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The Stability of Substituted Benzylpentazoles

Xiao-Fang Chen[1,2][1], Jian-Hua Bu[1], Tao Yu[1], Wei-Peng Lai[1], Zhong-Xue Ge[1]

[1] *Xi'an Modern Chemistry Research Institute, 168 Zhangba Road, Xi'an 710065, P. R. China*
[2] *State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China*

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Abstract: Pentazoles have been received increasing attentions in recent several decades. The most stable pentazole synthesized so far only exists for several hours at 0 ºC in methanol. Some *para*-substituted benzylpentazoles were explored in this study. The results elucidated that (4-oxobenzyl)pentazole anion is more stable than (4-oxophenyl)pentazole anion in either gas phase or methanol, while most of benzylpentazoles desiged are approximately ten-to-hundred times more stable than (4-oxophenyl)pentazole anion in methanol.

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Key words: Pentazole, Polynitrogen, Half-life, Decomposition, Kinetics, Density functional theory.

Pentazoles have been received increasing attentions in recent several decades, because of their potential application in forming energetic allogenic nitrogen. They were first successfully prepared by Huisgen and Ugi at -40 ºC in the late 1950s by adding an aqueous solution [1-3]. Nguyen et al [4] estimated that pentazole ion (N_5^-) has an energy barrier of at least 19.0 kcal/mol to decompose to stable N_3^- and N_2. Glukhovtsev et al [5] and Benin et al [6] have predicted that pentazole anion (N_5^-) has a half-life time ($t_{1/2}$) of 2.3 days, while $t_{1/2}$ is only about 10 min for HN_5 in methanol at 0 ºC. Those studies suggested that the half-life time of N_5^- is long enough to isolate. Unfortunately, pentazole ion can only be detected in spectrum

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* Corresponding author. *Email address*: xfchen@dicp.ac.cn Tel: 86-029-88294020

although many experimental efforts were made [7-16]. Both experimental [1-3] and theoretical [17] studies showed that (4-oxophenyl)pentazole anion is the most stable pentazole species known so far. Despite this, it only exists for several hours at 0 ºC in methanol [6].

Whether a pentazole derivative is capable to possess a half-life time of days or longer, it would contribute to its deposit and consequent dealing. Design and synthesize some long-lived pentazole derivatives are desirable. This study would explore some benzylpentazoles (**Figure 1**) at the B3LYP/6-311+G(2df,2p)//6-31+G(d) and PCM-B3LYP/6-31+G(d)//6-31+G(d) levels[18].

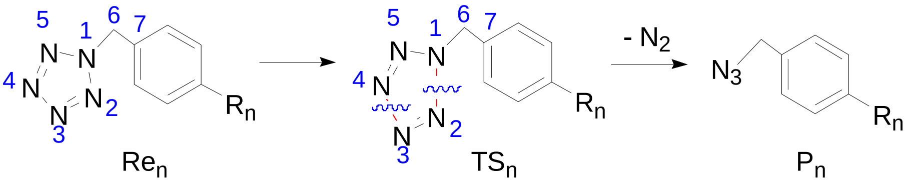


Figure 1: Degradation of benzylpentazoles (R_n = $-O^-$,$-N(CH_3)_2$, $-NHCH_3$, $-NH_2$, $-OCH_3$, -OH, $-CH_3$, and -H (n = 2-9)).

