Теоретические основы органической химии

Типы механизмов электрофильного ароматического замещения. Нитрование.

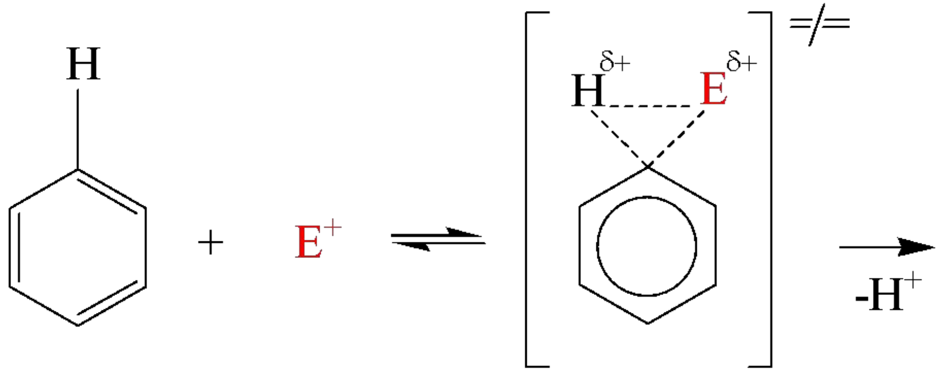
Лекция 28

(электронно-лекционный курс)

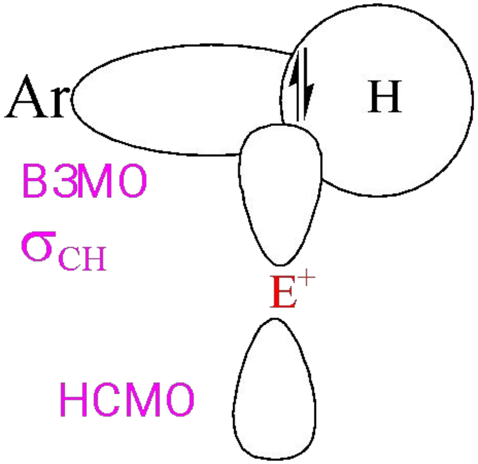
Проф. Бородкин Г.И.

Типы механизмов электрофильного ароматического замещения

1. Одностадийное бимолекулярное замещение

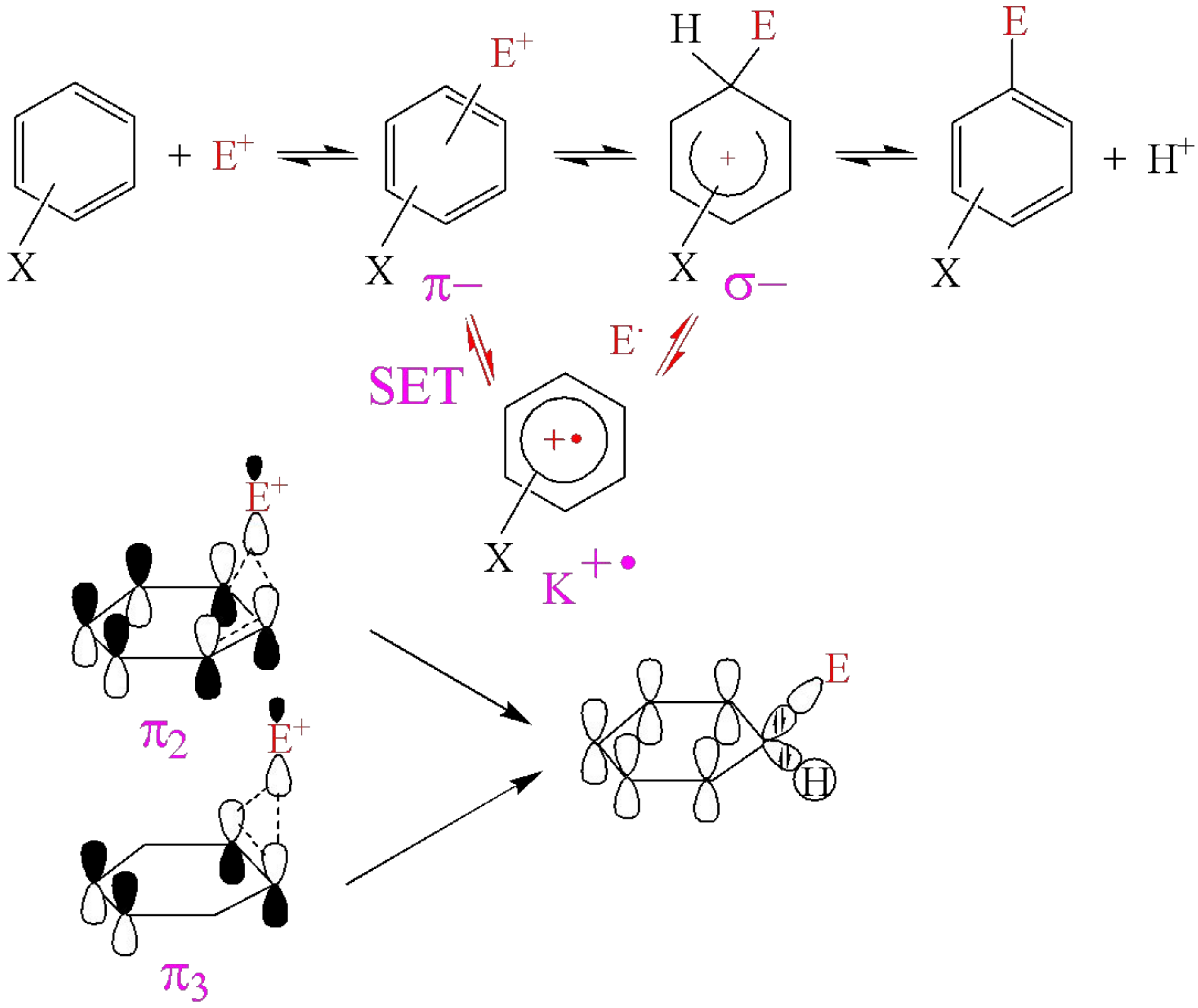


A

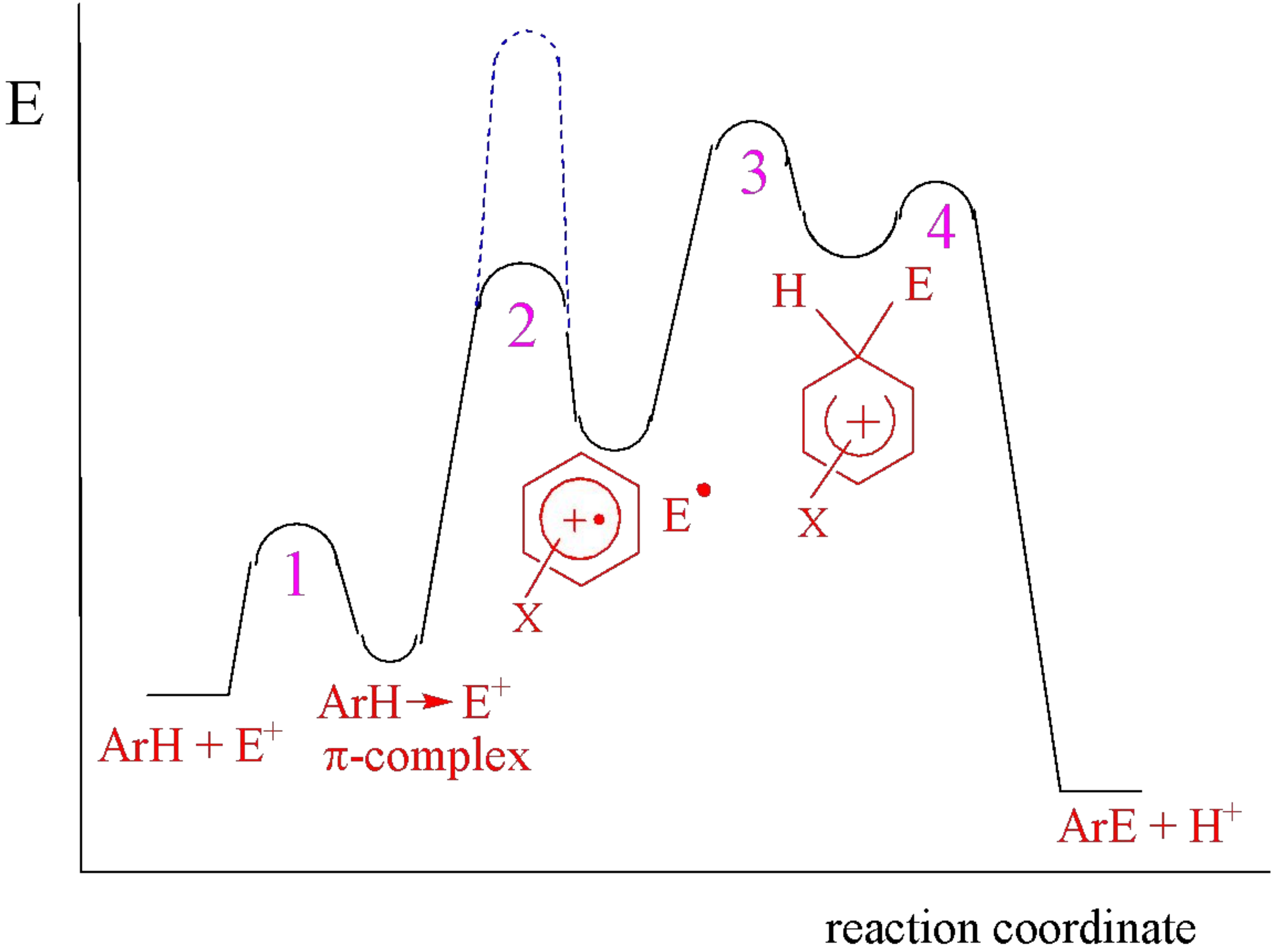


1) ПХ – ароматическое
2) КИЭ

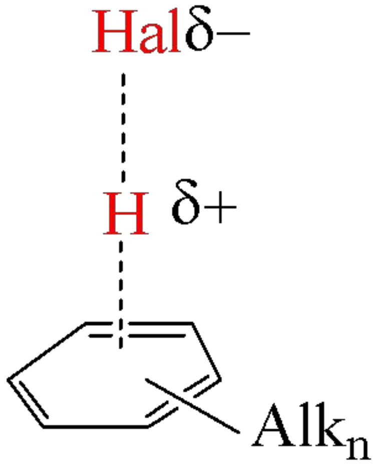
2. Обобщенный механизм S_E



Обобщенный механизм S_E



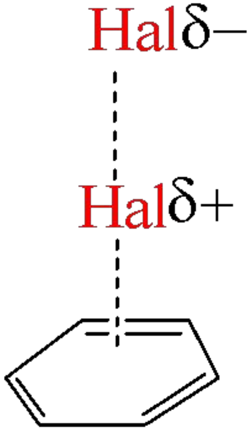
π-Комплексы



Hal = Cl, Br

-78°, гептан,

Г. Браун, 1952 г.

