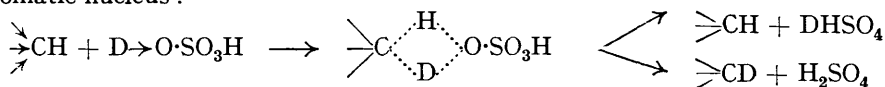


363. Direct Introduction of Deuterium into Aliphatic Systems. Part I. Hydrogen Exchange between Sulphuric Acid and Paraffinoid Hydrocarbons.

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INFORMATION on the direct introduction of deuterium into paraffins is limited. Taylor, Morikawa, and Benedict observed that methane could be induced to exchange its hydrogen atoms with those of molecular deuterium by means of photochemically excited mercury atoms, or through the agency of a nickel catalyst (*J. Amer. Chem. Soc.*, 1935, **57**, 383, 592); and very recently Steacie and Phillips have shown that the exchange can be effected by the use of free deuterium atoms formed by electric discharge (*J. Chem. Physics*, 1936, **4**, 461). The methods of deuteration thus indicated involve metastable reagents or heterogeneous catalysts, and hydrogen exchange with paraffins does not appear previously to have been realised as an ordinary substitution with a stable reagent. The experiments now reported show that hydrogen is exchanged between saturated aliphatic hydrocarbons and sulphuric acid, *i.e.*, that sulphuric acid containing deuterium can be used in order to introduce this isotope into paraffins.

We envisage the reaction as an electrophilic aliphatic substitution, having a transition state identical in pattern with that which we assume for the corresponding reaction with the aromatic nucleus :



However, the electronic displacements involved in activation, although they are similar in direction in the paraffinoid and the aromatic systems, must be less facile in the former; and hence we have to expect considerably more resistance to deuterium substitution in any simple paraffin than in benzene. But, for a precisely similar reason, sulphonation, which is always in competition with deuteration, is also expected to be (as in fact it is) considerably less facile in paraffins. Hence we are allowed a wider range of experimental conditions, and it was this consideration which rendered the experiments on the deuteration of paraffins worth trying. We found, as expected, that treatment at the room temperature with aqueous sulphuric acid of just over 50 mols. % concentration, conditions which would have effected a fairly rapid exchange with benzene, had no influence on simple paraffins such as hexane. We might have increased both the temperature and the concentration of the acid without risking serious sulphonation, but found it sufficient, in order to demonstrate the exchange and to show differences of reactivity between one aliphatic hydrocarbon and another, to retain room temperature and use acid of about 77 mols. % concentration.

The hypothesis that the deuteration of paraffins with sulphuric acid is an electrophilic substitution carries certain implications concerning the orientation of the exchange: it

should occur preferentially at those hydrogen-bearing carbon atoms which can acquire the strongest negative charge. The most favoured positions will therefore be tertiary carbon atoms, and, after these, methylene groups adjoining branching points of the skeleton. The orientation of hydrogen exchange should, indeed, be analogous to that of nitration; and Markownikoff's rule, which is known empirically to govern nitration, is substantially identical with the rule just stated. The main difference between deuteration and nitration with respect to their orientation is that in the former reaction the substituent will not inhibit further neighbouring substitution, so that we can foresee the possibility of introducing, not merely one, but several deuterium atoms into a molecule possessing a reactive region. Now we have not made any direct determinations of orientation in partly deuterated paraffins—indeed, it would not be easy to do so; nevertheless, the observed differences of reactivity in deuteration between the different hydrocarbons studied give definite support to the view that a branched chain is a region of special reactivity in this replacement, and that, not only the methine group at the branching point, but also the groups in proximity to it, undergo exchange with enhanced facility.

We refer below to observations made with *n*-hexane, *n*-heptane, cyclohexane, and methylcyclohexane. Experiments have also been carried out with β -dimethylhexane and $\beta\beta\delta$ -trimethylpentane, which undergo deuteration but with side reactions. The hydrocarbons, which were shown spectroscopically to be completely free from aromatic compounds, were shaken for various times at room temperature with sulphuric acid containing about 2 atoms % of deuterium; they were then separated, washed, dried, distilled, and burnt, the density of the combustion water being subsequently determined pyknometrically.

Unlike the deuteration of benzene derivatives containing strongly orienting substituents, the deuteration of aliphatic hydrocarbons does not appear to stop perfectly sharply at equilibrium in relation to a limited number of positions in the molecule. The amount of deuteration is a function of conditions, and as these were not precisely standardised, we confine the following detailed record to a single illustrative experiment with each hydrocarbon. These experiments are not accurately comparable, but they are sufficiently so to give significance to the differences between one hydrocarbon and another.

The data are best compared by reference to the "statistical exchange number." This is defined as the number of hydrogen atoms per molecule which, if in isotopic equilibrium subject to a partition-ratio of unity, would give the observed uptake of deuterium. As the deuterium partition-ratio is about unity for the reaction between sulphuric acid and benzene, it cannot be very far from unity for the corresponding reaction with paraffins, since the stretching frequencies of paraffinoid and benzenoid hydrogen are similar, and the bending frequencies contribute less strongly to the energy balance on which the exchange equilibrium depends. Therefore the statistical exchange number is at least a rough guide to the average number of hydrogen atoms per molecule actually exchanged.

Hydrocarbon †	<i>n</i> -Hexane	<i>n</i> -Heptane	<i>cyclo</i> -Hexane	Methyl <i>cyclo</i> -hexane
B. p.	68.0°	97.0°	80.3°	100.3°
Quantities of materials:				
Hydrocarbon (g.-mols.)	0.0773	0.0744	0.0952	0.0778
Sulphuric acid (g.-mols. H ₂ SO ₄) *	0.906	0.907	0.906	0.906
Water (g.-mols.) *	0.263	0.265	0.265	0.271
Concn. of aqueous acid (mols. % H ₂ SO ₄)	77.4	77.3	77.4	77.0
Ratio, (H of aqueous acid)/(H of hydrocarbon)	2.17	1.97	2.07	2.16
Time of shaking at room temp. (days)	15	9	12	15
Excess density (p.p.m.) of H ₂ O from H in:				
Aqueous acid (initial)	2780	2795	2800	2873
" (residual, by diff.)	2623	2790	2798	2435
Hydrocarbon (residual, by analysis)	340	10	4	947
Statistical exchange number	1.82	0.06	0.02	5.43
Atoms of H in hydrocarbon	14	16	12	14

* These quantities are inclusive of forms containing deuterium.

† *n*-Heptane was obtained from the Analytical and Synthetic Laboratories Ltd. and the other hydrocarbons from British Drug Houses Ltd. In each case the b.p. was constant and correct and olefinic and aromatic impurities were absent.

The most striking results are the extreme slowness of substitution in *cyclohexane* and the relatively rapid and extensive substitution in *methylcyclohexane*. In the former, all carbon-carbon links are equivalent, so that none possesses electrical dissymmetry. In the latter, the statistical exchange number suggests that, not only the methine hydrogen atom, but also the hydrogen of some other groups closely approach equilibrium in exchange during the period of the experiment.

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