RADICAL REACTIONS AT SURFACES

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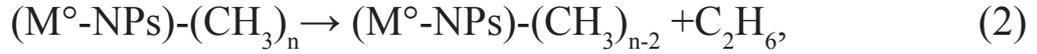[5]*Chemistry Department, Ben-Gurion University, Beer-Sheva, Israel*

Abstract

This short review discusses recent mechanistic studies concerning the reactions of alkyl radicals with surfaces of metals and semiconductors suspended in aqueous solutions. The results point out that these reactions are fast and involve the formations of transients with σ-bonds between the radical and the surface. The mechanism of decomposition of the transients thus formed depends on the nature of the surface; the radical; the solvent *etc*. In reaction with nano-particles supported on semiconductors or on insulators the nature of the support affects dramatically the mechanism of decomposition of these transients. These processes have to be considered in catalytic, electro-chemical, photo-chemical and environmental processes.

Alkyl radical reactions at surfaces have been suggested to be involved in variety of catalytic [1-3], photo-catalytic [4-6], electro-chemical [7, 8], synthetic [9, 10], geological [11], mechano-chemical [12] and environmental processes [6, 13] and for binding organic molecules to surfaces [14]. The surface chemistry of methyl radical has received considerable attention in recent years because of its relevance to the catalytic utilization of methane [15, 16]. Methyl radicals are proposed to be the surface reaction intermediates in the partial oxidation of methane to methanol and formaldehyde [17]. The first question asked was whether alkyl radicals formed in the reaction of zero-valent iron, ZVI, with halo-organic compounds react with the ZVI [18, 19]. The results pointed out that indeed these reactions are fast, and occur also for other metals [18, 19]. Furthermore the mechanisms of decomposition of the transients formed in these reactions depend on the nature of the metal and the substituents on the alkyl radicals [18-20].

In order of deriving rate constants of these reactions it was decided to measure the kinetics of reaction of methyl radicals with metal nano-

particles, M°-NPs. First the reactions with Ag°-NPs and Au°-NPs were studied [21]. The results pointed out that the reactions occurring are:

$$CH_3 + (M°\text{-}NPs)\text{-}(CH_3)_{n-1} \rightarrow (M°\text{-}NPs)\text{-}(CH_3)_n, \tag{1}$$

$$(M°\text{-}NPs)\text{-}(CH_3)_n \rightarrow (M°\text{-}NPs)\text{-}(CH_3)_{n-2} + C_2H_6, \tag{2}$$

or:

$$(M°\text{-}NPs)\text{-}(CH_3)_n + \cdot CH_3 \rightarrow (M°\text{-}NPs)\text{-}(CH_3)_{n-1} + C_2H_6, \tag{3}$$
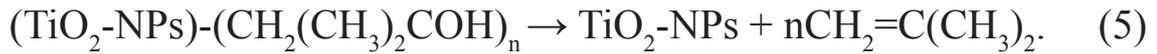
where the rate constants of reaction (1) are very fast and depend slightly on n [21, 22]. From the results one can estimate the minimal lifetimes of the transients (M°-NPs)-(CH$_3$), which are relatively long [22].

Analogous reactions were reported for the reactions of methyl radicals TiO$_2$-NPs [22]. Furthermore the reaction of $\cdot CH_2(CH_3)_2COH$ radicals with TiO$_2$-NPs was shown to proceed via [23]:

$$TiO_2\text{-}NPs + n\cdot CH_2(CH_3)_2COH \rightarrow (TiO_2\text{-}NPs)\text{-}(CH_2(CH_3)_2COH)_n, \tag{4}$$

$$(TiO_2\text{-}NPs)\text{-}(CH_2(CH_3)_2COH)_n \rightarrow TiO_2\text{-}NPs + nCH_2{=}C(CH_3)_2. \tag{5}$$
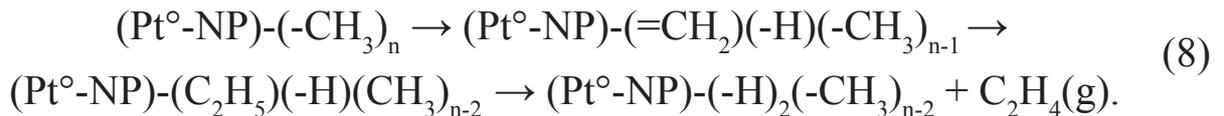
These results point out that the radicals obtained in solar energy conversion processes using semiconductors react with the surface and not in the homogeneous media.

