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COMMENT

Comment on "Decomposition mechanisms of trinitroalkyl compounds: a theoretical study from aliphatic to aromatic nitro compounds" by G. Fayet, P. Rotureau, B. Minisini, *Phys. Chem. Chem. Phys.*, 2014, 16, 6614

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In a recent paper[1] Fayet et al. scrutinized primary decomposition reactions for various derivatives of 1,1,1-trinitrobutane (TNB) and nitroaromatics using DFT computations. The authors compared the calculated Gibbs free energy of activation ($\Delta^{\neq}G^0_{298}$) for various competing reaction channels and inferred that the C-NO_2 bond fission dominates the gas-phase thermolysis of all species studied.

For clarity, we will consider the reactions of TNB at room temperature. In contrast to isomerisation channels (reactions R2 and R3 in the manuscript),[1] the C-NO_2 bond rupture (R1) is a barrierless process, and in such case the variational transition state theory (TST) is typically used to locate the transition state (TS).[2] In the framework of TST, either canonical or variational,[2] the rate constant of a unimolecular reaction reads as:

$$k_{TST} = \frac{k_B T}{h} exp\left(-\frac{\Delta^{\neq}G^0_T}{RT}\right) = \frac{k_B T}{h} exp\left(\frac{\Delta^{\neq}S^0_T}{R}\right) exp\left(-\frac{\Delta^{\neq}H^0_T}{RT}\right)$$
$$= \frac{k_B T}{h} \frac{z^{\neq}(T)}{z^{reag}(T)} exp\left(-\frac{\Delta^{\neq}H^0_0}{RT}\right) \qquad (1).$$

In my opinion, the methodologies employed by the authors[1] to calculate the ratio of partition functions $\frac{z^{\neq}}{z^{reag}}$ (or, almost equivalently, the activation entropy $\Delta^{\neq}S^0_{298}$) and activation barrier $\Delta^{\neq}H^0_0$ for a barrierless reaction R1 (more generally, the C-NO_2 bond rupture reactions as well), both have serious shortcomings.

Let us consider first $\frac{z^{\neq}}{z^{reag}}$. As an estimation to $\Delta^{\neq}G^0_{298}$ the authors[1] simply proposed the Gibbs free energy of a barrierless reaction $\Delta^r G^0_{298}$, (i.e., a variational TS corresponds to the asymptote •Rad1 + •NO_2 and $z^{\neq} \approx z^A z^B$). Assuming the usual

factorization of the partition function of N-atomic species $z = z^{(3)}_{tr} z^{(3)}_{rot} z^{(3N-6)}_{vib}$, the ratio of approximate and exact TS partition functions reads as:

$$\frac{z_A z_B}{z^{\neq}} = \frac{z^{A(3)}_{tr} z^{A(3)}_{rot} z^{A(3N_A-6)}_{vib} \cdot z^{B(3)}_{tr} z^{B(3)}_{rot} z^{B(3N_B-6)}_{vib}}{z^{\neq(3)}_{tr} z^{\neq(3)}_{rot} z^{\neq(3N-7)}_{vib}} =$$

$$= \left\{ \frac{\left(\frac{z^{A(3)}_{tr} \cdot z^{B(3)}_{tr}}{z^{\neq(3)}_{tr}}\right)\left(\frac{z^{A(3)}_{rot} \cdot z^{B(3)}_{rot}}{z^{\neq(3)}_{rot}}\right)}{z^{\neq(5)}_{vib/hind.rot}} \right\} \cdot \left[\frac{z^{A(3N_A-6)}_{vib} \cdot z^{B(3N_B-6)}_{vib}}{z^{\neq(3N-12)}_{vib}}\right] =$$

$$= \left\{ \frac{z^{eff(3)}_{tr} \cdot z^{eff(3)}_{rot}}{z^{\neq(5)}_{vib/hind.rot}} \right\} \cdot \left[\frac{z^{A(3N_A-6)}_{vib} \cdot z^{B(3N_B-6)}_{vib}}{z^{\neq(3N-12)}_{vib}}\right] =$$

$$= \left(\frac{\frac{V^0}{N_A}\frac{\left(2\pi m_{eff} k_B T\right)^{3/2}}{h^3}}{z^{\neq(2)}_{vib/hind.rot}}\right) \cdot \left\{ \frac{z^{eff(3)}_{rot}}{z^{\neq(3)}_{vib/hind.rot}} \right\} \cdot \left[\frac{z^{A(3N_A-6)}_{vib} \cdot z^{B(3N_B-6)}_{vib}}{z^{\neq(3N-12)}_{vib}}\right] \qquad (2).$$

