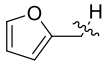
附录

Appendix

附表 1 一些共价键的键解离能

Annexed Table 1 The BDEs of some covalent bonds

No.	Substance	BDEs kJ/mol
1	PhO-H	368.2
2	Ph-OCH_3	416.7
3	Ph-Ph	478.6
4	CH_3-C_2H_3	426.3
5	Ph-H	472.2
6	$PhCH=CH_2$	688.3
7	$CH_2=CH_2$	728.4
8		361.9

附表 2 自由基诱导共价键的有效作用物理空间距离

Annexed Table 2 The effective physical-spatial distance of bonds induced by free radicals

	CH_3	**OH**	**H**		**CH_3**	**OH**	**H**
		Å				**Å**	
C_{al}-C_{al} Bond							
CH_3-CH_3				CH_3-C_2H_5			
X-B	3.9	3.7	3.3		3.9	3.7	3.3
X-A	1.9	1.8	1.4		1.9	1.8	1.4
A-B	1.9	2.0	1.8		1.9	1.9	1.8
CH_3-CH_2Ph				CH_3-$CH_2CH=CH_2$			
X-B	3.9	3.8	3.3		3.9	3.8	3.3
X-A	2.0	1.8	1.5		2.0	1.9	1.5
A-B	1.9	1.9	1.8		1.9	1.9	1.8
CH_3-CH_2OH				$HOCH_2$-C_2H_5			
X-B	3.9	3.7	3.3		3.9	3.8	3.3
X-A	2.0	1.8	1.4		2.0	1.8	1.4
A-B	1.9	1.9	1.8		2.0	2.0	1.9
$HOCH_2$-CH_2OH				CH_3-CH_2OCH_3			
X-B	3.8	3.7	3.2		3.8	3.8	3.2
X-A	1.9	1.8	1.4		1.9	1.8	1.4
A-B	1.9	1.9	1.8		1.9	1.9	1.8

续附表 2

Continued to Annexed Table 2

	-CH_3	-OH	-H		-CH_3	-OH	-H
		Å				Å	
C_{al}-C_{ar} Bond							
C_2H_5-C_2H_3				CH_3-Ph			
X-B	3.8	3.7	3.2		3.8	3.7	3.2
X-A	1.9	1.8	1.4		1.9	1.8	1.4
A-B	1.9	1.9	1.8		1.9	1.9	1.8
C_2H_5-Ph				nC_3H_7-Ph			
X-B	3.8	3.7	3.2		3.8	3.7	3.2
X-A	1.9	1.8	1.4		1.9	1.8	1.4
A-B	1.9	1.9	1.8		1.9	1.9	1.8
$HOCH_2$-Ph							
X-B	3.8	3.6	3.2				
X-A	1.9	1.8	1.3				
A-B	1.9	1.9	1.8				
C_{al}-H Bond							
H-CH_3				H-C_2H_5			
X-B	2.7	2.5	2.3		2.7	2.5	2.3
X-A	1.3	1.3	0.9		1.4	1.4	0.9
A-B	1.3	1.2	1.4		1.3	1.2	1.3
H-$CH_2C_2H_5$				H-CH_2-cyclopropane			
X-B	2.7	2.5	2.3		2.7	2.5	2.3
X-A	1.4	1.4	0.9		1.4	1.4	0.9
A-B	1.3	1.2	1.3		1.3	1.2	1.3
cyclobutene				cyclopentane			
X-B	2.7	2.6	2.3		2.7	2.6	2.3
X-A	1.4	1.4	1.0		1.4	1.5	1.0
A-B	1.3	1.2	1.3		1.3	1.2	1.3
cyclohexane				H-CH_2OH			
X-B	2.7	2.6	2.3		2.7	2.6	2.3
X-A	1.4	1.4	1.0		1.4	1.5	1.0
A-B	1.3	1.2	1.3		1.3	1.2	1.3

续附表 2

Continued to Annexed Table 2

	-CH_3	**-OH**	**-H**		**-CH_3**	**-OH**	**-H**
		Å				**Å**	
C_{al}-H Bond							
H-$CH_2CH=CH_2$							
X-B	2.7	2.6	2.3				
X-A	1.4	1.4	1.1				
A-B	1.3	1.2	1.2				
C_{ar}-H Bond							
H-$CH=CH_2$				H-$CH=CHCH_3$			
X-B	2.7	2.5	2.3		2.7	2.5	2.3
X-A	1.3	1.3	0.9		1.3	1.3	0.9
A-B	1.4	1.2	1.4		1.4	1.2	1.4
H-Ph				H-$C(OH)=CH_2$			
X-B	2.7	2.5	2.3		2.7	2.4	2.3
X-A	1.3	1.2	0.9		1.3	1.3	0.9
A-B	1.4	1.2	1.4		1.3	1.2	1.4
(naphthalene-αH)				(naphthalene-βH)			
X-B	2.7	2.5	2.3		2.7	2.5	2.3
X-A	1.3	1.3	0.9		1.3	1.2	0.9
A-B	1.4	1.2	1.4		1.4	1.2	1.4
C_{al}-O Bond							
HO-CH_3				HO-C_2H_5			
X-B	3.6	3.6	2.9		3.6	3.7	2.9
X-A	1.8	1.6	1.3		1.8	1.6	1.3
A-B	1.8	2.0	1.7		1.8	2.1	1.7
HO-$CH_2C_2H_5$				HO-CH_2CH_2OH			
X-B	3.6	3.7	2.9		3.6	3.7	2.9
X-A	1.8	1.6	1.3		1.8	1.6	1.3
A-B	1.8	2.1	1.7		1.8	2.0	1.7
HO-CH_2Ph				CH_3-OCH_3			
X-B	3.6	3.6	2.9		3.7	3.5	3.1
X-A	1.9	1.7	1.3		2.0	1.8	1.4
A-B	1.8	2.0	1.7		1.8	1.8	1.7

