Chemistry of Long-Chain Peroxy Acids Under Laundry Conditions[1]

T.A.B.M. Bolsman*, R. Kok and A.D. Vreugdenhil
Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research B.V.) P.O. Box 3003, 1003 AA Amsterdam, The Netherlands

Peroxycarboxylic acids are increasingly used as bleaching agents for the laundering process. These peroxy acids can be added as such to the wash liquor or may be generated in situ by reaction of a precursor component with hydrogen peroxide. Bleaching effectiveness appears to be determined by a delicate balance of chemical reactions of peroxy acid with the staining dyes and the rate of peroxy acid decomposition under the prevailing conditions. To improve our understanding of the chemistry involved we have carried out a systematic study using a range of aromatic and aliphatic mono- and diperoxycarboxylic acids with various carbon chain lengths and degrees of branching. We investigated peroxy acid decomposition, bleaching of stained fabric and bleaching of a water-soluble dye, and showed that the alkyl chain length of the peroxy acids, the presence of detergent components and the pH of the medium are important factors. Combination of the kinetic data for decomposition and bleaching reactions allows the selection of structures and conditions for optimum performance.

Bleaching is an essential process in fabric washing to remove certain stains. Traditionally, the European heavy-duty powders contain sodium perborate as the bleaching compound, whereas in the U.S. a separate hypochlorite bleach treatment is common practice. This difference in approach originates from the much higher washing temperature formerly used in most European countries (up to 95 C). However, the lowering in washing temperature from 90 to 40-60 C has reduced the effectiveness of the perborate system considerably. For proper hydrogen peroxide action, generated from perborate during the wash process, a temperature of at least 70 C is required. Therefore, new bleaching systems have been developed to maintain the performance at the reduced washing temperatures.

One option is the use of "activated systems," in which a peroxycarboxylic acid is generated in situ by reaction of the perhydroxyl anion with a precursor compound (1-3). Widely known are tetraacetylethylenediamine (TAED) and nonanoyloxybenzenesulphonate (NOBS), generating peroxyacetic and peroxynonanoic acid, respectively (4,5). Another approach is the direct use of peroxycarboxylic acids in the laundry formulation (6). Commercially available are magnesium monoperoxyphthalate (7) and diperoxydodecane-1,12-diacid (DPDDA) (8).

To improve our understanding of the relation between peroxy acid structure and bleaching performance, we have conducted a study using a range of aliphatic mono- and diperoxycarboxylic acids, of various carbon chain lengths and degrees of branching, and some aromatic peroxy acids. Bleaching of stained fabric, solution bleaching of a water-soluble dye and peroxy acid decomposition were investigated as a function of peroxy acid concentration, pH value and temperature. Results obtained were used to quantify the bleaching action of the peroxy acids in terms of an apparent bleaching rate constant, to facilitate the selection of peroxy acid structures and conditions for optimum performance.

EXPERIMENTAL

Peroxy acid synthesis. The peroxy acids have been prepared following standard procedures (9-15). The purity was determined by iodometric titration in a chloroform/acetic acid mixture (9). With the linear peroxyalkanoic acids a nearly quantitative conversion was reached, yielding peroxy acids with a purity above 90%. An increase in the amount of branching resulted in less pure peroxy acids (Table 1).

Fabric bleaching. The bleaching performance was evaluated by washing cotton and permanent-press polyester/cotton test fabric (size 10 × 10 cm) soiled with red wine, coffee and tea. This fabric was custom prepared by Waescherei Forschung Krefeld in Germany. The reflectance of the stained fabric was measured before (on average, ca. 51 for wine, 30 for coffee and 32 for tea) and after washings with an ElrephomatDFC5 with D65 light source, blue filter R46 and UV filter FL46. The reflectance data of each stain were averaged for the two fabrics, the stain removal being calculated with the Kubelka-Munk equation (16).

The washings were carried out in a Terg-O-Tometer (50 cycles/min) at a water hardness of 300 ppm (Ca ions only, expressed as $CaCO_3$). Each beaker contained six stained swatches (one cotton and one polyester/cotton for each stain) and two swatches (cotton and polyester/cotton) soiled with the standard Krefeld soil. During the washing experiments the pH value was kept constant by adding sodium hydroxide solution on a continuous basis. In most of the experiments the washing time was fixed at 20 min. After the washing cycle the fabric was squeezed and rinsed twice in one l water of the same hardness as used in the washing cycle.

The detergent solution consisted of a surfactant mixture of LAS/nonionic/soap and a phosphate-based builder system (Table 2, system A). No perborate was included in the basic system. After the wash solution had come to temperature, the soiled fabric was introduced, followed by the peroxy acids. In the experiments in which the variation of peroxy acid structure was investigated, the peroxy acids were added as solids. When peroxy acid concentration, pH value and washing time were varied, the peroxy acids were added as a 4 w% solution in tert-butanol, to minimize dissolution effects. In a separate experiment the effect of parent acid impurities was shown to be negligible.

