



Potential bleach activators with improved imide hydrolytic stability

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Received: 25 January 2019 / Accepted: 12 June 2020 / Published online: 29 July 2020
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Abstract

The commercially available bleach activator, *N,N,N',N'*-tetraacetylenediamine (TAED), has been widely used in laundry detergents to enable efficient low-temperature bleaching. However, the competitive hydrolysis of TAED limits its use in liquid detergents. Herein we report the synthesis of two TAED derivatives, *N,N,N',N'*-tetracetylpropylene-1,2-diamine (TA(Me)ED) and *N,N,N'*-triacetylpropylene-1,2-diamine (TriA(Me)ED), through the acetylation of propylene-1,2-diamine. The hydrolytic and perhydrolytic activity of the imide molecules were studied by HPLC to elucidate the structure–function relationship. Due to the increased steric hindrance imparted by the α -methyl group close to the imide, TA(Me)ED and TriA(Me)ED exhibited higher hydrolytic stability than TAED, with the hydrolytic rate constants (k_H) at pH 8.0 decreased by 58% and 84% for TA(Me)ED and TriA(Me)ED, respectively. On the other hand, TA(Me)ED and TriA(Me)ED showed comparable perhydrolytic activity with TAED in the presence of peroxide, enabling similar bleaching effect of a model food dye at room temperature. These results suggest these TAED derivatives may have potential being used as improved bleach activators.

Keywords Bleach activator · Hydrolysis · Perhydrolysis · Imides · Steric hindrance

Introduction

Since the 1970s, bleach activators have been widely used in laundry detergents to enable bleaching at low temperatures (40–60 °C) [1, 2], due to low efficiencies of peroxide derivatives at this temperature range. For instance, *N,N,N',N'*-tetraacetylenediamine (TAED) is the first activator used in a commercial product and is the main activator currently used in European detergents [1, 3]. The perhydrolysis of TAED in the presence of peroxide derivatives (e.g., sodium perborate and sodium percarbonate) leads to the formation of peracetic acid (PAA) [4], which is a more efficient bleach at low temperatures. Despite the great success, a major disadvantage for TAED is the competitive hydrolysis under basic conditions [5], which gradually converts TAED into

inactive acetic acid and lowers the equivalents of the generated PAA (lowered to 1.5–1.7 equivalents [2, 4], less than the theoretical value of 2 equivalents). As a result, TAED is generally used in powder detergents. To use TAED in liquid detergents, a significant amount of efforts have been made to encapsulate TAED in polymeric materials to improve its storage stability in liquid formulations [6–12]. While greater aqueous stability of TAED was achieved when coated with a surfactant or polymeric materials, the encapsulation strategy was limited with lower contents of active TAED in the final formulation as well as the safety concern of the coating materials.

In an attempt to improve the hydrolytic stability of TAED, it was hypothesized that an increase in steric hindrance close to the imide groups could potentially slow down the hydrolysis. We reasoned that the chemical modification of the activator structure may provide a novel and simple strategy compared with the encapsulation methods. Therefore, two TAED derivatives bearing an α -methyl group on the ethylenediamine core, *N,N,N',N'*-tetracetylpropylene-1,2-diamine (TA(Me)ED) and *N,N,N'*-triacetylpropylene-1,2-diamine (TriA(Me)ED), were prepared to study the structure–property relationship. It was found that these imides showed improved hydrolytic stability compared with TAED, while still maintaining a bleaching efficiency comparable

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to TAED. The improved hydrolytic stability and retained perhydrolytic activity of TA(Me)ED and TriA(Me)ED suggest that these derivatives could have significant potential in liquid laundry formulations.

Experimental procedure

Materials

All chemicals were purchased from MilliporeSigma (St. Louis, MO, USA) and used as received unless otherwise specified. *N,N,N',N'*-tetraacetylenediamine (TAED) (powder form) was purchased from Alfa Aesar (Tewksbury, MA, USA). *N,N'*-diacetylenediamine (DAED) was purchased from TCI America (Portland, OR, USA). Food dye with blue-color was purchased from Adams Extract (Gonzales, TX, USA). Citric buffer (0.1 M, pH 4.0 and 5.0) and Tris buffer (0.1 M, pH 7.2, 8.0, and 9.0) were prepared for further studies.

Instrumentation

Nuclear magnetic resonance (NMR) spectra were recorded on a Varian U500 spectrometer in the NMR laboratory, University of Illinois. Chemical shifts were reported in ppm and referenced to the residual protons in the deuterated solvents. MestReNova 8.1.1 was used for all NMR analysis. Electrospray ionization mass spectrometry (ESI-MS) spectra were obtained on a Waters Q-TOF Ultima ESI spectrometer in the MS laboratory, University of Illinois. High-performance liquid chromatography (HPLC) was performed on a Shimadzu LC system (Shimadzu, Columbia, MD, USA) with a pump (LC-20AT), a photodiode array (PDA) detector (SPD-M20A), and an LC column (Eclipse plus C18, 3.5 μ m, 4.6 \times 100 mm, Agilent, Santa Clara, CA, USA). Gradient method was adopted using 0.1% TFA-H₂O and acetonitrile (ACN) as a mobile phase. The UV wavelength for detecting the imide molecules was set at 218 nm.

