A Computational Study on the Kinetics and Mechanism for the Unimolecular Decomposition of o-Nitrotoluene

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The kinetics and mechanism for the unimolecular decomposition of o-nitrotoluene (o-CH$_3$C$_6$H$_4$NO$_2$) have been studied computationally at the G2M(RCC, MP2)//B3LYP/6-311G(d, p) level of theory in conjunction with rate constant predictions with RRKM and TST calculations. The results of the calculations reveal 10 decomposition channels for o-nitrotoluene and its six isomeric intermediates, among them four channels give major products: CH$_3$C$_6$H$_4$ + NO$_2$, C$_6$H$_4$C(H)ONO (anthranil) + H$_2$O, CH$_3$C$_6$H$_5$O (o-methyl phenoxy) + NO, and C$_6$H$_4$C(H)$_2$NO + OH. The predicted rate constants in the 500–2000 K temperature range indicate that anthranil production, taking place initially by intramolecular H-abstraction from the CH$_3$ group by NO$_2$ followed by five-membered ring formation and dehydration, dominates at temperatures below 1000 K, whereas NO$_2$ elimination becomes predominant above 1100 K and CH$_3$C$_6$H$_5$O formation by the nitro–nitrite isomerization/decomposition process accounts for only 5–11% of the total product yield in the middle temperature range 800–1300 K. The branching ratio for CH$_3$C$_6$H$_5$NO formation by the decomposition process of CH$_3$C$_6$H$_4$-NO(OH) is negligible. The predicted high-pressure-limit rate constants with the rate expression of $4.10 \times 10^{17}$ exp[−37000/T] s$^{-1}$ for the NO$_2$ elimination channel and $9.09 \times 10^{12}$ exp[−25800/T] s$^{-1}$ for the H$_2$O elimination channel generally agree reasonably with available experimental data. The predicted high-pressure-limit rate constants for the NO and OH elimination channels are represented as $1.49 \times 10^{14}$ exp[−30000/T] and $1.31 \times 10^{15}$ exp[−38000/T] s$^{-1}$, respectively.

Introduction

The thermal decomposition of o-nitrotoluene (1-nitro, 2-methyl benzene) has received much attention thanks to its relevance to the trinitrotoluene decomposition chemistry. Gonzalez and co-workers$^{1}$ studied the kinetics of the decomposition reaction in an experiment by high-power infrared laser heating (laser-enhanced homogeneous pyrolysis). In the experiment, they used a Lumonics K103 CO$_2$ laser (wavelength = 10.6 µm, duration = 1 µs, fluence = 1 J/cm$^2$) at a constant repetition rate (0.2 Hz) for the irradiation of a small portion of the reaction cell (typically 24%). They reported that the primary decomposition process occurred by the breaking of the C–NO$_2$ bond with 70.2 ± 2.5 kcal/mol activation energy at 1100 K. The rate expression for the dissociation process $o$-CH$_3$C$_6$H$_4$NO$_2$$ \rightarrow$ CH$_3$C$_6$H$_4$ + NO$_2$ at 110 Torr SF$_6$ pressure over the temperature range 110–1250 K was given by $k_1 = 10^{15.9} \pm 0.5$ exp[−33000 ± 1000/T] s$^{-1}$. Tsang and co-workers$^{2,3}$ also studied the decomposition reaction in a single-pulse shock tube at 2700–3400 Torr Ar pressure over the temperature range 1000–1180 K. They obtained the rate expressions of $k_1 = 6.4 \times 10^{14}$ exp[−30900/T] s$^{-1}$ for NO$_2$ production and $k_2 = 1.2 \times 10^{13}$ exp[−26000/T] s$^{-1}$ for $o$-CH$_3$C$_6$H$_4$NO$_2$$ \rightarrow$ C$_6$H$_4$C(H)ON (anthranil) + H$_2$O, respectively.

The photodissociation of nitrotoluene has been studied using a femtosecond laser photolysis/mass spectroscopic technique at 375 nm.$^4$ Both NO$_2$ and NO loss channels have been observed for all three nitrotoluene isomers ($o$-, $m$- and $p$-nitrotoluenes). In the dissociation of o-nitrotoluene, OH is a significant product that can be attributed to the so-called “ortho effect” (i.e., H-transfer from the CH$_3$- to the NO$_2$-group).$^{5-6}$ The NO fragment from the dissociation of o-nitrotoluene between 224 and 238 nm$^2$ and 220 and 250 nm$^3$ has also been observed.

