ORIGINAL PAPER

Mechanisms on inhibition of polyethylene electrical tree aging: a theoretical study

Hui Zhang · Yan Shang · Hong Zhao · Baozhong Han · Zesheng Li

Abstract A theoretical investigation is completed on inhibition mechanism of polyethylene electrical tree aging. Foremost it elucidates that it is one of the important factors for inhibiting initiation and propagation of polyethylene electrical tree through keto-enol tautomerism of acetophenone and its analogues. Geometries of the keto tautomer and the enol tautomer of acetophenone and its analogues, and its transition states are optimized at the B3LYP/6−311+G(d,p) level, the harmonic vibration frequencies of the equilibrium geometries are calculated at the same level. The minimum energy path (MEP) is obtained by the intrinsic reaction coordinate (IRC) theory at the same level. The calculated results show that the energy barriers of keto-enol tautomerism of acetophenone and its analogues are smaller than the average C—C bond energy of polyethylene, the acetophenone and its analogues adulterated in polyethylene composites can improve the strength of alternate current puncture that PE can endure as well as inhibit polyethylene electrical tree from initiation and propagation.

Keywords Acetophenone · Keto-enol tautomerism · Polyethylene · Transition state

H. Zhang (✉)
Key Laboratory of Engineering Dielectrics and Its Application, Ministry of Education & College of Chemical and Environmental Engineering, Harbin University of Science and Technology, Harbin 150080, People's Republic of China
e-mail: hust_zhanghui11@hotmail.com

Z. Li (✉)
Key Laboratory of Cluster Science of Ministry of Education & School of Chemistry, Beijing Institute of Technology, Beijing 100081, People's Republic of China
e-mail: zeshengli@hit.edu.cn

H. Zhao · B. Han (✉)
Key Laboratory of Engineering Dielectrics and Its Application, Ministry of Education, Harbin University of Science and Technology, Harbin 150080, People's Republic of China
e-mail: hbzhlj@163.com

Y. Shang
College of Chemical and Environmental Engineering, Harbin 150080, People's Republic of China

Introduction

Cross-linked polyethylene (XLPE) insulation cable has many advantages such as excellent electrical properties, high transmission capacity, and easy installation and maintenance. Since XLPE insulation cable was developed in 1959, its usage amount increases year after year. Especially over the last two decades, the voltage class of XLPE insulation cable has risen. Currently, XLPE is often used as insulation in high-voltage cable of up to 220 kV. Some XLPE insulation cable of 500 kV has also been used in extra high-voltage line [1]. During the application of high-voltage cable, it was found that the electrical tree aging is a leading factor to degradation and failure of XLPE insulation behavior of high-voltage cable. Therefore, the inhibition of electrical tree initiation and propagation inside the high-voltage XLPE cable has received more and more attention in recent years [2–5].

Since the 1960s, researchers have begun to use additives to improve the resistance capability of polyethylene to electrical tree [6–9]. For example, Tu et al. proved that the initial voltage of electrical tree of polythene (PE) was raised by as

much as 2–4 times by adding the voltage stabilizer in the 1980s. This is because the voltage stabilizer increases the high-field conduction through field-assisted dissociation and ionization, thus effectively homogenizing the electrical field distribution of defect inside PE and preventing the local high electrical field [10]. In 2009, Yamono et al. stated that addition of polycyclic aromatic hydrocarbons can improve the initial voltage of electrical tree and inhibit the electrical tree initiation, which is relative to the type of polycyclic aromatic hydrocarbons [11]. They considered that the π-bond absorbs the energy of moving electron, thus preventing the polymer molecule chain fracture caused by electron bombardment. This contributes to the acting mechanism of polycyclic aromatic hydrocarbons. In the same year, Englund et al. fabricated a new voltage stabilizer by grafting octane on four types of polycyclic aromatic hydrocarbons, and then dispersed them into high-voltage XLPE insulation cable fabricated by Northern Europe Chemical Company through the penetration method. Finally they embedded tungsten filament electrode with diameter of 10 μm during hot press molding of materials to prepare electrical tree initiation specimens. Their experimental results indicated that addition of moderate concentration of voltage stabilizer can effectively inhibit the electrical tree initiation and propagation. These authors stated [12] that the acting mechanism of voltage stabilizer to the electrical tree initiation and propagation is the same as that presented by Yamano et al. Our research group synthesizes the acetophenone/PE composites through the penetration method. We observed that the breakdown strength of these composites is 1.5 times that of plain PE, and the resistance capability to electrical tree is remarkably improved.

