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HAL Id: jpa-00251457

<https://hal.science/jpa-00251457>

Submitted on 4 Feb 2008

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Comparison of k_{ps} values in pure pentene isomers and in abs. EtOH/cis-2-pentene/Pt, abs. EtOH/cis-2-pentene/Pt-on-charcoal and D₂O mixtures

J.L. CIOTTONE, M. BROWN, K. FUHS and C. SHEEHAN

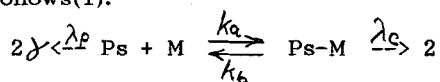
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ABSTRACT

k_{ps} values are an indication of o-Ps reactivity in molecular media via pseudo first order kinetics. Although pure pentene isomers exhibit similar o-Ps annihilation characteristics, cis-2-pentene shows rather unusual behavior when mixed with abs. EtOH and a heavy metal catalyst. In this study, comparison of k_{ps} values in pure 1-pentene, trans-2-pentene and cis-2-pentene isomers with those for various abs. EtOH/pentene isomers/Pt, abs. EtOH/pentene isomer/Pt-on-charcoal and D₂O/Pd mixtures will serve to further characterize o-Ps behavior in molecular liquids. The k_{ps} values will also be indirectly related to catalytic activity of Pt and Pt-on-charcoal.

INTRODUCTION

Chemical quenching of o-Ps in molecular liquids may be studied using classical transition state theory, in which o-Ps forms a complex with medium molecules, as follows(1):



where

λ_p = o-Ps pick-off annihilation rate

λ_c = o-Ps chemical quenching annihilation rate

k_a & k_b = rate constants for formation and dissociation of the Ps-M complex

Since medium molecules are present in large excess compared to o-Ps, the system may be treated using pseudo first order kinetics.

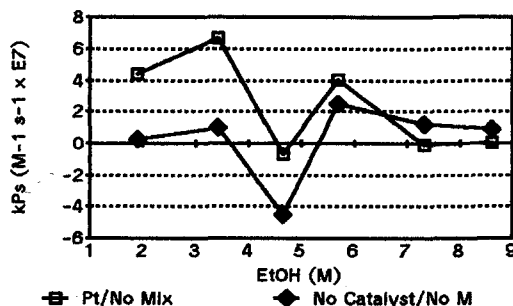
Pentene reaction mixtures consisted of 10 μ Ci ²²Na, absolute ethanol and pentene isomer. The abs. EtOH/pentene volume ratio was varied as shown in Table 1. Lifetime and intensity determinations were made for mixtures containing no catalyst, with catalyst, with no external mixing and with external mixing (2,3). D₂O mixtures consisted of 40 μ Ci ²²Na, 2ml D₂O and varying amounts of 5% Pd-on-

charcoal catalyst, shown in Table 5. In these mixtures, Ps is formed in the molecular medium outside the heavy metal catalyst and then interacts with the metal double surface layer, described by the Jellium model.

Table 1

Abs. EtOH/Pentene Volume Ratios

Pentene Isomer	Abs. EtOH/Pentene Vol. Ratios(ml)	Pt or 5% Pt-on-ch. catalyst(mg)
1-Pentene	2/1, 1/1, 1/2	0.6
trans-2-Pentene	2/1, 1/1, 1/2	0.6
cis-2-Pentene	2/1, 1/1, 1/2, 0.25/2, 0.75/2, 1.5/2	0.6



