

Neutral-Neutral Reactions

Ian Smith

Universities of Cambridge and Birmingham, UK

Panel Meeting
ISSI Bern
9th January 2008

Reported Interstellar and Circumstellar Molecules

N=2	N=2	N=3	N=3	N=4	N = 5	N = 6	N = 7	N = 8	N = 9	N = 10
H ₂	AlCl	H ₃ ⁺	HCP	NH ₃	CH ₄	CH ₃ OH	CH ₃ NH ₂	HCOOCH ₃	(CH ₃) ₂ O	(CH ₃)CO
CH	PN	CH ₂	OCS	H ₃ O ⁺	SiH ₄	CH ₃ SH	CH ₃ CCH	CH ₃ C ₂ CN	C ₂ H ₅ OH	CH ₃ C ₄ CN
CH ⁺	SiN	NH ₂	MgCN	H ₂ CO	CH ₂ NH	C ₂ H ₄	CH ₃ CHO	C ₆ H ₂	C ₂ H ₅ CN	CH ₃ CH ₂ CHO
NH	SiO	H ₂ O	MgNC	H ₂ CS	H ₂ C ₃	CH ₃ CN	c-CH ₂ OCH ₂	C ₇ H	CH ₃ C ₄ H	(CH ₂ OH) ₂
OH	SiS	H ₂ S	NaCN	<i>l</i> -C ₃ H	<i>l</i> -C ₃ H ₂	CH ₃ NC	CH ₂ CHCN	HOCH ₂ CHO	C ₈ H	
HF	CO ⁺	C ₂ H	SO ₂	c-C ₃ H	c-C ₃ H ₂	H ₂ CCHO	HC ₄ CN	CH ₃ COOH	HC ₆ CN	
C ₂	SO ⁺	HCN	N ₂ O	HCCH	H ₂ CCN	NH ₂ CHO	C ₆ H	H ₂ CCCHCN	CH ₃ CHCH ₂	
CN	PO	HNC	SiCN	HCNH ⁺	H ₂ NCN	HC ₃ NH ⁺	H ₂ CCHOH	H ₂ C ₆	CH ₃ CONH ₂	
CO	SH	HCO	CO ₂	H ₂ CN	CH ₂ CO	H ₂ C ₄	C ₆ H ⁻	CH ₂ CHCHO	C ₆ H ⁻	N = 11
CS	AlF	HCO ⁺	c-SiC ₂	c-C ₃ H	HCOOH	C ₅ H				HC ₈ CN
CP	FeO	HOC ⁺	SiNC	HCCN	C ₄ H	C ₅ N				CH ₃ C ₆ H
NO	SiC	HN ₂ ⁺	AINC	HNCO	HC ₂ CN	C ₅ O				
NS	CF ⁺	HNO		HOCO ⁺	HC ₂ NC	C ₅ S				N = 12
SO	? N ₂ ?	HCS ⁺		HNCS	C ₄ Si					C ₆ H ₆
HCl		C ₃		C ₂ CN	C ₅					
NaCl		C ₂ O		C ₃ O	C ₄ N					N = 13
KCl		C ₂ S		C ₃ S	H ₂ COH ⁺					HC ₁₀ CN
				SiC ₃	C ₄ H ⁻					

Neutral-Neutral Reactions: Summary of Experiments

- Canosa *et al.* list 93 reactions: 73 studied in continuous CRESU (Rennes, Birmingham, Bordeaux); 20 in pulsed CRESU (Arizona, Berkeley, Göttingen)
- Continuous CRESU reach as low as 13 K, more generally *ca.* 25 K; pulsed CRESU to 53 K
- **Radicals:** B(2P_J), C (3P_J), O (3P_J), Al (2P_J), and Si (3P_J)
CN, OH, CH, NH, C₂(X), C₂(a), C₂H, C₄H
- **Molecules:** alkenes/alkynes (52); saturated molecules (19); radicals (15); aromatics (2); others (5)

CRESU measurements of rate constants at low temperatures

- Signifies a pressure-dependent association reaction
- Metathesis reactions with $k(298\text{ K}) > 1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
- Metathesis reactions with $k(298\text{ K}) > 10 - 5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
- Metathesis reactions with $k(298\text{ K}) > 5 - 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