The compound, (4-oxophenyl)pentazole anion was also investigated for comparison and avoiding computational system errors in this study. Benzylpentazoles **2-9** are some pentazole derivatives with electron-donating groups of $-O^-$, $-N(CH_3)_2$, $-NH(CH_3)$, $-NH_2$, $-OCH_3$, -OH, $-CH_3$, and -H in the *para* position of the benzene ring respectively. Among five N-N bonds of pentazole ring, the N2-N3 bond is the shortest while the N3-N4 bond is the longest for benzylpentazoles **2-9**. The differences between the longest and shortest bond lengths were calculated to be 0.038, 0.044, 0.044, 0.044, 0.045, 0.045, 0.045, and 0.046 Å for benzylpentazoles **2-9**, respectively. Among eight benzylpentazoles, (4-oxobenzyl)pentazole anion possesses the largest electronic delocalization in the pentazole ring. However, the bond length difference between the longest and shortest ones was calculated to be 0.021 Å in (4-oxophenyl)pentazole. This allowed us to propose that the electronic delocalization effect of the pentazole ring in benzylpentazoles is less than that in (4-oxobenzyl)pentazole anion. Meanwhile, the N1-C6 bonds calculated are 1.514, 1.479, 1.479, 1.478, 1.476, 1.475, 1.474, and 1.504 Å in benzylpentazoles **2-9**, respectively, larger than the C-N bond (1.411 Å) of (4-oxobenyl)pentazole. This implies that the introduction of the methylene group makes the electronic overlap between the pentazole ring and the benzyl group less and loosens the C-N bond strength.

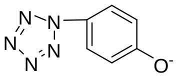
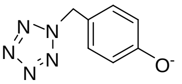
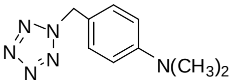
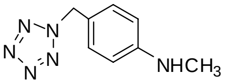
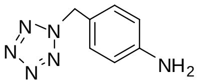
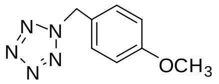
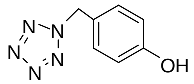
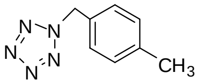
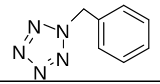
Benzylpentazoles **2-9** release N_2 through synchronous breakage of two N-N bonds readily (**Figure 1**). In transition states TS_2-TS_9, the N2-N3 bonds calculated are 1.173 Å, close to the experimental value (1.098 Å) of the N≡N bond length in nitrogen molecule; the N1-N5 distances calculated range from 1.276 to 1.291 Å, slightly larger than the experimental value (1.216 Å) of the N=N bond length of CH_3N_3, while the distances of N4-N5 were calculated to be 1.205-1.210 Å, in the range of the bond lengths of the double (1.113 Å) and triple (1.216 Å) nitrogen-nitrogen bonds of CH_3N_3 reported in experiments.

In N_2 evolution, benzylpentazoles **2**-**9** need submit activation internal energies ($\Delta E_g^{\neq}$) of 25.24, 22.67, 22.52, 22.51, 22.33, 22.27, 22.17, and 22.04 kcal/mol in gas phase, respectively. The energy decline of $\Delta E_g^{\neq}$ follows the order of substitutents of $-O^-$, $-N(CH_3)_2$, $-NH_2$, $-NH(CH_3)$, $-OCH_3$, -OH, $-CH_3$, and –H. It is well-known that the $-O^-$, $-N(CH_3)_2$, $-NH_2$, and $-NH(CH_3)$ groups are strongly activating groups, the $-OCH_3$ and –OH groups belong to moderately activating groups, and the $-CH_3$ group is weakly activating group. The reactivity of a molecule is opposite to its activation energy. Therefore, the order of degradation almost follows the electron-detonation ability of substituents. This is in line with para-substituted phenylpentazoles[17]. We also obtained that (4-oxyphenyl)pentazole anion is with a $\Delta E_g^{\neq}$ of 24.07 kcal/mol [19], close to the value (24.0 kcal/mol) of Carlqvist et al's[17]. By comparison, (4-oxobenyl)pentazole anion possesses the highest $\Delta E_g^{\neq}$ (25.24 kcal/mol) in those eight benzylpentazoles, which is 1.17 kcal/mol higher than (4-oxophenyl)pentazole anion; while benzylpentazoles **3**-**9** are ~1.40-2.03 kcal/mol lower than that of (4-oxophenyl)pentazole ion. **Table 1** also showed that the activation enthalpies ($\Delta H_g^{\neq 0}$) declines in the same trend as $\Delta E_g^{\neq}$. Only (4-oxobenzyl)pentazole anion is lower than (4-oxophenyl)pentazole anion in the gas activation free energy ($\Delta G_g^{\neq 0}$), contrary to neutral benzylpentazoles **3**-9. But, the $\Delta G_g^{\neq 0}$ decline trend is altered by the entropy effect. The degradation of benzylpentazoles **2**-**9** is all exothermic and the most exothermic benzylpentazole is (4-hydroxylbenzyl)pentazole while the least exothermic one is (4-oxobenzyl)pentazole anion. Overall, they are 4.45-9.96 kcal/mol below (4-oxophenylbenzyl) pentazole anion in $\Delta_r G_g$ in gas phase.

