Research article

Journal of Physical Organic Chemistry

Received: 12 October 2014, Revised: 14 March 2015, Accepted: 24 March 2015, Published online in Wiley Online Library: 6 May 2015

(wileyonlinelibrary.com) DOI: 10.1002/poc.3451

The relationships of catalytic activity of metal Schiff base catalysts and the Hammett constants of their anion–cationic substituents on ligand

Hang Chen[a], Lu Jia[a], Jia Yao[a], Jinghui Hu[b], Kexian Chen[a,b], Zhirong Chen[a] and Haoran Li[a,b]*

For quaternary ammonium, pyridinium, or imidazolium anion–cationic substituents, a linear relationship can be established between the reactivity of metal Schiff base catalysts and the Hammett constants of their anion–cationic substituents with multi-atomic anions on ligand based on the theoretical and experimental works. Copyright © 2015 John Wiley & Sons, Ltd.

Keywords: DFT calculation; electronic effect; Hammett constant; ionic-pair substituent; metal Schiff base

INTRODUCTION

The transition metal complexes are extensively investigated because of their importance in catalytic oxidation.[1–5] Various conventional organic substituents on the ligand of metal complexes result in different catalytic effects.[3,6,7] Unfortunately, these homogeneous catalysts have an intrinsic disadvantage, for example, unrecoverablility, and were not easily to be overcome by the conventional organic substituents.[8] As one of the alternative approaches for tackling these problems, ionic-pair substituents had been employed as the promising groups to modify the metal complexes.[9,10] Guillemine *et al.*[11]and Yao *et al.*[12]reported separately that ionic-pair-substituted ruthenium carbene can be reused by 10 times in ring-closing metathesis. Furthermore, the catalytic activities could be conveniently tuned by combining different cations and anions.[13–17] Such as, the ionic-pair-substituted Salen–Mn catalysts were found to be more effective than the unsubstituted one in the enantioselective epoxidation of styrene.[18,19] Grela *et al.* prepared Hoveyda–Grubbs catalysts with pyridinium or quaternary ammonium ionic-pair substituents and used in olefin metathesis. The results showed that they were highly active catalysts in ring closing metathesis.[20,21] When pyridinium or imidazolium-substituted acetyl acetone metal compounds were used in the C–H activation reactions, our group found that the catalysts with ionic-pair substituents have higher activity than the corresponding unsubstituted counterpart.[13–15]

To find out the cause of this tunability, most of the previous papers aimed at steric effect[22–26] and the interaction between the ions and the solvents.[25–27] Besides, several reports focused on the structural properties and reactivity of the catalysts with ionic-pair substituents.[8,28] The most requisite features of these metal complexes catalysts with ionic-pair substituents were that the ionic-pair substituents should connect with the ligand by conjugated double bond, consequently, the cation–anion interaction could easily deliver to the metal center.[14] Most studies predicted the influence of the ionic-pair substituents on the catalytic reactivity qualitatively.[14,17,29,30] The performances of Cu Salen catalysts with ionic-pair substituents on the oxidation of cyclohexene showed that the more nucleophilic the anion of the ionic-pair substituent on the ligand is, the higher the catalytic reactivity would be.[14] More recently, a pyridinium substituted metal Schiff base catalyst Co-[Salen-Py][PF_6]$_2$ showed more excellent catalytic performance in the oxidation of 4-methyl guaiacol to vanillin compared with other unsubstituted catalysts. It was believed that the pyridinium substituents could decrease the electron density of the metal center, thereby enhancing the catalytic activity of the Schiff base catalyst.[17] As far as we know, there are few works about the structure and reactivity of catalyst with ionic-pair substituents quantitatively.[8,28] By investigating the structure–reactivity relationships of acetyl acetone–Fe catalysts with ionic-pair substituents in C–H activation reaction, our group found that the introduction of ionic-pair substituents alters the spin density carried by Fe/O atoms (SD_{Fe}/SD_O), the charge carried by O atom (Q_O), and the isotropic Fermi contact couplings of O atom ($IFCC_O$) in the Fe = O part, thereby influencing the reactivity of the catalyst.[8] The introduction of the ionic-pair substituents that increases the SD_O, Q_O, and $IFCC_O$ or decreases the SD_{Fe} can make the catalyst more powerful. Although all these can be understood in terms of the electronic effect of ionic-pair substituents, it is still not easy to predict the influence of the ionic-pair substituents on the catalytic reactivity quantitatively.

