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Factors Enhancing the Reactivity of Carbonyl Compounds for Polycondensations with Aromatic Hydrocarbons. A Computational Study

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ABSTRACT: For the first time, reactions of acetophenone, 2,2,2-trifluoroacetophenone, fluorenone, and dinitrofluorenones with diphenyl and 4,4′-diphenoxybenzophenone in trifluoromethanesulfonic acid (TFSA) have been studied theoretically at the B3LYP/cc-pvtz(-f)//B3LYP/6-31G* level of theory as a model reaction for a superelectrophile involving polycondensation. It was found that the introduction of electron-withdrawing groups into the carbonyl compound reduces activation and total reaction energies of the aromatic electrophilic substitution reaction. The enhancement of the reactivity of carbonyl compounds bearing electron-withdrawing groups is due to lowering of LUMO energy. The electrophiles having highly delocalized LUMO are less active in the reaction of electrophilic aromatic substitution due to decreases of local LUMO density at the reaction center. General rules for the design of reactive monomer are formulated on the basis of calculational results.

1. Introduction

Friedel−Crafts aromatic substitution reactions − alkylation and acylation − are some of the most fundamental reactions in organic chemistry and have been widely (first mainly via polyalkylation reactions, later via polyacylation as well) explored in polymer chemistry.[1,2]

Cheaply available monomers and the promising properties of the polymers that might be obtained have greatly stimulated interest in that field.

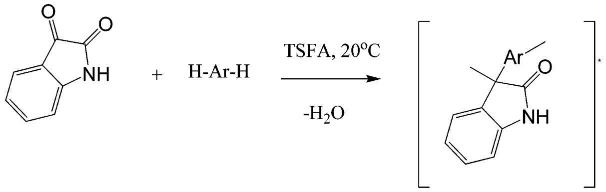
For a long time, however, polymer-forming Friedel−Crafts reactions were considered not to be regioselective. Indeed, such aromatic substitution reactions as alkylation and acylation basically lead to formation of isomer mixtures.

Nevertheless, over the last few decades, many linear, high molecular weight Friedel−Crafts polymers have been reported, and commercial technologies have been developed for some of them, such as the polyhydroxyarylene alkylene "Xylox", and the aromatic polyketones "Stilan", "Ultrapek", and "Declar".[3]

It is important to mention that, so far, only traditional types of electrophiles have been used in Friedel−Crafts polymer preparations. Obviously, the design of monomers bearing new types of electrophilic functional groups is of great importance for the advancement of Friedel−Crafts polymer chemistry.

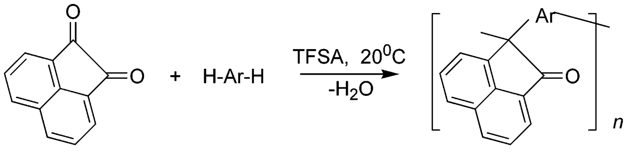
In this respect, the theory of superelectrophilic activation, suggested by G. A. Olah to explain the high reactivity of some electrophiles in superacid solutions, presents a promising challenge.[4] Superelectrophiles have since been proposed or studied in numerous superacid-catalyzed reactions.[4−7]

Recently, we reported the first application of superelectrophilic chemistry for polymer preparation, having synthesized new linear polymers − poly(arylene oxindole)s by reaction of isatine, containing 1,2-dicarbonyl groups as a part of the N-containing heterocycle, with aromatic hydrocarbons.[8]



It is believed that diprotonation of 1,2-dicarbonyl groups of isatin in a superacid medium generates a highly reactive electrophilic species.[7,9] After that, the superelectrophile-based approach was used successfully for the synthesis of hyperbranched poly(arylene oxindole)s.[10]

It has also been shown that cyclic diketones, containing 1,2-dicarbonyl groups, such as acenaphthenequinone, react with aromatic hydrocarbons (biphenyl, fluorene, phenyl ether, etc.) in superacid medium to give poly(arylene acenaphthenone)s.[11]



The simple, one-pot preparation method and properties of the polymers thus synthesized are very promising, clearly showing that polymer forming reactions, involving monocarbonyl compounds, would be of great importance.

Very recently, we found that condensations of carbonyl compounds containing adjacent or relatively close to a carbocation center electron-withdrawing substituents with nonactivated aromatic hydrocarbons, carried out in such a superacid system as TFSA at room temperature, afford linear, high-molecular-weight polymers.[12] For example, 2,2,2-trifluoroacetophenone reacts even with biphenyl under these conditions to give a high-molecular-weight film-forming polymer:

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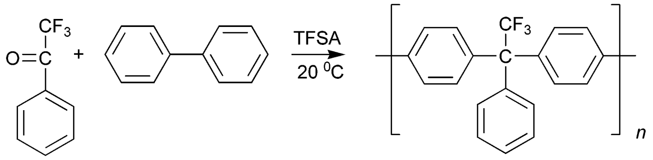


This is the first example of a Friedel–Crafts polycondensation using unsubstituted biphenyl as a comonomer. It is noteworthy that simple one-pot synthesis affords new polymers with promising properties.

Thus, the presence of electron-withdrawing groups in the carbonyl fragment is essential for the polycondensation to occur. Obviously, the clarification of the effect of the substituents would be of great significance for both superelectrophile organic and polymer chemistry.

The aim of the present work is to study effect of the electron-withdrawing groups on the reactivity of carbonyl compounds in the course of condensation with aromatic hydrocarbons in TSFA medium using quantum chemistry tools on real systems taking advantage of fast Jaguar code,[13] allowing one to treat large molecules at a reasonable time.

