Thermal decomposition of 2,4,6-trinitrotoluene in melt and solutions

V. V. Dubikhin,* V. G. Matveev, and G. M. Nazin

Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588

Thermal decomposition of 2,4,6-trinitrotoluene in the temperature range from 200 to 340 °C in melt and in solutions was studied. The main features of the process (high initial rates, activation energies lower than those in the gaseous phase, a higher acceleration at the catalytic stage, and the effect of nonpolar solvents on initial rates) are explained in terms of a kinetic scheme corresponding to a degenerate branched chain reaction.

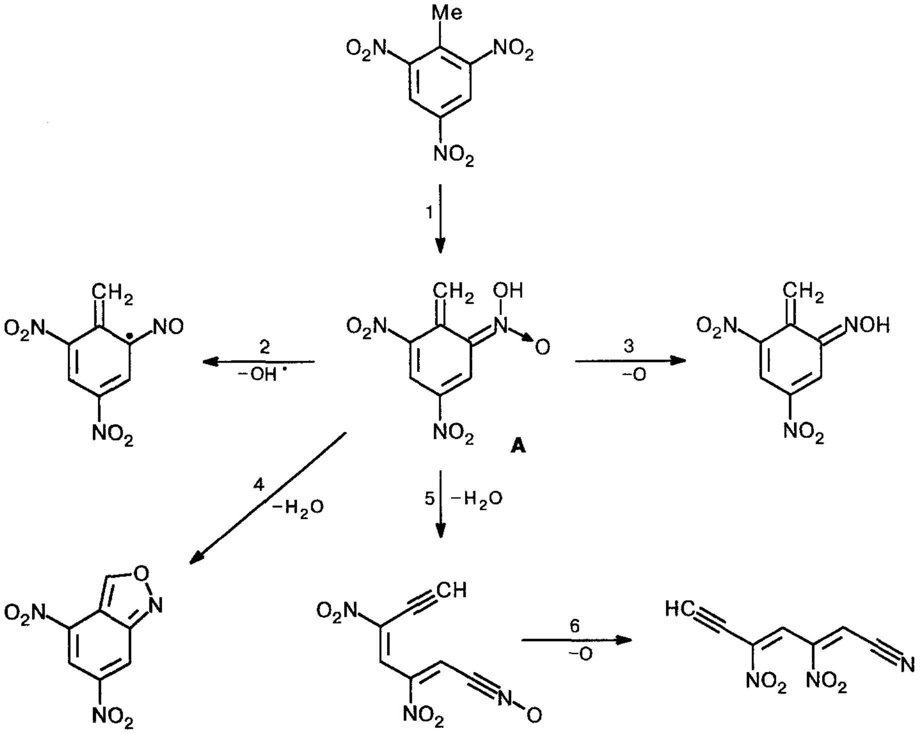
Key words: 2,4,6-trinitrotoluene, decomposition, chain mechanism.

Many works[1–4] have been devoted to the thermal decomposition of 2,4,6-trinitrotoluene (TNT). Isomerization of TNT into nitronic acid, which is rapidly decomposed[4] *via* the reactions presented in Scheme 1, is considered to be the first stage of its decomposition.

Reactions (3) and (4) have been experimentally confirmed,[5,6] while reactions (2), (5), and (6) are hypothetical, strongly exothermic processes. There are also other opinions concerning the stage of liquid phase decomposition.[4]

Decomposition *via* a molecular mechanism with the rate constant k_0 corresponding to stage (1) in Scheme 1 and occurs in the gaseous phase at low pressures of TNT vapor and is characterized by the following parameters: E_g = 196.5 kJ mol^{-1} and $\log(A_g\{c\})$ = 12.4 (see Ref. 3). When the initial pressure > 5 Torr decomposition proceeds *via* a chain mechanism and is complicated by heterogeneous reactions on the surface. The decomposition occurs faster in the liquid phase than at high pressures in the vapor phase: E_l = 142 kJ mol^{-1},

Scheme 1



Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 266—271, February, 1995.

$\log(A_l\{c\}) = 9.30$ (see Ref. 2). At 240 °C the ratio of the rate constants is $k_l/k_g = 138$.