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* Correspondence to: Haoran Li, Department of Chemistry, Zhejiang University, Hangzhou 310027, China.
E-mail: lihr@zju.edu.cn

a H. Chen, L. Jia, J. Yao, K. Chen, Z. Chen, H. Li
Department of Chemistry, ZJU-NHU United R&D Center, Zhejiang University, Hangzhou 310027, China

b J. Hu, K. Chen, H. Li
State Key Laboratory of Chemical Engineering, Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China

It is well known that the Hammett constant *σ* for a conventional substituent group gives a measure of its electronic effect on the reaction center.[31] Dissociation of substituted benzoic acids is the experimental method to obtain Hammett constants σ,[32–34] which was also chosen for the definition of σ,[35] primarily from the pK values in water. Because of the difficulty of the synthesis of some ionic substituted benzene, few Hammett constants σ of ionic substituents, which are important to design and improve the catalysts, can be found in literatures. Recently, we established a convenient method to predict the Hammett constants of ionic-pair substituents.[36] If a general relationship between the catalytic activity of metal Schiff base catalysts and the Hammett constants of their ionic-pair substituents on ligand is built, it will be helpful and convenient to design the catalysts and tune their reactivity. In this paper, we present our efforts to explore the relationship between the parameters of the reactivity, for example, reaction barrier, turnover frequency (*TOF*), and the Hammett constants of its anion–cationic substituents on ligand. By analyzing our previous works, a linear relation between the Hammett constants of its anion–cationic substituents on ligand and the reaction barrier or *TOF* was observed. We also report the metal Schiff base catalysts with imidazolium anion–cationic substituents on the ligand Co-[Salen-Mim][X]$_2$ (X = PF_6^-, ClO_4^-, BF_4^-, NO_3^-, and Br^-) in this paper. Then, the oxidation of 4-methyl guaiacol was carried out to investigate the electronic effect of anion–cationic substituents on ligand on their catalytic activities.

EXPERIMENTAL SECTION

Preparation and characterization of catalysts

The procedure to synthesize catalysts Co-[Salen-Mim][Br]$_2$ (Scheme 1) and their characterization are listed in the **SI**.

The $AgNO_3$ or $AgBF_4$ (2 mmol) was added to the Co-[Salen-Mim][Br]$_2$ (1 mmol) in ethanol (50 ml), and then the mixture was stirred away from light at room temperature for 8 h. The resulted mixture was filtered and the filtrate was evaporated under reduced pressure at 60 °C, and the obtained solid was dried in vacuum. Co-[Salen-Mim][X]$_2$ (X = BF_4^-, NO_3^-) were prepared. NH_4PF_6 or $NaClO_4$ (2 mmol) was added to the Co-[Salen-Mim][Br]$_2$ (1 mmol) in ethanol (50 ml), and then the mixture was stirred at room temperature for 8 h. The resulted mixture was filtered, and the obtained solid was dried in vacuum to give Co-[Salen-Mim][X]$_2$ (X = PF_6^-, ClO_4^-).

Co-[Salen-Mim][NO$_3$]$_2$: Yield: 91%. ICP-MS: Anal. Calcd. for $C_{20}H_{28}CoN_8O_8$: Co, 10.39%. Found: Co, 10.36%. ESI-MS, m/z = 505.15(M-NO$_3$)$^+$. FT-IR (KBr): 3436, 3142, 3093, 2959, 1716, 1582, 1472, 1428, 1387, 1285, 1204, 1098, 1066, 1017, 985, 936, 834, 765, 688, 627, 485 cm^{-1}.

