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The Effect of Radiation on Oil Drops

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Oil drops on a water surface increase their diameter when they are irradiated with β-rays, x-rays, or ultraviolet rays. The growth of the diameter depends on the amount of exposure to the radiation. Curves showing the increase of diameter with time have been made. If oil in a closed container is irradiated with x-rays, and drops from such irradiated oil are placed on a water surface, the drops spread and reach a limiting size after a few hours. The experiments made are of a preliminary nature and are intended to demonstrate the general nature of the phenomena.

THE behavior of oil on water has been studied by many investigators and articles by Langmuir[1] have stimulated us to undertake this study. When a small amount of fatty acid with a relatively long hydrocarbon chain is placed on a large water surface it spreads to form a monomolecular layer. The molecules are packed together side by side and become oriented so that they are approximately vertical, with the acid group in the water. A drop of long chain hydrocarbons, like petrolatum, on the other hand does not spread in a similar manner, but forms a lens that floats on the water. If one part of stearic acid is dissolved in about 20,000 parts of petrolatum, and a drop of this solution is placed on alkaline water, it gradually spreads and reaches a limiting size after a few minutes. According to Langmuir the area over which the drop spreads is proportional to the amount of stearic acid in the drop and independent of the amount of petrolatum, which indicates that all the stearic acid molecules go to the interface where each molecule contributes a certain size to the area. When a small amount of hydrocarbon in an open container is partially oxidized, for instance by heating, and a drop of this oil is placed on the water, it spreads in a similar manner. It seemed probable that irradiation of an oil drop with certain types of rays would result in oxidation of some of the molecules and as a consequence the drop would spread. Other chemical effects from irradiation indicate that one part in 20,000 can be changed with a large, but still reasonable dose.

For the first qualitative experiments, drops of petrolatum were placed on the surface of alkaline water in small shallow glass trays. Illumination was arranged so that light was reflected from the water surface and an image of the drop was projected, by means of a lens, to a vertically placed millimeter paper. One drop was irradiated with β-rays from a glass bulb containing about 90 mc of radon. Another drop was kept for control. The rays were filtered with about 0.2 mm brass and the bulb kept at about 1 cm distance from the drop. After one and a half hours the diameter of the drop had increased from 1.2 to 1.5 cm while the control drop had increased from 1.1 to 1.15 cm. After twelve hours of irradiation the diameters were 3.15 and 1.2 cm, respectively. The radon was removed and after twelve more hours the diameters were 3.25 and 1.2 cm. The second drop was then exposed for five and three quarters hours and the diameters afterwards measured 3.25 and 2.0 cm, respectively. This seemed to prove that the drops spread out over a larger surface as a consequence of exposure to rays from the radon. It seems reasonable to assume that the main effect is from the β-rays.

One drop of petrolatum on a water surface was next exposed to Röntgen rays. The container was placed inside the large drum containing the x-ray tube. The distance target to oil was 30 cm; the container was covered with black paper. Two hundred kilovolt peak and 30 ma were used and the drop was exposed for 64.5 minutes. The diameter increased 45 percent in size as compared to about 5 percent for the control drop. Evidently then Roentgen rays also have a spreading effect on oil drops on water.

Finally ultraviolet irradiation was tried. A quartz mercury lamp of the Cooper-Hewitt type

[1] Langmuir, Science **84**, 379 (1936); J. Chem. Phys. **1**, 756 (1933).

was used, running at 50 volts with about four amperes. The first drop was exposed for ten minutes at 12″ distance. It increased 80 percent in diameter and the control about 2 percent. A drop exposed under the same condition but with a piece of ordinary glass placed between the lamp and the container behaved like the control drop. When the exposure to ultraviolet radiation was extended for more than an hour the drop spread out to such a thin film that colored diffraction patterns could be seen.

From these preliminary experiments it is evident that β-rays, x-rays and ultraviolet rays, or radiation whose quanta are above a certain size, affect the oil drops in such a manner that they spread on water to an extent depending upon the amount of exposure. It seems reasonable to assume that a certain portion of the molecules are oxidized even though it would be difficult to determine the exact reaction.