The reasons for the faster rate in the liquid phase are still obscure. The addition of 30 % hexachlorobenzene as an inert solvent results in a fivefold decrease in the decomposition rate, which can be explained by the effect of TNT associates,[2] whose existence is indicated by a high value of the Trouton constant. However, it follows from the comparison of previously published data[3,7] that high k_l/k_g ratios are also typical of compounds with normal Trouton constants. A more careful measurement of the dependence of the observed rate constant (k_l) of the first stage of the decomposition on TNT concentration in hexachlorobenzene gives rise to a linear dependence of the type

$$k_l = k' + k''[\mathrm{TNT}]_0$$

for a large group of trinitrobenzene derivatives. The existence of a direct bimolecular reaction in the liquid phase in addition to the monomolecular reaction has also been postulated on the basis of these data.[8] Theoretical estimates do not rule out the possibility of this reaction.[4] However, it has not been observed in the gaseous phase and has not been rigorously proved in the liquid phase. The decrease in k_l with dilution can be related to the retardation of the catalytic reactions in the presence of admixtures and to a decrease in the contribution of autocatalytic stages to the k_l value. A distinctive feature of TNT decomposition is strong autocatalysis and wide scattering in the k_l data (see Ref. 1). Nitroxyl radicals are formed in the course of the reaction.[1] Therefore, it can be assumed that a free-radical chain reaction occurs both in the liquid phase and in vapor at elevated pressures. This reaction can explain both the high value of the liquid-phase k_l and its dependence on $[\mathrm{TNT}]_0$. This aspect of the reaction has not yet been considered.

In the present work, both pure TNT and its solutions in several solvents are studied with the purpose of developing a rigorous formal kinetic description of the reaction, determining the effects of the solvent nature and TNT concentration on the rate, and applying the concept of a chain mechanism to explain the data available and the results newly obtained.

Experimental

The kinetics of the thermal decomposition of TNT were studied by a manometric method by complete gas evolution. The setup was tailored to carry out the decomposition in a glass vessel (of the Bourdon type) and record an increase in gas pressure by the compensation method in the range from 1 Torr to 50 atm with an accuracy of ±1 Torr (below atmospheric pressure) and ±15 Torr (from 1 to 50 atm). The installation is fitted to work with any solvents, whose critical temperatures are higher than or close to the decomposition temperature of TNT.

The following samples of TNT were used in the work: a technical batch, GOST V-7059-73 (T1), T1 twice recrystallized from rectified ethanol (T2), T1 twice recrystallized from a chloroform—perfluorobenzene (1 : 5) mixture (T3), T1 twice recrystallized from a benzene—*n*-heptane (1 : 1) mixture (T4), T3 sublimated (T5) (the sample of T3 was sublimated at 10^{-4} Torr on a substrate at a temperature between 20 and 60 °C; 0.05 g of the sublimate was obtained from 5 g of T3), samples synthesized by the nitration of toluene (T6), and deuterated toluenes TNT-CD_3 (T7) and TNT-3,5-D_2 (T8). The samples were dried at 20 °C and 10^{-2} Torr over P_2O_5. All samples except T5 had the same melting points (from 80.5 to 81 °C), which attested to the small and approximately equal content of admixtures affecting the melting point. According to the GLC data (column of 1 m×2 mm filled with Chromaton SE, 130 °C), the sample of T1 contained *ortho*-nitrotoluene (0.1 %), *para*-nitrotoluene (0.03 %), 2,4- and 2,6-dinitrotoluenes (0.09 and 0.03 %, respectively), 2,3,4- and 2,4,5-trinitrotoluenes (0.001—0.002 %), and traces of heavier unidentified admixtures. The same content of volatile admixtures was found in the samples of T2—T4 within the accuracy of the analysis (15 %), although, judging by the change in the color, the amount of colored admixtures decreased after recrystallization. Sample T5 was enriched in mono- and dinitrotoluenes (their content was 5—10 times higher than that in T1) and its melting point was more blurred. Hexachlorobenzene (HCB), perfluoronaphthalene (PFN), naphthalene, benzene, and toluene were used as solvents. HCB, PFN, and naphthalene were recrystallized from anhydrous benzene. Toluene was dried over P_2O_5.

