

imum conditions of 2 units as the lipase concentration, 37 C as washing temperature and 10 min or longer as washing time.

Further, the effect of the lipase is more significant with the nonionic surfactant than with the anionic surfactant. It can be expected that the lipase will be used for laundry detergents.

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## Kinetics of the Thermal Decomposition of Alkyl Hydrogen Sulphates

D.W. Roberts, C.S. Fairclough and J.P. Conroy

Unilever Research, Port Sunlight Laboratory, Quarry Road East, Bebington, Wirral, Merseyside, L63 3JW, England

First order rate constants and Arrhenius parameters have been obtained for the thermal decomposition of 1-hexadecyl hydrogen sulphate. From published data on thermal decomposition of lauryl hydrogen sulphate and lauryl ether hydrogen sulphate, first order rate constants and Arrhenius parameters have been obtained. The agreement between the two sets of data for the two alkyl hydrogen sulphates is within the 95% confidence limits, a combined Arrhenius plot giving an activation energy of  $12.69 \pm 1.97$  K cal mol<sup>-1</sup> and pre-exponential factor of  $10^{(4.68 \pm 1.24)}$  sec<sup>-1</sup>. For lauryl ether hydrogen sulphate, a 3-point Arrhenius plot gives an activation energy of 9.4 K cal. mol<sup>-1</sup> and a pre-exponential factor of 10<sup>2</sup> sec<sup>-1</sup>.

Thermal decomposition of primary alkyl hydrogen sulphates is a conversion-reducing side reaction which should be minimized in the manufacture of primary alcohol sulphates by sulphonation of primary alcohols. In this paper we present kinetic data on the thermal decomposition of 1-hexadecyl hydrogen sulphate, and compare our findings with those published by Takei, Tsuto, Miyamoto and Wakatsuki (1), for lauryl hydrogen sulphate.

## EXPERIMENTAL

1-Hexadecyl hydrogen sulphate was prepared by the reaction of hexadecanol with chlorosulphonic acid, as described by Maurer, Stirton and Weil (2). After recrystallization from 30-40 C petroleum ether, the product was shown by nuclear magnetic resonance (NMR) to be ca 99% pure 1-hexadecyl hydrogen sulphate, containing ca 1% hexadecanol as the only impurity (triplet at 4.03 ppm, -CH<sub>2</sub>OSO<sub>3</sub>H; triplet at 3.75 ppm, -CH<sub>2</sub>OH; spectra recorded on solutions in chloroform/trifluoroacetic acid).

Di-(1-hexadecyl) sulphate and di-(1-hexadecyl) ether for use as analytical standards were prepared by the

methods of Barkenbaus and Owen (3) and Perron and Paquot (4), respectively.

Kinetic runs were carried out as follows. Hexadecyl hydrogen sulphate (ca 10 g) was placed in a 50 ml two-necked flask and, with magnetic stirring, heated at a constant temperature by means of an oil bath. Samples (ca. 0.2 g) were removed at measured times, weighed accurately and quenched immediately with N/10 ethanolic sodium hydroxide (15 ml). The quenched samples were then made up to 50 ml with distilled water, and these solutions were used to estimate the percent of anionic detergent (AD) in the samples by the two phase titration method of Epton, using methylene blue/cetyl dimethyl benzyl ammonium chloride (5).

The data of Takei, Tsuto, Miyamoto and Wakatsuki for lauryl hydrogen sulphate are given in their paper in the form of graphs of AD against time. We estimated numerical values for these data points by reading from the graphs.

The AD values are shown in Tables 1 and 2.

Qualitative analysis of nonionic decomposition products was carried out as follows. After the kinetic run at 104 C had been completed, a sample (3 g) was dissolved in ether (20 ml) and neutralized by addition of 100 ml of an aqueous 2M sodium hydroxide solution. The nonionic products were extracted with hexane (5 × 100 ml), with heating and addition of t-butanol (2 ml) as necessary to break emulsions. After evaporation of the hexane, the nonionic products were analyzed by thin layer chromatography (TLC) on plates of silica gel (0.025 in thickness) impregnated with sulphuric acid. This adsorbent was prepared by slurring silica (45 g Merck Kieselgel G) with a mixture of water (100 ml) and 98% sulphuric acid (2.25 ml). The TLC runs were carried out at 5 C. Plates were visualized by spraying with 50% aqueous sulphuric acid followed by heating at 180 C overnight. A 1-1.5% diethyl ether solution in hexane was found to be suitable for separation of the less polar components, which were identified by comparison of

