flame and slow reactions, but they are both degenerately branched processes, and the rate curves of the slow reaction (graphs of the time dependence of Δp and the aldehyde concentration) are sigmoid.

In sum the authors accept[95,99,100] that slow nitration (just like the cool-flame process) is a degenerately branched chain reaction, since steps of degenerate branching take place during its course, but one in which the rate of chain termination exceeds the rate of branching. When the rate of chain initiation is sufficient, as in nitration¶, such a reaction will mimic kinetically an unbranched-chain process.

According to the chain theory the limit equation in a degenerately branched chain reaction can be deduced from the formula

$$M = \{w_0/[k(\nu - 1) - k']\}\,[e^{[k(\nu-1)-k']t} - 1],$$

where the condition $k(\nu - 1) - k' = \varphi = 0$ defines the limit. Here M is the concentration of the branching agent (in the present case an aldehyde), ν the length of the chain, given by the ratio of the rates of chain propagation and chain termination, k the rate constant of degenerate branching, and k' the rate constant for termination of the branching agent. We shall see that termination of the branching agent must be introduced in order to obtain the limit. Termination of the aldehyde on the wall is assumed in the paper.

The transition from the cool-flame reaction through the limit to the slow reaction with variation in pressure (at constant temperature) can now be explained by the fact that $\varphi > 0$ in the region of cool-flame nitration. Decrease in pressure affects only k', which with termination in the diffusion domain will increase, so that φ will decrease.

¶Table 5 gives initiation rate constants for the nitration of propane. At 350°C, for example, $k_{init} = 10^{11} \times 8.5 \times 10^{-10} = 85$, which exceeds by 10^7 the value for the oxidation of propane by free oxygen.

At a certain pressure φ will become zero, and a slight further decrease in pressure will lead to transition through the limit into the region of the slow reaction.

With fall in temperature and the accompanying transition from cool-flame to slow reaction the rate constant of homogeneous termination remains unchanged, and that of surface termination decreases only slightly. A marked decrease is observed in the rate constant of branching, which, as always, has quite a high activation energy. Overall the rate of termination may exceed the rate of branching, and in contrast to ordinary branched processes, where reaction cannot in practice be measured below the limit ($\varphi < 0$), here (in nitration) a slow reaction mimicking an unbranched process is observed owing to relatively rapid initiation.

The establishment of a chain mechanism with degenerate branching for the slow and cool-flame nitration of methane and propane gave rise to the problem of the specific chemistry of this kinetic mechanism. In other words, a radical–chain scheme must be sought, unique to each hydrocarbon, calculations based on which would lead, depending on the temperature and the pressure, either to an autocatalytic cool-flame reaction ($\varphi > 0$) or to a slow reaction, involving the branching steps but mimicking an unbranched-chain process ($\varphi < 0$) because of the preponderance of termination over branching. The schemes suggested[95,99,100] for the nitration of methane and propane have the same fundamental structure, with that for methane forming part of the scheme for propane. The latter is more complicated only in involving radicals containing two and three carbon atoms in addition to those containing a single carbon atom.

Initiation is represented by the equation

$$RH + NO_2 \rightarrow \dot{R} + HNO_2 \ . \qquad (a)$$

Calculation of the activation energy of reaction (a) on the basis of the Polanyi–Semenov rule gave values of 30.8, 26.2, and 23.6 kcal mole^{-1} for the formation of methyl from methane and of propyl and isopropyl from propane. An important confirmation of this step (a) is the discovery by Soviet workers[103-107] that additions of nitrogen dioxide accelerate the oxidation of alkanes by free oxygen.

The alkyl radicals formed in reaction (a) undergo parallel reactions with nitrogen dioxide:

$$\dot{R} + NO_2 \rightarrow RNO_2 \qquad (b)$$

$$\dot{R} + NO_2 \rightarrow [RONO]^* \rightarrow R\dot{O} + NO \qquad (c)$$

the first of which terminates the chain, whereas step (c) propagates the chain. Rate constants of these steps and of $R\cdot + NO \rightarrow RNO$ were determined[94,96,97] directly for the reactions of the methyl radical with nitrogen dioxide and with nitric oxide†.

The alkoxy-radicals obtained in reaction (c) may undergo further change in three ways—(i) unimolecular decomposition with formation of an aldehyde and a lower alkyl radical

$$R\dot{O} \rightarrow R'CHO + R'' \qquad (d)$$

and for the methoxy-radical

$$CH_3\dot{O} \rightarrow HCHO + \dot{H} \qquad (e)$$

†The reaction $R\cdot + NO \rightarrow RNO$, whose rate constant was considerably smaller than that of the reaction $R\cdot + NO_2$, is ignored in the scheme for the initial stages of reaction, when the concentration of nitric oxide is still small.

(ii) hydrogen abstraction with formation of the alcohol

$$RO + RH \rightarrow ROH + \dot{R} \qquad (f)$$

and (iii) recombination with nitrogen dioxide and with nitric oxide, which is significant only at relatively low temperatures because of the thermal instability of alkyl nitrates and nitrites. (iv) Disproportionation of alkoxy-radicals with nitric oxide to form aldehydes (or ketones) becomes possible in the later stages, when the concentration of nitric oxide has become considerable. In the initial stages of nitration the main reaction of alkoxy-radicals is decomposition with formation of aldehydes.