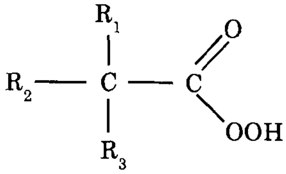
Bleaching of a water-soluble dye. The chemical bleaching activity of the peroxy acids was assessed via the rate of oxidation of the water-soluble dye Coomassie Brilliant Blue G250 (Aldrich) (15). The concentration of the dye was fixed at ca. 0.008 mmol/l, which allowed

---

[1] Presented at the AOCS meeting in New Orleans in May 1987.
*To whom correspondence should be addressed.

TABLE 1

Peroxy Acid Structure



Peroxy acid	Structure no.	R_1	R_2	R_3	Purity (%)
	I	n-C_8H_{17}	H	H	97
Aliphatic	II	n-$C_{10}H_{21}$	H	H	92
monoperoxy acid	III	n-$C_{12}H_{25}$	H	H	84
	IV	n-$C_{14}H_{29}$	H	H	95
	V	n-$C_{13}H_{23}$	CH_3	H	90
	VI	n-$C_{12}H_{21}$	C_2H_5	H	44
	VII	n-$C_{12}H_{21}$	CH_3	CH_3	25
Aliphatic	VIII	n-$C_{10}H_{21}$	H	CH_2CO_3H	92
diperoxy acid	IX	n-$C_{14}H_{29}$	H	CH_2CO_3H	88
	X	n-C_6H_{13} n-C_7H_{15}CH-	H	CH_2CO_3H	87
	XI	H	H	$(CH_2)_9CO_3H$	89
Aromatic	XII	p-tert-butylperbenzoic			82
peroxy acid	XIII	monoperoxyphthalic (Mg salt)			

TABLE 2

Detergent Systems

System A	
C_{11}-C_{13} linear alkylbenzenesulfonate	0.46 g/l
C_{16}-C_{18} alcohol + 14 EO C_{12}-C_{22} fatty acid soap	0.18 g/l 0.15 g/l
Sodium tripolyphosphate	1.70 g/l
Sodium silicate	0.23 g/l
Sodium sulfate	1.20 g/l
Ethylenediaminetetraacetic acid	0.01 g/l
Optical brightener	0.01 g/l
Carboxymethylcellulose	0.05 g/l
System B	
C_{10}-C_{13} linear alkylbenzenesulfonate	0.25 g/l
C_{12}-C_{15} alcohol + 7 EO	0.25 g/l
Sodium tripolyphosphate	1.50 g/l
Sodium silicate	0.24 g/l
Sodium sulfate	0.60 g/l

measurement in the linear part of the extinction vs dye concentration curve. The discoloration was monitored with a dipped probe photometer operating at a wavelength of 630 nm. The initial bleaching rate was calculated from the decrease in extinction from 100% to 70% of the initial value.

The pH was kept constant automatically by continuous addition of sodium hydroxide solution. The peroxy acids were added as 4 w% solutions in tert-butanol to the test solution containing the dye and a detergent system (Table 2, system B). Water hardness was 300 ppm Ca (expressed as $CaCO_3$). With the higher-molecular peroxy acids (from C_{14} upward) the extinction measurements had to be corrected for a background absorption caused by the turbidity in the system.

Peroxy acid decomposition. The rate of the decomposition of the peroxy acids was determined under the same conditions as used during fabric and solution bleaching. The experiments were carried out in a 500-ml double-walled vessel provided with a mechanical stirrer and with automatic pH control. Samples (50 g) were taken through a bottom stopcock and run into an acetic acid/chloroform mixture. The amount of peroxy acid was titrated potentiometrically. A number of samples were checked for the presence of hydrogen peroxide by repeating the titration in the presence of titanyl sulfate, which deactivates the hydrogen peroxide (19). Hardly any hydrogen peroxide was found; therefore, this procedure was omitted in most of the experiments.

RESULTS

Fabric bleaching. Table 3 presents the bleaching performance of a series of mono- and diperoxy acids. The highest level of stain removal is obtained with p-tert-butylperbenzoic acid (XII). Peroxydecanoic acid (I) and diperoxydecylsuccinic acid (VIII) perform at a slightly lower level, comparable to that of the reference TAED/perborate system. An increase in the length of the alkyl chain of both the peroxyalkanoic and the diperoxysuccinic acids reduces the bleaching activity considerably, and the performance drops below even that of the perborate only system. No clear effect of branching of peroxyhexadecanoic acids (V-VII) or diper-

TABLE 3

Fabric Bleaching: Effect of Peroxy Acid Structure[a]

Bleach		% Stain removal Red wine	 Coffee	 Tea
No bleach		81	90	74
Perborate[b]		89	93	80
TAED/perborate[c]		94	95	89
Aliphatic	I	94	96	86
monoperoxy acid	II	91	94	75
	III	89	94	77
	IV	86	92	75
	V	87	92	76
	VI	88	92	78
	VII	88	93	75
Aliphatic	VIII	91	95	87
diperoxy acid	IX	86	93	79
	X	89	93	74
Aromatic	XII	96	97	91
monoperoxy acid	XIII	89	94	85
LSD[d]		1.6	1.0	2.2

[a] Temp. 40 C; pH 9.5; 3.5 mmol active O per 1, assuming release of 1 mmol active O per mmol mono- and 2 mmol O per mmol diperoxy acid.