2. Computational Details

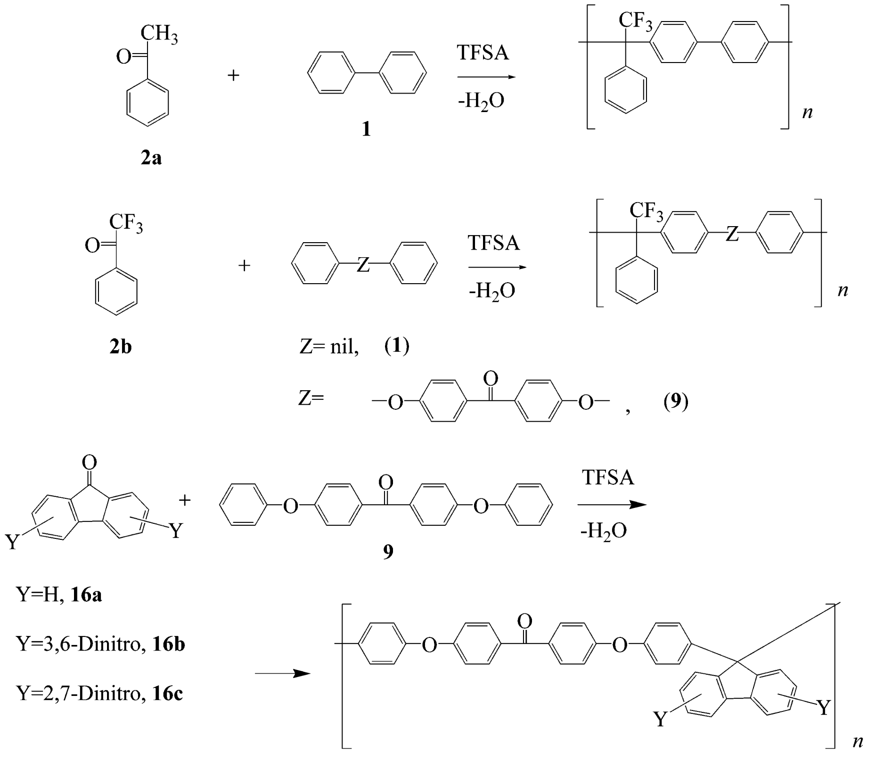
All calculations were carried out with the Jaguar v 5.0 program.[13] The geometry optimizations were run using the hybrid B3LYP functional without any symmetry restrictions at the B3LYP/6-31G* level of theory which is successful for the modeling of organic molecules.[14] Frequency calculations were run for transition state structures to make sure that a transition state (one imaginary mode) is located. Poisson–Boltzmann solver[15,16] implemented in Jaguar v 5.0 was used to calculate the solvation effects on the studied molecules in TFSA at the B3LYP/aug-cc-PVTZ(-f) level of theory. In other words, the structures have not been reoptimized in the presence of solvent since it has been shown previously that reoptimization has a very limited effect on the computed energies.[17–21] Because the present study is based on a comparison between series of similar reactions, total electronic energies can be used instead of free Gibbs energies, thus saving computational efforts. The calculations of local Fukui functions were carried out according to ref 22, assuming that the basis set is orthonormal.

3. Results and Discussion

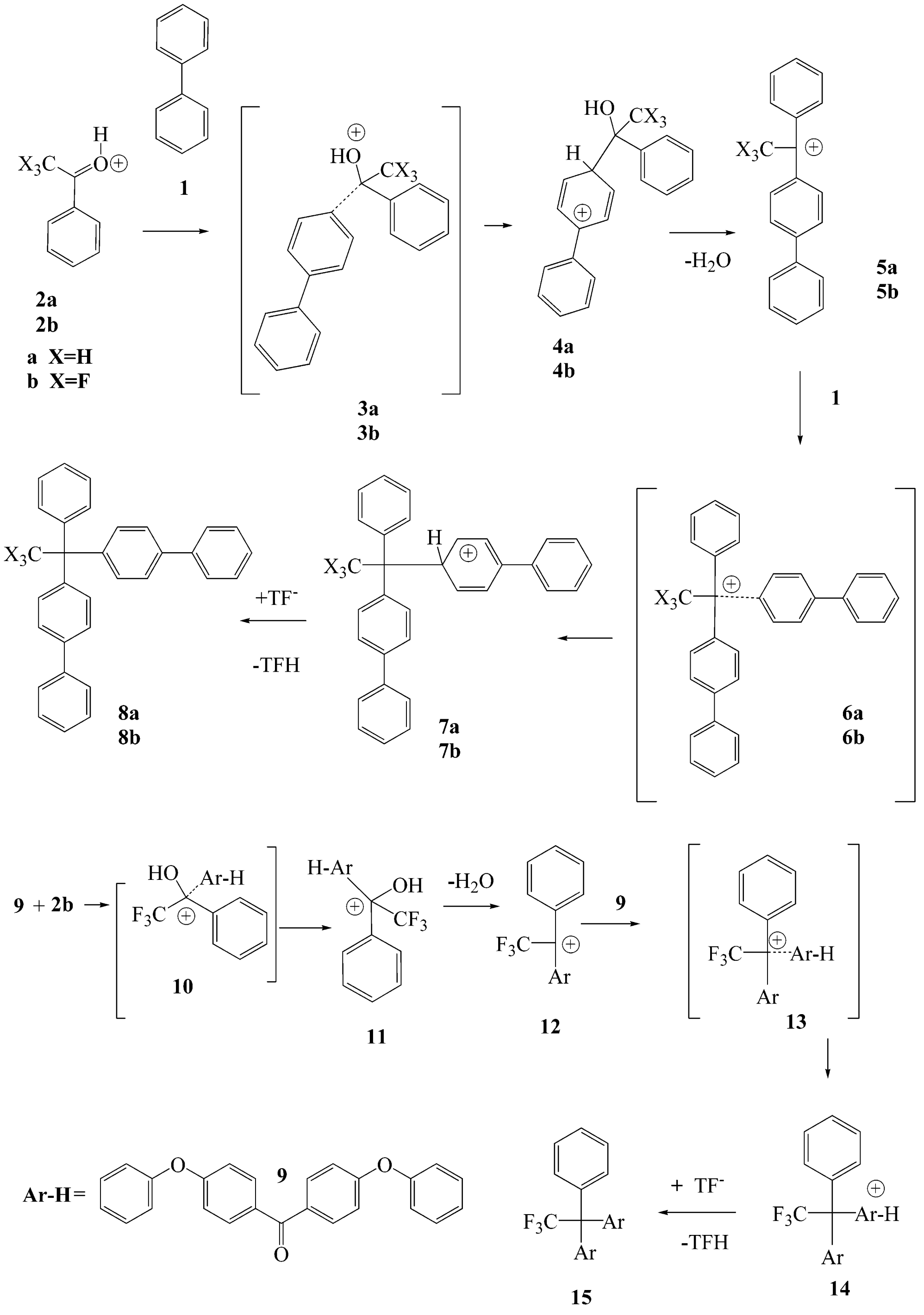
Scheme 1 shows the reaction paths to the synthesized polymers,[12] while Schemes 2 and 3 depict the elemental steps for TFSA-catalyzed polycondensation reactions of different carbonyl-containing molecules with aromatic molecules. It has been shown[23] that under superacid conditions diprotonated species are responsible for the unusually high reactivity carbonyl molecules toward some of the aromatic hydrocarbons. Therefore, it seems that diprotonated carbonyl species are of importance for the reaction being considered. However, experimental data show[12] that it is the presence of the electron-withdrawing group attached to the carbonyl fragment that makes the polycondensation possible. Therefore, diprotonation could hardly have to do with the acceleration of the polycondensation reaction because electron-withdrawing groups reduce the protonation equilibrium constant, and, therefore, the monoprotonated carbonyl component was considered to be the correct approximation for the electrophilic species participating in the polycondensation.