TABLE 1

AD Values at Various Reaction Times, for Thermal Decomposition of 1-Hexadecyl Hydrogen Sulphates (this work)

55 C		64 C		79 C		104 C		113 C	
t	AD	t	AD	t	AD	t	AD	t	AD
0	91.6 <sup>a</sup>	0	99.0	0	99.3	0	99.0	0	98.0
5	88.2	8	89.4	7	79.7	4	68.4	4	69.7
8	87.3	20	85.3	11	77.7	6	74.2	6	62.6
15	85.6	50	79.9	15	77.2	8	65.8	7.5	59.3
20	83.6	100	73.7	30	75.1	10	62.9	9	58.1
50	80.8	150	71.5	40	73.7	15	60.5	11	56.0
100	77.9	200	70.3	60	70.9	20	58.1	15	52.8
260	79.6	300	66.5	130	68.5	36	56.4	20	50.4
						62	50.4	30	49.7
								45	45.1

<sup>a</sup>Starting material contained ca 8% 1-hexadecanol.  
AD values quoted as mole % of initial starting material.  
t values in minutes.

TABLE 2

AD Values at Various Reaction times, for Thermal Decomposition of Lauryl Hydrogen Sulphate and Lauryl Ether Hydrogen Sulphate

t(min)	Lauryl hydrogen sulphate (temp in °C)				Lauryl ether hydrogen sulphate (temp in °C)		
	40	60	80	100	80	100	120
0	100	100	100	100	100	100	100
5	—	—	91.4	78.6	—	—	—
10	95.5	93.5	84.6	62.2	97.2	93.2	82.0
20	93.3	89.2	75.1	53.2	95.0	86.9	63.3
30	93.7	84.7	71.4	50.4	92.5	81.8	—
40	—	—	—	—	90.0	—	51.1
60	91.3	80.8	64.7	43.8	96.9	71.9	47.3
120	85.4	73.5	56.2	37.9	79.7	61.7	42.3

AD values quoted as mole % of initial starting material.

their  $R_f$  values against those of standard compounds chromatographed simultaneously. Using this eluent, di-n-hexadecyl ether, di-1-hexadecyl sulphate and hexadecenes were identified as reaction products. For separation of the more polar components, plates were eluted twice with a 60:40 v/v mixture of ether and hexane. Using this eluent 1-hexadecanol, secondary hexadecanols and internal sultones were identified by comparison of their  $R_f$  values with those of 1-hexadecanol, 2-hexadecanol, and a mixture of sultones obtained from sulphonation (6) of a commercial internal hexadecene, chromatographed simultaneously.

The mixture of nonionic products also was examined by gas liquid chromatography (GLC), using a Perkin Elmer F30 chromatograph fitted with a flame ionization detector (FID) and a 2 m stainless steel column (.125 in. OD) packed with 10% Carbowax 20M on Chromasorb W (HP)100/120 mesh. The temperature program was 50 to 200 C at 5 C/min with a 20-min hold at the final temperature. The carrier gas was helium (45 ml/min),

and the detector and injector temperatures were both 250 C. Comparison of retention times with those of 1-hexadecene and internal hexadecenes (a commercial material with unspecified double bond position was used as the standard) established the presence of both olefin types.

The presence of carbonyl compounds was established spectroscopically as follows. A sample (ca 0.1 g) of the nonionic product mixture was dissolved in absolute ethanol (50 ml) and to 5 ml of this solution was added 2 ml of a solution made by mixing 2,4-dinitrophenylhydrazine (0.4 g), absolute ethanol (100 ml) and concentrated hydrochloric acid (5 ml). After warming the mixed solutions together for 10 min at 75 C, the volume was made up to 25 ml with potassium hydroxide (1M) in absolute ethanol/water (70/30, v/v). After standing for 20 min, the solution was examined by ultraviolet spectroscopy (Beckman Model B spectrometer, 1 cm cell), which showed a band at 480 m $\mu$  characteristic of a 2,4-dinitrophenylhydrazone.

## DECOMPOSITION PRODUCTS

The nonionic products from decomposition of 1-hexadecyl hydrogen sulphate at 104 C, identified by a combination of chromatography and spectroscopy, are summarized as follows: major products:  $\alpha$  and internal olefins, dialkyl sulphate and primary and secondary alcohol; minor products: dialkyl ether, internal olefin-derived sultones and carbonyl compounds.

