o-Ps annihilation parameters in Pt, 5% Pt-on-charcoal, Pd and 5% Pd-on-charcoal powders

J. Ciottone, F. Lander, D. Leclair

► To cite this version:

J. Ciottone, F. Lander, D. Leclair. o-Ps annihilation parameters in Pt, 5% Pt-on-charcoal, Pd and 5% Pd-on-charcoal powders. Journal de Physique IV Proceedings, 1993, 03 (C4), pp.C4-185-C4-191. 10.1051/jp4:1993425 . jpa-00251468

HAL Id: jpa-00251468

<https://hal.science/jpa-00251468>

Submitted on 1 Jan 1993

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

o-Ps annihilation parameters in Pt, 5% Pt-on-charcoal, Pd and 5% Pd-on-charcoal powders

J.L. CIOTTONE, F. LANDER and D. LECLAIR

Chemistry Dept., Fitchburg State College, Fitchburg MA 01420, U.S.A.

ABSTRACT

o-Ps intensities and lifetimes show very good correlation to surface area and cavity size, respectively, of surface-active materials. τ_3 and I_3 values for Pt, 5% Pt-on-charcoal, Pd and 5% Pd-on-charcoal powders are presented. Surface area and cavity size are discussed and interpreted in terms of previously determined o-Ps lifetimes and intensities in abs. EtOH/pentene isomer/Pt or Pd mixtures.

INTRODUCTION

The surface area of catalytic materials may be determined from o-Ps intensities, calculated from positron lifetime spectra, using the following equations (1):

$$\begin{aligned}I_3 &= 3.0 + 0.033S \\I_3 &= 0.080S\end{aligned}$$

where

$$\begin{aligned}I_3 &= \text{longest observed o-Ps intensity} \\S &= \text{surface area in m}^2/\text{g}\end{aligned}$$

This equation is based on the standard linear curve determined by Venkateswaran, Cheng and Jean (2). Similarly, cavity size may be determined from o-Ps lifetimes, based on the following equation (3):

$$\tau_3 = 7.80V + 1.29$$

where

$$\begin{aligned}\tau_3 &= \text{o-Ps lifetime in ns} \\V &= \text{cavity size in nm}^3\end{aligned}$$

A linear correlation between τ_3 and pore size of various resins was also found by Venkateswaran et al. The curve deviates from linearity if chemical quenching groups are present on the surface-active material.

Interactions between o-Ps and Pt and Pd powders in simulated hydrogenation reaction mixtures have been previously studied in our laboratory(4,5). These mixtures contain 0.6mg heavy metal catalyst, ^{22}Na and abs.EtOH/cis-2-pentene in the following volume ratios: 2/1, 1/1, 0.25/2,

0.75/2, 1/2 and 1.5/2. The mixtures were studied with and without external mixing applied during the counting period. Several of the reaction mixtures; i.e., the 0.5/2, 1/2, and 0.25/2 ratios showed unusually long o-Ps lifetimes and high intensities. Lifetimes of 25ns and combined o-Ps intensities approaching 76% were obtained (4,5).

We have postulated the formation of a clathrate-type structure in which cis-2-pentene is adsorbed to the Jellium metal surface at the double bond. Solvation occurs via H-bonded EtOH molecules and o-Ps is trapped in the center. Recent calculations of k-Ps values in our laboratory indicate that o-Ps is forming some type of bond within the clathrate structure (6). Determination of pore size and surface area of the Pt and Pd catalysts will increase our understanding of these structures.

EXPERIMENTAL

Pt powder, particle size 0.27-0.47 microns, and Pd powder, particle size 0.25-0.55 microns, were obtained from Alfa. 5% Pt-on-charcoal and 5%Pd-on-charcoal were manufactured by DeGussa in Germany. ^{22}Na was obtained carrier free in the form of NaCl from New England Nuclear. Pentene isomers were obtained from Aldrich.

Catalysts, in powder form, were placed in round bottom 229mm NMR tubes. The height of catalyst in the tube was 1cm, while the mass was 0.4g-0.5g. 20 μCi ^{22}Na , in liquid form, were deposited on a 0.4cm square of Kapton foil and evaporated to dryness. The foil was embedded into the catalyst in the NMR tube so that it was approximately in the center. The tube was purged with nitrogen gas. The sample was counted, using a fast-slow coincidence system, until 200,000 counts accumulated in the peak channel. This was followed by determination of the resolution function (0.70ns).

RESULTS

Lifetimes, intensities, surface area and pore size of the catalysts studied are shown in Table 1.