The reaction of aromatic electrophilic substitution has been the subject of intensive theoretical studies.[24–26] It is well established that the reaction steps involve the complex formation between the electrophile and aromatic hydrocarbon which is transformed to the σ intermediate. The σ intermediate loses a proton to recover the aromaticity. It is suggested that the rate-determining step is the formation of the σ intermedi-

Scheme 1. General Scheme of the Studied Polycondensation Reaction



Scheme 2. Mechanism of Polycondensation (Part 1)



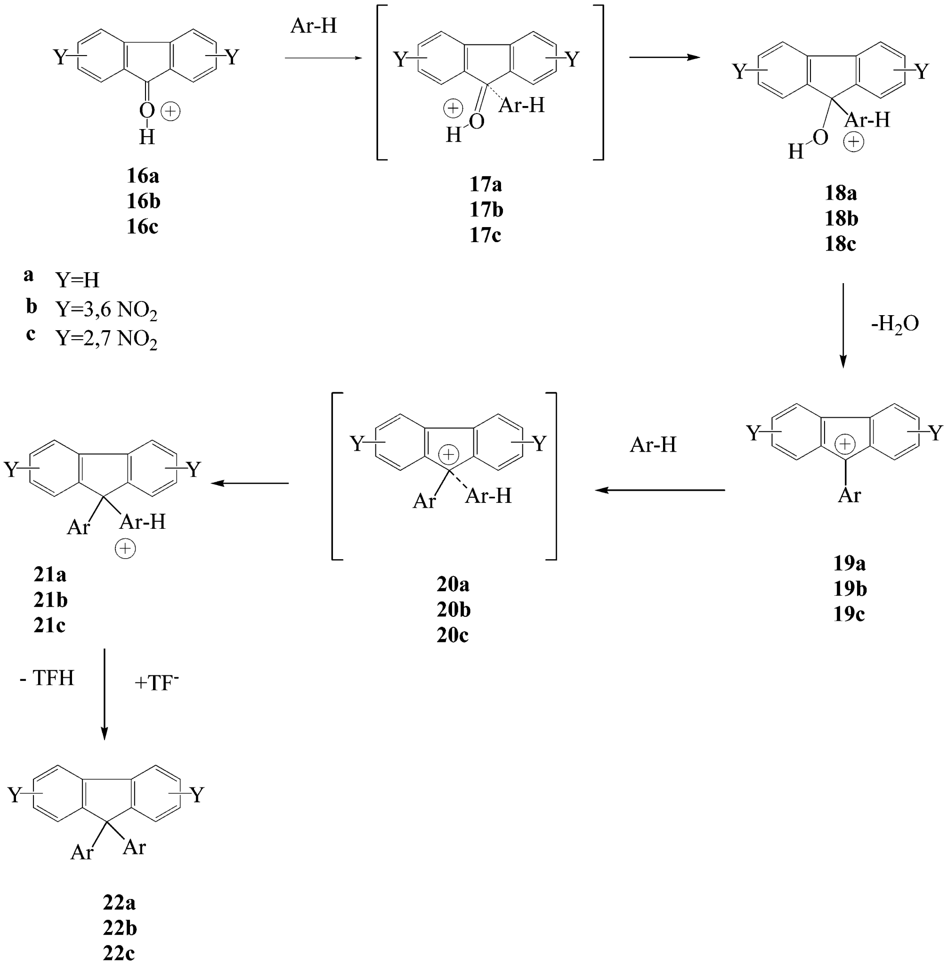
ate;[27] therefore, the transition state search was carried out only for the formation of σ intermediate to save computational time. The π-adduct formation previous to the formation of the σ intermediate was not taken into account for the following reasons:

(1) The formation of weak complexes is governed by dispersion interactions which are described incorrectly by modern DFT theory.[28] The high level theories correctly describing dispersion interactions are prohibitive due to the size of the treated molecules.

(2) The available calculated binding energies for π-adducts for the reaction of proton exchange and methylation of benzene do not exceed 4 kcal/mol.[26] Moreover, when comparing the difference of the activation energies, the formation of π-adducts will be affecting the energies even less due to the partial compensation effect.