Clearly, some of these products must result from secondary reactions. The nature of the initial decomposition reaction is under investigation, and we hope to report on it more fully in a future publication.

## ESTIMATION OF RATE CONSTANTS

In principle, rate constants should be obtainable from the AD values by plotting a function of  $(AD_t - AD_\infty)$ , the function chosen depending on the assumed order of reaction, against time,  $t$ .

However, the  $AD_\infty$  value is not readily measured, because the AD value observed after a prolonged reaction time will result partly from the secondary reactions. We therefore adopted the following approach: having chosen a function of  $(AD_t - AD_\infty)$  to plot against  $t$ , we used trial and error to find the  $AD_\infty$  value giving best linearity.

Initially we chose the function  $(AD_t - AD_\infty)^{-1}$ , corresponding to a second order reaction. For our data on 1-hexadecyl hydrogen sulphate, good straight lines were obtained for three of the reaction temperatures:

$$64^\circ (AD_t - 65.8)^{-1} = 9.65 \times 10^{-4}t + 3.01 \times 10^{-2}$$

linear up to  $t = 200$  min.

$$104^\circ (AD_t - 50.4)^{-1} = 5.46 \times 10^{-3}t + 2.06 \times 10^{-2}$$

linear up to  $t = 20$  min.

$$113^\circ (AD_t - 47.5)^{-1} = 5.25 \times 10^{-3}t + 1.81 \times 10^{-2}$$

linear up to  $t = 20$  min.

If the reaction were second order, the coefficients of  $t$  in these equations would be the rate constants. An Arrhenius plot of their logarithms against  $T^{-1}$ , where  $T$  is absolute temperature, should be linear. We found that such a plot in fact showed pronounced curvature. However, when logarithms of the initial rates (calculated as % per second from the above equations) were plotted against  $1/T$ , good linearity was observed. This implies that it is more realistic to treat the reaction as first order.

We next made plots of  $\ln(AD_t - AD_\infty)$  against  $t$ , again using trial and error to find the  $AD_\infty$  values giving the best fit. The first order, or pseudo first order, rate constants ( $k$ ) thereby obtained are shown in Tables 3 (1-hexadecyl hydrogen sulphate) and 4 (lauryl hydrogen sulphate), together with regression analysis data for the plots and the  $AD_\infty$  values used.

## ARRHENIUS PARAMETERS

Arrhenius plots of  $\log k$  again  $1/T$  are shown in Figure 1. Regression analysis was used to estimate activation energies ( $E_{act}$ ) and pre-exponential factors ( $A$ ) corresponding to the equation  $k = A \exp(-E_{act}/RT)$ .  $E_{act}$  and

$\log_{10} A$  values for thermal decomposition of 1-hexadecyl hydrogen sulphate and lauryl hydrogen sulphate are shown in Table 5.

The high linearity of the Arrhenius plots supports our conclusion that the reaction can realistically be treated as being first order. The differences between the Arrhenius parameters for the two chain lengths are not large; despite being from two different laboratories, the two sets of data can be combined together in a single Arrhenius plot with little loss in linearity.

It is of interest to consider the data point of 1-hexadecyl hydrogen sulphate at 55 C, for which the starting material contained 8% 1-hexadecanol. It can be seen from Figure 1 that this data point is in line with the other points in the Arrhenius plot for 1-hexadecyl hydrogen sulphate, and this is confirmed by comparison of the observed  $\log k$  value with that calculated from the 5 point regression equation:  $\log k$  (obs) = 4.90;  $\log k$  (calc) = 4.83. (Note that this rate constant, being obtained from the initial two AD,  $t$  points is likely to be an underestimate rather than an overestimate.) Thus, the presence of up to 8% of the corresponding alcohol in

TABLE 3

First Order Rate Constants,  $k$ , for Thermal Decomposition of 1-Hexadecyl Hydrogen Sulphate

T (°C)	$AD_\infty$	$k$ , min <sup>-1</sup> (± 95% confidence limits)	Regression data $n^a$	$-r^b$
55	<i>c</i>	$7.42 \times 10^{-3}$	<i>c</i>	
64	69.5	$(1.55 \pm .07) \times 10^{-2}$	6	.9995
79	<i>c</i>	$2.82 \times 10^{-2}$	<i>c</i>	
104	56.0	$(1.16 \pm .22) \times 10^{-1}$	7	.9881
113	49.6	$(1.83 \pm .46) \times 10^{-1}$	9	.9633

$n^a$  = number of data points used. Where this is smaller than the number of data points recorded (shown in Tables 1 & 2), the first  $n$  points were used.