The aldehydes react with nitrogen dioxide:

$$RCHO + NO_2 \rightarrow R\dot{C}O + \dot{H}NO_2 \ . \qquad (g)$$

This is a step of degenerate branching, since it entails replacement of the relatively inactive nitro-radical by an active aldehyde radical (formyl in the nitration of methane, and acetyl in that of propane). Published experimental rate constants k_{eff} for the reactions of acetaldehyde and of formaldehyde with nitrogen dioxide are closely similar to the rate constants of the primary steps (g). Although the assumed branching is of degenerate type, its rate constant is closer to the value for branching in the oxidation of molecular hydrogen than to the rate constant of degenerate branching in the oxidation of alkanes.

The resulting acetyl radical reacts mainly with nitrogen dioxide according to the equation

$$CH_3\dot{C}O + NO_2 \rightarrow \dot{C}H_3 + CO_2 + NO \ .$$

Competing processes—decomposition of the acetyl radical and its reaction with nitric oxide—are considerably slower under the given conditions, and therefore were omitted from the scheme. Examination of published information on the reaction of formaldehyde with nitrogen dioxide led to the inclusion of three reactions of the formyl radical—chain termination

$$H\dot{C}O + NO_2 \rightarrow CO + HNO_2 \qquad (i)$$

and chain propagation

$$H\dot{C}O + NO_2 \rightarrow CO_2 + \dot{H} + NO \qquad (j)$$

$$H\dot{C}O + M \rightarrow \dot{H} + CO + M \ . \qquad (k)$$

The hydrogen atoms formed in reactions (e), (j), and (k) undergo with nitrogen dioxide the rapid chain-propagating reaction

$$\dot{H} + NO_2 \rightarrow \dot{O}H + NO \qquad (l)$$

which takes place at almost every collision. The resulting hydroxyl radical reacts with the alkane:

$$RH + \dot{O}H \rightarrow \dot{R} + H_2O \ . \qquad (m)$$

The step $HO\cdot + NO_2 \rightarrow HNO_3$ is a third-order reaction which is considerably slower than (m). The nitrous acid formed in several stages breaks down almost immediately: $2HNO_2 \rightarrow H_2O + NO_2 + NO$. Heterogeneous termination of aldehydes has been introduced into the scheme.

Calculations based on the schemes for the reactions of propane and methane with nitrogen dioxide were made by the method of quasi-stationary states, on the hypothesis that, since aldehydes react relatively rapidly with nitrogen dioxide, they are the active centres of the reaction. Among all active centres only aldehydes (acetaldehyde and formaldehyde) show a non-zero variation of concentration with time, since they are involved in the slow stage of degenerate branching. Calculation on the

scheme for the nitration of propane was based on the assumptions that

$$k_1 = k_4 = k_7 = k_{17} = 0.45\,k_2\ ;\ k_2 = k_5 = k_8 = k_{18}; \quad (1)$$

$$[n\text{-}\dot{C}_3H_7] : [iso\text{-}\dot{C}_3H_7] = 0.25\ . \quad (2)$$

	Scheme of nitration of propane	Q, kcal mole^{-1}
0.	$C_3H_8 + NO_2 \xrightarrow{k_2} n\text{-}\dot{C}_3H_7 + HNO_2$	−19.6
	$C_3H_8 + NO_2 \xrightarrow{k_{21}} iso\text{-}\dot{C}_3H_7 + HNO_2$	−16.2
1.	$n\text{-}\dot{C}_3H_7 + NO_2 \rightarrow CH_2(NO_2)CH_2CH_3$	+59.6
2.	$n\text{-}\dot{C}_3H_7 + NO_2 \rightarrow n\text{-}C_3H_7ONO \rightarrow n\text{-}C_3H_7\dot{O} + NO$	+18.5
3.	$n\text{-}C_3H_7\dot{O} \rightarrow \dot{C}_2H_5 + HCHO$	−11.3
4.	$\dot{C}_2H_5 + NO_2 \rightarrow C_2H_5NO_2$	+55.6
5.	$\dot{C}_2H_5 + NO_2 \rightarrow [C_2H_5ONO^*] \rightarrow C_2H_5\dot{O} + NO$	+14.3
6.	$C_2H_5\dot{O} \rightarrow \dot{C}H_3 + HCHO$	−10.3
7.	$\dot{C}H_3 + NO_2 \rightarrow CH_3NO_2$	+59.7
8.	$\dot{C}H_3 + NO_2 \rightarrow [CH_3ONO^*] \rightarrow CH_3\dot{O} + NO$	+15.8
9.	$CH_3\dot{O} + NO \rightleftarrows CH_3ONO$	+40.7
10.	$CH_3\dot{O} \rightarrow \dot{H} + HCHO$	−20.9
11	$HCHO + NO_2 \rightarrow H\dot{C}O + HNO_2$	−8.7
12.	$H\dot{C}O + NO_2 \rightarrow CO + HNO_2$	+59.8
13.	$H\dot{C}O + NO_2 \rightarrow \dot{H} + CO_2 + NO$	+33.5
14.	$H\dot{C}O + M \rightarrow \dot{H} + CO + M$	−18.4
15.	$\dot{H} + NO_2 \rightarrow \dot{O}H + NO$	+29.0
16.	$\dot{O}H + C_3H_8 \xrightarrow{k_{16}} n\text{-}\dot{C}_3H_7 + H_2O$	+20.2
	$\dot{O}H + C_3H_8 \xrightarrow{k_{17}} iso\text{-}\dot{C}_3H_7 + H_2O$	+25.2
17.	$iso\text{-}\dot{C}_3H_7 + NO_2 \rightarrow CH_3CH(NO_2)CH_3$	+58.8
18.	$iso\text{-}\dot{C}_3H_7 + NO_2 \rightarrow [iso\text{-}C_3H_7ONO^*] \rightarrow iso\text{-}C_3H_7\dot{O} + NO$	+16.5
19.	$iso\text{-}C_3H_7\dot{O} \rightarrow CH_3CHO + \dot{C}H_3$	−6.9
20.	$iso\text{-}C_3H_7\dot{O} + C_3H_8 \xrightarrow{k_{20}} n\text{-}\dot{C}_3H_7 + iso\text{-}C_3H_7OH$	+4
	$iso\text{-}C_3H_7\dot{O} + C_3H_8 \xrightarrow{k_{21}} iso\text{-}\dot{C}_3H_7 + iso\text{-}C_3H_7OH$	+8
21.	$CH_3CHO + NO_2 \rightarrow CH_3\dot{C}O + HNO_2$	−8.9
22.	$CH_3\dot{C}O + NO_2 \rightarrow \dot{C}H_3 + CO_2 + NO$	+35.9
23.	$CH_3CHO \xrightarrow{walls}$ termination	—
24.	$HCHO \xrightarrow{walls}$ termination	—
25.	$2HNO_2 \rightarrow NO_2 + NO + H_2O$	—