Synthesis of TAED derivatives

Typically, propylene-1,2-diamine ((Me)ED) (1.0 g, 13.5 mmol) was first cooled to 0 °C in an ice bath, where acetic anhydride (Ac₂O) (5.74 mL, 60.7 mmol, 4.5 equiv.) was carefully added dropwise (Caution: the reaction between primary amine and acid anhydride is exothermic under solvent-free conditions. Careful cooling is needed to prevent overheating of the mixture). The conversion of (Me)ED to *N,N'*-diacetylpropylene-1,2-diamine (DA(Me)ED) was completed within 10 s under solvent-free conditions. Anhydrous

triethylamine (TEA) (6.58 mL, 47.2 mmol, 3.5 equiv.) was then added into the mixture, and the mixture was stirred at 100 °C for 20 h. The crude product was dissolved in dichloromethane (DCM), which was then washed three times with distilled (DI) water. The solvent DCM was removed under vacuum, and the products *N,N,N',N'*-tetracetylpropylene-1,2-diamine (TA(Me)ED) and *N,N,N'*-triacetylpropylene-1,2-diamine (TriA(Me)ED) were purified from silica gel column chromatography (EtOAc:hexane as eluent, from 1:2 to 10:1 ratio, v/v). TriA(Me)ED was further purified by recrystallization from DCM:ether:hexane, which was obtained as white needle-like crystals. TA(Me)ED was obtained as a light yellow viscous oil.

DA(Me)ED: ¹H NMR (CDCl₃, δ , 500 MHz): 6.44 (s, 1H, -NHCH(CH₃)CH₂NH-), 6.18 (s, 1H, -NHCH(CH₃)CH₂NH-), 4.03 (m, 1H, -NHCH(CH₃)CH₂NH-), 3.34 (m, 1H, -NHCH(CH₃)CH₂NH-), 3.20 (m, 1H, -NHCH(CH₃)CH₂NH-), 1.98 (s, 3H, CH₃C(=O)-), 1.96 (s, 3H, CH₃C(=O)-), 1.16 (d, *J* = 6.68 Hz, 3H, -NHCH(CH₃)CH₂NH-). ESI-MS: *m/z*, [M + H]⁺ Calcd. for C₇H₁₅N₂O₂ 159.1134; Found: 159.1130.

TriA(Me)ED: ¹H NMR (CDCl₃, δ , 500 MHz): 5.86 (s, 1H, -NHCH(CH₃)CH₂-), 4.16 (m, 1H, -NHCH(CH₃)CH₂-), 3.97 (dd, *J*₁ = 9.74 Hz, *J*₂ = 14.8 Hz, 1H, -NHCH(CH₃)CH₂-), 3.55 (dd, *J*₁ = 5.10 Hz, *J*₂ = 14.8 Hz, 1H, -NHCH(CH₃)CH₂-), 2.44 (s, 6H, CH₃C(=O)-), 1.91 (s, 3H, CH₃C(=O)-), 1.17 (d, *J* = 6.56 Hz, 3H, -NHCH(CH₃)CH₂-). ¹³C NMR (CDCl₃, δ , 500 MHz): 174.2, 170.2, 48.5, 46.0, 26.4, 23.5, 18.7. ESI-MS: *m/z*, [M + H]⁺ Calcd. for C₉H₁₇N₂O₃ 201.1239; Found: 201.1242.

TA(Me)ED: ¹H NMR (CDCl₃, δ , 500 MHz): 4.30 (m, 1H, -CH(CH₃)CH₂-), 4.04 (d, *J* = 6.88 Hz, 2H, -CH(CH₃)CH₂-), 2.38 (s, 6H, CH₃C(=O)-), 2.33 (s, 6H, CH₃C(=O)-), 1.38 (d, *J* = 6.93 Hz, 3H, -CH(CH₃)CH₂-). ¹³C NMR (CDCl₃, δ , 500 MHz): 174.8, 174.2, 53.0, 48.6, 26.4, 15.9. ESI-MS: *m/z*, [M + Na]⁺ Calcd. for C₁₁H₁₈N₂O₄Na 265.1164; Found: 265.1165.

Hydrolysis and perhydrolysis of imide molecules

TAED, TA(Me)ED, or TriA(Me)ED were dissolved in a water:ACN (3:1, v/v, 1 mg/mL, aqueous pH 4.0) and stored on ice to minimize the hydrolysis before analysis. The stock solution was then diluted with a water:ACN with target pH (5.0, 7.2, 8.0, or 9.0), such that the final concentration of imide molecules was 50 μ g/mL. The solution was then incubated at room temperature. At different time intervals, an aliquot of the solution was taken out and analyzed by HPLC. The concentration of imide molecules was calculated based on standard curves.

For analysis of perhydrolysis, sodium perborate was first dissolved in a water:ACN (3:1, v/v, 10 mg/mL, aqueous pH 7.2) and stored on ice. The molar ratio of sodium perborate and imide molecules is 10:1 in the final solution.

Bleaching test

The blue-color food dye was diluted 100 times with pH 8.0 buffer, which was then mixed with H₂O₂ (30%) at 1:1 ratio (v/v). TAED, TA(Me)ED, and TriA(Me)ED (20 mg) were then mixed with the dye-H₂O₂ solution (2.0 mL) under dark, which was checked at different time intervals for the color change. The hydrolytic/perhydrolytic degradation product, DAED and DA(Me)ED, were used as the control groups in the bleaching test.