	CH ₄	C ₂ H ₆	NH ₃	H ₂	D ₂	HBr	N ₂	CO	C ₂ H ₂	C ₂ H ₄	C ₃ H ₆	CH ₃ CCH	CH ₂ CCH ₂	butenes	O ₂	NO	NO ₂	O(³ P)
B(² P)									23	23					23			
Al(² P)															23			
C(³ P)									15	15		15	15		15	15		
Si(³ P)									15	15					15	15		
O(³ P)											23			27				
CH(² Π)	23	23	23	53	23		53	53	23	23				23	13	13		
OH(² Π)						23								23		23	53	38
CN(² Σ ⁺)		25	25						25	25		15	15		13			
C ₂ H(² Σ)									15	15	15	27	27		15			

also data for reactions of ¹C₂(¹Σ_g⁺), ³C₂(³Π_u) and C₄H

CRESU measurements of rate constants at low temperatures

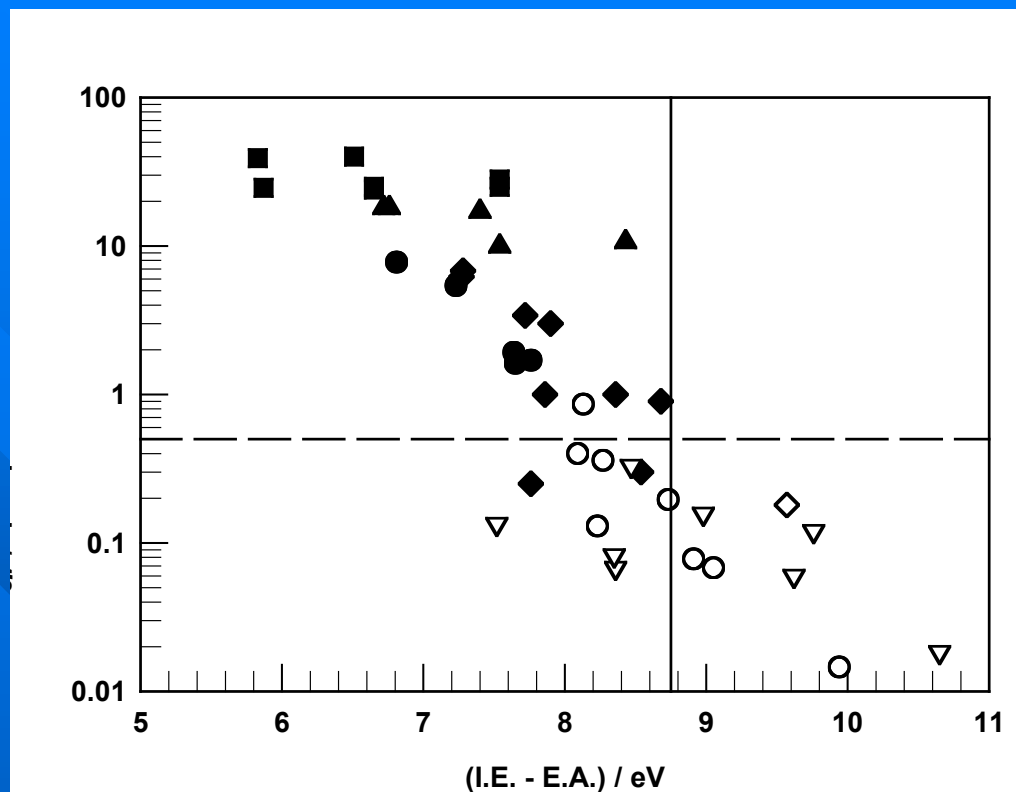
- - radical + saturated molecule
- - radical + unsaturated molecule
- - radical + radical

	CH ₄	C ₂ H ₆	NH ₃	H ₂	D ₂	HBr	N ₂	CO	C ₂ H ₂	C ₂ H ₄	C ₃ H ₆	CH ₃ CCH	CH ₂ CCH ₂	butenes	O ₂	NO	NO ₂	O(³ P)
B(² P)									23	23					23			
Al(² P)															23			
C(³ P)									15	15		15	15		15	15		
Si(³ P)									15	15					15	15		
O(³ P)											23			27				
CH(² Π)	23	23	23	53	23		53	53	23	23				23	13	13		
OH(² Π)						23								23		23	53	38
CN(² Σ ⁺)		25	25						25	25		15	15		13			
C ₂ H(² Σ)									15	15	15	27	27		15			

also data for reactions of ¹C₂(¹Σ_g⁺), ³C₂(³Π_u) and C₄H

Reactions of Radicals with Alkenes/Alkynes

- - CN radicals
- ▲ - C₂H radicals
- ◆, ◇ - OH radicals
- , ○ - O atoms
- ▽ - H atoms



Reaction will be fast at low temperatures (10 – 20 K) if:

- $k(298 \text{ K}) > 5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and/or
- $(\text{I.E.} - \text{E.A.}) > \text{ca. } 8.75 \text{ eV}$

Reactions of alkenes/alkynes with O(³P) atoms should provide crucial test

Why low temperature kinetics of O + alkenes?