Tables 1 and 2 show the total and solvation energies of the studied intermediates and reaction energies, respectively. The corresponding reaction energy profiles are shown in Figures 1 and 2. The effect of electron-withdrawing groups is clearly seen on the reaction energy profile. As seen from Table 2 in the case of **2a** and **2b**, there is a marked difference in both the activation energies and the total reaction energies. The presence of the CF_3 group in case of the reaction of ketones with diphenyl makes the formation of the first σ intermediate (**4b**) exothermic in the gas phase, while the formation of the corresponding intermediate for **2a** is an endothermic process. It is noteworthy that no

Scheme 3. Mechanism of Polycondensation (Part 2)



transition state was detected for the reaction **2a** + **1** = **4a**, while the activation energy of reaction **II** (Table 2) was determined as 1.68 kcal/mol in the gas phase. When solvation is taken into account, the formation of σ intermediate becomes less favorable, still maintaining the preference for reaction **II**. The elimination of water molecules (reactions **III** and **IV**) is exothermic for both intermediates **4a** and **4b**. Reaction **III** is less favorable

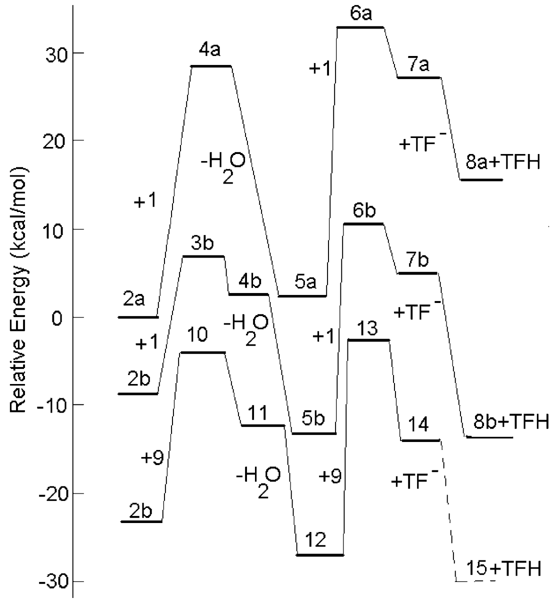


Figure 1. Energy profile for the polycondensation reaction involving acetophenone electrophiles. The solvation energy of the **14** + **TF**$^-$ = **15** + **TFH** reaction was estimated approximately (dotted line).

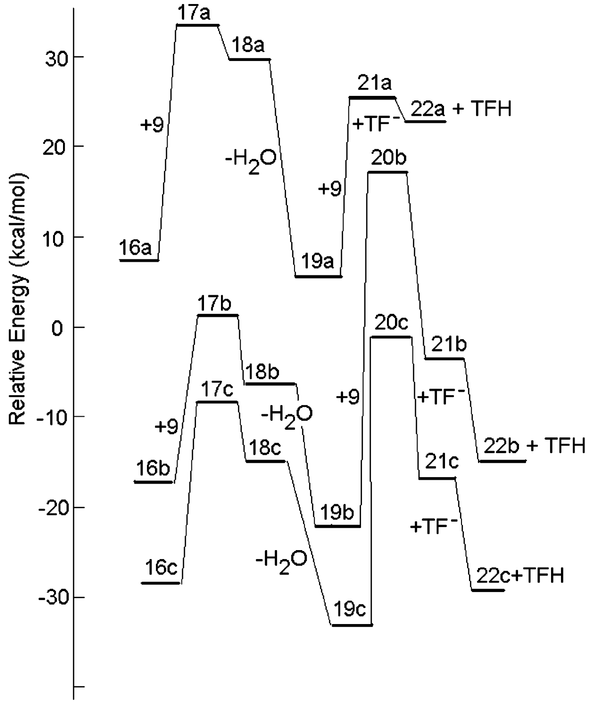


Figure 2. Energy profile for the polycondensation reaction involving fluorenone electrophiles.

Table 1. Total Electronic and Solvation Energies of the Studied Molecules Calculated at B3LYP/6-31G* Optimized Geometry[a]

molecule	B3LYP/6-31G*	B3LYP/aug-cc-pvtz(-f)	E_{solv}
1	−463.305328	−463.450233	−0.008106
2a	−385.240610	−385.368595	−0.090552
2b	−682.929460	−683.174383	−0.087108
3b	−1146.238962	−1146.621940	−0.073053
4a	−848.530770	−848.797287	−0.074735
4b	−1146.242366	−1146.625521	−0.076436
5a	−772.138838	−772.366189	−0.069648
5b	−1069.834918	−1070.179852	−0.069308
6a	−1235.409876	−1235.775621	−0.069811
6b	−1533.120096	−1533.602400	−0.067211
7a	−1235.415424	−1235.781672	−0.072881
7b	−1533.122019	−1533.604062	−0.074415
8a	−1235.077890	−1235.451788	−0.017168
8b	−1532.798291	−1533.288399	−0.015615
9	−1189.161836	−1189.537866	−0.023182
10	−1872.087349	−1872.702687	−0.089225
11	−1872.104447	−1872.718120	−0.086995
12	−1795.694209	−1796.270829	−0.079605
13	−2984.837624	−2985.781228	−0.091153
14	−2984.848769	−2985.793517	−0.097239
15	−2984.509478	−2985.460262	
16a	−575.785565	−575.961064	−0.083167
16b	−984.749052	−985.069737	−0.112107
16c	−984.752883	−985.073561	−0.112888
17a	−1764.932188	−1765.478579	−0.085067
17b	−2173.910380	−2174.601848	−0.111625
17c	−2173.914420	−2174.607099	−0.108406
18a	−1764.936146	−1765.483484	−0.086433
18b	−2173.919261	−2174.610730	−0.114742
18c	−2173.924696	−2174.616603	−0.109344
19a	−1688.546073	−1689.052380	−0.077741
19b	−2097.517028	−2098.168179	−0.104503
19c	−2097.523105	−2098.175540	−0.101429
20b	−3286.642971	−3287.661936	−0.109177
20c	−3286.664264	−3287.684015	−0.102776
21a	−2877.683479	−2878.561467	−0.097978
21b	−3286.667313	−3287.686703	−0.117423
21c	−3286.674717	−3287.695947	−0.116197
22a	−2877.336333	2878.216861	−0.042982
22b	−3286.336615	3287.361636	−0.056625
22c	−3286.338550	−3287.367468	−0.060300
TF^-	−1036.744484	−1037.071109	−0.085773
TFH	−1037.231674	−1037.549181	−0.011768
H_2O	−76.408933	−76.464481	−0.013544

[a] Total and solvation energies were calculated at the B3LYP/aug-cc-pvtz(-f) level of theory (E_{solv}) in au.