The primary treatment of the experimental S-like "pressure—time" curves was performed by the first-order equation of autocatalysis $d\eta/dt = -k_i(1-\eta) - k_{cat}\eta \cdot (1-\eta)$, (where $\eta = (p_t - p_0)/(p_\infty - p_0)$ is the degree of conversion, p_t is the current pressure, p_0 is the initial pressure (the vapor pressure of TNT or solvent), and p_∞ is the final pressure) on a computer in such a way that the deviation of the calculated curve from the experimental points did not exceed experimental error within the widest possible region of the curve. It turned out that this approach allowed one to describe the kinetic curves up to conversion values of 10—30 % by a first-order equation of autocatalysis. Both of the constants that characterized the autocatalysis were determined for each experiment: k_i/s^{-1}, which determined the initial rate, and $k_{cat} = K \cdot [\mathrm{TNT}]_0/\mathrm{s}^{-1}$ (K is the constant of autocatalysis in L (mol s)$^{-1}$), which determined the autoacceleration stage.

The majority of the experiments were performed in the temperature range from 200 to 270 °C in a reaction vessel (2 cm^3 and $m/V = 0.01$ g cm^{-3}). A large series of experiments on the decomposition of TNT was performed at 240 °C. The amount of gas evolution, φ (in moles of gas per mole of TNT), varied from 2.7 to 2.9. None of the samples gave good reproducibility at the initial rate (Fig. 1). The k_i values were the same and lay in the $(1.0—2.0) \cdot 10^{-6}$ s^{-1} range for T3, T4, and T6. Higher rates were characteristic of the samples of T1 and, especially, T2 and T5. The k_{cat} values were more constant and lay in the $(0.85—1.15) \cdot 10^{-3}$ s^{-1} range for all samples. Changing m/V from 0.001 to 1.0 g cm^{-3} had no effect on k_i and weakly affected k_{cat}. It was observed that the glass material had an effect on k_i. When fine glass powder (7, 17, and 40 mg) was added to the TNT sample (20 mg), k_i at 240 °C increased 5, 10, and 25 times, respectively, while the k_{cat} value remained almost unchanged. Experiments were performed in vessels of the same shape prepared from the same batch of the glass. After the experiment, the vessel was washed with acetone and

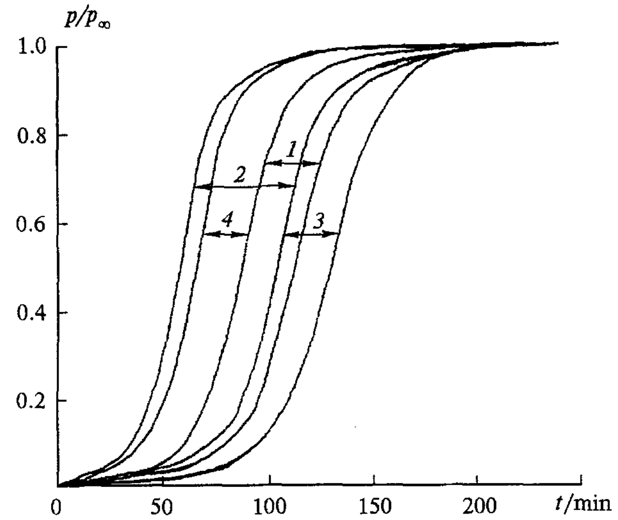


Fig. 1. Scatter in the experimental data for different samples of TNT at 240 °C: T1 (*1*), T2 (*2*), T3, T4, T6 (*3*), T5 (*4*).

calcinated. Despite this treatment, there was a scatter in the data for each sample (see Fig. 1). The Arrhenius parameters for k_i and K were determined with a sample of T3 in the 200 to 270 °C range.

$$k_\mathrm{i} = 10^{10.4\pm0.8} \exp\{-(159\pm4)/RT\}$$

$$K = 10^{10\pm2} \exp\{-(131\pm7)/RT\}.$$

An isotope effect was observed for T7 at 240 °C: $k_\mathrm{i}^\mathrm{H}/k_\mathrm{i}^\mathrm{D}$ = 1.58, $k_\mathrm{cat}^\mathrm{H}/k_\mathrm{cat}^\mathrm{D}$ = 1.82. No isotope effect was observed for T8.