- Extensive kinetics measurements at and above room temperature
 - Some reactions show positive T dependence (e.g. *propene* & *1-butene*) – some negative T dependence (e.g. *iso-butene* & *cis-2-butene*)
 - Rate constants and activation energies correlate with I.E. of the alkene (*Cvetanovic et al.*)
- ?? Will some $k(T)$'s decrease to low temperatures, some increase??

Kinetic Data for Reactions of O(³P) with Alkenes

	(I.E. – E.A.)/eV	<u>k(298 K)</u> 10 ⁻¹¹ cm ³ s ⁻¹	<u>T-dependence</u>
<i>trans</i> -2-butene	7.64	2.2	– ve
<i>cis</i> -2-butene	7.65	1.8	– ve
<i>iso</i> -butene	7.76	1.7	– ve
<hr/>			
1-butene	8.09	0.42	+ ve
propene	8.27	0.40	+ ve
<hr/>			
ethene	9.05	0.073	+ ve

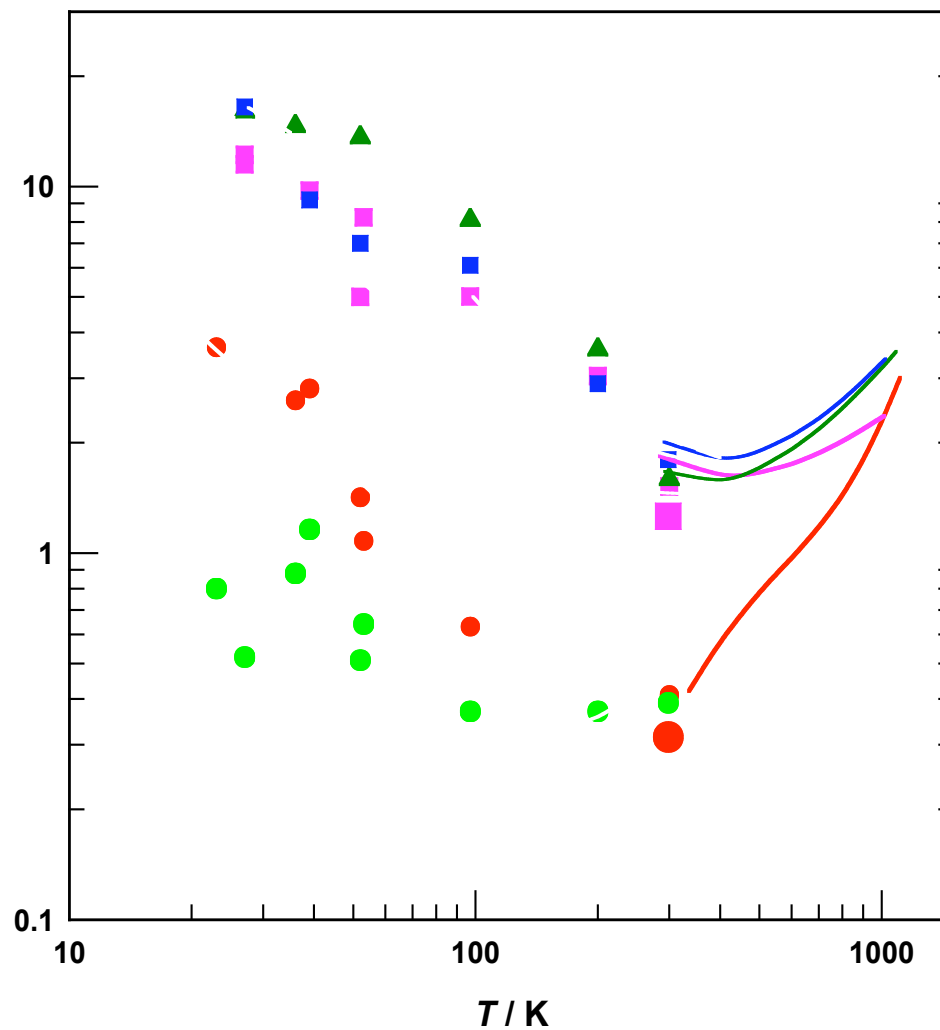
CRESU Experiments on Reactions of O(³P) with Alkenes