$r^b$  = correlation coefficient.

<sup>c</sup>For the 55 C and 79 C data, there was too much scatter for us to be able to unambiguously select the best  $AD_\infty$  value; therefore,  $k$  values could not be estimated graphically. Instead we used the initial rate approximation and calculated  $k$  values from the AD value at the first sampling time  $t_1$ , using the approximate formula  $k = (AD_0 - AD_1)/t_1 AD_0$ .

TABLE 4

First Order Rate Constants,  $k$ , for Thermal Decomposition of Lauryl Hydrogen Sulphate

T (°C)	$AD_\infty$	$k$ , min <sup>-1</sup> (± 95% confidence limits)	Regression data $n^a$	$-r^b$
40	<i>c</i>	$4.5 \times 10^{-3}$	<i>c</i>	
60	70.0	$(1.72 \pm .24) \times 10^{-2}$	6	.9951
80	63.0	$(5.09 \pm .30) \times 10^{-2}$	6	.9991
100	49.6	$(1.38 \pm .36) \times 10^{-1}$	5	.9991

<sup>a, b</sup>See corresponding footnotes to Table 3.

<sup>c</sup>Initial rate approximation used to estimate  $k$  (see corresponding footnote to Table 3).

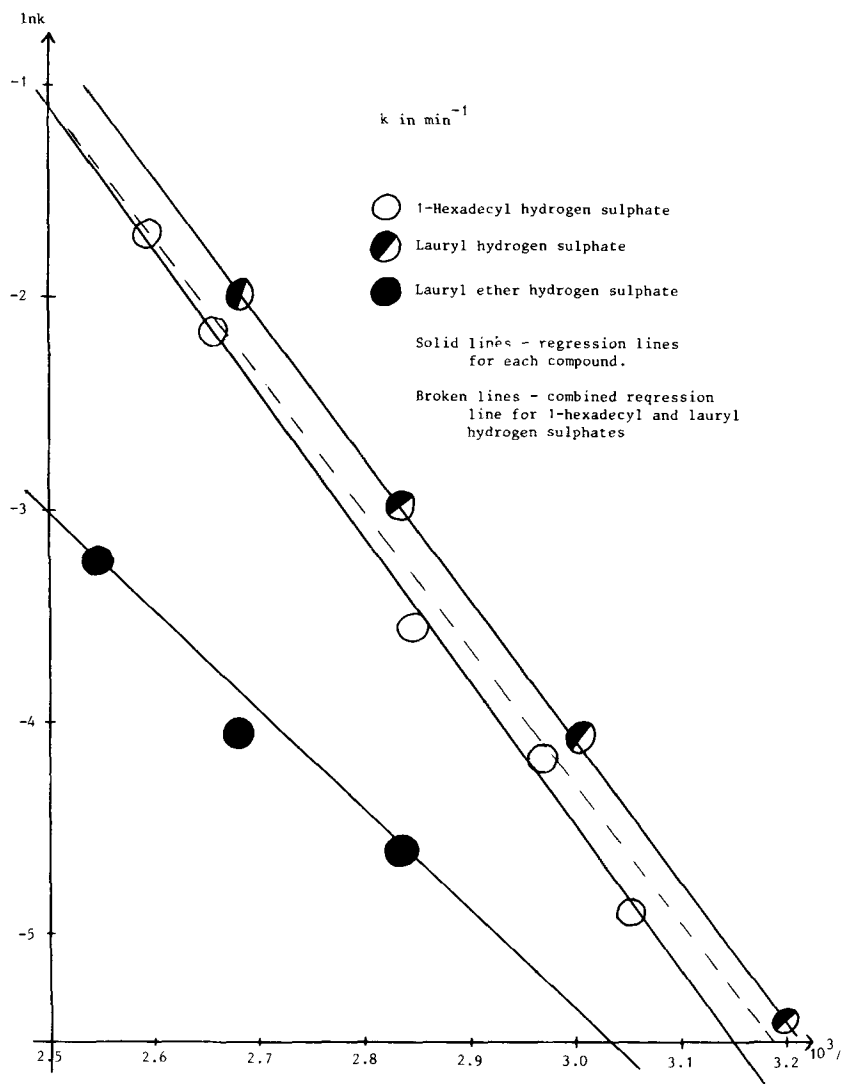


FIG. 1. Arrhenius plots for thermal decomposition of 1-hexadecyl, lauryl and lauryl ether hydrogen sulphates.