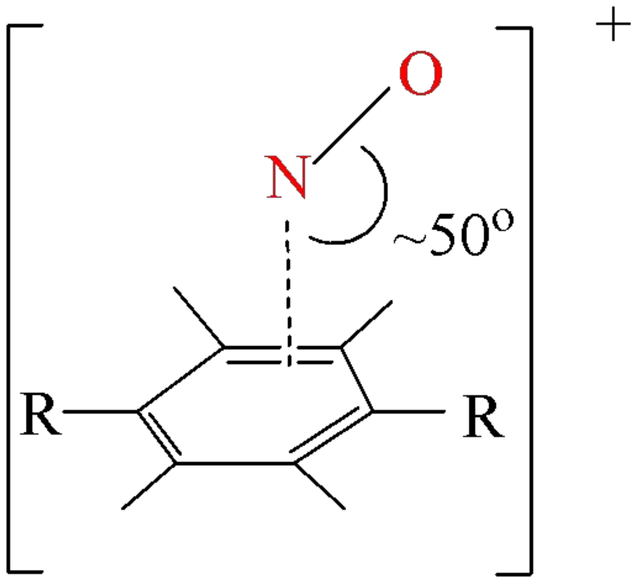


Hal = Cl, Br

X-ray

C_6

O. Hassel, Acta. Chem. Scand., **1958,** 1146



R = H, Me

2η, 3η (X-ray)

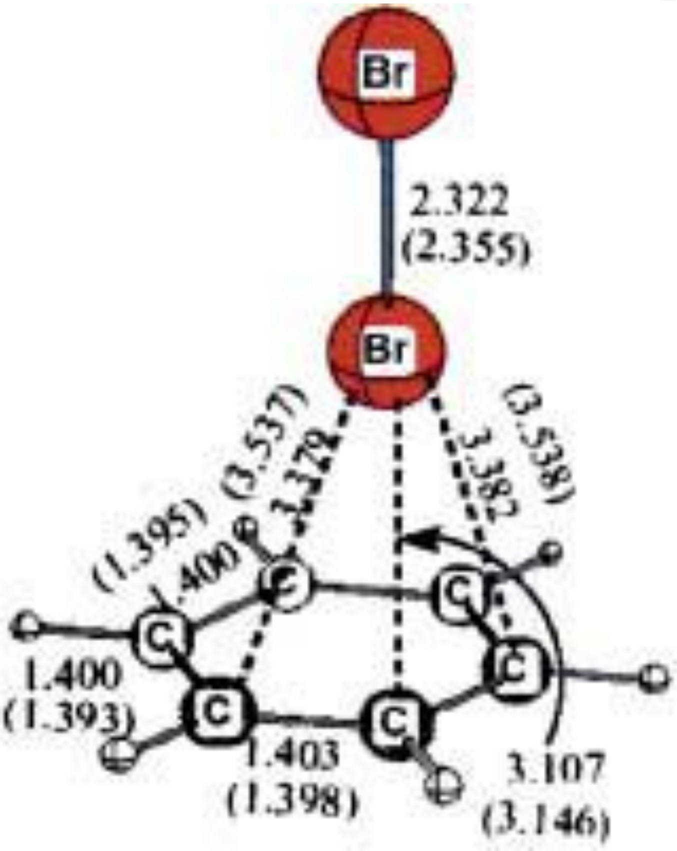
S. Brownstein et al. Can. J. Chem., 1986

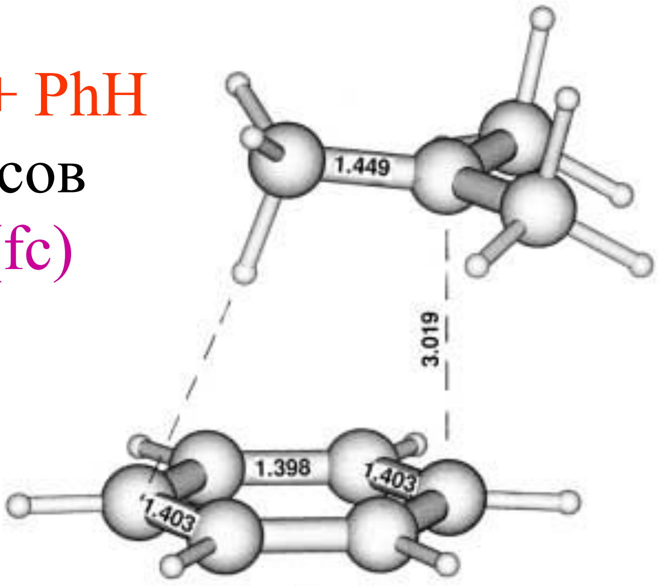
Г.И. Бородкин и др. ДАН, 1986

H^+, Me^+, i-Pr^+ + PhH

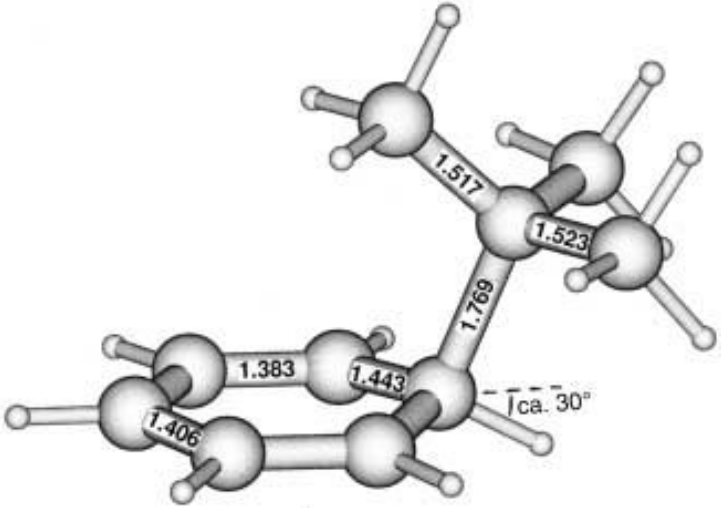
нет π-комплексов

MP2/6-31+G**(fc)



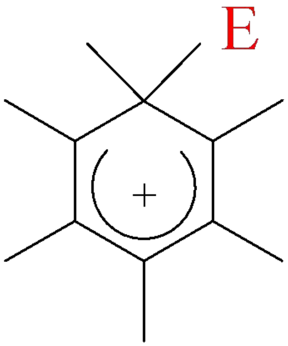


3



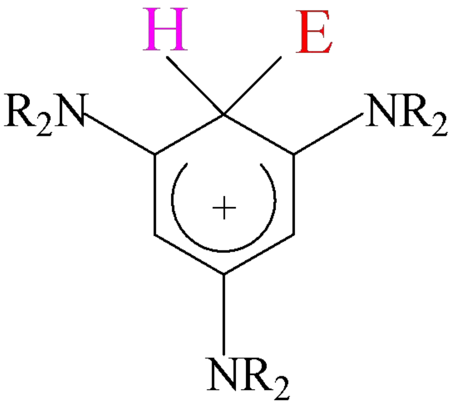
4

σ-Комплексы



E = H, Me, Et, CH_2Ph, CH_2Cl, Cl, Br, NO_2, SPh, SO_3H и др.

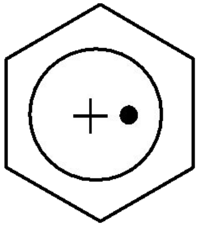
В.А. Коптюг и др. 1966 -1976 гг.



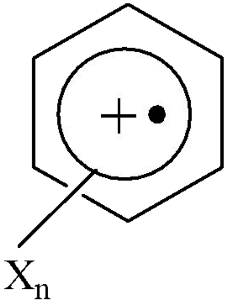
E = Me, Et, Cl, Br

Tetrah. Lett., **1968**, 4265;
Ang. Chem., **1972**, 954

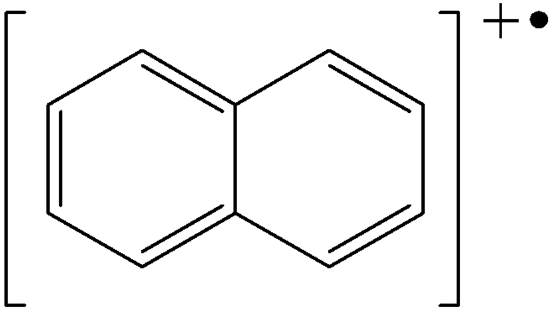
Катион-радикалы



$g = 2.00242$
$a_H = 0.444 mT$



X = Alk



Нитрование

$$ArH + HONO_2 \longrightarrow ArNO_2 + H_2O$$

Нитрующие реагенты, среда:

1. HNO_3
   $HNO_3 + H_2SO_4$
   HNO_3 ($MeNO_2$, $MeCOOH$ и др.)

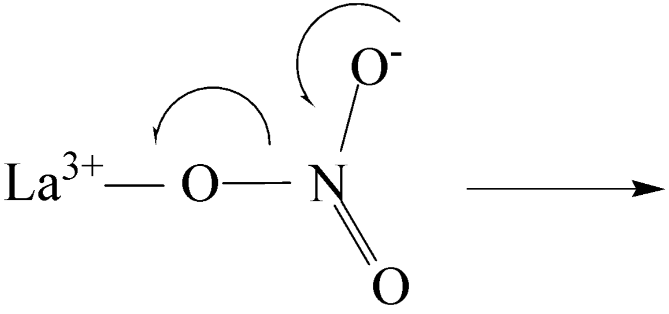
$$HNO_3 + 2\,H^+ \longrightarrow H_3O^+ + NO_2^+$$

2. $NO_2^+BF_4^-$, $NO_2^+PF_6^-$ (сульфолан, MeCN и др)

3. $(CF_3CO)_2O + M^+ NO_3^- \longrightarrow (CF_3COONO_2)$

$(CHCl_3, CH_2Cl_2)$ J. V. Crivello et al. *J. Org. Chem.*, **46**, 3056 (1981)

4. $Yb(O_3SCF_3)_3, Sc(O_3SCF_3)_3 + M^+ NO_3^-$



$\longrightarrow [O{=}N{=}O]^+$

F. J. Walker et al. *Chem. Commun.*,613 (1997).

A. Kawada et al. *Chem. Pharm. Bull.*, **50**, 1060 (2002)

5. $NO_2 + O_3 \longrightarrow NO_3 + O_2$

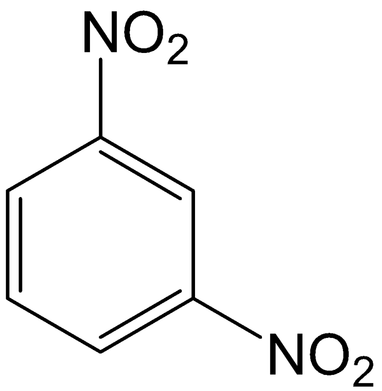
$ArH + NO_3 \longrightarrow [ArH]^{+\cdot} + NO_3^-$

$NO_2 + [ArH]^{+\cdot} \longrightarrow [ArHNO_2]^+ \longrightarrow ArNO_2 + H^+$

H. Suzuki and T. Mori, *J. Chem. Soc., Perkin Trans. 2*, 677 (1996)

1904 г. Мартинсон

$PhNO_2 + HNO_3 + H_2SO_4 \longrightarrow$



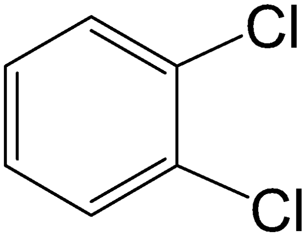
$W = k\,[PhNO_2]\,[HNO_3]$

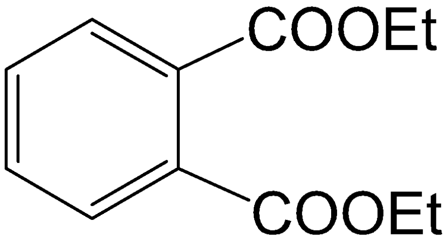
PhCOOH, $PhSO_3H$ и др.

