Supporting information for:

Comment on "Mechanism and Kinetics of the Wacker Process: A Quantum Mechanical Approach"

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Contents:

1. Calculation methods
2. Comparison of calculated energies
3. Relevant energies and geometries

1. Calculation methods:

We report relative free energies as differences between the calculated absolute free energy, G, of two species. For species involving transition metals, we define G as:

$$G_{mol} = E_{gas} + E_{solv} + ZPE + H_{vib298} + 3*RT - T*S_{vib298} + RT*\ln(24.5)$$

where RT = .592 kcal/mol at 298 K. See below for additional discussion of energy terms.

For H_2O:

$$G_{H2O} = -47962.6 \text{ kcal/mol.}$$

This value is obtained by taking our gas phase absolute free energy, $G_{H2O} = E_{gas} + ZPE + H_{vib,H2O} + 3*RT + pV - T*S_{tot,H2O}$, -47960.6 kcal/mol and adding -2.05 kcal/mol (the free energy of vaporization for H_2O).[1]

For Cl^-:

$$G_{Cl-} = -288908.8 \text{ kcal/mol.}$$

This value is obtained by taking our gas phase absolute free energy, $E_{gas} + 3/2*RT + pV - T*S_{tot,Cl-}$ ($S_{tot,Cl-}$ = 36.7 cal/mol*K)[2] and adding -74.6 kcal/mol (the free energy of solvation for Cl^-.)[3]

For H^+:

$$G_{H+} = -265.9 \text{ kcal/mol}$$

which is simply the free energy of solvation of H^+ at the standard state of 1M. See the supporting information of ref. 9 for a thorough discussion of why this energy is used rather than the full free energy of a proton in solution: -270.9 kcal/mol.

Discussion of Energy Terms:
E_{gas} and E_{solv} are calculated with computational techniques outlined below. ZPE, H_{vib}, S_{vib}, and S_{tot} contributions are obtained from vibrational frequency calculations with thermodynamic calculations at 298K unless otherwise noted.

Thermal contributions are added to account for translations (3/2*RT, in all species) and rotations (3/2*RT, in all species but Cl^-). We only use S_{vib} contributions in molecular species involving transition metals since

[1] Donald D. Wagman, William H. Evans, Vivian B. Parker, Richard H. Schumm, Iva Halow, Sylvia M. Bailey, Kenneth L. Churney, and Ralph L. Nuttall, The NBS Tables of Chemical Thermodynamic Properties, *J. Phys. Chem. Ref. Data*, Vol. 11, Suppl. 2 (1982).
[2] Chase, M.W., Jr., NIST-JANAF Themochemical Tables, Fourth Edition, *J. Phys. Chem. Ref. Data,* Monograph 9, **1998**, 1-1951.
[3] (a) Tissandier, M.D.; Cowen, K.A.; Feng, W.Y.; Gundlach, E.; Cohen, M.H.; Earhart, A.D.; Coe, J.V.; Tuttle, T.R.; *J. Phys. Chem. A.* **1998**, *102*, 7787. (b) Palascak, M. W.; Shields, G. C. *J. Phys. Chem. A* **2004**, *108*, 3692; (c) Camaioni, D. M.; Schwerdtfeger, C. A. *J. Phys. Chem. A* **2005**, *109*, 10795.

it is our experience that including S_{trans} and S_{rot} terms increases errors in associative ligand exchange barriers involving Pd and Pt complexes. All gas phase calculations include an additional term pV = RT = .592 kcal/mol. All calculations involving calculated values of E_{solv} include a free-energy correction to account for adjusting from standard states in gas to aqueous solution: RT*ln(24.5) = 1.9 kcal/mol.

All calculations were carried out with Jaguar 7.0[4] using the hybrid-density functional theory, B3LYP.[5] Molecular geometries and vibrational frequencies were obtained from solvent-relaxed geometries obtained with Jaguar's Poisson-Boltzmann implicit solvation program (ε = 80.37 and $r_{solvent}$ = 1.400 Å)[6] and with an overall double-zeta quality electronic core potential containing 18 explicit electrons, LACVP**[7] on Pd, and the 6-31G** basis set on all other atoms. From these "solvent-optimized" structures, we recalculated the single point gas phase energies with the LACVP**++ basis set and the single point solvent energies with the LACVP** basis set.