	Scheme of nitration of methane	Q, kcal mole^{-1}
0′.	$CH_4 + NO_2 \rightarrow \dot{C}H_3 + HNO_2$	−25.7
1′.	$\dot{C}H_3 + NO_2 \rightarrow CH_3NO_2$	+59.7
2′.	$\dot{C}H_3 + NO_2 \rightarrow [CH_3ONO^*] - CH_3\dot{O} + NO$	+15.8
3′.	$CH_3\dot{O} + CH_4 \rightarrow \dot{C}H_3 + CH_3OH$	−0.6
4′.	$CH_3\dot{O} \rightarrow HCHO + \dot{H}$	−20.9
5′.	$HCHO + NO_2 \rightarrow H\dot{C}O + HNO_2$	−8.7
6′.	$H\dot{C}O + M \rightarrow \dot{H} + CO + M$	−18.4
7′.	$H\dot{C}O + NO_2 \rightarrow CO + HNO_2$	+59.8
8′.	$H\dot{C}O + NO_2 \rightarrow \dot{H} + CO_2 + NO$	+33.5
9′.	$\dot{H} + NO_2 \rightarrow \dot{O}H + NO$	+29.0
10′.	$\dot{O}H + CH_4 \rightarrow \dot{C}H_3 + H_2O$	+15.3
11′.	$HCHO \xrightarrow{walls}$ termination	—
12′.	$2HNO_2 \rightarrow NO_2 + NO + H_2O$	—

Differential equations were obtained for the time dependence of the concentration of aldehydes, whose integration (with the condition that the aldehyde concentration is zero at $t = 0$) yielded for the nitration of propane the formula

$$[HCHO] = \frac{C}{A} \cdot \frac{k_0[C_3H_8] \cdot [NO_2]}{1+n} \cdot \frac{1}{\varphi} \cdot (e^{\varphi t} - 1)\ ,$$

where

$$\varphi = f - g = \frac{[NO_2]}{1+n}\left\{\left[k_{11}\frac{C}{A} + nk_{21}\left(\frac{C}{A} + B\right)\right] - \left(k_{11} + nk_{21}\left[1 + \frac{C}{1{,}4\,A}\left(0.4 + \frac{k_9[NO]}{k_9[NO] + k_{10}}\right)\right] + \frac{C}{A} \cdot \frac{k_{11}k_{12}[NO_2]}{(k_{12} + k_{13})[NO_2] + k_{14}[C_3H_8 + NO_2]}\right)\right\} - \frac{k_{24} + nk_{23}}{1+n}$$

in which

$$A = k_{19}\left(0.9 + \frac{0.83\,k_9[NO]}{k_9[NO] + k_1}\right) + k_{20}[C_3H_8]\left(0.62 + \frac{0.13\,k_9[NO]}{k_9[NO] + k_{10}}\right);$$

$$B = \frac{0.7\,k_{10}}{k_9[NO] + k_{10}}\ ;$$

$$C = (1+B)\,k_{19} + 0.25\,(k_{19} + k_{20}[C_3H_8])\left[1 + \frac{k_5}{k_4 + k_5}(1+B)\right];$$

$$n = [CH_3CHO]/[CH_2O],$$

and f and g are the rate constants of chain branching and termination respectively. An analogous calculation for the nitration of methane gave

$$[HCHO] = \frac{k_{2'}k_{4'}}{k_{1'}k_{3'}[CH_4] + k_{4'}} \cdot k_{0'}[CH_4][NO_2] \cdot \frac{1}{\varphi}(e^{\varphi t} - 1)\ ,$$

where

$$\varphi = k_{5'}[NO_2]\left[\frac{k_{2'}k_{4'}\{k_{6'}[CH_4 + NO_2] + k_{8'}[NO_2]\}}{k_{1'}\{k_{3'}[CH_4] + k_{4'}\}\{k_{6'}[CH_4 + NO_2] + k_{7'}k_{8'}[NO_2]\}} - 1\right] - k_{11'}\ .$$