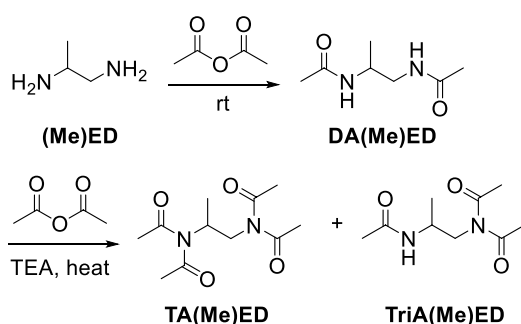


Fig. 1 Synthetic routes to TA(Me)ED and TriA(Me)ED

Table 1 Optimization of synthetic conditions for TA(Me)ED and TriA(Me)ED

Entry	Reaction time (h)	Anhydride equiv	<i>T</i> (°C)	Base ^a	Solvent	Conversion (%) ^b
1	1	5	100	–	–	11.2
2	3	5	100	–	–	24.6
3	9	5	100	–	–	53.5
4	17	5	100	–	–	69.0
5	9	6	100	–	–	60.6
6	9	7	100	–	–	68.4
7	9	8	100	–	–	79.2
8	9	5	130	–	–	60.1
9	9	5	150	–	–	59.5
10	9	5	170	–	–	36.8
11	17	4.5	100	TEA	–	87.1
12	17	4.5	100	–	Toluene	54.9
13	17	4.5	100	TEA	Toluene	44.7
14 ^c	20	4.5	100	TEA	–	83.1

All reactions were carried out with 100 mg (Me)ED unless specified. The added base is always 3.5 equiv compared with (Me)ED; the added solvent is always 1 mL

^aTEA triethylamine

^bConversion of DA(Me)ED to TriA(Me)ED, which was calculated by the integration ratio of peaks at 3.51–3.94 ppm (methylene protons from TriA(Me)ED) to peaks at 3.06–3.42 ppm (methylene protons from DA(Me)ED) in ¹H NMR spectra

^cStart with 1 g (Me)ED

Results and discussion

Optimization of synthetic conditions

TA(Me)ED and TriA(Me)ED were synthesized by treating propylene-1,2-diamine ((Me)ED) with a molar excess of acetic anhydride (Ac₂O) at elevated temperatures (Fig. 1), a similar process with the synthesis of TAED [13, 14]. To maximize the conversion, the synthetic conditions were first optimized in small scales. As shown in Table 1, (1) The elongation of reaction time resulted in a higher conversion of (Me)ED, where the conversion reached ~70% after 17 h heating at 100 °C (Entry 1–4). (2) The increase in anhydride equivalents led to higher conversion but caused potential purification issues due to the excessive Ac₂O (Entry 5–7). (3) Further increase of reaction temperature above 100 °C gave lower conversion, likely due to the decomposition of the imide product (Entry 8–10). (4) Addition of triethylamine (TEA) as a base significantly enhanced the conversion, which was attributed to the consumption of AcOH byproduct and the shift of reaction equilibrium (Entry 11). (5) Adding solvents did not improve the conversion (Entry 12–13). Therefore, we used the neat reaction at 100 °C for 20 h as the final condition for the large scale synthesis of TA(Me)ED and TriA(Me)ED, where the feeding ratio is [(Me)ED]₀: [Ac₂O]₀: [TEA]₀ = 1:4.5:3.5 (mol/mol/mol). This optimized reaction condition was tested with large

batch synthesis, where > 80% conversion was obtained by ^1H NMR that is consistent with the small scale trials (Entry 14). After the purification and separation through flash column chromatography, the molecular structures of both TA(Me)ED and TriA(Me)ED were confirmed by NMR and ESI-MS (Fig. 2).

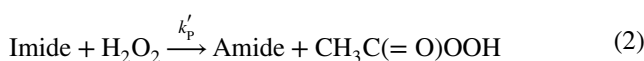
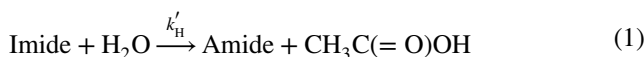
Hydrolytic and perhydrolytic activity

To get a quantitative understanding of how the added methyl group alters the hydrolytic behavior, HPLC was used to analyze the hydrolytic and perhydrolytic activity of both TA(Me)ED and TriA(Me)ED (Fig. 3a). Similar to TAED, the hydrolytic behaviors of both imide molecules were dependent on the pH value, with faster hydrolysis occurring at higher pH. The hydrolysis of TA(Me)ED and TriA(Me)ED were negligible at an acidic and neutral pH, with < 15% degradations after 30 days at room temperature (Fig. 3b, c). At a basic pH ($\text{pH} \geq 8$), however, both TA(Me)ED and TriA(Me)ED were degraded, with increased hydrolysis rates under more basic conditions (Fig. 3d, e). Compared with TAED, the improved hydrolytic stability of TA(Me)ED and TriA(Me)ED was attributed to the enhanced steric hindrance due to the incorporation of the methyl group close to the imide groups. The higher hydrolysis rate of TAED was attributed to the presence of imide groups with less steric hindrance, which exhibited faster hydrolysis compared with those closer to the methyl group. In addition, an increase in the hydrophobicity of TA(Me)ED and

TriA(Me)ED may also provide increased hydrolytic stability. Interestingly, all three molecules were rapidly perhydrolyzed in the presence of 10 equivalents of sodium perborate at pH 8.0, where more than 80% consumption was observed after 24 h (Fig. 3f). This result is consistent with previous studies, which demonstrated the stronger nucleophilicity of peroxide anions than hydroxide anions due to the alpha effect [15].