The addition of acetophenone to PE can improve their breakdown strength by alternate current puncture as well as inhibit polyethylene electrical tree from initiation and propagation. The present work targets to provide a systematic study on the micro-mechanism of tautomerism of acetophenone and its analogues. The energy barriers variation of keto-enol tautomerism of acetophenone and its analogues in cases of dissociated in or linked to PE have been calculated on the basis of density function theory [13]. The PE structural segments, $-\!(CH\!-\!CH\!)_n$ ($n=2, 3, 4$), were chosen to investigate energy barrier variation of keto-enol tautomerism of acetophenone and its analogues when linked to the carbon chain of PE via para- and meta-positions. Acetophenone with substituent groups of alkyl, saturated and unsaturated groups with heteroatoms have been chosen to evaluate the effect of these substituent groups on the energy barrier variation of keto-enol tautomerism. Meanwhile, the acetophenone' analogues, alkyl substituted benzamide and alkyl substituted benzoic acid, have been chosen to evaluate the effect of different functional groups on the energy barrier variation of keto-enol tautomerism.

Acetophenone and its analogues (keto tautomer) are abbreviated to K and the enol tautomers are abbreviated to E, while the transition state and reaction channel are abbreviated to TS and R, respectively. The following are 42 possible reaction channels that have been studied.

K→E (R)	K1→E1 (R1)
KC→EC (RC)	K2→E2 (R2)
KCC→ECC (RCC)	KO⁻→EO⁻ (RO⁻)
KPr^i→EPr^i (RPr^i)	KOH→EOH (ROH)
KBu^t→EBu^t (RBu^t)	KOC→EOC (ROC)
p-KP4→p-EP4 (p-RP4)	KOPr^i→EOPr^i (ROPr^i)
p-KP6→p-EP6 (p-RP6)	KOCOC→EOCOC (ROCOC)
p-KP8→p-EP8 (p-RP8)	KONO→EONO (RONO)
m-KP4→m-EP4 (m-RP4)	KSH→ESH (RSH)
m-KP6→m-EP6 (m-RP6)	KN→EN (RN)
m-KP8→m-EP8 (m-RP8)	KNC→ENC (RNC)
KOP4→EOP4 (ROP4)	KNCC→ENCC (RNCC)
KOP6→EOP6 (ROP6)	KNCOC→ENCOC (RNCOC)
KOP8→EOP8 (ROP8)	KF→EF (RF)
KOBP4→EOBP4 (ROBP4)	KCl→ECl (RCl)
KOBP6→EOBP6 (ROBP6)	KBr→EBr (RBr)
KOBP8→EOBP8 (ROBP8)	KCO→ECO (RCO)
KOBOP4→EOBOP4 (ROBOP4)	KCOOH→ECOOH (RCOOH)
KOBOP6→EOBOP6 (ROBOP6)	KCOOC→ECOOC (RCOOC)
KOBOP8→EOBOP8 (ROBOP8)	KCON→ECON (RCON)
KO→EO (RO)	KCN→ECN (RCN)

Computational methods

In the present work, the equilibrium geometries and frequencies of all the stationary points (keto tautomer of acetophenone and its analogues, enol tautomer of acetophenone and its analogues, and the corresponding transition states) are optimized by using B3LYP method [14–17] with the 6−311+G(d,p) basis set. The minimum energy path (MEP) is obtained by intrinsic reaction coordinate (IRC) theory in mass-weighted Cartesian coordinates with a gradient step-size of 0.05 (amu)$^{1/2}$ bohr. At the same level, the energy derivatives, including gradients and Hessians at geometries along the MEP, are obtained to calculate the curvature of the reaction path and the generalized vibrational frequencies along the reaction path. All the electronic structure calculations are performed by means of using GAUSSIAN09 program package [18].