Co-[Salen-Mim][BF$_4$]$_2$: Yield: 93%. ICP-MS: Anal. Calcd. for $C_{20}H_{28}B_2CoF_8N_6O_2$: Co, 9.55%. Found: Co, 9.47%. ESI-MS, m/z = 530.17(M-BF$_4$)$^+$. FT-IR (KBr): 3439, 3141, 1606, 1386, 1283, 1201, 1097, 1026, 934, 829, 758, 683, 619, 486 cm^{-1}.

Co-[Salen-Mim][ClO$_4$]^2: Yield: 89%. ICP-MS: Anal. Calcd. for $C_{20}H_{28}Cl_2CoN_6O_{10}$: Co, 9.18%. Found: Co, 9.22%. ESI-MS, m/z = 542.13(M-ClO$_4$)$^+$. FT-IR (KBr): 3540, 3140, 3095, 2964, 1701, 1583, 1544, 1421, 1349, 1278, 1200, 1081, 933, 813, 754, 685 cm^{-1}.

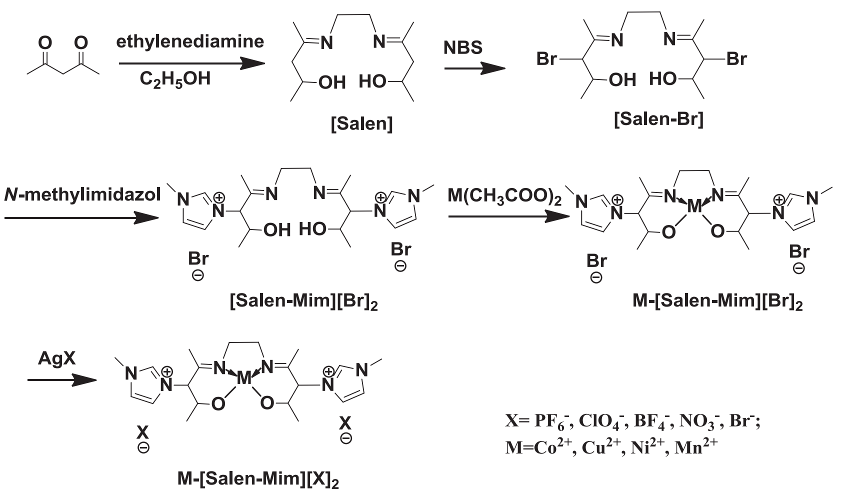
Co-[Salen-Mim][PF$_6$]$_2$: Yield: 96%. ICP-MS: Anal. Calcd. for $C_{20}H_{28}CoF_{12}N_6O_2P_2$: Co, 8.04%. Found: Co, 8.07%. ESI-MS, m/z = 588.12 (M-PF$_6$)$^+$. FT-IR (KBr): 3733, 3161, 1562, 1433, 1276, 1194, 1100, 1029, 935, 831, 750, 699 cm^{-1}.

Density functional theory calculation

The density functional theory was applied at the B3LYP/6-311++G* level. All calculations were performed with the Gaussian03 programs package.[37] All the structures were optimized without any restriction, and the final optimized structures were therefore all at the lowest point when referred to energy. To obtain a further understanding of electronic distribution, natural bond orbital (NBO) analysis was also performed by using the same basis set.

The calculation method of Hammett constants of ionic substituents

Based on the linear relationship between the para Hammett constants *σ* and the natural population analysis (NPA) charge *q* of the para carbon atom of the conventional monosubstituted benzenes ($\sigma = 3.762 + 18.467q$, $R^2 = 0.94$), the Hammett constants of ionic-pair substituents were obtained by calculating the natural population analysis charge *q* of their para carbon atom at the B3LYP/6-311++G* level in the gas phase.[36]



Scheme 1. Synthesis of M-[Salen-Mim][X]$_2$ (X = PF_6^-, ClO_4^-, BF_4^-, NO_3^-, and Br^-; M = Co^{2+}, Cu^{2+}, Ni^{2+}, and Mn^{2+})