It should be of interest to obtain some quantitative data and investigations of this nature have been started. The size of the drops have been measured by means of a telescope supplied with a scale arranged so that the diameter can be measured to within 0.1 mm. It is our intention to use some homogeneous hydrocarbons but the experiments reported here have been carried out with a mixture of long chain hydrocarbons in a heavy mineral oil referred to as Bacol which was easily obtainable.

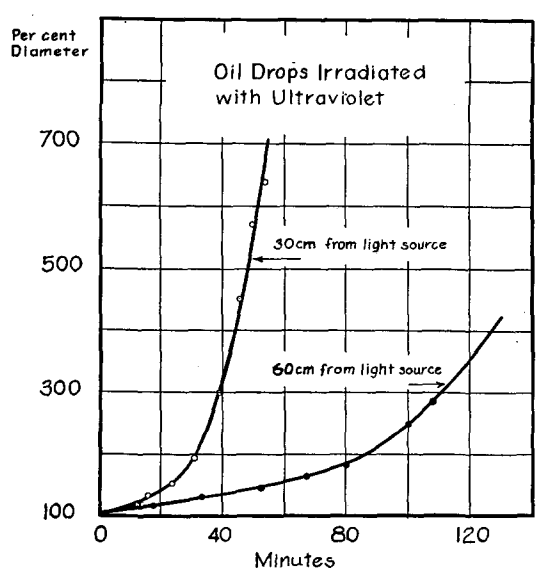

FIG. 1. Oil drops, on 0.01 N NaOH, irradiated with ultraviolet. Initial diameter of the drops was 5.3 mm.

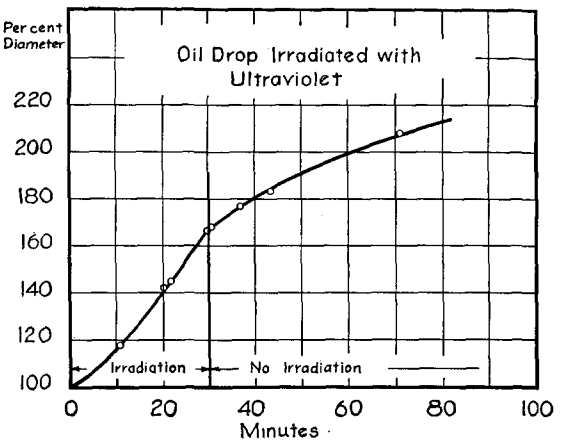

FIG. 2. An oil drop, on 0.01 N NaOH, irradiated for 30 minutes with ultraviolet at a distance of 30 cm from the lamp.

A number of factors may influence the spreading of the drop. The effect of impurities and of ions in the water is undoubtedly important. So far alkaline water consisting of 0.01 normal sodium hydroxide, made with distilled water, has been used for most experiments. No appreciable difference was, however, noticed in one experiment when 0.01 normal hydrochloric acid was used instead of sodium hydroxide. This was surprising as a drop of oil containing stearic acid behaved differently on acid water. The effect of temperature has not been determined as yet. The original size of the oil drop may be of considerable importance. Drops of nearly the same size and of an average weight of about 9 mg have been used for most experiments. The diameters of these drops were between $4\frac{1}{2}$ and 6 mm. For a few larger drops which were studied the percentage increase of the diameter during the time of irradiation with ultraviolet rays was smaller. If a large oil lens (consisting of about 25 drops) is given considerable radiation so that it becomes thin enough to show interference fringes and is left over night, the oil film becomes slightly thicker and a "solid" very thin and invisible film will cover the whole water surface. A small lens (one drop) behaves in a similar way but the film covering the water seems to have a "liquid" consistency. Mechanical agitation hastens the process. Apparently the attractive forces between the hydrophilic molecules and the oil molecules