Results and discussions

Stationary points

The optimized geometric structures of the keto tautomer of acetophenone and its analogues, the enol tautomer of acetophenone and its analogues, and the corresponding transition states for 42 reaction channels are completed at the B3LYP/6−311+G(d,p) level (Fig. 1). The optimized geometric structures of the keto tautomer and the enol tautomer of acetophenone and its analogues are presented in Fig. S1 as supplementary information. Optimized bond lengths of breaking and forming bonds and corresponding calculated harmonic vibrational frequencies for the 42 transition states are list in Table 1. All the transition states are confirmed by normal-mode analysis to have and only have
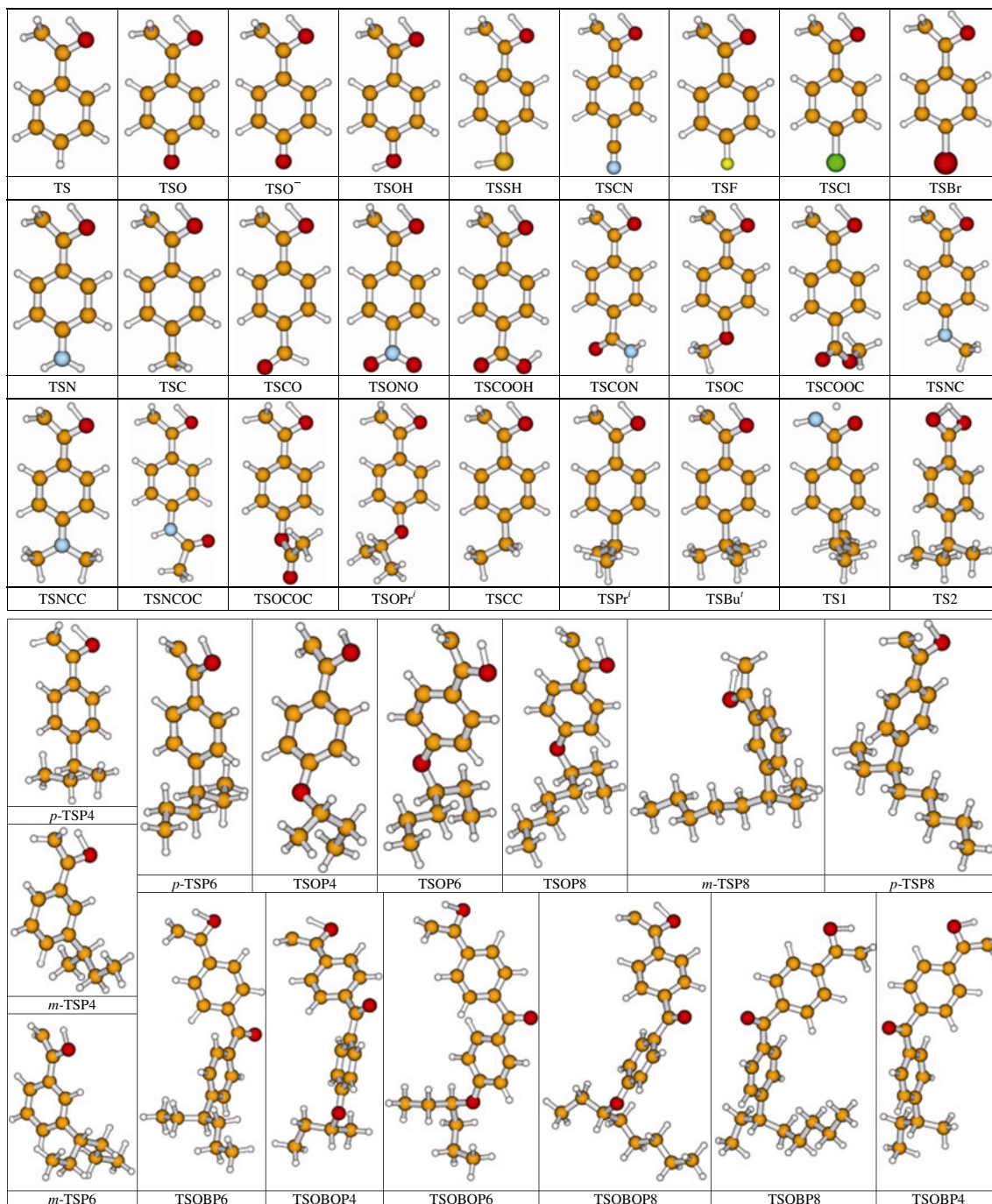
Fig. 1 Optimized geometric structures of the 42 transition states at the B3LYP/6-311+G(d,p) level