Procedure for the oxidation of 4-methyl guaiacol

In a typical reaction, 4-methyl guaiacol (290 mmol), NaOH (957 mmol), ethylene glycol (134.5 ml), water (25 ml) and Co-[Salen-Mim][X]$_2$ (1.38 mmol) were added into a 250 ml four-neck round bottom reactor, which was fitted with an overhead stirrer and a reflux condenser. The reaction temperature was kept constant in water bath. Oxygen was supplied to the reactor from the top using a single glass tube inlet. Timely samples were taken and analyzed on a high-performance liquid chromatography (HPLC) equipped with an ultraviolet detector (λ_{max} = 279 nm) on a 25 cm RP-18 column.

RESULTS AND DISCUSSION

Correlation of Hammett constant with reactivity parameters

Because changing anion is easier than replacing cation from the synthesis viewpoint,[38,39] the anion–cationic substituents have received more attention in the reported works.[8,14,15,17,28,40,41] Among them, quaternary ammonium, pyridinium, or imidazolium were commonly used.[8] For example, the acetyl acetone–Fe catalysts with anion-quaternary ammonium substituents were used in oxidation of methane by our group.[8] A linear relationship was found between the spin density carried by Fe/O atoms (SD_{Fe}/SD_O), or the charge carried by O atom (Q_O), or the isotropic Fermi contact couplings of O atom ($IFCC_O$) in the Fe=O part and the reactivity of the analogous catalysts. Because the C–H activation process undergoes electron transfer, SD_{Fe}/SD_O, Q_O, and $IFCC_O$ are terms of the electronic effect of ionic-pair substituents. We deduce that there should also be a linear relationship between the Hammett constants and the reactivity. The Hammett constants of their anion–cationic substituents on ligand were calculated via the method reported in our previous work,[36] and the reaction barriers (*RB*) were used as the reactivity parameter. Totally 10 different anions (PF_6^-, $AlCl_4^-$, BF_4^-, AsF_6^-, SbF_6^-, AlF_4^-, $CF_3CO_2^-$, $CF_3SO_3^-$, NO_3^-, and Cl^-) were used in our previous work.[8] We chose seven common anions (PF_6^-, $AlCl_4^-$, BF_4^-, AlF_4^-, $CF_3CO_2^-$, $CF_3SO_3^-$, and NO_3^-) for correlation. The reasons are that the bond between ionic-pair substituent $-NH_2(CH_3)X$ ($X = SbF_6$, AsF_6) and matrix moiety was broken during the structure optimization. Besides, the interaction between the mono-atomic anion of ionic-pair substituent in small size (such as Cl^- or Br^-) and central metal atom is direct, while the multi-atomic anion of ionic-pair substituent in large size has an effect on center metal atom indirectly through the direct interaction of ligand. The details of molecular structures are shown in **SI**. Therefore, the multi-atomic anion of ionic-pair substituent in large size is discussed in this paper.

The *RB* of the C–H activation and C–O rebound processes were correlated with the Hammett constants of their anion–cationic substituents on ligand. (Fig. 1) A linear relation can be found between the Hammett constants and the reactivity. The correlation coefficient R^2 is 0.78.

$$RB = -49.96\sigma + 99.76 \qquad R^2 = 0.78 \tag{1}$$

Because all the ionic-pair substituents are electron-withdrawing groups, the formula 1 suggests that the anion–cationic substituents on ligand with larger Hammett constant will make the catalyst more active. This result agrees with that reported in the literature.[8] It suggested that less negative charge carried by the O atom leads to higher reactivity.[8]

The methane C–H activation processes were also chosen to test the reactivity of the metalloporphyrin catalysts with anion-quaternary ammonium substituents in Hu's report.[28] A linear or almost linear relationship can also be found between the Hammett constants and the reactivity (Fig. 2). The correlation coefficient R^2 is 0.96.

$$RB = -81.05\sigma + 133.98 \qquad R^2 = 0.96 \tag{2}$$

The two metal Schiff base catalysts with ionic-pair substituents on the aforementioned ligand were reported in theoretical works.[8,28] The experimental data are also used to correlate the Hammett constants with reactivity. The oxidation of cyclohexene by molecular oxygen in the presence of Cu Salen catalysts with anion–pyridinium substituents was studied by our group.[14] *TOF* was used as the reactivity parameter. The *TOF* values were correlated with the Hammett constants of its anion–cationic substituents on ligand (Fig. 3). A linear relationship can be found between the Hammett constants and the reactivity. The correlation coefficient R^2 is 0.98.

