It also follows from the mechanism proposed by Adadurow and Didenko that the (per cent. reaction)-(time) curve for a single experiment must be autocatalytic in nature, since the reaction is assumed to be proceeding on zinc oxide formed by the decomposition of the reactant. No such effect was found, as is shown by Figure 1 of our paper.

It appears therefore that the criticisms of Adadurow and Didenko are based partly on an incorrect interpretation of their own data, and partly on an incorrect mechanism for the decomposition of methyl alcohol. On this basis they arrive at an alternative explanation of our experiments which is not in accord with the facts.

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RECEIVED JANUARY 21, 1936

COMMUNICATIONS TO THE EDITOR

THE PHOTOLYSIS OF ACETIC ACID

Sir:

In the course of a general investigation of the mechanism of the photolysis of acetic acid I applied the method of Paneth [*Ber.*, **62B**, 1335 (1929)] to the detection of free radicals. Using a light lead mirror followed in order by a heavy lead guard mirror and a light antimony mirror, approximately simultaneous disappearance of the two light mirrors was observed.

The efficacy of the guard mirror was checked by experiments with acetone. In a particular series of experiments, it was found that a guard mirror which was ineffective in preventing the removal of an antimony mirror in an acetic acid run was, after the lapse of a day, still effective in preventing such disappearance of a fresh antimony mirror in an acetone run, even though it itself was now visibly affected. The period of the latter run was equivalent (in free radical yield) to more than twice that of the acetic acid run. When, after the latter experiment, the guard mirror was reinforced by redeposition of lead, it was found that it was still ineffective in preventing the removal of the same antimony mirror in an immediately following run with acetic acid.

Except for the use of the guard mirror and the succeeding antimony mirror, the experiments bore a resemblance to those of Pearson [*J. Chem. Soc.*, 1718 (1934); *ibid.*, 1151 (1935)].

The effect on the lead mirrors may be attributed to the formation of free radicals, presumably methyl, and that on the antimony mirrors to the formation of atomic hydrogen in the photolysis of acetic acid in the vapor phase according to a mechanism

$$CH_3COOH + h\nu \longrightarrow CH_3 + COOH \quad (1)$$
$$COOH \longrightarrow CO_2 + H \quad (2)$$

Inasmuch as Farkas and Wansbrough Jones [*Z. physik. Chem.*, **B18**, 124 (1932)] offer good evidence [v. Franck and Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934)] for a primary formation of ultimate molecules according to the alternative mechanisms

$$CH_3COOH + h\nu \longrightarrow CH_4 + CO_2 \quad (3)$$
$$(CH_3COOH)_2 + h\nu \longrightarrow C_2H_6 + CO_2 + CO + H_2O \quad (4)$$

I am led to the conclusion that, in acetic acid, decomposition may occur either from a suitable constellation of atoms by rearrangement of bonds into equally stable constellations of other molecules or from a molecule of sufficient energy content into free radicals. The implications of this conclusion are being subjected to further test.

On the basis of the results of Pearson, Robinson and Stoddard, [*Proc. Roy. Soc.* (London), **A142**, 275 (1933)] the effect on the antimony mirror would have been unexpected since they report that the recombination of atomic hydrogen is catalyzed by a lead mirror. The results here indicate that at low concentrations of atomic hydrogen the recombination process is improbable. So far as known this is the first time that this method has been applied to the detection of hydrogen atoms in the presence of free radicals.

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