40 – 50 гг. Ингольд с сотр.

HNO_3 (изб.)/MeCOOH

W = k[ArH] для





W = const для PhH, PhAlk, PhOH

$$HNO_3 \underset{b}{\overset{a}{\rightleftarrows}} X$$ X истинный нитрующий агент

$$ArH + X \xrightarrow{c} ArNO_2$$

$$[X] = K_p [HNO_3]$$

1) Если $w_c << w_a$, тогда

$$w = k_c[ArH]\,[X] = k_c K_p\,[ArH]\,[HNO_3] = const\,[ArH]$$

2) Если $w_c >> w_a$, тогда

$$[X] = K_p\,[HNO_3]$$

$$w = const\,[HNO_3] = const$$

Природа X (варианты)

1) $HNO_3 + H^+ \longrightarrow H_2NO_3^+$

Перенос протона – быстрая реакция,1-ая стадия (a/b) не может быть лимитирующей

2) $HNO_3 + H_2O \rightleftarrows H_3O^+ + NO_3^-$

Добавка $K^+NO_3^-$ замедляет реакцию

3) NO_2^+ - истинный нитрующий агент

$$HNO_3 + 2\,H_2SO_4 \rightleftarrows NO_2^+ + H_3O^+ + 2HSO_4^-$$

в к. H_2SO_4 100%

в HNO_3 1%

В спектре КР:

1400 cm^{-1},

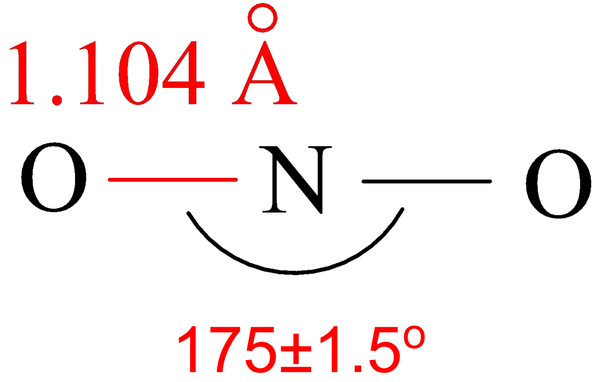
2370 cm^{-1}

1050 cm^{-1}

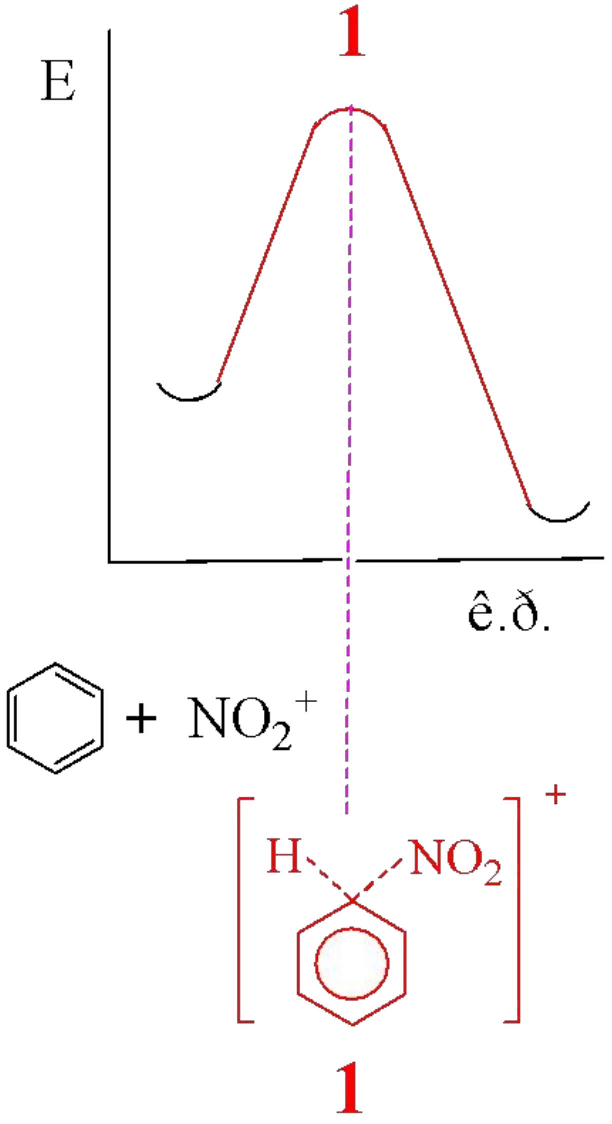
NO_2^+

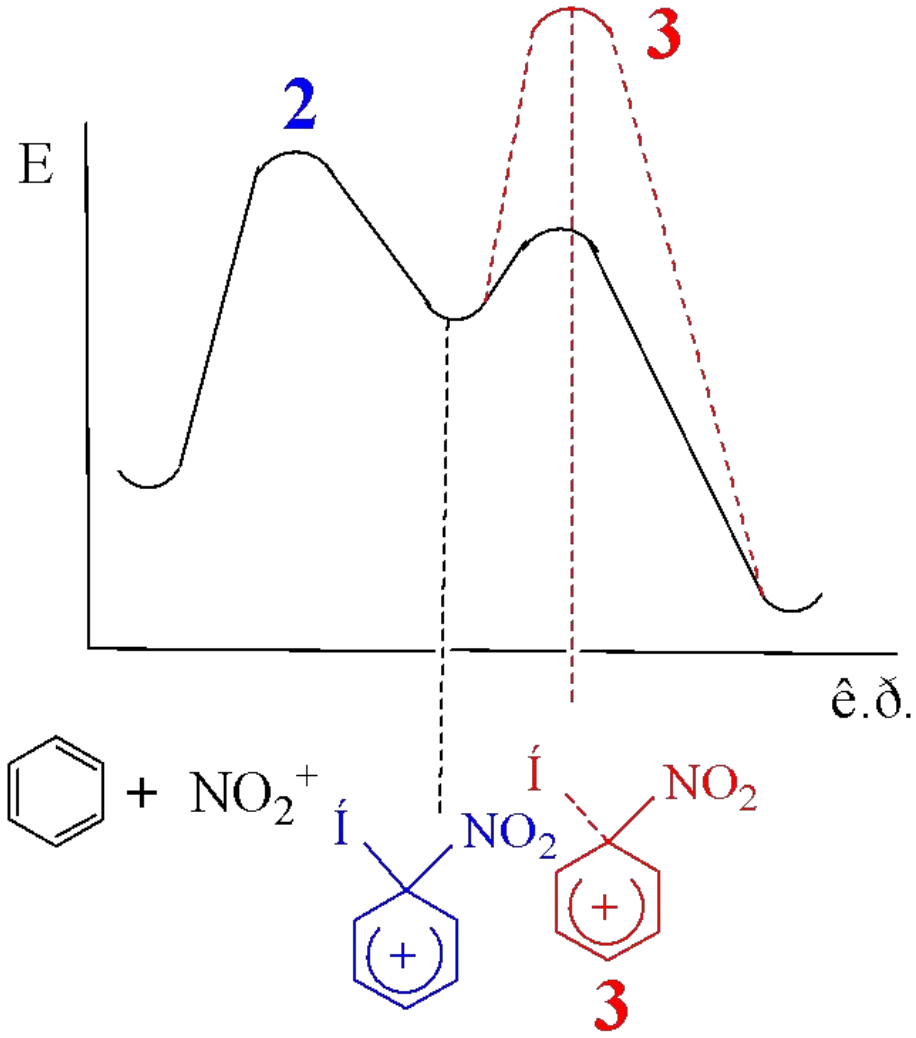
HSO_4^-

РСА:



ClO_4^-

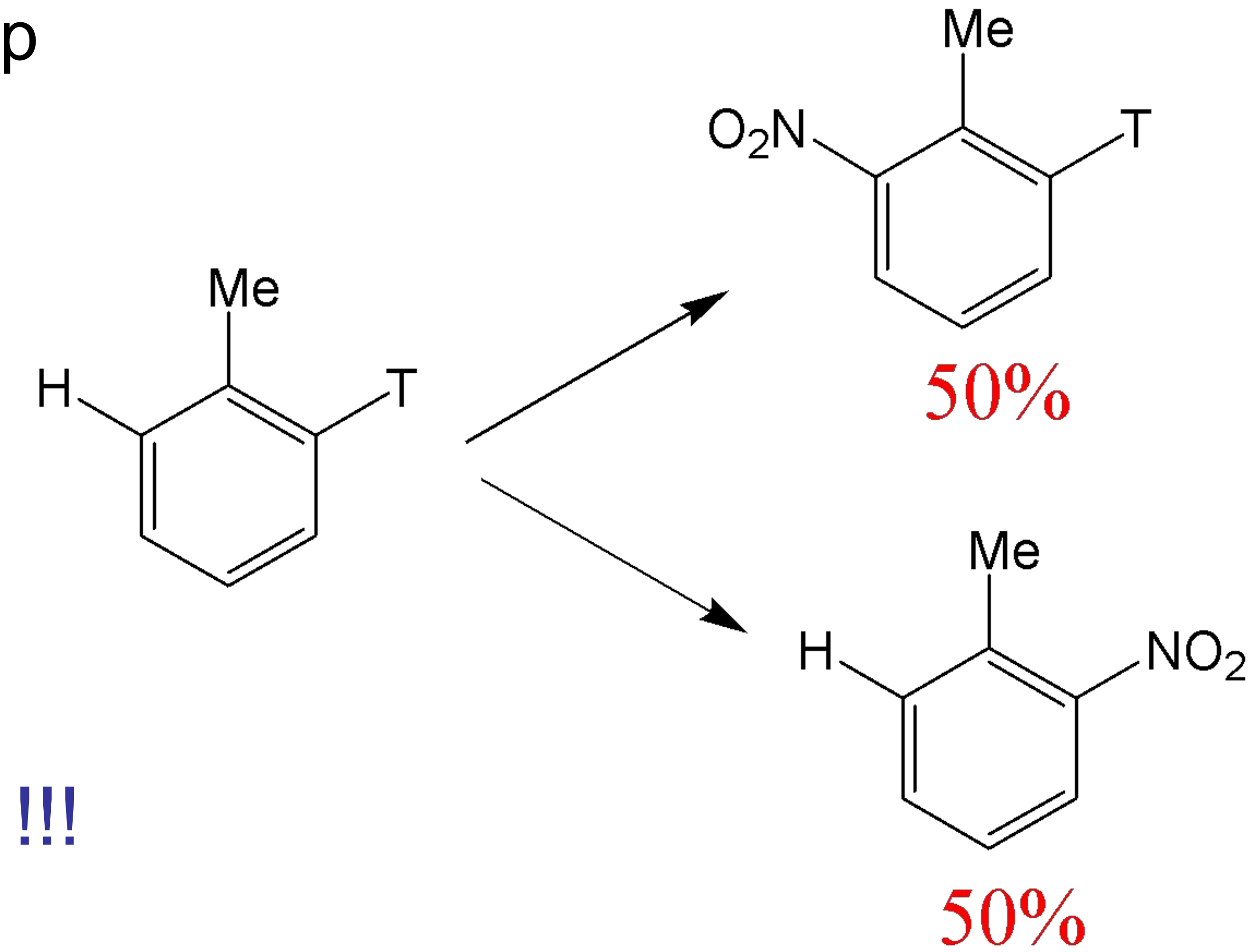




Варианты 1, 3: $k_H/k_D > 1$

Вариант 2: $k_H/k_D = 1$

Меландер



КИЭ нет !!!