Up to now, there has been no theoretical study on the decomposition of o-nitrotoluene, to our knowledge. In the present work, the kinetics and mechanism for the isomerization and decomposition of o-nitrotoluene have been computationally studied at the G2M(RCC, MP2) level of theory.$^7$ The potential energy surface (PES) and the rate constants for $o$-CH$_3$C$_6$H$_4$NO$_2$$ \rightarrow$ CH$_3$C$_6$H$_4$ + NO$_2$, C$_6$H$_4$C(H)ON (anthranil) + H$_2$O, CH$_3$C$_6$H$_5$O + NO, and CH$_3$C$_6$H$_5$NO + OH production channels have been predicted, and the results are reported herein for high-temperature combustion modeling applications.

Computational Method

The optimized geometries of o-nitrobenzene, its 8 stable isomers, 11 transition states, and products for the four dissociation channels have been calculated at the B3LYP/6-311G(d, p) level. To obtain more reliable values of energies for PES and rate constant predictions, we performed a series of single-point energy calculations for each molecule and transition state with the G2M(RCC, MP2) scheme$^8$ based on the optimized geometries at the B3LYP/6-311G(d, p) level. The G2M(RCC, MP2) or B3LYP method with larger basis sets is a reliable computational method for decomposition of phenyl compounds such as nitrobenzene$^{10}$ and nitrosobenzene.$^{11}$ The G2M(RCC, MP2) composite scheme is given as follows:

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$E_0[\text{G2M}] = \text{RCCSD(T)/6-311G(d,p)} + \text{MP2/6-311+G(3df,2p)} - \text{MP2/6-311G(d,p)} + \Delta \text{HLC} + \text{ZPE}$

where the higher level corrections ($\Delta \text{HLC}$) is given by $-5.3n_{3\beta} - 0.19n_\alpha$ in millihartree, where $n_\alpha$ and $n_{3\beta}$ are the numbers of $\alpha$ and $\beta$ valence electrons, respectively.

**Results and Discussion**

1. **Isomerization and Dissociation of o-Nitrotoluene.** The optimized structures of species 1–32 for o-nitrotoluene, its isomeric intermediates, transition states for the isomerization and dissociation reactions, and dissociated products calculated at the B3LYP/6-311G(d,p) level are presented in Figure 1. The energy diagram of the system, including various isomerization and decomposition reactions, computed with the G2M(RCC, MP2) method discussed above is shown in Figure 2. As shown in Figure 1, o-nitrotoluene has six different isomers: CH$_3$C$_6$H$_4$-t-N(OH)O (6), CH$_3$C$_6$H$_4$-e-N(OH)O (8), CH$_3$C$_6$H$_4$N(O)OH (10), CH$_3$C$_6$H$_4$ONO (13), CH$_3$C$_6$H$_4$NO (24), and CH$_2$C$_6$H$_4$NO (27); among them 27 is most stable, lying below the o-nitrotoluene at 4.1 kcal/mol. The geometries of o-nitrotoluene (1), 6, 8, and 10 have near $C_s$ symmetry. Due to the ortho effect, the H atom of the -CH$_3$ group of o-nitrotoluene is transferred to the NO$_2$ group of the 6 by an isomerization reaction. The 6 is the conformer of the 8 due to the internal rotation of OH in the HONO group. The 8 isomerizes to the 10 by the H atom transfer (HONO $\leftrightarrow$ ONOH). The 8 isomerizes to the 27 by the OH group transfer from HONO to the CH$_2$ group. Isomerization reactions can occur among the isomers by their corresponding transition states. Similar to the nitro isomerization reaction of nitrobenzene, o-nitrotoluene isomerizes to 24 by the nitro-nitrite isomerization reaction.