续附表 2

Continued to Annexed Table 2

	CH_3	**OH**	**H**		**CH_3**	**OH**	**H**
		Å				**Å**	
C_{al}-O Bond							
C_2H_5-OC_2H_5				CH_3-OC_2H_5			
X-B	3.8	3.5	3.1		3.8	3.5	3.1
X-A	2.0	1.8	1.4		2.0	1.8	1.5
A-B	1.8	1.8	1.7		1.8	1.8	1.7
CH_3-OPh				C_3H_7-OC_2H_3			
X-B	3.8	3.7	3.2		3.9	3.7	3.2
X-A	2.0	1.9	1.5		2.0	1.9	1.5
A-B	1.8	1.8	1.7		1.8	1.8	1.7
C_{ar}-O Bond							
HO-Ph				C_3H_7O-C_2H_3			
X-B	3.5	3.6	2.8		2.7	3.5	2.2
X-A	1.8	1.6	1.2		1.6	1.6	1.1
A-B	1.8	2.0	1.7		1.5	2.0	1.5
CH_3O-Ph				C_2H_5O-Ph			
X-B	2.8	3.5	2.3		2.8	3.5	2.3
X-A	1.7	1.6	1.1		1.7	1.6	1.1
A-B	1.5	2.0	1.5		1.5	2.0	1.5
O-H Bond							
H-OCH_3				H-OC_2H_5			
X-B	2.5	2.2	2.1		2.5	2.2	2.1
X-A	1.3	1.3	0.9		1.3	1.3	0.9
A-B	1.2	1.1	1.2		1.2	1.1	1.2
H-$OCH_2C_2H_5$				H-$OCH(CH_3)_2$			
X-B	2.5	2.2	2.1		2.5	2.2	2.1
X-A	1.3	1.3	0.9		1.3	1.3	0.9
A-B	1.2	1.1	1.2		1.2	1.1	1.2
H-OPh				H-OCH_2Ph			
X-B	2.5	2.3	2.1		2.5	2.3	2.1
X-A	1.4	1.4	1.0		1.3	1.3	0.9
A-B	1.2	1.0	1.1		1.2	1.1	1.2

续附表 2

Continued to Annexed Table 2

	·CH_3	·OH	·H	·CH_3	·OH	·H
		Å			Å	
O-H Bond						
H-OPhOH(p)				H-OPhCH_3(p)		
X-B	2.5	2.4	2.2	2.5	2.4	2.1
X-A	1.4	1.6	1.1	1.4	1.4	1.1
A-B	1.1	1.0	1.1	1.1	1.0	1.1

附表 3. 自由基诱导共价键的有效作用物理空间平均距离

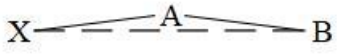
Annexed Table 3 The mean physical-spatial distance of bonds induced by free radicals

	·CH_3	·OH	·H	·CH_3	·OH	·H
		Å			Å	
C_{al}-C_{al} Bond				**C_{al}-C_{ar} Bond**		
X-B	3.9	3.7	3.3	X-B	3.8	3.7	3.2
X-A	1.9	1.8	1.4	X-A	1.9	1.8	1.4
A-B	1.9	2.0	1.8	A-B	1.9	1.9	1.8
C_{al}-H Bond				**C_{ar}-H Bond**		
X-B	2.7	2.5	2.3	X-B	2.7	2.5	2.3
X-A	1.4	1.4	1.0	X-A	1.3	1.3	0.9
A-B	1.3	1.2	1.3	A-B	1.4	1.2	1.4
C_{al}-O Bond				**C_{ar}-O Bond**		
X-B	3.6	3.6	2.9	X-B	3.0	3.5	2.3
X-A	1.8	1.6	1.3	X-A	1.7	1.6	1.1
A-B	1.8	2.0	1.7	A-B	1.5	2.0	1.5
O-H Bond				**C_{ar}-O Bond (HO-Ph)**		
X-B	2.5	2.3	2.1	X-B	3.5	3.6	2.8
X-A	1.3	1.3	0.9	X-A	1.8	1.6	1.2
A-B	1.2	1.1	1.2	A-B	1.8	2.0	1.7

附表 4. 自由基诱导共价键的有效作用物理空间范围

Annexed Table 4 The range of the effective physical-spatial distance of bonds induced by free radicals

	·CH_3	·OH	·H
		Å	
X-B	2.5~3.9	2.3~3.7	2.1~3.3
X-A	1.3~1.9	1.3~1.8	0.9~1.4
A-B	1.2~1.9	1.1~2.0	1.2~1.8

如右图所示， 

，X 为自由基中诱导原子，A 为被诱导原子，B 为反应后将成为自由基产物的、与 A 直接相连的原子。以 X-B、X-A 和 A-B 的距离来描述“各类自由基有效作用的物理空间距离”，相关数据列于附表 2~3。附表 4 汇总了各类自由基有效作用的物理空间范围。

由附表 2 可知，确实存在自由基移动范围对诱导过程的影响；可以发现，自由基和共价键种类一定下，X-A 的距离与 X-B 的距离近似为 X-B 的距离，这说明，自由基中原子 X 近乎沿着 X-A-B 键角呈 180°的方向去诱导 A-B 键断裂。根据附表 3 可知，距离空间位阻可按共价键种类分为以下五种：C-C 键、C-H 键、C_{al}-O 键、C_{ar}-O 键和 O-H 键，例如，相同自由基诱导 C_{al}-C_{al} 和 C_{ar}-C_{ar} 键的有效作用物理空间平均距离 X-B、X-A、A-B 近乎相同。