Реакция протекает ступенчато по варианту 2

История SET в S_E

Pfeiffer P., Wizinger R., 1928 г.: предположили участие катион-радикалов в нитровании

Kenner J., Weiss J., 1945 г.:

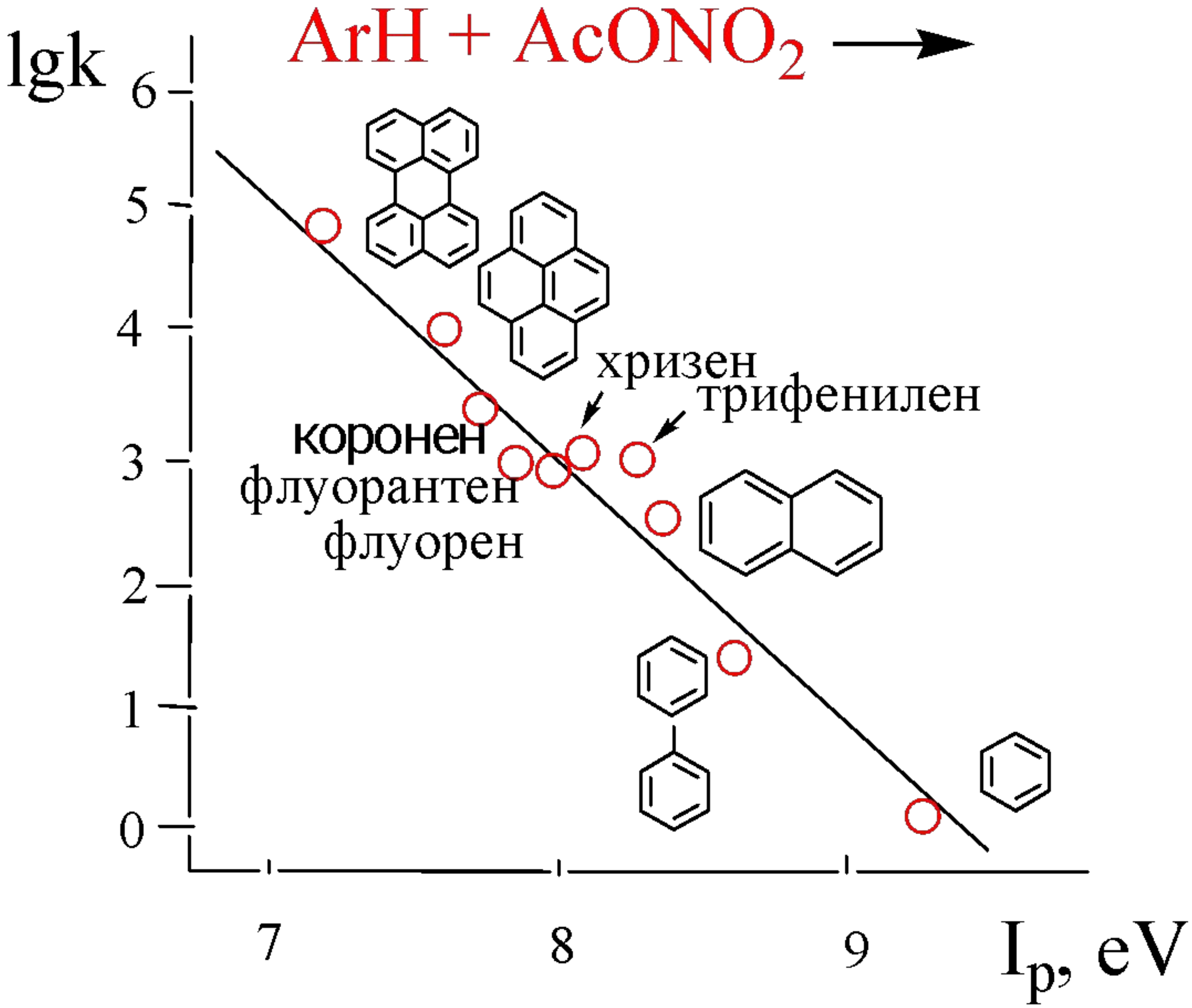
$$ArH + NO_2^+ \longrightarrow ArH^{+\bullet} + NO_2$$

$$ArH^{+\bullet} + HSO_4^- \longrightarrow Ar^{\bullet} \xrightarrow{NO_2} ArNO_2$$

Nagakura S., Tanaka J., 1954, 1959,1963 гг.:

Газ: NO_2^+ (-11.0 eV), I^+ (-10.4 eV). Br^+ (-11.8 eV)
PhH (-9.24 eV)

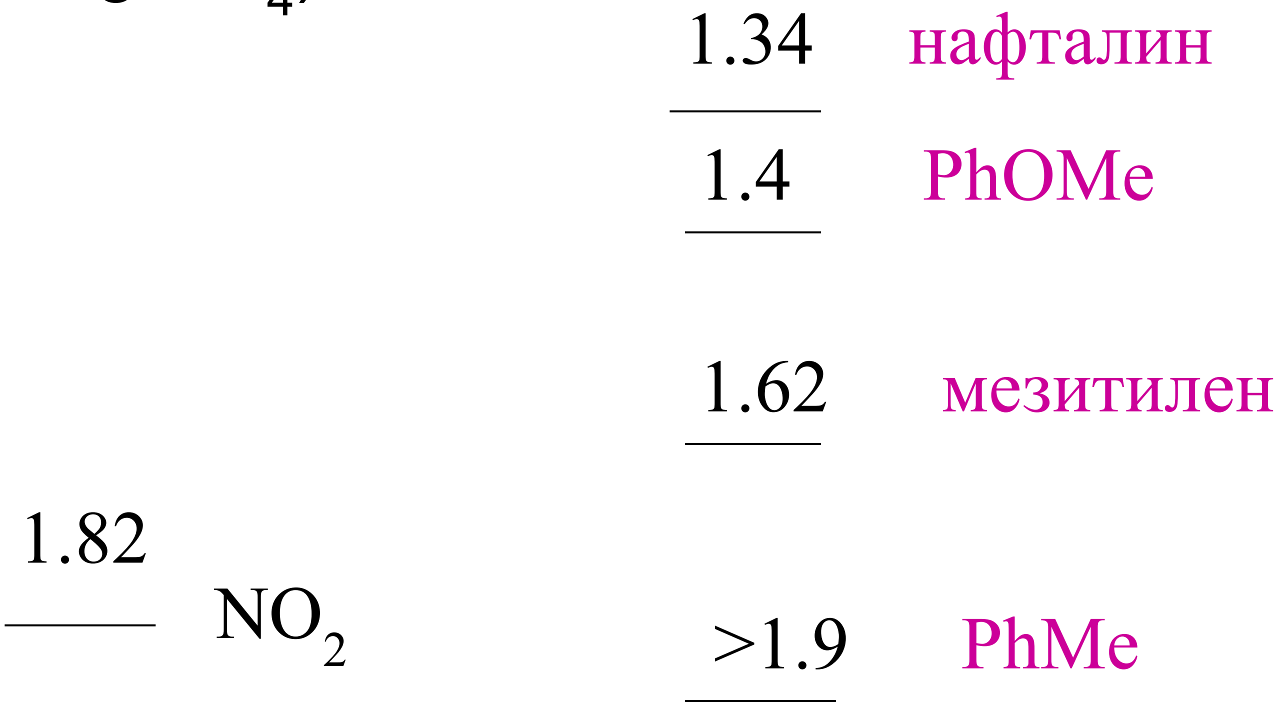
Pederson et al., *T.L.*,**1973**, 579



$ArH + AcONO_2 \rightarrow$

Энергетика SET в нитровании

Анодные потенциалы (MeCN, Ag [0.01 M $AgClO_4$), V



1.34 нафталин

1.4 PhOMe

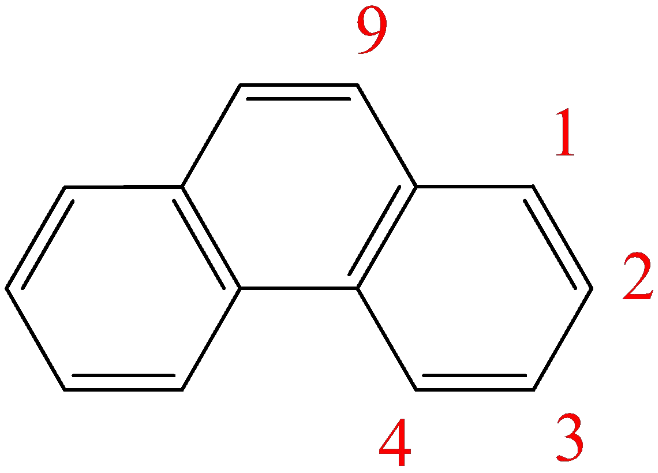
1.62 мезитилен

1.82 NO_2

>1.9 PhMe

C.L. Perrin, *J. Am. Chem. Soc.* **1977,** 5516

Позиционная селективность в нитровании:



9 > 1 > 3 >> 2 > 4

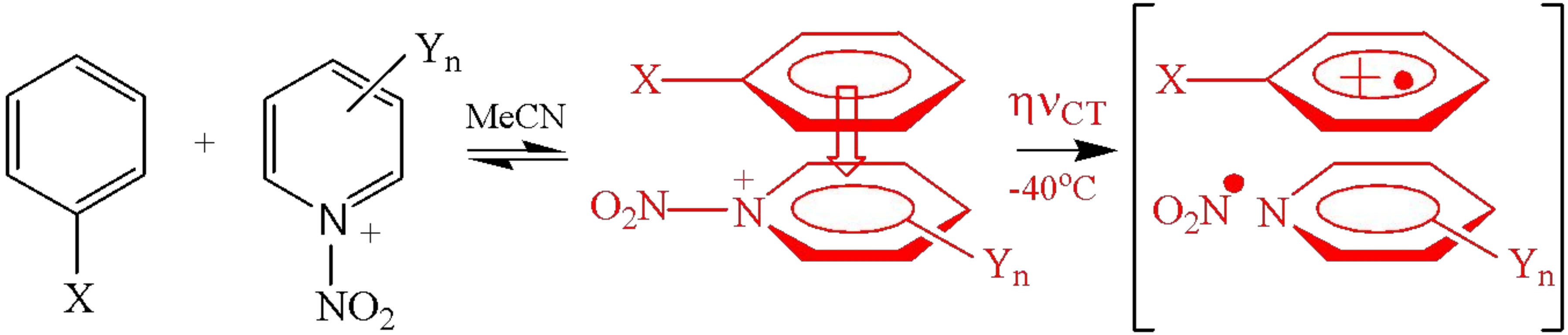
энергия локализации по Дьюару:
9 > 1 > 4 >> 3 > 2

