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Correction to "Experimental Evidence for pK_a -Driven Asynchronicity in C–H Activation by a Terminal Co(III)–Oxo Complex"

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J. Am. Chem. Soc. 2019, 141 (9), 4051-4062. DOI: 10.1021/jacs.8b13490

Read Online Cite This: https://dx.doi.org/10.1021/jacs.0c02031 ACCESS Metrics & More Article Recommendations **SUPPORTING Information** t has been brought to our attention that our previous Α analysis of kinetic data for C–H activation was incomplete. 1.00 $\log(k_{obs})$ 0 5 = 9.2(4)*10⁻⁴ s Absorbance 0. 0.75 0.3 0.2 Absorbance 0. 0.50 400 600 Time (s) 800 100 74 0.25 78 82 84 76 80 BDE_{C-H} (kcal/mol) В 0.00 С 400 500 600 700 800 900 1000 1100 300 Wavelength (nm) Figure 1. UV-vis spectra of the reaction between 3 (dark red trace) and 10 equiv of DHA to produce 1 and anthracene (purple trace). $\log(k_{obs})$ Gray traces indicate 1 min time points. Inset: Pseudo-first-order kinetic analysis of the reaction monitored at 470 nm.

For the reaction of PhB(^tBuIm)₃Co^{III}O (3) with various substrates, the observed rate constants, k_{obs} , were originally determined by plotting the natural log of the UV-vis absorbance at 470 nm at time $t(A_t)$ divided by the initial absorbance (A_0) versus time in seconds to give k_{obs} as the slope of the linear fit of the data. However, this method implicitly assumes that the absorbance at infinite time, A_{inf} is equal to 0. This is not true for these reactions due to absorbances from the reaction products, resulting in an underestimation of the true k_{obs} values for each substrate. In order to obtain more accurate k_{obs} values, the data were reanalyzed by fitting the absorbance versus time data at 470 nm to an exponential function, $A_t = A_{inf} + (A_0 - A_{inf}) e^{-kt}$. This method explicitly accounts for A_{inf} in the fitting parameters, providing more accurate values for the k_{obs} for each substrate. For the Eyring analysis of the reaction between 3 and 9,10-dihydroanthracene, the noise and subsequent error in the measurements precluded good exponential fits of the variable-temperature data. Therefore, these data were analyzed by finding k_{obs} as the slope of the linear fit of a plot of $\ln((A_t - A_{inf})/(A_0 - A_{inf}))$ versus t in seconds, where A_{inf} was estimated from reactions carried out in a cuvette at room temperature. These new



pK_a (DMSO)

24

28

32

36

-5

16

20

analyses result in the following corrections to the original Article:





Figure 3. Hammett substituent plot for the reaction of **3** with 9-(4-X-phenyl)-9H-fluorenes. The red line shows the linear fit of the data: $\rho = 0.87(3)$, $R^2 = 0.996$.

Table of Contents. The $log(k_{obs})$ vs substrate pK_a plot has been updated with the more accurately determined k_{obs} values. The corrected graphic is shown here:



Experimental Evidence for Asynchronous pKa-Driven C-H Activation

Pages 4053–4055. The more accurately determined k_{obs} values have been changed in Table 1, Figure 1, Table 2, Figure 2, Table 3, and Figure 3. The updated tables, figures, and captions are given here. Any values from these tables, figures, and captions mentioned explicitly in the text should be those from these updated tables, figures, and captions. We would also like to note that exponential fits of the data for diphenylmethane were sensitive to the inclusion of initial time points,

and the fits to these data were qualitatively poor, suggesting that caution must be employed in quantitatively interpreting data for this substrate. Nevertheless, the data were fit to an exponential to maintain consistency between different substrates.

