

## The Influence of Water on the Autoxidation of Methyl Linoleate

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In the presence of water the autoxidation of methyl linoleate has a short induction period. This is supposed to depend on water interfering with the reactions initiating the autoxidation, while peroxides have not yet formed, rather than on an inhibition of the autoxidation reactions. The pH of the water has no effect on the length of the induction period in the range of pH 5.1—9.2.

Many foods and technical products based on fats contain water which may influence their stability against autoxidation. In the literature divergent views are found on the existence of such an influence. Thus Greenbank and Holm<sup>1</sup> state that water increases the stability of fat, whilst French *et al.*<sup>2</sup> and Mukherjee<sup>3</sup> consider water to have no influence at all.

This lack of agreement may depend upon the fact that these authors used different fats for their investigations. It therefore seemed to be of interest to study the autoxidation of a pure unsaturated fatty acid ester in the presence of water.

### EXPERIMENTAL

#### The investigation method

The investigation was carried out by measuring manometrically the oxygen absorption of methyl linoleate in contact with borate buffers at 40° C.

For investigations of this type vegetable fats are unsuitable, because of their content of natural antioxidants. The influence of water on the autoxidation rate may then be indistinguishable from an effect on the antioxidants. Animal fats have a very low antioxidant content but show, like the vegetable fats, considerable variations also for the same type of fat, which renders difficult the comparison of results obtained with different fats.

As linoleic acid is the most unsaturated acid of several valuable fats, thus strongly affecting their stability (*cf.* Gunstone and Hilditch<sup>4</sup>), methyl linoleate is a suitable model substance for fats in autoxidation studies. It does not possess the disadvantages of natural fats mentioned above, as linoleic acid is easily obtained in a sufficiently pure state. Furthermore its autoxidation reactions have been extensively studied (*e. g.* by Farmer<sup>5</sup> and Bolland and Gee<sup>6</sup>). Methyl linoleate also autoxidizes rapidly enough to permit the investigation to be carried out at a low temperature at conditions similar to those of "normal" storage.

Table 1. The oxygen absorption in ml at NTP of 1 g methyl linoleate.

Dry		pH 5.1		pH 6.5		pH 8.0		pH 9.2	
min.	ml O <sub>2</sub>	min.	ml O <sub>2</sub>	min.	ml O <sub>2</sub>	min.	ml O <sub>2</sub>	min.	ml O <sub>2</sub>
67	0.06	113	0.04	138	0.06	96	0.06	144	0.01
157	0.12	193	0.09	228	0.07	176	0.09	189	0.10
207	0.18	258	0.13	333	0.18	405	0.16	339	0.24
262	0.25	422	0.17	608	0.50	549	0.38	559	0.44
477	0.66	563	0.42	1 338	2.29	1 291	1.98	1 339	2.27
537	0.73	1 308	2.14	1 478	2.90	1 431	2.46	1 419	2.66
1 267	3.39	1 448	2.70	1 523	3.10	1 476	2.62	1 474	2.95
1 352	3.80	1 553	3.17	1 573	3.36	1 536	2.88	1 524	3.14
1 403 <sup>a</sup>	4.00	1 663	3.70	1 635	3.70	1 667	3.68	1 609	3.57
		1 711 <sup>a</sup>	4.00	1 689 <sup>a</sup>	4.00	1 709 <sup>a</sup>	4.00	1 705 <sup>a</sup>	4.00

<sup>a</sup> Interpolated value

### Materials

*Methyl linoleate.* Tetrabromostearic acid was prepared as described by McCutcheon <sup>7</sup> and was recrystallized from ligroin until a melting point of 115.0–115.3° C was reached. It was then debrominated in boiling methanol acidulated with sulphuric acid to which zinc dust was added in portions. After decantation from the zinc residue more sulphuric acid was added and the linoleic acid was esterified to methyl linoleate by boiling under reflux (*cf.* Ref. <sup>8</sup>). The ester was then transferred into an ether solution and deacidified with alkali. At last the methyl linoleate was fractionally distilled under reduced pressure, the fraction having a b. p. of 149–151° C at 1 mm Hg was collected and sealed in ampullae.

From the debromination step onwards all operations were carried out in an atmosphere of oxygen-free nitrogen. The distillation apparatus and the ampullae were carefully cleaned.

The methyl linoleate thus obtained contained no detectable amounts of free fatty acid, peroxides or heavy metal soaps.