спиновая плотность, ВЗМО:

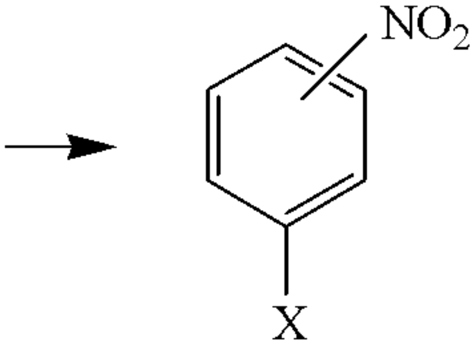
9 > 1 > 3 > 4 > 2

Аналогично,
трифинилен

Фотоактивация СТ-комплексов в нитровании



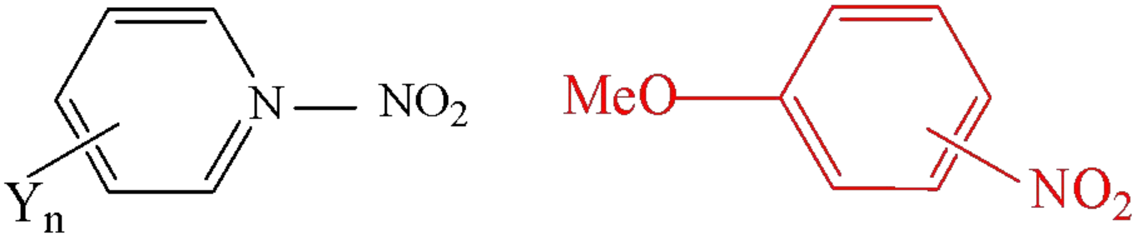
X = Me, MeO, t-Bu и др.



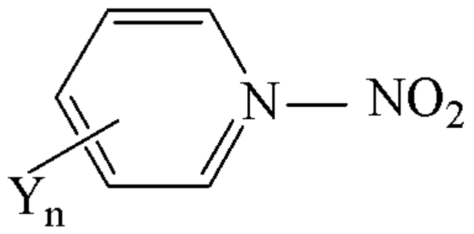
λ_{CT} ~ 400 nm,

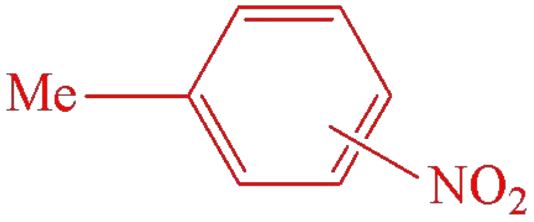
УФ-фильтр 350 - 580 nm, лазер 30-ps

J.K. Kochi et al. *J. Am. Chem. Soc.* **1993**, 3091



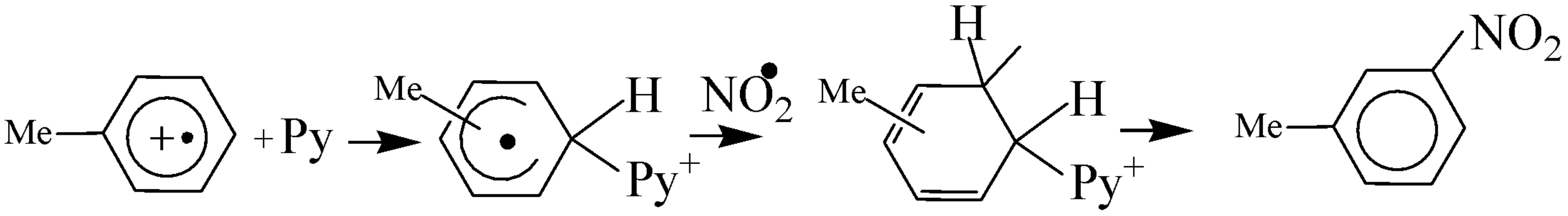
Y		орто-	пара-	t,°C /h
H	350nm	51	49	-30/6
4-Me	350nm	51	49	10/9
4-MeO	350nm	41	56	-40/7
2,6-Me$_2$	400nm	65	35	-40/35
4-MeO	dark	69	31	60/21



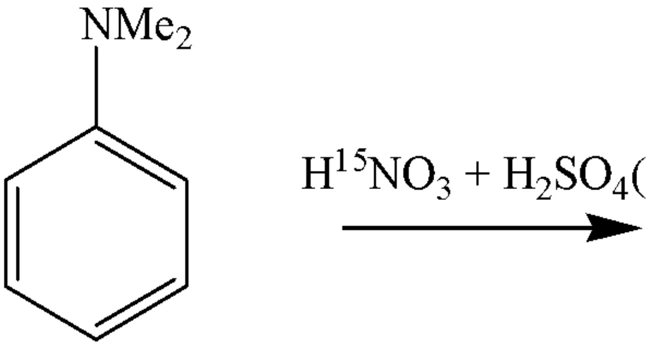


Y		%, орто-	мета-	пара-	t,°C/h
H	380nm	24	60	16	-20/1
4-Me	350nm	23	54	23	23/21
4-MeO	350nm	20	43	37	-65/40
4-MeO	380nm[a]	66	5	28	-40/17
2,6-Me_2	410nm	70	2	28	-40/16