The ratio $\frac{z_A z_B}{z^{\neq}}$ is dominated by the first term in parentheses. For brevity, we estimate from below the second term in curly brackets (in a very conservative manner) as unity. The third term comprises contributions from approximately conserved vibrational modes and is supposed to be close to unity as well. Assuming $z^{eff(3)}_{tr} = 7.5 \cdot 10^6$ ($m_{eff} = 35$ a.e.m.) and the partition function of every TS vibrational (or hindered rotation) mode $z^{\neq(1)}_{vib/hind.rot} \leq 10$ (corresponds to a harmonic vibration with a wavenumber higher than ~20 cm^{-1}); the lower estimation of the first term in (2) yields $\frac{z_A z_B}{z^{\neq}} \geq 7 \cdot 10^4$.

More generally, the main error stems from contributions from one entirely spurious translational degree of freedom and two vibrations/hindered rotations in the TS erroneously considered to be translations as

well. In the case of (R1), this yields at room temperature a spurious contribution to $\Delta^{\neq}G^0_{298}$ of $RT \cdot \left(ln\left(\frac{z_A z_B}{z^{\neq}} \right) - 1 \right) \geq 6\,\text{kcal/mol}$. Such fictitious overestimation of $\Delta^{\neq}S^0_{298}$, inter alia, leads to an unrealistically high value of the preexponential factor $A \approx \frac{k_B T}{h} exp\left(1 + \frac{\Delta^r S^0_{298}}{R} \right) = 10^{24}\,\text{s}^{-1}$.

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Table 1. Activation Barriers of Thermal Reactions of Nitroalkanes ($\Delta^{\neq}H_0^0$) Calculated Using Various Coupled Cluster Methods, Multi-Level, and DFT Procedures. In the Case of Barrierless Radical Decomposition Reactions, the C-NO$_2$ Bond Energies ($\Delta^r H_0^0$) are Listed in Parentheses. All Values are in kcal/mol.

Reactions	$\Delta^{\neq}H_0^0$ ($\Delta^r H_0^0$), kcal/mol				
	CCSD(T)/ CBS(T,Q)[a,b]	CCSD(T)-F12/ CBS(D,T)[a,b]	**CCSD(T)-F12/ VDZ-F12[b]**	**PBE0[c]**	M06-2X[d]
$C_3H_7C(NO_2)_3 \rightarrow \bullet C_3H_7C(NO_2)_2 + \bullet NO_2$ (R1)[e]			**(44.0)**	**(35.0)**	**(44.0)**
$C_3H_7C(NO_2)_3 \rightarrow C_3H_6=C(NO_2)_2 + HONO$ (R3)[e]			**42.7**	**37.9**	**41.7**
$C_3H_7C(NO_2)_3 \rightarrow C_3H_7C(NO_2)_2ONO$ (R2)[e]			**59.5**	**59.2**	**62.1**
$CH(NO_2)_3 \rightarrow \bullet CH(NO_2)_2 + \bullet NO_2$		(46.5)	**(46.0)**	**(38.9)**	(46.1)
$CH(NO_2)_3 \rightarrow C(NO_2)_2N(O)OH$		50.4	**50.7**	**45.7**	48.7
$CH(NO_2)_3 \rightarrow CH(NO_2)_2ONO$		61.1	**60.5**	**60.6**	62.8
$CH_3CH(NO_2)_2 \rightarrow \bullet CH_3CH(NO_2) + \bullet NO_2$		(48.5)	**(47.8)**	**(41.1)**	(47.4)
$CH_3CH(NO_2)_2 \rightarrow CH_2=CH(NO_2) + HONO$		44.4	**45.0**	**41.3**	43.6
$CH_2(NO_2)_2 \rightarrow \bullet CH_2(NO_2) + \bullet NO_2$	(49.1)	(49.3)	**(48.6)**	**(44.3)**	(48.8)
$CH_2(NO_2)_2 \rightarrow CH(NO_2)N(O)OH$	54.7	54.7	**54.8**	**51.1**	53.2
$CH_3CH_2NO_2 \rightarrow \bullet CH_3CH_2 + \bullet NO_2$ (NE1)	(61.0)	(61.1)	**(60.2)**	**(57.5)**	(62.1)
$CH_3CH_2NO_2 \rightarrow CH_2=CH_2 + HNO_2$ (NE2)	47.4	47.3	**47.8**	**45.6**	47.0

[a] The two-point complete basis set extrapolations (aVTZ:aVQZ and VDZ-F12:VTZ-F12, respectively) were employed. [b] Single point CCSD(T)/aug-cc-pVTZ, CCSD(T)/aug-cc-pVQZ, CCSD(T)-F12b/cc-pVDZ-F12, and CCSD(T)-F12b/cc-pVTZ-F12 energies were calculated using the M06-2X/6-311++G(2df,p) optimized geometry. ZPE and thermal corrections to enthalpy were computed at the same level of theory. [c] PBE0/6-31+G(d,p) level of theory was used. [d] M06-2X/6-311++G(2df,p) level of theory was used. [e] The reactions are named in accordance with ref 1.