Table 1 Optimized bond lengths of breaking and forming bonds (in angstrom) for the 42 transition states, and calculated frequencies (in cm^{-1}) for the 42 transition states at the B3LYP/6−311+G(d,p) level

Reaction equation	Breaking bonds	Forming bonds	Frequencies
K→E (R)	1.491	1.276	2175 i
KC→EC (RC)	1.492	1.273	2163 i
KCC→ECC (RCC)	1.492	1.272	2161 i
KPr^j→EPr^j (RPr^j)	1.492	1.274	2163 i
KBu^t→EBu^t (RBu^t)	1.492	1.273	2164 i
p-KP4→p-EP4 (p-RP4)	1.491	1.273	2164 i
p-KP6→p-EP6 (p-RP6)	1.491	1.274	2164 i
p-KP8→p-EP8 (p-RP8)	1.492	1.273	2161 i
m-KP4→m-EP4 (m-RP4)	1.491	1.274	2169 i
m-KP6→m-EP6 (m-RP6)	1.491	1.275	2170 i
m-KP8→m-EP8 (m-RP8)	1.491	1.274	2169 i
KOP4→EOP4 (ROP4)	1.494	1.270	2140 i
KOP6→EOP6 (ROP6)	1.494	1.269	2138 i
KOP8→EOP8 (ROP8)	1.494	1.268	2137 i
KOBP4→EOBP4 (ROBP4)	1.490	1.278	2190 i
KOBP6→EOBP6 (ROBP6)	1.490	1.278	2190 i
KOBP8→EOBP8 (ROBP8)	1.490	1.278	2191 i
KOBOP4→EOBOP4 (ROBOP4)	1.489	1.278	2185 i
KOBOP6→EOBOP6 (ROBOP6)	1.490	1.278	2185 i
KOBOP8→EOBOP8 (ROBOP8)	1.490	1.278	2186 i
KO→EO (RO)	1.474	1.288	2418 i
K1→E1 (R1)	1.326	1.315	1953 i
K2→E2 (R2)	1.491	1.274	1950 i
KO$^-$→EO$^-$ (RO$^-$)	1.514	1.224	1869 i
KOH→EOH (ROH)	1.493	1.271	2149 i
KOC→EOC (ROC)	1.495	1.269	2143 i
KOPr^j→EOPr^j (ROPr^j)	1.495	1.268	2140 i
KOCOC→EOCOC (ROCOC)	1.492	1.275	2172 i
KONO→EONO (RONO)	1.487	1.286	2223 i
KSH→ESH (RSH)	1.492	1.274	2163 i
KN→EN (RN)	1.496	1.266	2126 i
KNC→ENC (RNC)	1.496	1.265	2116 i
KNCC→ENCC (RNCC)	1.496	1.266	2115 i
KNCOC→ENCOC (RNCOC)	1.493	1.272	2156 i
KF→EF (RF)	1.491	1.276	2173 i
KCl→ECl (RCl)	1.490	1.278	2181 i
KBr→EBr (RBr)	1.490	1.278	2183 i
KCO→ECO (RCO)	1.487	1.282	2211 i
KCOOH→ECOOH (RCOOH)	1.488	1.283	2209 i
KCOOC→ECOOC (RCOOC)	1.489	1.281	2197 i
KCON→ECON (RCON)	1.489	1.280	2195 i
KCN→ECN (RCN)	1.488	1.284	2212 i

one imaginary frequency corresponding to the stretching modes of the coupling breaking and forming bonds.

