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Energetics of organometallic species: the entropic factor

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Abstract

A rather simple procedure to estimate entropy changes of organometallic reactions is described. It merely consists in finding organic or inorganic reactions, for which the gas phase standard entropies are well known, that can mimic a given organometallic reaction. The merits and limitations of the method are discussed, and it is concluded that a careful use of model reactions can at least provide a reliable guideline to estimate or even to assess entropy data for many organometallic reactions.

Keywords: Gas phase reactions; Organometallic reactions; Entropy data

1. Introduction

The thermodynamic driving force of a chemical reaction is measured by the Gibbs energy change $\Delta_r G$ associated with the conversion of reactants to products, spontaneous reactions having $\Delta_r G < 0$. Under equilibrium conditions $\Delta_r G = 0$ and the standard Gibbs energy $\Delta_r G^0$ of the reaction is related to the equilibrium constant K of the reaction by

$$\Delta_r G^0 = -RT \ln K \quad (1)$$

where R is the gas constant and T the absolute temperature. As K reflects the relative amounts of reactants and products present in the reaction mixture (and therefore the reaction yield), the prediction of the feasibility of a given reaction or of a postulated elementary step in a composite reaction, on thermodynamic grounds, implies that one is able to calculate $\Delta_r G^0$ for the process under study.

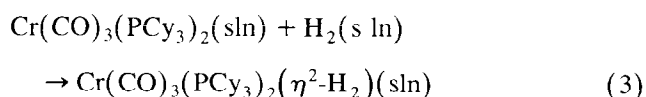
The standard Gibbs energy of a reaction is related to the corresponding enthalpy $\Delta_r H^0$ and entropy $\Delta_r S^0$ by

$$\Delta_r G^0 = \Delta_r H^0 - T\Delta_r S^0 \quad (2)$$

In the case of reactions involving organometallic compounds much more is known about the enthalpy term than about the entropy term in Eq. (2). Most experimental studies in organometallic thermochemistry available

in the literature report the determination of enthalpies of reaction, from which other enthalpies of reaction, enthalpies $\Delta_r H^0$ of formation and bond dissociation enthalpies $DH^0(M-L)$ (M = metal centre; L = ligand) were (or can be) derived [1–7]. Some methods of estimating $\Delta_r H^0$, $\Delta_f H^0$ and $DH^0(M-L)$ data have also been discussed [8]. Although these estimating procedures are not as accurate and general as several existing schemes for predicting thermochemical data of organic compounds [9–12], they are often used to assess experimental data and to discuss the energetics of bond cleavage and formation in organometallic reactions. Thus, in the absence of direct experimental measurements, it is now possible, for many organometallic reactions, to make reliable predictions of the enthalpy term in Eq. (2).

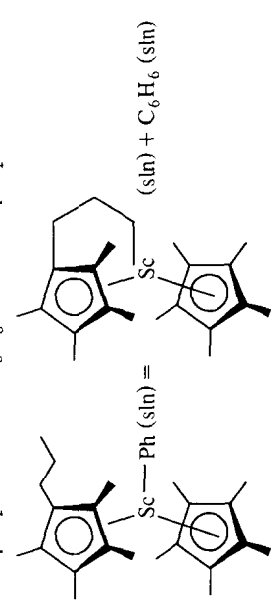
Much less attention has been given to the measurement and estimation of entropy changes in organometallic reactions, despite the fact that, in some cases, the value of $T\Delta_r S^0$ makes an important contribution to $\Delta_r G^0$, or even determines if the reaction is spontaneous. For example, in the reaction (see Table 1)



$\Delta_r H^0 = -30.5 \text{ kJ mol}^{-1}$ and $T\Delta_r S^0 = -31.9 \text{ kJ mol}^{-1}$, leading to $\Delta_r G^0 = 1.4 \text{ kJ mol}^{-1}$. Therefore, although the reaction is exothermic, the entropy change leads to a positive value for $\Delta_r G^0$. Note that, in this

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Table 1
Entropies of selected organometallic reactions

No.	Reaction ^a	Solvent, Ref.	T/K	$\Delta_r S / \text{J K}^{-1} \text{mol}^{-1}$
1	$\text{Sc}(\text{Cp}^*)_2\text{H}(\text{sln}) + \text{C}_6\text{H}_6(\text{sln}) = \text{Sc}(\text{Cp}^*)_2\text{Ph}(\text{sln}) + \text{H}_2(\text{sln})$	benzene, [13]	279–353	-4.2 ± 4.2
2	$\text{Sc}(\text{Cp}^*)_2(\text{thf})\text{H}(\text{sln}) + \text{C}_6\text{H}_6(\text{sln}) = \text{Sc}(\text{Cp}^*)_2\text{Ph}(\text{sln}) + \text{thf}(\text{sln}) + \text{H}_2(\text{sln})$	benzene, [13]	298–353	100.4 ± 8.4
3	 $(\text{sln}) + \text{C}_6\text{H}_6(\text{sln})$	benzene, [14]	323–373	43.2 ± 1.3
4	$\text{Th}(\text{Cp}^*)_2(\text{CH}_2\text{SiMe}_3)_2(\text{sln}) = (\text{Cp}^*)_2\text{Th}(\text{CH}_2)_2\text{Si}(\text{CH}_3)_2(\text{sln}) + \text{SiMe}_4(\text{sln})$	cyclohexane, [15]	333–373	69.5 ± 20.9
5	$\text{Th}(\text{Cp}^*)_2(\text{OR})\text{H}(\text{sln}) + \text{CO}(\text{sln}) = \text{Th}(\text{Cp}^*)_2(\text{OR})\text{C}(\text{O})\text{H}(\text{sln})$	toluene, [16]	180–220	-49.0 ± 18.0
6	$\text{R} = \text{CH}^t\text{Bu}_2$		180–200	-100.0 ± 31.0
7	$\text{R} = 2,6\text{-C}_6\text{H}_3\text{tBu}_2$		445–540	272 ± 58
8	$\text{U}(\text{cot})_2(\text{g}) = \text{U}(\text{cot})_2(\text{g}) + \text{cot}(\text{g})$	[17]	243, 268	-85 ± 20
9	$[\text{Ti}(\text{Cp})_2\text{Cl}]_2(\text{sln}) + 2\text{CO}(\text{sln}) = 2\text{TiCp}_2(\text{CO})\text{Cl}(\text{sln})$	toluene, [18]	300–318	145.6 ± 10.0
	$\text{Ti}(\text{C}_6\text{H}_9)_2\text{PEt}_3(\text{sln}) = \text{Ti}(\text{C}_6\text{H}_9)_2(\text{sln}) + \text{PEt}_3(\text{sln})$	thf, [19]		
	$\text{Ti}(\text{C}_7\text{H}_{11})_2\text{L}(\text{sln}) = \text{Ti}(\text{C}_7\text{H}_{11})_2(\text{sln}) + \text{L}(\text{sln})$	thf, [19]		
10	$\text{L} = \text{PF}_3$		270–300	130.5 ± 10.5
11	$\text{L} = \text{PMe}_3$		313–332	142.7 ± 10.0
12	$\text{L} = \text{PEt}_3$		224–269	134.7 ± 1.3
13	$\text{L} = \text{PMe}_2\text{Ph}$		276–303	139.3 ± 7.9
14	$\text{L} = \text{P}(\text{OMe})_3$		269–303	125.9 ± 13.4
15	$\text{L} = \text{P}(\text{OEt})_3$		259–290	114.6 ± 8.8
16	$\text{Hf}(\text{Cp})_2\text{R}_2(\text{sln}) + \text{CO}(\text{sln}) = \text{Hf}(\text{Cp})_2\text{RC}(\text{O})\text{R}(\text{sln})$	toluene, [20]	269–307	-138.1 ± 23.4
17	$\text{R} = \text{Me}$		269–307	-120.1 ± 2.5
18	$\text{R} = \text{Bz}$	benzene, [14]	373–444	-14.6 ± 2.6
19	$\text{Hf}(\text{Cp}^*)_2\text{H}_2(\text{sln}) + \text{C}_6\text{H}_6(\text{sln}) = \text{Hf}(\text{Cp}^*)_2(\text{Ph})\text{H}(\text{sln}) + \text{H}_2(\text{sln})$	benzene, [14]	343–387	139.4 ± 20.4

