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| Title | A MASS SPECTROMETRIC DEMONSTRATION OF HYDROGEN-DEUTERIUM EXCHANGE AND HYDROGEN REDISTRIBUTION DURING CATALYTIC DEUTERATION OF SOME METHYL OCTADECENOATES |
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Short Note

A MASS SPECTROMETRIC DEMONSTRATION OF HYDROGEN-DEUTERIUM EXCHANGE AND HYDROGEN REDISTRIBUTION DURING CATALYTIC DEUTERATION OF SOME METHYL OCTADECENOATES

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A previous paper¹⁾ reported on the extensive replacement of hydrogen by deuterium during the catalytic deuteration of some olefinic and halogenated esters. In the present investigation some information has been obtained on the addition reaction, the hydrogen-deuterium exchange reactions, and the hydrogen (or deuterium) redistribution phenomenon, using both neutral and ionic media (dioxane, acetic acid, and acetic acid-*d*).

All experiments were carried out with Adams' platinum catalyst at room temperature. All figures given in this paper are from the high-mass end of mass spectra of the final saturated esters. For accurate interpretation, the heights of the molecule-ion peaks have been corrected by subtracting the contribution due to the natural content of ¹³C.

Deuteration of methyl oleate by shaking with 5 percent of catalyst in a system containing deuterium and dioxane, led to the formation of large percentages of methyl stearate ($M=298$) and methyl monodeuterostearate ($M=299$), together with methyl dideuterostearate ($M=300$) and higher deuterated methyl stearates ($M=301$ to about $M=311$), as shown by a whole series of molecule-ion peaks in Fig. 1. When the reduction was carried out with 10 percent of catalyst¹⁾, the high-mass end of the spectrum of the final product showed that the peaks at $m/e=298$ and $m/e=299$ were respectively only about 7 and 40 percent of the peak at $m/e=300$.

Deuteration of methyl oleate in acetic acid-*d* and 1 percent of catalyst also gave a product with a mass spectrum (Fig. 2) of high molecule-ion peaks for methyl stearate ($M=289$), methyl monodeuterostearate ($M=299$) and methyl dideuterostearate ($M=300$), followed by a whole series of molecule-ion peaks of

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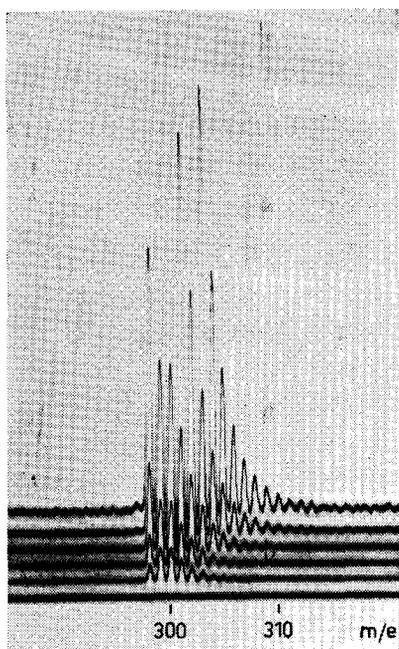


Fig. 1.

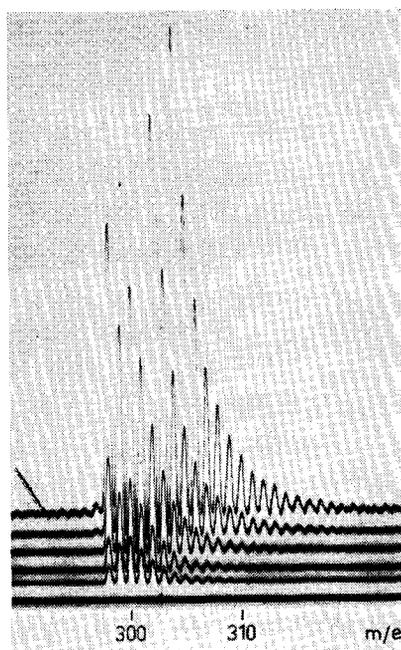


Fig. 2.

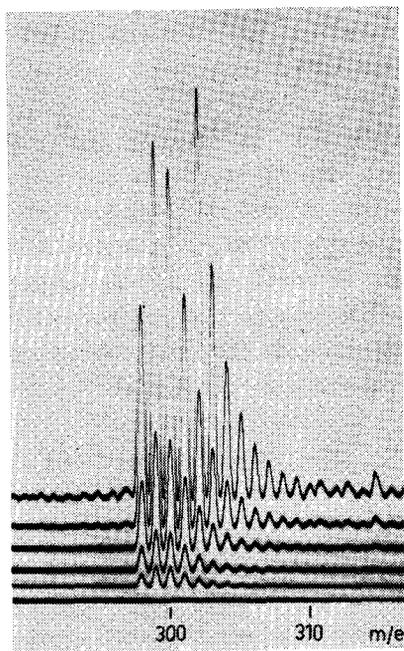


Fig. 3.