Moreover, even higher error to $\Delta^{\neq}G_{298}^0$ is introduced by quantum chemical calculations of $\Delta^{\neq}H_0^0$.[3] As we have previously demonstrated,[4] some DFT functionals remarkably underbind polynitromethanes (e.g., B3LYP lowers D_0(C-NO$_2$) in trinitromethane by ~11 kcal/mol).[4] PBE0 performs similarly and underestimates D_0(C-NO$_2$) in TNB by ~9 kcal/mol in comparison with CCSD(T)-F12 values (cf. the benchmark results in Table 1). More generally, the results of Table 1 indicate poor performance of PBE0 for decomposition and H-transfer reactions of polynitroalkanes.

Thus, the difference between a true $\Delta^{\neq}G_{298}^0$ and reported[1] $\Delta^r G_{298}^0$ of the reaction (R1) is at least ~15 kcal/mol (*ca.* 11 orders of magnitude in k_{TST} at room temperature). At the same time, the $\Delta(\Delta^{\neq}G_{298}^0)$ of the reactions (R1) and (R3) was reported to be 16.4 kcal/mol.[1] However, PBE0 also underestimates the activation barrier of (R3) by ~5 kcal/mol (Table 1) and (R1) most likely remains a dominating primary reaction. The correct conclusion is therefore a result of partial error compensation between the computed activation energies of (R1) and (R3).

On the other hand, PBE0 reproduces well the activation barriers of nitro-nitrite rearrangements (Table 1). Thus, calculations of $\Delta^r H_0^0$ at PBE0 level along with incorrect estimations of $\Delta^{\neq}S_{298}^0$ render branching ratios intrinsically biased towards radical decomposition of nitroalkanes. E.g., the calculated in such manner $\Delta(\Delta^{\neq}G_{298}^0)$ of reactions NE1 and NE2 (Table 1) is less than 1 kcal/mol, while the isokinetic temperature for these channels was estimated to be higher than 600 K.[5]

Note that the M06-2X functional[6] provides reasonable accuracy (Table 1, last column) and can be used for feasible calculations in the case of large nitroaliphatics and nitroaromatics.

Notes and references

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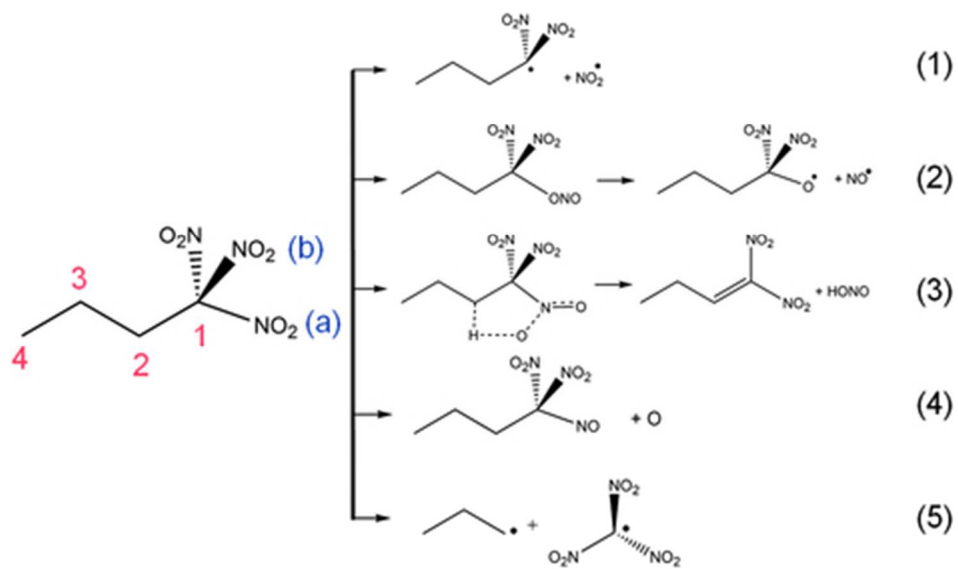
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