The decomposition of TNT in solutions was performed with the T3 sample in the temperature range from 200 to 340 °C. Data on the temperature dependence of the density of TNT and the solvents are needed for exact determination of TNT concentration and gas evolution. These data have been determined for toluene, TNT, and HCB.[8] For PFN and naphthalene these dependences were experimentally determined on the installation mentioned. A weighed sample of a solvent was placed in an evacuated vessel with a rigid membrane. The vessel was heated smoothly up to a sharp jump in pressure. The temperature observed at the instant of this jump corresponded to the vessel filled with a substance. This temperature varied within one degree in repeated measurements.

Typical kinetic curves of TNT decomposition in solution are presented in Fig. 2. The reproducibility of k_i was rapidly improved by dilution and the scatter in the k_i values did not exceed ±20 % when $[\mathrm{TNT}]_0 < 40$ % was reached. The dependences of gas evolution, φ (used for the calculation of k_i and k_cat), on the initial TNT concentration ($[\mathrm{TNT}]_0$) are shown in Fig. 3. The dependences of k_i on $[\mathrm{TNT}]_0$ are shown in Fig. 4. A typical dependence of $\log k_\mathrm{i}$ on $\log[\mathrm{TNT}]_0$ is shown in Fig. 5. For dilute solutions of TNT in PFN (from 200 to 340 °C), benzene, and HCB (240 °C), k_i is found to have the same value within the limits of error and to obey the Arrhenius law:

$$k_\mathrm{i} = 10^{10.3\pm0.6} \exp[-(161\pm3)/RT].$$

For dilute solutions in naphthalene (from 200 to 310 °C)

$$k_\mathrm{i} = 10^{10.5\pm0.5} \exp[-(156\pm2)/RT].$$

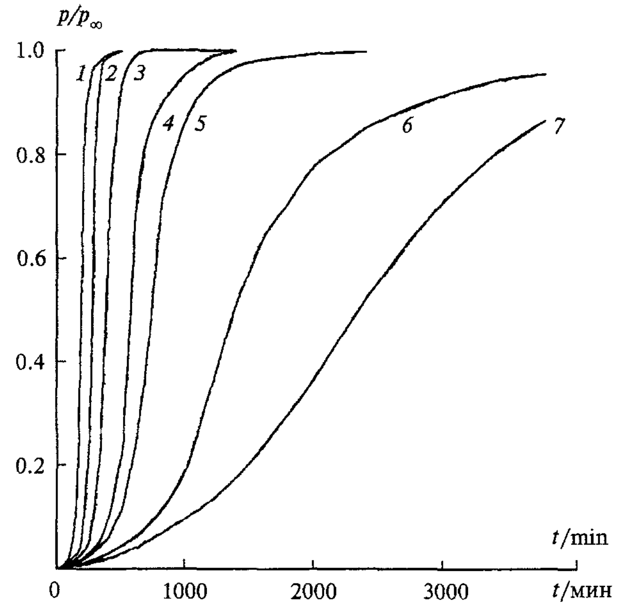


Fig. 2. Examples of the kinetic curves of TNT decomposition in HCB at 240 °C. $[\mathrm{TNT}]_0$, mol. %: 85 (*1*), 70 (*2*), 56 (*3*), 41 (*4*), 31 (*5*), 21 (*6*), 10 (*7*).