Graph 2

Abs. EtOH/cis-2-Pentene

RESULTS

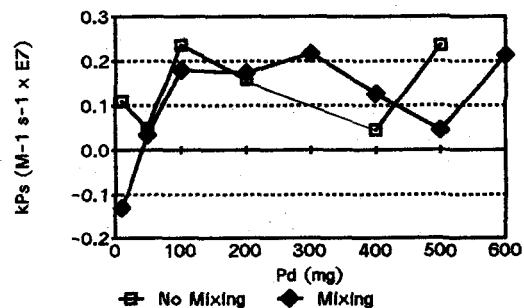
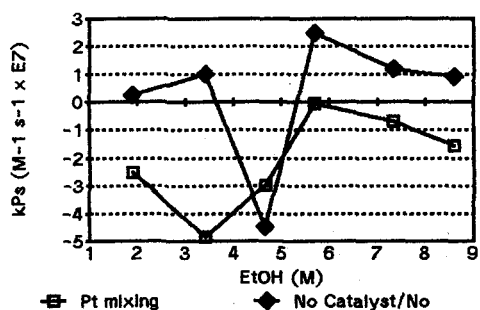
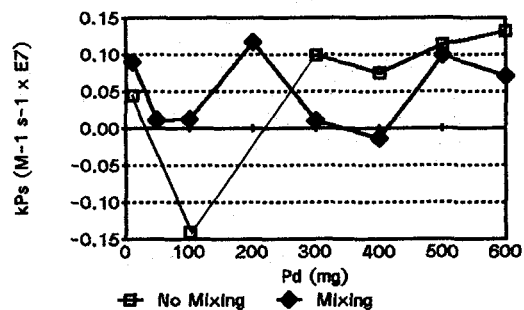
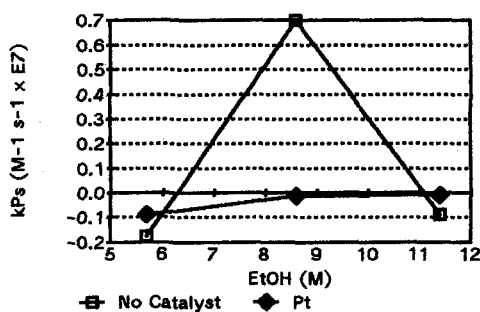
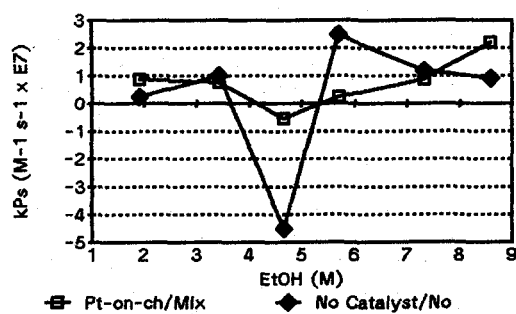
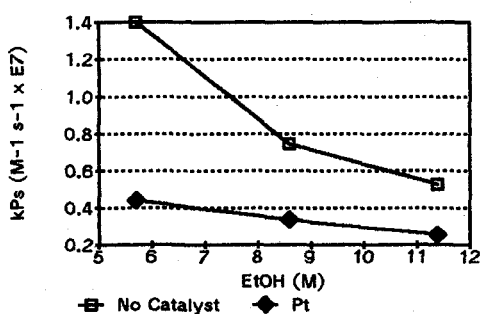
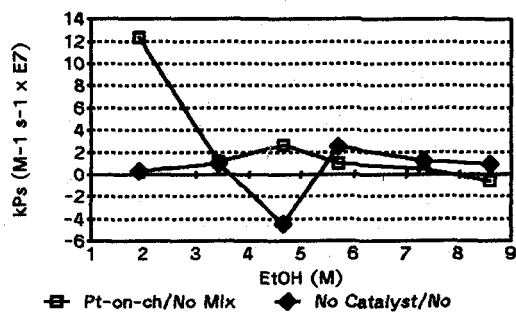
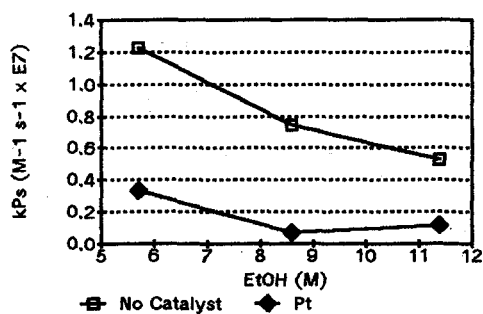
Abs. EtOH/Pentene mixtures

Graph 1 shows k_{ps} values for 2/1, 1/1 and 1/2 abs. EtOH/pentene ratios with no catalyst and upon addition of 0.6mg Pt powder. Although τ_3 did not change appreciably for 1-pentene, trans-2-pentene or cis-2-pentene, comparison of k_{ps} values is interesting. One pentene and trans-2-pentene show similar k_{ps} trends. When catalyst was added, k_{ps} values were lower for all three abs. EtOH/pentene ratios. One would expect lower k_{ps} values upon addition of catalyst since double bond electron density would be less available to Ps if pentene were adsorbed to the catalyst surface at the double bond.

The cis-2-pentene isomer shows very different and interesting behavior. For the 1/2 and 2/1 ratios marked increases in k_{ps} were observed when Pt powder was added, while the 1/1 mixture showed a large decrease. The increased k_{ps} values for the 1/2 and 1/1 ratios indicate the possible formation of some type of bound, cage-like species between o-Ps and medium molecules.