Table 2. Reaction and Activation Energies (kcal/mol) Calculated at the B3LYP/Aug-cc-pvtz(-f)//B3LYP/6-31G* Level of Theory in the Gas Phase (ΔE, E_a) and in TFSA Solution (ΔE_s, E_{as})

run	reactions	ΔE_{gs}	E_a	ΔE_s	E_{as}
I	$1 + 2a = 4a$	13.52		28.53	
II	$1 + 2b = [3] = 4b$	−0.57	1.68	11.21	15.58
III	$4a = 5a + H_2O$	−20.95		−26.26	
IV	$4b = 5b + H_2O$	−11.80		−15.83	
V	$1 + 5a = [6a] = 7a$	21.81	25.60	24.86	30.59
VI	$1 + 5b = [6b] = 7b$	16.33	17.37	18.21	23.77
VII	$7a + TF^- = 8a + TFH$	−92.99		−11.59	
VIII	$7b + TF^- = 8b + TFH$	−101.91		−18.58	
IX	$9 + 2b = [10] = 11$	−3.68	6.00	10.93	19.22
X	$11 = 12 + H_2O$	−10.79		−14.65	
XI	$9 + 12 = [13] = 14$	9.52	17.24	13.01	24.54
XII	14+TF-=15+ TFH	−90.87			
XIII	$9 + 16a = [17a] = 18a$	9.69	12.77	22.19	26.13
XIV	$9 + 16b = [17b] = 18b$	−1.96	3.61	10.93	18.46
XV	$9 + 16c = [17c] = 18c$	−3.25	2.72	13.52	20.07
XVI	$18a = 19a + H_2O$	−20.94		−23.99	
XVII	$18b = 19b + H_2O$	−13.76		−15.84	
XVIII	$18c = 19c + H_2O$	−14.69		−18.23	
XIX	$9 + 19a = 21a$	18.06		19.91	
XX	$9 + 19b = [20b] = 21b$	12.14	27.68	18.58	39.29
XXI	$9 + 19c = [20c] = 21c$	11.00	18.40	16.30	32.10
XXII	$21a + TF^- = 22a + TFH$	−83.75		−2.80	
XXIII	$21b + TF^- = 22b + TFH$	−96.01		−11.42	
XXIV	$21c + TF^- = 22c + TFH$	−93.90		−12.40	

Table 3. Local Fukui Functions (f^+) and HOMO and LUMO Energies Calculated at the HF/cc-pvtz(-f)//B3LYP/6-31G* Level (au)

molecule	E_{HOMO}	E_{LUMO}	f^{+a}
1	−0.30082	0.05486	
2a	−0.50336	−0.14421	0.348
2b	−0.52328	−0.17669	0.327
5a	−0.41795	−0.14452	0.286
5b	−0.42943	−0.16956	0.260
9	−0.31851	0.04903	
12	−0.38178	−0.15981	0.287
16a	−0.45386	−0.16122	0.245
16b	−0.49096	−0.20666	0.223
16c	−0.50173	−0.1958	0.228
19a	−0.3746	−0.15474	0.237
19b	−0.37008	−0.19142	0.210
19c	−0.37686	−0.17914	0.216

[a] $\sum C_i^2$, where C_i are the coefficients of basis functions localized on the bond-forming atom which contribute to LUMO calculated at the HF/cc-pvtz(-f)//B3LYP/6-31G* level of theory.

due to the presence of the electron-withdrawing group destabilizing carbocation **5b** with respect to **5a**. The second step of the condensation (reactions **V** and **VI**) represents the electrophilic attack of carbocations **5a** and **5b** at second molecule of diphenyl. The second step is notoriously more difficult than the first. In both cases, the formation of the σ intermediate is less favorable kinetically and thermodynamically; however, similar to the first step, the presence of a CF_3 group decreases both the activation energy and the total reaction energy. The last step of the reaction sequence is deprotonation of the σ intermediates **7a** and **7b** by triflate anion to give stable derivatives **8a** and **8b**. These reactions are exothermic both in the gas phase and in solution, and complex **8b** is a stronger acid due to the presence of the trifluoromethyl group.

The estimation of the reactivity of the activated carbonyl compound **2b** toward the other donor molecule **9** also has been carried out for the purpose of comparison. As seen from Table 2 and Figure 1, the reaction profile of the reaction **2b** + **9** is very similar to that calculated for **2b** + **1**. Unfortunately, it was impossible to estimate the solvation energies for molecule **15** due to technical problems; however, it seems reasonable to suggest that this energy is similar to other neutral molecules such as **8a** and **8b**.

The introduction of nitro groups into the fluorenone moiety provokes a similar effect on the reaction energetic. As seen from Table 2 and Figure 2 (molecules **16a**, **16b**, and **16c**), the introduction of nitro groups in positions 3,6 and 2,7 of the fluorenone moiety result in similar changes in the reaction energies profile. The formation of the first σ intermediate (reactions **XIII**, **XIV**, **XV**, Table 2) is strongly facilitated in the presence of the nitro group independent of their position in the ring. Similar to the CF_3 group, nitro groups destabilize carbocations **19b** and **19c** as compared to **19a** as follows from the comparison of the reaction energetic (reactions **XVI**, **XVII**, and **XVIII**, Table 2). The second reaction step is less favorable in all cases. However, similar to the CF_3 group in kenone **2b**, the presence of nitro groups in fluorenone decreases the activation and reaction energies of the second substitution step (Table 2, Figure 2).

