Chain decomposition of 2,4,6-trinitrotoluene in hydrocarbon solvents

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

The rate constants for the thermal decomposition of 2,4,6-trinitrotoluene have been measured in toluene and other hydrocarbon solvents. The initial, observed rate constant (k_i) increases with dilution with toluene. The concentration dependence is described by the chain decomposition scheme with the transfer of the free valence to a solvent molecule. The activation energy and $\log k_i$ were found to linearly correlate with the dissociation energy of the C—H bond of the solvent.

Key words: 2,4,6-trinitrotoluene, thermal decomposition, solvent effect, chain mechanism, dissociation energy of C—H bond, kinetics.

The study of the decomposition of 2,4,6-trinitrotoluene (TNT) and other aromatic nitrocompounds in solutions aimed at elucidating the mechanism of the process and the reasons for a sharp increase in its rate in melt compared to that in the gas phase showed[1,2] that bimolecular reactions, which have been later interpreted[3] as stages of a chain process, play a substantial role in the liquid-phase decomposition of the majority of *ortho*-derivatives of nitrobenzene. Therefore, when a solution is diluted with an inert solvent, such as perfluoronaphthalene and perchlorobenzene, the overall rate of the decomposition of TNT decreases, approaching the reaction rate in the gas phase.[4] However, as has been shown previously,[3] the dilution with toluene does not result in a decrease in the decomposition rate of TNT and, by contrast, the rate increases. This fact was rationalized in terms of the chain mechanism with the transfer of a free valence to toluene, which possesses a low-energy C—H bond, and involvement of this molecule in the chain decomposition reaction. This work performed a more detailed experimental study of the decomposition of TNT in toluene and other hydrocarbon solvents, especially in a low-concentration range and presents the model description of these reactions.

Results and Discussion

The kinetics of decomposition of TNT in solutions was studied by the manometric method on a high-pressure installation[3] at 200 and 240 °C. For toluene, the TNT concentrations ranged mainly from 0.07 to 3 mol L^{-1} (or 0.7 to 50 mol. %), *i.e.*, they covered the dilution at which the effect of toluene was pronounced.[3] In other solvents, the measurements were carried out at 0.5 to 2 mol. % TNT. In all cases, the reaction occurs with self-acceleration. The typical kinetic curves of gas release in toluene at 240 °C are shown in Figs. 1 and 2. The value of 100 in these figures corresponds to the melt of TNT. The calculations were performed using the first-order equation of autocatalysis

$$d\eta/dt = k_i(1-\eta) + k_{cat}\eta(1-\eta),$$

where $\eta = (p_t - p_0)/(p_\infty - p_0)$ is the degree of conversion (p_t and p_∞ are the current and final pressures, respectively, p_0 is the pressure of the solvent vapor over the solution at the temperature of the experiment), k_i and k_{cat} are the observed first-order rate constants for the initial and catalytic stages, respectively. The true rate constant of autocatalysis can be obtained by dividing k_{cat} by the initial concentration $[TNT]_0$ expressed

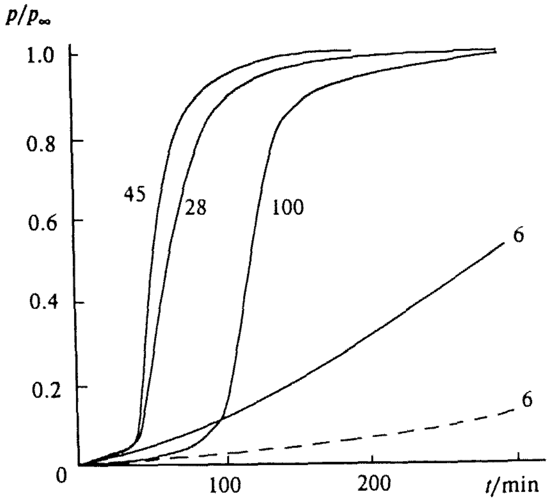

Fig. 1. Kinetic curves of the TNT decomposition in toluene at 240 °C. Figures at the curves designate concentrations of TNT in mol. %. The decomposition of TNT in toluene-CD_3 is shown by the dotted line.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1977—1980, August, 1996.

