a maximum over-all quantum yield of 2 if our mechanism is correct, or of 1 if that of Ross and Kistiakowsky is right. The fact that the values of Ross and Kistiakowsky are less than unity at 3650 and somewhat exceed it at 3130 lends probability to the correctness of our theory.

If this view is not taken it is difficult to reconcile the low value of the quantum efficiency at λ 3650 Å. with the diffuse character of the absorption in that region. It is improbable that the fraction of excited molecules which do not decompose could lose their energy by collision for this would involve a life of the excited state of the order of 10^{-8} second, which is about 10^5 times greater than that necessary to produce so diffuse a spectrum.

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RECEIVED JUNE 7, 1934

THE ADDITION OF HYDROGEN BROMIDE TO PENTENE-1 AND HEPTENE-1

Sir:

In reply to the communication by Kharasch, Hinckley and Gladstone in which they question the validity of our conclusions concerning the importance of the solvent as an influencing factor in hydrogen bromide addition to pentene-1 and heptene-1, we would emphasize the particular conditions under which our addition reactions were carried out. The highly purified hydrocarbons gave no test for peroxide before the addition of hydrogen bromide nor did they give the colored reaction mixtures which we have always obtained in hydrogen bromide addition to hydrocarbons known to contain peroxide. The addition reactions in organic solvents, where we obtained the so-called "abnormal" products, 1-bromopentane and 1-bromoheptane, took place in the absence of air, whereas in water solution the reaction mixtures were shaken for many days in contact with air. The probability of a peroxide effect in the latter solvent is therefore much greater than in the organic solvents but our results gave conclusive evidence of the formation of only the "normal" product 2-bromopentane and 2-bromoheptane in water solution. Careful analysis of the experimental data would seem to justify our conclusion that any peroxide effect was eliminated in these reactions.

Furthermore, our reactions were carried out at atmospheric pressure while those of Kharasch and co-workers must have taken place under increased pressure. This factor complicates any comparison of results since the effect of pressure may be of importance in determining the products of the reaction. In drawing conclusions from our experiments there was no intentional disregard of the importance of the peroxide effect in hydrogen halide addition to unsaturated compounds which has been demonstrated by Kharasch and co-workers. Our results, however, seem to give conclusive evidence that in the absence of peroxide the solvent is an influencing factor.

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RECEIVED JUNE 11, 1934

PREPARATION OF PURE METALLIC HYDROXIDES

Sir:

A recent article by J. H. Long, J. C. W. Frazer and Emil Ott [THIS JOURNAL, **56**, 1101 (1934)] refers to a dissertation by O. G. Bennett [Johns Hopkins University, 1930] which describes the purification of metallic hydroxides by washing the oxides (or hydroxides) by decantation until peptization occurs and then electrodialyzing to remove the alkali salts adsorbed by the oxide hydrate at the moment of precipitation and which cannot be removed from the (usually gelatinous) oxide by mere washing. This ultrapurification is necessary if one is to obtain cobalt or nickel trioxides or manganese dioxides in a state sufficiently pure so as to be capable of catalyzing the reaction of carbon monoxide with oxygen at room temperature.

According to Bennett's dissertation, which was kindly made available by Dr. J. C. W. Frazer, the process of electrodialysis is long and tedious, sometimes requiring weeks. If the oxide could be precipitated in the absence of alkali or metal compound other than manganese or nickel salts, respectively, it would not be necessary to remove adsorbed salts by electrodialysis. It has been found in this Laboratory that passing ozone through neutral solutions of manganous acetate or chloride precipitated a manganese oxide which, after a short washing with concentrated nitric acid and drying by evacuation at 100°, was a very active catalyst for the oxidation of carbon monoxide. The electrolysis of manganous nitrate (with the cathode surrounded by a porous cup containing ammonium nitrate solution) gave a manganese dioxide of equal activity and in greater quantities. (Similarly, ozonizing basic lead acetate solution precipitated an oxide which, after washing with nitric acid and drying *in vacuo* at 100°, was active at 80°, whereas Bennett's PbO_2 did not catalyze the reaction except above 180°.)

It is hoped that this communication will be of aid to workers interested in preparing manganese dioxide (or other higher oxides) free of adsorbed alkali salts and capable of catalyzing gas-oxidation reactions. At no time did these oxides or the salts from which they were obtained come in contact with alkali other than that derived from glass, porcelain, etc., or with any foreign material other than nitric acid and volatile ammonium salts. Further work is now in progress.

