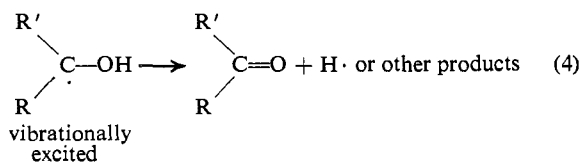
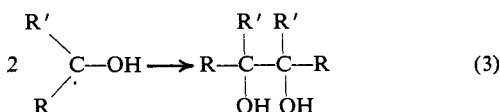
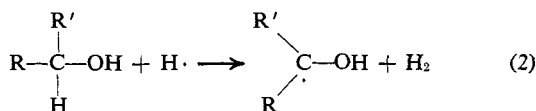
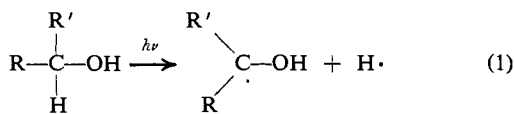


2-propanol, and 2-methyl-2-propanol are summarized below, and the products are expressed in units of mmoles per hour: methanol: H₂, 2.97; CO, 0.098; CH₄, 0.012; HCHO, 0.32; (CH₂OH)₂, 1.92; glycerine, 0.26; ethanol: H₂, 2.54; CO, 0.75; CH₄, 0.81; CH₃CHO, 0.10; 2,3-dihydroxybutane, 1.63; 2-propanol: H₂, 1.72; CO, 0.68; CH₄, 1.27; C₂H₆, 0.05; acetone, 0.23; pinacol, 1.52; 2-methyl-2-propanol: CH₄, 5.10; CO, 0.42; acetone, 0.35; pinacol, 1.25; 3-hydroxy-3-methyl-2-butanone, 0.33; 2,5-dihydroxy-2,5-dimethylhexane, 1.74.

The gas evolutions in these photolyses were inhibited by cyclohexene and were completely suppressed by the presence of 5% of cyclohexene (0.6 M). In all cases, cyclohexene only absorbs a minor portion of the light. In the case of photolysis of 2-propanol in the presence of 5% of cyclohexene, the following products were obtained in units of millimoles per hour: acetone, 2.0; pinacol, 0.09; cyclohexane, 0.60; cyclohexyldimethylcarbinol, 0.51; cyclohexenyldimethylcarbinol, 0.40; bicyclohexyl, 0.12; cyclohexenylcyclohexane, 0.05; high boiling residue (0.04 g/hr).

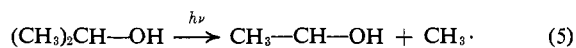
The principal gaseous product is hydrogen in all cases except 2-methyl-2-propanol and the principal higher boiling products are the corresponding carbonyl compounds and the glycol. When the results of photolysis of 2-propanol in the presence of cyclohexene, a radical scavenger, were compared with the results of photolysis of pure 2-propanol, it is interesting to note that the evolution of hydrogen, methane, and carbon monoxide was completely suppressed and the yield of acetone became much higher. On the basis of the above observations, hydrogen is most likely formed from a radical process such as indicated by reactions 1 and 2 and acetone is not formed directly from 2-propanol by a molecular elimination of hydrogen. One possible



explanation is that the 2-hydroxy-2-propyl radical formed in reaction 1 may be vibrationally excited. The light at 185 m μ is very energetic and is equivalent to 6.5 eV or 148.7 kcal/einstein. After the initial cleavage of the α -C-H bond in photoexcited 2-propanol, which has a bond energy estimated at about 85 kcal, the excess energy may remain preferably in the form of vibrational energy in the 2-hydroxy-2-propyl radical rather than in the form of kinetic energy of the hydrogen atom. The vibrationally excited 2-hydroxy-2-

propyl radical thus generated may differ in its behavior from the normal 2-hydroxy-2-propyl radical which usually dimerizes to give pinacol (reaction 3) or is scavenged by cyclohexene. It is probable that the vibrationally excited 2-hydroxy-2-propyl radical may disproportionate, dissociate, or react with cyclohexene to give acetone prior to its deactivation (reaction 4). The accumulation of acetone in the photolysis of 2-propanol in the presence of cyclohexene may be attributed to the quenching effect of cyclohexene on the secondary decomposition of acetone by the 254-m μ emission of the light source.

The α -C-C bond in 2-propanol has a bond energy comparable to that of the α -C-H bond. An initial cleavage of photoexcited 2-propanol will give a methyl radical and a 1-hydroxyethyl radical (reaction 5). The products which may be derived from these radicals are conspicuously absent in the photolysis of 2-propanol in the presence of cyclohexene or among the higher boiling products in the photolysis of pure 2-propanol. Therefore, the formation of methane and carbon monoxide in the photolysis of 2-propanol is probably derived from the secondary photolysis of acetone. This fact was readily demonstrated by photolyzing acetone in 2-propanol.^{5,9}



We wish to suggest that the principal primary process in the liquid phase photolysis of simple primary and secondary alcohols is the cleavage of an α -C-H bond, while the primary process for tertiary alcohols is the cleavage of an α -C-C bond. Our preliminary investigations indicate that photochemical reactions in the liquid phase with 185 m μ light might be quite selective and the investigations are being extended to other organic compounds.

Acknowledgment. The authors wish to thank the Atomic Energy Commission for the support of this work.

(9) A detailed analysis of gas evolved from the photolysis of 2-propanol at 60-min intervals indicated that the gas evolved earlier is considerably richer in hydrogen, but we are not able as yet to obtain a sample completely free of methane. Acetaldehyde, if formed, would have been detected under the reaction conditions.

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Dependence of the Quantum Yield of Photoreduction of Benzophenone in 2-Propanol on Light Intensity. Possibility of Triplet Quenching by the Radical Intermediates in Solution

Sir:

The photoreduction of benzophenone in 2-propanol has been extensively investigated.¹ The reaction is

(1) (a) G. Ciamician and P. Silber, *Ber.*, **34**, 1530 (1901); (b) J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Martin, *J. Am. Chem. Soc.*, **81**, 1068 (1959); (c) J. N. Pitts, Jr., H. W. Johnson, Jr., and T. Kuwana, *J. Phys. Chem.*, **66**, 2456 (1962); (d) W. M. Moore, G. S. Hammond, and R. P. Ross, *J. Am. Chem. Soc.*, **83**, 2789 (1961); (e) G. S. Hammond, W. P. Baker, and W. M. Moore, *ibid.*, **83**, 2795 (1961); (f) G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, **57**, 1686 (1961).