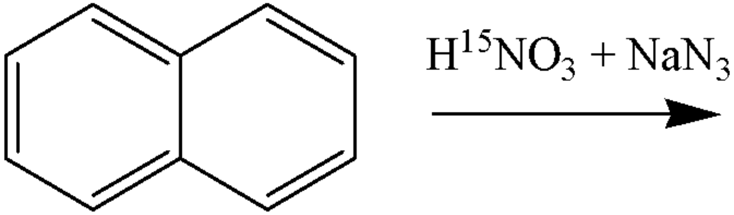
[a] Избыток NO_2



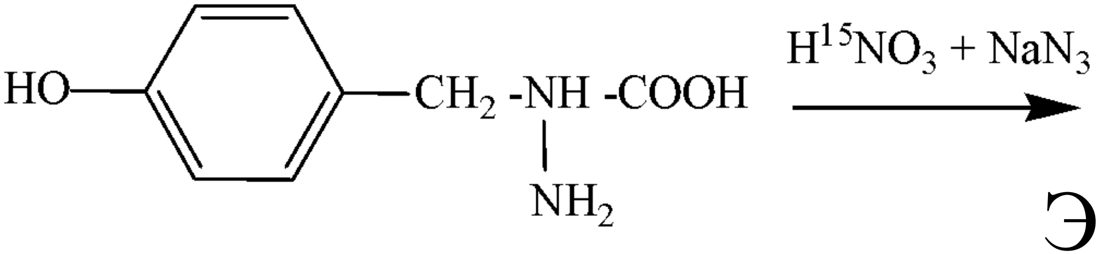
ХПЯ



J.H. Ridd, Chem. Comm.
1981, 402

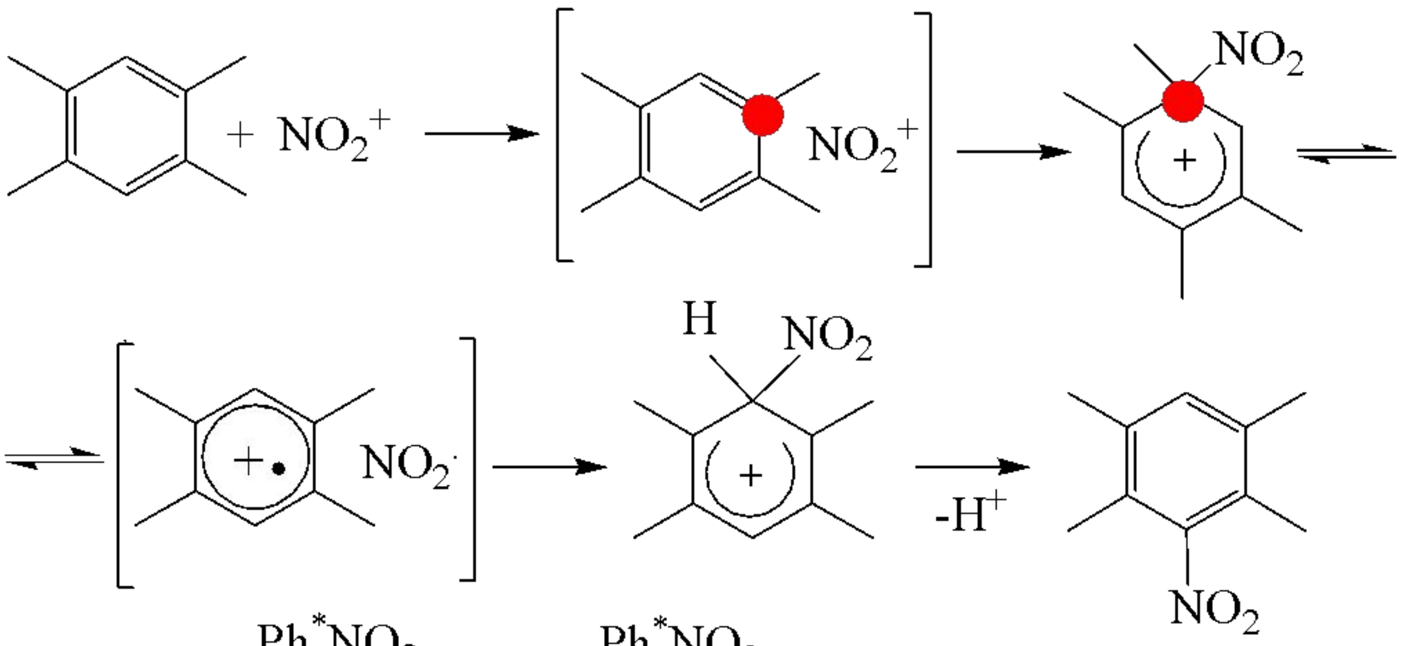


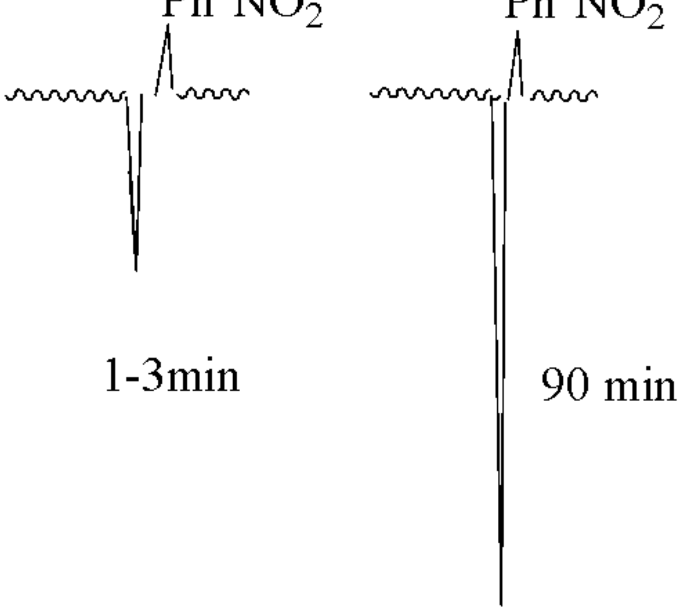
J.H. Ridd et al., JCS PT2,
1991, 623



A.R. Butler et al.,
Chem. Commun. **1997**, 669

Эмиссия в ЯМР ^{15}N



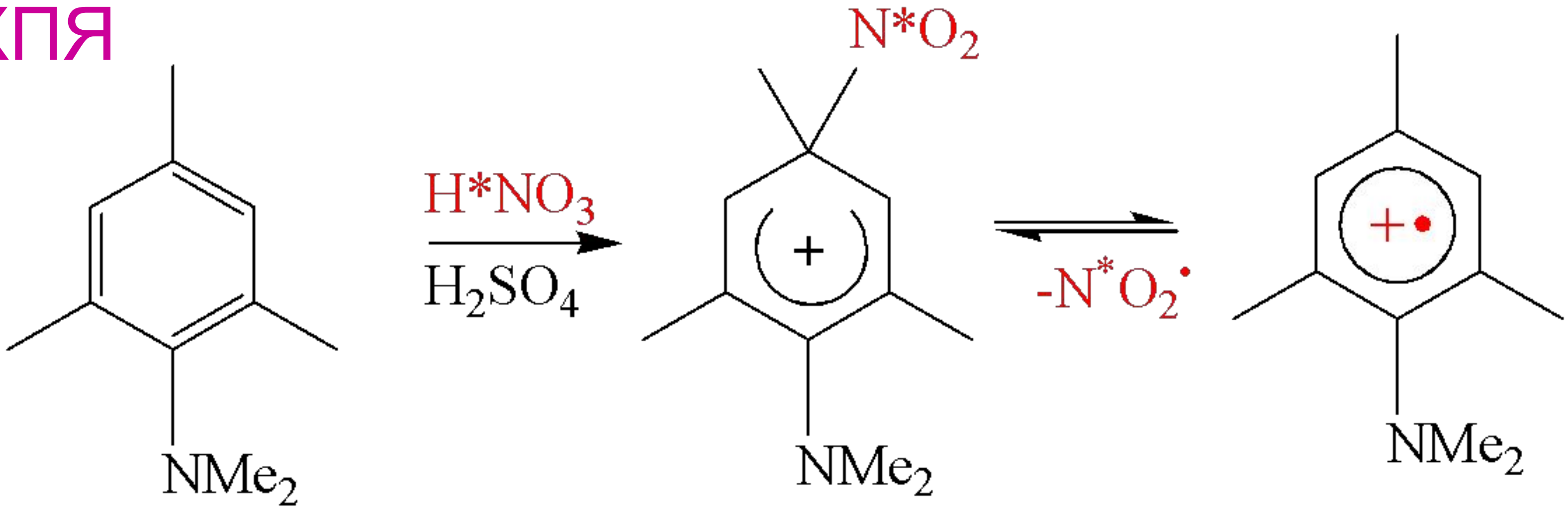


ХПЯ в

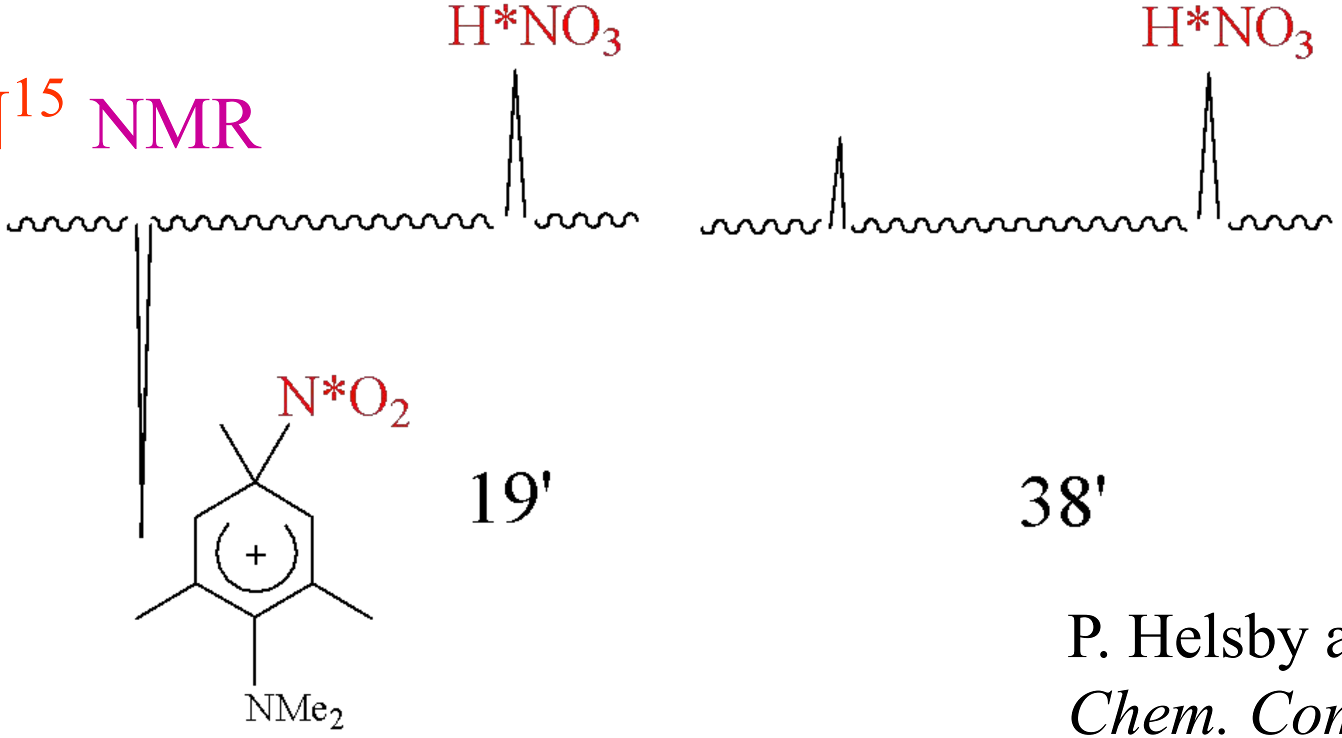
$H^{15}NO_3$ + CF_3COOH,
CH_3COONa

J.H. Ridd et al.,
JCS PT2 1985, 1227

ХПЯ

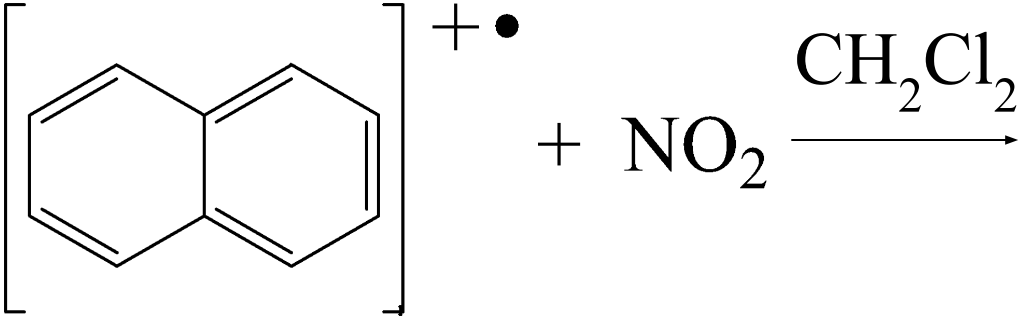


N^{15} NMR



P. Helsby and J.H. Ridd,
Chem. Comm. **1981**, 825

Против механизма SET

	Соотношение 1-NO_2/ 2-NO_2Npht:
1. Perrin C., MeCN	10.9
2. Achord J., et al. *J. Electrochem. Soc.* **1981**, 2556	17
3. Olah G. et al., MeCN, Proc. Nat. Acad. Sci. USA, **1981**	11-24
4. 	35-60

Eberson L. *Acta Chem. Scand. B.*, **1980,** 739

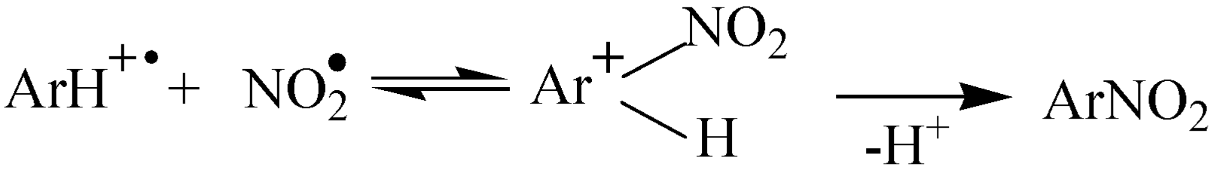
Против механизма SET

2. Корреляция $a_{\text{H}} \rightarrow E^{+}_{\text{лок.}}$

3. Катализ NO^+ и ХПЯ

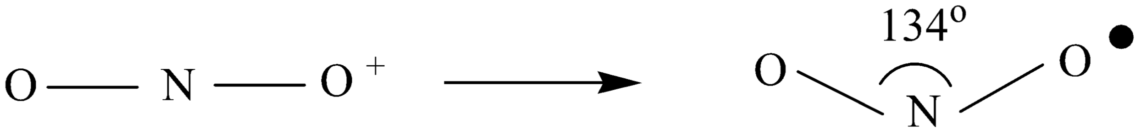
$$ArH + NO^+ \rightleftharpoons ArH^{+\bullet} + NO^{\bullet}$$

$$NO^{\bullet} + NO_2^+ \rightleftharpoons NO^+ + NO_2^{\bullet}$$



$$ArH^{+\bullet} + NO_2^{\bullet} \rightleftharpoons Ar^{+}(NO_2)(H) \xrightarrow[-H^+]{} ArNO_2$$

4. Большая энергия реорганизации ~50 ккал/моль



Кинетические изотопные эффекты

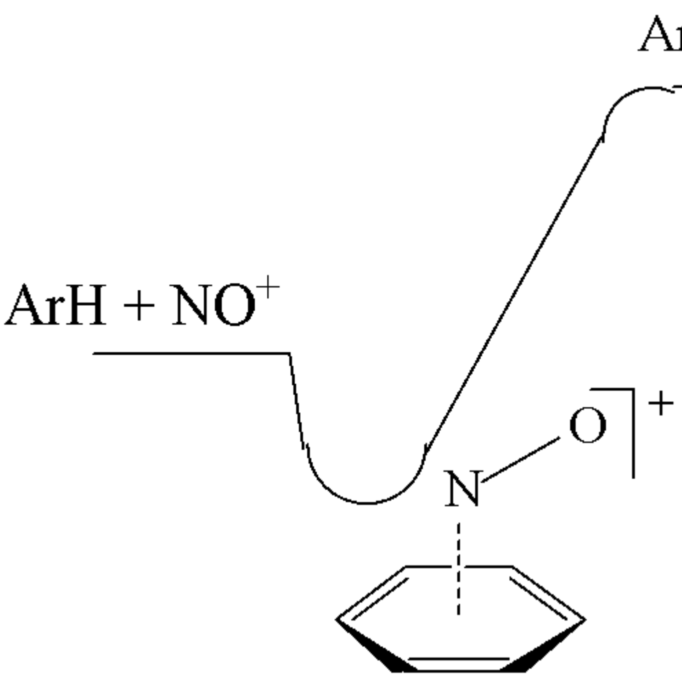
Газовая фаза, ICR $C_6D_nH_{6-n}$ + NO_2^+ $k_H/k_D = 1$

в CH_2Cl_2 $C_6D_nH_{6-n}$ + NO_2BF_4 $k_H/k_D = 0.86$

В растворе SET не может быть лимитирующей стадией (модель не локализованного электрона и вертикальный перенос электрона)

В газовой фазе и в растворе лимитирующие стадии разные!