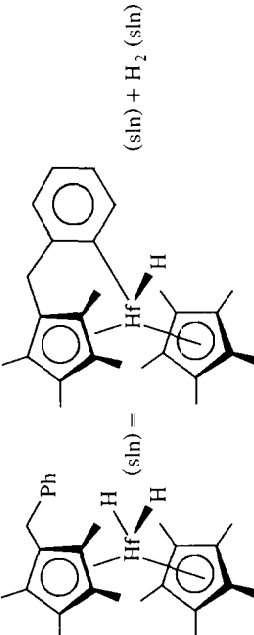
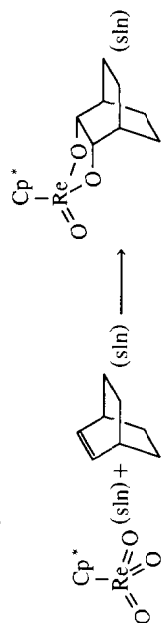
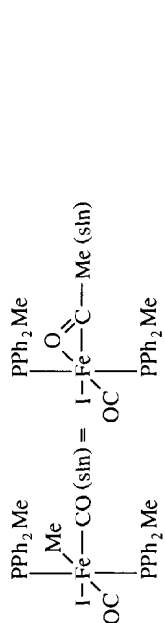
20		benzene, [14]	332–386	78.8 ± 9.8
21	$\text{V}(\text{Cp})_2(\text{CO})(\text{sln}) = \text{V}(\text{Cp})_2(\text{CO})\text{I}(\text{sln})$	toluene, [21]	272–316	-144.8 ± 14.2
22	$\text{Cr}(\text{CO})_3(\text{PCy}_3)_2(\text{sln}) + \text{L}(\text{sln}) = \text{Cr}(\text{CO})_3(\text{PCy}_3)_2(\eta^2\text{-L})(\text{sln})$	thf, [22]		
23	L = N ₂		283–318	-148.1 ± 9.6
24	L = H ₂		291–318	-107.1 ± 7.1
25	$\text{Cr}(\text{CO})_3(\text{PCy}_3)_2\text{py}(\text{sln}) = \text{Cr}(\text{CO})_3(\text{PCy}_3)_2(\text{sln}) + \text{py}(\text{sln})$	toluene, [23]	278–298	120.5 ± 23.8
26	$[\text{Cr}(\text{Cp})(\text{CO})_3]_2(\text{sln}) = 2\text{Cr}(\text{Cp})(\text{CO})_3(\text{sln})$	toluene, [24]	208–368	155.2 ± 5.9
27		toluene, [25]	298–333	212.1 ± 9.2
28		toluene, [26]	283–338	146.9 ± 3.8
29	$[\text{Cr}(\text{Cp}^* \text{XCO})_3]_2(\text{sln}) = 2\text{Cr}(\text{Cp}^* \text{XCO})_3(\text{sln})$	thf, [24]	208–368	143.5 ± 5.4
30		toluene, [27]	247–314	229.3 ± 9.2
31		toluene, [26]	273–323	179.1 ± 12.1
32	$[\text{Cr}(\text{Cp})(\text{CO})_2(\text{P}(\text{OMe})_3)]_2(\text{sln}) = 2\text{Cr}(\text{Cp})(\text{CO})_2\text{P}(\text{OMe})_3(\text{sln})$	thf, [26]	223–273	169.0 ± 5.4
33		toluene, [25]	243–263	288.7 ± 6.3
34	$\text{Mo}(\text{CO})_3(\text{CD}_3\text{CN})_3(\text{sln}) + \text{CpH}(\text{sln}) = \text{Mo}(\text{Cp})(\text{CO})_3\text{H}(\text{sln}) + 3\text{CD}_3\text{CN}(\text{sln})$	thf, [26]	198–235	175.7 ± 12.6
35	$\text{Mo}(\text{CO})_3(\text{thf})_3(\text{sln}) + \text{PhMe}(\text{sln}) = \text{Mo}(\eta^6\text{-PhMe})(\text{CO})_3(\text{sln}) + 3\text{thf}(\text{sln})$	CD ₃ CN, [28]	316–355	214.6 ± 8.4
36	$\text{W}(\text{CO})_5\text{Xe}(\text{sln}) = \text{W}(\text{CO})_5(\text{sln}) + \text{Xe}(\text{sln})$	thf, [29]	308–354	173.6 ± 5.0
37	$\text{W}(\text{CO})_5(\text{PhNH}_2)(\text{sln}) + \text{L}(\text{sln}) = \text{W}(\text{CO})_5\text{L}(\text{sln}) + \text{PhNH}_2(\text{sln})$	liquid Xe, [30]	173–198	66.9 ± 20.9
38	L = PBu ₃	toluene, [31]	308–318	151 ± 33
39	L = PPh ₃			360 ± 21
40	L = P(OBu) ₃			222 ± 25
41	L = P(OPh) ₃			372 ± 8
42	L = AsPh ₃			280 ± 25
43	$\text{W}(\text{CO})_3(\text{PR}_3)_2(\eta^2\text{-H}_2)(\text{sln}) + \text{H}_2\text{O}(\text{sln}) = \text{W}(\text{CO})_3(\text{PR}_3)_2(\text{H}_2\text{O})(\text{sln}) + \text{H}_2(\text{sln})$	thf, [32]	203–298	-69.0 ± 8.4
44	R = Cy			-78.7 ± 8.4
45	R = iPr	toluene, [32]	193–293	129.7 ± 10.5
46	$\text{W}(\text{CO})_3(\text{PR}_3)_2(\text{thf})(\text{sln}) = \text{W}(\text{CO})_3(\text{PR}_3)_2(\text{sln}) + \text{thf}(\text{sln})$	toluene, [33]	273–309	10.0 ± 5.9
47	R = cy-C ₆ H ₁₁		265–305	5.0 ± 8.8
48	$\text{Mn}_2(\text{CO})_{10}(\text{sln}) + \text{H}_2(\text{sln}) = 2\text{Mn}(\text{CO})_5\text{H}(\text{sln})$	supercritical CO ₂ , [34]	353–453	35.6 ± 3.3

Table 1 (continued)