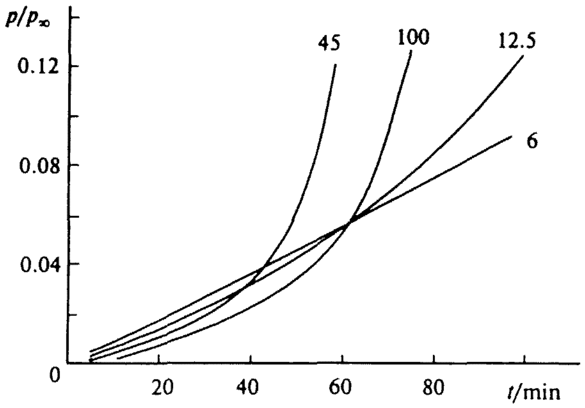

Fig. 2. Initial regions of kinetic curves of the TNT decomposition at 240 °C. Figures at the curves designate concentrations of TNT in mol. %.

in mol L^{-1}. The p_∞ parameter depends strongly on dilution[3]; therefore, the reaction was carried out to completion in all cases, and the calculation was performed using the overal kinetic curve by the method described previously.[3]

The dependences of k_i on $[TNT]_0$ in toluene at 200 and 240 °C are presented in Fig. 3. At the TNT concentration of 2 mol. %, the decomposition rate is three times higher than that obtained at [TNT] = 50 mol. % and it is ten times higher than that observed in a melt.[3] The dependences of $\log k_{cat}$ on $\log[TNT]_0$ are presented in Fig. 4. It is seen that in the catalytic reaction the first order with respect to TNT is fulfilled over a wide range of $[TNT]_0$. In a dilute solution of toluene-CD_3, the decomposition rate is lower than in ordinary toluene and also increases as $[TNT]_0$ decreases. The kinetic isotope effect of the solvent at $[TNT]_0$ = 2 mol. % is equal to 3.0 for k_i and 1.68 for k_{cat}.

The Arrhenius dependences of k_i in various solvents at $[TNT]_0$ = 2 mol. % for the temperatures of 200—240 °C are shown in Fig. 5. Each point in Fig. 5 was obtained by averaging the results of several (not less than three) parallel measurements. The kinetic parameters for k_i calculated from Fig. 5 are presented in Table 1.

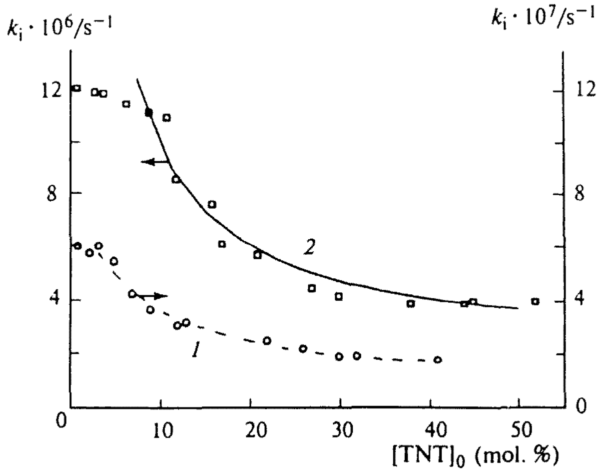

Fig. 3. Experimental dependences of k_i on $[TNT]_0$ in toluene at 200 (*1*) and 240 °C (*2*). The solid line shows the caculation by Eq. (7).