Determination of hydrolytic and perhydrolytic rate constants

The kinetics of hydrolysis and perhydrolysis of imide molecules can be written as follows:



In the absence of sodium perborates, the imide molecules were only consumed by hydrolysis. Due to the large excess of water, the hydrolysis followed a pseudo first-order kinetics:

$$-\frac{d[\text{Imide}]}{dt} = k'_H[\text{Imide}][\text{H}_2\text{O}] = k_H[\text{Imide}] \quad (3)$$

In the presence of sodium perborates, the imide molecules were consumed by both hydrolysis and perhydrolysis. The large excess of water and sodium perborates (10 equiv.)

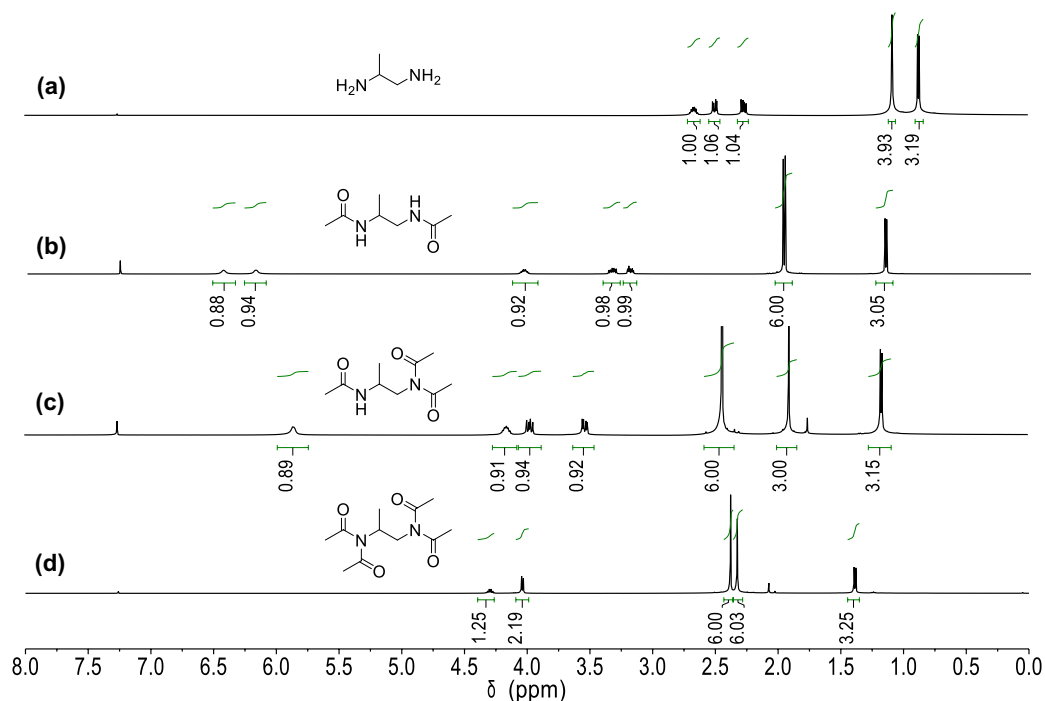


Fig. 2 Stacked ^1H NMR spectra of (Me)ED (a), DA(Me)ED (b), TriA(Me)ED (c), and TA(Me)ED (d) in CDCl_3 (500 MHz)