A Mass Spectrometric Demonstration of Hydrogen-deuterium Exchange

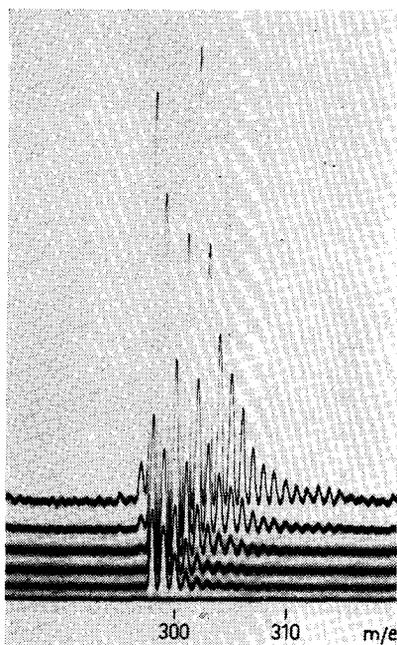


Fig. 4.

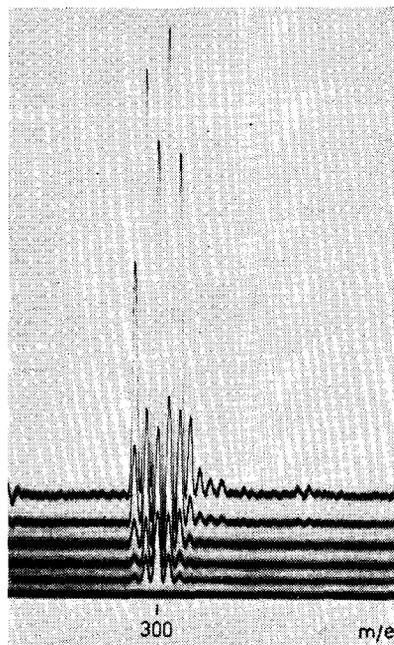


Fig. 5.

decreasing intensity of higher deuterated methyl stearates ($M=301$ to about $M=316$). On reduction of the unsaturated ester with deuterium in acetic acid, a final product gave a spectrum (Fig. 3) which had the highest molecule-ion peak for methyl monodeuterostearate ($M=299$), but otherwise it was similar to the foregoing. When the reduction was carried out with hydrogen in acetic acid- d , the mass spectrum of the resulting product (Fig. 4) had the highest molecule-ion peak at the $m/e=298$ corresponding to that of the molecule-ion of methyl stearate. A whole series of molecule-ion peaks of partly deuterated methyl stearates ($M=299$ to about $M=314$) is also present in the mass spectrum of Fig. 4.

Hydrogenation of methyl 9, 10-dideuteroöleate*) in dioxane and 10 percent of catalyst gave a mixture of saturated compounds with a mass spectrum (Fig. 5) in which the highest molecule-ion peak is due to methyl dideuterostearate ($M=300$), which is followed by about five molecule-ion peaks of decreasing intensity. The latter are due to a small amount of higher deuterated methyl stearates. After deuteration of the unsaturated ester under the same conditions, the resulting product contained methyl trideuterostearate ($M=301$) as the main component, and methyl stearate ($M=298$), methyl monodeuterostearate ($M=299$), methyl dideuterostearate

*) This ester was prepared by deuteration of methyl stearolate over LINDLAR's catalyst (Pb-Pd/CaCO₃). This catalyst gave no unspecific exchange of hydrogen for deuterium.

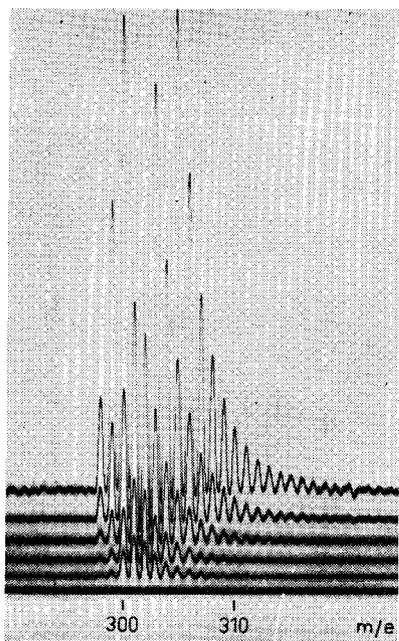


Fig. 6.