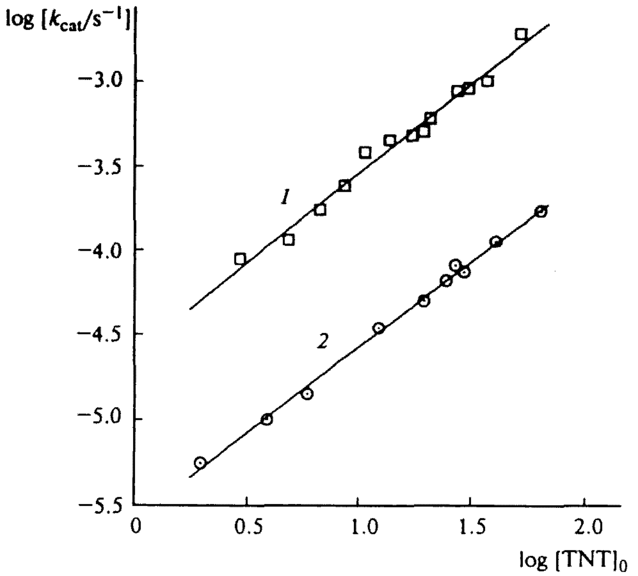

Fig. 4. Dependences of $\log k_{cat}$ on $\log[TNT]_0$ in toluene at 240 (*1*) and 200 °C (*2*).

The values of k_{cat} are the same in all solvents, E_{cat} = 130±7 kJ mol^{-1}, and $\log A_{cat}$ = 10.35.

An increase in k_i with dilution with toluene is evidence of the solvent effect on the initial stage of decomposition. This is also confirmed by the existence of a deuterium isotope effect when the reaction is carried out in toluene-CD_3. In the case of the TNT melt, the initial stage was interpreted[3] as a chain nonbranched process involving $^{\cdot}OH$, $PicCH_2^{\cdot}$, $PicCH_2O^{\cdot}$, $Pic^{\cdot}$, $PicO^{\cdot}$, and

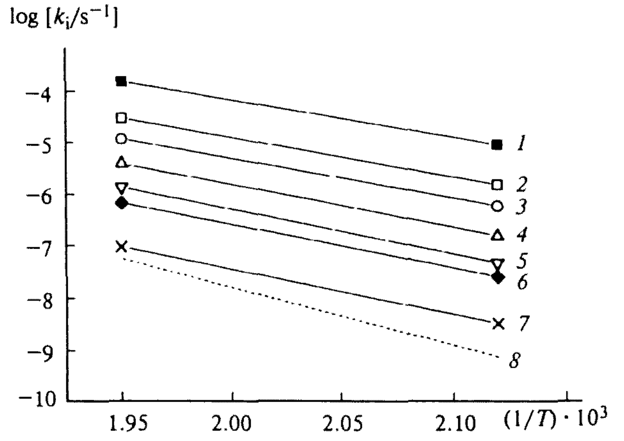

Fig. 5. Arrhenius plots of k_i for the decomposition of TNT in dilute (2 mol. %) solutions of diphenylmethane (*1*), *m*-xylene (*2*), toluene (*3*), naphthalene (*4*), in melt of TNT (*5*), and in benzene, hexachlorobenzene, and perfluoronaphthalene (*6*). Constant k_1 (*7*) is calculated taking into account reactions (1)—(6). Decomposition of TNT in the gas phase[4] (*8*).

Table 1. Kinetic parameters of the TNT decomposition in solutions (initial stage)

Medium	E_i /kJ mol^{-1}	$\log(A_i/s^{-1})$	k_i^{rel} at 240 °C
Melt	159.0	10.40	1
Diphenylmethane	139.2	10.40	100
m-Xylene	146	10.37	18.6
Toluene	151	10.51	8.1
Chloroform	156	10.26	1.3
Benzene	162.2	10.39	0.46
Perchlorobenzene	159.7	10.30	0.64
Perfluoronaphthalene	160	10.11	0.39

other free radicals. All these radicals can detach easily a hydrogen atom from toluene or other solvents with low-energy C—H bonds and transfer thereby the free valence to the solvent. Then the general scheme of the initial chain decomposition of TNT in solutions (which takes into account the scheme suggested[3] for the melt) will be as follows.

$$T \rightarrow R^\cdot + P_1 \quad (1)$$

$$R^\cdot + T \rightarrow R^\cdot + P_2 \quad (2)$$

$$R^\cdot + LH \rightarrow RH + L^\cdot \quad (3)$$

$$L^\cdot + T \rightarrow LH + R^\cdot \quad (4)$$

$$R^\cdot + M \rightarrow P_5 + M \quad (5)$$

$$R^\cdot + R^\cdot \rightarrow R{-}R \quad (6)$$

Here T is TNT; R · are free radicals (generally speaking, they can be different, but with similar reactivities); LH is the solvent; M are the products of the TNT decomposition, which quench R · radicals; P_1, P_2, and P_5 are the gaseous decomposition products. Stages (1) and (2) are not elementary processes. The elementary reactions involved and the structure of R · have been discussed previously.[3]