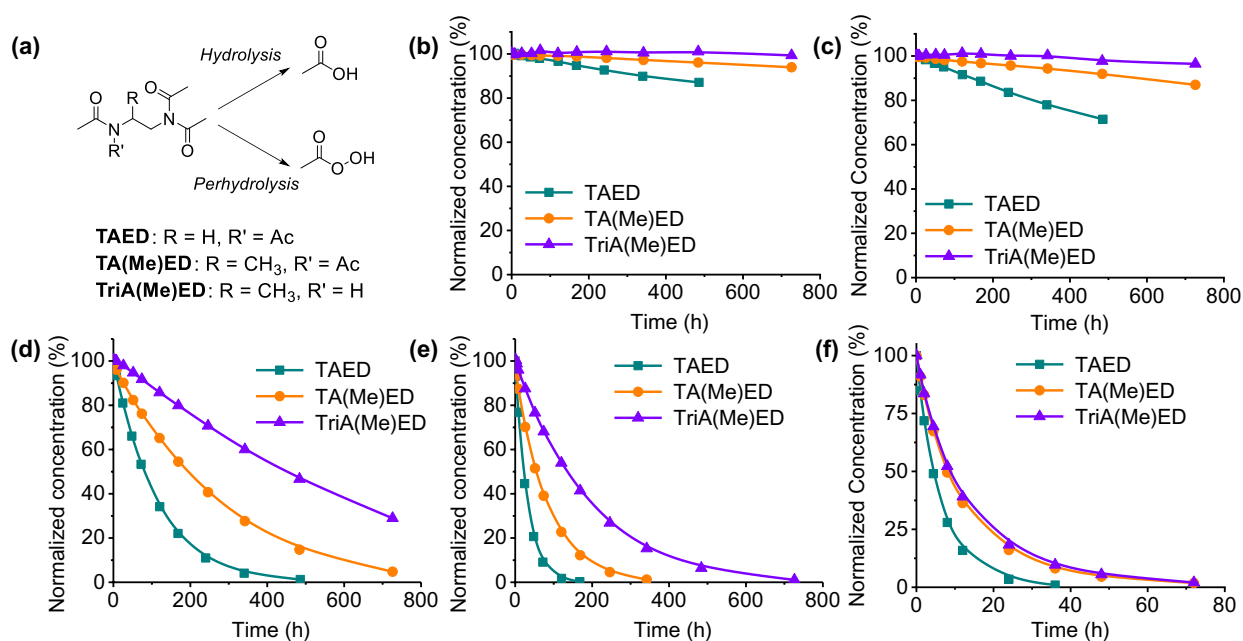


Fig. 3 Hydrolytic and perhydrolytic kinetics of imide molecules. **a** Scheme illustrating the hydrolysis and perhydrolysis of TAED, TA(Me)ED, and TriA(Me)ED. **b–e** Hydrolysis of TAED, TA(Me)ED, and TriA(Me)ED at aqueous pH 5.0 (**b**), 7.2 (**c**), 8.0 (**d**), and 9.0 (**e**)

in water:ACN (3:1, v/v). **f** Perhydrolysis of TAED, TA(Me)ED, and TriA(Me)ED in the presence of sodium perborate (10 equiv.) at aqueous pH 8.0 in water:ACN (3:1, v/v). [Imide]₀ = 50 μg/mL

makes a pseudo first-order kinetics, where the apparent rate constant is the sum of k_H and k_P :

$$-\frac{d[\text{Imide}]}{dt} = k'_H[\text{Imide}][\text{H}_2\text{O}] = k'_P[\text{Imide}][\text{H}_2\text{O}_2] \\ = k_H[\text{Imide}] + k_P[\text{Imide}] = (k_H + k_P)[\text{Imide}] \quad (4)$$

Therefore, k_H and k_P were obtained from the linear fitting of $\ln([\text{Imide}]_0/[\text{Imide}]_t)$ vs time plot according to Eqs. 3 and 4 (Fig. 4 and Table 2).

The hydrolysis of all three molecules followed pseudo first-order kinetics [16], where the hydrolytic rate constant (k_H) at pH 8.0 was determined to be $9.1 \times 10^{-3} \text{ h}^{-1}$,

$3.8 \times 10^{-3} \text{ h}^{-1}$, and $1.5 \times 10^{-3} \text{ h}^{-1}$ for TAED, TA(Me)ED, and TriA(Me)ED, respectively (Table 2). Compared with TAED, k_H decreased by 58% and 84% for TA(Me)ED and TriA(Me)ED, respectively, suggesting their better hydrolytic stability due to the added α -methyl group. On the other hand, the perhydrolytic rate constant (k_P) was similar among three imide molecules, which was determined to be $1.26 \times 10^{-1} \text{ h}^{-1}$, $5.8 \times 10^{-2} \text{ h}^{-1}$, and $5.7 \times 10^{-2} \text{ h}^{-1}$ for TAED, TA(Me)ED, and TriA(Me)ED, respectively (Table 2).

The ratio of k_P to $(k_H + k_P)$ allowed us to estimate the theoretical values of generated PAA equivalents of the bleach activators, which were calculated to be 1.87 and 0.97 for TA(Me)ED and TriA(Me)ED at pH 8.0, respectively. While

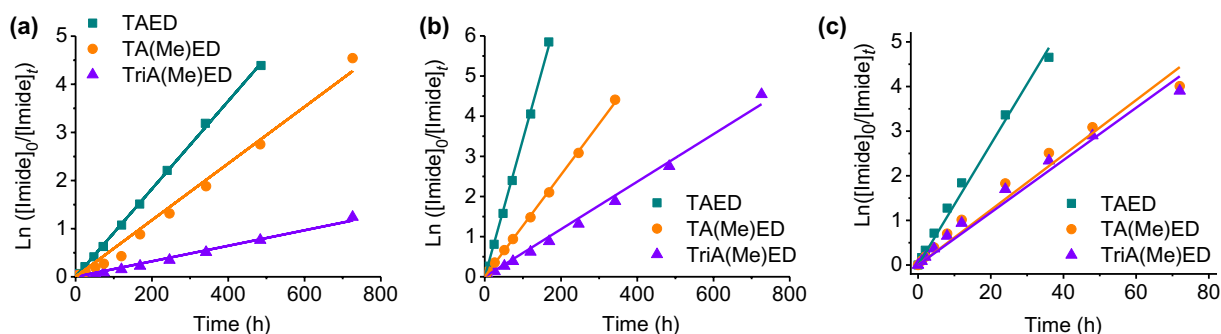


Fig. 4 Determination of hydrolytic and perhydrolytic rate constants. **a, b** $\ln([\text{Imide}]_0/[\text{Imide}]_t)$ vs time plot for the hydrolytic degradation of TAED, TA(Me)ED, and TriA(Me)ED at pH 8.0 (**a**) and 9.0 (**b**) in

water:ACN (3:1, v/v). **c** $\ln([\text{Imide}]_0/[\text{Imide}]_t)$ vs time plot for the perhydrolytic degradation of TAED, TA(Me)ED, and TriA(Me)ED at pH 8.0 in water:ACN (3:1, v/v)

