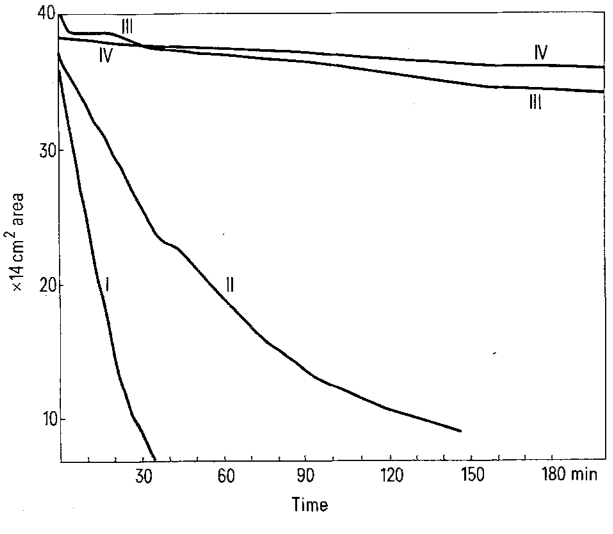
Photo Contraction of Unsaturated Monolayers at the Air/Liquid Interface

Although monolayers of long-chain fatty acids constitute one of the favoured systems for studies by the Langmuir trough technique[1], little is known about spontaneous changes in compressed fatty acid films. However changes in redox potentials in emulsions of[2] oleic acid exposed to UV-light have been reported. We have examined[3] for some years the properties of monolayers at the gas/liquid interface. During an investigation of the effects of radiation on monolayers of oleic acid, we have observed that the films contracted in a series of alternating slow and fast steps. Further experiments showed that the overall rate of contraction was related to the intensity of ambient light. Since the process might be affected by the physical state of the monolayers, similar studies were made with elaidic acid, the *trans* isomer of the *cis*-octadecenoic (oleic) acid. Because of its relatively straight carbon skeleton, elaidic acid exhibits condensed 'liquid' film properties, in contrast to the 'liquid expanded' films of oleic acid[4]. Our results show that considerable care should be taken to exclude light if degradative changes in unsaturated monolayers are to be minimized.

Materials and methods. Solutions containing 1 mg/ml of oleic or elaidic acid (> 99% pure, Applied Science Laboratory, State Coll., Pa., USA) were made up in petroleum ether and kept in complete darkness. A 'Hydrophil' balance (Cenco S.A., Fribourg, Switzerland) was enclosed in a box which eliminated light but allowed free exchange with the atmosphere. It had a sensitivity of 0.15–0.20 dynes/cm. The balance was modified so that the position of the floating and moveable barriers could be read in the dark. In this way, constant pressure could be maintained on the monolayer without disturbing the light shield. The balance trough was filled with deionized water at 19–21 °C. All experiments were made in an atmosphere of air. Presence of dust was checked by testing the stability of a film of behenic alcohol at 11 dynes/cm. Over a 2-h- period the pressure increased by only 10% and was greatly reduced again by the use of the dust box.

Oleic and elaidic acid films were spread from an Agla microsyringe, using 0.056 to 0.072 ml of solution which covered about 45 × 14 cm^2 of the water surface at zero pressure. After 1 min equilibration, the films were compressed to the required pressure, which was maintained by movement of the barrier every 0.5 to 2 min, depending on the rate of change of film pressure. The maximum deviation from the chosen equilibrium pressure was less than 1 dyne/cm. Most experiments were performed at a constant pressure of 11 dyne/cm. Rates of film contraction were measured in darkness or again on a new monolayer under a mercury vapour fluorescent light. Many other experiments were performed in the open darkened laboratory without the dust cover and yielded similar results. Also other experiments with a greatly reduced intensity light source yielded a much reduced rate of contraction of the film.



Contraction of monolayers of oleic (I) and elaidic acid (II) under fluorescent light and in the dark (III and IV).

Experimental results are summarized in the Figure. Presence of light caused a rapid contraction of both oleic and elaidic acid monolayers. The overall rate of change was faster for the former, but for each compound, the contraction was made up of a series of alternating fast and slow steps. Behaviour in absence of light was almost identical for both acids, except for a rapid initial contraction of the oleic monolayer. Presence of light increased the average dark contraction rate by a factor of 30 to 40. At higher pressures, the contraction was reduced for both compounds.

It is clear that even the relatively weak fluorescent light employed was a powerful catalyst for the physical contraction of the films. Also, the rate of film contraction may be a function of the state of the film, since the more condensed elaidic acid monolayers collapsed at a slower rate. The area change is probably caused by the autoxidation of the acids. For oleic acid, autoxidation in bulk and in thin films has been shown to lead first to the formation of hydroperoxides, followed by their splitting and degradation, and then by further secondary autoxidation of products[5]. Among the final products identified were saturated C-6 to C-12 aldehydes, together with formic, acetic, butyric and propionic acids. All these are soluble in water and some are volatile.

To explain the occurrence of slow and fast steps in monolayer contraction, we postulate that in the slow steps peroxides are formed in the well-documented chain mechanism for olefin oxidation[6]. This causes expansion of the monolayer, but the peroxides break down continuously to soluble and volatile derivatives, which slowly leave the film causing a net gradual contraction. The fast steps occur when sufficient breakdown products accumulate in the surface to interrupt the reaction chains. Further oxidation cannot then proceed rapidly until the chainbreaking molecules leave the film, when once again the contraction is slowed by production of fresh peroxides. In studies of the oxidative contraction of linoleic acid monolayers, Porter et al.[7] noticed a steady contraction but did not observe the fine details of the change because film areas were measured every 10 min only. Linoleic acid films would be expected to collapse more quickly than

---

[1] N. K. Adam, *The Physics and Chemistry of Surfaces* (Oxford University Press, Oxford 1941).