(Ludovic Bennier, Hassan Sabbah, Ian Sims & IWMS)

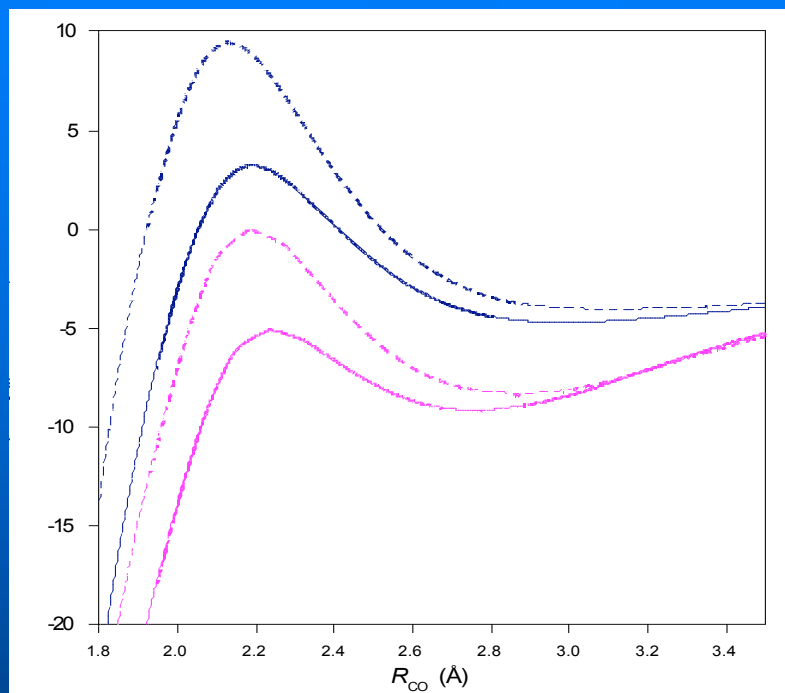
- O(³P) atoms are generated by pulsed laser photolysis of NO₂ at 355 nm (tripled Nd:YAG laser)
- a small-ish concentration of NO is included in the reaction mixture, and variation in the O(³P) atom concentration is followed by observing the intensity of the chemiluminescence from NO₂*

Rate constants for reaction of O(³P) with alkenes

- ▲ *cis*-butene
 - *trans*-butene
 - *iso*-butene
 - 1-butene
 - propene
- and ■ from IWMS 1967!!



Theoretical calculations on O(³P) + alkene reactions (Yuri Georgievskii and Stephen Klippenstein)



Ab initio calculations characterise the long-range potentials

--- *trans*-butene --- ethene

Generally two maxima – two transition states – ‘outer’ and ‘inner’

- Dynamics treated by μJ version of TST
- For O(³P) + ethene, inner TS is dominant (‘real’ barrier)
- For O(³P) + alkenes with low values of (I.E. – E.A.), outer TS is dominant, barrier is well-submerged
- For intermediate cases, influence of both barriers is important with their relative importance depending on temperature

