Radical Reactions at Surfaces

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Importance of radical reactions at surfaces

1. Catalytic processes.

2. Electrochemical reactions.

3. Photochemical processes in which the light is absorbed by the solid.

4. Reduction of halo-organic compounds by metals, a process of environmental implications.

Reaction of aliphatic carbon-centered radicals with transition metal complexes in aqueous solutions

$\longrightarrow M^{n\pm1}L_m + R^{-/+}$ **Outer sphere**

M-C σ-bond

$\longrightarrow L_mM^{n+1}\text{-}R$ or $L_{m-1}M^{n+1}\text{-}R + L$

Inner sphere

$M^nL_m + R\cdot \longrightarrow M^{n-1}L_{m-1} + L\text{-}R$ or $L^{\pm} + R^{-/+}$

$\longrightarrow L_{m-1}M^n\text{-}LR\cdot \longrightarrow M^{n\pm1}L_{m-1} + L\text{-}R^{-/+}$

or $+ L^{\pm} + R$

$\longrightarrow L_{m-1}M^n(L\cdot^{\pm}) + R^{-/+} \longrightarrow M^{n\pm1}L_m + R^{-}$

/+

Mechanisms of decomposition of the transient complexes L_mM^{n+1}-R

- Heterolysis
- Homolysis
- β- Elimination
- β- Hydride Shift
- CO insertion
- Rearrangement of the carbon skeleton (R)

Methyl radicals

$$\cdot CH_3 + (CH_3)_2SO \longrightarrow CH_4 + \cdot CH_2S(O)(CH_3)$$

$$\cdot CH_3 + \cdot CH_3 \longrightarrow C_2H_6$$

$E^o(\cdot CH_3)$ is not known.

Estimation: using the redox potentials of hydrogen atoms and the dissociation energy of:

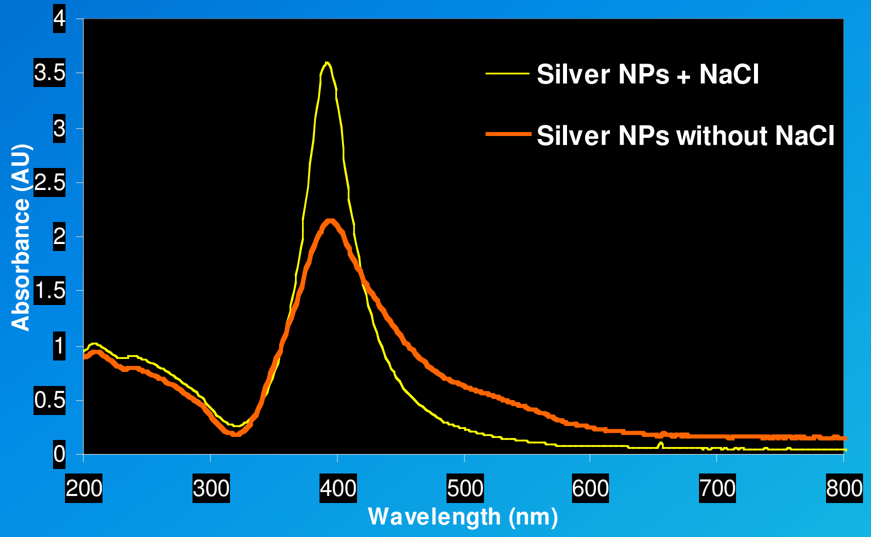
Bond Type	Dissociation Energy (kcal/mol)
$H - H$	104
$H - CH_3$	105
$H - OH$	119
$CH_3 - OH$	91

$E(\cdot H/H^+) = 2.25$ V

$E(H_2/\cdot H + H^+) = -2.25$ V

Synthesis of Silver NPs

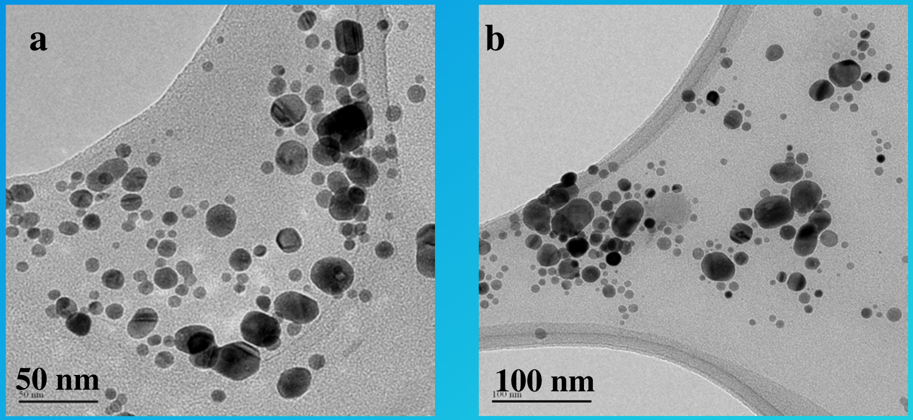
Experimental, Ag^+ reduction using $NaBH_4$



Solutions composition:

a) Ag_2SO_4 (2.5×10^{-4} M of Ag^+), $NaBH_4$ (1.5×10^{-3} M before the reduction), at pH 9.5.

b) Same solution as (a) with the addition of NaCl (1.0×10^{-4} M) .



TEM Micrographs of: a – Ag NPs; b – Ag NPs + NaCl

$[Ag^o\text{-NPs}] = (7 \pm 2) \times 10^{-9}$ M

Creighton, J. A.; Blatchford, C. G.; Albrecht, M. G. *J. Chem. Soc., Faraday Trans. 2* 1979, *75*, 790.

Irradiation of the NPs dispersions in the γ source

Sample[a]	NPs × 10^8 [M]	$G(CH_4)$	$G(C_2H_6)$	$G_{total}(\cdot CH_3)$ b	$G(CH_4)/G(C_2H_6)$
Blank (water)	0	4.2	0.8	5.8	5.3
Blank (aqueous borate) [b]	0	4.2	0.8	6.0	5.6
$[Ag]_{NP}$	0.7	1.7	2.2	6.1	0.78
$[Ag]_{NP}/2$	0.35	2.6	1.5	5.7	1.7
$[Ag]_{NP}/5$	0.14	4.0	0.82	5.6	4.9
$[Ag]_{NP}/6$	0.12	4.55	0.87	6.3	5.2
$[Au]_{NP}$	17	0.43	3.73	7.9	0.11
$[Au]_{NP}/2$	8.50	0.52	3.7	7.9	0.14
$[Au]_{NP}/7$	2.43	2.85	2.6	8.0	1.10
$[Au]_{NP}/10$	1.70	2.89	1.83	6.5	1.58
$[Au]_{NP}/12$	1.42	3.15	1.65	6.4	1.91