The condition $\varphi = 0$ implies a transition from a slow steady-state reaction to the non-stationary cool-flame reaction. Calculation of φ by means of equations based on the schemes showed that with rise in temperature and increase in pressure φ passes from negative to positive values, i.e. that the slow reaction passes into the cool-flame reaction. This transition agrees satisfactorily with experiment (the bottom line in Table 4 gives the observed limits of cool-flame ignition).

Table 4. Variation of φ (s^{-1}) with temperature and pressure (for the mixtures $C_3H_8 + NO_2$ and $4CH_4 + NO_2$).

p_{init}, mmHg	$C_3H_8+NO_2$			$4CH_4+NO_2$
	300° C	350° C	400° C	450° C
50	—	—	−2.4	—
100	−1.6	−1.2	−0.04	−1.9
200	−0.7	+0.15	+2.3	+0.04
400	+0.02	+0.70	—	+1.5
500	—	—	—	+1.9
Expt. p_{lim}, mmHg	360	164	70	160

Values of φ were calculated from the rate constants listed in Table 5. Rate constants for the loss of aldehydes on the walls of the reaction vessel were calculated for termination of the aldehydes by reactions *23*, *24*, and *11′* in the diffusion range: $k_{loss} = 8D/r^2$, in which the diffusion coefficient was found by means of the formula $D = \frac{1}{3}u\lambda$, where u is the velocity of the molecules, λ the free path, and r the radius of the reaction vessel. The rate constants of the loss of formaldehyde and acetaldehyde at the walls are $k_{24} = 1.0\ s^{-1}$ and $k_{23} = 0.7\ s^{-1}$ for the nitration of propane under an initial pressure of 200 mmHg at 350°C, and $k_{11'} = 1.3\ s^{-1}$ for the nitration of methane under the same initial pressure at 450°C.

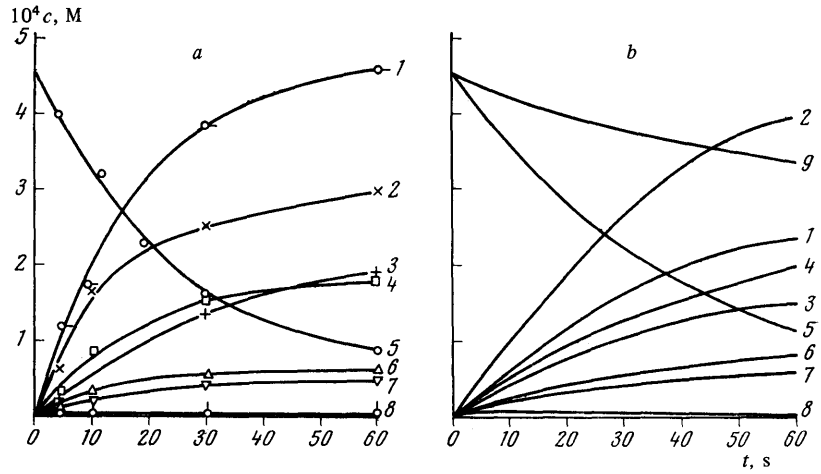


Figure 4. Comparison of (*a*) experimental and (*b*) computed curves for the accumulation of reaction products and the consumption of starting materials (C_3H_8 + NO_2 initially at 320 mmHg and 300°C): 1) CO_2; 2) 2-$C_3H_7NO_2$; 3) CO; 4) CH_3NO_2; 5) NO_2 (×0.1); 6) 1-$C_3H_7NO_2$; 7) $C_2H_5NO_2$; 8) CH_3CHO; 9) C_3H_8.

Table 5. Rate constants of primary steps.

Numbered reactions in schemes		lg *A*	*E*, kcal mole^{-1}	Experimental or estimated, Ref.
C_3H_8	CH_4			
0		11 (cm^3 mole^{-1} s^{-1})	26	est. [108]
0t		11 »	24	est.
1, 4, 7, 17	1′	12.1 »	0	expt. [75]
2, 5, 8, 18	2′	12.3 »	0	expt.
3		9.6 (s^{-1})	13	est. [108, 95]
6		9.6 »	13	expt. [109]
9		10.5 (cm^3 mole^{-1} s^{-1})	0	calc. [110]
10	4′	13 (s^{-1})	24	est. [108]
11	5′	12 (cm^3 mole^{-1} s^{-1})	19	expt. [111]
12	7′	11.48 »	0	est. [108]
13	8′	11.88 »	0	est.
14	6′	14.5 »	12	est.
15	9′	13.63 »	0	expt. [112]
16		12.86 »	1.3	expt. [113]
19		11.8 (s^{-1})	17.3	expt. [114]
20		12.8 (cm^3 mole^{-1} s^{-1})	9.0	est. [108]
21		11.28 »	15.2	expt. [115]
22		12 »	0	expt. [116]
23		0.5* s^{-1}	—	est. [95]
24		0.9* s^{-1}	—	est. [95]
	3′	11.8 (cm^3 mole^{-1} s^{-1})	11	est. [117]
25		11.8** »	—	est. [108]

*Rate constant at 300°C and 320 mmHg.
**Rate constant at 300°C.

