The study of the radiation chemical oxidation of unsaturated hydrocarbons by oxygen is of considerable interest. The possibility of carrying out the radiolysis at any temperature, in particular, at room and lower temperatures, makes it possible to isolate from the oxidation products unstable intermediate compounds, which is usually impossible in the study of thermal oxidation processes. Despite the great difference in the conditions, results obtained in the radiation chemical oxidation of lower olefins apparently can shed some light on the mechanism of thermal oxidation, which has not been elucidated up to now.

Very little work has been done on the oxidation of lower olefins under the action of radiation. There are only three communications on the radiolysis of water containing a dissolved mixture of ethylene and oxygen. Henley et al. [1,2] established that in this case, ethanol, acid, hydrogen peroxide, organic peroxide, and aldehydes are formed and according to the data of the authors, acetaldehyde was obtained in a yield of 60 molecules/100 ev. However, in the work of Clay, Johnson, and Weiss [3] it was stated that acetaldehyde is formed in considerably lower yields and that the only reaction products are formaldehyde, acetaldehyde, glycolaldehyde, and peroxides.

We studied the oxidation of ethylene by oxygen in the gas phase under the action of a beam of fast electrons. The effect of irradiation time, the ratio of the initial gases, the temperature, and the material of the reaction vessel was studied. We established the qualitative composition of the reaction products and carried out a quantitative analysis of both liquid and gaseous oxidation products and this made it possible to draw up a balance of carbon and oxygen between the starting gases and the reaction products.

Experiments on the effect of the total dose on the oxidation were carried out with ethylene-oxygen mixtures in a ratio of 1:1 in an aluminum chamber at room temperature and an initial pressure equal to atmospheric. The irradiation time was varied over the range 5 to 45 min (dose 0.2-1.0 × 10^2 to 1.7-10^3 ev, respectively).

The results of the experiments, which are given in Figs. 1-4, show that over the dose range studied, ethylene reacts at a higher rate than oxygen and this difference increases considerably with a reduction in the total dose. This phenomenon is explained by an increase in the yield of acetylene and carbon monoxide in the initial period of the reaction and at first glance, it seems surprising as carbon monoxide is regarded as a secondary product in oxidation processes and its yield should fall with a decrease in exposure. In the given case, the increase in the carbon monoxide and acetylene yield at low doses may be explained by the catalytic effect of the chamber walls; in the initial period of radiation there is dehydrogenation of active molecules and primary peroxide products on the walls of the chamber which are covered with aluminum oxide, so that the reaction is displaced toward the formation of acetylene, carbon monoxide, and hydrogen with an increase in the ethylene consumption; however, after some time, the walls of the chamber are covered with a layer of liquid oxidation products and the catalytic effect of the walls is reduced to a considerable extent.
This argument was confirmed by the following experiment: the starting mixture was irradiated for 4 min and after gas had been taken for analysis, mixture was introduced into the chamber up to atmospheric pressure and irradiation continued for a further 20 min; the gas was then completely removed from the chamber and the latter filled with fresh starting mixture, which was irradiated for 4 min. Gas analysis showed that less acetylene and considerably less carbon monoxide was formed in the second 4-min experiment than in the first.

The data presented show that the main oxidation products were glycolaldehyde, formic acid, carbon monoxide, acetylene and organic peroxides (hydrogen peroxide was formed in an insignificant yield)*. Formaldehyde was formed in a yield of 0.15 molecules/100 ev. After a reaction period of approximately 15 min, there was no sharp change in the relation of the yields of oxidation products to the total dose.

The relation of the oxidation process to the ratio of the starting gases was investigated in the same chamber at room temperature and an initial pressure equal to atmospheric and with an exposure of 15 min (dose $0.55 \times 10^{23}$ ev). The data presented in Fig. 5-8 show that the rates of the reaction of ethylene and oxygen depended strongly

* ROOR denotes the sum of the peroxides in all graphs and tables.