No.	Reaction ^a	Solvent, Ref.	T/K	$\Delta_f S / J K^{-1} mol^{-1}$
49	$Mn(CO)_5R (sin) + CO (sin) = Mn(CO)_5C(O)R (sin)$	2,2'-diethoxydiethyl ether, [35]		
50	R = Me			-125.5
51	R = Et			-64.9
52	R = Pr			-37.2
53	R = Ph			-114.6
54	$Mn_2(CO)_{10} (sin) + Re_2(CO)_{10} (sin) = 2(CO)_5MnRe(CO)_5 (sin)$ $Mn_2(CO)_{10} (sin) + Co_2(CO)_8 (sin) = 2(CO)_5MnCo(CO)_4 (sin)$	decalin, [36] supercritical CO ₂ , [34]	353–453	80.3 ± 2.5 2.9 ± 3.3
55		C ₆ D ₆ , [37]	378–402	-117.1 ± 16.7
56		CH ₂ Cl ₂ , [38]	220, 309	-6.5 ± 2.0
57	$[FeCo_2(CO)_9(CPh)H] (sin) = [FeCo_2(CO)_9(HCPh)] (sin)$	toluene, [39]	170–298	-5.0 ± 0.8
58	$Ru_7Cp_4 (g) = 2RuCp_2 (g)$	[40]	500–625	129.9 ± 5.9
59	$Ru(Cp^* \lambda PMe_3)_2(OH) (sin) + Ph_2NH (sin) = Ru(Cp^* \lambda PMe_3)_2(NPh_2) (sin) + H_2O (sin)$	thf, [41]		-25.5 ± 0.8
60	$Ru_3(CO)_{12} (sin) + 3CO (sin) = 3Ru(CO)_5 (sin)$	n-hexane, [42]		-114.0 ± 5.0
61		i-octane, [43]		-60.8 ± 2.6
62	$Ru(H)(\eta^2-H_2XCl)(CO)[P(iPr_3)]_2 (sin) = Ru(HXCl)(CO)[P(iPr_3)]_2 (sin) + H_2 (sin)$	toluene- <i>d</i> ₆ , [44]	373–448	97.1 ± 4.1
63	$Os_5Cp_4 (g) = 2OsCp_2 (g)$	[40]	180–190	118.6 ± 5.9
64	$Os_3(CO)_{12} (sin) + PhC=CPh (sin) = Os_3(CO)_{11}(PhC=CPh)(sin) + CO (sin)$	decalin, [45]	500–625	38.5 ± 28.0
65	$Co_2(CO)_8 (sin) + H_2 (sin) = 2Co(CO)_4H (sin)$	supercritical CO ₂ , [46]	333–453	-17.6 ± 2.1
66	$Co_2(CO)_8 (sin) + H_2 (sin) = 2Co(CO)_4H (sin)$	heptane, [47]	307–428	18.4
67		hexane, [42]		18.4 ± 2.1
68	$Co(CO)_4H (sin) = Co(CO)_3H (sin) + CO (sin)$	heptane, [48]	288–298	121.3
69	$Co(CO)_4C(O)Pt (sin) = Co(CO)_4C(O)Pt (sin)$	octane, [49]	298–358	8.9 ± 2.5
70	$2Me-B_{12} (sin) = [Me-B_{12}]_2 (sin)$	water, [50]	280–350	-138.1
71	$2Rh(TMP) (sin) + CH_4 (sin) = Rh(TMP)Me (sin) + Rh(TMP)H (sin)$	benzene, [51]	353–393	-79.5 ± 20.9
72	$Rh(OEP)H (sin) + CO (sin) = Rh(OEP)CHO (sin)$	benzene, [52]	298–335	-123 ± 15
73	$[Rh(OEP)]_2 (sin) + H_2 (sin) = 2Rh(OEP)H (sin)$	benzene, [53]	294, 335	3.3 ± 8.4
74	$[Rh(TXP)]_2 (sin) + CH_4 (sin) = Rh(TXP)CH_3 (sin) + Rh(TXP)H (sin)$	benzene, [51]	353, 393	-29.3 ± 12.6
75	$[Rh(OEP)]_2 (sin) + C_3H_6 (sin) = (OEP)RhC_3H_5MeRh(OEP) (sin)$	benzene, [54]	280–330	-84 ± 21
76	$[Rh(OEP)]_2 (sin) + CO (sin) = (OEP)RhC(O)Rh(OEP) (sin)$	toluene, [55]		-130 ± 21
77	$[Rh(OEP)]_2 (sin) + 2CO (sin) = (OEP)RhC(O)C(O)Rh(OEP) (sin)$	toluene, [55]		-259 ± 30
78	$(OEP)RhC(O)Rh(OEP) (sin) + CO (sin) = (OEP)RhC(O)C(O)Rh(OEP) (sin)$	toluene, [55]		-130 ± 29
79	$[Rh(OEP)]_2CO (sin) + CO (sin) = (OEP)RhC(O)C(O)Rh(OEP) (sin)$	toluene, [55]		-151 ± 12

80	$\text{Rh}(\text{acac})\text{C}_2\text{H}_4)_2(\text{sln}) + \text{L}(\text{sln}) = \text{Rh}(\text{acac})\text{C}_2\text{H}_4\text{L}(\text{sln}) + \text{C}_2\text{H}_4(\text{sln})$	toluene, [56]	-3.3 ± 12.1
81	L = CH ₂ CHF		-31.4 ± 15.9
82	L = CH ₂ CHCl		-2.1 ± 2.1
83	L = CH ₂ CHMe		-7.1 ± 20.9
84	L = CH ₂ CHEt		-20.5 ± 12.6
85	L = <i>cis</i> -C ₄ H ₈		-25.5 ± 10.9
86	L = <i>trans</i> -C ₄ H ₈		-10.9 ± 10.5
87	$\text{Ir}(\text{H})_2(\eta^2\text{-H}_2\text{X})[\text{PMe}(\text{t-Bu})_2]_2(\text{sln}) = \text{Ir}(\text{H})_2(\text{X})[\text{PMe}(\text{t-Bu})_2]_2(\text{sln}) + \text{H}_2(\text{sln})$	toluene-d ₈ , [57]	250–294
88	X = Cl		80.3 ± 2.9
89	X = Br		82.4 ± 13.4
90	X = I		95.0 ± 3.3
91	$\text{Ir}(\text{D})_2(\eta^2\text{-D}_2\text{XCl})[\text{PMe}(\text{t-Bu})_2]_2(\text{sln}) = \text{Ir}(\text{D})_2(\text{Cl})[\text{PMe}(\text{t-Bu})_2]_2(\text{sln}) + \text{D}_2(\text{sln})$	toluene-d ₈ , [57]	260–294
92	$\text{Ir}(\text{CO})_2(\text{SIR}_3\text{XHX})(\mu\text{-CH}_2)(\text{TaCp}_2\text{Xsln}) = \text{Ir}(\text{CO})_2(\mu\text{-CH}_2)(\text{TaCp}_2\text{Xsln}) + \text{R}_3\text{SiH}(\text{sln})$	S, [58]	273–313
93	S = thf-d ₈ R = Me		103.8 ± 5.9
94	S = thf-d ₈ R = Et		263–313
95	S = toluene-d ₈ R = Et		253–343
96	S = thf-d ₈ R = Ph		104.6 ± 10.5
97	$\text{Ni}[\text{P}(\text{O-}o\text{-tol})_3]_3(\text{sln}) + \text{C}_2\text{H}_4(\text{sln}) = \text{Ni}[\text{P}(\text{O-}o\text{-tol})_3]_3(\text{C}_2\text{H}_4\text{Xsln}) + \text{P}(\text{O-}o\text{-tol})_3(\text{sln})$	toluene, [59]	294–338
98	$\text{Ni}[\text{P}(\text{O-}o\text{-tol})_3]_3(\text{C}_2\text{H}_4\text{Xsln}) + \text{P}(\text{O-}o\text{-tol})_3(\text{sln}) = \text{Ni}[\text{P}(\text{O-}o\text{-tol})_3]_3(\text{C}_2\text{H}_4\text{Xsln})$	toluene, [59]	213–243
99	$\text{Ni}[\text{P}(\text{O-}o\text{-tol})_3]_3(\text{sln}) + \text{L}(\text{sln}) = \text{Ni}[\text{P}(\text{O-}o\text{-tol})_3]_3\text{L}(\text{sln}) + \text{P}(\text{O-}o\text{-tol})_3(\text{sln})$	benzene, [60]	-58.6 ± 41.8
	L = C ₆ H ₁₀		-175.7 ± 33.4
	L = 1-hexene		4.2 ± 12.6
	<i>trans</i> -Pt(PEt ₃) ₂ (Cl)Et(sln) = <i>trans</i> -Pt(PEt ₃) ₂ (Cl)H(sln) + C ₂ H ₄ (sln)	cyclohexane, [61]	8.4 ± 12.6
			113.0 ± 5.4

^a acac = acetylacetonate; C₆H₉ = 3-methylpentadienyl; C₇H₁₁ = 2,4-dimethylpentadienyl; cor = 1,3,5,7-cyclooctatetraene; Cp* = η⁵-C₅H₅; Cp⁺ = η⁵-C₅Me₅; Cy = cyclohexyl; Me-B₁₂ = methylcobalamine; OEP = octaethylporphyrin; py = pyridine; thf = tetrahydrofuran; TMP = tetramethylporphyrin; tol = tolyl; TXP = tetraethylporphyrin.

case, $K = 0.57$, and ignoring the entropic contribution to $\Delta_r G^0$ (i.e. making $\Delta_r G^0 \approx \Delta_r H^0$) results in an enormous error in the value of the equilibrium constant ($K = 1.8 \times 10^5$ instead of $K = 0.57$).