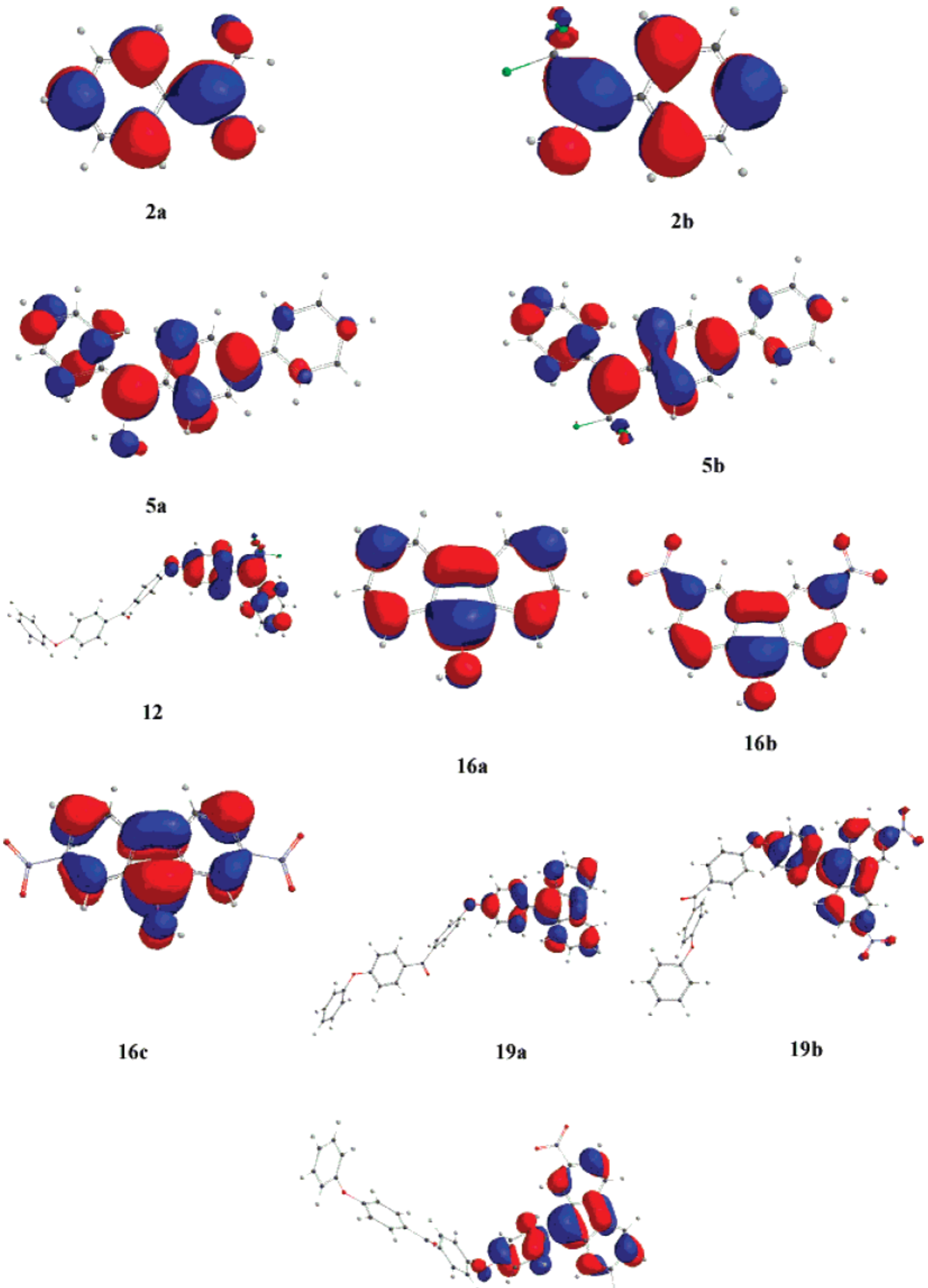

2a 2b 5a 5b 12 16a 16b 16c 19a 19b 19c

Figure 3. LUMO of the electrophilic species calculated at the HF/cc-pvtz(-f)//B3LYP/6-31G* level.

There are no available experimental data on the reactivity of 3,6-dinitrofluorenone. However, according to calculational data, the reactivity of 3,6-dinitrofluorenone and 2,7-dinitrofluorenone must be very close. This fact is rather surprising, because 3,6-dinitrofluorenone has nitro groups para to carbonyl, thus enhancing the electrophilicity of the carbonyl group. To understand the electronic factors which are responsible for the enhancement of reactivity of carbonyl compounds on the introduction of electron-withdrawing groups, the hard soft acids bases (HSAB) principal can be applied.[29] The interaction between soft acids and bases (where a soft acid is the cation and a soft base is the aromatic hydrocarbon) is orbital controlled. Table 3 shows the energies of HOMO and LUMO Hartree−Fock orbitals of the reaction intermediates calculated at the HF/cc-pvtz(-f)//B3LYP/6-31G* level of theory. The interaction between an electrophile (carbonyl compound) and a nucleophile can be represented as the interaction of the LUMO and HOMO of the electrophile and nucleophile, respectively. Thus, the smaller is the energy difference between the LUMO of the electrophile and the HOMO of the nucleophile, the lower is the activation energies and the total energy difference of the reactions; in other

