

Electron transfer reactions (ETR) of *tert*-butyl perbenzoates with dimethyl sulfide: the rates controlled by translational entropy

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ABSTRACT: Various *tert*-butyl perbenzoates were prepared according to the known methods. The mixtures of *tert*-butyl perbenzoate and dimethyl sulfide underwent thermolysis at several temperatures ($T^{\circ}\text{C}$: 80, 90, 100, and 110). The rates of consumption of the peresters (k_{obs}) were obtained from $\ln C_0/C_t = k_{\text{obs}} \times t$ where C_0 and C_t are the concentration of the perester at time 0 and t , respectively. For example: The decrease of the perester satisfied pseudo first order kinetics, and k_{obs} were determined. k_{Hom} and k_{ET} were obtained from $k_{\text{obs}} = k_{\text{Hom}} + k_{\text{ET}}[\text{CH}_3\text{SCH}_3]$ where $[\text{CH}_3\text{SCH}_3]/[\text{perester}] > 10$. k_{ET} and its relative rates are produced from plot of k_{obs} against $[\text{CH}_3\text{SCH}_3]$. Hammett correlation are plotted against σ and σ^+ in which σ is better correlated than σ^+ . Hammett ρ could be considered selectivity which stays constant irrespective of temperature. The phenomenon is not consistent with reactivity/selectivity principle. The differential activation entropies linearly increase with substituent constant σ to give slope of 2.63 while the similar slope for differential enthalpies shows much lower value of 0.892. The dominance of differential entropic terms clearly indicates the entropy control of the rates. Copyright © 2006 John Wiley & Sons, Ltd.

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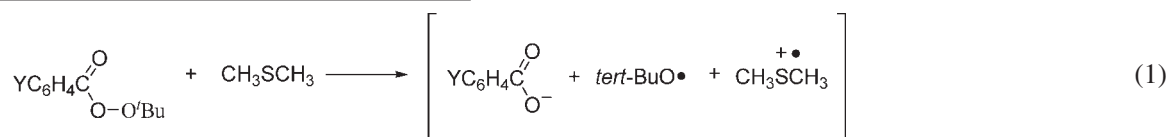
KEYWORDS: *tert*-butyl perbenzoates; dimethyl sulfide; entropy control of the rates

INTRODUCTION

Hydrogen atom abstractions from toluenes¹ and cumenes² by bromine atoms, β -scissions of the carbinyl radicals,³ and thermolysis of *tert*-butyl phenylperacetates⁴ proceed through polar transition state (TS) and reveal entropy control of rates. The relative rates at several temperatures provide differential activation terms ($\Delta\Delta H_{\text{Y-H}}^{\ddagger}$ and $\Delta\Delta S_{\text{Y-H}}^{\ddagger}$) derived from Eyring equation.⁵ The sign and magnitude of differential activation entropies ($\Delta\Delta S_{\text{Y-H}}^{\ddagger}$) outweighs those of differential enthalpies ($\Delta\Delta H_{\text{Y-H}}^{\ddagger}$).^{1–4} When the substituent approaches electron-donating character, that is, the value of σ^+ maintains larger negative value, $\Delta\Delta S_{\text{Y-H}}^{\ddagger}$ becomes much bigger positive magnitudes than $\Delta\Delta H_{\text{Y-H}}^{\ddagger}$. The activation parameters for abstraction of phenolic hydrogen from *p*-methoxyphenol by *tert*-butoxyl radical⁶

shows dominance of entropic term over enthalpy. Triplet δ -hydrogen abstraction by *o-tert*-butyl benzophenones⁷ shows an entropy-controlled inductive effect. Recently the rate of hydrogen abstractions by *tert*-butoxyl radicals^{6–8} are suggested to involve entropy-controlled process.⁹ *tert*-Butyl peroxybenzoate (TBP) underwent electron transfer reaction (ETR) with dimethyl sulfide through reactions 1–4.¹⁰ The kinetic isotope effect suggests that dimethyl sulfide-TBP system involves ET while dimethylaniline-benzoylperoxide system proceeds through $\text{S}_{\text{N}}2$ mechanism.

The three intermediates occur in Eqn (1) which then react via Eqn (2), Eqn (3) to give the intermediates **I** which rearranges to give benzoyloxy dimethyl sulfide. A similar ET mechanism between TBP and thiophenol has also been reported by us.¹¹ We would like to herein show that the rate of ETR is controlled by entropy.