The importance of evaluating $\Delta_r S^0$ for the thermodynamic analysis of organometallic reactions led us to search for a simple and reliable method for estimating (and assessing) $\Delta_r S^0$ data. We have found that for many of those reactions reasonable estimates of $\Delta_r S^0$ can be obtained by using entropy data for model reactions for which the standard entropy changes are well known.

2. Selected entropy data for organometallic reactions

The values in Table 1 [13–61] were selected to illustrate the merits as well as the limitations of the estimation method discussed below. These data seldom refer to the reactants and products in their standard states [9], since concentrations and not activities were used to derive the equilibrium constants, but it will be assumed that the overall corrections are smaller than the experimental uncertainties. In any case, the organometallic reaction entropies presented in Table 1 and in the text below will be represented by $\Delta_r S$ and not by $\Delta_r S^0$.

In general, $\Delta_r S^0$ values are obtained from van't Hoff plots [9,62,63]:

$$\ln K = -\frac{\Delta_r H^0}{RT} + \frac{\Delta_r S^0}{R} \quad (4)$$

The calculation of $\Delta_r S^0$ from the plot of $\ln K$ vs. $1/T$ assumes that both $\Delta_r S^0$ and $\Delta_r H^0$ do not vary with temperature. An alternative and (in principle) more accurate method consists in combining a calorimetrically derived $\Delta_r H^0$ value with the corresponding equilibrium constant at a single temperature T , to obtain $\Delta_r S^0$ at that temperature from Eq. (4) [9,62,63]. To our knowledge this method has not been applied to organometallic reactions. Note also that the errors of the $\Delta_r S$ values in Table 1, which reflect the precision of the measurements, are frequently of the order of 10% or more and do not include Student's t factors [64]. In general, not more than 10 experimental points were used to fit Eq. (4) by a linear regression. Therefore, if Student's t factors for 95% confidence level were taken into account, the errors in Table 1 would at least double, in most cases.

3. The estimation method

The method used to estimate the entropy changes of organometallic reactions is rather simple and can be illustrated by considering several reactions in Table 1.

Take, for example, reaction 16, an intermolecular carbonyl insertion into a hafnium–methyl bond. As far as entropy is concerned, this reaction can be modelled by reaction M14 or by reaction M15 (“M” for model; see Table 2 [62,65]). It is seen that $\Delta_r S(16) = -138.1 \pm 23.4 \text{ J K}^{-1} \text{ mol}^{-1}$ is close to $\Delta_r S^0(\text{M14}) = -132.3 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta_r S^0(\text{M15}) = -137.8 \text{ J K}^{-1} \text{ mol}^{-1}$. Consider now the σ -bond metathesis reaction 1, for which $\Delta_r S(1) = -4.2 \pm 4.2 \text{ J K}^{-1} \text{ mol}^{-1}$. In this case, the model reactions M28, M29, and M30 yield an average $\Delta_r S^0 = -7.8 \text{ J K}^{-1} \text{ mol}^{-1}$, in good agreement with the experimental value. Finally, note that the entropy of reaction 3 in Table 1, $\Delta_r S(3) = 43.2 \pm 1.3 \text{ J K}^{-1} \text{ mol}^{-1}$, which involves a cyclization process, can be modelled by reaction M3, where $\Delta_r S^0(\text{M3}) = 49.5 \text{ J K}^{-1} \text{ mol}^{-1}$.

The above three examples indicate that the entropy changes of the organometallic reactions in Table 1 can be approximated to the entropy changes of organic and inorganic reactions of the same type, in the gas phase, at 298 K. A collection of these simple model reactions, for which the entropies are known, is presented in Table 2, together with an indication of the corresponding reactions in Table 1. The deviations δ found between the experimental and predicted $T\Delta_r S$ data are summarized in Table 3. Before proceeding into a more detailed discussion of these results it is stressed that $\delta = T|\Delta_r S(\text{exp}) - \Delta_r S^0(\text{model})|$, at $T = 298 \text{ K}$, is usually less than 10 kJ mol^{-1} .

4. Discussion

The agreement between the experimental and predicted entropy values can be understood within the framework of statistical thermodynamics of ideal gas phase reactions [10a,11,66]. Only a very brief analysis is given below.

The entropy of a substance in the gas phase can be considered as a sum of several contributions, namely translation (S_t^0), rotation (S_r^0), vibration (S_v^0), internal rotation (S_{ir}^0), and electronic (S_e^0):

$$S^0 = S_t^0 + S_r^0 + S_v^0 + S_{ir}^0 + S_e^0 \quad (5)$$

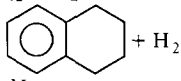
Other contributions may have to be accounted for [10a,11], but those in Eq. (5) are enough for the present discussion. The equations used in the computation of S_t^0 , S_r^0 , S_v^0 , and S_e^0 (in $\text{J K}^{-1} \text{ mol}^{-1}$), assuming a rigid rotator–harmonic oscillator model for the molecule, are

$$S_t^0 = -9.57577 + 20.78628 \ln T + 12.47177 \ln M \quad (6)$$

$$S_r^0 = 877.39503 + 8.31451 \ln T + 8.31451 \ln I - 8.31451 \ln \sigma \quad (7)$$

(linear molecules)

Table 2
Standard molar entropies of model reactions in the ideal gas state at 298 K ^a