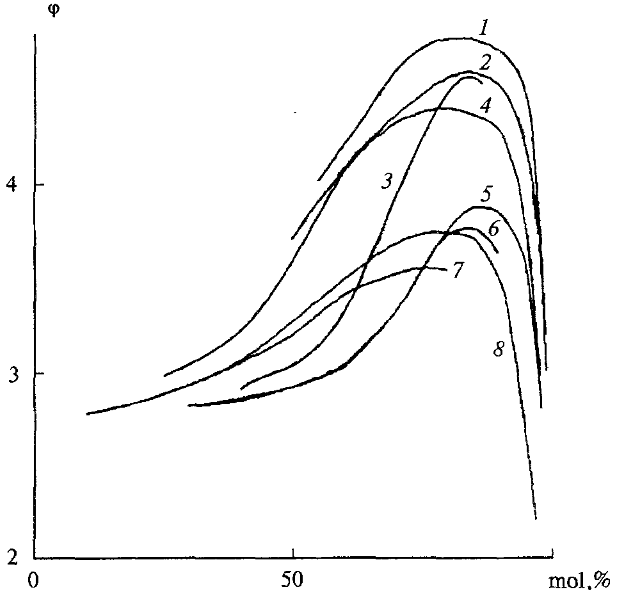


Fig. 3. Dependence of the molar yield (φ) of gaseous products on $[\mathrm{TNT}]_0$ in solutions (solvent, °C): PFN, 310 (*1*), PFN, 290 (*2*), toluene, 240 (*3*), PFN, 270 (*4*), naphthalene, 240 (*5*), toluene, 200 (*6*), PFN, 200 (*7*), PFN, 240 (*8*).

The Arrhenius parameters were also found for K, which in HCB and PFN solutions at $[\mathrm{TNT}]_0 < 70$ % was constant (see Fig. 5) and equal to

$$K = 10^{9.7\pm0.5} \exp[-(136\pm2)/RT].$$

K has the same Arrhenius parameters for dilute solutions in benzene and naphthalene as for the melt.

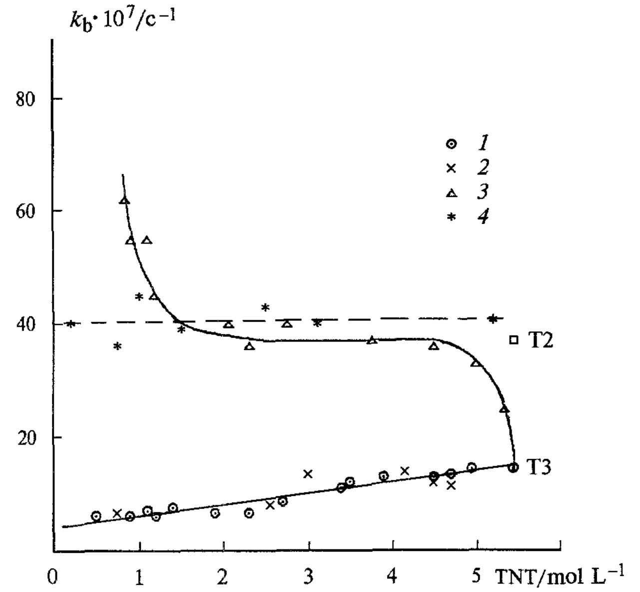


Fig. 4. Dependence of k_i on $[TNT]_0$ at 240 °C in solutions of HCB (*1*), PFN (*2*), toluene (*3*), and naphthalene (*4*).

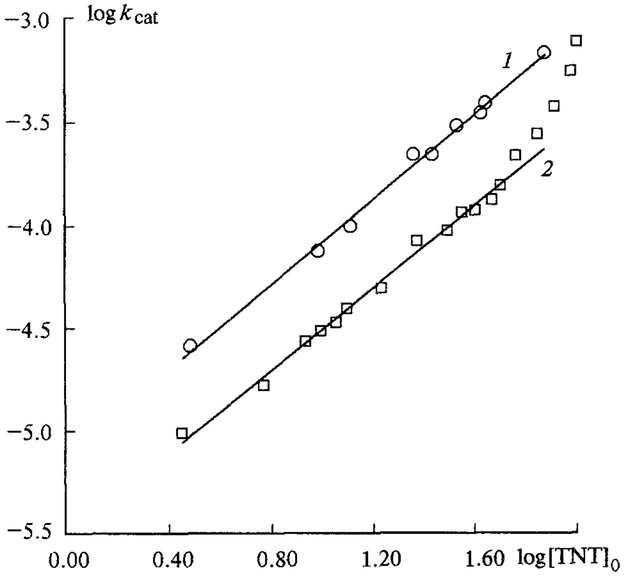


Fig. 5. Effect of $[TNT]_0$ on k_{cat} at 240 °C in solutions of naphthalene (*1*) and HCB (*2*).