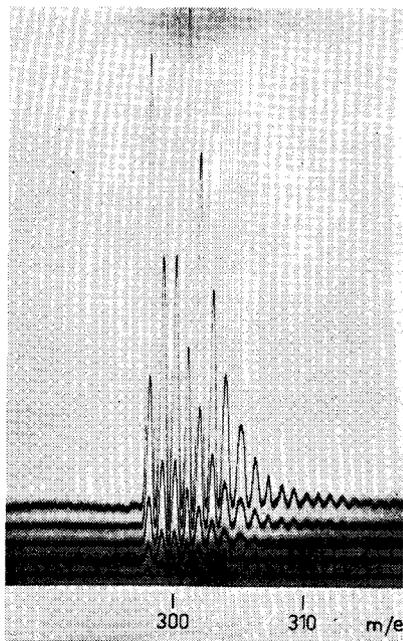


Fig. 7.

($M=300$), methyl teratedeuterostearate ($M=302$) and more highly deuterated methyl stearates ($M=303$ to about $M=318$), as shown by a whole series of molecule-ion peaks in Fig. 6.

Deuteration of methyl *cis*-petroselinate in dioxane and 10 percent of catalyst gave a product with a mass spectrum (Fig. 7) having high molecule-ion peaks for methyl stearate ($M=298$), methyl monodeuterostearate ($M=299$) and methyl di-deuterostearate ($M=300$), followed by a whole series of molecule-ion peaks of decreasing intensity of higher deuterated methyl stearates ($M=301$ to about $M=312$).

No hydrogen-deuterium exchange occurred between methyl stearate and acetic acid-*d* and deuterium over 1 percent of catalyst.

The experiments above show that addition of two deuterium (or hydrogen) atoms to the double bond may take place faster than the exchange between them and an acidic solvent, and the chemisorbed deuterium (or hydrogen) used for the reduction is thus not in equilibrium with the liquid phase². It is clear, that in the case of the hydrogenation of methyl oleate in acetic acid-*d*, exchange between chemisorbed hydrogen atoms and deuterium ions had occurred to a large extent. All deuteration, in neutral as well as in ionic media, led to formation of both methyl stearate and methyl monodeuterostearate. This is probably due to the so-

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called hydrogen redistribution phenomenon reported by several authors²⁻⁹. In all deuterations and in one case of hydrogenation in acetic acid-*d*, an extensive replacement of hydrogen by deuterium took place in the hydrocarbon chain of the esters. It is possible that this is due to double-bond shifts and to exchange reactions which are known to occur during the catalytic hydrogenation of olefins^{7,8}.

The hydrogen redistribution in the present cases may be explained on the basis of the "associative" mechanism⁸⁻¹² for the metal-catalysed hydrogenation of olefins involving double-bond shifts and exchange reactions. It is possible that an adsorbed molecule of olefinic ester successively remove two adsorbed hydrogen atoms that have been abstracted by the catalyst from other molecules of the ester by hydrogen-deuterium exchange in the course of deuteration; this would give methyl stearate. The formation of the methyl monodeuterostearate may be due to the completion of the reduction of a half-deuterated complex by an adsorbed hydrogen atom. The deuterium redistribution in the case of the hydrogenated methyl 9,10-dideuteroöleate can be explained in a similar manner.

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References

- 1) Ng. DINH-NGUYEN and R. RYHAGE, *Acta Chem. Scand.* **13**, 1032 (1959).
- 2) D. RITTENBERG, R. RATNER and H. D. HOBERMAN, *J. Am. Chem. Soc.* **62**, 2249 (1940).
- 3) J. TURKEVICH, D. O. SCHISSLER and P. IRSA, *J. Phys. Colloid Chem.* **55**, 1078 (1951).
- 4) C. D. WAGNER, J. N. WILSON, J. W. OTVOS and D. P. STEVENSON, *J. Chem. Phys.* **20**, 338, 1331 (1952).
- 5) M. C. MARKHAM, M. C. WALL and K. J. LAIDLER, *ibid.*, 1331.
- 6) J. N. WILSON, J. W. OTVOS, D. P. STEVENSON and C. D. WAGNER, *Ind. Eng. Chem.* **45**, 1480 (1953).
- 7) Cf. T. I. TAYLOR, *Catalysis*, Reinhold, New York 1957, vol. 5, chap. 5.
- 8) J. HORIUTI and M. POLANYI, *Trans. Faraday Soc.* **30**, 1164 (1934).
- 9) J. HORIUTI, *Shokubai (Catalyst)* **2**, 1 (1947).
- 10) J. HORIUTI, *J. Res. Inst. Catalysis, Hokkaido Univ.* **6**, 250 (1958).
- 11) T. KEII, *ibid.* **3**, 36 (1953).
- 12) T. KEII, *J. Chem. Phys.* **23**, 210 (1955).