No.	Reaction	$\Delta_r S^0(\text{g})/\text{J K}^{-1} \text{mol}^{-1}$	No. of reaction in Table 1
<i>1 particle = 1 particle</i>			
M1	$\text{C}_4\text{H}_{10} = {}^i\text{C}_4\text{H}_{10}$	-15.5	69
M2	$\text{C}_5\text{H}_{12} = {}^i\text{C}_5\text{H}_{12}$	-5.3	69
<i>1 particle = 2 particles</i>			
M3	$\text{CH}_3(\text{CH}_2)_5\text{Ph} = \text{cy-C}_6\text{H}_{12} + \text{C}_6\text{H}_6$	49.5	3
M4	$\text{C}_2\text{H}_6 = 2\text{CH}_3$	158.8	7, 9–15, 24–33, 44, 45, 58, 63, 70
M5	$\text{H}_2\text{O}_2 = 2\text{OH}$	134.8	7, 9–15, 24–33, 44, 45, 58, 63, 70
M6	$\text{N}_2\text{H}_4 = 2\text{NH}_2$	151.5	7, 9–15, 24–33, 44, 45, 58, 63, 70
M7	$\text{C}_2\text{H}_4 + \text{H}_2\text{O}_2 = \text{HOCH}_2\text{CH}_2\text{OH}$	-128.7	55
M8	$\text{CH}_3 + \text{CO} = \text{CH}_3\text{CO}$	-122.0	21, 68
M9	$\text{C}_5\text{H}_{12} = \text{cy-C}_4\text{H}_8 + \text{CH}_4$	102.7	4
M10	$\text{C}_6\text{H}_{14} = \text{cy-C}_5\text{H}_{10} + \text{CH}_4$	90.7	4
M11	$\text{CH}_4 + \text{CO} = \text{CH}_3\text{C(O)H}$	-119.7	5, 6, 72
M12	$\text{H}_2 + \text{CO} = \text{HC(O)H}$	-109.6	5, 6, 72
M13	$\text{C}_2\text{H}_6 + \text{CO} = \text{C}_2\text{H}_5\text{C(O)H}$	-122.6	5, 6, 72
M14	$\text{C}_2\text{H}_6 + \text{CO} = \text{CH}_3\text{C(O)CH}_3$	-132.3	16, 49–51, 76, 78
M15	$\text{C}_4\text{H}_{10} + \text{CO} = \text{C}_2\text{H}_5\text{C(O)C}_2\text{H}_5$	-137.8	17, 49–51, 76, 78
M16	$\text{PhCH}_3 + \text{CO} = \text{CH}_3\text{C(O)Ph}$	-145.5	52
M17	$\text{C}_6\text{H}_{14} = \text{cy-C}_6\text{H}_{12} + \text{H}_2$	40.5	19
M18	$\text{CH}_3(\text{CH}_2)_3\text{Ph} = $  $+ \text{H}_2$	64.4	20
M19	$\text{CH}_2 + \text{N}_2 = \text{CH}_2\text{N}_2$	-143.7	22
M20	$\text{CH}_2 + \text{H}_2 = \text{CH}_4$	-139.3	23
M21	$\text{C}_2\text{H}_6 = \text{H}_2 + \text{C}_2\text{H}_4$	220.5	99
M22	$\text{C}_3\text{H}_8 = \text{CH}_4 + \text{C}_2\text{H}_4$	135.8	99
M23	$\text{CH}_3\text{Cl} = \text{CH}_3 + \text{Cl}$	124.8	36
M24	$\text{CH}_3\text{F} = \text{CH}_3 + \text{F}$	130.2	36
M25	$\text{Si}(\text{CH}_3)_4 = \text{CH}_2 + (\text{CH}_3)_3\text{SiH}$	166.9	91–94
M26	$\text{C}_2\text{H}_6 + \text{C}_3\text{H}_6 = \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_3$	-152.8	75
M27	$\text{H}_2 + \text{C}_3\text{H}_6 = \text{C}_3\text{H}_8$	-127.7	75
<i>2 particles = 2 particles</i>			
M28	$\text{H}_2\text{O} + \text{C}_6\text{H}_6 = \text{PhOH} + \text{H}_2$	-11.7	1, 18
M29	$\text{CH}_4 + \text{C}_6\text{H}_6 = \text{PhCH}_3 + \text{H}_2$	-4.1	1, 18
M30	$\text{H}_2\text{S} + \text{C}_6\text{H}_6 = \text{PhSH} + \text{H}_2$	-7.5	1, 18
M31	$\text{C}_2\text{H}_6 + \text{H}_2 = 2\text{CH}_4$	12.2	48, 65–67, 73
M32	$\text{H}_2\text{O}_2 + \text{H}_2 = 2\text{H}_2\text{O}$	14.2	48, 65–67, 73
M33	$\text{N}_2\text{H}_4 + \text{H}_2 = 2\text{NH}_3$	15.7	48, 65–67, 73
M34	$\text{N}_2\text{H}_4 + \text{CH}_4 = \text{CH}_3\text{NH}_2 + \text{NH}_3$	10.3	74
M35	$\text{H}_2\text{O}_2 + \text{CH}_4 = \text{CH}_3\text{OH} + \text{H}_2\text{O}$	9.5	74
M36	$\text{C}_2\text{H}_6 + \text{OH} = \text{CH}_3\text{OH} + \text{CH}_3$	20.6	64
M37	$\text{CH}_3\text{OH} + (\text{CH}_3)_2\text{NH} = (\text{CH}_3)_3\text{N} + \text{H}_2\text{O}$	-36.8	59
M38	$\text{CH}_3\text{OH} + (\text{CH}_3)\text{NH}_2 = (\text{CH}_3)_2\text{NH} + \text{H}_2\text{O}$	-21.2	59
<i>2 particles = 3 particles</i>			
M39	$\text{C}_2\text{H}_6 + 2\text{CO} = 2\text{CH}_3\text{CO}$	-85.2	8
M40	$2\text{OH} + \text{CH}_4 = \text{H}_2\text{O} + \text{CH}_3\text{OH}$	-125.2	71
M41	$\text{C}_2\text{H}_6 + \text{C}_6\text{H}_6 = \text{PhCH}_3 + \text{CH}_2 + \text{H}_2$	147.4	2
<i>2 particles = 4 particles</i>			
M42	$\text{CH}(\text{C}_2\text{H}_5)_3 + \text{H}_2 = \text{CH}_3 + 3\text{C}_2\text{H}_5$	340.8	34, 35
M43	$\text{CH}(\text{C}_2\text{H}_5)_3 + \text{H}_2\text{O} = \text{CH}_3\text{O} + 3\text{C}_2\text{H}_5$	318.6	34, 35
M44	$\text{CH}(\text{C}_2\text{H}_5)_3 + \text{PhH} = \text{PhCH}_2 + 3\text{C}_2\text{H}_5$	331.5	34, 35
<i>4 particles = 3 particles</i>			
M45	$\text{cy-C}_3\text{H}_6 + 3\text{CO} = 3\text{CH}_2\text{CO}$	-87.5	60, 61
M46	$\text{cy-C}_3\text{H}_6 + 3\text{HCO} = 3\text{CH}_3\text{CO}$	-101.9	60, 61
M47	$\text{cy-C}_3\text{H}_6 + 3\text{H}_2 = 3\text{CH}_4$	-70.7	60, 61

^a Standard entropies of gaseous reactants and products were taken from Refs. [62] and [65].

Table 3

Deviations $\delta = |T\Delta_r S(\text{exp}) - T\Delta_r S^0(\text{model})|$ of the estimated values of $T\Delta_r S^0(\text{model})$ from the corresponding experimental values $T\Delta_r S(\text{exp})$ for the reactions in Table 1 ($T = 298 \text{ K}$)