*Water.* The water used had been doubly distilled in an all-glass apparatus.

*Boric acid and sodium tetraborate p. a.* The solutions were prepared according to Palitzsch <sup>9</sup>. The pH-values were measured with the solutions in equilibrium with an equal amount of fatty acid ester at 25° C.

### Apparatus

The oxygen absorption was measured with a Barcroft apparatus. This consists essentially of a U-tube manometer having both ends connected to flasks. One flask contains the sample and the other one acts as a compensating vessel. For details of construction and application of this apparatus *cf.* Dixon <sup>10</sup>.

### EXPERIMENTAL RESULTS

The autoxidation of dry methyl linoleate was first studied. Fig. 1 gives the oxygen absorption curve as constructed from the values given in Table 1. The oxygen absorption is initially very slow but increases as the oxygen absorption increases due to autocatalysis <sup>\*</sup>.

Experiments were then made with methyl linoleate to which an equal amount of borate buffer solutions of the pH-values 5.1, 6.5, 8.0 and 9.2 respectively had been added. The oxygen absorption curves obtained were identical and the times necessary for the sorption of 4 ml O<sub>2</sub> at NTP per g methyl linoleate differ only by a few minutes. The oxygen absorption is very slow and fairly constant for about 300 min., but then takes the same course as in the experiment with dry methyl linoleate.

<sup>\*</sup> For a discussion of autoxidation curves of this type see *e. g.* Robertson and Waters <sup>11</sup>.

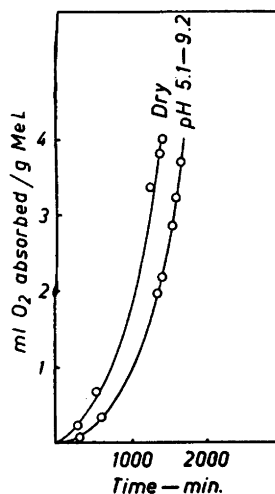


Fig. 1. The autoxidation of methyl linoleate in absence and in presence of water.

#### DISCUSSION

The experimental results presented above show that water retards the autoxidation reaction of the methyl linoleate but it has no influence on the chain reaction, when this has once started. Such a behaviour is typical of an inhibitor. Water can, however, not act as an inhibitor, since reactions between radicals and water, involving liberation of a hydrogen atom, are generally highly endothermic, because of the high dissociation energy of the reaction  $\text{H}_2\text{O} \rightarrow \text{H} + \text{OH}^{12}$ . If water had been an inhibitor the induction period should have lasted until all water had been consumed. The only reasonable explanation of the induction period seems to be that water interferes with the reactions by which the autoxidation is initiated while peroxides have not yet formed. However, these reactions are not known with any degree of certainty (cf. however Farmer<sup>5</sup>).

The pH of the water had no effect on the length of the induction period in the pH-range 5.1—9.2 (cf. Ref.<sup>13</sup>).

#### REFERENCES

- Greenbank, G. R. and Holm, G. E. *Ind. Eng. Chem.* **16** (1924) 598.
- French, R. B., Olcott, H. S. and Mattill, H. A. *Ind. Eng. Chem.* **27** (1935) 724.
- Mukherjee, S. *J. Indian Chem. Soc.* **27** (1950) 607.
- Gunstone, F. D. and Hilditch, T. P. *J. Chem. Soc.* **1946** 1022.
- Farmer, H. *Trans. Faraday Soc.* **42** (1946) 228.
- Bolland, J. L. and Gee, G. *Trans. Faraday Soc.* **42** (1946) 236.
- McCutcheon, J. W. *Organic Syntheses* **22** (1942) 75.
- Frankel, J. B. and Frankel, J. J. *Am. Chem. Soc.* **60** (1938) 54.
- Palitzsch, S. *Bull. Inst. Océanographique*, No. 49 cit. from Clark, W. M. *The Determination of Hydrogen Ions*, Baltimore 1928.
- Dixon, M. *Manometric Methods*, 2nd Ed. Cambridge 1943, p. 20.
- Robertson, A. and Waters, W. A. *Trans. Faraday Soc.* **42** (1946) 201.
- Dainton, F. S. *J. Chem. Soc.* **1952** 1533.
- Lea, C. H. *J. Soc. Chem. Ind.* **55** (1936) 293T.

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