Results and Discussion

The decomposition of pure TNT is not described by a first-order equation of autocatalysis (Fig. 6). Burning out[9] contributes an insignificant correction, because only ~20 % of the weight of TNT is transformed into gases after its complete decomposition. To provide the necessary increase in the specific rate, it is necessary to introduce several subsequent catalytic stages of decomposition, which is quite reasonable for such a polyfunctional molecule as TNT. The observed rate constant (k_i) is not elementary; it does not decrease to k_0 at high dilutions and even increases in some solvents (toluene, naphthalene) as $[TNT]_0$ decreases. The effect of a nonpolar solvent on the rate can be caused by its involvement in a chain decomposition reaction.

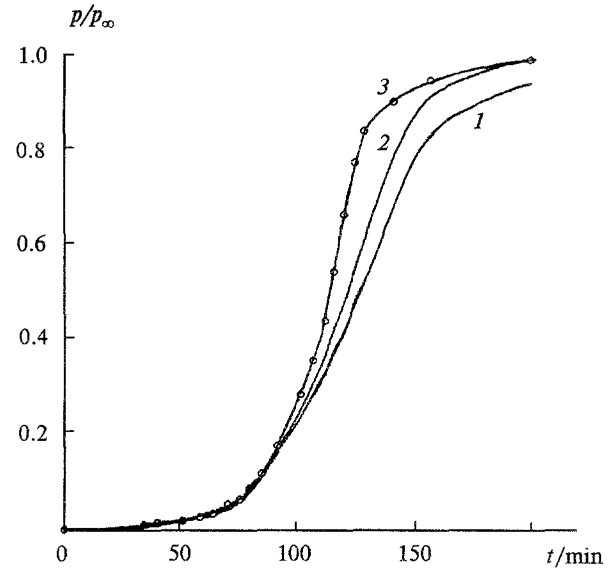


Fig. 6. Description of the kinetic curve: *1*, first-order autocatalysis, *2*, the same with account for burning out, *3*, according to Scheme 2 (the experiment is indicated by points).

Based on the aforesaid, a kinetic scheme of the process was developed. This scheme formally corresponds to a degenerate branched chain reaction and describes the experimental curves of gas evolution at all temperatures for conversion > 95 %. Using successive approximations, the number of stages and components in the scheme were minimized and it was reduced to the following:

Scheme 2

$T \rightarrow R_1 + G_1$ (1)
$T + R_1 \rightarrow R_1 + P_1 + G_2$ (2)
$P_1 \rightarrow R_2 + G_3$ (3)
$T + R_2 \rightarrow R_2 + P_2 + G_4$ (4)
$P_2 \rightarrow R_2 + G_5$ (5)
$R_1 + M \rightarrow P_3 + M$ (6)
$R_2 + M \rightarrow P_4 + M$ (7)
$P_2 \rightarrow R_3 + G_8$ (8)
$T + R_3 \rightarrow R_3 + P_3 + G_9$ (9)
$P_2 + R_3 \rightarrow R_3 + P_3 + G_{10}$ (10)
$P_3 \rightarrow R_3 + G_{11}$ (11)
$R_3 \rightarrow P_4 + M,$ (12)

where T is TNT; P_1, P_2, and P_3 are intermediate nonvolatile compounds; G_1—G_{11} are gaseous products: any

G can be N_2, NO, N_2O, CO, CO_2, or H_2O or a set of these compounds; the number i relates G_i to the corresponding stage of the process; P_4 are the final condensed products; R are free radicals or catalysts that unite particles with similar reactivities with the same index. Reaction (1) is the sum of elementary stages leading to the formation of primary free radicals. Its rate is determined by the first elementary stage of decomposition, such the rate constant k_1 in Scheme 2 must correspond to the gas-phase k_0. Reactions (1), (2), and (6) describe the noncatalytic decomposition as a nonbranched chain reaction and result in the k_i rate constant experimentally observed. The stage of acceleration is described by two processes of degenerate branching *via* products P_2 and P_3. Under the quasi-stationary conditions in R_1—R_3, the kinetic equation for the pressure takes the form:

$$dp/dt = k_1T + k_1(k_2/k_6M)T^2 + (k_4/k_2M)(k_3P_1 + k_5P_2)T + k_3P_1 + k_5P_2 + k_8P_2 + (k_9/k_{12}M)(k_8P_2 + k_{11}P_8)T(k_{10}/k_{12}M)(k_8P_3 + k_{11}P_3) + k_{11}P_3. \qquad (13)$$

