

An E.S.R. Study of the Oxidation of Sodium Alkyl Sulphates by Hydroxyl Radicals

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Abstract

Radicals detected by electron spin resonance show that hydrogen abstraction in the oxidation of alkyl sulphates by the $\text{TiCl}_3/\text{H}_2\text{O}_2$ system is not selective. In the light of these results and of evidence obtained by reduction of γ -iodocaproic acid, the previous claim¹ that hydrogen abstraction from aliphatic carboxylic acids containing 6-8 carbons occurs chiefly at the α and $\omega-1$ positions can no longer be supported.

In a previous paper¹ we described e.s.r. spectra from the oxidation of aliphatic acids by the hydroxyl radical, generated in a flow system from $\text{TiCl}_3/\text{H}_2\text{O}_2$. The unexpected selectivity of α and $\omega-1$ hydrogen abstraction in acids of medium length was explained in terms of an intermolecular reaction involving an oxidizing species complexed through titanium to the carboxyl group; and to extend this investigation to other compounds with similar properties we have examined the oxidation of a series of sodium alkyl sulphates.

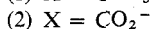
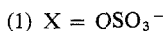
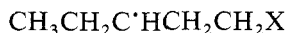
Table 1. Radicals from the oxidation of sodium alkyl sulphates
 a_{H} , hyperfine splitting (G); 1 G = 10^{-4} T. g -value, 2.0026 throughout. C_{rel} , $C(\gamma \text{ to } \omega-2 \text{ abstraction})/C(\omega-1 \text{ abstraction})$

Sulphate	$a_{\text{H}}(5)$	$a_{\text{H}}(2)$	$a_{\text{H}}(6)$	$a_{\text{H}}(2)$	C_{rel}
$\text{CH}_3(\text{CH}_2)_5\text{OSO}_3^- \text{Na}^+$	24.6	20.8	24.4	20.4	0.6
$\text{CH}_3(\text{CH}_2)_6\text{OSO}_3^- \text{Na}^+$	24.6	20.8	24.4	20.4	1.5
$\text{CH}_3(\text{CH}_2)_7\text{OSO}_3^- \text{Na}^+$	24.6	20.8	24.4	20.4	2.3
$\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^- \text{Na}^+$	24.6	20.8			

The spectra obtained in this way were at least five times as strong as those from the corresponding carboxylates, and the resulting increase in resolution and reduction in noise greatly simplified their interpretation. Splittings shown in Table 1 indicate the presence of two types of radical: one a sextet of doublets due to the radical formed by $\omega-1$ hydrogen abstraction, and the other a quintet of doublets. As the chain length increases, the proportion of the radical due to $\omega-1$ abstraction decreases, until in sodium lauryl sulphate this radical is no longer detectable. The corresponding

¹ Hewgill, F. R., and Proudfoot, G. M., *Aust. J. Chem.*, 1976, 29, 637.

increase in the quintet of doublets with increasing chain length is only consistent with the assignment of this spectrum to the group of presumably indistinguishable radicals produced by random abstraction of hydrogen from methylene groups elsewhere in the chain, e.g. (1). Abstraction of hydrogen from the α , β and ω carbons could not be detected but may have occurred.



As it seemed unlikely that the oxidation of alkyl carboxylates should be more selective than that of alkyl sulphates, we re-examined the spectra of the former. Computer simulation of the spectra from hexanoic, heptanoic and octanoic acids showed that these could also be interpreted as mixtures of radicals arising from a combination of $\omega-1$ and random $\omega-2$ to γ abstraction of methylene hydrogens if the outermost lines of the quintets were obscured by noise. Our previous assignments as mixtures of $\omega-1$ and α radicals were based mainly on the presence of a triplet of doublets arising from α hydrogen abstraction, and in view of our results for the alkyl sulphates we now believe that the triplets are the inner three lines of quintets, and that in fact random abstraction of methylene hydrogens also occurs in the carboxylic acids. This interpretation is also more in accord with the view that, although titanium ions complex with hydroperoxy radicals, the actual oxidizing species is the free hydroxyl radical itself.²

Further confirmation was provided by the reduction of γ -iodocaproic acid by the method of Beckwith and Norman.³ The resulting radical (2), typical of those that would be obtained by random hydrogen abstraction, was observed as a quintet of doublets with $a_{\text{H}}(5)$ 25.0 and $a_{\text{H}}(2)$ 21.2 G. These splitting constants were, within experimental error, in even better agreement with those from the C_6 to C_8 acids (25.0, 21.6 G) than the triplet of doublets previously obtained from α -bromocaproic acid. Moreover, a comparison of the g -values showed that whereas the signals from both the radicals obtained by oxidation of caproic acid were centred at g 2.0026, that from α -bromocaproic acid had g 2.0032. We are therefore now of the opinion that oxidation of the alkyl chain of aliphatic acids by the hydroxyl radical is a relatively non-specific process.

Experimental

General

E.s.r. spectra were recorded with a Varian V4 500-10A spectrometer. The flow system used was similar to that described by Dixon and Norman.⁴ With weak spectra the flow rate was increased by connecting the effluent tube to a water pump. Splitting constants and g -values were determined by reference to those of Frémy's salt, and splitting constants are estimated to have an accuracy of ± 0.5 G.

Sodium alkyl sulphates were prepared by reaction of the corresponding alcohol with chlorosulphonic acid in acetic acid as described by Dreger *et al.*⁵ γ -Bromocaproic acid was prepared from

² Gilbert, B. C., and Dobbs, A. J., in 'Organic Peroxides' (Ed. D. Swern) Vol. 3, p. 271 (Interscience: New York 1972).

³ Beckwith, A. L. J., and Norman, R. O. C., *J. Chem. Soc. B*, 1969, 400.

⁴ Dixon, W. T., and Norman, R. O. C., *J. Chem. Soc.*, 1963, 3119.

⁵ Dreger, E. E., Keim, G. I., Miles, G. D., Shedlovsky, L., and Ross, J., *Ind. Eng. Chem.*, 1944, **36**, 610.

hex-3-enoic acid as described by Heine and Lane,⁶ and converted into the iodo acid by exchange with sodium iodide in acetone.

Preparation of Solutions

(i) *Oxidation of sodium alkyl sulphates*.—One solution contained titanous chloride (15%, 10 ml), ethylenediaminetetraacetic acid (6 g) and water (1 l.), while the second contained hydrogen peroxide (100 vol., 4 ml), the sodium alkyl sulphate (x g) and water (1 l.). The quantity x was varied from 2.5 to 30 g without altering the composition of the spectrum, only its strength.

(ii) *Oxidation of carboxylic acids*.—As above, except that 20 g of the sodium salt of the carboxylic acid were used instead of the sodium alkyl sulphate.

(iii) *Reduction of γ -iodocaproic acid*.—One solution contained titanous chloride (15%, 10 ml), concentrated sulphuric acid (3 ml), formic acid (17 ml) and water (1 l.), while the second contained hydrogen peroxide (100 vol., 4 ml), concentrated sulphuric acid (3 ml), formic acid (17 ml), γ -iodocaproic acid (2 g) and water (1 l.).

Acknowledgments

We are grateful to Dr M. F. Chiu and Mr J. A. Hewgill for the spectral simulation program, and to the Australian Research Grants Committee for the spectrometer.

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⁶ Heine, H. W., and Lane, J. F., *J. Am. Chem. Soc.*, 1951, **73**, 1348.

Corrigendum

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Pages 152, 155: In structures (5a), (5b), (14a) and (14b) there should only be a partial bond between the oxygen and the developing carbonium site, e.g.