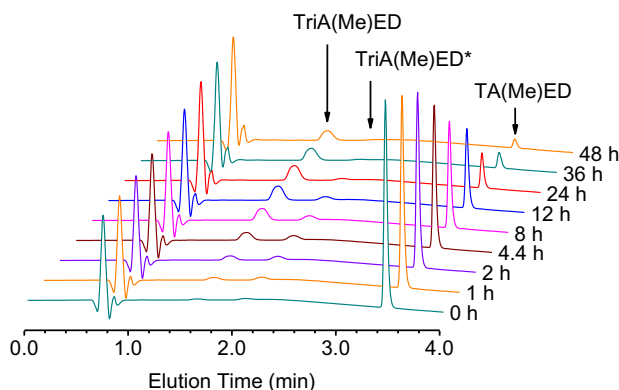


Table 2 Hydrolytic and perhydrolytic kinetics of TAED, TA(Me)ED, and TriA(Me)ED

Compound	pH 8.0			pH 9.0
	k_H (h^{-1}) ^a	$(k_H + k_p)$ (h^{-1}) ^a	k_p (h^{-1})	k_H (h^{-1}) ^a
TAED	$(9.1 \pm 0.1) \times 10^{-3}$	$(1.35 \pm 0.03) \times 10^{-1}$	1.26×10^{-1}	$(3.4 \pm 0.1) \times 10^{-2}$
TA(Me)ED	$(3.8 \pm 0.1) \times 10^{-3}$	$(6.2 \pm 0.2) \times 10^{-2}$	5.8×10^{-2}	$(1.3 \pm 0.1) \times 10^{-2}$
TriA(Me)ED	$(1.5 \pm 0.1) \times 10^{-3}$	$(5.9 \pm 0.2) \times 10^{-2}$	5.7×10^{-2}	$(5.9 \pm 0.1) \times 10^{-3}$

All hydrolytic and perhydrolytic reactions were carried out in water:ACN (3:1, v/v). Rate constants: k_H , hydrolytic rate constant; k_p , perhydrolytic rate constant

^aDetermined by the slopes in Fig. 4

**Fig. 5** Stacked HPLC traces revealing the intermediates during the perhydrolysis of TA(Me)ED at pH 8.0 in water:ACN (3:1, v/v)

TriA(Me)ED shows higher efficiency of perhydrolysis due to slower hydrolysis rate, it only contains one imide group molecule that leads to lower PAA equivalents than TA(Me)ED.

Analysis of intermediates

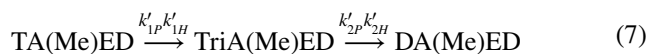
During the perhydrolysis of TA(Me)ED, two new peaks were observed on the HPLC traces (Fig. 5). While the first peak had the same elution time compared with TriA(Me)ED, the second peak was attributed to the other triacetyl-substituted propylene-1,2-diamine, where an imide group was formed on the more sterically hindered side (Fig. 6a, referred to as TriA(Me)ED*). The perhydrolytic intermediates were separated using semi-preparative HPLC and their molecular structures were confirmed by NMR (Fig. 7).

In the presence of sodium perborates, TA(Me)ED was first converted to both TriA(Me)ED and TriA(Me)ED* through hydrolysis and perhydrolysis. Both TriA(Me)ED and TriA(Me)ED* were then reacted with water or hydrogen peroxide to generate the final product, *N,N'*-diacetylpropylene-1,2-diamine (DA(Me)ED) (Fig. 6a). In such a cascade reaction, the intermediate compound (*i.e.*, TriA(Me)ED and TriA(Me)ED*) reached a maximum concentration at $t = t_{\max}$. The value of t_{\max} was directly related to the rate constants [17]:



$$t_{\max} = \frac{\ln(k_1/k_2)}{k_1 - k_2} \quad (6)$$

Based on Eq. 5, the cascade reactions in the hydrolysis and perhydrolysis of TA(Me)ED was described as follows:



The t_{\max} values were obtained from Fig. 6b, where $t'_{\max} = 19.5$ h for TriA(Me)ED, and $t''_{\max} = 5.5$ h for TriA(Me)ED*. Since $(k'_{1P} + k'_{1H}) + (k''_{1P} + k''_{1H}) = 0.062$ h^{-1} , $(k'_{2P} + k'_{2H}) = 0.058$ h^{-1} (Table 2), it is, therefore, straightforward to calculate $(k'_{1P} + k'_{1H})$ and $(k''_{2P} + k''_{2H})$ according to Eq. 6, which was determined to be 0.045 h^{-1} and 0.70 h^{-1} , respectively. The summary of all rate constants involved in the perhydrolysis of TA(Me)ED at pH 8.0 was shown in Fig. 6d.