A quasi-stationary system of differential equations and the method of steepest descent[10] are used to find the rate constants. An example of the description of the kinetic curve is presented in Fig. 6. The numerical values of the constants at 240 °C for sample T3 are the following: $k_1 = 6.65 \cdot 10^{-8}$ s^{-1}, $k_2T_0/k_6M = 43.3$, $k_3 = 2.99 \cdot 10^{-5}$ s^{-1}, $k_5 = 2.29 \cdot 10^{-4}$ s^{-1}, $k_8 = 4.40 \cdot 10^{-7}$ s^{-1}, $k_4T_0/k_7M = 6.23$, $k_9T_0/k_{12}M = 2.26$, $k_{10}T_0/k_{12}M = 3.65$, $k_{11} = 1.23 \cdot 10^{-3}$ s^{-1}. The calculated k_1 value is close to k_0 ($3.0 \cdot 10^{-8}$ s^{-1}). The activation energy for k_1 is equal to 167±10 kJ mol^{-1}, which is 28.9 kJ mol^{-1} lower than E_{gas}. The calculated value of log$A$ is equal to 10.1±2.1 for k_1. The initial rate is determined by the first two terms of Eq. (13), whence the expression for k_i takes the form

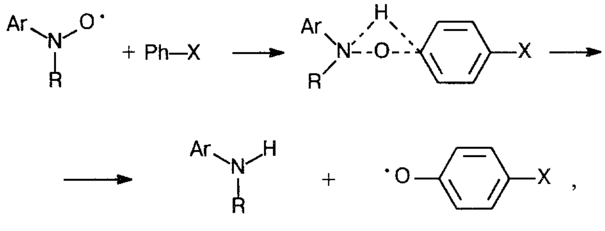
$$k_i = k_1 + k_1k_2T_0/k_6M = 2.4 \cdot 10^{-6}\ \text{s}^{-1}.$$

The magnitude of k_i virtually coincides with the experimental value. Some excess of k_1 over k_0 can be related to the positive effect of the medium on the rate of the initial isomerization, which, undoubtedly, occurs *via* a polar transition state.

The scheme suggested is not the only one possible. It is justified by the following points: first, the reaction cannot be described by a simpler scheme; second, none of the stages of the Scheme, including the initial stage, are elementary; and third, the acceleration is caused by at least two successive autocatalytic stages. The formal kinetic description in terms of the chain reaction agrees better with the other data, *e.g.*, the formation of free nitroxyl radicals during decomposition.

Scheme 2 has no chemical meaning without a detailed analysis; however, based on commonly accepted views about the reactions of aryl radicals, it can be assumed that R_1 is mainly $PicCH_2^{\cdot}$ (Pic is symmetric trinitrophenyl), which appears in reactions of TNT with OH or O (see Scheme 1), and $PicCH_2O^{\cdot}$, which alternates with $PicCH_2^{\cdot}$.

The P_1 product is $PicCH_2OH$, *viz.*, it is one of the mononitroso compounds formed by the elimination of the O atom from one of the NO_2 groups of the TNT molecule. $PicCH_2OH$ decomposes faster than TNT *via* the same mechanism but with deeper oxidation of the CH_3 group. The decomposition of $PicCH_2O^{\cdot}$ yields the more active $Pic^{\cdot}$ radical and then $PicO^{\cdot}$ (the series of R_2 radicals), which give rise to such final products as trinitrobenzene and picric acid. Substituted phenyl radicals are also formed by the elimination of the NO group from nitroso compounds. The latter are very important for the increase in acceleration. The interaction of nitroso compounds with any free radical ($R^{\cdot}$) results in the formation of stable nitroxyl radicals ($ArN(R)O^{\cdot}$), which are catalysts for the decomposition. Their reaction with the activated aromatic ring



results in aromatic amines (*i.e.*, new catalysts) and the O radical thus causing chain branching.