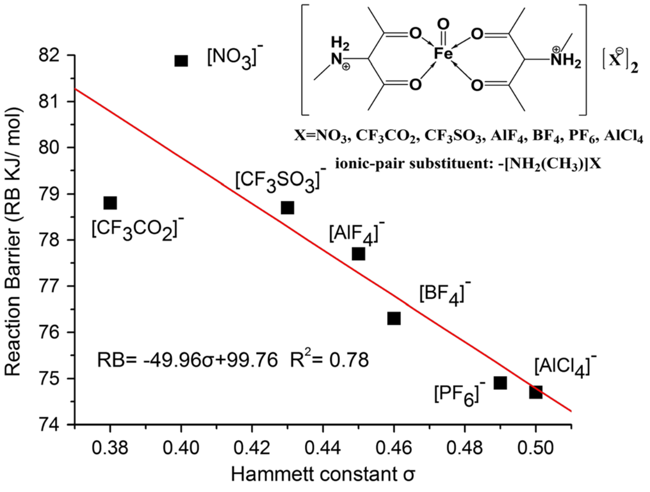


Figure 1. The reaction barrier[a] of the C-H activation process during methane oxidation by the acetyl acetone–Fe catalysts with anion-quaternary ammonium substituents[b] plotted against the Hammett constant σ^c. [a] The reaction barrier data was selected from reference. 8 [b] The multi-atomic anions of ionic-pair substituent in large size were chosen. [c] The Hammett constant were calculated according to reference. 36 *RB*, reaction barriers

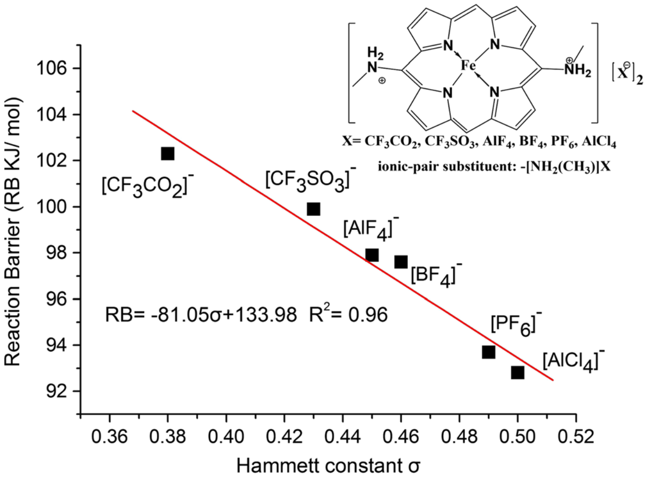


Figure 2. The reaction barrier[a] of the C–H activation process during methane oxidation by the metalloporphyrin catalysts with anion-quaternary ammonium substituents[b] plotted against the Hammett constant σ^c. [a] The reaction barrier data was selected from reference. 28 [b] The multi-atomic anions of ionic-pair substituent in large size were chosen. [c] The Hammett constant were calculated according to reference. 36 *RB*, reaction barriers

$$TOF = 153.41\sigma - 50.84 \qquad R^2 = 0.98 \tag{3}$$

The oxidation of 4-methyl guaiacol to test the metal Schiff base catalysts with imidazolium anion–cationic substituents

To better understand the relativity between the electronic effect and reactivity, the metal Schiff base catalysts with imidazolium anion–cationic substituents on ligand Co-[Salen-Mim][X]$_2$ ($X = PF_6^-$, ClO_4^-, BF_4^-, NO_3^-, and Br^-) were synthesized to investigate the relationship between the Hammett constants of their anion–