[b] 8.3 mmol/l sodium perborate.

[c] 1.75 mmol/l TAED, 8.3 mmol/l sodium perborate.

[d] Least significant difference at 95% confidence level (in all tables).

oxytetradecylsuccinic acids (VIII-X) on the bleaching performance was seen.

For the most promising peroxy acids the effect of the peroxy acid concentration on the degree of stain removal is presented in Table 4. With peroxydecanoic- (I) and p-tert-butylperbenzoic (XII) acid a performance plateau is reached at 2 mmol active oxygen (avox)/1. The bleaching by diperoxydecylsuccinic acid (VIII) and monoperoxyphthalic acid (XIII) does not reach the performance of I and XII.

A reduction in pH value from 9.5 to 8.5 improves the bleaching properties of monoperoxyphthalic acid (XIII), whereas the performance of the other three peroxy acids is affected only marginally over the indicated pH range (Table 5).

Soil removal data as a function of washing time (Table 6) show the concurrent stain removal by the detergent and the bleach system. In these experiments the inferior performance of peroxytetradecanoic acid is confirmed, stain removal being brought about only by detergency of the surfactant. A reasonable fit for the stain removal against time was found by treating stain removal as a third-order reaction. Figure 2 presents $1-(S_o/S_t)^2$ versus time for the removal of coffee and tea stains by peroxy acids (I and VIII) and by the sole detergent as a reference (S_o and S_t are amounts of stain on the fabric at times zero and t).

Bleaching of a water-soluble dye. In order to facilitate the study of the intrinsic difference in bleaching performance between lyphophilic peroxy acids, thus excluding, for instance, adsorption phenomena, we measured the rate of oxidation of Coomassie Brilliant Blue G250, a water-soluble dye (15). The rate of bleaching is best represented by a log dye concentration versus time plot. Typical plots obtained for a number of peroxy acids are presented in Figure 2. The derived initial bleaching rate constants of all peroxy acid structures are presented in Table 7.

A notable difference is observed for the various peroxy acid structures between solution bleaching and fabric bleaching. In the case of solution bleaching the diperoxyalkylsuccinic acids show the highest bleaching rates, whereas during fabric bleaching the p-tert-butylperbenzoic acid gave the best performance. With the peroxyalkanoic acids an increase in rate was found with increasing alkyl chain length, the highest rate

TABLE 4

Fabric Bleaching: Effect of Peroxy Acid Concentration[a]

Beach		Peroxy acid conc. mmol O per 1[b]	% Stain removal Red wine	 Coffee	 Tea
No bleach			80	90	70
Aliphatic	I	1	89	94	80
monoperoxy acid		2	91	95	89
		3	92	95	84
Aliphatic	VIII	1	88	93	78
diperoxy acid		2	88	93	81
		3	89	94	85
Aromatic	XII	1	91	95	86
monoperoxy acid		2	93	95	90
		3	93	96	88
	XIII	1	85	92	79
		2	86	93	80
		3	87	93	80
LSD			1.4	0.8	2.0

[a] Temp. 40 C; pH 9.5.

[b] Assuming release of 1 mmol active O per mmol mono- and 2 mmol O per mmol diperoxy acid.