When the solvent effect of methanol being added, solvent activation free energies ($\Delta G_{sol}^{\neq 0}$) have been raised by 1.58-3.75 kcal/mol for these eight benzylpentazoles relative to $\Delta G_g^{\neq 0}$. The polar solvent of methanol slows the degradation of pentazole derivatives down. This is likely caused by the fact that the dipole moments of transition states are larger than the corresponding ground states for neutral benzylpentazoles **3**-**9** (**Table 1**). This brings about the transition states are dissolved more easily than the corresponding ground state in the polar solvent of methanol for pentazoles **3**-**9**, and then the entropy change of transition states is larger than that of ground states. In methanol, the additions of activation free energy are 1.58, 3.51, 3.75, 3.6, 3.54, 3.71, 3.66, and 3.71 kcal/mol for benzylpentazoles **2**-**9**, respectively, while it is only 1.1 kcal/mol for (4-oxophenyl)pentazole ion. As a result, the $\Delta G_{sol}^{\neq 0}$ of eight benzylpentazoles **2**-**9** are 1.21-1.93 kcal/mol higher than that of (4-oxophenyl)pentazole. This leads to the degradation of these eight benzylpentazoles more difficult than (4-oxophenyl)pentazole in methanol. Also, the solvent effect makes the product systems possess higher Gibbs free energies and then the degradation of benzylpentazoles releases much less Gibbs free energies. The nitrogen evolution from benzylpentazoles **3**-**9** is slightly easier than that from (4-oxophenyl)pentazole anion dynamically in methanol under standard condition.

In methanol, the half-life time (t1/2) is 8.76, 3.30, 10.53, 5.33, 2.90, 4.95, 5.33, and 7.02 for benzylpentazoles 2-9 at 0 ºC, respectively. Benzylpentazoles 2-9 are 25.99, 9.79, 31.25, 15.82, 8.61, 14.69, 15.82, and 20.83 times than (4-oxophenyl)pentazole anion in the half-life time within the same system errors.

Table 1: Activation and reaction energies (in kcal/mol), the half-life ($t_{1/2}$) (in days) and dipole moment (Debye) for pentazoles at 273.15 K and 1atm in methanol, as well as imaginary frequencies ($-\nu_i$) (in cm^{-1}) of their transition states.$^{\alpha}$