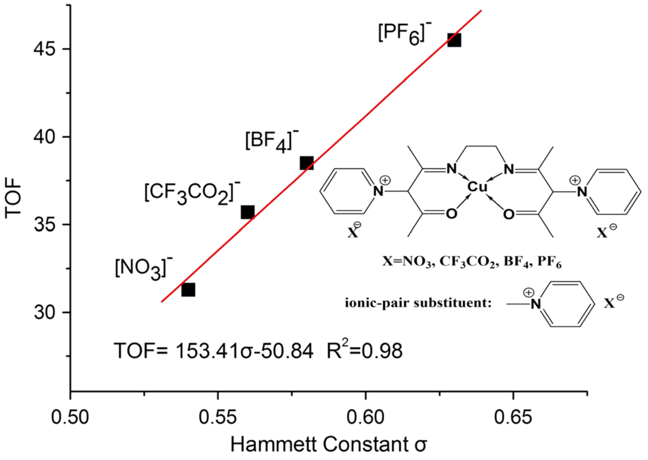


Figure 3. The turnover frequency[a] of the oxidation of cyclohexene by the Cu Salen catalysts with anion–pyridinium substituents[b] plotted against the Hammett constant σ[c]. [a] The turnover frequency was selected from reference. 14 [b] The Hammett constant were calculated according to reference. 36 [c] The multi-atomic anions of ionic-pair substituent in large size were chosen. *TOF*, turnover frequency

Table 1. The results of the oxidation of 4-methyl guaiacol with different catalysts[a]

Entry	Catalyst	Time (h)	Conv. (%)	*TOF* (h^{-1})[b]
1	Co-[Salen-Mim][Br]$_2$	5	53	22.3
2	Co-[Salen-Mim][NO$_3$]$_2$	5	54	22.7
3	Co-[Salen-Mim][BF$_4$]$_2$	5	55	23.1
4	Co-[Salen-Mim][ClO$_4$]$_2$	5	62	26.0
5	Co-[Salen-Mim][PF$_6$]$_2$	5	64	26.9
6	Co-[Salen]	5	45	18.9

TOF, turnover frequency.
[a] Reaction conditions: 4-methyl guaiacol (290 mmol), oxygen flow rate (40 cm^3/min), stirring rate rpm 1000, NaOH (957 mmol), ethylene glycol (150 g), water 25 g, temperature75 °C, and catalyst (1.38 mmol).
[b] *TOF* is calculated by expression of (moles of 4-methyl guaiacol)/[(mole of catalyst)*time (h)].

Table 2. The Hammett constants of the Co-[Salen-Mim][X]$_2$

Entry	Substituent[a]	*TOF*	Hammett constant[b]
1	−[Mim][Br]	22.3	0.25
2	−[Mim][NO$_3$]	22.7	0.14
3	−[Mim][BF$_4$]	23.1	0.36
4	−[Mim][ClO$_4$]	26.0	0.37
5	−[Mim][PF$_6$]	26.9	0.39

TOF, turnover frequency.
[a] [Mim]$^+$: imidazolium [$C_4H_6NN^+$].
[b] The Hammett constant were calculated according to reference.36