Jaguar 7.0 is only capable of solving numerical frequencies integrals numerically under an implicit solvent. Occasionally, we encountered small (less than 50 cm^{-1}) and/or extra imaginary frequencies relating to torsions of coordinated water molecules or other soft bending modes. Comparisons of these frequencies to those from gas phase calculations with analytic vibrational frequencies suggest that these discrepancies more likely attributed to Jaguar's frequency code rather than as an error with our geometries. Since we expect our optimized geometries to be accurate, E_{gas} and E_{solv} terms will be unaffected by these small frequencies. However, thermodynamic contributions, S_{vib} in particular, will be drastically affected by spurious small frequencies. In order to treat these cases consistently, we chose to replace all vibrational frequencies that were unexpectedly less than 50cm^{-1} with frequencies valued at 50cm^{-1} and recalculate ZPE, H_{vib}, and S_{vib} according to the standard procedure.[8]

Additional discussion of these energy terms and the derivation of an empirical correction for calculations undergoing deprotonation are found in the supporting information for ref 9.

Comparison of calculated energies:

Table I. shows summarized results of QM data on *anti*- and *syn*- nucleophilic attacks. As seen in the table, nucleophilic attacks with the two different olefins show the same qualitative agreement between the two modes of nucleophilic attack. This is used as evidence to suggest that conclusions made in ref 10 are valid for ethylene olefin.

Table I. Comparison of *anti*- and *syn*- barriers with two olefins: ethylene, and the allyl-alcohol utilized in ref. 2. Energies in (kcal/mol)

Species	**L = "C_2H_4"**	**L = "$CH_3CHOHCH{=}CHCH_3$" (AA)**
$PdCl_3(L)$	0.0	0.0
External attack (anti-)	23.9	27.5
Internal attack (syn-)	18.0	17.1

[4] Jaguar 7.0, Schrodinger, LLC, New York, NY, 2007.
[5](a) Becke, A.D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Stephens, P.J.; Devlin, F.J.; Chabalowski, C.F.; Frisch, M.J. *J. Phys. Chem.* **1994**, *98*, 11623.
[6] Tannor, D.J.; Marten, B.; Murphy, R.; Friesner, R.A.; Sitkoff, D.; Nicholls, A.; Ringnalda, M.; Goddard, W.A.; Honig, B. *J. Am. Chem. Soc.* **1994**, *116*, 11875.
[7] Hay, P.J.; Wadt, W.R. *J. Chem. Phys.* **1985**, *82*, 270.
[8] See any physical chemistry textbook's chapter on statistical thermodynamics for equations of partition functions.
[9] Keith, J.A.; Nielsen, R.J.; Oxgaard, J.; Goddard, W.A. *J. Am. Chem. Soc.* **2007**, *129*, 12342-12343.
[10] (a) Hamed, O.; Henry, P.M.; Thompson, C. *J. Org. Chem.*, **1999**, *64*, 7745. (b) Hamed, O.; Thompson, C.; Henry, P.M. *J. Org. Chem.*, **1997**, *62*, 7082.

2. Relevant energies and geometries:

The following energies and geometries were used:

H_2O:
G = -47962.6 kcal/mol (see section 1.)

O1	-0.0015682281	0.0000000000	-0.0011860418
H2	0.0185631919	0.0000000000	0.9662305522
H3	0.9351445621	0.0000000000	-0.2439039161

Cl-:
G = -288908.8 kcal/mol (see section 1.)

$PdCl_3(C_2H_4)$:
G = -995343.0 kcal/mol
Escf = -1586.14468442097 au
Esolv= -0.09311243001 au

Pd1	-0.6165650000	5.2331810000	2.5702650000
Cl2	1.4703030000	6.2284040000	2.0238250000
Cl3	-0.3322830000	3.6085670000	0.8223940000
Cl4	-2.7093400000	4.2747110000	3.1594970000
C5	-1.1752300000	7.0820130000	3.6847980000
C6	-0.5404500000	6.2277680000	4.5659740000
H7	-2.2579390000	7.1120420000	3.6195770000
H8	-0.6266450000	7.8703460000	3.1798760000
H9	-1.1102880000	5.5672850000	5.2113980000
H10	0.5205270000	6.3255480000	4.7716510000