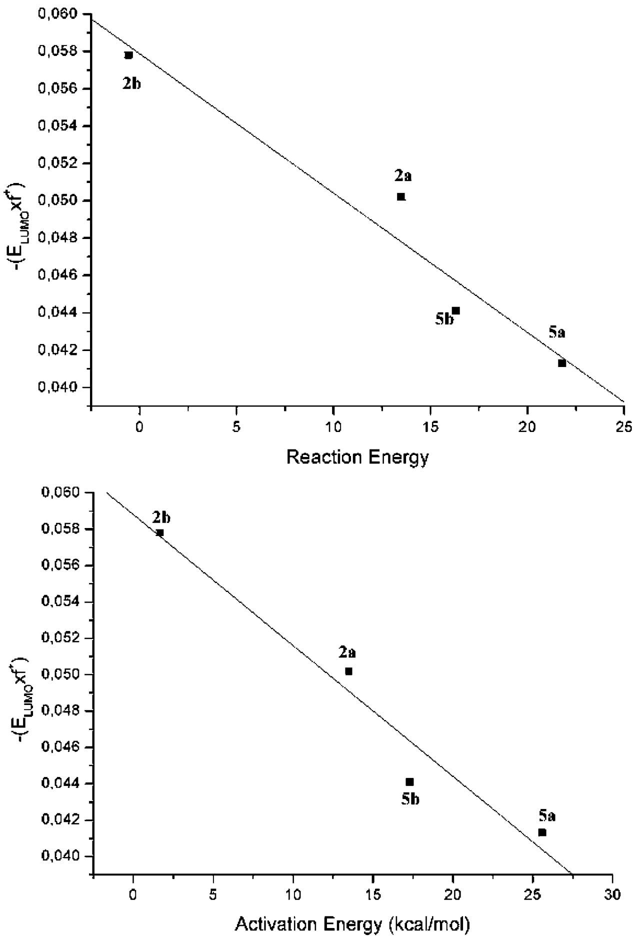


Figure 4. Correlation between reaction and activation energies and $-(E_{\mathrm{LUMO}} \times f^{+})$ values of cationic species for the reactions with biphenyl (Table 3).

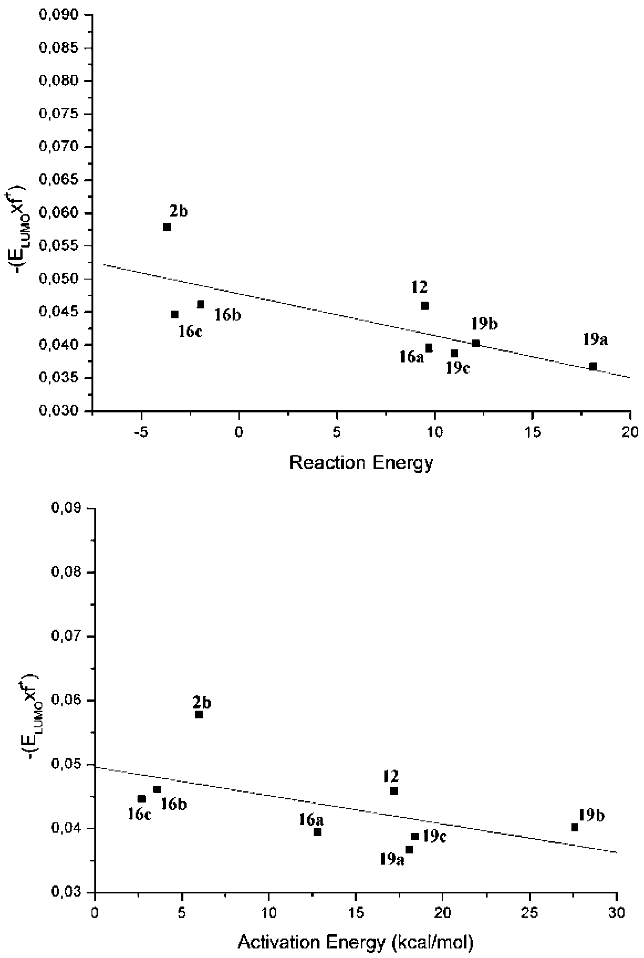


Figure 5. Correlation between reaction and activation energies and $-(E_{\mathrm{LUMO}} \times f^{+})$ values of cationic species for the reactions with molecule **9** (Table 3).

words, the reaction is favored kinetically and thermodynamically. As seen from Table 3, the introduction of electron-withdrawing groups in carbonyl compounds decreases the LUMO energy of the electrophile (**2a** and **2b**, **5a** and **5b**, **16a**, **16b**, and **16c**, **19a**, **19b**, and **19c**). There is a clear correlation between the reactivity of the above-mentioned compounds and the LUMO energy. From this point of view, it is easy to understand the similar reactivity of the molecules **16b** and **16c** despite the different positions of the nitro groups because the energies of the LUMO for these two molecules are very much the same.

As seen from the reaction energy profiles (Figures 1 and 2), the second substitution is more difficult than the first one (higher activation energies and total reaction energies). As seen from Table 3, the electrophilic species that participate in the second substitution step have higher LUMO energies as compared to those of electrophiles participating in the first step, with one exception, the **2a**, **5a** pair, in accordance with HASB theory considering that reactive intermediates participating in polycondensation are soft acids and bases.

However, the orbital energy characterizes the entire molecule, while the electron density distribution in molecules is not generally uniform. To monitor the reactivity of the reaction sites in electrophilic intermediates, the local quantities such as local Fukui functions were calculated. The calculated local Fukui functions has a physical meaning of virtual electron density at the LUMO on the bond-forming atoms of electrophilic intermediates and represents a measure of the electrophilicity of the atomic center. As seen from Table 3, the electrophiles participating in the second substitution step always have lower local Fukui function values as compared to those participating in the first step. Therefore, all other things being equal, the electrophilicity of the bond-forming carbon decreases for the second substitution step. This effect can be understood in terms of higher delocalization of the LUMO for these electrophiles, thus decreasing the LUMO amplitude on the reaction center, which is seen from Figure 3. On the other hand, the local Fukui functions at bond-forming atoms for **2a**, **5a**, and **16a**,**b** are higher as compared to those for **2b**, **5b**, and **16b**,**c**, meaning that the reactivity of the studied electrophiles is defined primarily by the LUMO energy and the local Fukui functions are of secondary importance.