No. of reaction in Table 1	$T\Delta_r S(\text{exp})/\text{kJ mol}^{-1}$	No. of model reaction in Table 2	$T\Delta_r S^0(\text{model})/\text{kJ mol}^{-1 \text{ a}}$	$\delta/\text{kJ mol}^{-1}$
1	-1.3 ± 1.3	M28, M29, M30	-2.3	1.0
2	29.9 ± 2.5	M41	43.9	14.0
3	12.9 ± 0.4	M3	14.8	1.9
4	20.7 ± 6.2	M9, M10	28.8	8.1
5	-14.6 ± 5.4	M11, M12, M13	-34.5	20.3
6	-29.8 ± 9.2	M11, M12, M13	-34.5	5.1
7	81.1 ± 18.3	M4, M5, M6	44.2	36.9
8	-25.3 ± 6.0	M39	-25.4	0.1
9	43.4 ± 3.0	M4, M5, M6	44.2	0.8
10	38.9 ± 3.1	M4, M5, M6	44.2	5.3
11	42.5 ± 3.0	M4, M5, M6	44.2	1.7
12	40.1 ± 0.4	M4, M5, M6	44.2	4.1
13	41.5 ± 2.4	M4, M5, M6	44.2	2.7
14	37.1 ± 4.0	M4, M5, M6	44.2	7.1
15	34.2 ± 2.6	M4, M5, M6	44.2	10.0
16	-41.5 ± 7.0	M14	-39.4	2.1
17	-35.8 ± 0.7	M15	-41.1	5.3
18	-4.4 ± 0.8	M28, M29, M30	-2.3	2.1
19	41.5 ± 6.1	M17	12.1	29.4
20	23.5 ± 2.9	M18	19.2	4.3
21	-43.2 ± 4.2	M8	-36.4	6.8
22	-44.1 ± 2.9	M19	-42.8	1.3
23	-31.9 ± 2.1	M20	-41.5	9.6
24	35.9 ± 7.1	M4, M5, M6	44.2	8.3
25	46.2 ± 1.8	M4, M5, M6	44.2	2.0
26	63.2 ± 2.7	M4, M5, M6	44.2	19.0
27	43.8 ± 1.1	M4, M5, M6	44.2	0.4
28	42.8 ± 1.6	M4, M5, M6	44.2	1.4
29	68.3 ± 2.7	M4, M5, M6	44.2	24.1
30	53.4 ± 3.6	M4, M5, M6	44.2	9.2
31	50.4 ± 1.6	M4, M5, M6	44.2	6.2
32	86.0 ± 1.9	M4, M5, M6	44.2	41.8
33	52.4 ± 3.4	M4, M5, M6	44.2	8.2
34	64.0 ± 2.5	M42, M43, M44	98.4	34.4
35	51.7 ± 1.5	M42, M43, M44	98.4	46.7
36	19.9 ± 6.2	M23, M24	38.0	18.1
37	45.0 ± 9.8	b,c	0	45.0
38	107.3 ± 6.3	b,c	0	107.3
39	66.2 ± 7.5	b,c	0	66.2
40	110.9 ± 2.4	b,c	0	110.9
41	83.4 ± 7.5	b,c	0	83.4
42	-20.6 ± 2.5	b,c	0	20.6
43	-23.5 ± 2.5	b,c	0	23.5
44	38.7 ± 3.1	M4, M5, M6	44.2	5.5
45	42.4 ± 2.5	M4, M5, M6	44.2	1.8
46	3.0 ± 1.8	c,d	0	3.0
47	1.5 ± 2.6	c,d	0	1.5
48	10.6 ± 1.0	M31, M32, M33	4.2	6.4
49	-37.4	M14, M15	-40.3	2.4
50	-19.3	M14, M15	-40.3	21.0
51	-11.1	M14, M15	-40.3	29.2
52	-34.2	M16	-43.4	9.2
53	23.9 ± 0.7	b,c	0	23.9
54	0.9 ± 1.0	b,c	0	0.9
55	-34.9 ± 5.0	M7	-38.4	3.5
56	-1.9 ± 0.6	c,d	0	1.9
57	-1.5 ± 0.2	c,d	0	1.5
58	38.7 ± 1.8	M4, M5, M6	44.2	5.5
59	-7.6 ± 0.2	M37, M38	-8.7	1.1

Table 3 (continued)

No. of reaction in Table 1	$T\Delta_r S(\text{exp})/\text{kJ mol}^{-1}$	No. of model reaction in Table 2	$T\Delta_r S^0(\text{model})/\text{kJ mol}^{-1}$ ^a	$\delta/\text{kJ mol}^{-1}$
60	-34.0 ± 1.5	M45, M46, M47	-25.8	8.2
61	-18.1 ± 0.8	M45, M46, M47	-25.8	7.7
62	28.9 ± 1.2	^{c,e}	42	13.1
63	35.3 ± 1.8	M4, M5, M6	44.2	8.9
64	11.5 ± 8.3	M36	6.1	5.4
65	-5.2 ± 0.6	M31, M32, M33	4.2	9.4
66	5.5	M31, M32, M33	4.2	1.3
67	5.5 ± 0.6	M31, M32, M33	4.2	1.3
68	36.1	M8	36.4	0.3
69	2.7 ± 0.7	M1, M2	-3.1	5.8
70	-41.2	M4, M5, M6	-44.2	3.0
71	-23.7 ± 6.2	M40	-37.3	13.6
72	-36.7 ± 4.5	M11, M12	-34.2	2.5
73	1.0 ± 2.5	M31, M32, M33	4.2	3.2
74	-8.7 ± 3.8	M34, M35	3.8	12.5
75	-25.0 ± 6.3	M26, M27	-41.8	16.8
76	-38.7 ± 6.3	M14, M15	-40.2	1.5
77	-77.2 ± 8.9	^c	-80.5	3.3
78	-38.7 ± 8.6	M14, M15	-40.2	1.5
79	-45.0 ± 3.6	M8	-36.3	8.7
80	-1.0 ± 3.6	^{b,c}	0	1.0
81	-9.4 ± 4.7	^{b,c}	0	9.4
82	-0.6 ± 0.6	^{b,c}	0	0.6
83	-2.1 ± 6.2	^{b,c}	0	2.1
84	-6.1 ± 3.8	^{b,c}	0	6.1
85	-7.6 ± 3.2	^{b,c}	0	7.6
86	-3.2 ± 3.1	^{b,c}	0	3.2
87	23.9 ± 0.9	^{c,e}	42	18.1
88	24.6 ± 4.0	^{c,e}	42	17.4
89	28.3 ± 1.0	^{c,e}	42	13.7
90	25.8 ± 2.2	^{c,e}	42	16.2
91	23.8 ± 1.9	M25	49.7	25.9
92	30.9 ± 1.8	M25	49.7	18.8
93	31.2 ± 3.1	M25	49.7	18.5
94	29.8 ± 1.8	M25	49.7	19.9
95	-17.5 ± 12.5	^{b,c}	0	17.5
96	-52.4 ± 10.0	^e	-42	10.4
97	1.3 ± 3.8	^{b,c}	0	1.3
98	2.5 ± 3.8	^{b,c}	0	2.5
99	33.7 ± 1.6	M21, M22	38.2	4.5

^a Average of the results obtained with different models, when applicable.^b 2 particles = 2 particles.^c See discussion in text.^d 1 particle = 1 particle.^e 1 particle = 2 particles.

$$S_r^0 = 1320.85148 + 12.47177 \ln T + 4.157255 \ln(I_A I_B I_C) - 8.31451 \ln \sigma \quad (8)$$

(non-linear molecules)

$$S_v^0 = R \sum_i \left\{ \frac{1.438 \bar{\nu}_i / T}{\exp(1.438 \bar{\nu}_i / T)} - \ln[1 - \exp(-1.438 \bar{\nu}_i / T)] \right\} \quad (9)$$

$$S_e^0 = R \ln \omega_0 \quad (10)$$

were T is the temperature (in K), M is the molar mass (in g mol^{-1}), I is the moment of inertia of a linear molecule, $I_A I_B I_C$ is the product of the principal moments of inertia of a non-linear molecule, σ is the symmetry number, $\bar{\nu}_i$ is the wavenumber of the i th normal mode of vibration of the molecule (in cm^{-1}), ω_0 is the electronic ground state degeneracy, and R is the gas constant.

The translational entropy given by Eq. (6) refers to a standard pressure of 1 bar. According to this equation, S_r^0 is proportional to $\ln M$, and therefore it is not strongly dependent on changes of molar mass. This implies, for example, that in reactions where one parti-

cle yields two particles, if the molar masses of the reactant and one of the products are of the same magnitude, the translational contribution to the reaction entropy will be close to the translational entropy of the second product. This is seen, for instance, in the case of intermolecular carbonyl insertion reactions and in H_2 oxidative additions, where the translational entropy changes are nearly identical to $S_t^0(CO)$ and $S_t^0(H_2)$ respectively.

The previous discussion can be easily extended to other types of reaction involving several numbers of particles, displayed in Tables 1 and 2. It also applies to the case of the rotational contribution: Eqs. (7) and (8) show that S_r^0 is rather insensitive to changes in the moment of inertia.

Although the vibrational contribution to entropy can be negligible compared with S_t^0 and S_r^0 , particularly in molecules with a small number of light atoms, such as hydrogen and carbon, in the case of most organometallic species it has to be considered. While this is true for entropies of individual species, it becomes less relevant when the vibrational entropy change $\Delta_r S_v^0$ of a reaction is calculated. In many reactions shown in Table 1, the overall change in vibration degrees of freedom is small and leads to a small $\Delta_r S_v^0$ (see, however, discussion below).