TABLE 5

Arrhenius Parameters for Thermal Decomposition of 1-Hexadecyl Hydrogen Sulphate, Lauryl Hydrogen Sulphate and Lauryl Ether Hydrogen Sulphate

	$E_{Act}$	$\log_{10} A$	Regression data		
			$n^a$	$-r^b$	$s^c$
1-hexadecyl hydrogen sulphate <sup>d</sup>	$13.96 \pm 2.35$	$5.03 \pm 1.45$	5	.9957	.142
Lauryl hydrogen sulphate <sup>d</sup>	$13.19 \pm .81$	$5.09 \pm .52$	4	.9998	.036
Combined data for both chain lengths <sup>d</sup>	$12.69 \pm 1.97$	$4.68 \pm 1.24$	9	.9852	.240
Lauryl ether hydrogen sulphate	9.3	2.0	3	.9902	.135

<sup>a, b</sup>See corresponding footnotes to Table 3.

<sup>c</sup> $s$  = standard deviation of residuals.

<sup>d</sup>Omission of the data points estimate by the initial rate approximation does not significantly modify the  $E_{Act}$  and  $\log_{10} A$  values.

$\pm$  95% confidence limits are shown for  $E_{Act}$  and  $\log_{10} A$ .

Units are  $k$  cal. mole<sup>-1</sup> ( $E_{Act}$ ) and sec<sup>-1</sup>( $A$ ).

THERMAL DECOMPOSITION OF RSO<sub>4</sub>H

the alkyl hydrogen sulphate does not significantly retard the decomposition. It is well known that higher alcohol levels do stabilize alkyl hydrogen sulphates sufficiently to enable detergent chain-length alcohols to be sulphated to about 70% conversion with SO<sub>3</sub> in batch reactors, without significant decomposition occurring (7). A possible explanation for this apparent discrepancy is that at the 8% level the alcohol is completely protonated and, as a result, is unable to exert a stabilizing effect.

The pre-exponential factors whose logarithms are shown in Table 5 correspond to entropy of activation ( $\Delta S^\ddagger$ ) values in the range  $-30$  to  $-40$  cal deg<sup>-1</sup> mole<sup>-1</sup>. Negative  $\Delta S^\ddagger$  values of this magnitude suggest two things, first, that although this reaction behaves kinetically as first order, the rate determining step is bimolecular, and second, that the transition state is more polar, and hence more highly solvated, than the alkyl hydrogen sulphate.

#### DECOMPOSITION OF LAURYL ETHER HYDROGEN SULPHATE

Takei, Tsuto, Miyamoto and Wakatsuke present graphic data on thermal decomposition of lauryl ether hydrogen sulphate, C<sub>12</sub>H<sub>25</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>OSO<sub>3</sub>H, at 80, 100 and 120 C.

By reading numerical values for these data points (Table 2) from the graphs, and using the same trial and error method as for the primary alkyl hydrogen sulphates to find the best values for AD<sub>∞</sub>, we obtained first order or pseudo first order rate constants, in the same way as for the primary alkyl hydrogen sulphates. The linearity of these rate plots was very high (Table 6).

An Arrhenius plot for lauryl ether hydrogen sulphate is shown, together with those for the alkyl hydrogen sulphates, in Figure 1.

From the slope and intercept of the best straight line, values for E<sub>act</sub> and Log<sub>10</sub>A can be calculated (Table 5); because of the small number of data points, realistic 95%

TABLE 6

First Order Rate Constants, k, for Thermal Decomposition of Lauryl Hydrogen Sulphate

T (°C)	AD <sub>∞</sub>	k, min <sup>-1</sup> (± 95% confidence limits)	Regression data	
			n <sup>a</sup>	-r <sup>b</sup>
80	71.0	(1.01 ± .03) × 10 <sup>-2</sup>	6	.9997
100	56.4	(1.75 ± .02) × 10 <sup>-2</sup>	6	.9999
120	41.8	(3.92 ± .34) × 10 <sup>-2</sup>	6	.9980

<sup>a, b</sup>See corresponding footnotes to Table 3.

confidence limits cannot be estimated. However, it seems likely from comparison of the Arrhenius parameters that the greater stability of lauryl ether hydrogen sulphate compared with alkyl hydrogen sulphates results from a larger negative entropy of activation, not from a higher activation energy. This is consistent with a transition state more highly solvated than the starting material, because the ether oxygens should increase the solvating power of lauryl ether hydrogen sulphate relative to that of alkyl hydrogen sulphates.

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