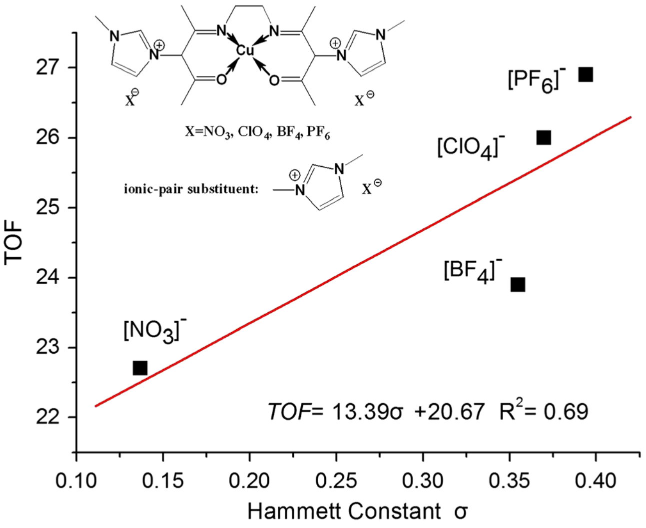


Figure 4. The turnover frequency of the oxidation of 4-methyl guaiacol by the Co Salen catalysts with imidazolium anion–cationic substituents[a] plotted against the Hammett constant σ[b]. [a] The multi-atomic anions of ionic-pair substituent in large size were chosen. [b] The Hammett constant were calculated according to reference.36 TOF, turnover frequency

cationic substituents on ligand and their catalytic activity. In this section, the catalysts Co-[Salen-Mim][X]$_2$ were evaluated in the oxidation of 4-methyl guaiacol to vanillin. According to our previous report on the oxidation of 4-methyl guaiacol, Co metal and the solvent (ethylene glycol/water (V/V) = 85:15) was the better choice for this reaction.[17] As shown in Table 1, it was found that the reactivity of the catalyst Co-[Salen] without substituents was low (Entry 6), in comparison to Co-[Salen-Mim][X]$_2$. The introduction of ionic-pair substituents could improve the reactivity. It was found that the anions have a subtle effect on the catalytic activity (Entry 1–5). The *TOF* value of Co-[Salen-Mim][PF$_6$]$_2$ (26.9) (Entry 5) is the largest among the studied Co-[Salen-Mim][X]$_2$ (Entry1–5). The catalytic activities of the catalysts with different anions follow the order: $PF_6^- > ClO_4^- > BF_4^- > NO_3^- > Br^-$. It is shown that the reactivity of Co-[Salen-Mim][X]$_2$ is increased with increasing of the Hammett constant of its substituent. However, the mono-atomic anion Br^- is an exception to this rule. The Hammett constants of their anion–cationic substituents on ligand and the *TOF* values are collected in Table 2. We chose the multi-atomic anions (PF_6^-, ClO_4^-, BF_4^-, and NO_3^-) for correlation. The correlation between *TOF* and the Hammett constants in Fig. 4 suggests that there is a linear relationship as follows:

$$TOF = 13.39\sigma + 20.67 \qquad R^2 = 0.69 \qquad (4)$$

CONCLUDING REMARKS

As far as we know, despite that they are important in designing and improving the catalysts, few Hammett constants of ionic-pair substituents were reported in literatures. In this paper, the Hammett constants of their anion–cationic substituents on ligand were calculated via the method reported in our previous works,[36] then we explored the relationship between the parameters of the reactivity (such as reaction barrier or TOF) of metal Schiff base catalysts and the Hammett constants of their anion–cationic substituents on ligand. The anion–cationic substituents often contain quaternary ammonium, pyridinium, or imidazolium cations.[8] Based on the analysis on the previous theoretical and experimental works, it was found that the reactivity was correlated with the Hammett constants of their quaternary ammonium or pyridinium anion–cationic substituents with multi-atomic anions in large size on ligand linearly. To better understand the relativity between the electronic effect and reactivity, we synthesized metal Schiff base catalysts with imidazolium anion–cationic substituents on ligand Co-[Salen-Mim][X]$_2$ (X = PF_6^-, ClO_4^-, BF_4^-, NO_3^-, and Br^-), and calculated the Hammett constants of their anion–cationic substituents on ligand. The oxidation of 4-methyl guaiacol was then carried out to investigate the electronic effect of these anion–cationic substituents on the catalytic activities of catalysts. The results show that a linear relativity also exists between the Hammett constants of the anion–cationic substituents with multi-atomic anions and their reactivity. The quantitative electronic effect and reactivity relationships proposed in the present study are expected to be useful in designing a more powerful catalyst with anion–cationic substituents with multi-atomic anions in large size on ligand.

Acknowledgements

This work was supported by the Program for Zhejiang Leading Team of S&T Innovation (2011R50007), and the Fundamental Research Funds of the Central Universities.

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