The o-nitrotoluene molecule can dissociate directly to the products CH$_3$C$_6$H$_4$ (19) $\rightarrow$ NO$_2$ with the dissociation energy at 0 K of 76.3 kcal/mol and to CH$_3$C$_6$H$_4$NO (18) $\rightarrow$ CH$_3$ with the high dissociation energy at 0 K of 103.0 kcal/mol. The predicted C═NO$_2$ dissociation energy at 1100 K of 75.7 kcal/mol may be compared with the experimental activation energy measured at 1100 K and 110 Torr SF$_6$ pressure, 70.2 ± 2.5 kcal/mol.$^{11}$ CH$_3$C$_6$H$_4$NO can also dissociate directly to give the products CH$_3$C$_6$H$_4$NO (22) $\rightarrow$ HONO with a 63.6 kcal/mol enthalpy change after overcoming the 104.3 kcal/mol barrier at TS$_1$, and the products CH$_3$C$_6$H$_4$NO (22) $\rightarrow$ HONO with the predicted enthalpy of reaction, 72.9 kcal/mol, after overcoming the 74.3 kcal/mol barrier at TSs. In these reactions, species ONOH$\cdots$CH$_2$C$_6$H$_2$ (3) and ONOH$\cdots$CH$_2$C$_6$H$_2$ (21) appearing in the PES are product complexes. Isomer 13, which can be formed by ring-closure from isomers CH$_3$C$_6$H$_4$-e-N(OH)O (8) and CH$_3$C$_6$H$_4$-N(O)OH (10) via TS$_6$ and TS$_5$, respectively, can eliminate H$_2$O to give the double-ring product CH$_3$C$_6$H$_4$(HON) (16, anthranil) by overcoming the 37.7 kcal/mol barrier at TS$_5$ with -60.0 kcal/mol overall energy change from the reactant. Isomer CH$_3$C$_6$H$_4$-ONO (24), formed by the nitro-nitrite isomerization reaction from the reactant via TS$_5$ (57.9 kcal/mol), can dissociate readily to the products CH$_3$C$_6$H$_4$ (25) $\rightarrow$ NO with an endothermicity of 14.3 kcal/mol or to the less favored products CH$_3$C$_6$H$_4$ (19) $\rightarrow$ NO with an endothermicity of 76.3 kcal/mol as cited above for the direct dissociation process. Both dissociation reactions occur without intrinsic barriers. Isomer 8 and its isomer through HONO internal rotation, CH$_3$C$_6$H$_4$-t-N(OH)O (6)—the initial H-abstraction product from CH$_3$ by the nitro-group via TS$_2$ (46.3 kcal/mol)—can dissociate to produce CH$_3$C$_6$H$_4$NO (17) $\rightarrow$ OH with 84.9 kcal/mol overall endothermicity and to CH$_3$C$_6$H$_4$ (30) $\rightarrow$ HONO with 92.2 kcal/mol endothermicity; both occur by direct dissociation mechanism. Finally, isomer o-hydroxymethyl nitrosobenzene (27), predicted to be the most stable isomer, can dissociate to give the products CH$_3$(OH)C$_6$H$_4$ (28) $\rightarrow$ NO and CH$_3$C$_6$H$_4$NO (29) $\rightarrow$ CH$_3$OH with 55.6 and 104.5 kcal/mol overall endothermicities, respectively, both by direct dissociation processes.

In summary, there are 10 decomposition channels for o-nitrotoluene and its isomers, where the channels giving rise to NO$_2$, H$_2$O, and NO products are major reactions. In addition, the OH loss process was also reported in some photodissociation experiments.$^{6}$ This process may involve the dissociation channels CH$_3$C$_6$H$_4$N(O)OH (10) $\rightarrow$ CH$_3$C$_6$H$_4$C(H$_2$)NO (14) $\rightarrow$ OH and CH$_3$C$_6$H$_4$-t-N(OH)O (6) or CH$_3$C$_6$H$_4$-e-N(OH)O (8) $\rightarrow$ CH$_3$C$_6$H$_4$NO (17) $\rightarrow$ OH with 74.2 and 84.9 kcal/mol overall endothermicities, respectively; among them the first reaction with a much lower dissociation energy should dominate. Products 17 and 14 formed above are the two structural isomers of o-nitrosobenzyl radicals connected by the -NO torsional isomerization transition state.

2. **Rate Constants Calculations.**

a. **Production of NO$_2$.** The NO$_2$ elimination reaction

$$o$-CH$_3$C$_6$H$_4$NO$_2$ $\rightarrow$ CH$_3$C$_6$H$_4$ + NO$_2$  \hspace{1cm} (1)$$