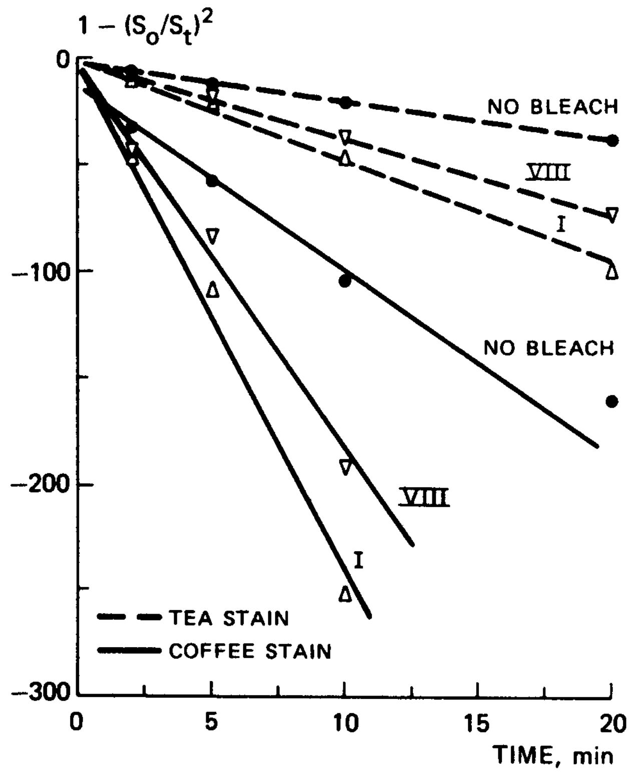


FIG. 1. Fabric bleaching by peroxy acids: Stain removal from cotton and polyester/cotton. (Peroxy acid) 2 mmol O per l; Temp. 40 C; pH 9.5.

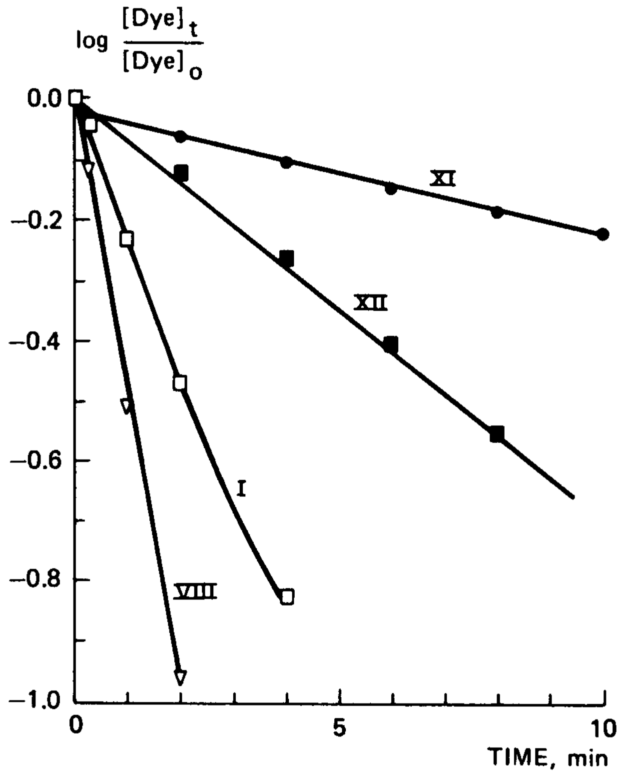


FIG. 2. Bleaching of Coomassie Brilliant Blue: Effect of peroxy acid structure. (Peroxy acid) 1 mmol O per l; Temp. 40 C; pH 9.5; (Dye) 0.008 mmol/l.

TABLE 5

Fabric Bleaching: Effect of pH[a]

Bleach		pH	% Stain removal Red wine	Coffee	Tea
No bleach		8.5	77	90	74
		9.5	79	90	70
Aliphatic monoperoxy acid	I	8.5	93	95	86
		9.5	91	95	89
Aliphatic diperoxy acid	VIII	8.5	90	93	82
		9.5	88	93	81
Aromatic monoperoxy acid	XII	8.5	94	97	88
		9.5	93	95	90
	XIII	8.5	91	94	81
		9.5	86	93	80
LSD			1.4	0.8	2.0

[a] Temp. 40 C; 2 mmol active O/1, assuming release of 1 mmol active O per mmol mono- and 2 mmol O per mmol diperoxy acid.

TABLE 6

Fabric Bleaching: Effect of Washing Time[a]

Bleach		Time (min)	% Stain removal Red wine	Coffee	Tea
No bleach		2	87	82	63
		5	92	87	72
		10	94	90	78
		20	95	92	84
Aliphatic monoperoxy acid	I	2	89	85	67
		5	95	90	78
		10	98	94	85
		20	99	96	90
	III	2	85	80	63
		5	89	86	69
		20	95	92	81
Aliphatic diperoxy acid	VIII	2	89	85	68
		5	94	89	78
		10	96	93	84
		20	98	95	88
Aromatic monoperoxy acid	XII	2	88	83	70
		5	93	89	78
		20	99	96	90
LSD			1.1	1.2	2.2

[a] Temp. 40 C; pH 9.5; (Peroxy acid) 2 mmol active O/1 assuming release of 1 mmol active O per mmol mono- and 2 mmol O per mmol diperoxy acid; cotton fabric.

being found for peroxydodecanoic acid. This strongly contrasts to fabric bleaching, where the C_{14}-peroxy acids hardly contributed to the performance.

In general, the short-chain peroxy acids give a low solution bleaching rate. Similarly low rates were observed for monoperoxyphthalic acid (XIII) and diperoxydodecane-1,12-diacid (XI). These findings point to a strong influence of micellar interactions during soluble-dye oxidation.