[a] The solutions were irradiated at a dose rate of 18 rad/min (=1.8×10^{-9} $M \cdot s^{-1}$) (total dose: 200-450 Gy). All samples contained $(CH_3)_2SO$ and were N_2O saturated [b] $G_{total}(\cdot CH_3) = G(CH_4) + 2G(C_2H_6)$. Error limits ±15%

T. Zidki, H. Cohen, D. Meyerstein, Phys. Chem. Chem. Phys. 2006 ,8, 3552 –3556

Plausible reactions in solution:

(1) $\cdot CH_3 + \cdot CH_3 \rightarrow C_2H_6$ $k_1 = 1.6x10^9\, M^{-1}s^{-1}$

(2) $\cdot CH_3 + (CH_3)_2SO \rightarrow CH_4 + \cdot CH_2S(O)CH_3$ $k_2 = 100\, M^{-1}s^{-1}$

(3) $\cdot CH_3 + (NP)-(CH_3)_{n-1} \rightarrow (NP)-(CH_3)_n$ $k_3 = ?$

(4) $(NP)-(CH_3)_n \rightarrow (NP)-(CH_3)_{n-2} + C_2H_6$

(5) $(NP)-(CH_3)_n + \cdot CH_3 \rightarrow (NP)-(CH_3)_{n-1} + C_2H_6$

(6) $(NP)-(CH_3)_n + H_3O^+ / H_2O \rightarrow (NP)^+ -(CH_3)_{n-1} + CH_4 + H_2O / OH^-$

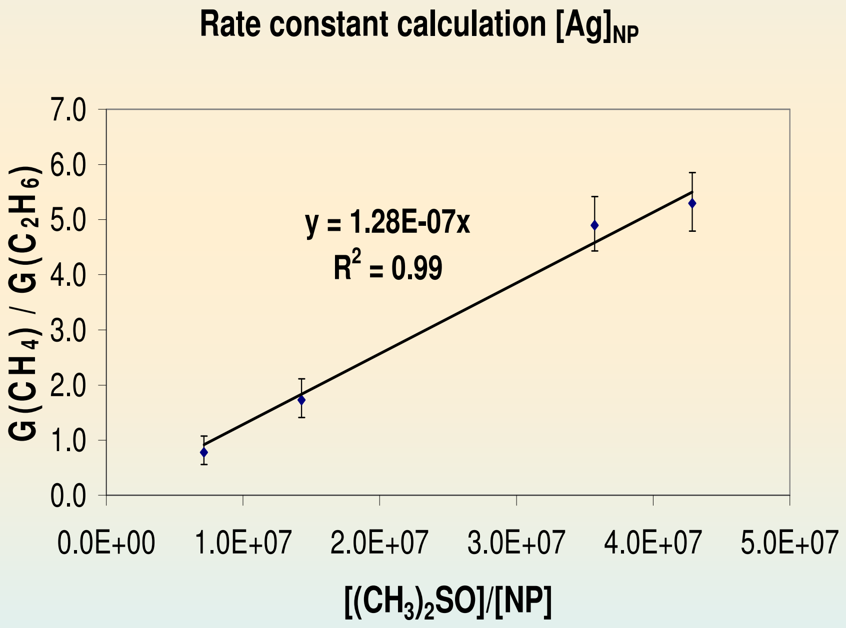
Assumptions for k_3 calculation:

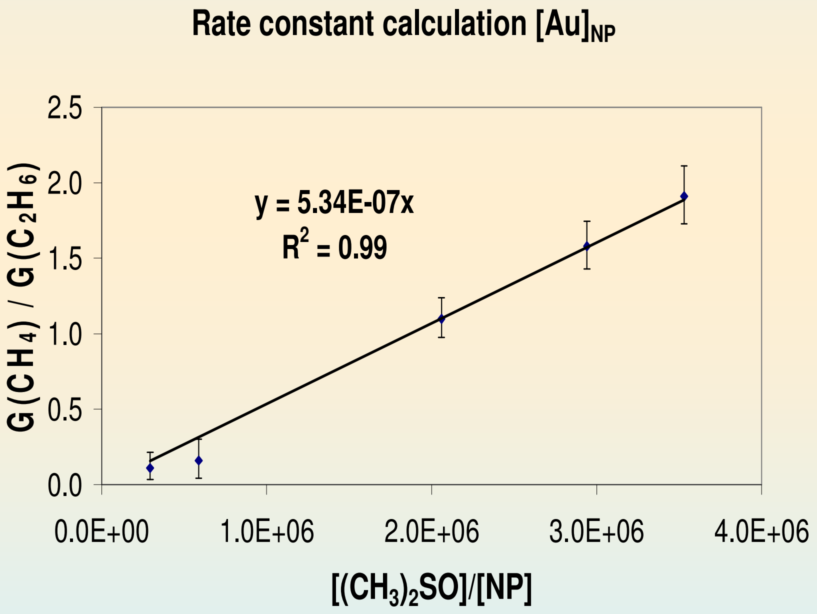
- **Reaction 1 does not contribute to the ethane production in the presence of the NPs.**
- **k_3 is independent of n.**
- **Reaction (5) is negligible**
- **Reaction (6) does not occur.**
- **[$\cdot CH_3$] is in a steady-state.**

k_3 is calculated using the equation:

$$\frac{G(CH_4)}{G(C_2H_6)} = \frac{k_2[\cdot CH_3]_{ss}[(CH_3)_2SO]}{k_3[\cdot CH_3]_{ss}[NP]} = \frac{k_2[(CH_3)_2SO]}{k_3[NP]}$$

Slope = k_2/k_3





Plots of the ratios $G(CH_4)/G(C_2H_6)$ vs. $[(CH_3)_2SO]/[NP]$ in order to derive k_3 for the reaction between methyl radicals and (i) silver NPs (ii) gold NPs.

R. Bar-Ziv, I. Zilbermann, O. Oster-Golberg, T. Zidki,, G. Yardeni, H. Cohen, D. Meyerstein, Chemistry Eur. J., 18, 4699-4705, 2012.