The solution of the system of kinetic equations describing this scheme under quasi-steady-state conditions with respect to R · and L, neglecting the contribution of several insignificant stages, results in the following approximate expression for k_i:

$$k_i = k_1 + k_1\frac{k_2T_0}{k_5M} + k_1\frac{k_2T_0}{k_5Mk_2}\frac{k_3}{k_2}\left(\frac{1-C}{C}\right), \quad (7)$$

where T_0 is the concentration of TNT in the melt and C is the molar fraction of TNT in the solution. The processing of the experimental data for the TNT melt gave the following values[3]: $k_1 = 7.47 \cdot 10^{-6}$ s^{-1} and $k_2T_0/k_5M = 48.6$. Taking into account these values, the experimental data on dilution (see Fig. 3) at $k_3/k_2 = 0.27$ can be described well by dependence (7), which testifies to an approximately fourfold increase in the efficiency of the interaction of R · on going from TNT to toluene. This is explained by possible reactions of R · with TNT involving not only C—H bonds, but the nitro groups as well. An increase in k_i with dilution occurs due to the involvement in the decomposition process of a second channel of the chain propagation, which competes with termination reactions. The replacement of primary O-centered radicals, which cannot react with TNT at nitro groups, by C-centered radicals of the solvent reacting with TNT at N—O and C—H bonds also plays a significant role. At low TNT concentrations, the accuracy of the description of the initial process by Eqs. (1)—(6) decreases, and the experimental points deviate from the theoretical dependence (see Fig. 3).

Unlike k_i, k_{cat} is independent of the TNT concentration and the solvent type. Thus, the acceleration stage is not associated with the development of chain processes and is a normal autocatalytic reaction.

The observed activation energy for k_i can be obtained from the formula

$$E_i = \frac{RT^2}{k_i}\frac{dk_i}{dT}.$$

The existence of stage (3) suggests that E_i depends on the C—H bond dissociation energy in the solvent. In fact, after differentiating Eq. (7) by T under the conditions of sufficiently great dilution, *i.e.*, when $k_2T_0/k_5M \gg 1$ and $k_3/k_2C \gg 1$, a rather simple dependence $E_i = E_1 + E_3 - E_5$ can be obtained. Then, expressing E_3 through the heat of reaction (3) Q_3 according to the Semenov—Polany equation, $E = a + bQ_3$, and expressing Q_3 through the enthalpies of formation of LH, L ·, and D(C—H) in LH, we obtain the linear relationship

$$E_i = \alpha + \beta D(\text{C—H}). \quad (8)$$

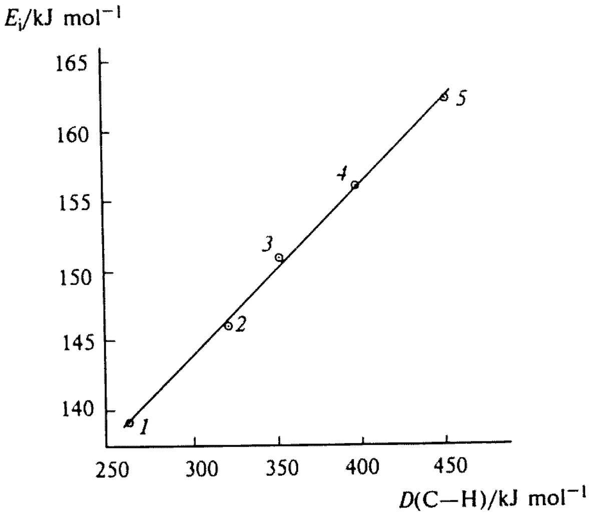

Fig. 6. Dependence of E_i on D(C—H) of the solvent: diphenylmethane (*1*), *m*-xylene (*2*), toluene (*3*), chloroform (*4*), and benzene (*5*).