TABLE 7

Bleaching Rate of Coomassie Brilliant Blue G: Effect of Peracid Structure[a]

Peroxy acid		Bleaching rate[b] (1 mol O^{-1} s^{-1})
Aliphatic monoperoxy acid	I	9
	II	19
	III	14
	IV	6
	V	19
Aliphatic diperoxy acid	VIII	19
	IX	23
	XI	0.8
Aromatic monoperoxy acid	XII	3.8
	XIII	0.09

[a] Temp. 40 C; pH 9.5; detergent system B; (dye) 0.008 mmol/l Coomassie Brilliant Blue G250; (peroxy acid)1.0 mmol active O/1, added as a 4 wt% solution in tert-butanol.
[b] Observed bleaching rate per mol active O.

The influence of peroxy acid concentration and pH value were investigated for peroxydecanoic acid (I), peroxytetradecanoic acid (III), diperoxydecylsuccinic acid (VIII) and p-tert-butylperbenzoic acid (XII). Plots of log concentration versus time are shown only for peroxydecanoic acid (Figs. 3 and 4). The derived initial bleaching rate values are presented in tables 8 and 9.

The concentration dependence of the bleach rate appears to be first order in peroxy acid concentration for all four peroxy acids (Table 8). In the case of the monoperoxy acids the peroxy acid anion has been proposed as the active component (17,18). With diperoxy acids the situation is more complex as several peroxy components can be formed. In general, formation of the anion is determined by the peroxy acid equilibrium constants and the pH of the solution.

The observed bleaching rates of the monoperoxy acids increase at increasing pH value, whereas the diperoxydecylsuccinic acid shows the reverse trend (Table 9). The latter observation rules out the possibility that the di-anion participates in the rate-determining step. Correlation of the peroxy acid anion concentrations as calculated from estimated pK values for the peroxy acids with the observed first-order bleaching rate constant (Table 9, values in brackets) confirm that the rate-determining component in bleaching by peroxyalkanoic acids is the peroxy alkanoate anion. With diperoxydecylsuccinic acid (VIII) the mono-anion of the diperoxy acid appears to be the rate-determining component. This implies that bleaching rates of peroxyalkanoic acids and perbenzoic acids are optimal at a high pH value, wheras the diperoxyalkylsuccinic acids have their optimum around a pH value of 8.5, the exact pH depending on the values of the acid equilibrium constants.

PEROXY ACID SIDE REACTIONS

In aqueous solutions monoperoxy acids are known to decompose into oxygen via a bimolecular mechanism, which has been described as a reaction between the peroxy acid anion and the parent peroxy acid (18).

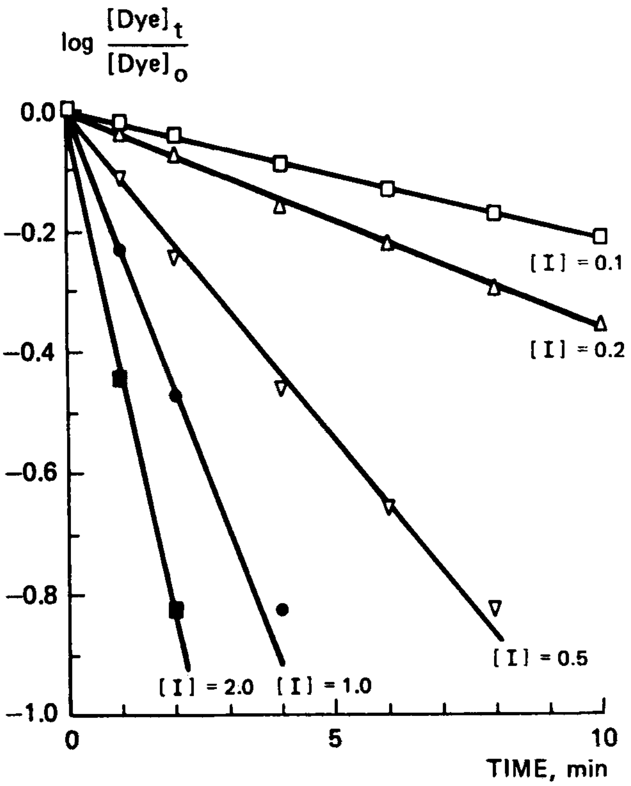


FIG. 3. Bleaching of Coomassie Brilliant Blue: Effect of peroxydecanoic acid (I) concentration, mmol/l. (Dye) 0.008 mmol/l; Temp. 40 C; pH 9.5.