Table 1

Catalyst	τ_2 (ns)	I_2 (%)	S (m^2/g)	Particle size(microns)	V($\text{\AA}^3$)
Pt	1.53 $\pm$ 0.03	6.53 $\pm$ 0.46	82	0.27-0.47	31
Pt-on-Ch.	1.55 $\pm$ 0.05	2.14 $\pm$ 0.21	27		33
Pd	1.71 $\pm$ 0.04	4.07 $\pm$ 0.28	51	0.25-0.55	54
Pd-on-Ch.	1.58 $\pm$ 0.04	7.94 $\pm$ 0.67	99		37

Although the catalysts have surface areas below $100\text{m}^2/\text{g}$, they can be fit very well to a linear curve (Graph 1). This is also the case for the pore sizes (Graph 2). The Pd catalysts generally have larger pore size than the Pt catalysts of comparable particle size. This is anticipated since Pt is paramagnetic ($5d^9 6s^1$), thereby increasing pick-off quenching, while Pd is diamagnetic ($5d^{10}$).

Graph 1
Dependence of Surface Area
on o-Ps Intensity

Graph 2
Dependence of Cavity Size
on o-Ps Lifetime

The low surface area obtained for Pt-on-charcoal is an unexpected result. The particle size of this catalyst is not known, but the consistency is comparable to that of the Pd-on-charcoal, obtained from the same manufacturer. Although a complete explanation cannot be offered at this time, there is a correlation to the erratic behavior shown by this catalyst in previous experiments with cis-2-pentene, which is discussed below.

DISCUSSION

The low surface area and rather small pore size obtained for the Pt and Pd catalysts confirm our hypothesis regarding annihilation of o-Ps in the simulated hydrogenation reaction mixtures previously studied in our laboratory. Our data indicate that o-Ps is not annihilating within or at the surface of the

catalyst. It is annihilating in the surrounding molecular medium. K_{Ps} values calculated for these reaction mixtures also support this view.

Since the abs.EtOH/pentene mixture is present in large excess compared to o-Ps, pseudo first order kinetics may be used; i.e.,

$$k_{Ps} = \frac{\lambda - \lambda_p}{M}$$

where

$$\begin{aligned} \lambda &= \text{decay constant of pure solvent} \\ \lambda_p &= \text{decay constant of pentene isomer} \\ M &= \text{molarity of abs.EtOH} \end{aligned}$$

Table 2

k_{Ps} values for Abs. EtOH/Pentene Volume Ratios
with no catalyst and with Pt powder

	No Catalyst				With Catalyst			
Abs. EtOH/Pentene	EtOH (M)	τ_3 (ns)	$\lambda \cdot 10^8$ (s ⁻¹)	$k_{PS} \cdot 10^7$ (M ⁻¹ s ⁻¹)	τ_3 (ns)	$\lambda \cdot 10^8$ (s ⁻¹)	$k_{PS} \cdot 10^7$ (M ⁻¹ s ⁻¹)	
Abs. EtOH/1-Pentene								
2/1	11.4	3.8	2.60	0.526	3.9	2.56	0.114	
1/1	8.6	3.9	2.56	0.744	3.8	2.60	0.0698	
1/2	5.7	4.0	2.50	1.23	4.0	2.50	0.333	
Abs. EtOH/trans-2-Pentene								
2/1	11.4	3.0	3.30	0.526	4.2	2.40	0.254	
1/1	8.6	3.8	2.60	0.744	4.2	2.40	0.337	
1/2	5.7	3.0	3.30	1.40	4.1	2.44	0.439	
Abs. EtOH/cis-2-Pentene								
2/1	11.4	3.8	2.60	-0.0877	3.7	2.70	0.008	
1/1	8.6	3.9	2.56	0.698	3.7	2.70	0.0116	
1/2	5.7	5.7	2.40	-0.175	3.65	2.74	0.0877	

Table 2 shows k_{Ps} values for pentene isomers as well as o-Ps lifetimes and decay constants. Lifetimes were all in the 3ns- 4ns range and did not change significantly when catalyst was added. k_{Ps} values showed very similar trends for 1-pentene and trans-2-pentene. They decreased when catalyst was added. Cis-2-pentene, however, showed very different and interesting behavior. When catalyst was added, k_{Ps} values increased for the 1/2 and 2/1 ratios but decreased for the 1/1 ratio. This isomer has repeatedly shown unusual behavior in experiments done in our laboratory. o-Ps intensities approaching 100% and 76% and lifetimes as long as 25ns have been obtained for specific abs.EtOH/cis-2-pentene ratios. The increased k_{Ps} values upon addition of catalyst indicate increased reactivity of o-Ps with medium molecules and the possible formation of a transition state or other bound species within the clathrate-type structure.

Table 3 shows similar results for six abs.EtOH/cis-2-pentene ratios with no external mixing. The 0.25/2, 0.5/2 and 1/2 ratios showed unusually long lifetimes upon addition of catalyst accompanied by increased k_{Ps} values, again indicating formation of a bound species. External mixing is expected to disrupt the clathrate structures and quench lifetimes, intensities and k_{Ps} values. This was

indeed the case for mixtures containing Pt catalyst, as shown in Table 4. For mixtures containing Pt-on-charcoal, however, inconsistent behavior was observed. The 1/1 ratio showed a large increase in τ_3 , while the other mixtures showed slight increases or decreases.

