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Photochemical Initiation of Polymerization of Tetrafluoroethylene by Mercury Bromides

Although tetrafluoroethylene can usually be stored indefinitely in glass vessels, polymerization on surfaces was observed in some vessels attached to mercury manometers. Bromine had been used in part of the apparatus and it was thought that the polymerization followed slight contamination of the mercury with mercury bromide. Polymerization did not occur when the vessels were shielded from light. These observations indicated that mercury bromide might initiate photochemically a polymerization of tetrafluoroethylene. Experiments to test this theory were performed.

Equal portions of pure tetrafluoroethylene¹ were condensed into cleaned glass tubes, volume about 6 cm³, containing various materials and the tubes were sealed under vacuum. Except when the additive included mercury, the tetrafluoroethylene was freed from mercury by passage through a trap at -130°C. The pressure of the gas in the tubes was about 25 cm and the additives used, separately, were redistilled mercury, mercury treated with bromine vapour to form mercurous bromide with mercury in excess, mercuric bromide crystals, and dibromotetrafluoroethylene. One set of tubes was exposed in the laboratory and a duplicate set was kept in the dark.

No polymerization took place in tubes containing pure tetrafluoroethylene, or in the tubes kept in the dark, with the exception of that containing dibromotetrafluoroethylene which showed traces of polymer after some weeks. In the light, obvious polymerization was produced by mercurous bromide in three days and by mercuric bromide in a week. Polymerization caused by dibromotetrafluoroethylene was greater in the light than in the dark but still very slow. Mercury in the light produced traces of polymer dust after exposure for some months. Further observations were made with filtered light from an ME/D 250 watt mercury lamp. No polymerization was produced by 4358 Å light. With 3650 Å light both mercuric and mercurous bromide produced obvious polymerization in 24 h, mercurous bromide being more effective. Mercurous bromide solid has an orange fluorescence in 3650 Å light. Polymer formed in the presence of mercury bromides was attached either to the mercury bromide surfaces or to the glass surfaces and was not deposited as a dust from the gas phase. It was concluded that polymerization initiated by mercury bromides in room light is caused by the near ultra-violet light present. Contamination of tetrafluoroethylene with dibromotetrafluoroethylene reduces its stability even in the absence of light, but the effect is apparent only over a long period of time.

DOYLE² has observed that the absorption threshold of mercuric bromide solid is in the near ultra-violet and the above results show that this is also true for mercurous bromide. Light in the far ultra-violet causes dissociation of mercuric bromide vapour into HgBr and Br with one of the products excited³. The energy required for dissociation into unexcited products is 62 kcal per mole, which is less than the energy provided by 3650 Å light, 78 kcal, but dissociation of the excited state in this manner may be forbidden. The fluorescence observed with mercurous bromide solid is at longer wavelengths than that of HgBr in the vapour observed by WIELAND³. There may be an excited state of Hg₂Br₂ about 50 kcal above the ground state. This discussion gives no grounds for assuming that absorption by solid mercury bromides at 3650 Å leads to the formation of bromine atoms. Although a free radical polymerisation of tetrafluoroethylene is produced, this again does not prove that free gaseous bromine atoms are formed. The reaction is obviously heterogeneous and direct transfer of bromine atoms from the solid to adsorbed tetrafluoroethylene may take place.

B. ATKINSON

Department of Chemistry, Imperial College of Science and Technology, London, May 12, 1958.

Zusammenfassung

Eine heterogene Polymerisation von Tetrafluoräthylen wurde durch Merkuri- und Merkurobromide in natürlichem Licht oder solchem von 3650 Å Wellenlänge, nicht aber in blauem Licht, ausgelöst. Es ist möglich, dass Bromatome vom angeregten Quecksilberbromid zum adsorbierten Tetrafluoräthylen übertragen werden.

Untersuchungen über Aktinpolymerisation

Der quergestreifte Muskel enthält ungefähr 0,2-0,3% ATP, das vielleicht bei der Kontraktion eine wichtige Rolle spielt. Auch ist bekannt, dass die Struktur-Proteine des Muskels ATP enthalten oder durch ATP stark beeinflusst werden.

Weiter wissen wir, dass das Aktin ungefähr 1% gebundenes ATP enthält. Dieses ATP wird während der Polymerisation gespalten. STRAUB¹ meinte, dass Polymerisation und Spaltung eng zusammenhängen und dass die Spaltung kein enzymatischer Prozess ist. Dieser Zusammenhang wurde von mehreren Forschern angenommen (LAKI *et al.*, BÍRÓ, TURBA *et al.*, MOMMAERTS, BÁRÁNY *et al.*), von anderen abgelehnt (DUBUISSON, SNELLMAN and GELOTTE).

Im Aktin zerfällt während der Polymerisation das ATP durch einen unbekanntem Mechanismus in ADP und anorganischen Phosphor. Nach der Spaltung wird anorganischer Phosphor an das Aktin gebunden (MORALES *et al.*²), während das ADP an demselben gebunden bleibt (FEUER *et al.*³). Wir wissen jedoch bis heute noch nicht, welche

¹ F. B. STRAUB und G. FEUER, *Biochim. biophys. Acta* **4**, 455 (1950).

² M. F. MORALES, K. LAKI, J. GERGELY und L. P. CECCHINI, *J. cell. comp. Physiol.* **37**, 477 (1950); zitiert M. DUBUISSON, *Muscular Contraction* (Springfield 1954), p. 77.

³ G. FEUER und M. WOLLEMAN, *Acta physiol. Hung.* **3**, 267 (1952).

¹ B. ATKINSON, *J. chem. Soc.* **1952**, 2684.

² W. P. DOYLE, Thesis, University of London, 1951.

³ K. WIELAND, *Z. Phys.* **77**, 157 (1932).