$k_3(Ag) = (7.8 \pm 1.5)x10^8\ M^{-1}s^{-1}$
$k_3(Au) = (1.9 \pm 0.4)x10^8\ M^{-1}s^{-1}$

These rate constants are lower by a factor of ca. 2, from those derived from results using a γ source with a higher dose rate

This systematic difference suggests that one of the assumptions taken in the derivation of the rate constants is not completely accurate:

- •k_3 is somewhat dependent of n
- •n increases with the dose rate of the γ source, *i.e.* more methyl radicals are covalently bound to a given particle at higher dose rates
- •The increase of n increases the electron density on the NPs and therefore probably increases k_3
- •This suggests that the lifetime of, $(NP)\text{-}(CH_3)_n$, has to be relatively long in order of enabling n to increase significantly beyond $n = 1$

Lifetime of (NP)-CH_3

$$(1)\qquad \cdot CH_3 + (NP) \rightarrow (NP)-CH_3$$

$$(2)\qquad (NP)-(CH_3)_{n-1} + \cdot CH_3 \rightarrow (NP)-(CH_3)_n$$

$$(3)\qquad (NP)-(CH_3)_n \rightarrow (NP)-(CH_3)_{n-2} + C_2H_6$$

$$(4)\qquad (NP)-(CH_3)_n + \cdot CH_3 \rightarrow (NP)-(CH_3)_{n-1} + C_2H_6$$

The rate of $\cdot CH_3$ radical production, r:

$$r = 18\frac{rad}{\min}\cdot\frac{1\min}{60\sec}\cdot 10^{-9}\frac{M}{rad}\cdot 6 = 1.8\cdot 10^{-9} M\sec^{-1}$$

The minimal lifetime (τ) of the methyls bound to the NPs, (NP)-CH3:

$$\mathrm{Au} \rightarrow \tau \geq \frac{2[\mathrm{Au}]_{\mathrm{NP}}}{\mathrm{r}} = \frac{2\times 1.7\cdot 10^{-7}\,\mathrm{M}}{1.8\times 10^{-9}\,\mathrm{M}\cdot\mathrm{sec}^{-1}} \geq 188\ \mathrm{sec}$$

$$\mathrm{Ag} \rightarrow \tau \geq \frac{2[\mathrm{Ag}]_{\mathrm{NP}}}{\mathrm{r}} = \frac{2\times 7\cdot 10^{-9}\,\mathrm{M}}{1.8\times 10^{-9}\,\mathrm{M}\cdot\mathrm{sec}^{-1}} \geq 8\ \mathrm{sec}$$

Estimation of the (NP)-CH_3 bond strength:

From the value of τ using Frenkel equation,

$$\tau = \tau^0 \exp(-\Delta H / RT) \ , \tau^0 = 10^{-13} \text{ sec.}$$

One can calculate that the **(NP)-CH_3 bond strengths are $\geq$ 70 kJ/mole**

i.e. the bond strengths are of at least the same order of magnitude as many metal-carbon σ bonds in organo-metallic complexes. For the Au^0-NPs this conclusion is in accord with recent conclusions regarding the (Au^0-NP)-H bond strength, as it is reasonable to expect that the (Au^0-NP)-CH_3 and (Au^0-NP)-H bond strengths are similar.

Reactions of radicals with TiO_2

Surprisingly TiO_2-NPs react similarly:

$[TiO_2\text{-NPs}] + n{\cdot}CH_3 \rightarrow [TiO_2\text{-NPs}]\text{-}(CH_3)_n$

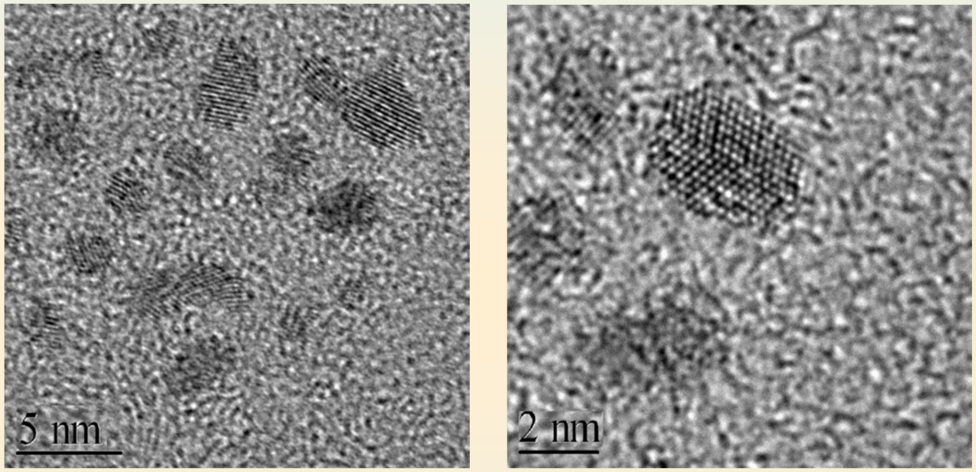
$[TiO_2\text{-NPs}]\text{-}(CH_3)_n \rightarrow [TiO_2\text{-NPs}]\text{-}(CH_3)_{n\text{-}m} + (m/2)C_2H_6$

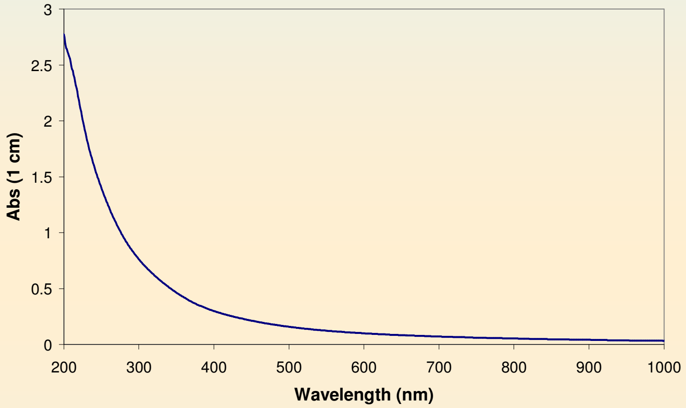
$t_{1/2} \sim 8$ sec.

$[TiO_2\text{-NPs}] + {\cdot}CH_2(CH_3)_2COH \rightarrow$
$[TiO_2\text{-NPs}]\text{-}CH_2(CH_3)_2COH$

$[TiO_2\text{-NPs}]\text{-}CH_2(CH_3)_2COH \rightarrow [TiO_2\text{-NPs}]^+ +$
$(CH_3)_2C{=}CH_2 + OH^-$

- **Platinum NPs** aqueous suspension was prepared by the reduction of Pt^{IV} ions with $NaBH_4$
- The resultant color observed was brown, typical to Pt NPs





HR-TEM micrographs of the Pt NPs

$[Pt]_{NP} = 2.2 \times 10^{-7}$ M , d=3.2 nm (ca. 500 surface atoms/NP)

Solution composition:

$Pt(SO_4)_{2(aq)}$ (2.5×10^{-4} M of Pt^{4+}), $NaBH_4$ (2×10^{-3} M before the reduction). The NPs final pH was 8.0 (±0.2)