is a direct dissociation process, which is similar to C$_6$H$_5$NO$_2$ $\rightarrow$ C$_6$H$_5$ + NO$_2$. The predicted dissociation energy, 76.3 kcal/mol, is close to the analogous dissociation energy, 74.1 kcal/mol in C$_6$H$_4$NO$_2$. The rate constant for reaction 1, $k_1$, has been predicted with the Variflex code$^{12}$ based on the G2M(RCC) PES and the molecular parameters and frequencies computed by B3LYP/6-311G(d,p). For $k_1$ evaluation, the minimum energy path (MEP) representing the direct dissociation process was obtained by calculating the potential curve along the reaction coordinate $C \rightarrow$ N of o-CH$_3$C$_6$H$_4$NO$_2$ $\rightarrow$ CH$_3$C$_6$H$_4$ + NO$_2$. Along the path, the $C \rightarrow$ N bond length was stretched from the equilibrium value 1.483 to 5 Å with the step size of 0.1 Å and each geometry with a fixed $C \rightarrow$ N bond length was fully optimized at the B3LYP/6-311G(d,p) level. The MEP with the separation of 2.3 to 5.0 Å in the variational TST calculation is approximated with the Morse potential, $V(r) = D_0[1 - \exp(-\beta(R - R_0))]^2$, where $R$ is the reaction coordinate, $R_0$ is the equilibrium value, and $D_0$ is the bond energy without zero-point energy corrections. The parameters of the Morse potential obtained by fitting the MEP are $R_0 = 1.483$ Å, $\beta = 1.31$ Å$^{-1}$, and $D_0 = 81.0$ kcal/mol, which was scaled slightly to the G2M value without ZPE-correction. The CH$_3$ groups in CH$_3$C$_6$H$_4$ and o-CH$_3$C$_6$H$_4$NO$_2$ were treated as free rotors with the rotational constants of 5.563 cm$^{-1}$ for CH$_3$C$_6$H$_4$ and 5.415 cm$^{-1}$ for o-CH$_3$C$_6$H$_4$NO$_2$ evaluated with the ChemRate program.$^{13}$ In addition, the Lennard-Jones pairwise potential and the anisotropic potential (a potential anisotropy form assuming a bonding potential which is cylindrically symmetric with respect to each fragment) are also added to form the final potential for the variational rate constant evaluation. To compare the theory with experiments, we have calculated the rate constants in the temperature range 500–2000 K under different experimental conditions. The Lennard-Jones (L-J) parameters for different bath gases employed are as follows: Ar, $\sigma = 3.47$ Å, $\epsilon/k = 114$ K; SF$_6$, $\sigma = 5.20$ Å, $\epsilon/k = 212$ K; o-CH$_3$C$_6$H$_4$NO$_2$, $\sigma = 5.6$ Å, $\epsilon/k = 690$ K, derived from its critical temperature (769 K) and volume (376 cm$^3$/mol) using the formulas ($\epsilon/k = 0.897 T_c$, $\sigma = 0.785 V_c^{1/3}$).$^{14}$ The average step-sizes for collisional deactivation by Ar and SF$_6$ were taken as $\langle \Delta E \rangle_{\text{coll}} \simeq 400$ and 2200 cm$^{-1}$, respectively, as previously employed for the C$_6$H$_5$NO$_2$ decomposition reaction.$^{10}$
The predicted high-pressure first-order and low-pressure second-order rate constants for the decomposition reaction in the temperature range 500–2000 K can be represented by

\[ k_{1m} = 4.10 \times 10^{17} \exp\left[-37000/T\right] \text{s}^{-1}, \]

\[ k_1^0 = 5.41 \times 10^{10} \times T^{-24.3} \exp\left[-43500/T\right] \text{cm}^3 \text{mol}^{-1} \text{s}^{-1} \]

for the Ar-bath gas. The high value of the high-pressure A-factor given above is consistent with those obtained for \( \text{C}_6\text{H}_5\text{NO}_1 \) and \( \text{C}_6\text{H}_5\text{NO}_2 \) fragmentation reactions.

The predicted values shown in Figure 3 for the conditions close to those employed experimentally compare reasonably with the experimental results cited in the Introduction. The rate constants measured by Gonzalez et al.\(^1\) using the SF\(_6\) as bath gas at 110 Torr pressure are evidently higher than those measured by Tsang and co-workers\(^2,3\) using Ar as bath gas at 2700–3400 Torr. The values predicted for the conditions employed by Gonzalez et al.\(^1\), represented by \( k_1 = 1.5 \times 10^{15} \exp\left[-30900/T\right] \text{s}^{-1} \), though slightly lower than their experimental results given by \( k_1 = 7.9 \times 10^{15} \exp\left[-(33000 \pm 1000)/T\right] \text{s}^{-1} \), are well within the given error bars as shown in the
A similar nitro–nitrite isomerization/decomposition process has been studied in the nitrobenzene decomposition reaction.10 Because the barrier at TS9 is 43.6 kcal/mol higher than the dissociation energy of CH₃C₆H₄ONO (24) → CH₃C₆H₄O (25) + NO with 14.3 kcal/mol, this decomposition reaction can be treated as a one-step dissociation via TS9. The predicted barrier, 57.9 kcal/mol, may be compared with that of the parallel nitrobenzene decomposition reaction, 61.1 kcal/mol. The statistical factor for the decomposition reaction is 2 because there are two optical isomers in TS9.