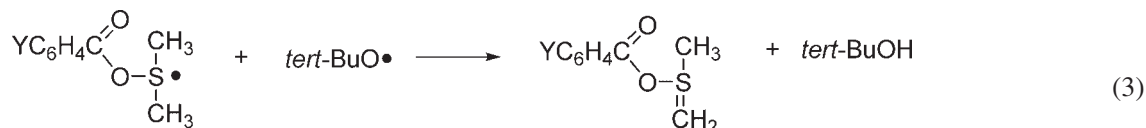
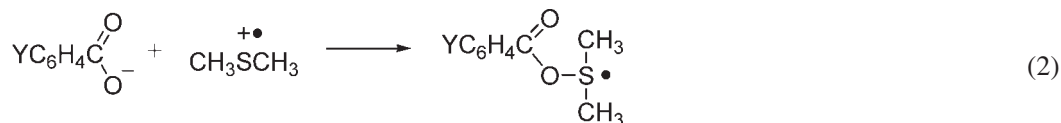


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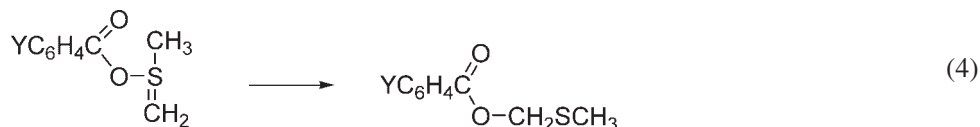
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I



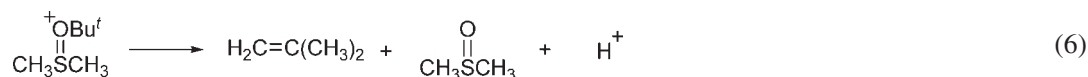
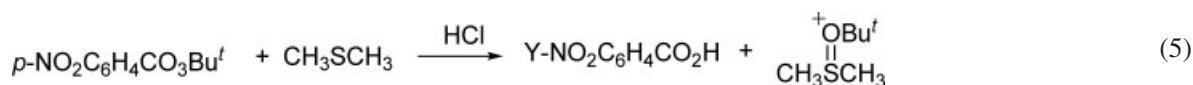
RESULTS AND DISCUSSION

Preparation and thermolysis of the peresters and relevant kinetic data

Various $\text{YC}_6\text{H}_4\text{CO}_2\text{Bu}^t$ [Y: *p*-OCH₃, *p*-CH₃, *p*-Cl, *m*-Cl, and *p*-NO₂] (TBP) were prepared according to the known method.¹⁰ TBP (0.05 M), CH₃SCCH₃ (0.5 ~ 2.0 M), α -methoxycumene (0.02 M, internal standard) and trans-stilbene (0.2 M)¹² were dissolved in CDCl₃ and divided into Pyrex ampoules. Potassium fluoride (KF) was added to each ampoule which was then degassed and underwent thermolysis at several temperatures. KF is to neutralize HCl which is slightly contained in the solvent CDCl₃. In the presence of HCl reactions (5) and (6) occur to reduce the yield of benzoxyloxy dimethyl sulfide and *tert*-butyl alcohol. Product analysis in absence and presence of KF are shown in Table 1. That clearly shows that reaction (5) is effectively inhibited by scavenging HCl with KF.

Table 1. Product analysis of thermolysis of *tert*-Butyl *p*-nitroperbenzoate and dimethyl sulfide in absence and presence of KF

Products	Mole of Product/Mole of Perester before Reaction	
	Without KF	With KF
$\text{p-NO}_2\text{C}_6\text{H}_4\text{C}(=\text{O})\text{OCH}_2\text{SCH}_3$	0.44	0.96
<i>tert</i> -BuOH	0.42	0.97
<i>p</i> -NO ₂ C ₆ H ₄ COOH	0.56	—
(CH ₃) ₂ C=CH ₂	0.53	—
$\text{CH}_3\text{C}(=\text{O})\text{SCH}_3$	0.58	—



The rates of consumption of TBP (k_{obs}) were obtained by measuring the disappearing NMR peak of *tert*-butyl group of TBP. Equation (7) has been utilized to calculate k_{obs} at various temperatures and with different substituent (Y).