Page 4059. In the Experimental Section under the subsection Procedure for Kinetic Studies, the text originally read: "To determine the observed rate k_{obs} values, the data were analyzed by plotting the natural log of the absorbance at 470 nm at time *t* divided by the initial absorbance versus time in seconds to give k_{obs} as the slope of the linear fit of the data. For diphenylmethane, this plot was generated using the absorbance at 470 nm from the radical product generated." This text should be replaced with the following:

"To determine the observed rate k_{obs} values, the data were analyzed by plotting the absorbance at 470 nm at time *t* versus time in seconds and fitting the data to an exponential function, $A_t = A_{inf} + (A_0 - A_{inf}) e^{-kt}$, where A_{inf} is the absorbance at infinite time, A_0 is the initial absorbance, and *k* is the observed rate constant, k_{obs} . For diphenylmethane, this plot was generated using the absorbance at 556 nm due to a convoluting absorbance at 470 nm upon injection of substrate."

Page 4059. In the Experimental Section under the subsection Determination of Activation Parameters for the Reaction between 3 and DHA, the text originally read: "To determine the observed rate k_{obs} values, the data were analyzed by plotting the natural log of the absorbance at 470 nm at time t divided by the initial absorbance versus time in seconds to give k_{obs} as the slope of the linear fit of the data." This text should be replaced with the following:

"To determine the observed rate k_{obs} values, the data were analyzed by plotting $\ln((A_t - A_{inf})/(A_0 - A_{inf}))$ (where A_{inf} was estimated from reactions carried out in a cuvette at room temperature) versus time in seconds to give k_{obs} as the slope of the linear fit of the data."

Supporting Information. Figures S3, S5, S8–S10, S12, S14–S16, S18, and S21–S24 have been replaced with new representative exponential fits. Figures S4, S11, S13, S17, S20, and S29 have been updated accordingly. Figure S6 has been replaced with the new fits for the variable-temperature

Table 1. Thermodynamic Data for Selected Transition Metal Oxo/Hydroxo Complexes and Their Reactivity Parameters with DHA

| complex | ΔH^{\ddagger} (kcal/mol) ^a | ΔS^{\ddagger} (e.u.) ^{<i>a</i>} | $k_2 (M^{-1} s^{-1})^a$ | $_{(k_{\rm H}/k_{\rm D})}^{\rm KIE}$ | $(DMSO)^{b}$ | E^0 (V vs Fc/Fc ⁺) ^c | BDFE _{O-H} (kcal/mol) | ref |
|---|---|--|-------------------------|--------------------------------------|--------------|--|-----------------------------------|-----------|
| PhB(^t BuIm) ₃ Co ^{III} O ^d | 13(2) | -20(6) | 0.0584(8) | 9.2(6) | ~15 | -0.23 | 84.6 | this work |
| $[(H_3 buea)Fe^{IV}O]^{-e}$ | n.r. | n.r. | n.r. | n.r. | 11 | 0.036 | 87 | 35 |
| $[(H_3 buea)Mn^{IV}O]^{-e}$ | 5(1) | -49(4) | 0.026(2) | 6.8 | 15 | -0.11 | 89 | 27 |
| $[(H_3 \text{ buea})Mn^{III}O]^{2-e}$ | 14(2) | -14(6) | 0.48(4) | 2.6 | 28.3 | -1.51 | 77 | 27 |
| $[Fe^{IV}O(TMC)(MeCN)]^{2+f}$ | n.r. | n.r. | 0.14 | 10 | n.r. | n.r. | 84(1) | 19 |
| (Cz)Mn ^V O ^g | n.r. | n.r. | $1.8(5) \times 10^{-5}$ | n.r. | ~11 | -0.33 | ~80 | 17 |
| $LCu^{III}OH^{h}$ | 5.4(2) | -30(2) | 186 | 29 | ~18 | -0.076 | 90(3) | 20 |
| $[Ru^{IV}O(bpy)_2 py]^{2+}$ | n.r. | n.r. | 125 | 35(5) | <-2 | >2.2 | 84.8 | 36, 37 |
| $Fe^{IV}O(TPFPP)^{i}$ | n.r. | n.r. | 13(2) | 20 | n.r. | n.r. | n.r. | 38 |

