Micellar Control of the Rate and Stereochemical Course of the Hydrolysis of 1-Methylheptyl Trifluoromethanesulphonate

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Summary Hydrolytic alkyl–oxygen bond fission of optically active 1-methylheptyl trifluoromethanesulphonate is extensively retarded by micelles of cetyltrimethylammonium bromide and sodium lauryl sulphate and proceeds with predominant retention of configuration.

ALTHOUGH the micellar effect on nucleophilic substitution at carbonyl carbon[1] has been extensively studied, including micellar control of stereochemistry,[2] little work has been reported on saturated compounds, except 3-bromo-3-phenylpropionate ion,[3] 2-phenylethyl bromide,[4] 1-methylheptyl *p*-(trimethylammonium)benzenesulphonate,[5] and 2-amino-octane.[6] We now report the striking effectiveness of micellar control on the rate and stereochemical course of the hydrolysis at a saturated carbon atom.

The alkoxy-^{18}O-labelled 1-methylheptyl trifluoromethanesulphonate† (Oct^{18}OTf) gave non-labelled octan-2-ol when it was hydrolysed after solubilization by 0·1 M surfactants [cetyltrimethylammonium bromide (CTABr) or sodium lauryl sulphate (NaLS)] at 25 °C, indicating that the hydrolysis proceeds *via* alkyl–oxygen bond fission even in the presence of the surfactants. The hydrolysis rates, measured by conductometry, are only 1/300 (for CTABr) or 1/350 (for NaLS) as fast as the rate in pure water; the value in pure water was estimated by extrapolation from the rate constants in aqueous acetone solvents because of very low solubility ($< 1{\cdot}0 \times 10^{-4}$ M) of the substrate in pure water. When the optically active triflate OctOTf‡ was hydrolysed in 40—75% aqueous acetone, the octan-2-ol formed shows net inversion of configuration, similar to the results obtained for the usual 1-methylheptyl systems;[7] the extent of inversion extrapolated to pure water was 70%. However, when

Surfactant/M		$10^3k_1{}^a/\mathrm{s}^{-1}$	Octan-2-ol Net steric course (%)[b]	Octan-2-ol Yield (%)[c]
CTABr	0·025	1·11	46·0 ret.	67·1
	0·050	0·979	35·6 ret.	59·0
	0·081	—	48·5 ret.	68·6
	0·100	1·25	47·2 ret.	62·0
NaLS	0·025	0·940	68·0 inv.	62·3
	0·049	0·948	6·0 inv.	63·0
	0·074	—	27·5 ret.	62·2
	0·100	0·875	27·4 ret.	57·6
None[d]		(330±20)	(70·0 inv.)	(75·0)

[a] Determined by conductometry to 80—85% completion; probable error, ±3%. The spectrophotometric rate constant for 0·100 M NaLS was $(0{\cdot}850 \pm 0{\cdot}050) \times 10^{-3}\,\mathrm{s}^{-1}$. [b] [Optical purity of OctOH, isolated]/[optical purity of OctOTf] × 100. [c] Determined by g.l.c.; the yields for octan-2-ol, isolated by extraction with Et_2O–MeOH (3 : 1 v/v) and by subsequent preparative t.l.c., were *ca.* 2/3 of the figures determined by g.l.c.; oct-1-ene, and *cis*- and *trans*-oct-2-ene were identified besides octan-2-ol. [d] k_1 was determined by graphical extrapolation of the log k_1 *vs.* Y-values plot for 35—60% aqueous acetone solvents; the % stereochemical course and % yield were extrapolated from the data for 40—70% aqueous acetone solvents.

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† ^{18}O content: 1·47—1·54 excess atom %; prepared from Oct^{18}OH and $(CF_3SO_2)_2O$ at 0 °C in the presence of solid NaOH.

‡ $[\alpha]_D$ −3·25° (CH_2Cl_2); prepared from OctOH, $[\alpha]_D$ −4·62° (EtOH).

the triflate was hydrolysed in the solubilized state with surfactant concentrations greater than their critical micelle concentrations, the stereochemical course changed to net retention (*ca.* 48% for CTABr or *ca.* 27% for NaLS). The results are summarized in the Table.

The rate constants, very much lower than those in the absence of micelles, indicate that the reaction proceeds completely in the micelles, most probably at the co-micelles of surfactant and OctOTf. The partial racemization of the octan-2-ol isolated strongly suggests that the hydrolysis proceeds *via* ionization of OctOTf as in the S_N1 hydrolysis in homogeneous solution. If this is the case, hydrolysis *via* ionization of OctOTf may be suppressed in media with low dielectric constant like micelles. Further studies are under way to clarify the mechanistic details that can explain the rate constants, which are essentially independent of surfactant concentration or head-group charge, and the stereochemical course, which is dependent on the surfactant concentration for the reaction with NaLS.

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[1] For recent reviews, see E. H. Cordes, Ed., 'Reaction Kinetics in Micelles,' Plenum Press, New York, 1973; J. H. Fendler and E. J. Fendler, 'Catalysis in Micellar and Macromolecular Systems,' Academic Press, New York, 1975.

[2] For a recent example, see J. M. Brown and C. A. Bunton *J.C.S. Chem. Comm.*, 1974, 969.

[3] C. A. Bunton, A. A. Kamego, and P. Ng, *J. Org. Chem.*, 1974, **39**, 3469.

[4] C. Lapinte and P. Viout, *Tetrahedron Letters*, 1973, 1113.

[5] C. H. Sukenik, B.-A. Weissman, and R. G. Bergman, *J. Amer. Chem. Soc.*, 1965, **97**, 445.

[6] R. A. Moss, C. J. Talkowski, D. W. Reger, and C. E. Powell, *J. Amer. Chem. Soc.*, 1973, **95**, 5215, and references cited therein.

[7] K. Okamoto and T. Kinoshita, *Bull. Chem. Soc. Japan*, 1972, **45**, 2802, and references therein.