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RECEIVED JUNE 13, 1934

ASYMMETRIC REARRANGEMENT

Sir:

For some time there has been under way in this Laboratory an investigation of the effect called by Kuhn [*Ber.*, **65**, 49 (1932)] asymmetric rearrangement of the first type (asymmetrische Umlagerung erster Art). Our experiments (as yet unpublished) indicate that Kuhn's hypothesis is not generally valid, and that if it has any field of applicability, that field has not yet been clearly defined. The present communication is prompted by the recent paper of Lesslie and Turner [*J. Chem. Soc.*, 347 (1934); we have searched carefully for the mutarotation described by Lesslie and Turner, but have not been able to find any such phenomenon] in support of Kuhn's idea.

Kuhn bases his hypothesis chiefly on the "anomalous" optical rotation of quinine 4,4'-dinitrodiphenate in chloroform solution; Lesslie and Turner's supporting evidence is derived from the similar behavior of quinine diphenate in the same solvent. The divergences from the normal rotation are explained by what might be called a "dissymmetrizing" effect exerted by the optically active base on the acid. According to this view, the solution of the free acid is an equimolecular mixture of the *d* and *l* forms in labile equilibrium. The dissymmetric base disturbs this equilibrium, and the observed rotation is the resultant of the rotations of the base and the optically activated acid. As soon as the dissymmetrizing base is removed, the equilibrium between the two forms of the acid shifts back very rapidly to form the equimolecular mixture. Physical separation of the stereomeric acids is thus impossible.

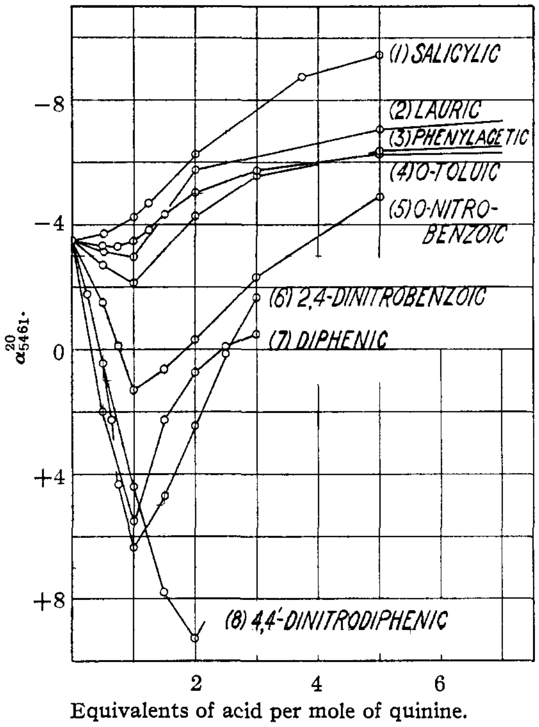

Fig. 1.—Rotations of salts of quinine in chloroform: Curves 1, 2, 3, 4, 5 and 6 were obtained with 0.04 molar solutions, curves 7 and 8 with 0.01 molar solutions of quinine, in a 2-dm. tube. The discrepancy thus introduced is, however, negligible, *e. g.*, for a 0.04 molar solution of quinine containing one equivalent of 4,4'-dinitrodiphenic acid α_{5461}^{20} 4.43°; calculated to the above concentration from a 0.01 molar solution of quinine and one equivalent of acid α_{5461}^{20} 4.40°. Curve 1: Similar curves were obtained with anthranilic, *o*-chlorobenzoic and *o*-iodobenzoic acids. Curves 2 and 3: Similar curves were obtained with acetic, crotonic, chloroacetic, palmitic, phenylpropionic and trichloroacetic acids. Curve 5: Similar curves were obtained with anisic, cinnamic, *m*- and *p*-nitrobenzoic, *p*-toluic and 3,5-dinitrobenzoic acids. Curves 6 and 7: A similar curve was obtained with 2,4,6-trinitrobenzoic acid.

This theory of Kuhn implies an important departure from classic chemical practice. The principle that isomer numbers can be determined from anomalies in the optical rotations of solutions may well have far reaching consequences. It therefore seemed desirable to us, before accepting so radical an idea, to investigate thoroughly the rotations of salts of various optically active