It can be seen that the transition state structure TS2 of reaction R2, the length of the O—H bond which will be broken stretches by 35 % over the O—H regular bond length in K2, and the product-forming H—O bond is elongated by about 34 % over the equilibrium bond length in equilibrium E2. Thus, reaction R2 proceeds *via* a symmetrical barrier. On the other hand, the elongation of the breaking bond is larger than that of the forming bond of the other keto-enol tautomerism transition state structure of acetophenone and its analogues reaction systems are all

product-like, *i.e.*, those reaction channels will proceed *via* "late" transition states, which is consistent with Hammond's postulate [19], applied to for an endothermic reaction.

Energetics

The reaction enthalpies at 298 K (ΔH_{298}^0) and the potential barrier heights (ΔE^{TS}) with zero-point energy (ZPE) corrections for the 42 reactions calculated at the B3LYP/6−311+ G(d,p) level are listed in Tables 2, 3 and 4, as well as the relative difference values of potential barrier energies (ΔE) between acetophenone with its analogues. Energy barrier variation of keto-enol tautomerism of acetophenone with alkyl group at the para- or meta-positions is provided in Table 2. From Table 2, all the energy barriers of keto-enol tautomerism of acetophenone with alkyl group at the para- or meta-positions decrease compared to K. However, the decrease extent is lowered from KC to KBu^t. For example, the value of ΔE for KC is −0.25 kcal mol^{-1}, but it reduces to −0.15 kcal mol^{-1} for KBu^t. The alkyl groups linked to benzene ring will exhibit electron donating inductive effect and σ-π hyper conjugation effect. When alkyl linked to the para-position of acetyl group in acetophenone (KC、KCC、KPr^i、KBu^t), the strength of σ-π hyper conjugated effect varies along with the type of α-C, and is proportional to the number of H atoms in α-C. Furthermore, the electron-donating effect follows the order of $-CH_3 > -CH_2R > -CHR_2 > -CR_3$. As a result, from KC to KBu^t, all the energy barriers decrease compared with K, but their decrease extent is contracted. To simulate the conditions of acetophenone linked to the chain of PE, energy barriers of keto-enol tautomerism of acetophenone' analogues, *p*-KPn and *m*-KPn($n=4,6,8$) with all the α-C as -CH, have been calculated. The calculated results suggest that energy barrier of keto-enol tautomerism gradually decreases as the alkyl chain length increases. Certain amount of energy, which is far lower than the carbon-carbon single bond energy, is needed to complete the keto-enol tautomerism of acetophenone and its analogues. When high-energy electrons are injected into PE, the energy will be mainly consumed by the keto-enol tautomerism of acetophenone and its analogues, which will efficiently prevent the carbon-carbon bond in main chain from breakage and avoid the generation of secondary electron, and thus inhibit polyethylene electrical tree from initiation. Energy barrier of keto-enol tautomerism decreases as the length of alkyl chain, at para- or meta-position of acetophenone, increases. As a result, the energy of high-energy electrons can be absorbed and transferred more easily, and then inhibit polyethylene electrical tree from initiation. We replaced the -CH$_3$ in the acetyl group of *p*-KP4 with -NH$_2$ (K1) or -OH (K2). The H in -NH$_2$ and -OH will be more active than that in -CH$_3$ due to the larger electronegativity of N and O than that of C.

Therefore, H in -NH$_2$ and -OH dissociate easier and lead to more facile tautomerism, and thus lower energy barriers. Moreover, these are the two compounds with the lowest energy barriers among all the reaction systems that have been evaluated.