The sum of hydrolytic and perhydrolytic rate constants ($k_H + k_p$) of TriA(Me)ED* (0.70 h^{-1}) was much larger than that of TriA(Me)ED (5.8×10^{-2} h^{-1}), suggesting the poor stability of TriA(Me)ED* in the presence of hydroxide or perhydroxide anions. Because of its instability, TriA(Me)ED* was not observed during the hydrolysis of TA(Me)ED (Fig. 6c).

Since the new bleach activators and their degradation products have similar structures with that of TAED, we expect they show similar biodegradability and safety profile with TAED [18]. More detailed safety study will be included in future publications.

Bleaching test

Compared with TAED, the enhanced hydrolytic stability and the comparable rapid perhydrolysis of TA(Me)ED and TriA(Me)ED makes them promising candidates as new bleach activators for liquid laundry formulations.

Fig. 6 Analysis of the intermediates during hydrolysis and perhydrolysis of imide molecules. **a** Scheme showing the intermediates and final products during the hydrolysis and perhydrolysis of TA(Me)ED. **b, c** The reaction profile vs reaction time for the perhydrolysis (**b**) and hydrolysis (**c**) of TA(Me)ED at aqueous pH 8.0 in water:ACN (3:1, v/v). **d** Summary of rate constants involved during the perhydrolysis of TA(Me)ED. $[\text{Imide}]_0 = 50 \mu\text{g/mL}$, for perhydrolysis, $[\text{sodium perborate}] = 10 \text{ equiv.}$ of imide molecules

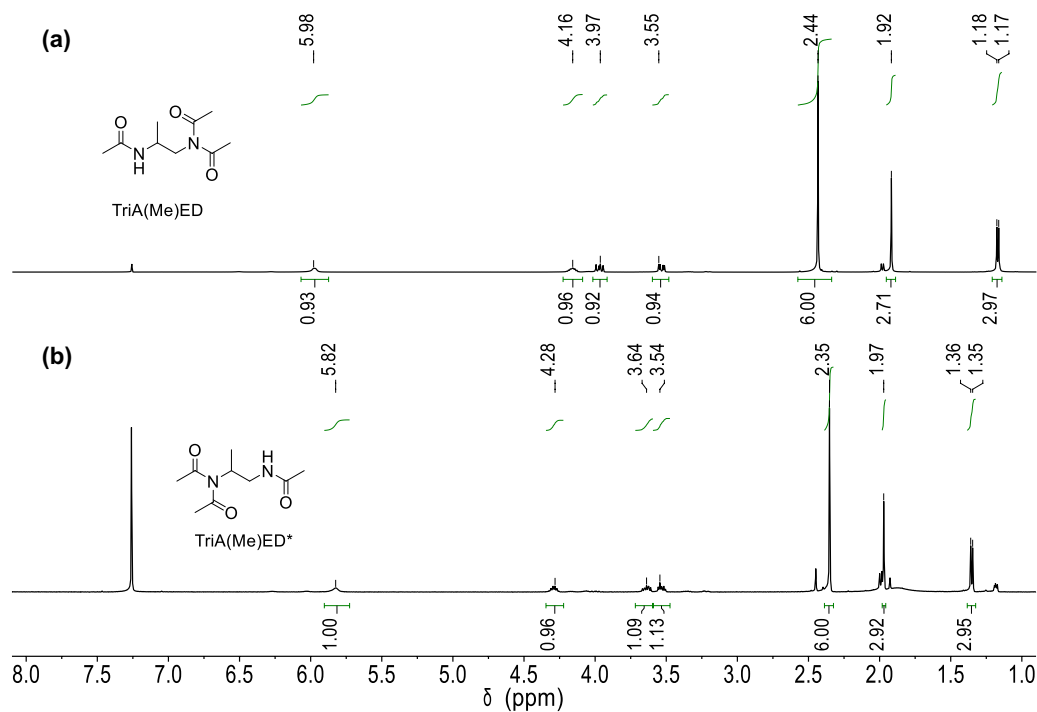
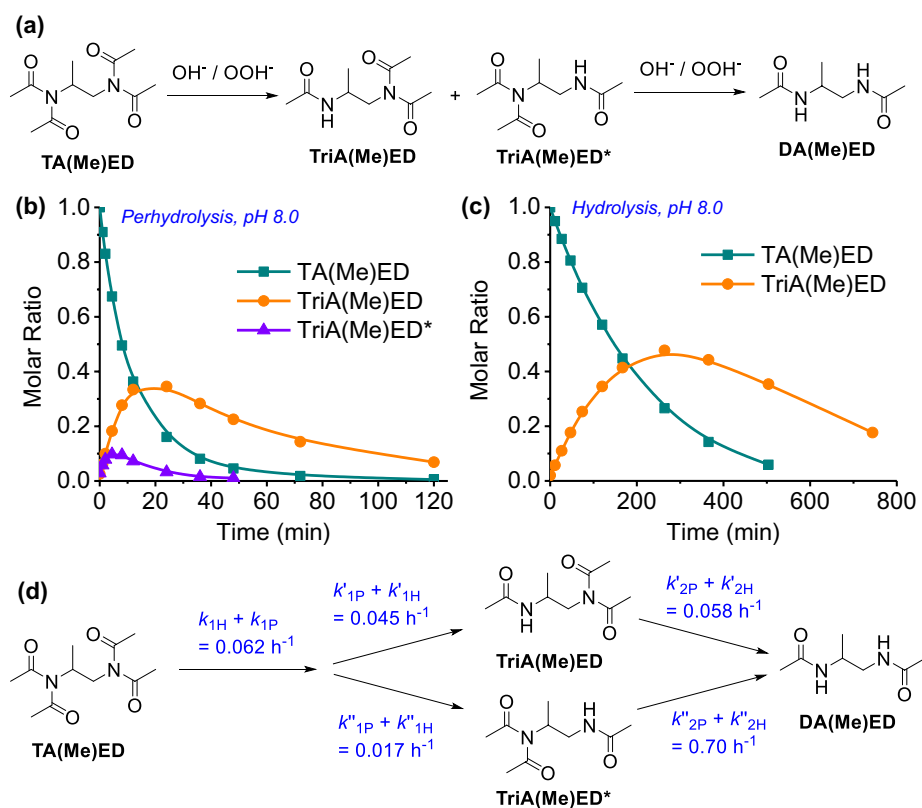