$$\ln \frac{C_0}{C_t} = k_{\text{obs}} \times t \quad (7)$$

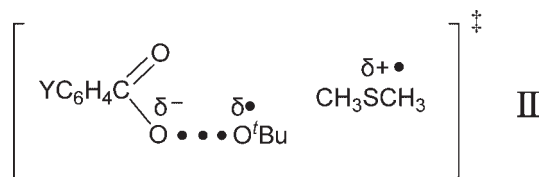
where C_0 is the initial concentration of the perester, C_t is the concentration of the perester at time t . k_{obs} is obtained from Eqn (7) that could be dissected into the rate constants caused by homolysis of the perester

and by ET between the perester and dimethyl sulfide to give

$$k_{\text{obs}} = k_{\text{Hom.}} + k_{\text{ET}}[\text{CH}_3\text{SCH}_3] \quad (8)$$

$k_{\text{Hom.}}$ and k_{ET} can be obtained from the linear relation between k_{obs} and concentration of dimethyl sulfide. In the case of a large excess of dimethyl sulfide ($C_{\text{MeSMe}}/C_{\text{Perester}} > 10$), Eqn (8) follows a pseudo-first order reaction. $k_{\text{Hom.}}$ corresponds to the intercept and k_{ET} becomes the slope of the linear line. Utilizing this method, k_{obs} and k_{ET} are obtained for numerous TBP (refer to Supporting Information).

Absolute and relative rates of ETR at various temperatures ($T^{\circ}\text{C}$: 80, 90, 100, and 110°C) were obtained. Hammett correlations at each temperature are also studied (Table 2). Hammett correlations are positive and better correlated with σ rather than σ^+ . This indicates that negative charge resides on benzoyloxy group without conjugation with the phenyl ring (refer to II). This is well compared with the previous entropy-controlled reactions¹⁻⁴ where the positive charge is delocalized into phenyl ring for $\rho^+\sigma^+$ correlations.



The relative rates of ETR, $k_{\text{ET}}^{\text{Y}}/k_{\text{ET}}^{\text{H}}$ remains nearly invariable irrespective of temperature. This means that substituent effect is constant at various temperatures in order to give the identical Hammett ρ value ($\rho = 1.06 \pm 0.02$) (refer to Table 2). The constant ρ^+ with temperature (not ρ in those cases) had already been observed with photobromination of cumenes² and homolytic fragmentation of carbinoyloxy radicals.³ The Hammett reaction constant either ρ or ρ^+ can be considered selectivity and the invariance with temperature apparently inconsistent with reactivity/selectivity principle (RSP).¹³ The activation parameters and their differential values are tabulated in Table 3. The isokinetic relationship is observed to give the straight line indicating isokinetic temperature $T = -146^{\circ}\text{C}$ (Fig. 1). The magnitudes of differential activation parameters also suggest that cleavage of $-\text{O}-\text{O}-$ in II is systematically controlled by the substituents for the linearity.

Translational entropy responsible for the rates

Benzoyloxy group attains partial negative charge and *tert*-butoxy becomes radical type in II. The extent of heterolytic (into radical and anion) bond cleavage of $-\text{O}-\text{O}-$ is variable depending upon the substituent (Y). The values of differential activation terms (Table 3) indicate that electron-withdrawing groups (Y) boost more bond cleavage than hydrogen H. The substituent effect may weakly influence the magnitude of $\Delta H_{\text{Y}}^{\ddagger}$ to give relatively smaller values of $\Delta\Delta H_{\text{Y-H}}^{\ddagger}$. The plot of $\Delta\Delta H_{\text{Y-H}}^{\ddagger}$ versus σ is shown in Fig. 2 with slope of 0.891. Absolute rate theory⁵ suggests that the vibration of $-\text{O}-\text{O}-$ bond in TBP should be replaced by translation during the activation process. The transition from vibration to translation should accompany dramatic entropic increase since vibration is of one dimension while translation occurs with three dimensions. Therefore, the increase (decrease) in differential activation entropy multiplied by the absolute temperature

Table 2. Absolute Rates, Relative Rates and Hammett Correlations for ETR between *tert*-Butyl Perbenzoates and Dimethyl Sulfide