This conclusion can be quantified by using a parameter that takes into account two of these factors at the same time. Thus, the $-(E_{\mathrm{LUMO}} \times f^{+})$ value satisfies this requirement. Figures 4 and 5 show a correlation between the $-(E_{\mathrm{LUMO}} \times f^{+})$ parameter and the activation and reaction energies for the reactions of cationic species with biphenyl and molecule **9**, respectively. As seen from Figure 4, there is a very good correlation between the reactivity and $-(E_{\mathrm{LUMO}} \times f^{+})$ parameter in the reaction with biphenyl. Cation **2b** is the most active electrophile, while the less active is **5a**. In the case of the reactions with molecule **9**, the best electrophile is **2b** and the

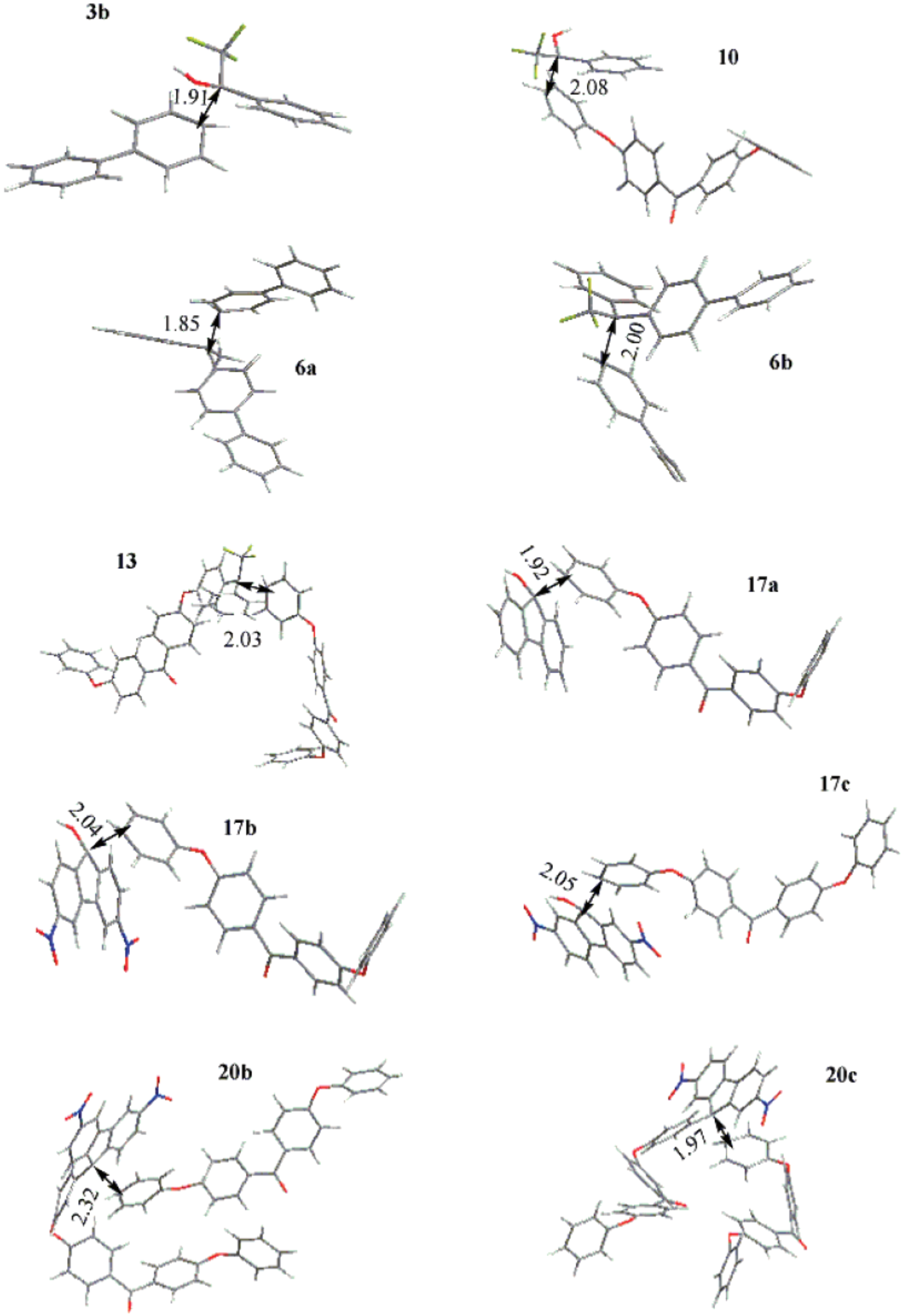


Figure 6. Geometries of located transition states optimized at the B3LYP/6-31G* level.

worst is **19a**. In this case, the correlation is not as good as for biphenyl-involved reactions, but still remains valid. Thus, the $-(E_{\mathrm{LUMO}} \times f^{+})$ parameter can be very useful for quick estimation of the reactivity of electrophiles in the reactions of aromatic electrophilic substitutions.

Figure 6 shows the optimized geometries of the located transition states, in accordance with the Hammond postulate:[30] reactions which are more favorable thermodynamically (Table 2) show early transition states, while those less favorable show late ones. Because polycondensation reactions are strongly affected by steric factor, the incorporation of electron-withdrawing groups into carbonyl compounds will additionally reduce the reaction activation energies due to looser transition states reducing steric hindrances in the transition state.

4. Conclusions

The first computational study of the reactivity of carbonyl compounds in superelectrophile-involved polycondensation allows one to make conclusions important for the reactivity tuning of carbonyl-containing monomer in the Friedel−Crafts-type polycondensation.

The reactivity enhancement of carbonyl-containing monomers on the introduction of electron-withdrawing groups is due to reduction of LUMO energy. Carbonyl compounds bearing electron-withdrawing groups show early transition state in accordance with the Hammond postulate;[30] therefore, steric factor is less important for highly reactive monomers due to the loose structure of the transition states.

All other things being equal, the electrophiles having highly delocalized LUMOs are less active in the reaction of electrophilic aromatic substitution due to a decrease of the local LUMO amplitude at the reaction center. This statement can be quantified by introducing the $-(E_{\mathrm{LUMO}} \times f^{+})$ parameter as a measure of the reactivity of the cationic species in the studied reactions.

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