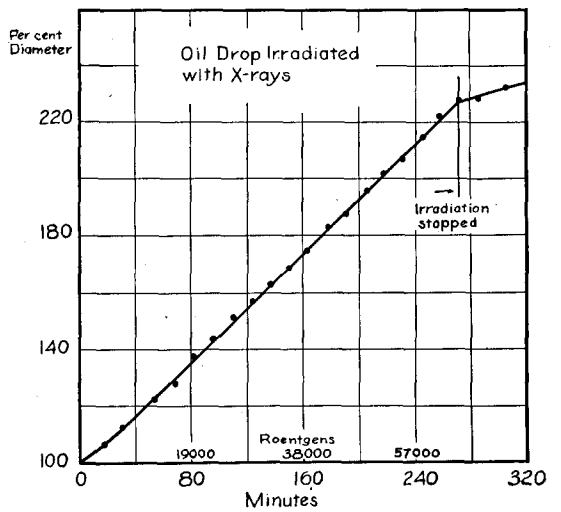

FIG. 3. An oil drop, on 0.01 *N* NaOH, irradiated with x-rays at 100 KVP, 5 ma, 20 cm distance from the target. Irradiation was stopped after 271 minutes.

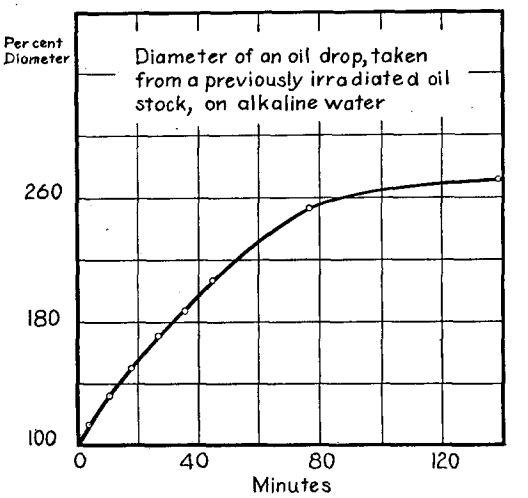

FIG. 4. Oil, completely filling a 25 cc glass-stoppered flask, was irradiated with x-rays at 200 KVP, 30 ma, 30 cm distance from target, for 232 minutes. Eighteen hours after the exposure a drop of this oil was placed on a 0.01 *N* NaOH and the relation between its diameter as a function of time was determined.

are not as great as those between the oil molecules.

For most of these experiments large watch glasses were used and the alkaline water had a surface measuring about 11 cm in diameter. A change in this diameter did not affect the spreading appreciably as long as the final diameter of the drop was less than half the diameter of the water surface.

The drops keep on spreading for a considerable length of time after the irradiation is discontinued. This is evidently due to a gradual diffusion of the changed molecules to the oil-water interface.

Fig. 1 shows the growth of two drops that were exposed to ultraviolet radiation. The growth is expressed in percent of the original diameter. Drop I was exposed at 30 cm distance and drop II at 60 cm distance from the lamp.

While it is impossible, from the curves, to say how closely the velocity of spreading is proportional to the intensity of radiation, because of the diffuse source of light, still there appears to be an approximate proportionality. The velocity of spreading of the drop at 60 cm distance compared to that at 30 cm distance, is probably greater than that expected from the ratio of the intensities, due to the greater proportion of chemically changed molecules having had time to diffuse to the water surface. To find the effect of a given quantity of radiation it will be necessary to compare the final diameters of the drops.

Fig. 2 shows the growth of a drop during and after the irradiation with ultraviolet light. The drop was at 30 cm distance from the lamp. Fig. 3 shows the growth of a drop during and after irradiation with x-rays. The diameter of the drop immediately before the irradiation was 7.2 mm; 100 KVP, 5 ma, 20 cm target skin distance, and no filter except a piece of black paper, was used. The half-value layer was 0.8 mm aluminum, and the intensity amounted to 240 roentgens per minute as measured in air. The container was placed on paraffin blocks and a large field was used. A drop exposed to β-rays from a radon bulb grew in a similar manner. These results give an idea of the velocity of the growth of the drops when they are exposed directly on the water surface. It is possible that this method could be used for measurements of intensity of radiation. The number of roentgens required for an appreciable growth of a drop is, however, so large that the method would be impractical for the measurements of x-rays. It may prove satisfactory for measurements of short wave ultraviolet radiation. It may also be tried to compare the surface effects of different types of rays, as the maximum thickness of the drops does not exceed 4 mm.