	<i>p</i> -OMe	<i>p</i> -Me	H	$k_{\text{ET}} \times 10^4, \text{M}^{-1} \text{s}^{-1\text{a}}$	$(k_{\text{ET}}^{\text{Y}}/k_{\text{ET}}^{\text{H}})^{\text{b}}$	<i>p</i> -Cl	<i>m</i> -Cl	<i>p</i> -NO ₂	ρ (r)	ρ^+ (r)
80°C	0.0715 ^c (0.585)	0.0931 ± 0.0039 (0.716)	0.130 ± 0.006 (1.00)	0.260 ± 0.003 (2.00)	0.343 ± 0.015 (2.64)	0.987 ± 0.027 (7.52)			1.05 ± 0.03 (0.998)	0.72 ± 0.12 (0.949)
90°C	0.167 ± 0.005 (0.603)	0.215 ± 0.016 (0.776)	0.277 ± 0.005 (1.00)	0.554 ± 0.021 (2.00)	0.737 ± 0.012 (2.66)	2.27 ± 0.10 (8.19)			1.06 ± 0.03 (0.998)	0.73 ± 0.12 (0.946)
100°C	0.347 ± 0.020 (0.595)	0.438 ± 0.009 (0.751)	0.583 ± 0.036 (1.00)	1.19 ± 0.06 (2.04)	1.65 ± 0.08 (2.83)	4.76 ± 0.32 (8.16)			1.07 ± 0.03 (0.998)	0.74 ± 0.12 (0.948)
110°C	0.710 ± 0.012 (0.607)	0.837 ± 0.033 (0.715)	1.17 ± 0.03 (1.00)	2.46 ± 0.12 (2.10)	3.29 ± 0.06 (2.81)	9.66 ± 0.17 (8.26)			1.08 ± 0.04 (0.997)	0.74 ± 0.13 (0.944)

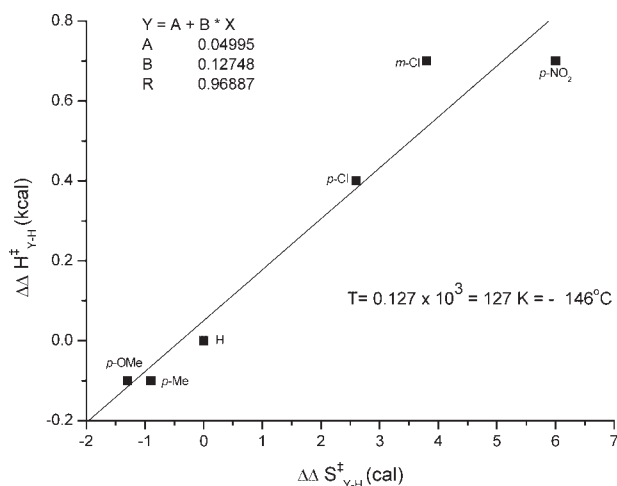
^a Absolute rate constants of ETR.

^b Relative rate constants of ETR.

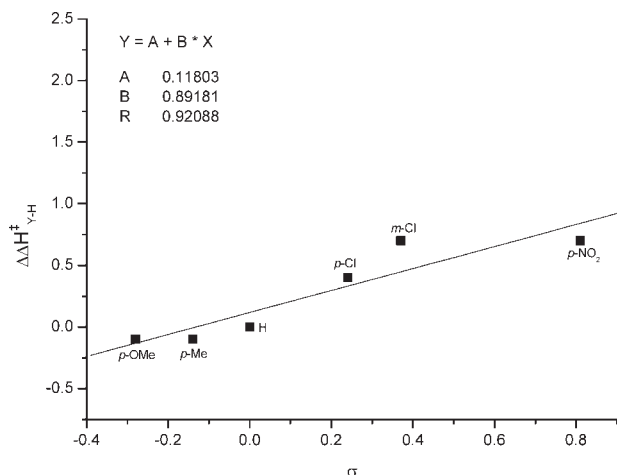
^c The value is obtained by extrapolation because of very slow rate of decomposition.