It is known that alcohols at concentrations <0.05 mol fraction enhance Ps formation by hole scavenging when added to hydrocarbons (7):

In the 1/2 abs.EtOH/cis-2-pentene mixture, the EtOH mol fraction is 0.48. Antiinhibition due to EtOH should be nonexistent at this mol fraction. It is apparent that the catalyst is very effective in removing electron density from o-Ps and that catalytic activity may be directly correlated to antiinhibition in these mixtures.

Table 3

k_{ps} values for Abs. EtOH/cis-2-Pentene Volume Ratios
with No External Mixing

Abs. EtOH/Pentene	EtOH (M)	τ_3 (ns)	$\lambda \cdot 10^8$ (s^{-1})	$k_{ps} \cdot 10^7$ ($M^{-1}s^{-1}$)
Abs. EtOH (No Catalyst)	17.10	3.02	3.31	
1/1	8.60	3.97	2.52	0.919
0.25/2	1.90	3.07	3.26	0.263
0.5/2	3.42	3.38	2.96	1.02
0.75/2	4.66	1.85	5.41	-4.51
1/2	5.70	5.26	1.89	2.49
1.5/2	7.33	4.12	2.43	1.20
Abs. EtOH (with Pt catalyst)	17.10	3.72	2.69	
1/1	8.60	3.80	2.63	0.0698
0.25/2	1.90	5.42	1.85	4.42
0.5/2	3.42	24.90	0.400	6.70
0.75/2	4.66	3.33	3.00	-0.665
1/2	5.70	25.50	0.390	4.04
1.5/2	7.33	3.63	2.75	-0.0819
Abs. EtOH (with Pt-on-ch)	17.10	3.20	3.13	
1/1	8.60	2.72	3.68	-0.640
0.25/2	1.90	12.90	0.780	12.4
0.5/2	3.42	3.66	2.73	1.17
0.75/2	4.66	5.31	1.88	2.68
1/2	5.70	3.89	2.57	0.982
1.5/2	7.33	3.57	2.80	0.450

Table 4

k_{ps} values for Abs. EtOH/cis-2-Pentene Volume Ratios
with External Mixing

Abs. EtOH/Pentene	EtOH (M)	τ_3 (ns)	$\lambda \cdot 10^8$ (s^{-1})	$k_{ps} \cdot 10^7$ ($M^{-1}s^{-1}$)
		τ_2		
Abs. EtOH (with Pt catalyst)	17.10	3.72	2.69	
1/1	8.60	2.49	4.02	-1.55
0.25/2	1.90	3.15	3.17	-2.53
0.5/2	3.42	2.30	4.35	-4.85
0.75/2	4.66	2.45	4.08	-2.98
1/2	5.70	3.68	2.72	-0.0526
1.5/2	7.33	3.13	3.19	-0.682
Abs. EtOH (with Pt-on-ch)	17.10	3.20	3.13	
1/1	8.60	8.23	1.22	2.22
0.25/2	1.90	3.38	2.96	0.895
0.5/2	3.42	3.49	2.87	0.760
0.75/2	4.66	2.96	3.38	-0.536
1/2	5.70	3.35	2.99	0.246
1.5/2	7.33	4.04	2.48	0.887

CONCLUSIONS

Antiinhibition of o-Ps lifetimes and intensities occurs for simulated hydrogenation reaction mixtures containing 0.6mg Pt or Pd catalyst and abs.EtOH/cis-2-pentene present in specific volume ratios; i.e. 1/2, 0.5/2 and 0.25/2. When these ratios are changed, antiinhibition no longer occurs.

We have postulated the formation of a clathrate type structure in which cis-2-pentene is adsorbed to the metal surface at the double bond (3,4). The metallic surface is represented as a Jellium double surface layer. Solvation by hydrogen bonded abs.EtOH molecules completes the cage. When external mixing is applied to the Pt containing mixtures, the τ_3 component disappears and all lifetimes and intensities are quenched. This is due to disruption of the clathrate structures, which results in increased pick-off annihilation.

K_{ps} values for these mixtures increase when antiinhibition occurs. This correlation suggests the possible formation of a loose bond between o-Ps and the surrounding medium molecules. Future work in our laboratory will involve determination of activation energies for the simulated hydrogenation mixtures. Computer simulation will be used to construct the clathrate structures.

References

1. Schrader, D.M. and Jean,Y.C.; Positron and Positronium Chemistry, Elsevier, 1988
2. Ventekateswaran,K., Cheng,K. and Jean,Y.; J.Phys.Chem.,88, 2465 (1984)
3. Jean,Y., Sandreczki,T. and Ames,D.; J.Poly.Sci. B24,1247 (1986)
4. Ciottone,J.L.; J. Chem. Phys.,78 (11) 1983
5. Ciottone,J.L. and Lander,F.; J. Chem. Phys. 92 (11) 1990
6. Ciottone,J.L., Brown,M., Fuhs,K. and Sheehan,C.; PPC4 Poster presentation
7. Byakov,V., Grafutin,V., Koldaeva,O., Miniachev,E. and Stepanova,O.; Khim.Vys.En.17, 506(1983)