Results- reactions between methyl radicals and Pt-NPs

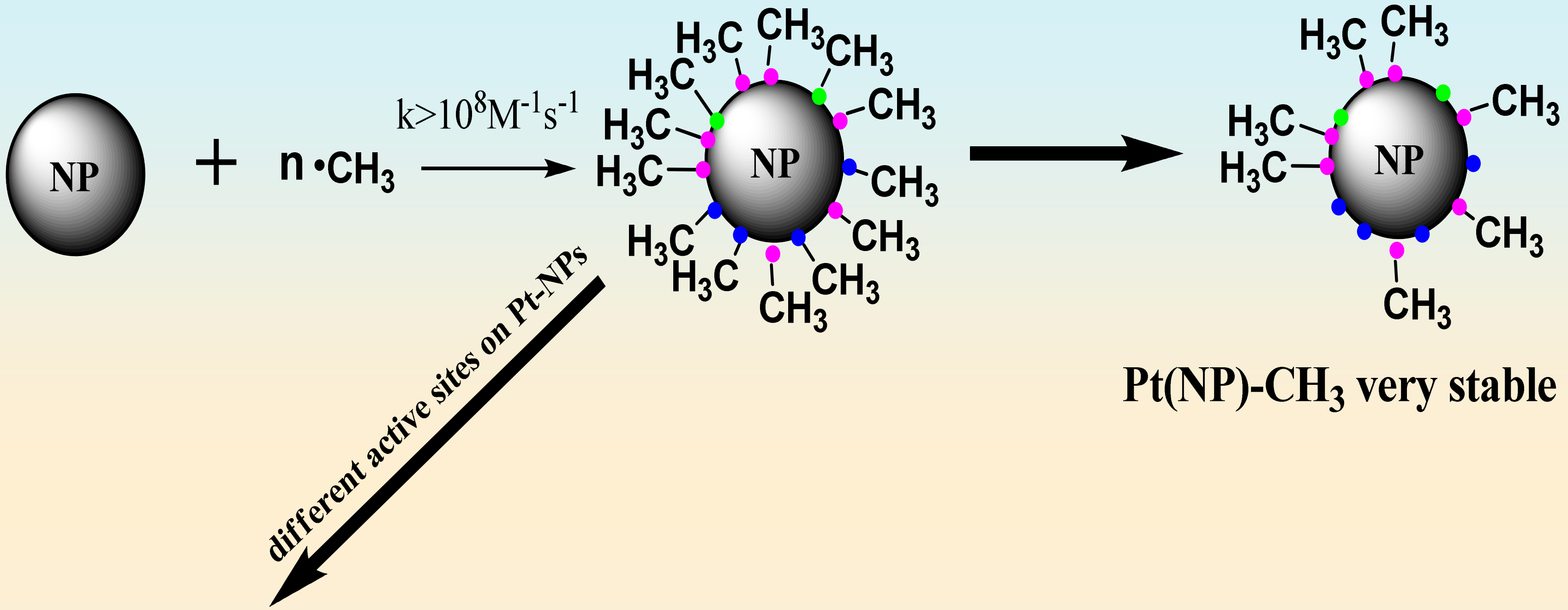
Sample [a]	**G(CH_4)**	**G(C_2H_6)**	**G(C_2H_4)**	**CH_4/C_2H_6**	**$G_{(total)}$**[c]
Pt^0-NPs (0.05 M DMSO)	0.59	0.80	0.10	0.74	2.39
Pt^0 -NPs (0.05 M DMSO) after H_2 [b]	2.08	-	-	-	2.08 (G_t=2.08 +2.39 =4.47)
Blank (0.05 M DMSO)	1.7	2.4		0.70	6.5

[a] The solutions were irradiated at a dose rate of 12 Gy/min (total dose 184 Gy), all samples contained 2.2x10^{-7}M Pt^o-NPs and 0.05 M $(CH_3)_2SO$ at pH 8.0 ± 0.2. (blank- an aqueous solution containing $(CH_3)_2SO$ without NPs). [b] After H_2 injection (2 ml, 1 atm into a 14 ml vial containing 5 ml of an irradiated sample).

[c] Gtotal ($\cdot CH_3$)= G(CH_4) + 2G(C_2H_6) + 2G(C_2H_4) .Error limits ± 10%. (C_2H_4 ± 20%).

R. Bar-Ziv, I. Zilbermann, O. Oster-Golberg, T. Zidki,, G. Yardeni, H. Cohen, D. Meyerstein, Chemistry Eur. J., 18, 4699-4705, 2012.

Reaction mechanism



Pt(NP)-CH_3 very stable

(2) (NP)-$(CH_3)_n \longrightarrow$ (NP)-$(CH_3)_{n-2}$ + C_2H_6

(3) (NP)-$CH_3 \rightleftharpoons CH_2$=(NP)-H (α-elimination)

(4) (NP)=CH_2 + $\cdot CH_3 \longrightarrow$ (NP)-$CH_2CH_3 \longrightarrow$ (NP)-H + C_2H_4 (β-hydride elimination)

$\xrightarrow{=CH_2}$ (NP) + C_2H_4

$\xrightarrow{=CH_2}$ (NP)-$CH_2CH_2CH_3$ (polymerization)

Surface Coverage

G = 2.1 for CH_4 released from the NPs by the addition of H_2 is equivalent to 38.3 μM.