Table 3. Activation parameters and their differential values

	<i>p</i> -OMe	<i>p</i> -Me	H	<i>p</i> -Cl	<i>m</i> -Cl	<i>p</i> -NO ₂
$\Delta H_{Y-H}^\ddagger$ ^a	18.9 ± 0.1	18.9 ± 0.4	19.0 ± 0.1	19.4 ± 0.2	19.7 ± 0.3	19.7 ± 0.2
$\Delta S_{Y-H}^\ddagger$ ^b	-28.7 ± 0.1	-28.3 ± 1.3	-27.4 ± 0.3	-24.8 ± 0.8	-23.6 ± 0.8	-21.4 ± 0.7
$\Delta\Delta H_{Y-H}^\ddagger$ ^{a,c}	-0.1	-0.1	0	0.4	0.7	0.7
$\Delta\Delta S_{Y-H}^\ddagger$ ^{b,d}	-1.3	-0.9	0	2.6	3.8	6.0
$T\Delta\Delta S_{Y-H}^\ddagger$ ^a $T = 373$ K	-0.47	-0.33	0	0.94	1.38	2.18

^a unit: kcal/mol.^b unit: cal/mol, K.^c $\Delta\Delta H_{Y-H}^\ddagger = \Delta H_{Y-H}^\ddagger - \Delta H_{H-H}^\ddagger$ where the subscript Y and H indicate the substituents Y and H in the perester.^d $\Delta\Delta S_{Y-H}^\ddagger = \Delta S_{Y-H}^\ddagger - \Delta S_{H-H}^\ddagger$ where the subscript Y and H indicate the substituents Y and H in the perester.**Figure 1.** Plot of isokinetic relationship

($T\Delta\Delta S_{Y-H}^\ddagger$) should be much higher than that corresponding to differential activation enthalpy to control the magnitude of $\Delta\Delta G_{Y-H}^\ddagger$ ($T\Delta\Delta S_{Y-H}^\ddagger \gg \Delta\Delta H_{Y-H}^\ddagger$). The plot of $T\Delta\Delta S_{Y-H}^\ddagger$ versus σ gives a straight line with slope = 2.63 (Fig. 3). The polarity of II is opposite to

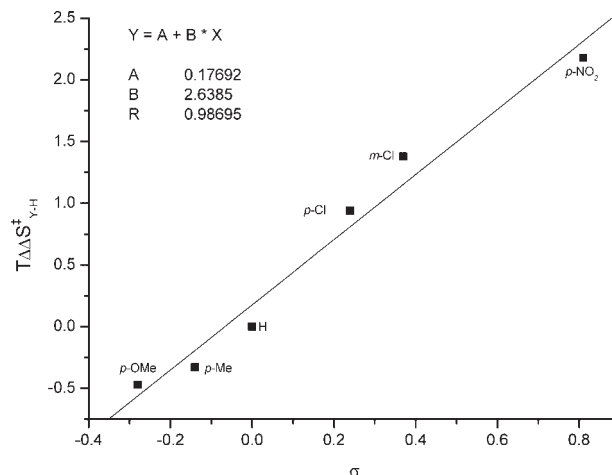
**Figure 2.** Plot of $\Delta\Delta H_{Y-H}^\ddagger$ vs. σ

that of TS's involved with the previous entropy dominating reactions.¹⁻⁴ The negative charge is localized on benzyloxy group (refer to II) to give $\rho\sigma$ correlation while the positive charge is dispersed into the benzene ring for $\rho^+\sigma^+$ relationship.¹⁻⁴

The selectivity S of a species with competing peresters harboring substituents Y and H, respectively could be defined as $S = \ln k_{ET}^Y/k_{ET}^H = -(\Delta G_Y^\ddagger - \Delta G_H^\ddagger)/RT = -\Delta\Delta G_{Y-H}^\ddagger/RT$ with k and $\Delta G^\ddagger$ being the corresponding rate constant and free energy of activation of ETR. $S = -\Delta\Delta G_{Y-H}^\ddagger/RT$ can be subdivided into two parts: $-\Delta\Delta G_{Y-H}^\ddagger/RT = \Delta\Delta S_{Y-H}^\ddagger/R - \Delta\Delta H_{Y-H}^\ddagger/RT$. The present ETR involve $\Delta\Delta H_{Y-H}^\ddagger/RT$ close to zero. Therefore, S is mainly controlled by $\Delta\Delta S_{Y-H}^\ddagger/R$ which is temperature-independent and takes almost constant figures with the substituent (refer to values of k_{ET}^Y/k_{ET}^H of Table 2).