The effect of the radiation may take place

throughout the oil, at the whole surface of the drop, or at one of the interfaces. The fact that the drop grows after the irradiation is discontinued, indicates that the oil-water interface is not the sole place for immediate action. It may be considered possible that activated water molecules contribute to the reaction, but that could hardly explain the delayed effect. More information could evidently be obtained by irradiating the oil before the drop was placed on the water. In the first experiment of this type oil was kept in the same type of containers as used before, namely large watch glasses. A large surface thus was exposed to air. After the irradiation a drop of the oil was placed on a water surface. Such a drop has at first about the same diameter as a drop from unirradiated oil. It spreads, however, rather rapidly and reaches a limiting size after several hours. The final size depends upon the amount of radiation given. It might be expected that the amount of oil surface exposed to the air during irradiation would make a large difference in the chemical change. However, Fig. 4 shows that with oil completely filling a closed container during irradiation with x-rays, this change took place. This does not exclude air from the reaction, as amounts absorbed on the container walls and in the oil may be sufficient for the reaction.

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Reactions in the System Containing Nitrogen Dioxide, Carbon Monoxide and Oxygen; NO_3 as an Intermediate in the Classical Trimolecular Oxidation of Nitric Oxide

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The kinetics of some reactions in the system containing carbon monoxide, oxygen, and nitrogen dioxide have been studied over the temperature range from 658° to 800°K. It has been shown that the reaction is heterogeneous for the lower pressures of nitrogen dioxide and homogeneous for pressures above 10 mm. The homogeneous portion of the reaction appears to include the oxidation of nitric oxide and the oxidation of carbon monoxide by "oxides" of nitrogen. A bimolecular reaction involving nitric oxide and oxygen has been studied. Evidence is presented which indicates that the oxidation of nitric oxide involves two consecutive bimolecular reactions instead of the classical termolecular mechanism.

INTRODUCTION

THE effect of small amounts of nitrogen dioxide upon certain thermal oxidation reactions has been described by several investigators. The rate of the oxidation of hydrogen catalyzed by traces of nitrogen dioxide has been studied by Hinshelwood and co-workers.[1] Norrish[2] has shown that a photochemical reaction proceeds in hydrogen-oxygen mixtures containing nitrogen dioxide at temperatures which are far too low to permit a measurable thermal reaction.

Mixtures of carbon monoxide and oxygen exhibit definite explosion areas which are sharply defined by temperature and pressure of the gases. Semenoff[3] found that these explosive peninsulas could be extended a hundred degrees or more in the direction of lower temperatures if a small quantity of nitrogen dioxide was added to the mixture. This work was primarily concerned with the study of the effect of various inert gases, water vapor, etc. upon the explosion limits. No data relative to the rate of the nonexplosive catalyzed reaction were reported.

A study of the nitrogen dioxide catalyzed oxidation of carbon monoxide in the nonexplosive region has been made by Crist and Roehling.[4] They indicated that the catalytic effect of nitrogen dioxide was probably due to

[1] (a) Gibson and Hinshelwood, Trans. Faraday Soc. **24**, 559 (1928); (b) Thompson and Hinshelwood, Proc. Roy. Soc. **124A**, 219 (1929).
[2] Norrish and Griffiths, Proc. Roy. Soc. **139A**, 147 (1933).
[3] Semenoff, *Chemical Kinetics and Chain Reactions* (Oxford University Press, 1935).
[4] Crist and Roehling, J. Am. Chem. Soc. **57**, 2196 (1935).