Table 3. Thermodynamic stability constants of the chelates of salicylaldehyde-5-sulphonic acid (L) and the values of the parameters of eqn. (1).

Chelate	$\log \beta_1{}^\circ$	$\log \beta_2{}^\circ$	α	B
NiL	4.42		1.83	0.21
NiL$_2$$^{2-}$		6.99	1.52	0.33
ZnL	3.61		2.01	-0.11
ZnL$_2$$^{2-}$		5.43	1.43	0.42

$\log \beta_1 = 3.0$ (at an unspecified ionic strength and 25°C) for the first zinc(II) chelate can be compared with the values at low ionic strength found in this study. No other values seem to be available in the literature. The stabilities of the metal complexes of salicylaldehyde derivatives are linearly correlated with the acid strengths of the ligands.[3,4]

Experimental. Sodium salicylaldehyde-5-sulphonate was prepared and purified as described earlier.[1] The nickel salt used was nickel(II) perchlorate from the G. Frederick Smith Chemical Co. The other reagents were of analytical grade.

The stability constants of the chelates were calculated using a modified SCOGS programme[5] on a Burroughs B 6500 electronic computer. The equation used to calculate required values of the second dissociation constant of the ligand was:[1]

$$pK_2 = 7.322 - \frac{2.036 \sqrt{I}}{1 + 1.577 \sqrt{I}} + 0.234 \, I$$

The other details of the procedure were the same as described earlier.[1]

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Determination of the Bond Ruptured in the Alkaline Hydrolysis of Vinyl Acetate

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It was recently confirmed in our laboratory by the oxygen-18 method that the acid-catalysed hydrolysis of vinyl acetate in dilute aqueous acid solutions takes place by acyl-oxygen fission [1]* in accordance with kinetic results [2] but in contrast to earlier opinions based on oxygen-18 measurements.[3] More recent results of Noyce and Pollack [4] show without any doubt that vinyl acetate is hydrolysed by the $A_{AC}2$ mechanism in dilute acid solutions. There is some controversy about the site of bond fission in the alkaline hydrolysis of vinyl esters. Kiprianova and Rekasheva hydrolysed vinyl acetate and vinyl benzoate [3] in alkaline aqueous solutions enriched in ^{18}O and several vinyl esters with an excess of ^{18}O in the ethereal or the ethereal and carbonyl oxygen atoms in alkaline solutions of normal isotopic composition.[5] The results could not be interpreted without assuming that both vinyl-oxygen and acyl-oxygen fission takes place.[3,5,6] On the other hand, the kinetics of the alkaline hydrolysis of vinyl esters does not differ significantly from that of corresponding saturated esters,[5-7] and their hydrolysis mechanism is believed to be the normal $B_{AC}2$ mechanism.[7,8]

To clarify this controversy, we determined the bond ruptured in the alkaline hydrolysis of vinyl acetate and, for comparison, ethyl acetate by the oxygen-18 method. The results are given in Table 1. The values of R ($= m(46)/m(44)$ in CO_2 from the formed acetate ion) obtained for vinyl acetate are in accordance with the value

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* The expression for r on p. 1293 in Ref. 1 should be $\frac{1}{2}([A^*] + 2[A^{**}])/\sum[A]$ rather than $\frac{1}{2}[A^*]/\sum[A]$ if the distribution of the oxygen isotopes is statistical. Because this is not the case, the correct way would have been to compare calculated and observed R values as is done in this paper. Because of the small excess of ^{18}O in the water employed, the differences are insignificant and the conclusions drawn in Ref. 1 are unaffected.

Table 1. Values of $R(=m(46)/m(44)$ in carbon dioxide obtained from the acetate ion formed in hydrolysis) for the alkaline hydrolysis of acetate esters in aqueous sodium hydroxide solutions at 25°C.

Ester	t min	R (%)		
		Experimental	Calculated[a] for	
			acyl-oxygen fission	alkyl-oxygen fission
$CH_3COOCH=CH_2$	19 $(=1000t_{1/2})$	2.31 2.38	2.35	0.41
$CH_3COOCH_2CH_3$	840 $(=1000t_{1/2})$ 0.83 $(=t_{1/2})$	2.24 2.28		

[a] Calculated from the approximate equation $R = ([A*]+2 \times 0.00204[A])/(1-2 \times 0.00204)[A] = 1.004[A*]/[A]+0.0041$, with $[A*]/[A]=[*OH^-]/[OH^-] = (2.095-0.204)/97.8 = 0.0214$ for acyl-oxygen fission ($A* =$ produced acetate ion with excess ^{18}O).

calculated for acyl-oxygen fission. The small differences are not significant when expected systematic errors in the experimental method are taken into account. It should be noted that the experimental R values are higher for vinyl acetate than for ethyl acetate. These facts indicate unequivocally that the alkaline hydrolysis of vinyl acetate takes place by the normal $B_{AC}2$ mechanism with acyl-oxygen fission.

Experimental. The *materials* were the same as used earlier.[1] The aqueous sodium hydroxide solution (0.188 M) was prepared by dissolving sodium metal in ^{18}O enriched water (2.095 at. % ^{18}O).

The *oxygen-18 analyses* were performed as before by precipitating the acetate ion as silver acetate, which was pyrolysed to carbon dioxide.[1] The mass ratios were determined with a Perkin-Elmer 270 mass spectrometer equipped with an additional Servogor RE 511 recorder. The peaks $m/e=44$ and 46 were recorded in succession and interpolated graphically to the same time. Standard curves were constructed using data for carbon dioxide samples of known ^{18}O content.

Determination of the site of bond fission. Equimolar amounts of ester and oxygen-18 enriched aqueous sodium hydroxide solution were mixed, shaken, and allowed to stand in a thermostat for a preselected time. The reaction mixture was chilled and neutralised to about

pH 6 with a 0.9 M perchloric acid solution. Unreacted ester and formed acetaldehyde or ethanol were extracted with methylene chloride. The volume of the aqueous layer was reduced by evaporation and the acetate ion was precipitated as silver acetate, which was washed, dried, and pyrolysed as before.[1] By separate experiments, it was confirmed that no oxygen exchange takes place between the sodium hydroxide solution and the acetate ion or acetaldehyde in the employed experimental conditions.

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