$PdCl_3$(AA):
G = -1116513.0 kcal/mol
Escf = -1779.31290730134 au
Esolv = -0.10477063768 au

Pd1	0.0055072500	0.1071071905	0.0362172884
Cl2	0.2869773209	0.2144464894	2.3954857780
Cl3	2.3632925747	0.5394300167	-0.2081501576
Cl4	-0.2157746367	-0.0052233093	-2.3371476480
C5	-2.2465274657	0.4211089717	0.1690569030
C6	-2.0148890588	-0.9486620092	0.1555249816
H7	-2.3477648425	0.8994469726	-0.8028386672
H9	-1.9712687638	-1.4304785857	-0.8202797955
C10	-2.7024204260	1.2469948562	1.3354588990
H11	-2.5235382521	0.7712612290	2.2995208419
H12	-2.2093231854	2.2237863406	1.3299091388
H13	-3.7801112782	1.4295323581	1.2215915440
C14	-2.1990349793	-1.9167372849	1.3044177143
H15	-1.8126581242	-1.4881010271	2.2311074327
C16	-3.6848861529	-2.2578866815	1.4816632096
H17	-4.0990409088	-2.6961446706	0.5663658938

H18	-3.7890625197	-2.9831861892	2.2945115305
H19	-4.2680179115	-1.3671502589	1.7331857195
O20	-1.4298176123	-3.1016233808	1.0864905130
H21	-1.8059118552	-3.5762287628	0.3280473584

External Attack (C_2H_4):
G = -1043286.3 kcal/mol
Escf = -1738.98994867709 au
Esolv = -0.12588708083 au

Pd1	-0.1920885767	-0.0276401039	0.2321502511
C2	-0.1598462640	1.8494677786	2.0279461519
O3	-0.0908480089	2.6166171227	3.8151125875
C4	-0.8849773025	0.6253265300	2.1039392102
H5	0.4004197250	1.8636053308	4.2466502699
Cl6	-2.1829818569	0.8392489387	-0.7444709026
H7	-1.9694317861	0.6961423826	2.0788940162
H8	-0.4933169789	-0.1240648309	2.7855305217
Cl9	0.5448944124	-1.0503977272	-1.9005713194
Cl10	1.8110201735	-0.7683884630	1.3679606383
H11	0.9227525003	1.8327488159	2.0171697043
H12	-0.6104417987	2.7086042713	1.5396481653
H13	-0.9886273034	2.6024377515	4.1903595352
O14	1.4262777346	0.4903118951	4.5311070659
H15	1.0176379539	-0.2315544965	5.0326780190
H16	1.7420667360	0.0671047370	3.7111604263

External Attack (AA):
G = -1164448.2 kcal/mol
Escf = -1855.68926044077 au
Esolv = -0.14247482302 au

Pd1	0.0027427493	-0.0024717408	0.0002517816
C2	0.0046413896	0.0015480911	2.8102973326
O3	0.8193102892	0.0050650993	4.3362985489
C4	0.7769527984	-0.7661708302	1.8077765691
H5	1.7506188531	0.2894484646	4.2617187894
Cl6	-1.7303760209	-1.6904729028	-0.1721523256
H8	1.7814999374	-0.3444352339	1.7293548325
Cl9	-0.6996335605	0.8810883838	-2.2566568184
Cl10	1.6067578925	1.7816295032	0.2351576642
H11	0.1254995572	1.0722839481	2.6570389720
H13	0.8122794153	-0.8518935137	4.8031056430
C16	-1.3933101186	-0.3670955030	3.2455504139
H17	-1.4523218724	-1.3938834158	3.6072883135
H18	-1.7539407998	0.3315860271	4.0045706103
H19	-2.0407663000	-0.2933105027	2.3673413187
C19	0.8984354343	-2.2983801985	1.8425253990
H21	1.2048047814	-2.5993005664	0.8283689977
C22	1.9955004525	-2.7873318095	2.7949033313
H23	2.9521018245	-2.3093972693	2.5656520753
H24	1.7427927753	-2.5783849149	3.8393911445
H25	2.1167231457	-3.8700965306	2.6913299374
O25	-0.2952319733	-2.9861722183	2.2001636577