^{*a*}Values for reaction with DHA at room temperature. ^{*b*} pK_a value for M^{*n*+}-O/M^{*n*+}-OH adjusted using the correlation between pK_a values in DMSO, MeCN, THF, and H₂O as necessary. ^{*c*} E^0 for M^{*n*+}-OH/M^{(*n*-1)+}-OH adjusted versus Fc/Fc⁺ as necessary. ^{*d*}PhB(⁺BuIm)₃⁻ = tris(1-tert-butylimidazol-2-ylidene)phenylborate. ^{*e*}H₃ buea³⁻ = tris[(N₃-tert-butylureayl)-N-ethylene]aminato. ^{*f*}TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane. ^{*g*}Cz³⁻ = octakis(*para-tert*-butylphenyl)corrolazinato. ^{*h*}L²⁻ = N,N'-bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamide. ^{*i*}TPFPP²⁻ = *meso*-tetrakis(pentafluorophenyl)porphinato. Entries depicting n.r. indicate values not reported to the best of our knowledge. See original Article for references.

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Table 2. Kinetic Data for the Reaction of 3 with Various C-H Substrates

| substrate | $k_{\rm obs} \ (10^{-4} \ {\rm s}^{-1})^a$ | $k_2 (10^{-2} \text{ M}^{-1} \text{ s}^{-1})$ | KIE $(k_{\rm H}/k_{\rm D})$ | $pK_a (DMSO)^b$ | BDE _{C-H} (kcal/mol) ^c |
|-------------------------------------|--|---|-----------------------------|-----------------|--|
| 9,10-dihydroanthracene ^d | 9.2(4) | 5.84(8) | 9.2(6) | 30.1 | 76.3 |
| xanthene | 14.1(8) | n.d. | n.d. | 30.0 | 75 |
| 1,1,3,3-tetraphenylpropene | 1.0(3) | n.d. | n.d. | 25.8 | 77 |
| diphenylmethane | 1.5(4) | 1.2(4) | n.d. | 32.3 | 84.5 |
| 1,3-cyclohexadiene ^d | 0.60(7) | 0.27(2) | n.d. | 35 | 74.3 |
| 9-X-9H-fluorene | | | | | |
| X = H | 95(3) | 61(4) | 3.1(1) | 22.6 | 82 |
| $X = {}^{t}Bu$ | 11(3) | n.d. | n.d. | 24.4 | 79.9 |
| X = Ph | 3700(500) | n.d. | n.d. | 17.9 | 74 |

^{*a*}Determined using 10 equiv of substrate per equiv of Co complex either directly or from the k_2 value. ^{*b*}Data taken from the Bordwell p K_a table.⁴³ ^{*c*}Data taken from the CRC's Handbook of Bond Dissociation Energies.⁴⁴ ^{*d*}Rates corrected for stoichiometry. Entries depicting n.d. indicate values that were not determined. See original Article for references.

Table 3. Rates for Substrates Used in Hammett Analyses

| substrate | $k_{\rm obs} \ (10^{-2} \ {\rm s}^{-1})^a$ | $\sigma_{\rm p}^{-b}$ | | |
|---------------------------------|--|-----------------------|--|--|
| 9-(4-X-phenyl)-9H-fluorene | | | | |
| X = OMe | 22(3) | -0.26 | | |
| X = Me | 28(4) | -0.17 | | |
| X = H | 37(5) | 0.00 | | |
| CF ₃ | 140(40) | 0.65 | | |
| 3-X-xanthene | | | | |
| X = Me | 0.11(2) | -0.17 | | |
| X = H | 0.141(8) | 0.00 | | |
| 3-X-xanthene X = Me X = H | 0.11(2) 0.141(8) | -0.17 0.00 | | |

"Values obtained using 10 equiv of substrate. ^bHammett parameters obtained from Hansch, Leo, and Taft.⁴⁵ See original Article for references.

kinetic data for the reaction of **3** with DHA, and Figure S7 has been updated accordingly.

The conclusions of the paper remain unchanged after the reevaluation of the kinetic data, and indeed a slightly better correlation between pK_a and rate constants is observed.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c02031.

Supplementary derivations, figures, tables, and schemes (updated) (PDF)

ACKNOWLEDGMENTS

We thank Professor David M. Stanbury of Auburn University for bringing to our attention our incomplete treatment of the kinetic data and for his suggestions and insight regarding our updated analysis.