Table 3 shows the energy barriers of keto-enol tautomerism of acetophenone's analogues, which are formed by linking heteroatoms (N, O, S, and X) to acetonpheone *via* single bonds. Distinct electron-donating conjugated effect and relatively weak electron-withdrawing effect present when –NH$_2$ is linked to benzene ring (KN, KNC, and KNCC). The combined result is that evident energy barrier decrease for acetophenone with the amido at the para-position, and all the energy barrier differences are higher than 1 kcal mol^{-1}. The electron-withdrawing effect is strengthened when the substituent group is acylamino (KNCOC), a bit higher energy barrier than KN will be the result, though still lower than K. All the energy barriers of keto-enol tautomerism decrease when -OR, -OH and -O$^-$, particularly -O$^-$ with an energy barrier decrease of 7.76 kcal mol^{-1}, are linked to the para-positon of acetophenone directly. It is analyzed that their interaction mechanism is as follows: O linked directly to benzene ring exhibit electron-withdrawing inductive effect and electron-donating conjugated effect at the same time, where the latter is stronger than the former and results in good electron-donating effect. Among them O$^-$ possesses the strongest electron-donating effect, and the increased electron density in benzene ring will further impel the transfer of π electrons of −C=O to O. The increased electron density in O will in turn exerts stronger attraction to H in acetyl, and thus tautomerization occurs in an easier fashion. Moreover, theoretical calculated results show that the energy barrier decreases gradually as the alkyl chain becomes larger from KOP4 to KOP8, this is in line with the above-mentioned calculated results of *p*-KPn and *m*-KPn ($n=4, 6, 8$). In the case of KSH, S and O belong to the same oxygenic group and possess similar electron effect, except that S has a larger atomic radius and conjugates less efficiently with benzene ring than O. Hence, decreased energy barrier of tautomerization, though with less extent than that of -OH, can be expected when -SH linked to the para-position of acetophenone. Electron density in benzene will decrease when the para-positon of acetophoene is linked with halogen atoms (F, Cl, and Br), due to the fact that halogen atoms are deactivation groups. Therefore, C in −C=O becomes more electropositive, which will impel electron transfer to C in −C=O. The decreased electron density will weaken the attraction of O to H, and hence increased energy barrier of tautomerization. We also investigated the energy barriers variation of keto-enol tautomerism of acetophenone's analogues, which are formed by linking C, N, O, and F atoms or groups (KC, KN, KOH, and KF) to para-position of acetophenone. C, N, O, and F

