the ether solution for three or four hours with three successive portions of powdered calcium chloride. I only employed a quantity just sufficient to fix the alcohol which was mixed with ketene acetal. When being shaken in this way ketene acetal is held by the great surplus of solid calcium chloride, which is not the case when a concentrated aqueous solution of calcium chloride is used. The separation of alcohol is better performed in such a manner. The directions given by me should be changed as follows.

After drying with anhydrous sodium sulfate, the ethereal solution from the extraction of the "primary reaction product" triturated with water, is distilled through a fractionating column. The residue containing ether only in a little amount is shaken intermittently during six hours with four parts of saturated aqueous solution of calcium chloride. Then it is extracted with ether in a continuous extraction apparatus and the resulting solution is dried with anhydrous sodium sulfate. Observing the precautionary measures mentioned before, ether and finally ketene acetal are distilled; yield, 13 g. or 11.2% of the calculated amount based on 23 g. of sodium used.

The preparation of dimethyl ketene diethyl acetal from ethyl isobutyrate was not successful with sodium ethoxide. It was performed in another manner which will be described later.

TECHNISCHE HOCHSCHULE OF BERLIN   HELMUTH SCHEIBLER
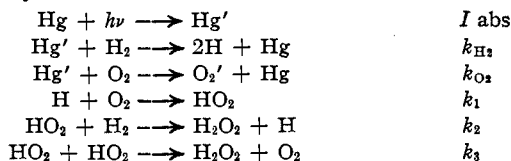LABORATORY OF ORGANIC CHEMISTRY
BERLIN-LICHTERFELDE, GERMANY

KINETICS OF THE MERCURY SENSITIZED REACTION BETWEEN HYDROGEN AND OXYGEN

Sir:

Investigations of the mercury sensitized photo-reaction between hydrogen and oxygen have given rise to a large number of conflicting and unconnected data. These have been used to set up mutually conflicting theories of the mechanism of the reaction of hydrogen atoms with oxygen. It can, however, be demonstrated that almost all the known facts can be correlated and be completely in accord if we assume as the true mechanism:

$$
\begin{array}{ll}
\mathrm{Hg} + h\nu \longrightarrow \mathrm{Hg}' & I\ \text{abs} \\
\mathrm{Hg}' + \mathrm{H_2} \longrightarrow 2\mathrm{H} + \mathrm{Hg} & k_{\mathrm{H_2}} \\
\mathrm{Hg}' + \mathrm{O_2} \longrightarrow \mathrm{O_2}' + \mathrm{Hg} & k_{\mathrm{O_2}} \\
\mathrm{H} + \mathrm{O_2} \longrightarrow \mathrm{HO_2} & k_1 \\
\mathrm{HO_2} + \mathrm{H_2} \longrightarrow \mathrm{H_2O_2} + \mathrm{H} & k_2 \\
\mathrm{HO_2} + \mathrm{HO_2} \longrightarrow \mathrm{H_2O_2} + \mathrm{O_2} & k_3
\end{array}
$$

These give the kinetic expression

$$
\frac{d\,[\mathrm{H_2O_2}]}{dt} = \frac{k_2\,[\mathrm{H_2}]}{\sqrt{k_3}} \sqrt{\frac{[\mathrm{H_2}]\,k_{\mathrm{H_2}}\,I\ \text{abs}}{[\mathrm{H_2}]\,k_{\mathrm{H_2}} + [\mathrm{O_2}]\,k_{\mathrm{O_2}}}} + \frac{[\mathrm{H_2}]\,k\mathrm{H_2}\,I\ \text{abs}}{[\mathrm{H_2}]\,k_{\mathrm{H_2}} + [\mathrm{O_2}]\,k_{\mathrm{O_2}}}
$$

Assuming $k_2/\sqrt{k_3} = 10^{-3}$, this equation fits exactly the data of Marshall [This Journal, **49**, 2763 (1927)] on the influence of [H$_2$] and [O$_2$] on the rate, if we put for k_{H_2} 1.1 × 10^7, k_{O_2} 0.68 × 10^7 as determined by Zemansky [*Phys. Rev.*, **36**, 919 (1930)]. The constant (I abs) so obtained is constant to within less than 3% for all the experiments of Marshall not indicated as uncertain. Furthermore, the value of the quantum yield as calculated, using $k_2/\sqrt{k_3} = 10^{-3}$ lies between 1 and 2 in those experiments, in close agreement with those experimentally determined (1–2.5). In addition, the discrepancy between the quantum yield measurements of Frankenburger and Klinkhardt [*Z. physik. Chem.*, **15B**, 421 (1931)] and by Marshall [*J. Phys. Chem.*, **30**, 1078 (1926); This Journal, **54**, 4460 (1932)] is explained, in that the former used a light intensity a hundredfold greater than the latter. The mechanism postulated calls for a higher quantum yield with lower intensities, which is again in agreement with the experiments. This subject will be given a complete exposition in a paper shortly to be submitted to the Journal.

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FURTHER REMARKS ON THE PREPARATION OF KETENE ACETAL

Sir:

Scheibler [This Journal, **55**, 425 (1933)] ascribes our failure to obtain ketene acetal [*ibid.*, **55**, 416 (1933)], first, to too long standing of the "primary reaction product" over sulfuric acid, and second, to the use of excessive amounts of calcium chloride in the purification of the product. The first reason is not valid because we did not use a "primary reaction product" which had attained constant weight over sulfuric acid, but rather the residue left after the evaporation of the reaction mixture at room temperature under diminished pressure in a vacuum desiccator as described by the original investigators [Scheibler and co-workers, *Ann.*, **458**, 28 (1927)]. On account of the second reason Scheibler now revises his original extraction procedure.

In consideration of this revised procedure we have made two further attempts to prepare ketene acetal. The same quantities of materials that were used in our earlier work were employed. The preparation of the "primary reaction product" was carried out in a tared 3-liter round-bottomed Pyrex flask. In this way it was possible to evaporate the ether and ethyl acetate from the reaction mixture and obtain a dry residue in about six hours, whereas evaporation in a vacuum desiccator according to the original procedure required about ten hours. It is not apparent to us how the time for this evaporation can be further decreased without