Another important contribution to the entropy of a large molecule comes from internal rotations [10a,11]. However, as in the case of vibration, in many reactions the net change of the internal rotation degrees of freedom is small, leading to a small contribution to the reaction entropy.

When the information about the electronic configuration of the ground state is known, it is possible to calculate the electronic contribution to the entropy by using Eq. (10) (it is assumed that the energy difference between the first electronic excited state and the ground state is much higher than $k_B T$). In a chemical reaction where reactants and products have different ground state degeneracies, the electronic contribution to the entropy change must be considered if a very accurate value is to be derived. Take, for example, the reaction of dissociation of I_2 , yielding two iodine atoms. The ground state electronic degeneracies $\omega_0(I_2) = 1$ and $\omega_0(I) = 4$ lead to $T\Delta_r S_e^0 = 3.4 \text{ kJ mol}^{-1}$. In many organometallic reactions involving coordinatively saturated complexes, however, the variation of the ground state degeneracies is not as large and therefore neglecting the electronic contribution to the entropy leads to errors which are often comparable with the experimental uncertainties.

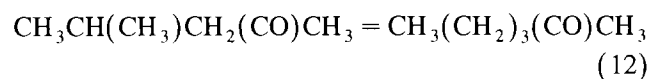
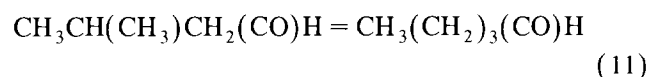
In conclusion, $\Delta_r S_t^0$ and $\Delta_r S_r^0$ are frequently the most important contributions to the entropy of a reaction. Owing to their insensitivity to changes in molar mass and moments of inertia, these contributions have roughly constant values for organic, inorganic or organometallic reactions of the same type (CO inser-

tions, σ -bond metathesis, etc.). Even though the entropy of a gas phase reaction can be accurately calculated from statistical thermodynamics, the method is laborious and often the necessary structural and vibrational data for reactants and products are not available or are difficult to predict. The use of model reactions which mimic the changes in the external and internal degrees of freedom provides an alternative and easy way of estimating $T\Delta_r S$ for organometallic reactions within ca. 10 kJ mol^{-1} . Other methods for predicting entropy changes avoiding detailed statistical thermodynamic calculations have been reported and applied to biochemical systems [67–72].

Let us now analyse in more detail some of the reactions in Tables 1 and 2, paying particular attention to those for which $\delta > 10 \text{ kJ mol}^{-1}$ (Table 3). Just for a matter of convenience, the discussion below follows the classification of reactions given in Table 2, according to the number of particles as reactants and products.

4.1. 1 particle = 1 particle

Small entropy changes for reactions where the number of particles is conserved can be predicted, particularly when only structural rearrangements are involved. This is indeed the case for reactions 46, 47, 56, 57, and 69. Although no models could be found for reactions 46, 47, 56, and 57, the reported experimental entropies are close to zero, as expected for 1 particle = 1 particle reactions. The negative value obtained for reaction 56 is probably due to the formation of the three-membered ring in the product. Note, however, that although a negative entropy value is predicted for reaction 69 based on models M1 and M2, and a positive value is experimentally found, the obtained δ value in Table 3 is reasonably small, ca. 6 kJ mol^{-1} . Note also, for example, that Benson's additivity scheme [10] also gives a negative value ($T\Delta_r S^0 = -0.9 \text{ kJ mol}^{-1}$) for the entropy of the reactions



which may be better models for reaction 69.

4.2. 1 particle = 2 particles

Reaction 3 corresponds to a σ -bond metathesis and ring closure reaction. In this case the model M3 estimates $T\Delta_r S^0$ within 2 kJ mol^{-1} . A good agreement is also observed for reaction 20, where model M18 was used. However, it is surprising that the estimated $T\Delta_r S^0$ value for reaction 19 (model M17) leads to a large

deviation (29.4 kJ mol^{-1}) from the experimental value. A similar comment applies to reactions 5 and 6, which are CO insertions into M–H bonds. Although the model reactions M11–M13 predict $T\Delta_r S^0$ for reaction 6 within the experimental error, the corresponding estimate for reaction 5 leads to a discrepancy of 20 kJ mol^{-1} .

Reaction 7 is a ligand dissociation reaction. Based on the model reactions M4–M6 it is expected that $T\Delta_r S^0$ for reaction 7 is about 44 kJ mol^{-1} . The large discrepancy found between the estimated and the experimental value (37 kJ mol^{-1}), as well as the large uncertainty of the experimental value, strongly suggest that the entropy of reaction 7 in Table 1 is in error.

Models M4–M6 were also used for estimating the entropies of reactions 24–33. As seen in Table 1, reactions 25–28 describe the cleavage of the Cr–Cr bond in the complex $[\text{Cr}(\text{Cp})(\text{CO})_3]_2$ and were studied by different groups. The same happened with reactions 29–31 for the analogue Cp^* complex, and reactions 32, 33 for $\{\text{Cr}(\text{Cp})(\text{CO})_2[\text{P}(\text{OMe})_3]\}_2$. It is noted that the experimental values of $T\Delta_r S$ for reactions 26, 29, and 32, all measured by the same group, are considerably higher than predicted by the model and are also in disagreement with the other experimental values.

The experimental value of the entropy of reaction 36 is considerably smaller than the value predicted for the model reactions M23 and M24. Both reaction 36 and the models involve the formation of a monoatomic species and a polyatomic fragment, implying identical changes in translational, rotational and vibrational degrees of freedom. From the above discussion after Eqs. (6)–(8) it is expected that the translational and rotational contributions to $\Delta_r S^0$ are similar in reactions 36, M23 and M24. However, the frequencies of the three vibration modes lost upon dissociation of the model compounds (CH_3F and CH_3Cl) are certainly much higher than the corresponding frequencies in the case of the dissociation of $\text{W}(\text{CO})_5\text{Xe}$. Therefore, according to Eq. (9), the negative vibrational contribution to $\Delta_r S^0$ will be much larger for reaction 36 than for the models M23 and M24, leading to a considerably lower $\Delta_r S^0$ value in the former case [73].

The experimental values of the entropies for the CO insertion reactions 49–52 show unexpected differences. Indeed, while the models used for estimating $T\Delta_r S$ for $\text{R} = \text{Me}$ and Ph lead to errors smaller than 10 kJ mol^{-1} , the discrepancies found for $\text{R} = \text{Et}$ and Pr are considerably higher.

The reported entropies of reactions 62 and 87–90 seem too low when compared with typical data for 1 particle = 2 particles reactions, ca. $T\Delta_r S^0 = 42 \text{ kJ mol}^{-1}$. These discrepancies must be related to the internal rotation of the $\eta^2\text{-H}_2$ moiety in the reactant complex and to the loss of internal rotation degrees of freedom of the phosphine group upon formation of a C–H \rightarrow M agostic interaction in the organometallic

product [74]. Both effects act in the same direction, i.e. the former increases the entropy of the reactant and the latter reduces the entropy of the product. While the explanation seems reasonable, it could also be used to predict that reactions 46 and 47 should have negative (albeit small) entropies, which conflicts with the experimental data in Table 1. Note, however, that the error bars for the entropies of these reactions do not seem to invalidate the prediction $T\Delta_r S < 0$.

A large deviation is found between $T\Delta_r S$ for reaction 75 and for the model reactions M26 and M27 (16.8 kJ mol^{-1} ; Table 3). This discrepancy and the large experimental error quoted for $T\Delta_r S(75)$ suggest that the reported entropy of reaction 75 is too high.