The mechanism suggested for the nitration of propane was tested also by numerical integration on an electronic computer of the set of differential equations describing the mechanism[108]. In view of the peculiarity of schemes comprising reactions of stable species and free radicals having rate constants differing by many orders of magnitude, use was made of a special algorithm and a programme developed in the Moscow State Pedagogic Institute[118,119]. The algorithm was based on solution of the set of differential equations by a finite-difference method with a "reverse step" procedure. Rate curves were computed for the consumption of the starting materials and the accumulation of the final products from an initial equimolecular mixture of propane and nitrogen dioxide under 320 mmHg at 300°C. The rate constants used for the calculation are given in Table 5‡. The computed curves are shown in Fig. 4*b*, and the corresponding experimental results are plotted in Fig. 4*a*. Since the reaction scheme has been set up for the initial stages and disregards secondary reactions of stable species (e.g. further reactions of the nitroalkanes), the suggested mechanism must be regarded as describing satisfactorily the nitration of propane by nitrogen dioxide.

The situation is less satisfactory with respect to the mechanism of the nitration of alkanes by nitric acid. As has been shown above, no agreement is apparent in the literature even on the nature of the direct nitrating agent, whether nitric acid itself or nitrogen dioxide formed by its decomposition. This question must be settled first of all, since if the role of nitric acid were mainly to generate nitrogen dioxide, the whole of the above mechanism should form the major part of the mechanism of nitration by nitric acid. This does not mean, of course, that changing from nitrogen dioxide to nitric acid does not introduce any changes into the reaction mechanism. In particular, the formation of hydroxyl radicals (by the decomposition of nitric acid) would increase the rate of nitration. Nor is heterogeneous decomposition of the acid excluded, which would affect the whole course of the reaction. Overall, however, the mechanism of nitration by nitric acid, with R + NO_2 → RNO_2 as the principal step, will be closely similar to the suggested mechanism of nitration by nitrogen dioxide.

These considerations led the Reviewers to undertake, at the Institute of Petrochemical Synthesis during recent years, experimental studies of the nitration of propane by nitric acid with the primary aim of ascertaining whether nitrogen dioxide is involved in formation of the nitro-compound[108]. Several facts have now been established: (i) the reaction of propane with nitric acid follows (as with nitrogen dioxide) three kinetic types—slow, cool-flame, and with a hot flame—depending on the temperature and

‡For computer purposes reactions *23*, *24*, and *11′* were written CH_3CHO → CH_4 + CO *23* and HCHO → H_2 + CO *24*.

the pressure; (ii) the products at the ends of slow and cool-flame reactions are closely similar in composition to the corresponding products obtained with nitrogen dioxide; (iii) in the slow reaction autocatalysis is observed both in the accumulation of nitrogen dioxide and of nitroalkane and in the increase in pressure Δp; (iv) the time variation of the concentration of nitrogen dioxide passes through a maximum; and (v) the ratio of the rates of accumulation of nitroalkanes to the rate of accumulation of nitrogen dioxide approaches zero at shorter times. These five points can be supplemented by (vi) the Reviewers' calculation (Section II, 2) of the rates of $R\cdot + HNO_3 \rightarrow RNO_2 + OH\cdot$ and $R\cdot + NO_2 \rightarrow RNO_2$, which indicated that at 350°C the rate of the latter exceeded that of the former reaction by $\sim 10^5$. Points (i) and (ii) are evidence of the far reaching similarity in phenomenology and closely related chemistry of the actions of nitric acid and of nitrogen dioxide on propane. Point (iv) confirms that nitrogen dioxide is actually present during the reaction with nitric acid. Point (v) implies that nitroalkanes and nitrogen dioxide are formed in two consecutive reactions, with the latter formed first, i.e. that nitrogen dioxide is involved in the formation of nitroalkanes.

Together with point (vi) all this leads to adoption of $R\cdot + NO_2 \rightarrow RNO_2$ as immediate step in nitralkane formation even when nitric acid is used. As noted above, the consequence of this should be a fundamental similarity in the mechanisms of nitration of alkanes by nitrogen dioxide and by nitric acid. Only slight differences can be expected, one of which is indicated by point (iii). The continuing study of the nitration of alkanes by nitric acid being conducted at the Institute of Petrochemical Synthesis has the aim of revealing also the detailed mechanism of this reaction.

The above outline reflects the evolution of views and modern ideas on the mechanism of the gas-phase nitration of alkanes, a field in which the main contribution was made by Konovalov, Markovnikov, Nametkin, Titov, ad and Topchiev. The present issue is dedicated to the memory of S. S. Nametkin, who was the first to help elucidate the mechanism of nitration by the fruitful application of contemporaneous physicochemical concepts—e.g. the influence of the relative concentrations of the initial reactants on yields of nitration and oxidation products, the dependence of the yields of nitro-products on reaction velocity and of the latter on the "mass" of the acid, and the concept of oxidation and nitration as parallel reactions—which made nitration a subject of investigation also in physical chemistry, in particular chemical kinetics. The study of nitration in relation to neighbouring branches of chemistry has been responsible for the considerable progress made in establishing its mechanism that we now witness.