Scheme 2 includes the bimolecular chain termination at M particles, whose concentration is comparable to that of the initial substance. The calculated model predicts the linear dependence of k_i on T_0 (in molar fractions) in an inert solution with the slope $k_1k_2T_0/k_6M = 2.9 \cdot 10^{-6}$ s^{-1} and $k_i = k_1 = 6.65 \cdot 10^{-8}$ s^{-1}. In fact, k_i is equal to $6.0 \cdot 10^{-7}$ s^{-1} in dilute solutions of HCB and PFN, and the slope of the dependence is equal to $1.05 \cdot 10^{-7}$ s^{-1} (the k_2T_0/k_6M value is a dimensionless quantity). These deviations appear to be due to the fact that benzene, HCB, and PFN (which were considered inert) are actually not quite inert solvents. They support the decomposition by being involved into the chain process. This is also indicated by the change in the rate constant of autocatalysis and the dependence of the yield of gaseous products on $[TNT]_0$. Other solvents (naphthalene and toluene) are aninert: the decomposition rate in their solutions increases rather than decreases. This phenomenon can be explained most easily by the chain mechanism and deserves further investigation. It is noteworthy that a considerable increase in the rate is caused by small additions of such substances as naphthalene and toluene. It is likely that the irreproducibility of k_i is related to the effect of small amounts of admixtures. Partial sublimation of TNT results in the enrichment of its samples with volatile admixtures and an increase in the decomposition rate. The k_i scatter within one sample is probably related to the effect of the vessel surface. The high sensitivity to admixtures and the surface can easily be explained by the chain nature of the decomposition. It is likely that the liquid-crystalline structure of TNT and its change under the action of admixtures play a certain role in the decomposition.

References

1. R. M. Guidry and L. P. Davis, *Thermochim. Acta,* 1979, **32**, 1.
2. Yu. Ya. Maksimov and V. F. Sopranovich, *Gorenie i vzryv, Materialy IV Vses. sympoziuma po goreniyu i vzryvu* [*Combustion and Explosion, Proc. of IV All-Union Symp. on Combustion and Explosion*], Nauka, Moscow, 1977, 619 (in Russian).
3. V. G. Matveev, V. V. Dubikhin, and G. M. Nazin, *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1978, 474 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1978, **27**, 411 (Engl. Transl.)].
4. L. Peide and K. K. Brower, *Proc. of 17-th Intern. Pyrotechnics Seminar Combined with the 2nd Beijing Intern. Symp. of Pyrotechnics and Explosives, October 23 31, 1991 Beijing, China,* 1991, 473.
5. Y. E. He, J. P. Cui, W. C. Mallard, and W. Tsang, *J. Am. Chem. Soc.*, 1988, **110**, 3754.
6. C. P. Allen and G. P. Happ, *Canad. J. Chem.*, 1964, **42**, 650.
7. K. K. Andreev, *Termicheskoe razlozhenie i gorenie vzryvchatykh veshchestv* [*Thermal Decomposition and Combustion of Explosive Compounds*], Nauka, Moscow, 1966, 98 (in Russian).
8. Yu. Ya. Maksimov and E. N. Kogut, *Zh. Fiz. Khim.,* 1978, **52**, 1400 [*Russ. J. Phys. Chem.*, 1978, **52** (Engl. Transl.)].
9. F. I. Dubovitskii, G. B. Manelis, and A. G. Merzhanov, *Dokl. Akad. Nauk SSSR*, 1958, **121**, 668 [*Dokl. Chem.*, 1958, **12** (Engl. Transl.)].
10. E. F. Brin and B. V. Pavlov, *Kinet. Katal.*, 1975, **16**, 233 [*Kinet. Catal.*, 1975, **16** (Engl. Transl.)].

Received December 21, 1993;
in revised form May 10, 1994