H26	-0.9589818471	-2.7598460254	1.5190900047

Internal Attack (C_2H_4):
G = -802344.8 kcal/mol – 16 kcal/mol* (see supporting information for ref 9)
Escf = -1278.63500691376 au
Esolv = -0.06010908438 au

Pd1	0.0000000000	0.0000000000	0.0000000000
O2	0.0000000000	0.0000000000	2.1579240063
C3	1.8725904454	0.0000000000	1.9211196948
C4	2.0267999675	-0.0401769821	0.4887288192
Cl5	0.4361681724	0.0983728632	-2.2997338944
H6	-0.3283195562	-0.8020015264	2.6052074303
H7	2.4148700902	-0.9717352912	0.0809089122
H8	2.4311026124	0.8659915081	0.0391527257
H9	2.0263982772	0.9324517024	2.4568093170
H10	2.0274892904	-0.9018820565	2.5066885188
Cl11	-2.4585797642	0.2945354754	-0.1897940754
H12	-0.5715676117	0.8754269570	2.3937631627
O13	-1.4490655108	1.9899205990	2.3558654008
H14	-1.0045801376	2.8267925782	2.1408065081
H15	-2.0279487937	1.7963886068	1.5884159266

Internal Attack (AA):
G = -923512.4 kcal/mol – 16 kcal/mol* (see supporting information for ref 9)
Escf = -1471.79850581057 au
Esolv = -0.07253405439 au

Pd1	-0.0040241459	-0.0143876399	-0.0382406458
O2	0.0222150321	-0.0222872735	2.1162759743
C3	1.8657488604	0.0161532479	1.9017401122
C4	2.0045057457	-0.2599423489	0.4574934227
Cl5	0.3348403883	0.0423666006	-2.3593294680
H6	-0.3227092781	-0.8168016192	2.5658402748
H8	2.4325651366	0.6175788809	-0.0348462758
H9	1.9232114945	1.0688603856	2.1697707334
Cl11	-2.4718364189	0.5413627451	-0.1368393956
H12	-0.5475541646	0.8760418111	2.3495269403
O13	-1.2726682468	2.0512624965	2.3392473389
H14	-0.7483390408	2.8088707570	2.0277290123
H15	-1.9226729603	1.8827148228	1.6196026970
C18	2.3283423609	-0.9142417506	2.9699522727
H19	2.0821953916	-1.9605800068	2.7727246080
H20	3.4250287920	-0.8255742355	2.9986900416
H21	1.9486127579	-0.6100398074	3.9479523956
C21	2.7460819920	-1.5354247130	-0.0000098646
H24	3.4680717633	-1.7998038413	0.7881472299
O24	3.4646905456	-1.2738346333	-1.2026132654
H25	4.1874796941	-0.6624998573	-0.9952809563
C25	1.8751666894	-2.7615069197	-0.2609924718
H26	1.1805836969	-2.5600720181	-1.0808610463
H27	2.5085432030	-3.6129365791	-0.5305809559
H28	1.2948317168	-3.0288227978	0.6269845502

Anti-attack on $[Pd(OH)(Cl)_2(C_2H_4)]^-$
G = -802056.74 kcal/mol – 16 kcal/mol* (see supporting information for ref 9)
Escf = -1278.140144 au
Esolv = -0.110215033 au

Pd1	0.0000000000	0.0000000000	0.0000000000
C2	0.0000000000	0.0000000000	3.0879495225
O3	2.0709478302	0.0000000000	2.5637753658
H4	1.9166562667	0.5943639204	1.7345405271
H5	0.2121994052	0.9281989098	3.6058381070
C6	-0.8929921381	-0.0340797302	2.0080413775
H7	2.5070197226	0.5694392157	3.2188387120
H8	-1.4657319833	0.8785942174	1.8346001604
Cl9	0.9848643285	0.1697114310	-2.2291203641
H10	0.2184103052	-0.9100523129	3.6358427811
H11	-1.4393738470	-0.9646936882	1.8827167433
Cl12	-1.6838525471	-1.5772274111	-0.7147439796
O13	1.3783402058	1.3588581897	0.5789006119
H14	1.9960930653	1.3695430909	-0.1702819197