

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  $k_{H_2}$   $1.1 \times 10^7$ ,  $k_{O_2}$   $0.68 \times 10^7$  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 Frankenburg 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

the application of heat. The weight of the dry residue obtained in our latest experiments was in one case 77 g. and in the other 78 g. instead of 125 g. reported by the original investigators. In fact, intermittent weighings of the tared evaporation flask during the latter period of the evaporation showed that when its contents weighed 125 g. they were still liquid.

On working up these residues according to the revised procedure of Scheibler we obtained in one case 7 g. (A) and in the other 9 g. (B) of product at the point where ketene acetal should appear. In each of these products the amount of ethyl acetate was determined by saponification of an aliquot with 0.1 *N* potassium hydroxide and the amounts of ethyl alcohol and water were estimated by treatment of an aliquot with phenyl isocyanate followed by the isolation of the phenyl urethan and diphenyl urea. The following summary shows the percentages of these substances which were found to be present in the products which we obtained.

Product	Ethyl acetate, %	Alcohol, % <sup>a</sup>	Water, %	Total % found
A	13.0	72.5	2.2	87.7
B	0	87.5	1.5	89.0

<sup>a</sup> Analyses of a known mixture of alcohol and ethyl acetate, containing 85% of the former and 15% of the latter showed that only 85-90% of the alcohol could be recovered as the phenyl urethan, m. p. 52°.

These results show that the products which we obtained were mainly alcohol containing small amounts of water and ethyl acetate. It is our opinion that the failure of the found values to total 100% is due to the limitations of the procedure used for the determination of alcohol.

On the basis of our experiences, we believe that our failure to prepare ketene acetal is traceable to the discrepancy between the results reported by Scheibler and those obtained by us in connection with the formation of the so-called "primary reaction product" from ethyl acetate and sodium ethoxide. The results which we report now confirm our earlier conclusion that there is not only no evidence for, but definite evidence against, the existence of such a reaction product.

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## BROMINE SENSITIZED PHOTO-DECOMPOSITION OF CHLORINE DIOXIDE

Sir:

Chlorine dioxide is decomposed by light with production of  $\text{Cl}_2\text{O}_6$ , light in the blue and ultraviolet being equally effective [Finkelnburg and Schumacher, *Z. physik. Chem.*, Bodenstein Band, 704 (1931); Spinks, *THIS JOURNAL*, 54, 1689 (1932)]. Since the region of predissociation in