REFERENCES

1. M. I. Konovalov, Zhur. Russ. Khim. Obshch., 19, 157 (1887).
2. M. I. Konovalov, Zhur. Russ. Khim. Obshch., 23, 217 (1891).
3. M. I. Konovalov, Zhur. Russ. Khim. Obshch., 25, 389, 472, 509 (1893).
4. M. I. Konovalov, Zhur. Russ. Khim. Obshch., 26, 68 (1894).
5. M. I. Konovalov, Zhur. Russ. Khim. Obshch., 27, 421 (1895).
6. M. I. Konovalov, Ber., 28, 1855 (1895).
7. M. I. Konovalov, Zhur. Russ. Khim. Obshch., 31, 254 (1899).
8. M. I. Konovalov, Zhur. Russ. Khim. Obshch., 36, 232 (1904).
9. M. I. Konovalov and Kh. L. Gurevich, Zhur. Russ. Khim. Obshch., 37, 537 (1905).
10. M. I. Konovalov, Zhur. Russ. Khim. Obshch., 37, 134 (1905).
11. V. V. Markovnikov, Annalen, 302, 15 (1898).
12. V. V. Markovnikov, Zhur. Russ. Khim. Obshch., 31, 47, 215, 530 (1899).
13. V. V. Markovnikov, Zhur. Russ. Khim. Obshch., 32, 302, 1441 (1900).
14. V. V. Markovnikov, Zhur. Russ. Khim. Obshch., 35, 1023 (1903).
15. V. V. Markovnikov, Ber., 33, 1906 (1900).
16. V. V. Markovnikov, Zhur. Russ. Khim. Obshch., 20, 118 (1888).
17. V. V. Markovnikov, Zhur. Russ. Khim. Obshch., 27, 174 (1895).
18. V. V. Markovnikov, Zhur. Russ. Khim. Obshch., 28, 125 (1896).
19. V. V. Markovnikov, Zhur. Russ. Khim. Obshch., 30, 151 (1898).
20. S. S. Nametkin, Zhur. Russ. Khim. Obshch., 40, 184, 1570 (1908).
21. S. S. Nametkin, Zhur. Russ. Khim. Obshch., 41, 145 (1909).
22. S. S. Nametkin, Zhur. Russ. Khim. Obshch., 42, 581, 585, 691 (1910).
23. S. S. Nametkin, Ber., 42, 1372 (1909).
24. S. S. Nametkin, Zhur. Russ. Khim. Obshch., 43, 1603, 1611 (1911).
25. S. S. Nametkin, Zhur. Russ. Khim. Obshch., 45, 1414 (1913).
26. S. S. Nametkin and E. I. Pozdnyakova, Zhur. Russ. Khim. Obshch., 45, 1420 (1913).
27. S. S. Nametkin and A. K. Ruzhentseva, Zhur. Russ. Khim. Obshch., 46, 1540 (1914).
28. Wilhelm Ostwald, "Grundlinien der anorganischen Chemie" (Translated into Russian), Moscow, 1902, p. 204.
29. "Kirk-Othmer Encyclopedia of Chemical Technology", Wiley, New York, 2nd Edition 1967, Vol. 13.
30. P. P. Shorygin and A. V. Topchiev, Ber., 67, 1362 (1934)
31. P. P. Shorygin and A. V. Topchiev, Zhur. Obshch. Khim., 5, 549 (1935).
32. H. B. Hass, E. B. Hodge, and M. B. Vanderbilt, US P. 1 967 666 (24th July 1934); Chem. Abs., 28, 5830 (1934).
33. H. B. Hass, E. B. Hodge, and M. B. Vanderbilt, Ind. Eng. Chem., 28, 339 (1936).
34. H. B. Hass and J. A. Patterson, Ind. Eng. Chem., 30, 67 (1938).
35. L. B. Seigle and H. B. Hass, Ind. Eng. Chem., 31, 648 (1939).
36. H. B. Hilsman, E. H. Piersen, and H. B. Hass, Ind. Eng. Chem., 32, 427 (1940).
37. H. B. Hass, J. Dorsky, and E. B. Hodge, Ind. Eng. Chem., 33, 1138 (1941).
38. T. Boyd and H. B. Hass, Ind. Eng. Chem., 34, 300 (1942).
39. H. B. Hass and E. F. Riley, Chem. Rev., 32, 373 (1943).
40. M. H. Danzig and H. B. Hass, J. Amer. Chem. Soc., 66, 2017 (1944).