[2] D. S. van Fleet, Biodynamica *5*, 297 (1945).

[3] J. G. Hawke and I. White, J. phys. Chem. *74*, 2788 (1970).

[4] J. T. Davies and E. K. Rideal, *Interfacial Phenomena* (Academic Press, New York 1966), chapter 5.

[5] M. Loury, C. r. Acad. Sci., Paris *255*, 2458 (1962).

[6] J. L. Bolland, Q. Rev. chem. Soc. *3*, 1 (1949).

[7] W. L. Porter, A. S. Henick and M. Clifford, J. Am. Oil Chemists Soc. *44*, 185 (1967).

oleic or elaidic monolayers and would need continuous monitoring for the detection of short-term changes.

The slower photo-contraction of elaidic acid films may be due to their different structure or to the lower oxidation rate of the *trans*-isomer[8]. The rapid initial contraction of oleic acid films, even in the dark, is due to dissolution of oxidation products present in the bulk phase. The slow contraction in the absence of light indicates that thermal oxidation and breakdown of monolayer molecules also occurs.

Zusammenfassung. Nachweis, dass die Photokontraktion von *cis*- und *trans*-Isomeren der 9-Oktadecensäure, als monomolekulare Schicht auf einer Luft/Wasser-Oberfläche ausgebreitet, stufenweise erfolgt. Daraus wird geschlossen, dass der Kettenbildungsprozess der Selbstoxidation, der zur Vergrösserung Oberfläche/Molekül führt, von einem Kettenabbruch gefolgt wird, den die aus dem Spaltungsprozess gebildeten kleinen Moleküle bewirken.

C. Golian, J. G. Hawke[10,11], J. H. Green and J. M. Gebicki[9]

School of Chemistry, Macquarie University, Sydney (N.S.W. 2113, Australia), 10 December 1973.

---

[8] N. P. Bulatskiĭ, Trudy odess. Univ., Sbornik Khim. Fak. *3*, 33 (1953).

[9] School of Biological Sciences.

[10] To whom communications should be addressed.

[11] This work was supported by grants from the Australian Research Grants Committee and the Australian Institute of Nuclear Science and Engineering.

Mitochondrial Morphological Changes in Mucosal Epithelial Cells

Morphological and biochemical evidence has consistently shown that the matrix containing regions of mitochondria are surrounded by a rather complex system of membranes[1-7]. The complexity is due to or is largely associated with the functions of the cristae. These membranous invaginations contain mitochondrial constituents which are essential in oxidative processes and energy conservation. Cellular energy demands can cause rapid changes in mitochondrial respiration rates, nucleotide and ion distribution, enzyme activities, and substrate levels. Such noted metabolic and chemical alterations frequently are indicated by conformational changes in the structure of the mitochondria[8]. During high rates of coupled respiration the matrix of mitochondria becomes greatly condensed and the inner membrane system undergoes

---

[1] C. J. Bentzel and A. K. Solomon, J. gen. Physiol. *50*, 1547 (1967).

[2] H. Tedeschi and D. L. Harris, Arch. Biochem. Biophys. *58*, 52 (1955).

[3] G. E. Palade, J. Histochem. Cytochem. *1*, 188 (1953).

[4] D. K. Jasper and J. R. Bronk, J. Cell Biol. *38*, 277 (1968).

[5] F. S. Sjostrand and J. Rhodin, Expl Cell Res. *4*, 426 (1953).

[6] L. Packer, J. M. Wrigglesworth, P. A. G. Fortes and B. C. Pressman, J. Cell Biol. *39*, 382 (1968).

[7] C. L. Hackenbrock, J. Cell Biol. *37*, 345 (1968).

[8] D. K. Jasper and J. R. Bronk, J. Cell Biol. *47*, 98A (1970).

Fig. 1. A condensed mitochondrion in the nuclear region of a mucosal epithelial cell of the rat jejunum after 3 min incubation in a mixture of amino acids (1 mg/ml) with added D-glucose (28 m*M*). Note slight mid-region constriction (arrow) suggestive of mitochondrial division. Compare with Figures 2 and 3. ×60,000.

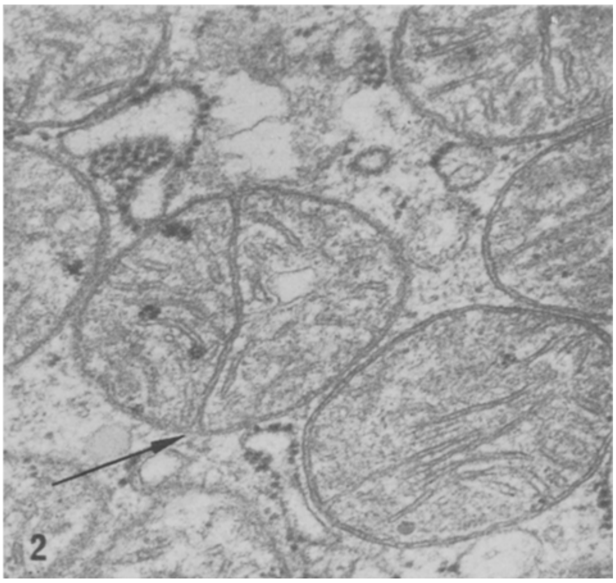


Fig. 2. A portion of the nuclear region of a mucosal epithelial cell in which paired cristael membranes of an orthodox-appearing mitochondrion extends from one side to the other where they join the inner membrane (arrow). The sample is from an intestinal slice incubated in 28 m*M* D-glucose for 30 sec. ×50,000.