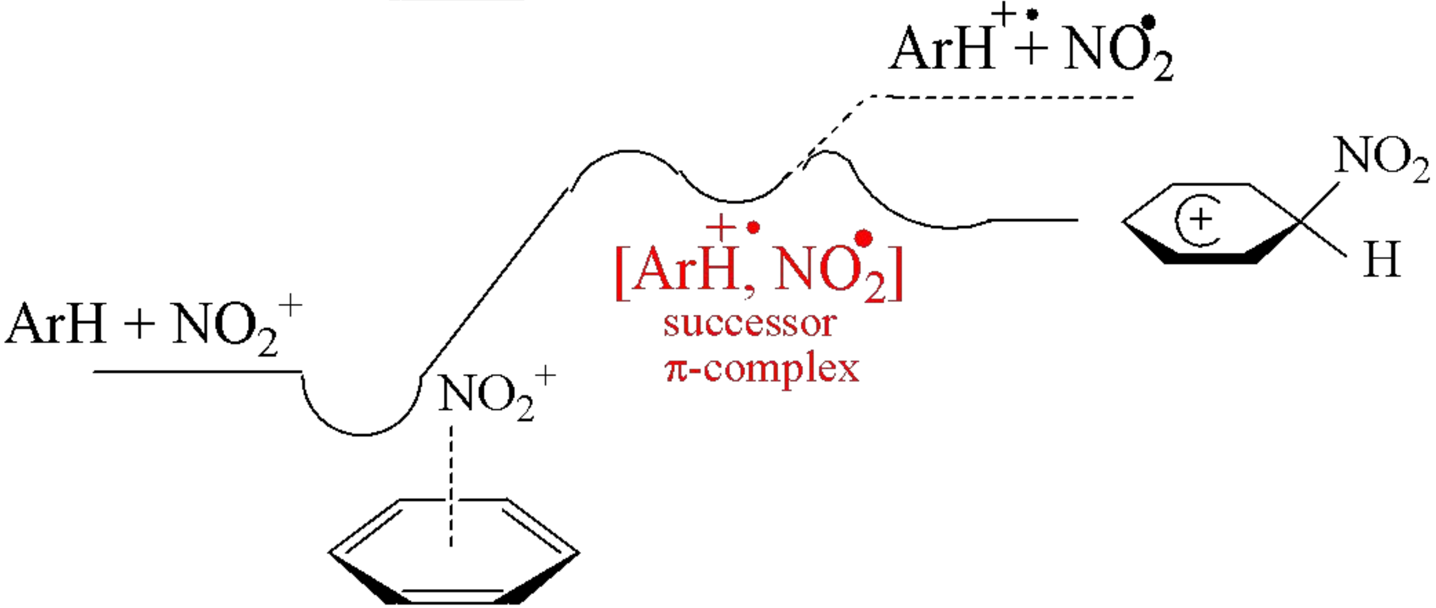
G.A. Olah et al. *J. Am. Chem. Soc.*, **2003,** 4836



$ArH^{+\bullet} + NO^{\bullet}$

$ArH + NO^{+}$

$[N{-}O]^{+}$



$ArH^{+\bullet} + NO_2^{\bullet}$

NO_2

H

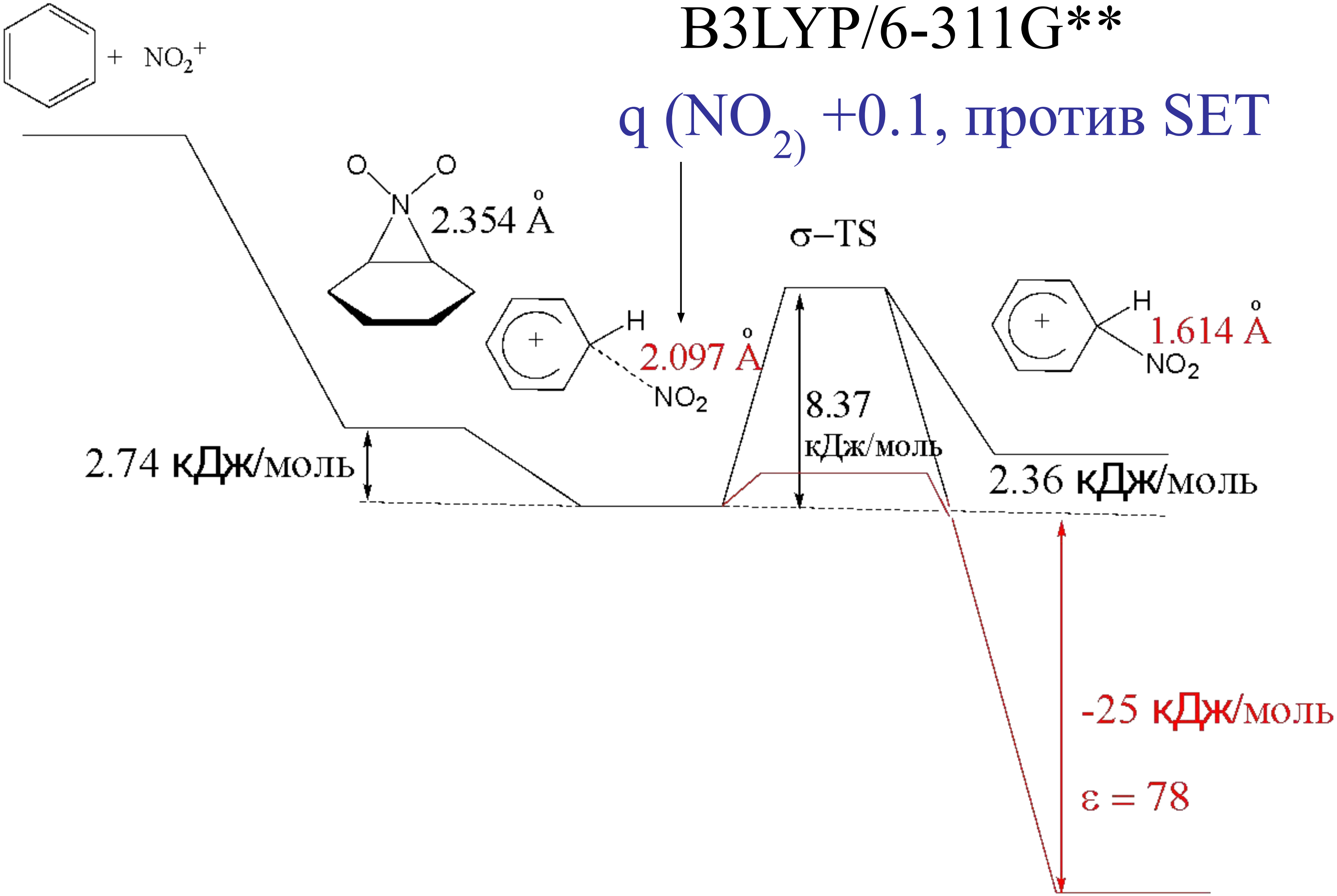
$[ArH^{+\bullet}, NO_2^{\bullet}]$
successor
π-complex