41. A. P. Howe and H. B. Hass, Ind. Eng. Chem., 38, 251 (1946).
42. H. B. Hass and H. Schechter, Ind. Eng. Chem., 39, 817 (1947).
43. H. B. Hass, H. Schechter, J. G. Alexander, and D. B. Hastsher, Ind. Eng. Chem., 39, 919 (1947).
44. H. B. Hass and J. G. Alexander, 41, 2266 (1949).
45. H. B. Hass and H. Schechter, J. Amer. Chem. Soc., 75, 1382 (1953).
46. G. B. Bachman, L. M. Addison, I. V. Havett, L. Kohn, and A. Millikan, J. Org. Chem., 17, 906 (1952).
47. G. B. Bachman, H. B. Hass, and L. M. Addison, J. Org. Chem., 17, 914 (1952).
48. G. B. Bachman, H. B. Hass, and J. V. Hevett, J. Org. Chem., 17, 928 (1952).
49. G. B. Bachman, J. V. Hevett, and A. G. Millikan, J. Org. Chem., 17, 935 (1952).
50. G. B. Bachman and L. Kohn, J. Org. Chem., 17, 942 (1952).
51. G. B. Bachman, M. T. Atwood, and M. Pollak, J. Org. Chem., 19, 312 (1953).
52. G. B. Bachman and M. Pollak, Ind. Eng. Chem., 46, 713 (1953).
53. G. B. Bachman and N. W. Standish, J. Org. Chem., 26, 570 (1961).
54. M. Szwarc, Chem. Rev., 47, 75 (1950).
55. R. Shaw, Internat. J. Chem. Kinetics, 5, 261 (1973).
56. R. N. Spokes and S. W. Benson, J. Amer. Chem. Soc., 89, 6030 (1967).
57. R. F. McCleary and E. Degering, Ind. Eng. Chem., 30, 64 (1938).
58. W. J. Faith, D. B. Keyes, and D. E. Clark, "Industrial Chemicals", Wiley, New York, 1965.
59. A. I. Titov, Zhur. Obshch. Khim., 6, 1855 (1936).
60. A. I. Titov, Zhur. Obshch. Khim., 7, 1695 (1937).
61. A. I. Titov, Zhur. Obshch. Khim., 10, 1878 (1940).
62. A. I. Titov, Zhur. Obshch. Khim., 16, 1896 (1946).
63. A. I. Titov, Zhur. Obshch. Khim., 18, 465, 534 (1948).
64. A. I. Titov, Zhur. Obshch. Khim., 18, 1312 (1948).
65. A. I. Titov, Zhur. Obshch. Khim., 19, 1472 (1949).
66. A. I. Titov, Zhur. Obshch. Khim., 19, 1461 (1949).
67. A. I. Titov, Zhur. Obshch. Khim., 19, 1464 (1949).
68. A. I. Titov and N. V. Shchitov, Dokl. Akad. Nauk SSSR, 81, 1085 (1951).
69. A. I. Titov, Uspekhi Khim., 21, 881 (1952).
70. F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals" (Translated into Russian), ONTI, Leningrad, 1937.
71. G. Geiseler and H. Reinhardt, Z. Elektrochem., 61, 296 (1957).
72. H. S. Johnston, L. Foering, and J. R. White, J. Amer. Chem. Soc., 77, 4208 (1955).
73. H. Harrison, H. S. Johnston, and E. R. Hardwick, J. Amer. Chem. Soc., 84, 2478 (1962).
74. E. F. Greene and I. P. Toennies, "Chemical Reactions in Shock Waves", New York, 1964.
75. N. L. Shlyapnikova, I. V. Patsevich, A. P. Ballod, and V. Ya. Shtern, Arm. Khim. Zhur., 20, 972 (1967).
76. M. T. H. Zin and K. I. Laidler, Canad. J. Chem., 46, 479 (1968).
77. T. S. Godfrey, E. D. Hughes, and C. Ingold, J. Chem. Soc., 1063 (1965).
78. P. Gray, Trans. Faraday Soc., 51, 1367 (1955),
79. A. D. Yoffe, Research, 6, 11S (1953).
80. P. Gray, Discuss. Faraday Soc., 10, 310 (1951).
81. A. L. Myerson, F. R. Taylor, and B. G. Faunce, Sixth Symposium on Combustion, New Heaven, Connecticut, 1956, p. 154.
82. A. D. Yoffe, Sixth Symposium on Combustion, New Heaven, Connecticut, 1956, p. 156.
83. A. B. Gagarina and N. M. Emanuel', Zhur. Fiz. Khim., 33, 1641 (1959) [Russ. J. Phys. Chem., No. 7 (1959)].
84. A. B. Gagarina and N. M. Emanuel', Zhur. Fiz. Khim., 33, 1872 (1959) [Russ. J. Phys. Chem., No. 8 (1959)].
85. S. K. Ermakova, V. M. Cherednichenko, and S. Ya. Pshezhetskii, Zhur. Fiz. Khim., 35, 2352 (1961) [Russ. J. Phys. Chem., No. 10 (1961)].
86. A. P. Ballod, S. I. Molchanova, A. V. Topchiev, T. V. Fedorova, and V. Ya. Shtern, Dokl. Akad. Nauk SSSR, 123, 464 (1958).
87. A. P. Ballod, S. I. Molchanova, I. V. Patsevich, A. V. Topchiev, and V. Ya. Shtern, Zhur. Anal. Khim., 14, 188 (1959).
88. A. P. Ballod, N. L. Galanina, I. V. Patsevich, A. V. Topchiev, and A. M. Yanyukova, Neftekhimiya, 2, 924 (1962).
89. A. V. Topchiev, T. V. Fedorova, A. P. Ballod, and V. Ya. Shtern, Neftekhimiya, 2, 71 (1962).
90. S. A. Gol'din, A. P. Ballod, and V. Ya. Shtern, Dokl. Akad. Nauk SSSR, 164, 371 (1965).
91. A. P. Ballod, S. I. Molchanova, and V. Ya. Shtern, Neftekhimiya, 6, 894 (1966).
92. A. P. Ballod, S. I. Molchanova, and V. Ya. Shtern, Neftekhimiya, 7, 115 (1967).
93. S. I. Molchanova, A. P. Ballod, and V. Ya. Shtern, Neftekhimiya, 7, 896 (1967).
94. A. V. Topchiev, A. P. Ballod, S. I. Molchanova, I. V. Patsevich, T. V. Fedorova, and V. Ya. Shtern, Aspecte din Chimia Hidrocarburilor, Bucurest, 1960.
95. A. P. Ballod, S. I. Molchanova, and V. Ya. Shtern, Kinetika i Kataliz, 12, 1365 (1971).
96. T. A. Titarchuk, A. P. Ballod, V. A. Kulikova, and V. Ya. Shtern, Dokl. Akad. Nauk SSSR, 208, 1404 (1973).
97. T. A. Titarchuk, A. P. Ballod, N. G. Prokhortseva, and V. Ya. Shtern, Kinetika i Kataliz, 15, 1375 (1974).
98. S. A. Gol'din, A. P. Ballod, and V. Ya. Shtern, Kinetika i Kataliz, 16, 7 (1975).
99. A. V. Topchiev, A. P. Ballod, T. V. Fedorova, and V. Ya. Shtern, Neftekhimiya, 2, 211 (1962).
100. V. Ya. Shtern, in "Khimicheskaya Kinetika i Tsepnye Reaktsii" (Chemical Kinetics and Chain Reactions), Nauka, Moscow, 1966, p. 286.
101. B. S. Rabinovitch, J. F. Meagher, K. I. Chac, and I. R. Barker, J. Chem. Phys., 60, 2932 (1974).
102. J. M. Parson, Faraday Discuss. of Chem. Soc., 55, 344 (1973).
103. Z. K. Maizus and N. M. Emanuel', Dokl. Akad. Nauk SSSR, 83, 717 (1952).
104. N. S. Enikolopov, N. A. Kleimenov, L. V. Karmilova, A. M. Markevich, and A. B. Nalbandyan, Zhur. Prikl. Khim., 32, 913 (1959).
105. S. F. Gudkov, A. K. Ivanov, V. F. Kornilov, B. I. Lur'e, A. B. Nalbandyan, and P. S. Rudenko, Gaz. Prom., 351 (1963).
106. A. B. Nalbandyan, L. V. Karmilova, and N. S. Enikolopov, Zhur. Fiz. Khim., 30, 798 (1956).
107. V. T. Minasyan, T. A. Vardanyan, and A. B. Nalbandyan, Arm. Khim. Zhur., 26, 187 (1973).
108. A. P. Ballod, Doctoral Thesis, Institute of Petrochemical Synthesis of the USSR Academy of Sciences, Moscow, 1975.