Earlier lifetime and intensity measurements for this isomer resulted in an o-Ps intensity approaching 100% for the 1/2 abs. EtOH/cis-2-pentene ratio. Subsequent repetition of this trial resulted in an o-Ps intensity of approximately 75%. Several very long lifetimes were obtained. The 1/2 ratio again showed unusual results. For the series with no catalyst, this ratio has the longest lifetime (5.26ns). Upon addition of Pt powder, a dramatic increase in lifetime occurred (from 5.26ns to 25.5ns). The 0.5/2 ratio showed a similar lifetime increase. With Pt-on-charcoal catalyst, a large lifetime increase was obtained for the 0.25/2 ratio. k_{ps} values increased for four of these reaction mixtures, including the 1/2 and 0.5/2 ratios, when Pt catalyst was added (see Graph 2). Since this indicates increased reactivity of o-Ps with medium molecules, it is again an indication of formation of a loosely bonded o-Ps species.

When external mixing was applied with a Vortex mixer during the counting period, all lifetimes for samples with Pt catalyst were markedly quenched. Note that k_{ps} values decreased for five of the six samples (Graph 3). This clearly indicates disruption of the cage-like structures during mixing.



For samples containing Pt-on-charcoal, increases in k_{ps} were observed for three reaction mixtures when catalyst was added (Graph 4). The 0.5/2 ratio showed only a slight increase, while the 0.25/2 ratio showed a very large increase. An unusually long lifetime was obtained for this sample (12.9ns) and the combined o-Ps intensity was approximately 43%. Although a long lifetime was not obtained for the 1/2 ratio, the combined o-Ps intensity was 66%. Antiinhibition is again occurring here due to enhancement of o-Ps reactivity with medium molecules. External mixing resulted in decreases in k_{ps} values for three samples, the largest decreases occurring for the 0.5/2 and 1/2 ratios (Graph 5). This was accompanied by a decrease in lifetime for four samples.

D₂O/Pd mixtures

k_{ps} were calculated for several D₂O/Pd and D₂O/Pd-on-charcoal mixtures. For samples containing Pd with no mixing, k_{ps} values generally increased with decreasing Pd content, as did the intensity values (Graph 6). Mixing and non-mixing produced almost exactly opposite effects with respect to Ps reactivity. For samples containing Pd-on-charcoal erratic behavior was observed (Graph 7).

DISCUSSION

k_{ps} values in weak Ps acceptors are known to vary in different solvents and are strongly influenced by polarity differences(4). The dipole moments of EtOH and D₂O are similar; i.e., 1.66D and 1.85D, respectively (5). The dipole moment for pentene isomers is approximately 0.34D. Substitution of D₂O for EtOH in the cis-2-pentene reaction mixtures is necessary for a valid comparison of these two solvents.

The k_{ps} values reported here have clarified our hypothesis that clathrate-type structures are forming in several abs. EtOH/cis-2-pentene mixtures with catalyst. They have also indicated that a transition state or other loosely bonded species involving o-Ps is forming(6). This could be verified by activation energy determination from temperature controlled experiments followed by computer simulation of the potential energy surface and geometry of the bonded species. Future work in our laboratory will concentrate in this direction.

Table 5

D ₂ O(2ml)/Pd/ ²² Na(40μCi)					D ₂ O(2ml)/Pd-on-charcoal/ ²² Na(40μCi)				
Pd (mg)	Mixing		No Mixing		Mixing		No Mixing		
	τ_3 (ns)	$k_{ps} \cdot 10^7$ (M ⁻¹ s ⁻¹)	τ_3 (ns)	$k_{ps} \cdot 10^7$ (M ⁻¹ s ⁻¹)	τ_3 (ns)	$k_{ps} \cdot 10^7$ (M ⁻¹ s ⁻¹)	τ_3 (ns)	$k_{ps} \cdot 10^7$ (M ⁻¹ s ⁻¹)	
0			1.74						
0			1.78						
600	1.89	0.0707	2.02	0.1320	2.22	0.2140	----	-----	
500	1.95	0.0997	1.98	0.1140	1.84	0.0453	2.29	0.2370	
400	1.74	-0.0127	1.90	0.0761	2.01	0.1270	1.84	0.0453	
300	1.78	0.0109	1.95	0.0997	2.23	0.2180	----	-----	
200	1.99	0.1180	----	-----	2.12	0.1740	2.08	0.1580	
100	2.03	0.1360	1.55	-0.1400	2.13	0.1790	2.29	0.2370	
50	1.99	0.1180	----	-----	1.82	0.0344	1.85	0.0489	
10	1.93	0.0906	1.84	0.0453	1.56	-0.1320	1.97	0.1090	

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