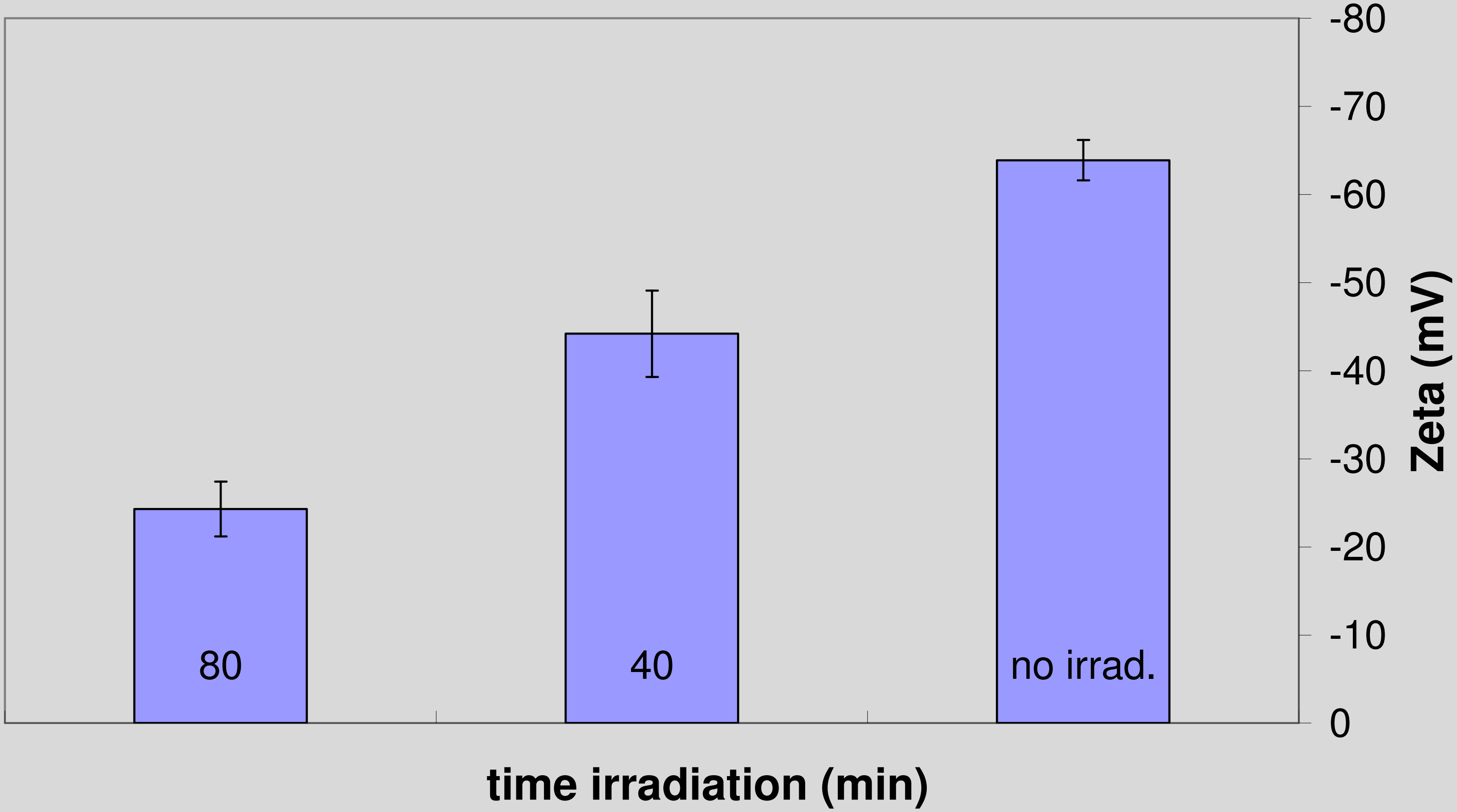
A rough calculation of the number of Pt^o atoms on the surface of the NPs gives ~ 500 atoms per NP.

As the concentration of the NPs is $2.2x10^{-7}$ M the concentration of Pt^o surface atoms is ~ $1.1x10^{-4}$ M.

Thus the results point out that methyls are bound to ca. 35 % of the surface atoms, a relatively dense coverage.

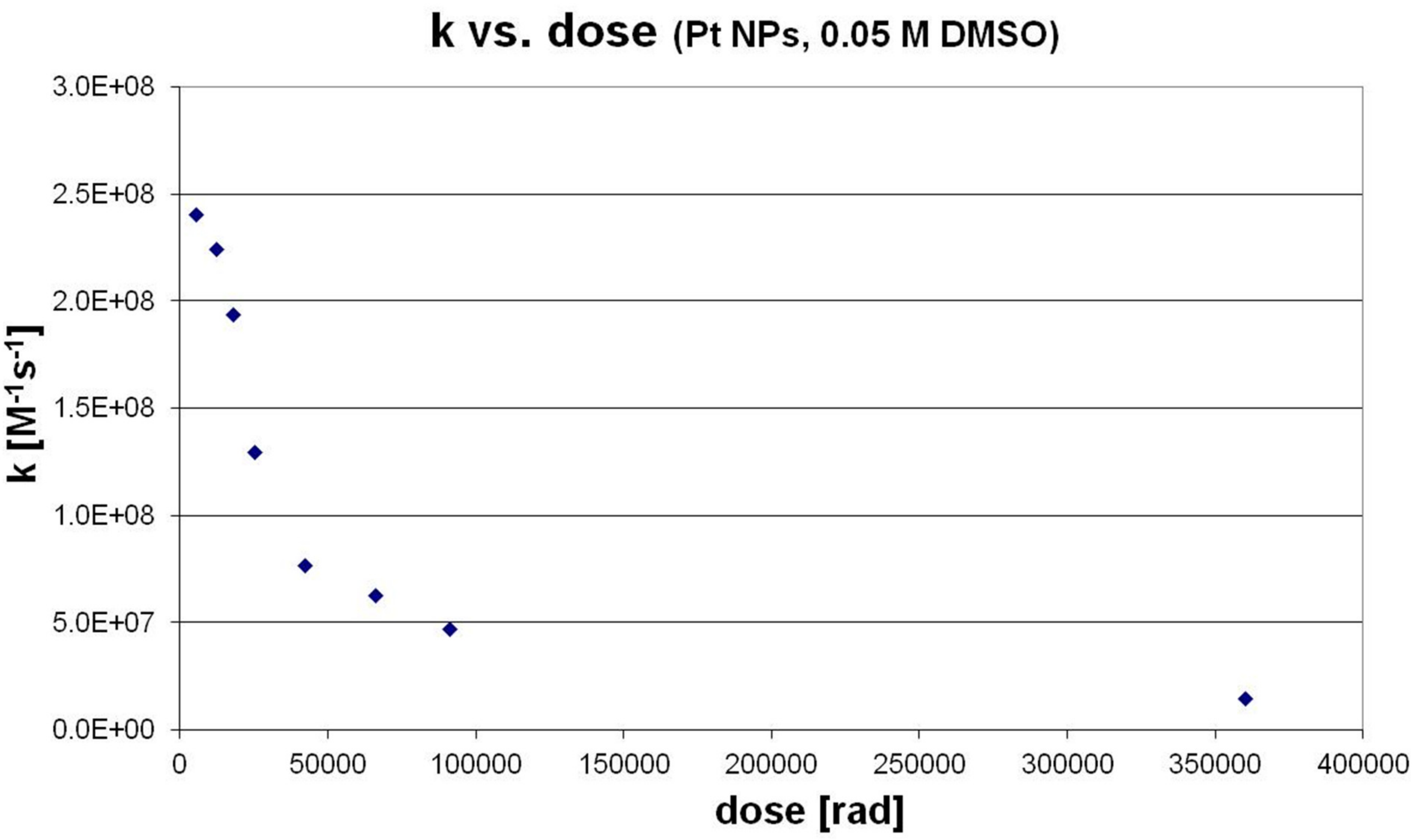
This coverage might depend on the total dose delivered to the sample and might affect $k(\cdot CH_3 + Pt^o\text{-NPs})$.