Table 2 The reaction enthalpies at 298 K $\left(\Delta H_{298}^0\right)$, the potential barrier heights TSs (ΔE^{TS}) (kcal mol^{-1}) with zero-point energy (ZPE) corrections, relative difference values of potential barrier energies (ΔE) for the acetophenone with its analogues reactions calculated at the B3LYP/6−311+G(d,p) level
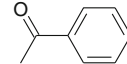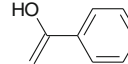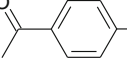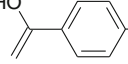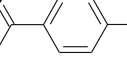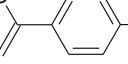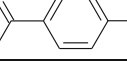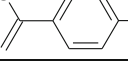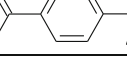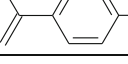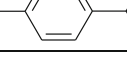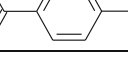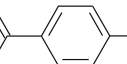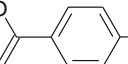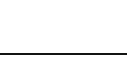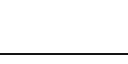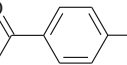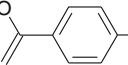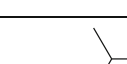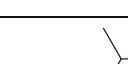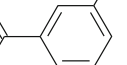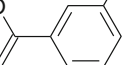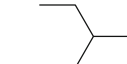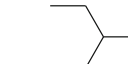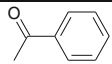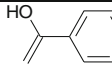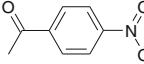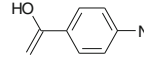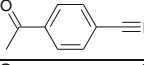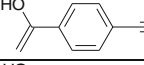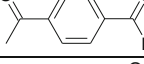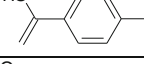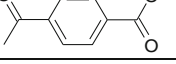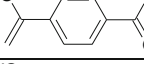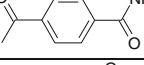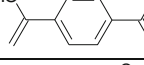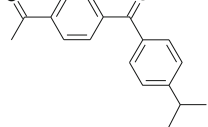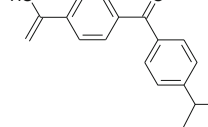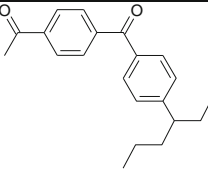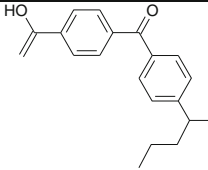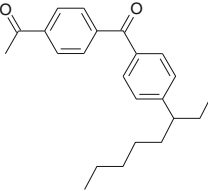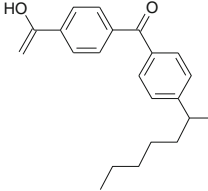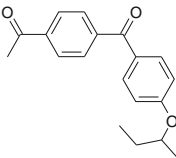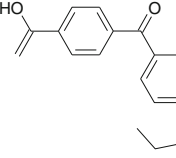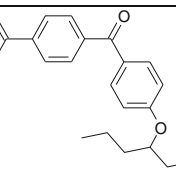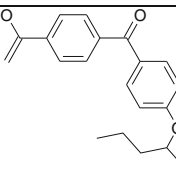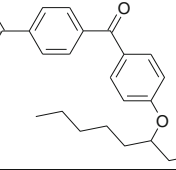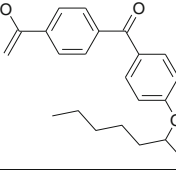
ab.	molecular formula	ab.	molecular formula	ΔE^{TS}+ZPE	ΔH_{298}^0	ΔE
K		E		62.31	13.81	0
KC		EC		62.06	14.20	-0.25
KCC		ECC		62.10	14.32	-0.21
KPr^i		EPr^i		62.13	14.16	-0.18
KBu^t		EBu^t		62.16	14.27	-0.15
p-KP4		p-EP4		62.10	14.25	-0.21
p-KP6		p-EP6		62.07	14.14	-0.24
p-KP8		p-EP8		62.00	14.12	-0.31
m-KP4		m-EP4		62.24	14.04	-0.07
m-KP6		m-EP6		62.21	13.96	-0.10
m-KP8		m-EP8		61.91	14.02	-0.40
K1		E1		42.00	13.08	-20.31
K2		E2		31.84	0.02	-30.47

Table 3 The reaction enthalpies at 298 K $\left(\Delta H_{298}^0\right)$, the potential barrier heights TSs (ΔE^{TS}) (kcal mol^{-1}) with zero-point energy (ZPE) corrections, relative difference values of potential barrier energies (ΔE) for the acetophenone with its analogues reactions calculated at the B3LYP/6−311+G(d,p) level

ab.	molecular formula	ab.	molecular formula	ΔE^{TS}+ZPE	ΔH_{298}^0	ΔE
K		E		62.31	13.81	0
KN		EN		61.17	15.44	-1.14
KNC		ENC		60.87	15.59	-1.44
KNCC		ENCC		60.88	15.65	-1.43
KNCOC		ENCOC		61.81	14.18	-0.50
KO$^-$		EO$^-$		54.55	22.70	-7.76
KOH		EOH		61.77	14.69	-0.54
KOC		EOC		61.71	14.88	-0.60
KOPr^i		EOPr^i		61.53	14.96	-0.78
KOP4		EOP4		61.62	14.97	-0.69
KOP6		EOP6		61.54	15.00	-0.77
KOP8		EOP8		61.50	15.01	-0.81
KOCOC		EOCOC		62.28	13.88	-0.03
KSH		ESH		62.05	14.18	-0.26
KF		EF		62.34	13.93	0.03
KCl		ECl		62.47	13.62	0.16
KBr		EBr		62.51	13.55	0.20