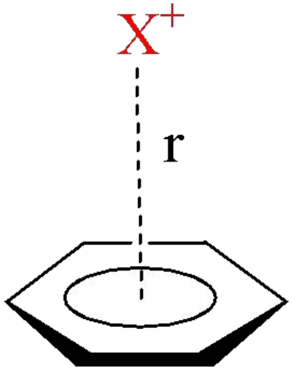
$ArH + NO_2^{+}$

NO_2^{+}

B3LYP/6-311G**

q (NO$_{2)}$ +0.1, против SET





CASSCF/cc-pVDZ

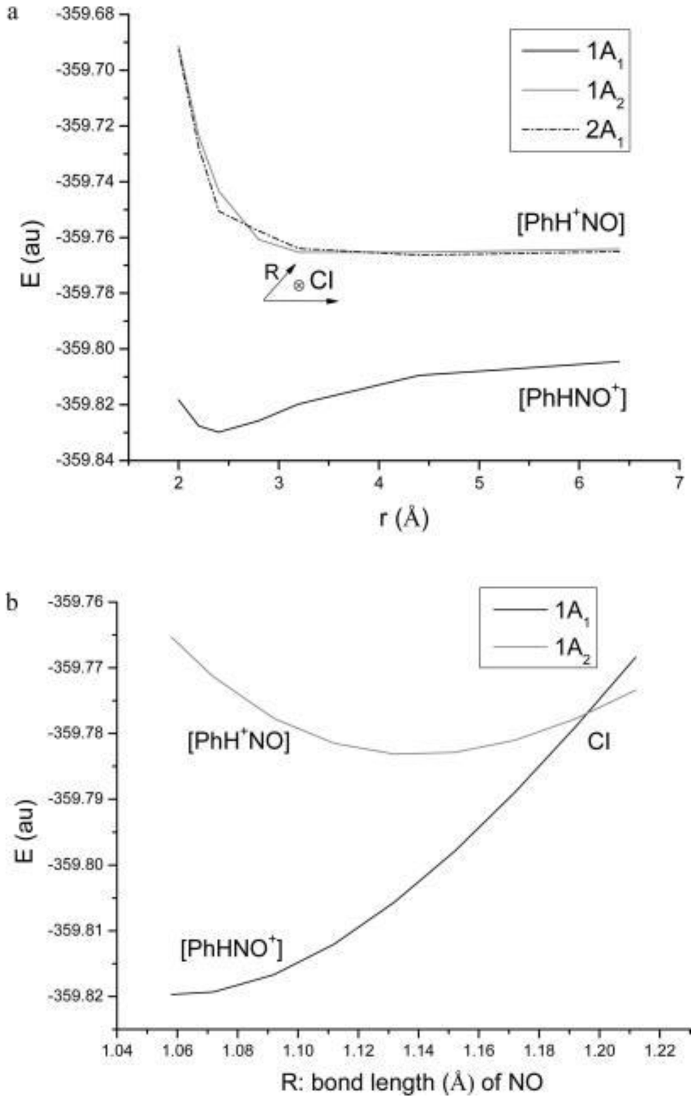
C_{6v}, C_{2v}

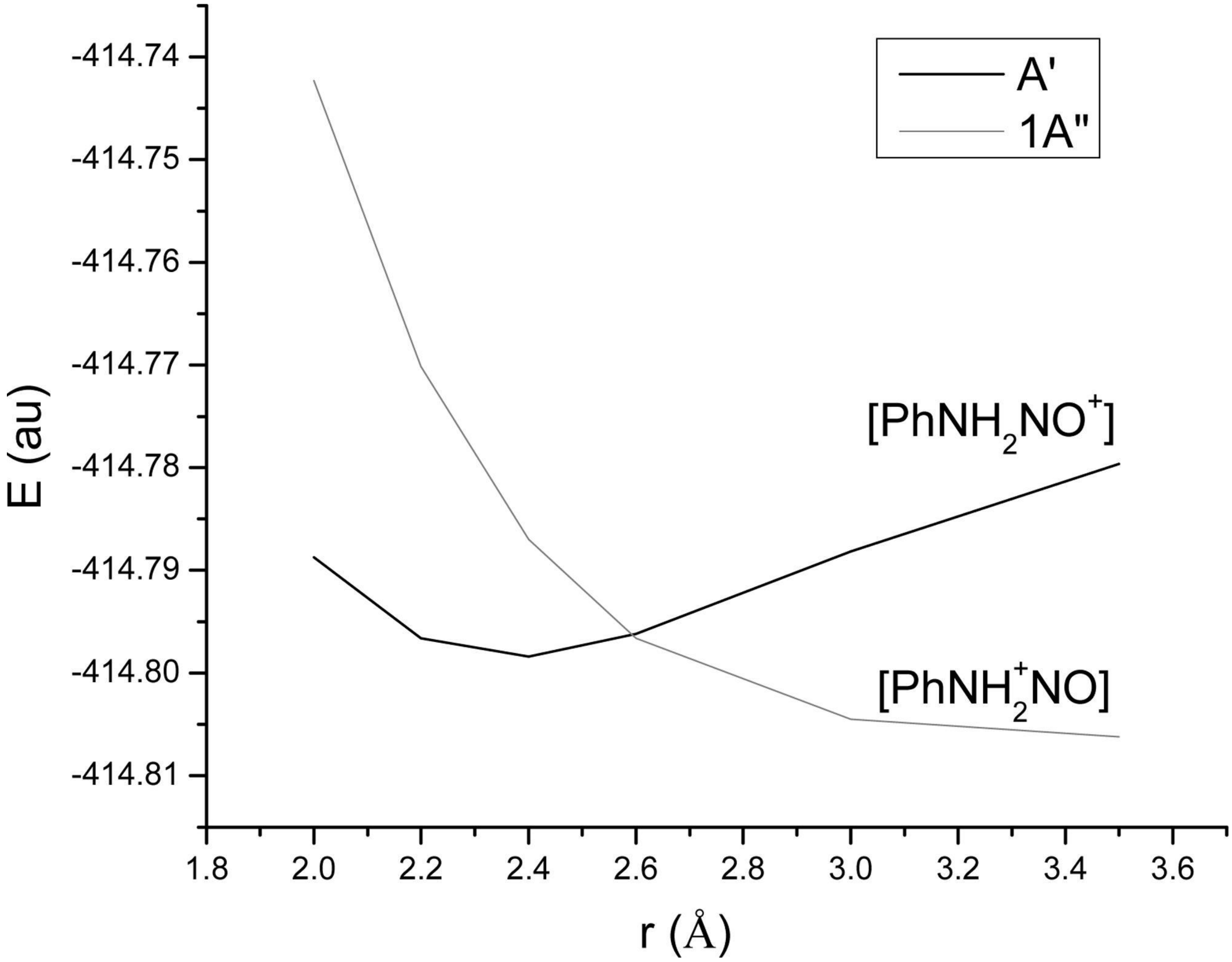
$I_p = 9.24$ eV

X^+	H^+	Cl^+	$C\equiv CH^+$	CH_3^+	NO_2^+	NO^+
EA, eV	13.60	12.97	11.61	9.84	9.59	9.26

Гарпунный механизм переноса электрона

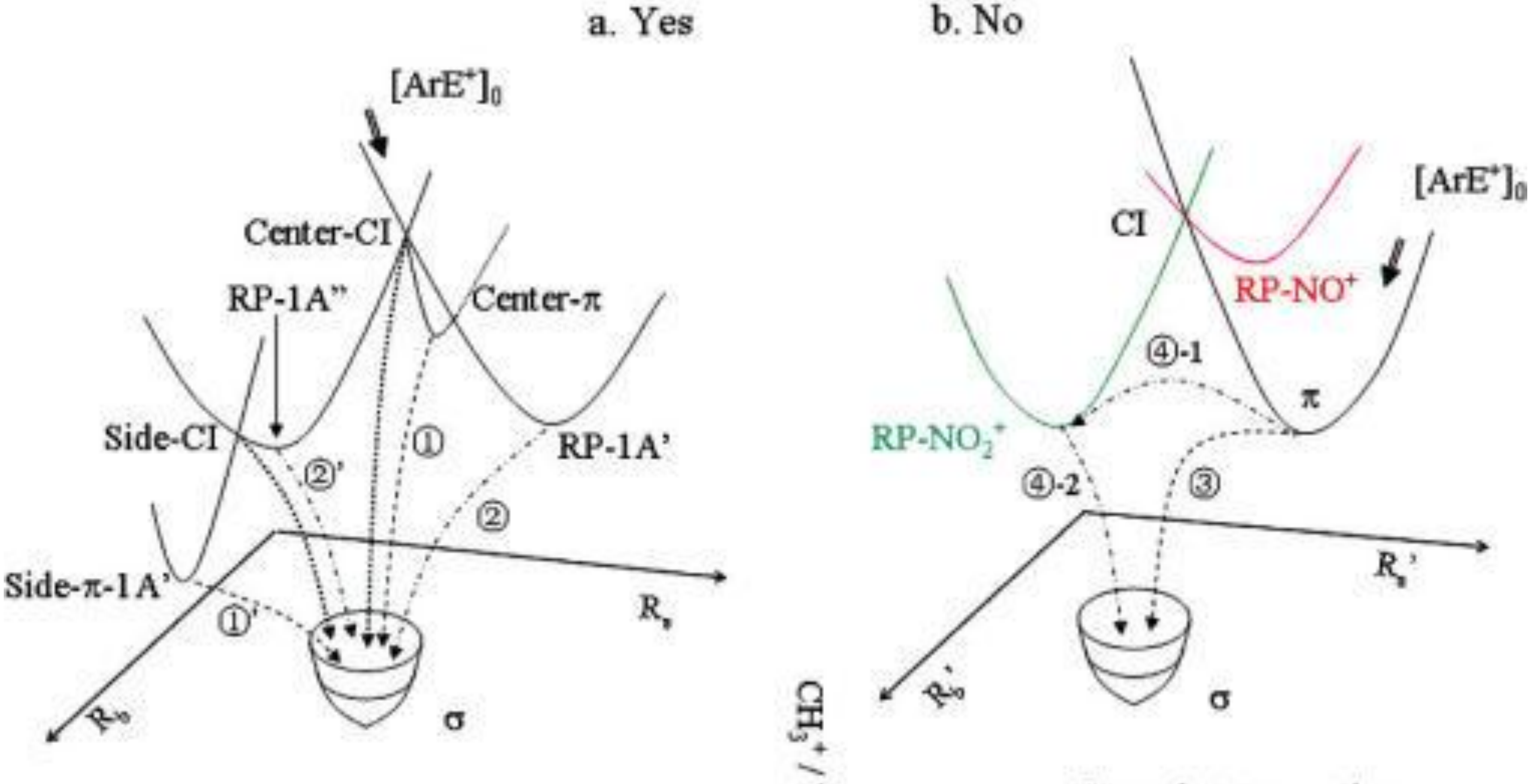
Роль электронно-возбужденных состояний





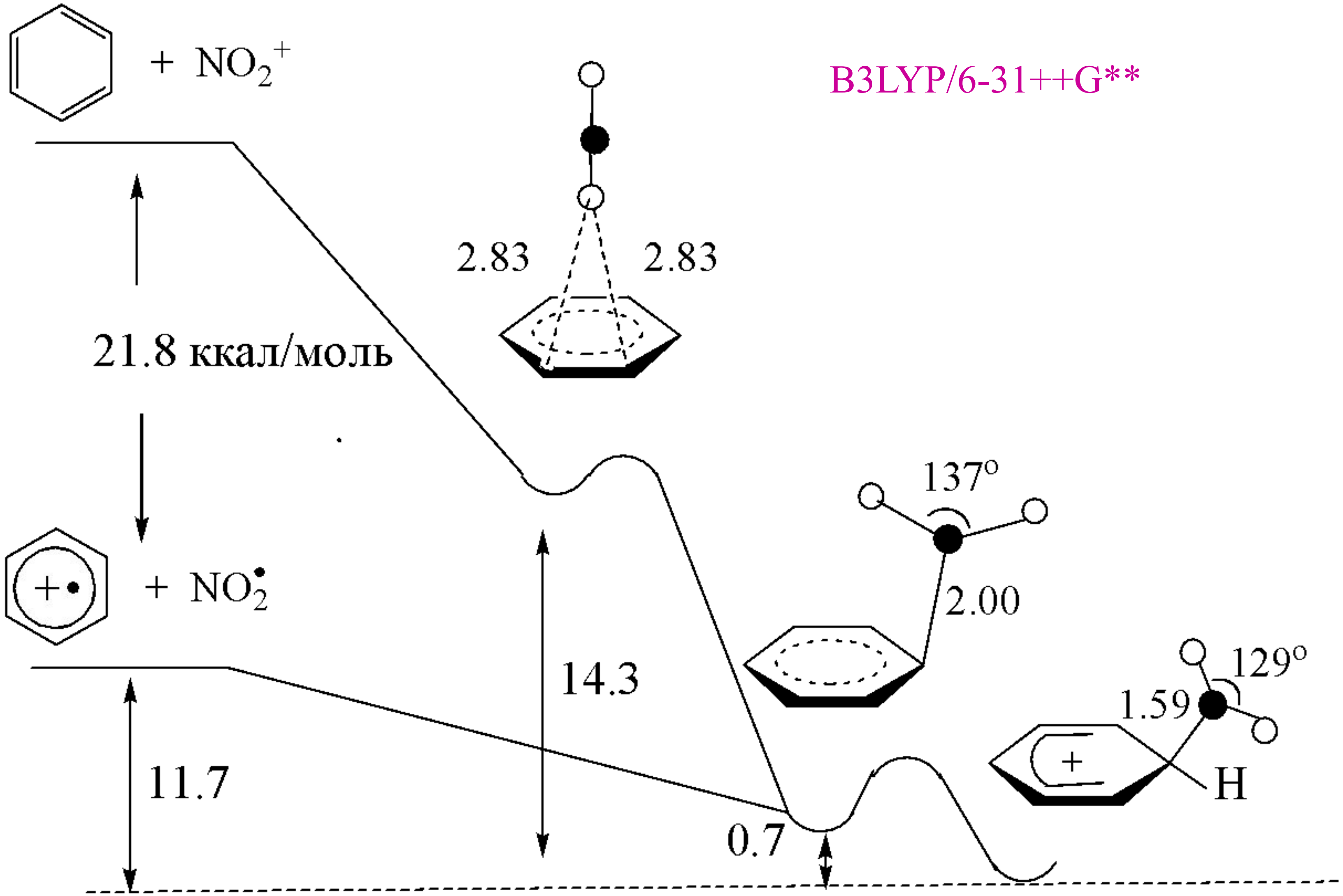
A'
1A"
[PhNH$_2$NO$^+$]
[PhNH$_2^+$NO]
E (au)
-414.74
-414.75
-414.76
-414.77
-414.78
-414.79
-414.80
-414.81
r (Å)
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6

Is $[ArE^+]_0$ excited state?



Relatively Strong E^+: H^+, Cl^+, $C{\equiv}CH^+$ vs benzene
NO^+ vs aniline

Ground-state reaction
Relatively Weak E^+: NO_2^+, NO^+ vs benzene



B3LYP/6-31++G**