Zeta Potential Pt NPs vs. time irr. (dose)



Pt NPs + 0.05 M $(CH_3)_2SO$ before and after irradiation (dose rate 1150 rad/min)

R. Bar-Ziv *et. al*. to be published.


k vs. dose (Pt NPs, 0.05 M DMSO)
k [M^{-1}s^{-1}]
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
0
50000
100000
150000
200000
250000
300000
350000
400000
dose [rad]

Summary of the Reactions of Methyl Radical with NPs dispersed in aqueous solutions

NPs[a]	major product	minor product	traces
Au	C_2H_6	-	-
Ag	C_2H_6	-	-
Pt	(NP)-CH_3	C_2H_6, CH_4	C_2H_4, polymerization
Pd	(NP)-CH_3	CH_4, C_2H_6	C_2H_4, polymerization
Au-Pt	C_2H_6	(NP)-CH_3	C_2H_4
Cu	CH_4	C_2H_6	-
Cu@CuO	C_2H_6	CH_4	-
TiO_2	C_2H_6	-	-

[a] The suspensions were irradiated at ^{60}Co gamma source and contained $(CH_3)_2SO$ and were N_2O saturated

Catalysis of water reduction, HER

$H_2O \xrightarrow{\gamma,\ e^-} e^-_{aq}$ (2.65); $^{\cdot}OH$ (2.65); $H^{\cdot}$ (0.60); H_2 (0.60); H_2O_2 (0.75)

$HC(CH_3)_2OH + \cdot OH/H\cdot \rightarrow \cdot C(CH_3)_2OH + H_2O/H_2$

$(CH_3)_2CO + e^-_{aq} + H_3O^+ \rightarrow \cdot C(CH_3)_2OH$

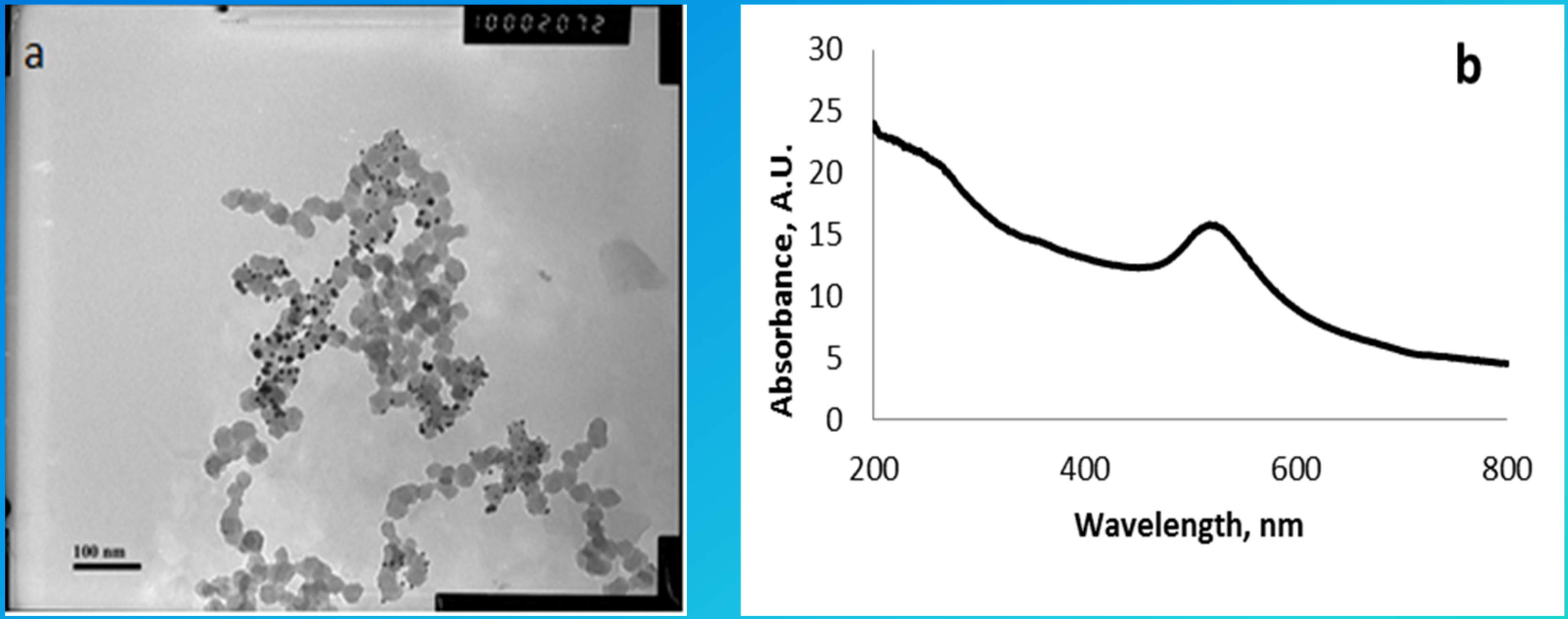
$2\cdot C(CH_3)_2OH \rightarrow (CH_3)_2CO + HC(CH_3)_2OH$

$n\cdot C(CH_3)_2OH + NP \rightarrow n(CH_3)_2CO + nH_3O^+ + NP^{n-}$

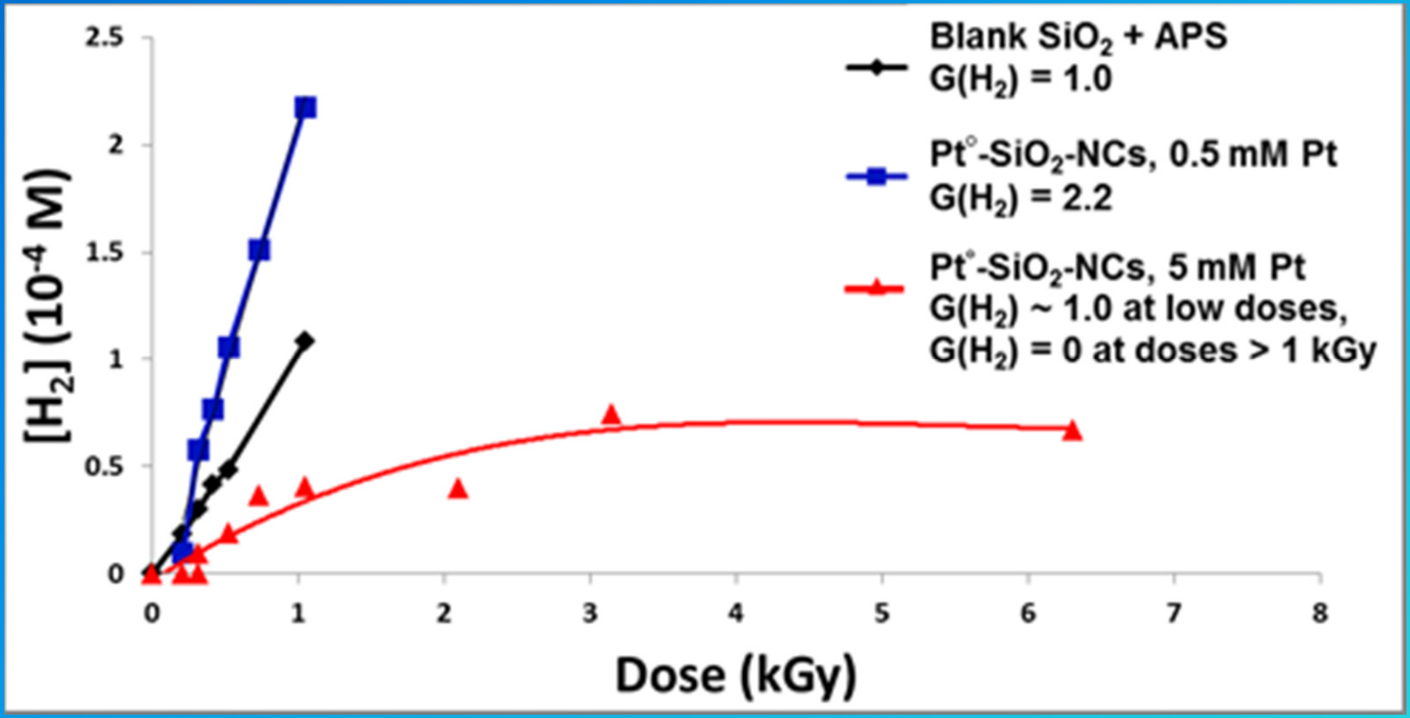
$NP^{n-} + mH_3O^+ \rightarrow NP^{n-m}\text{-}H_m$