Table 4 The reaction enthalpies at 298 K $\left(\Delta H_{298}^0\right)$, the potential barrier heights TSs (ΔE^{TS}) (kcal mol^{-1}) with zero-point energy (ZPE) corrections, relative difference values of potential barrier energies (ΔE) for the acetophenone with its analogues reactions calculated at the B3LYP/6−311+G(d,p) level

ab.	molecular formula	ab.	molecular formula	ΔE^{TS}+ZPE	ΔH_{298}^0	ΔE
K		E		62.31	13.81	0
KONO		EONO		63.19	12.02	0.88
KCN		ECN		63.00	12.46	0.69
KCO		ECO		62.93	12.55	0.62
KCOOC		ECOOC		62.83	12.95	0.52
KCON		ECON		62.76	13.16	0.45
KOBP4		EOBP4		62.60	13.10	0.29
KOBP6		EOBP6		62.52	13.05	0.21
KOBP8		EOBP8		62.52	13.08	0.21
KOBOP4		EOBOP4		62.46	13.21	0.15
KOBOP6		EOBOP6		62.44	13.20	0.13
KOBOP8		EOBOP8		62.40	13.20	0.09

all belong to the same second period of element, and follow an electron-donating capability order of -NH$_2$> −OH>−R>−X. Therefore, the corresponding energy barriers of tautomerization will gradually increase accordingly as shown in Table 3.

Table 4 presents energy barriers variation of keto-enol tautomerism of acetophenone's analogues, which are formed by linking unsaturated groups (−NO$_2$, −CN, and −C=O) to para-position of acetonphenone. In the case of −C=O, both the inductive effect and conjugated effect are electron-withdrawing, which will cause π electron transfer to C in −C=O of acetyl. The decreased electron density in O of −C=O will reduce its attraction to H, and thus a more difficult tautomerization process, which has been well confirmed by the calculated energy barrier result. As shown in Table 4, the energy barriers of keto-enol tautomerism of KCOOC, KCON, 4-acetyl-4'-alkyl (alkoxy) benzophenone (KOBPn and KOBOPn, $n=4, 6, 8$) are all higher than that of acetopheone. In comparison with −C=O, the −NO$_2$ and −CN linked to acetophenone exhibit stronger electron-withdrawing inductive effect and conjugated effect, and hence larger energy barriers increase of keto-enol tautomerism of KONO and KCN can be expected.

Through analyzing the data shown in Tables 2, 3 and 4, it can be concluded that the better electron-donating ability of groups linked to acetophenone, the more energy barrier decrease of keto-enol tautomerism, and vice versa. That is to say, the better electron-donating ability of groups linked to acetophenone, the easier keto-enol tautomerism will be when high-energy electrons are injected. Therefore, remarkable increased anti-electrical tree aging ability of PE can be expected when acetophenone and its analogues, which are formed by linking electron-donating groups to para- or meta-position of acetophenone, are doped into or bonded to the chains of PE.

Conclusions

In this paper, a systematic theoretical study on the micro-mechanism of tautomerism of acetophenone and its analogues has been carried out at the B3LYP/6−311+G(d,p) level. According to the theoretical calculation results, the following conclusions can be deduced.

1. There are energy barriers for all the tautomerism reactions of acetophenone and its analogues (42 reaction systems). Certain energy barriers are needed to overcome for both reactions from enol to keto and from keto to enol.
2. In comparison with acetophenone, the energy barriers of keto-enol tautomerism decrease when alkyl groups are linked to para- or meta-position of acetophenone. When

electron-donating groups (−NH$_2$, −OH, −OR, −O$^-$, *etc.*) are linked to the para-position, the energy barrier needed for keto to enol decreases obviously. The energy barriers of tautomerism for benzamide's analogues and benzoic acid's analogues decrease further, which is closely related to the larger electronegativity of N and O.
3. The energy barriers of all 42 keto-enol tautomerism for acetophenone and its analogues are lower than the energy needed to break C-C bond (average bond energy: 82.95 kcal mol^{-1}).
4. Either acetophenone dissociated in acetophenone/PE composite or linked to PE chains can inhibit polyethylene electrical tree from initiation and propagation as well as improve the strength of alternate current that PE can endure.

Supporting information available Geometric structures of theoretical calculation for the 42 keto enol tautomer and its analogues at the B3LYP/6−311+G(d,p) level.

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