

significant inhibiting effect upon the action of hyaluronidase on connective tissue. The explanation of their inhibition of the spreading phenomenon *in vivo* is therefore probably referable to their influence upon some other of the several factors upon which this phenomenon depends.

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<sup>1</sup> Hechter, O., *Ann. N.Y. Acad. Sci.*, 52, 1028 (1950).

<sup>2</sup> Pelloja, M., *Lancet*, 233 (1952).

<sup>3</sup> Day, T. D., *J. Physiol.*, 117, 1 (1952).

### Position of Radical Attack during Oxidation of Long-Chain Paraffins

MUCH work has been done on the liquid-phase oxidation of hydrocarbons; but strangely enough very few experiments of a fundamental nature have included what would appear to be the simplest models, namely, straight-chain paraffins. Any suggestions made so far concerning the point of oxygen attack when there is no preferred tertiary or activated hydrogen atom have been largely speculative. Ivanov *et al.*<sup>1</sup> claim, on the basis of certain products isolated from the oxidation of *n*-heptane, that attack takes place predominantly at the 2-position. Asinger<sup>2</sup> found that in the chlorination of dodecane and cetane attack was equal on all methylene groups, and suggested that the same would hold for oxidation.

In our research on the mechanism of liquid-phase oxidation of paraffins, we have determined the proportion of attack on the different carbon atoms of *n*-decane.

Pure *n*-decane was autoxidized at 145° C. with oxygen until the hydroperoxide concentration had reached 2.5 per cent w/w. From previous work in these laboratories it was known that at this extent of oxidation more than 80 per cent of the decane oxidized retains its original carbon skeleton, the oxygen being present as hydroperoxy- and carbonyl-groups; of these functional groups, 80 per cent are present in mono-functional compounds, the isomer distribution of which indicates the points of attack.

The oxidate was first hydrogenated on palladium black to reduce the hydroperoxides to the corresponding alcohols. In one case the oxygenated compounds were then separated from the unchanged hydrocarbon by chromatography and treated with lithium aluminium hydride to reduce the ketones to alcohols, thus yielding a mixture (*A*) of the total isomers from which the diols had to be removed.

Samples of the same hydrogenated oxidate were also subjected to chromatography by two different operators to separate hydroperoxide-derived alcohols (*B*<sub>1</sub> and *B*<sub>2</sub>) from ketones. The two ketone fractions, on reduction with LiAlH<sub>4</sub>, yielded isomeric decanol mixtures (*C*<sub>1</sub> and *C*<sub>2</sub>). During chromatography a partial resolution of the isomeric alcohols was noted.

The infra-red spectra of all five mixtures were recorded and the proportion of isomers determined by matching against standard mixtures of the pure decanols. In some cases, for example, *C*<sub>2</sub>, traces of non-decanol material compromised accurate matching.

Mixture *A* should give the more accurate picture since fewer manipulations were involved in this case.

Decanol isomer	Each isomer as percentage of total isomers in the fraction					Limits of accuracy of infra-red analyses
	Decanols from total oxidate	Decanols from peroxides		Decanols from ketones		
		<i>A</i>	<i>B</i> <sub>1</sub>	<i>B</i> <sub>2</sub>	<i>C</i> <sub>1</sub>	
1-ol	3	De- tected	<3	De- tected	Not de- tected	± 2
2-ol	31	23	20	25	22	± 3
3-ol	25	23	28	22	[35]	± 3
4-ol	22	22	17	25	22	± 5
5-ol	19	22	23	28	22	± 3

The sum of *B* and *C* in the correct proportions is in reasonable agreement with *A*. Part of the ketones may have arisen from the hydroperoxide during hydrogenation; after allowing for this, and considering the limits of accuracy of analysis, we believe that the isomeric distribution of the ketones is substantially the same as that of the hydroperoxides.

By continuous counter-current extraction, decane monohydroperoxide of purity greater than 97 per cent was isolated from an *n*-decane oxidate prepared at 145° C. The isolated peroxide, which contained 20 per cent of the oxygen absorbed, was hydrogenated over Adams's catalyst and the product was an equimolar mixture of the four secondary decanol isomers with possibly a trace of decan-1-ol. No other products could be detected by infra-red spectroscopy.

Our results show that there is a small proportion of attack at the terminal methyl groups, but that the major attack is distributed almost equally on the methylene groups of the *n*-decane chain. Allowing for the limits of accuracy of the infra-red analysis, the preference for the methylene groups near the ends of the chain is only slight.

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<sup>1</sup> Ivanov, K. I., Savinova, V. K., and Zhakhovskaya, V. P., *Doklady Akad. Nauk. S.S.S.R.*, 72, 903 (1950).

<sup>2</sup> Asinger, F., *Ber.*, 75 B, 668 (1942).

### A Rapid Method for the Extraction of Radioiodide from Urine

THE extraction of radioiodide from urine is important in radioiodide therapy, since without it the large quantities of highly radioactive urine which accumulate must be stored until the activity decays sufficiently to allow disposal.

Purves has described<sup>1</sup> a method for removing iodide from boiled, acidified and filtered urine by passing it through a filter bed of asbestos impregnated with silver chloride, the iodide being retained in the filter bed, from which it can be afterwards removed as iodic acid by treatment with a solution of chlorine