The reductive elimination reactions 91–94 have entropies (79.9 ± 6.3 , 103.8 ± 5.9 , 104.6 ± 10.5 , and $100.0 \pm 5.9 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively), considerably smaller than expected on the basis of the data for the model reaction M25 in Table 2 ($166.9 \text{ J K}^{-1} \text{ mol}^{-1}$), leading to an average δ value of ca. 21 kJ mol^{-1} . We are unable to explain this discrepancy. Steric effects in the reactant complex, hindering the internal rotations of the SiMe_3 group, would imply an upward correction of $T\Delta_r S^0$ predicted by the model.

4.3. 1 particle = 3 particles

No model is presented for reaction 77. Note, however, that this reaction corresponds to a double CO insertion. Therefore it is expected that $\Delta_r S(77)$ is approximately twice the value given in Table 2 for models M14 and M15, which yields $T\Delta_r S^0 = -80.5 \text{ kJ mol}^{-1}$. This is in good agreement with the experimental value.

4.4. 2 particles = 2 particles

Reactions 37–41 should have entropies close to zero. As stated by Angelici and Ingemanson [31], the abnormally large experimental values are not understood.

Kubas et al. [32] have explained the negative entropies of reactions 42 and 43 by the interaction of solvent (thf) molecules with the coordinated water. As one would expect that, in the absence of such specific interactions, $T\Delta_r S \approx 0$ and, as also one cannot rule out the solvation of free water reactant molecules, the experimental values imply that the coordination of thf to the organometallic product produces a larger entropy decrease than in the case of the free water molecule (see below for more comments on solvation).

Although no specific model was used for reactions 53 and 54, the comparison between the corresponding $\Delta_r S$ values suggests that the value reported for reaction 53 is in error. While $\Delta_r S$ for reaction 54 is in the range found for 2 particles = 2 particles reactions (i.e. $\Delta_r S \approx 0$), the value for reaction 53 is much higher than expected.

The entropies of reactions 65–67 are close to zero as predicted for this type of 2 particles = 2 particles reaction. The negative value of $\Delta_r S$ for reaction 65 is, however, unexpected, judging from the positive entropies of reactions 66, 67 and of the model reactions M31–M33.

The model reactions M34 and M35 predict a small positive value for the entropy of reaction 74. In contrast, the experimental value found is small but negative. This discrepancy suggests that the experimental value should be redetermined, since it is based on measurements at two temperatures only and has a large experimental error.

We could not find appropriate organic analogues for reactions 80–86, where an η^2 -ethylene is replaced by another η^2 -olefin, and for reactions 95, 97, and 98. The values of $\Delta_r S$ reported for reactions 80–86 are, however, nearly within the expected range for 2 particles = 2 particles reactions, i.e. $T\Delta_r S \approx 0$, particularly if the experimental uncertainties are considered. The same is observed for reactions 95, 97, and 98, although in the case of reaction 95 the recommended $T\Delta_r S$ value is about 18 kJ mol⁻¹ higher than predicted.

4.5. 2 particles = 3 particles

Reaction 2 can be decomposed in a σ -bond metathesis and a ligand dissociation reaction. It is expected that $\Delta_r S \approx 0$ for the former process (reactions M28–M30) and $\Delta_r S^0 \approx 130$ – 150 J mol⁻¹ K⁻¹ for the latter (see reactions M4–M6). The model reaction M41 has $\Delta_r S^0 = 147.4$ J mol⁻¹ K⁻¹, which corresponds to $T\Delta_r S^0 = 43.9$ kJ mol⁻¹. The estimate exceeds the experimental $T\Delta_r S$ value by 14.1 kJ mol⁻¹. This significant difference may reflect a loosely bound thf molecule in the organometallic reactant: the internal rotation and the low frequency vibrational modes involving the coordinated thf moiety, which will increase the entropy of the organometallic adduct, are lost upon dissociation.

The value of $T\Delta_r S^0 = -37.3$ kJ mol⁻¹ for the model reaction M40 is about 14 kJ mol⁻¹ lower than the corresponding value for reaction 71 (-23.7 ± 6.2 kJ mol⁻¹). We note, however, that the experimental value relies on a van't Hoff plot involving only three temperatures.

4.6. 2 particles = 4 particles

Reactions 34 and 35 involve changes of ligand hapticity and provide an example for which it is not possible to find suitable organic models. Therefore, large discrepancies between the entropies of models, such as M42–M44, and the entropies of those organometallic reactions could be expected.

4.7. 4 particles = 3 particles

The reactions M45–M47 predict, as observed experimentally, that the absolute values of the entropies of reactions 60 and 61 are smaller than the typical range for 2 particles = 1 particle reactions. The agreement between the estimated and the experimental data is fair: the prediction $\Delta_r S^0 = -86.7$ J mol⁻¹ K⁻¹ leads to errors of 8.1 and 7.7 kJ mol⁻¹ for reactions 60 and 61, respectively (Table 3). These discrepancies are within our accepted limits for the estimates. However, it is somewhat surprising that the entropies of reactions 60 and 61 differ by 53 J mol⁻¹ K⁻¹. This difference is hardly justifiable by invoking solvent effects (see below). Unfortunately, the entropies of the model reactions M45–M47 vary over a wide range, making it difficult to assess which is the most reliable experimental value.

5. Final comments

It is understood that the use of gas phase models at 298 K to estimate entropies of organometallic reactions in solution is somewhat crude, since a more detailed analysis of the internal and external degrees of freedom of reactants and products (whenever possible), together with temperature and solvent effects, might allow more accurate predictions. However, the method discussed above is extremely simple to apply and in most cases it is sufficiently accurate to assess or to predict entropy changes of organometallic reactions. It is of course recognized that an error of 10 kJ mol⁻¹ in $T\Delta_r S$ leads to a very large error in the equilibrium constant (see Introduction) and, in this regard, the method is not satisfactory. Yet, as mentioned before, a fair amount of the experimental data is probably less reliable than the values obtained through the model reactions.

Let us finally address the temperature and solvent effects on the reaction entropies. The fact that the large majority of organometallic reactions is studied in solution limits the temperature range of the experiments. For example, all reactions in Table 1, except three (7, 58, 63), were studied in solution at temperatures ranging from ca. 170–450 K. As can be concluded from

$$\Delta_r S(298) = \Delta_r S(T) + \Delta_r C_p \ln \frac{298}{T} \quad (13)$$

the temperature corrections to derive $\Delta_r S$ at 298 K are well within the uncertainty accepted for the present estimation method. $\Delta_r C_p$, which represents the average reaction heat capacity change in the temperature range 298– T , is small for most reactions in Table 1 ($|\Delta_r C_p|$ less than ca. 30 J mol⁻¹ K⁻¹ [75]) and is multiplied by

a factor smaller than one. We therefore decided not to apply any temperature corrections to our model.

With regard to solvation effects, the difference between the entropy of a reaction in the gas phase and in solution has been discussed, and it does not seem to be well understood [69,72,76]. It is generally agreed that the transfer from the gas phase to solution of a reaction where there is no net change in the number of particles does not lead to a significant entropy difference. However, for reactions involving a different number of particles as reactants and products there is conflicting evidence about the expected entropy differences in the gas phase and in solution [69,72,76]. According to Hammett [76], in the case of 2 particles = 1 particle reactions, it should be expected that entropies in solution are considerably less negative than in the gas phase. However, as discussed by Page [69], similar entropies should be expected for many association reactions in the gas phase and in solution. Most data in Table 1 refer to reactions involving neutral species, in solvents where solvation effects are expected to be small. The fact that the method of estimation discussed in this paper leads to a satisfactory agreement with experimental data, suggests that gas phase and solution values of $T\Delta S$ for most reactions in Table 1 are similar within the maximum accepted error for the estimations (10 kJ mol^{-1}), even for reactions where the number of particles is not conserved.

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