CONCLUSION

The ETR proceeds through TS II in which —O—O— bond is cleaved. Comparison of magnitude of $\Delta\Delta H_{Y-H}^\ddagger$ and $\Delta\Delta S_{Y-H}^\ddagger$ tells that the relative rates are controlled by $T\Delta\Delta S_{Y-H}^\ddagger$. The entropic dominance is derived from the

**Figure 3.** Plot of $T\Delta\Delta S_{Y-H}^\ddagger$ vs. σ

translational degree of freedom occurring in breakage of —O—O— bond. Entropy-controlled rates may not be uncommon for the ETR and the homolysis reactions take place via polar TS.

EXPERIMENTAL SECTION

Materials and methods

Substituted benzoic acids, *tert*-butyl hydroperoxide and other chemicals were purchased from the major suppliers. Liquids were distilled with center-cut collection and solids were purified according to standard procedures if necessary.¹⁴ An NMR spectrometer was used for the analysis of the peresters.

Preparation of various *tert*-butyl perbenzoates

All the peresters were prepared according to the known method.¹⁵ IR C=O stretchings are shown between 1747 ~ 1757 cm⁻¹. *p*-CH₃O, *p*-CH₃ and H peresters are liquid while *p*-Cl (48 °C), *m*-Cl (46 °C), and *p*-NO₂ (79 °C) peresters are solid with melting point indicated in the parenthesis. The melting points are exactly match the reported values.¹⁵ ¹H NMR spectra various YC₆H₄CO₂-Bu^t are as follows: *p*-OCH₃: 6.8 ~ 8.0 (m, 4H), 3.86 (s, 3H), 1.40 (s, 9H); *p*-CH₃: 7.2 ~ 7.8 (m, 4H), 2.41 (s, 3H), 1.41 (s, 9H); H: 7.2 ~ 7.9 (m, 5H), 1.42 (s, 9H); *p*-Cl: 7.4 ~ 7.9 (m, 4H), 1.40 (s, 9H); *m*-Cl: 7.3 ~ 7.8 (m, 4H), 1.38 (s, 9H); *p*-NO₂: 8.1 ~ 8.3 (m, 4H), 1.42 (s, 9H).

ETR of *tert*-butyl perbenzoates with dimethyl sulfide

tert-Butyl perbenzoate (0.05 M), dimethyl sulfide (0.5 ~ 2.0 M), α -methoxy cumene (0.02 M: internal standard), *trans*-stilbene (0.2 M: inhibitor) and KF (30 mg) were dissolved in CDCl₃ (0.4 mL) in a tube. This mixture was freeze, degassed three times and sealed. The ampoule (lid. 4 mm, length 3 cm, 2/3 full) was immersed in a constant temperature bath for more than 200 sec for the thermolysis. Less than 20 sec were required for complete thermal equilibration, which was measured by a Copper-Constantan thermo couple. At various intervals, the tubes were removed from the bath, quenched in ice water and opened for NMR analysis.

Concentration of the perester at time *t* can be obtained by measuring the magnitude of proton peaks of *tert*-butyl group of perester and of methyl of α -methoxy cumene utilizing Eqn (9).

$$\frac{I_{\text{per},t}}{I_{\text{st},t}} = \frac{9}{6} \times \frac{C_{\text{per},t}}{C_{\text{st},t}} = \alpha C_{\text{per},t} \quad (9)$$

- $I_{\text{per},t}$: Magnitude of proton peak of *tert*-butyl group of the perester at time *t*.
- $I_{\text{st},t}$: Magnitude of proton peak of methyl group of α -methoxy cumene.

Accordingly k_{obs} is obtained from Eqn (10).

k_{Hom} and k_{ET} are thus acquired by plotting k_{obs} against concentration of dimethyl sulfide.

$$\ln \frac{I_{\text{per},0}/I_{\text{st},0}}{I_{\text{per},t}/I_{\text{st},t}} = \ln \frac{C_{\text{per},0}}{C_{\text{per},t}} = k_{\text{obs}}t \quad (10)$$

$$k_{\text{obs}} = k_{\text{Hom}} + k_{\text{ET}}[\text{CH}_3\text{SCH}_3] \quad (11)$$

Acknowledgements

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