109. M. H. J. Wijnen, J. Amer. Chem. Soc., 82, 3034 (1960).
110. K. N. Bascombe, M. Cowperthwaite, and R. Shaw, J. Chem. Soc., 3868 (1965).
111. F. H. Pollard and W. M. H. Wyatt, Trans. Faraday Soc., 45, 760 (1949).
112. E. A. Arden and L. Phillips, J. Chem. Soc., 5118 (1964).
113. N. B. Greiner, J. Chem. Phys., 53, 1074 (1970).
114. D. L. Cox, R. A. Livermoore, and L. Phillips, J. Chem. Soc. B, 245 (1966).
115. A. E. Pedler and F. H. Pollard, Trans. Faraday Soc., 53, 44 (1957).
116. M. I. Christie and M. A. Voisey, Trans. Faraday Soc., 63, 2459 (1967).
117. R. Shaw and J. C. J. Thynne, Trans. Faraday Soc., 62, 104 (1966).
118. I. T. Levitina, "Reshenie Sistemy Differentsial'nykh Uravnenii Khimicheskoi Kinetiki Ustoichivo-raznostnym Metodom. Standartnaya Programma dlya EVM Tipa BSM-4. Gosudarstvennyi Fond Algoritmov i Programm. Inventarnyi No. P0000669. Annotatsiya No. 62 v Vypuske No. 2 Informats. Byulletenya 'Algoritmy i Programmy'" (Solution of a Set of Differential Equations of Chemical Kinetics by a Constant-difference Method. Standard Programme for a BSM-4 Computer. State Stock of Algorithms and Programmes. Listed No. P0000669. Note No. 62 in Issue No. 2 of the Information Bulletin "Algorithms and Programmes"), Izd. VMTITs, 1974, p. 34.
119. S. V. Adel'son, I. G. Levitina, V. I. Nikonov, and A. V. Sakovich, Kinetika i Kataliz, 13, 1327 (1972).

Topchiev Institute of Petrochemical Synthesis, USSR Academy of Sciences, Moscow