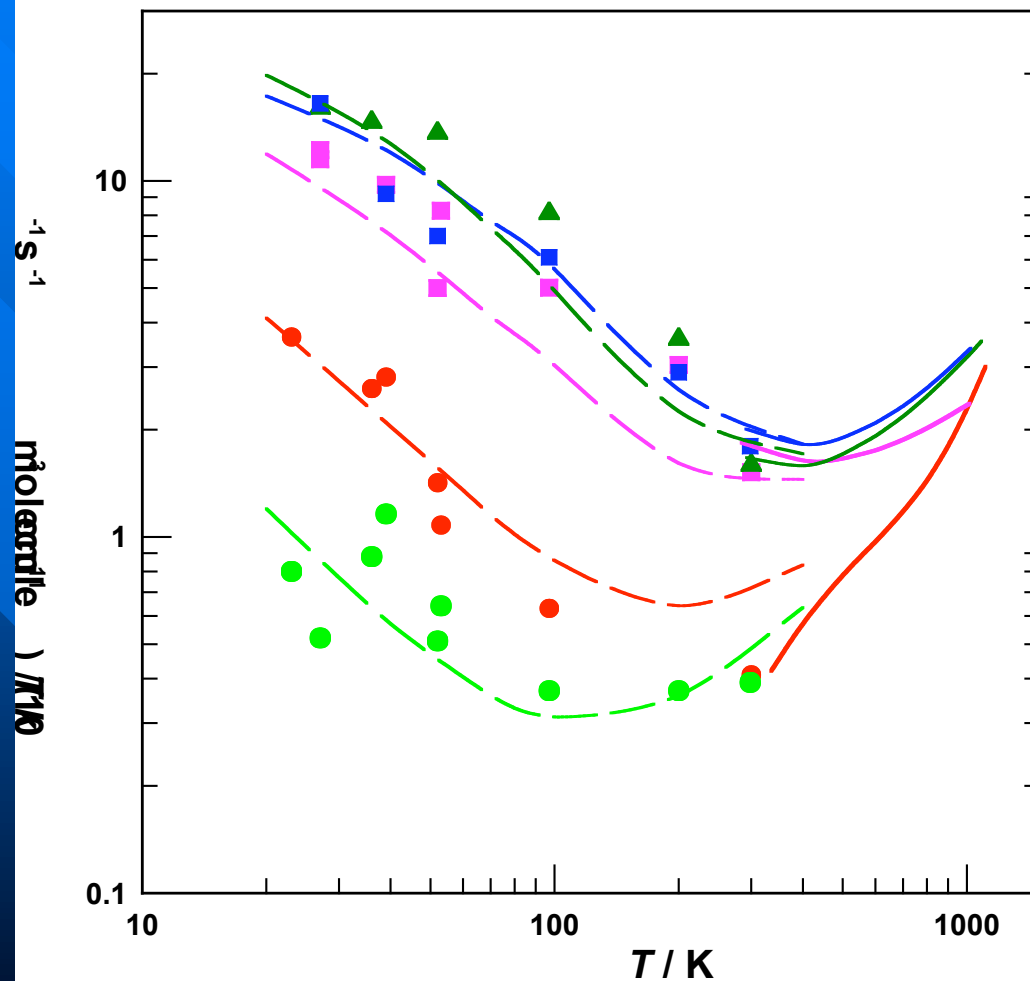
Rate constants for reaction of O(³P) with alkenes

- ▲ *cis*-butene
- *trans*-butene
- *iso*-butene
- 1-butene
- propene

Solid lines from expts of Fontijn

Dashed lines from μJ -TST calculations

O(³P) + ethene – too slow to measure



Conclusions

- Rate constants for reaction of O(³P) atoms with alkenes show a complex dependence on temperature
- The semi-empirical arguments introduced in the Faraday Discussion paper of Smith et al. that reactants with (I.E. – E.A.) < ca. 8.75 eV will occur rapidly at low temperature hold up rather well
- The values of $k(T)$ and their dependence on T are well-matched by a two transition state model using μJ version of TST

Radical-Radical Reactions

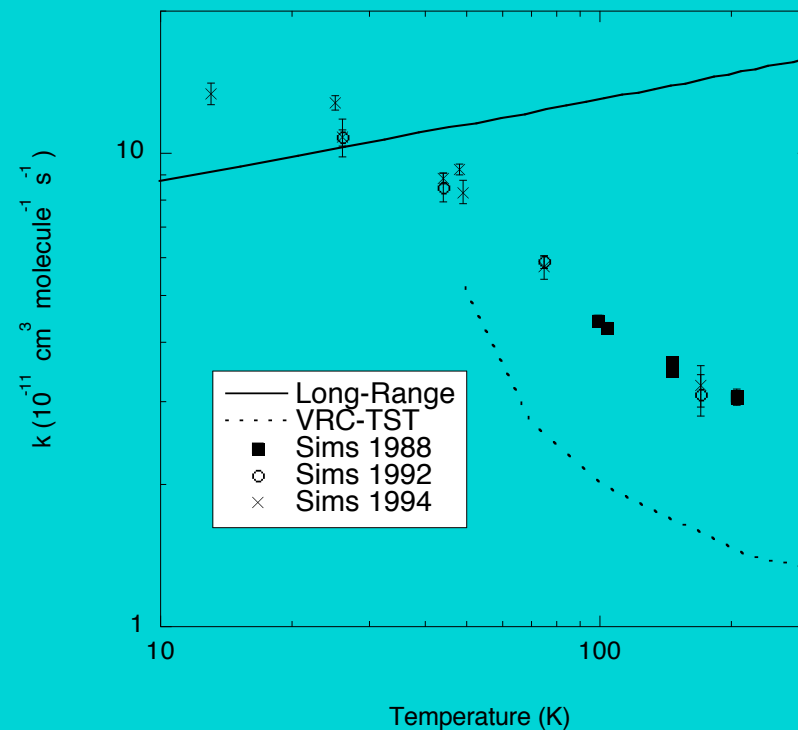
- At least one PES should have no maximum and probably a 'deep' minimum
- Several PES's probably correlate with reactants not all leading (without a barrier) to products
- $k(T)$ may be lowered by degeneracies and near-degeneracies
- Can an inner transition state lower rate below that for capture?