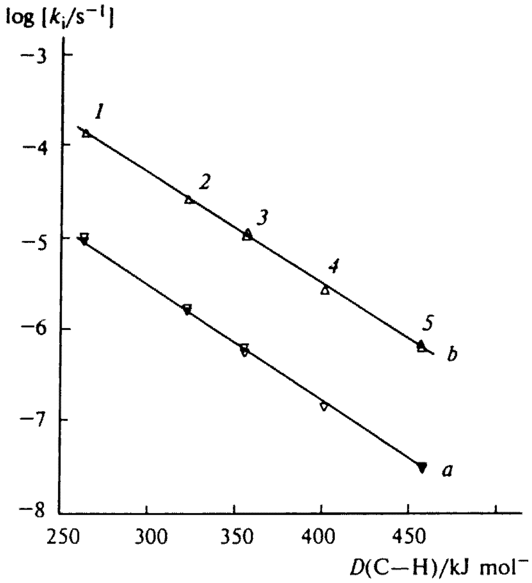

Fig. 7. Dependences of logk_i on D(C—H) at 200 °C (*a*) and 240 °C (*b*) in various solvents: diphenylmethane (*1*), *m*-xylene (*2*), toluene (*3*), chloroform (*4*), and benzene (*5*).

Dependence (8) agrees with the experimental data (Fig. 6) (the published[5] values of D(C—H) have been used)

$$E_i = (107.3\pm1.3) + (0.12\pm0.003)D(\mathrm{C{-}H})\ (\mathrm{kJ\ mol^{-1}})$$

and can be used for the determination of D(C—H) on the basis of the measurements of E_i. This can be done more precisely from the dependence of logk_i on D(C—H) presented in Fig. 7

$$\log k_i = 10.35 - [(107.3\pm1.3) + (0.12\pm0.003)D(\mathrm{C{-}H})]/2.3RT. \qquad (9)$$

At 240 °C

$$\log k_i = -(0.605\pm0.04) - (0.0122\pm0.0001)D(\mathrm{C{-}H}),$$

and at 200 °C

$$\log k_i = -(1.505\pm0.04) - (0.0133\pm0.0001)D(\mathrm{C{-}H}),$$

where D(C—H) is expressed in kJ mol^{-1}.

Thus, the results of the present work not only confirmed the chain scheme of the TNT decomposition, but they also allowed one to suggest a new method for the determination of the C—H bond energy in hydrocarbons and their haloderivatives. This method can be probably applied to alcohols, ethers, esters, and some other compounds, in which the detachment of a hydrogen atom is a sole reaction with free radicals. At the accuracy of measurement of k_i of 20 %, the error in determination of D(C—H) will be ±6.7 kJ mol^{-1}. Compounds with C—H bonds of the same type or in which the weakest C—H bond differs from the others by ~16 kJ mol^{-1} are appropriate for the determination of D(C—H) by Eq. (9).

This work was financially supported by the International Science Foundation (Grant NJ9 000).

References

1. Yu. Ya. Maksimov and V. F. Sopranovich, *Gorenie i vzryv, Materialy IV Vsesoyuz. simp. po goreniyu i vzryvu* [*Combustion and Explosion, Proc. IV All-Union Symp. on Combustion and Explosion*], Nauka, Moscow, 1977, 619 (in Russian).
2. Yu. Ya. Maksimov and E. N. Kogut, *Zh. Fiz. Khim.*, 1978, **52**, 1400 [*Russ. J. Phys. Chem.*, 1978, **52** (Engl. Transl.)].
3. V. V. Dubikhin, V. G. Matveev, and G. M. Nazin, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 266 [*Russ. Chem. Bull.*, 1995, **44**, 258 (Engl. Transl.)].
4. 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.)].
5. L. V. Gurvich, G. V. Karachevtsev, V. N. Kondrat'ev, Yu. A. Lebedev, V. A. Medvedev, V. K. Potapov, and Yu. S. Khodeev, *Energii razryva khimicheskikh svyazei. Potentsialy ionizatsii i srodstvo k elektronu* [*Dissociation Energies of Chemical Bonds. Ionization Potentials and Electron Affinity*], Nauka, Moscow, 1974, 351 pp. (in Russian).

Received December 29, 1995