Index	Species	$\Delta E_g^{\neq}$ ($\Delta_r E_g$)	$\Delta H_g^{\neq 0}$ ($\Delta_r H_g$)	$\Delta G_g^{\neq 0}$ ($\Delta_r G_g$)	$\Delta G_{sol}^{\neq 0}$ ($\Delta_r G_{sol}^{\neq 0}$)	$\Delta\Delta G^{\neq}_{sol}$ $\Delta\Delta_r G_{sol}$	ν_i	$^{\delta}t_{1/2}$	Dipole moment$^{\gamma}$
1		24.07 24.0$^{\beta}$ (-19.99) (-20.0$^{\beta}$)	21.61 21.4$^{\beta}$ (-22.67) (-22.7$^{\beta}$)	20.58 20.8$^{\beta}$ (-33.77) (-34.6$^{\beta}$)	21.74 22.0$^{\beta}$ 21.0$^{\gamma}$ (-35.82) (-37.9$^{\beta}$)	1.16 (-2.05)	(530.6)	0.34 0.54$^{\beta}$ 0.09$^{\gamma}$	8.62 (9.29)
2		25.24 (-24.70)	22.91 (-27.19)	21.93 (-38.24)	23.51 (-36.94)	1.58 (1.30)	(556.9)	8.76	7.25 (5.89)
3		22.67 (-29.59)	20.32 (-32.07)	19.47 (-42.90)	22.98 (-37.79)	3.51 (5.11)	(552.1)	3.30	7.53 (5.11)
4		22.51 (-29.78)	20.24 (-32.20)	19.86 (-42.87)	23.61 (-37.50)	3.75 (5.37)	(552.2)	10.53	7.38 (5.83)
5		22.52 (-29.84)	20.21 (-32.28)	19.62 (-43.12)	23.34 (-37.78)	3.72 (5.34)	(551.7)	5.33	6.21 (5.01)
6		22.33 (-30.04)	20.02 (-31.26)	19.37 (-41.43)	22.91 (-36.15)	3.54 (5.28)	(551.3)	2.90	5.72 (3.99)
7		22.27 (-30.21)	19.99 (-32.66)	19.49 (-43.47)	23.20 (-38.05)	3.71 (5.42)	(551.6)	4.95	5.86 (4.32)
8		22.17 (-30.31)	19.90 (-32.74)	19.58 (-43.48)	23.24 (-38.14)	3.66 (5.34)	(550.6)	5.33	5.49 (4.10)
9		22.04 (-30.55)	19.76 (-32.96)	19.68 (-43.35)	23.39 (-37.93)	3.71 (5.42)	(550.1)	7.02	3.26 (4.50)

$^{\alpha}$Energies of TS relative to respective *para*-substituted arylpentazoles, estimated at the B3LYP/6-311+G(2df,2p) level. Geometries optimized at the B3LYP/6-31+G(d) level with thermal corrections to the energy calculated at the same level. Definitions of the energies: $\Delta E^{\neq}$: internal energy. $\Delta H_g^{\neq o} = \Delta E^{\neq} + \Delta H_g$, ΔH_g is the enthalpy correction. $\Delta G_g^{\neq o} = \Delta E^{\neq} + \Delta G_g$, ΔG_g is the free energy correction. ΔH_g and ΔG_g are calculated at 273.15 K and 1 atm. $\Delta G_{sol}^{\neq o} = \Delta G_g^{\neq o} + \Delta\Delta G^{\neq}_{sol}$, $\Delta\Delta G^{\neq}_{sol}$ is PCM solvation free energy correction.

$^{\beta}$Values reported by Carlqvist et al's theoretical study.

$^{\gamma}$Values estimated from reaction rates in methanol at 273.15 K in Huisgen et al's experiments.

$^{\delta}$Half-life time of the degradation of pentazole derivatives estimated by using our results.

[γ] Values in parenthesis are dipole moments for transition states.

In summary, the computation results indicated that benzylpentazole derivatives exist as stable species, and the decline of both $\Delta E_g^{\neq 0}$ and $\Delta H_g^{\neq 0}$ in their degradation follow the order of the electron-detonation ability of substituents. While the decline trend of $\Delta G_g^{\neq 0}$ is altered by the entropy effect. For neutral pentazoles, the transition states are polar than the ground states. But, this trend becomes reverse in the case of anionic pentazole derivatives. The polarity difference between transition states and ground states contributes to accounting for the computational results that the solvation free energy correction of neutral benzylpentazoles is higher than that of anionic pentazoles. Most of benzylpentazoles in this study are approximately ten-to-hundred times more stable than (4-oxophenyl)pentazole anion in methanol under standard condition.

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