$NP^{n-m}\text{-}H_m \rightarrow NP^{n-m}\text{-}H_{m-l} + \tfrac{1}{2} H_2$

The Effect of Silica-Nanoparticles Support on the Catalytic Reduction of Water by Gold and Platinum NPs.



(a) TEM micrograph of the SiO_2-Au^0-NCs and (b) the UV-VIS spectrum of a suspension of these composite particles. The absorbance was measured in in a 1 mm optical path cuvette and the spectrum is normalized to 1 cm optical path.



H_2 yields from irradiated SiO_2-NPs, blank, (black line) and Au^0-SiO_2-NCs suspensions at [Au] = 5 and 25 mM (blue and red lines, respectively) at a constant molar ratio $[(SiO_2)_p]/[Au] = 17.8$.

Catalysis and deactivation of water reduction by various [M° -NPs] and [M° -SiO_2-NCs]

	Catalysis		Deactivation		
Catalyst	**$G(H_2)_{Max}$**	**[M], mM**	**$G(H_2)_{Min}$**	**[M], mM**	**Dose Rate, Gy/min**
Ag° -NPs	3.0	0.25			8.3
Ag° -NPs	2.9	1.4-170			106
Au° -NPs	4.2	0.54			160
Au° -NPs	3.9	1.4-170			72
Pt° -NPs (pH 1)	6	0.05			13.8
Pt° -NPs (pH 8)			0	0.25	10
Ag° -SiO_2-NCs	1.9	0.12	0	120	106
Ag° -SiO_2-NCs	1.0	12	1.0	12	106
Au° -SiO_2-NCs	2.9	5			106
Au° -SiO_2-NCs	1.7	25			106

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Catalytic H_2 formation	Full deactivation/destruction	Non catalytic H_2 formation

Conclusions

- Radicals react in fast reactions with surfaces forming transients with σ-bonds to the surface.
- The mechanism of decomposition of the transients thus formed depends on the nature of the surface; the radical; the solvent *etc.*
- The support of the NPs affects dramatically their properties.
- These processes have to be considered in catalytic, electrochemical, photo-chemical and environmental processes.

The work of the righteous is done by others:

Beer-Sheva:

Prof. H. Cohen
Dr. A. Masarwa
Dr. I. Zilbermann
Dr. I. Rusonik
Dr. T. Zidki
Dr. O. Oster-Golberg
Mr. R. Bar-Ziv
Ms. A. Elisseev

Thanks for your attention

Heterolysis

$$\begin{tikzcd}
 & M^{n+1}L_m + RH + OH^- \\
L_mM^{n+1}\text{-}R + H_2O \arrow[ur, "a)"] \arrow[dr, "b)"'] & \\
 & M^{n-1}L_m + ROH/R_{-H} + H_3O^+
\end{tikzcd}$$

Homolysis

$$L_mM^{n+1}\text{-}R + L \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} M^nL_m + R\cdot$$

Followed by:

$$2\ R\cdot \longrightarrow R_2/RH + R_{-H}$$

$$R\cdot + S \longrightarrow P$$

$$\cdot R + L_{m-1}M^{n+1}\text{-}R \xrightarrow{L} M^nL_m + R_2/(R^+ + R^-)$$

$$\cdot R + O_2 \longrightarrow RO_2\cdot$$

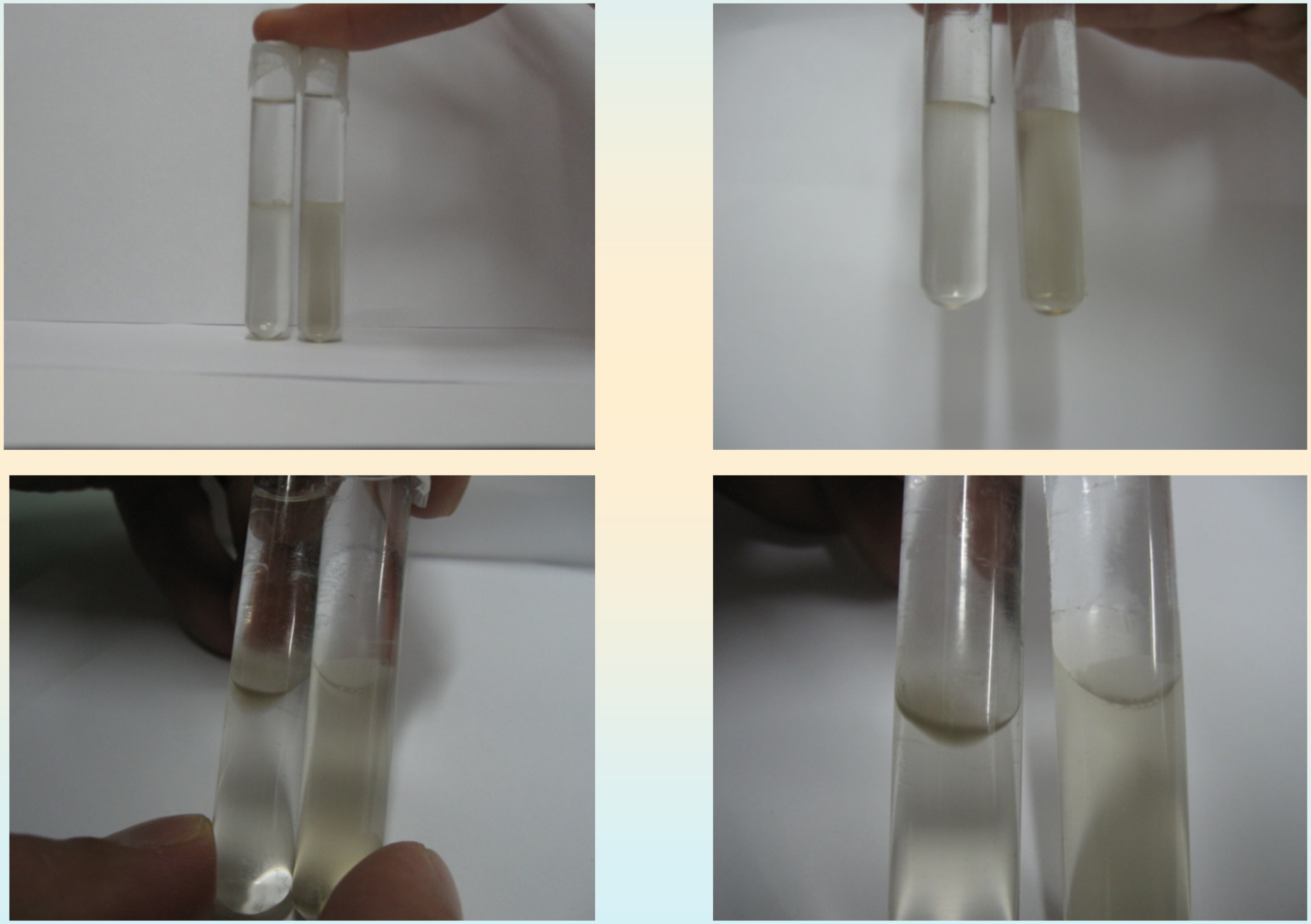
β- Eliminations

$$L_mM^{n+1}\text{-}CR^1R^2CR^3R^4X \longrightarrow M^{n+1}L_m + R^1R^2C{=}CR^3R^4 + X^-$$

X = OR, NR_2, OPO_3^{2-}, Cl, NHC(O)R

good leaving group bound to β-carbon

Pt NPs solutions- extraction with dodecane - before and after irradiation , *i.e.* after reaction with $\cdot CH_3$ radicals



From the results one concludes that

$G(\cdot CH_3 + Pt^o\text{-}NPs) = 6.5 - (0.59 + 2x0.29) \sim 5.4.$

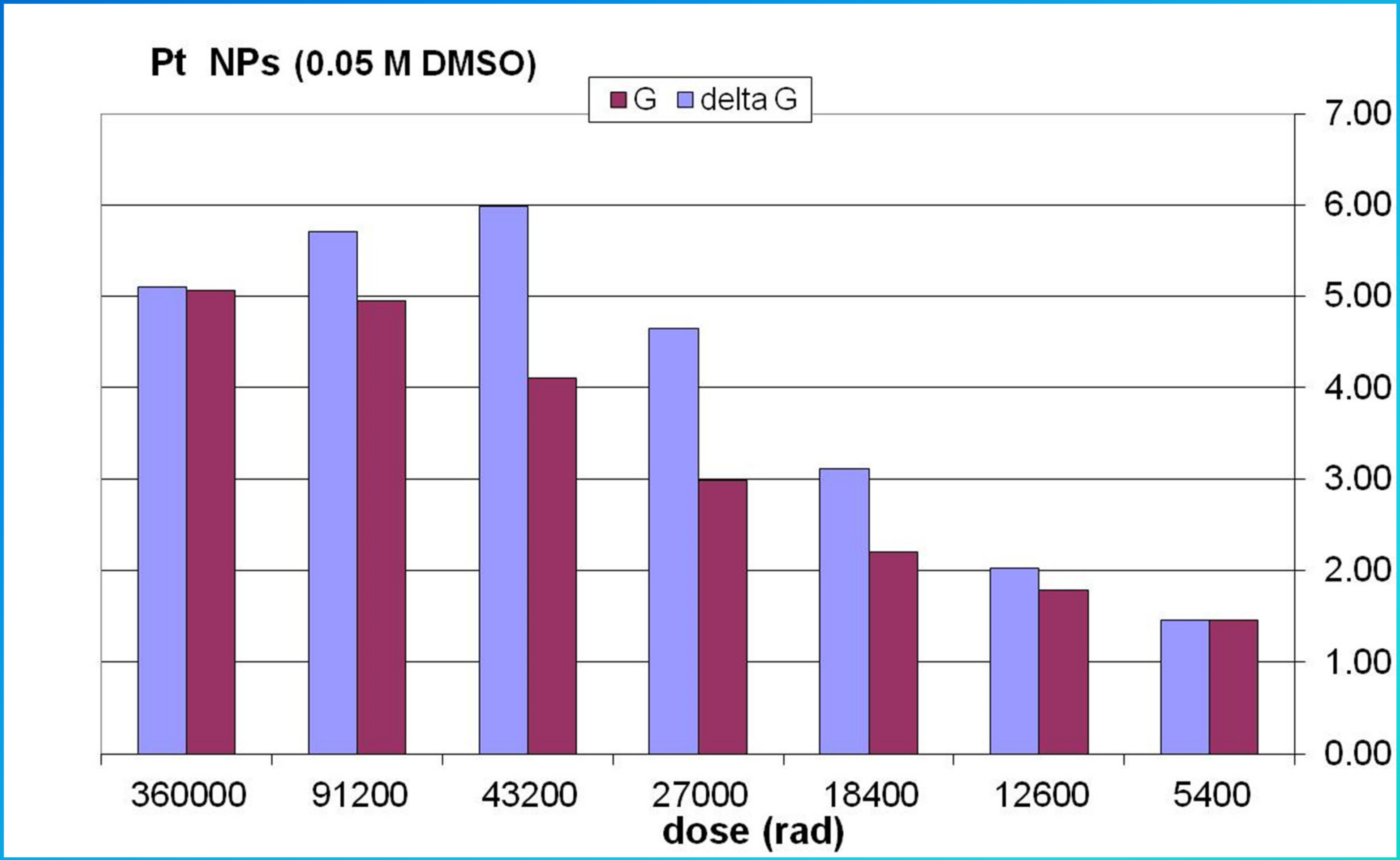
i.e. under the experimental conditions 82% of the methyl radicals react with the NPs.

Therefore to derive $k(\cdot CH_3 + Pt\text{-}NPs)$, the following expression should be applied:

$G(\cdot CH_3 + (CH_3)_2SO) / G(\cdot CH_3 + Pt\text{-}NPs) = k[\cdot CH_3]\cdot[(CH_3)_2SO]/k[\cdot CH_3]\cdot[NP]$

$0.59/5.4 = 100[\cdot CH_3]\cdot[(CH_3)_2SO]/ k[\cdot CH_3]\cdot[NP]$ **=>**

$k = 100x0.05x5.4/0.59x2.2x10^{-7} \sim$ **$2\ x10^{8}\ M^{-1}s^{-1}$**



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