Recently [24, 25], it has been shown that platinum nanoparticles (Pt^0-NPs) react with methyl radicals differently than with other noble metal NPs, the major reaction with the Pt^0-NPs is:

$$(Pt°\text{-}NP) + n{\cdot}CH_3 \rightarrow (Pt°\text{-}NP)\text{-}(\text{-}CH_3)_n. \tag{6}$$

This reaction is in principle identical to reaction (1), however in this case the major stable product is the nano-particle coated with methyl groups, (Pt°-NPs)-(CH$_3$)$_n$. Several minor gaseous products *e.g.* C$_2$H$_6$ and C$_2$H$_4$ are also formed at different sites on the platinum surfaces according to the following processes:

$$(Pt°\text{-}NP)\text{-}(\text{-}CH_3)_n \rightarrow (Pt°\text{-}NP)\text{-}(\text{-}CH_3)_{n-2} + C_2H_6(g), \tag{7}$$

$$(Pt°\text{-}NP)\text{-}(\text{-}CH_3)_n \rightarrow (Pt°\text{-}NP)\text{-}({=}CH_2)(\text{-}H)(\text{-}CH_3)_{n-1} \rightarrow$$
$$(Pt°\text{-}NP)\text{-}(C_2H_5)(\text{-}H)(CH_3)_{n-2} \rightarrow (Pt°\text{-}NP)\text{-}(\text{-}H)_2(\text{-}CH_3)_{n-2} + C_2H_4(g). \tag{8}$$

The layer of the methyl groups bound to the surface of the NPs decreases the rate constant of reaction (6), k$_6$, and affects the NPs' properties

and reactivity. The surface layer of methyls can be released as methane via the reaction of the $(Pt^0$-NPs$)$-$(CH_3)_n$ with H_2 [25] The nano-particles after the release of the methyls bound to their surface are more reactive towards methyl radicals than the original particles and than nano-particles pre-treated with H_2 [26].

Analogous studies concerning the reactions of methyl radicals with other NPs suspended in aqueous solutions were carried out, the results are summed up in Table 1.
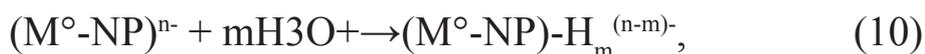
Table 1

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

NPs	Major product	Minor products	Trace products
Au°	C_2H_6	-	-
Ag°	C_2H_6	-	-
Pt°	$(Pt°$-NP$)$-$(-CH_3)_n$	C_2H_6; CH_4	C_2H_4; Oligomerization products
Pd° [27]	$(Pd°$-NP$)$-$(-CH_3)_n$	CH_4; C_2H_6	C_2H_4; Oligomerization products
Pt°/Pd° = 1 [27]	$(M°$-NP$)$-$(-CH_3)_n$	C_2H_6; CH_4	C_2H_4; Oligomerization products
Pt°/Au° = 1 [27]	C_2H_6	$(M°$-NP$)$-$(-CH_3)_n$	C_2H_4
Cu° [28]	CH_4	C_2H_6	-
Cu@CuO [27]	C_2H_6	CH_4	-
TiO$_2$	C_2H_6	-	-

The results point out that Pd°-NPs have similar properties to those of the Pt°-NPs, though the ethane and methane yields are considerably higher than those in the Pt°-NPs system [27]. The results for the Pt°/Pd° alloy are about the average of those obtained for the neat M°-NPs [27]. On the other hand the results for the Pt°/Au° alloys are similar to those of the Au°-NPs [27], i.e. in this case a considerable synergistic effect is observed. The results for the Cu°-NPs point out that the considerably stronger reducing agent, Cu°-NPs, reduces the methyl radicals. On the other hand the Cu°@CuO-NPs behave similarly to the TiO$_2$-NPs, a result that suggests that oxide covered NPs react with methyl radicals to yield ethane [28].

The observation that all the reactions of methyl radicals with metal or semiconductor nano-particles are very fast is attributed to the fact that the electrons in the conduction bands are really unpaired electrons and behave therefore as radicals.

It is known that noble-metal-NPs catalyze the reduction of water by reducing radicals, e.g. by $\cdot C(CH_3)_2OH$ [3, 29-43]. The rate constants of reaction (10) depend strongly on the nature of the NPs.

$$n\cdot C(CH_3)_2OH + M°\text{-}NP \rightarrow n(CH_3)_2CO + nH_3O_+ + (M°\text{-}NP)^{n-}, \quad (9)$$

$$(M°\text{-}NP)^{n-} + mH3O+ \rightarrow (M°\text{-}NP)\text{-}H_m^{(n-m)-}, \quad (10)$$

$$(M°\text{-}NP)\text{-}H_m^{(n-m)-} \rightarrow (M°\text{-}NP)\text{-}H_{m-2}^{(n-m)} + H_2 \quad (11)$$

or:

$$(M°\text{-}NP)\text{-}H_m^{(n-m)-} + H^+ \rightarrow (M°\text{-}NP)\text{-}H_{m-}^{(n-m+1)} + H_2. \quad (12)$$

The rate constants of reaction (10) depend on the nature of M°. It was shown that this rate constant depends on the over-potential for hydrogen evolution that has built on the $(M°\text{-}NP)^{n-}$. Consequently, for $M° = Ag°$ or $Au°$ the reaction is relatively slow [37, 44], while the reaction is very fast for $M° = Pt°$ [45].Surprisingly recent results point out that when the M°-NPs are supported on SiO2-NPs the support has a major effect on the catalytic activity of the M°-NPs [46, 47]. At present we have no explanation to the effect of the "inert" support on the catalytic properties of the NPs.

Recent results point out that $(M°\text{-}NP)\text{-}H_m^{(n-m)-}$, $M° = Au°$ or $Pd°$, or in the case of $Pd°$ $(Pd°\text{-}NP)n\text{-}$ are catalysts for the reduction of perchlorate in neutral aqueous solutions [48].

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