	O ₂	NO	NO ₂	O(³ P)
B(² P)	23			
Al(² P)	23			
C(³ P)	15	15		
Si(³ P)	15	15		
O(³ P)				
CH(² Π)	13	13		
OH(² Π)		23	53	38
CN(² Σ ⁺)	13			
C ₂ H(² Σ)	15			

Radical-Radical Reactions: CN + O2

■ experimental $k(T)$ show strong negative T -dependence – in contrast to ‘capture’ calculations

■ main features of experimental $k(T)$ are reproduced by 2-TS model (Klippenstein)



Reactions of Radical with Saturated Molecules

- Data set from CRESU experiments is limited

	CH ₄	C ₂ H ₆	NH ₃	H ₂	D ₂	HBr
B(² P)						
Al(² P)						
C(³ P)						
Si(³ P)						
O(³ P)						
CH(² Π)	23	23	23	53	23	
OH(² Π)						23
CN(² Σ ⁺)		25	25			
C ₂ H(² Σ)						

Reactions of Radicals with Saturated Molecules

Values of $k(298\text{ K}) / 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$

	E.A./eV	H ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	i-C ₄ H ₁₀	n-C ₄ H ₁₀
I.E./eV		15.43	12.51	11.52	10.95	10.57	10.53
C(³ P)		(17)	?	?	?	?	?
CH(² Π)	1.238	(160)	91	280	425	448	483
H(² S)	0.754	10 ⁻⁴	1.5(-7)	2.8(-5)	1.5(-4)	1.1(-3)	2.9(-4)
O(³ P)	1.461	9(-6)	1.7(-5)	1.4(-4)	9.4(-3)	0.11	2.6(-2)
OH(² Π)	1.827	1.7(-3)	6.1(-3)	0.25	1.1	2.1	2.4
CN(² Σ ⁺)	3.862	2.8(-2)	0.60	28	75	100	
C ₂ H(² Σ)	2.969	0.7	2.7	43	80	96	120

Reactions of Radical with Saturated Molecules

- $C(^3P)$ and $CH(^2\Pi)$ react rapidly with saturated molecules – if exothermic reaction is available
- Alkanes will not react with $H(^2S)$, $O(^3P)$ or $OH(^2\Pi)$ – probably the reactions of these radicals with saturated molecules can be ignored
- Most alkanes will react rapidly with $CN(^2\Sigma^+)$ and $C_2H(^2\Sigma)$
- Reactivity of $C(^3P)$ atoms ?

Values of $k(298\text{ K}) / 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$

	E.A./ eV	CH_4	C_2H_6	C_3H_8	<i>i</i> - C_4H_{10}	<i>n</i> - C_4H_{10}
I.E./eV		12.51	11.52	10.95	10.57	10.53
$C(^3P)$						
$CH(^2\Pi)$	1.238	91	280	425	448	483
$H(^2S)$	0.754	1.5(-7)	2.8(-5)	1.5(-4)	1.1(-3)	2.9(-4)
$O(^3P)$	1.461	1.7(-5)	1.4(-4)	9.4(-3)	0.11	2.6(-2)
$OH(^2\Pi)$	1.827	6.1(-3)	0.25	1.1	2.1	2.4
$CN(^2\Sigma^+)$	3.862	0.60	28	75	100	
$C_2H(^2\Sigma)$	2.969	2.7	43	80	96	120

Some final thoughts !

- Examination of available rate data suggests that for any neutral-neutral reaction with $k(298\text{ K}) > 5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ there is no 'real' barrier on the MEP and $k(10\text{-}20\text{ K})$ is likely to be *ca.* $2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (factor of 2 uncertainty ?)
- For radical-radical reactions $k(10\text{-}20\text{ K})$ may be lowered by 'electronic degeneracy factor'
- **Theoretical point for discussion:** how does two-TS model with dependence on E and J mesh with dependence of $k(T)$ on rotational states of reactants?