Fig. 7 ^1H NMR spectra of separated perhydrolysis intermediates of TA(Me)ED, TriA(Me)ED (**a**) and TriA(Me)ED (**b**), in CDCl_3 (500 MHz)



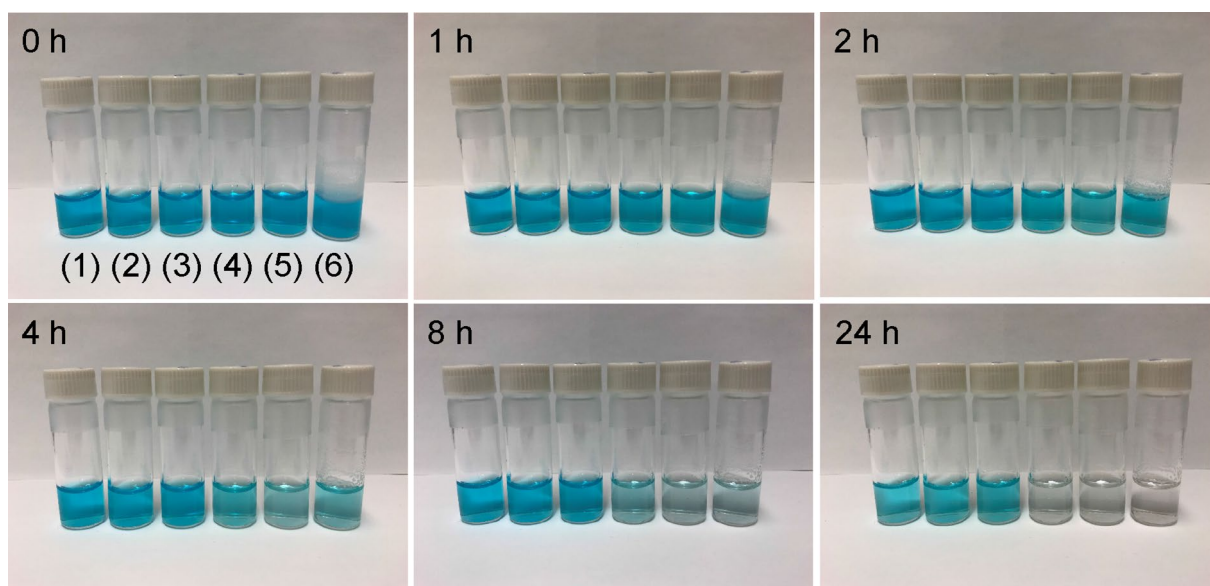


Fig. 8 Photographs showing the quenching of a blue-color food dye over time with H_2O_2 in the presence of various imide/amide molecules. (1) control, (2) DAED, (3) DA(Me)ED, (4) TriA(Me)ED, (5)

TA(Me)ED, (6) TAED. Final conditions: pH 8.0, $[\text{H}_2\text{O}_2]_0 = 15\%$, $[\text{imide/amide}]_0 = 10 \text{ mg/mL}$

To demonstrate their bleaching activity, TA(Me)ED and TriA(Me)ED were mixed with hydrogen peroxide (H_2O_2) at pH 8.0, and their ability to bleach a blue-color food dye was monitored for 24 h. In the presence of TA(Me)ED and TriA(Me)ED, the blue colors began to fade away ~4 h after mixing, and completely disappeared after 24 h (Fig. 8). The bleaching profiles of TA(Me)ED and TriA(Me)ED resembled that of TAED, indicating similar activity as bleach activators. TriA(Me)ED exhibited slightly slower bleaching kinetics, which was attributed to the lower PAA equivalents compared with TAED and TA(Me)ED. On the contrary, the control molecules without imide groups, including DA(Me)ED and *N,N'*-diacetylenediamine (DAED), exhibited negligible bleaching activity after 24 h, further validating that the bleaching originates from the imide groups of the molecules.

Conclusion

In summary, it was demonstrated that the hydrolytic activity of imide molecules was improved by adding a methyl group to the ethylenediamine core structure. The resulting compounds, TA(Me)ED and TriA(Me)ED, exhibited a slower hydrolysis and similar perhydrolysis compared with TAED, rendering them as promising bleach activators for liquid laundry formulations.

Acknowledgements This work was supported by The Dow Chemical Company.

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