The predicted rate constant for reaction 3 in the temperature range 500–2000 K calculated by the Variflex code12 for the high-pressure first-order and low-pressure second-order limits...
Figure 5. Calculated branching ratios for the four channels of \( o \)-nitrotoluene decomposition to NO\(_2\) (solid curve), H\(_2\)O (dotted curve), NO (dashed curve), and OH (dash–dotted curve) products in the temperature range 500–2000 K.

in Ar can be represented by the expressions,

\[
k_3^\infty = 1.49 \times 10^{14} \exp[-30000/T] \text{ s}^{-1},
\]

\[
k_3^0 = 6.21 \times 10^{92} \times T^{-21.8} \exp[-36000/T] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.
\]

To our knowledge, there are no experimental rate constants available for the decomposition channel of NO product.

d. Production of OH. As mentioned in the last section,

\[
\text{CH}_3\text{C}_6\text{H}_4\text{N(O)OH (10)} \rightarrow \text{CH}_2\text{C}_6\text{H}_4\text{NO (14)} + \text{OH (4)}
\]

with 74.2 kcal/mol dissociation energy is the primary channel of the OH product. The isomerization process from \( o \)-CH\(_3\)C\(_6\)H\(_4\)NO\(_2\) to CH\(_3\)C\(_6\)H\(_4\)N(O)OH (10) is the same as reaction 2.

The predicted rate constant for reaction 4 in the temperature range 500–2000 K calculated by the ChemRate program\(^3\) for the high-pressure first-order and low-pressure second-order limits in Ar can be represented by the expressions

\[
k_4^\infty = 1.31 \times 10^{13} \exp[-39000/T] \text{ s}^{-1},
\]

\[
k_4^0 = 2.67 \times 10^{38} \times T^{-3.7} \exp[-34000/T] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.
\]

To our knowledge, there are no experimental data available for the decomposition channel producing the OH product.

e. The Branching Ratios for Formation of NO\(_2\), H\(_2\)O, NO, and OH. The branching ratios of high-pressure rate constants for \( o \)-nitrotoluene to produce NO\(_2\), H\(_2\)O, NO, and OH are shown in Figure 5. The channel for H\(_2\)O production dominates at temperatures below 1000 K, whereas that for NO\(_2\) production becomes predominant over 1100 K. The channel producing NO accounts for only 5–10% of the total decomposition rates in the temperature range from 800 to 1300 K. The channel producing OH contributes negligibly to the total decomposition rate.

Conclusions

The potential energy surface for the isomerization and decomposition of \( o \)-nitrotoluene, a model compound for TNT, has been calculated at the G2M(RCC, MP2)/B3LYP/6-311G(d, p) level. There are 10 decomposition channels for \( o \)-nitrotoluene and its six isomeric derivatives, where the channels producing CH\(_3\)C\(_6\)H\(_4\) + NO\(_2\), CH\(_3\)H\(_2\)C(H)ON (anthranil) + H\(_2\)O, and CH\(_3\)C\(_6\)H\(_4\)O (\( o \)-methyl phenoxy) + NO are primary processes. The predicted rate constants for NO\(_2\) elimination (\( k_1 \)) and for anthranil formation (\( k_2 \)) are generally in reasonable agreement with available experimental data. The predicted rate constants for production of NO and OH (giving CH\(_3\)C\(_6\)H\(_4\)NO) were found to be much smaller. The branching ratios for \( o \)-nitrotoluene decomposition to produce NO\(_2\), H\(_2\)O, NO, and OH in the temperature range 500–2000 K indicate that the dehydration process dominates at temperatures below 1000 K, whereas the NO\(_2\) elimination reaction becomes dominant at temperature over 1100 K, and the NO product accounts for only 5–10% of the total yield in the temperature range from 800 to 1300 K. The channel producing OH is negligible over the entire range of temperature studied.

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Supporting Information Available: Table S1 lists the frequencies and moments of inertia \( I_i \) of the decomposition reaction of \( o \)-nitrotoluene calculated at the B3LYP/6-311G(d, p) level. Table S2 lists the predicted forward and reverse rate constants of each and final rate constants of reaction 1, 2a, 2b, 3, and 4 at the high-pressure limit condition. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes