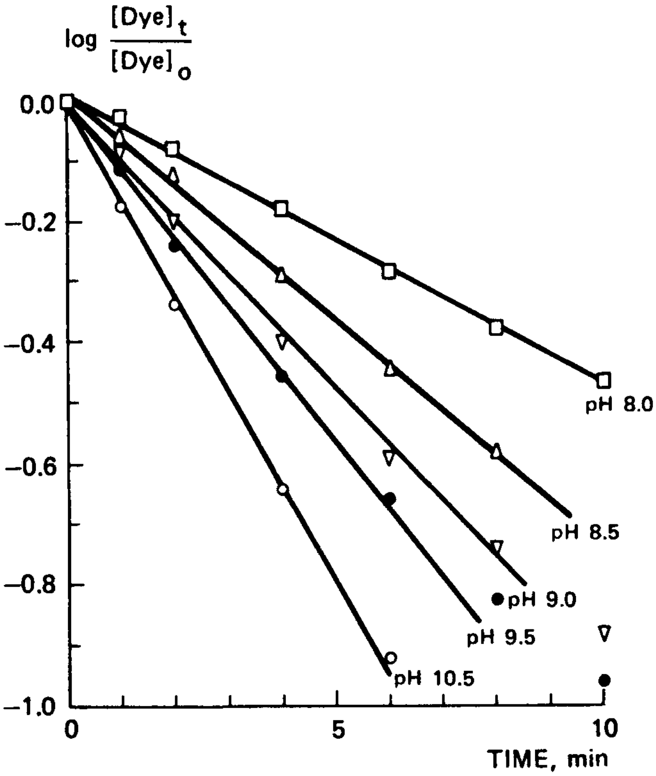


FIG. 4. Bleaching of Coomassie Brilliant Blue: Effect of pH. (I) 0.5 mmol O per l; Temp. 40 C; (Dye) 0.008 mmol/l.

TABLE 8

Bleaching of Coomassie Brilliant Blue G: Effect of Peroxy Acid Concentration[a]

Peroxy acid		Bleaching rate, $(10^{-3}\ s^{-1})$[b] (Peroxyacid), mmol O/l 0.1	0.2	0.5	1.0	2.0
Aliphatic monoperoxy acid	I	0.84 (8.4)	1.5 (7.4)	3.7 (7.4)	7.9 (7.9)	18.0 (9.0)
	III	-	3.6 (18)	8.5 (17)	15.7 (16)	-
Aliphatic diperoxy acid	VIII	-	4.7 (23)	11.2 (22)	19.5 (20)	-
Aromatic monoperoxy acid	XII	-	0.91 (4.5)	1.9 (3.9)	3.3 (3.3)	-

[a]Detergent system B: Temp. 40 C; pH 9.5; (Dye) 0.008 mmol/l Coomassie Brilliant Blue G250.

[b]Observed bleaching rate; value in brackets is rate per mol active O/l $(1\ mol^{-1}\ s^{-1})$.

TABLE 9

Bleaching of Coomassie Brilliant Blue G: Effect of pH[a]

Peroxy acid		Bleaching rate $(1\ mol\ O^{-1}\ s^{-1})$[b] at pH 8.0	8.5	9.0	9.5	10.5
Aliphatic monoperoxy acid	I	3.5 (14)	5.0 (10)	7.7 (10)	7.4 (8.1)	13.3 (13)
	III	- -	3.5 (21)	- -	17 (25)	24 (25)
Aliphatic diperoxy acid	VIII	- -	40 (48)	- -	22 (40)	12 (106)
	XI	1.5	-	-	0.74	0.38
Aromatic monoperoxy acid	XII	- -		- -	3.7 (3.8)	3.8 (3.9)

[a]Detergent system B: Temp. 40 C; 0.5 mmol active O/l, [Dye] 0.008 mmol/l Coomassie Brilliant Blue G250.

[b]Observed bleaching rate per mol active O/l. Value in brackets is bleaching rate per mol of peroxy anion as calculated from the estimated pK values of the peroxy acids. [pK (I) 8.5; pK (III) 9.2; pK_1 (VIII) 7.6; pK_2 (VIII) 9.6; pK (XII) 7.6].

TABLE 10

Peroxy Acid Decomposition: Effect of Peroxy Acid Concentration and pH[a]

Peroxy acid		Detergent system	pH	Decomposition rate[b] $1\ mol^{-1}\ s^{-1}$ (acid) 1.0 mmol O/l	(acid) 2.0 mmol O/l
Aliphatic monoperoxy acid	I	B	8.0	0.84	-
			8.5	0.96	-
			9.0	0.87	-
			10.0	0.25	-
		None	8.5	-	0.34
			9.0	-	0.16
			10.5	-	0.02
	III	B	9.5	2.9	-
		None	9.5	-	0.35
			10.5	-	0.27
Aliphatic diperoxy acid	VIII	B	9.5	0.85	-
			10.5	0.14	-
		None	9.5	0.25	-
			10.5	-	0.04
	XI	B	8.5	0.41	-
			9.5	0.14	-
Aromatic monoperoxy acid	XII	B	8.0	0.13	-
		None	8.5	-	0.01

[a]Temp. 40 C, peroxy acid added as 2-4% solution in tert-butanol.

[b]Observed rate per mol active O/l derived from a $(1\text{-}C_0/C_t)$/time plot.

The decomposition rates of several peroxy acids were determined under conditions used both during stain and dye bleaching. In addition, a number of decomposition experiments were performed in demineralized water, to study the effect of added detergent components. Data obtained are presented in Table 10. Typical plots of $(1-C_0/C_t)$ versus time for the monoperoxy acids confirm findings reported earlier (Fig. 5) (18). Variation of the pH value shows a low rate of decomposition at high values and a high decomposition at the pH near the pK of the peroxy acid. A deviation from a normal decomposition behavior was observed for the high-molecular-weight peroxytetradecanoic acid (III). Immediately after addition of the peroxy acid a very

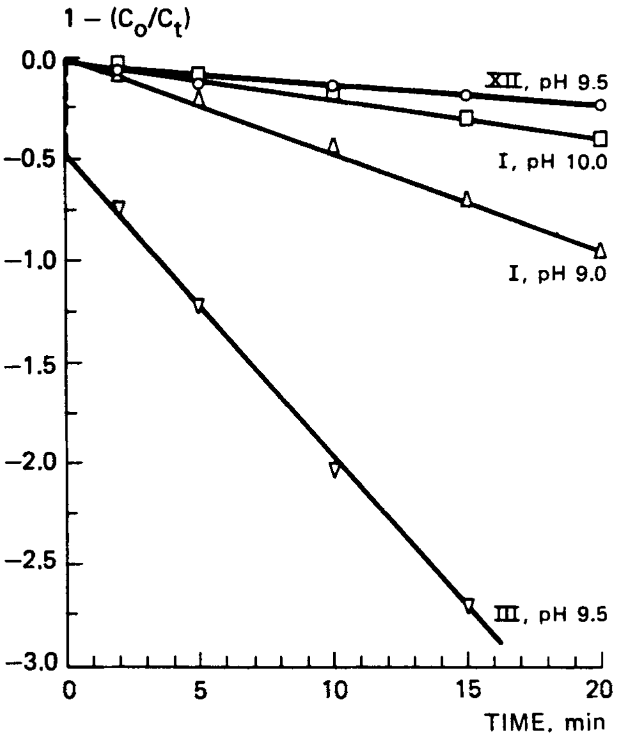


FIG. 5. Decomposition of monoperoxy acid in aqueous solution: Effect of peroxy acid structure. Detergent system B (Table 2); (Peroxy acid) 1.0 mmol/l; Temp. 40 C.

high rate of decomposition was observed, which probably is due to a strong interaction of the peroxy acid anion with unionized peroxy acid in the micelles. After this rapid initial decomposition, the rate was on a much lower level. At pH values applied in wash solutions the most stable monoperoxy acid was the p-tert-butylperbenzoic acid. This is not surprising because under these conditions hardly any free acid is available to react with the perbenzoate anion.

The decomposition behavior of the diperoxydecylsuccinic acid proved to be much more complex. At low pH values (10–11) and high peroxy acid concentrations, high initial decomposition rates were observed. Measurements at higher pH values indicate that the diperoxy mono-anion is an essential component in the decomposition reaction.

Noteworthy is the significant effect of the presence of the detergent system. Observed rates of decomposition in detergent system B were considerably higher than those observed in demineralized water. This finding again indicates that interaction of peroxy acids with surfactant micelles is an important factor in peroxy acid stability.

Peroxy acid decomposition measured under the conditions used in the fabric bleaching experiments also shows that the peroxyalkanoic acids with an alkyl chain length of $C_n > 10$ decompose very fast in the first few minutes, which may explain their moderate performance in fabric bleaching. By contrast, the stability of p-tert-butylperbenzoic acid may explain the excellent performance.

KINETIC SCHEME FOR CALCULATION OF RELATIVE BLEACHING RATE CONSTANT

In the model for the calculation of bleaching rate constants from stain removal or solution bleaching data, we have included the following processes:

(a) protolysis reactions
(b) decomposition reactions
(c) stain removal reactions

Each of these processes can be represented by chemical reactions with a forward and (if necessary) a backward reaction rate constant. For our calculations we have adopted the following reactions:

(a) Protolysis reactions

Monoperoxy acids: $AOH \rightleftharpoons AO^- + H^+$ [1]

Diperoxy acids: $AO_2H_2 \rightleftharpoons AO_2H^- + H^+$ [2]

$AO_2H^- \rightleftharpoons AO_2{}^{2-} + H^+$ [3]

where AO^-, AO_2H^- and $AO_2{}^{2-}$ are peroxy acid anions, AOH is parent monoperoxy acid and AO_2H_2 is parent diperoxy acid. $[H^+]$ is kept constant by buffering.

(b) Peroxy acid decomposition

The monoperoxy acids decompose via a reaction between the peroxy acid anion and the parent acid (16). This gives:

$$AO^- + AOH \rightarrow A^- + AH + 2''0'' \quad [4]$$

The decomposition mechanism of diperoxy acids is much more complex. On the basis of decomposition studies at various peroxy acid concentrations the rate-determining component is assumed to be the diperoxy monoanion. This gives:

$$AO_2H^- \rightarrow \text{decomp. products} + \text{“0”} \quad [5]$$

(c) Stain removal reactions

The active components in the bleaching of stains are assumed to be the percarboxylate anion of the monoperoxy acid and the diperoxy mono-anion of the diperoxy acid. Further, the bleaching of stains from fabric is treated as a reaction with a third order in stain. This gives the following equations:

Solution bleaching: $S + AO^- \rightarrow L + A^-$ [6]

Fabric bleaching: $3S + AO^- \rightarrow L + 2S + A^-$ [7]

in which S is stain and L is the oxidized (colourless) stain. In addition, there is a strong action of the detergent (D) itself in fabric bleaching, which can be represented by:

$$3S + D \rightarrow L + 2S + D \quad [8]$$

When writing equations [6], [7] and [8] in the form of an apparent bleach rate equation, one obtains:

Solution bleaching: $d[S]/dt = -[S] .k_6 [AO^-]$ [9]

Fabric bleaching: $d[S]/dt = [S]^3 \{-k_7 [AO^-] - k_8]D]\}$ [10]

in which: [S] is concentration stain; $[AO^-]$ is concentration peroxy acid anion (diperoxy mono-anion in the case of diperoxy acids); [D] is concentration of detergent; k_6, k_7 and k_8 are the apparent bleaching rate constants of equations [6], [7] and [8].

CORRELATION OF BLEACHING AND DECOMPOSITION

Via a computer program solving rate equations, we determined the bleaching rate relative to that of perborate for the various peroxy acid structures. Table 11 summarizes these data, together with the rates found for the bleaching of the water-soluble dye. The data show that solution bleaching is strongly enhanced by micellar interactions, leading to a high relative bleaching rate for the long-carbon-chain peroxy acids. In contrast, fabric bleaching is most likely promoted by a high adsorption of the peroxy acid to the fabric, which is optimal at C_9-C_{10} carbon chain lengths.

This concept provides us with a tool to predict bleaching performance under a wide range of conditions, enabling us to optimize the peroxyacid in terms of pH, peroxy acid concentration and washing temperature.

TABLE 11

Relative Bleaching Rates

Peracid		Average value for coffee, wine, tea Fabric	 Solution dye
Perborate		1	1
Aliphatic monoperoxy acid	I	23	800
	II	8	1700
	III	11	1300
	IV	10	550
	V	12	1700
	VI	10	
Aliphatic diperoxy acid	VIII	15	1700
	IX	9	2100
	XI		73
Aromatic monoperoxy acid	XII	41	350
	XIII	7	8

REFERENCES

1. Gilbert, H., *Detergent Age*, June 18 (1967).
2. Gilbert, H., *Ibid.* July 30 (1967).
3. Gilbert, H., *Ibid.* Aug. 26 (1967).
4. Smidrkal, J., and J. Smimunek, *Proceedings of the World Surfactant Congress*, Munich, May 1984, Volume IV, p. 513.
5. Sommer, U., and H. Milster, *Tenside Detergents 23*:76 (1986).
6. Dankowski, M., P. Kuzel and T. Lieser, *Fette, Seifen, Anstrichm. 88*:159 (1986).
7. Hignett, G.J., *Tenside Detergents 23*:69 (1986).
8. Kuzel, P., T. Lieser and M. Dankowski, *Seifen-Oele-Fette-Wachse 111*:448 (1985).
9. Swern, D., *Organic Peroxides*, Volume I, Wiley Interscience, New York, 1970, p. 313.
10. Silbert, L.S., E.S. Siegel and D. Swern, *J. Org. Chem. 27*:1336 (1962).
11. Silbert, L.S., E.S. Siegel and D. Swern, *Org. Syn. 43*:93 (1963).
12. Parker, W.E., C. Ricutti, C.L. Ogg and D. Swern, *J. Am. Chem. Soc. 77*:4037 (1955).
13. Mayer, J.M., U.S. Patent 4,435,335 (1984).
14. Blumbergs, J.H., U.S. Patent 3,235,584 (1966).
15. Mayer, J.M., European Patent 0,083,560 (1983).
16. Kissa, E., in *Surfactant Science Series*, Vol. 20, edited by W.G. Cutler and E. Kissa, Marcel Dekker, New York, 1987, p. 64.
17. Davies, D.M., and P. Jones, *J. Soc. Dyers Colour 98*:17 (1983).
18. Goodman, J.F., P. Robson and E.R. Wilson, *Trans. Faraday. Soc. 58*:1846 (1962).
19. Ledaal, T., and E. Bernatek, *Anal. Chim. Acta 28*:332 (1963).

[Received May 28, 1987;
accepted October 29, 1987]