a few hours for a type of adsorption having all of the characteristics of activated adsorption [Taylor, THIS JOURNAL, **53**, 578 (1931)]. The energy of activation of the adsorption was about 9000 calories. The isobar at 760 mm. showed a gradual decrease from an adsorption of 7 to 8 cc. at −78° to about 5 or 6 cc. at 0°.

Type B Activated Adsorption.—At 100° or higher an additional but much slower adsorption (type B) set in, the total adsorption (type A and type B) reaching at 100° a value of 8 to 9 cc. within two hours. At 212 and 450° the adsorptions were 5.5 and 3.5 cc., respectively, and reached an apparent equilibrium in less than an hour. Isotherms taken at 350 and 410° were reversible and indicated a heat of adsorption of about 8500 calories.

In a previous communication [Harkness and Emmett, THIS JOURNAL, **55**, 3496 (1933)] it was pointed out that the adsorption of hydrogen by the promoted iron catalyst at 100° and at 212° strongly inhibited the low temperature (−190°) catalytic conversion of ortho to para hydrogen. In continuing this study it has now been found that this inhibition produced by the adsorption of a given volume of hydrogen by the catalyst at 100° is about eight times as great as that produced by the same volume of hydrogen adsorbed at −78°.

From the combined adsorption data and measurements of the absolute and relative poisoning effects of types A and B adsorption on the low temperature ortho–para hydrogen conversion it therefore may be concluded (1) that both types A and B are primarily surface adsorptions and not solutions within the metal, and (2) that types A and B represent two distinctly different kinds of activated adsorption, the B type not being merely a slow continuation of type A.

BUREAU OF CHEMISTRY AND SOILS R. W. HARKNESS
WASHINGTON, D. C. P. H. EMMETT

RECEIVED DECEMBER 26, 1933

MOLECULAR REARRANGEMENTS OF OPTICALLY ACTIVE RADICALS

Sir:

Previous investigations in this Laboratory have shown that in certain molecular rearrangements involving optically active radicals, notably of the Hofmann, Curtius and Lossen types, the optically active group maintains an asymmetric configuration during the rearrangement. It has also been shown that such transformations are accompanied with little or no racemization. The optical stability of such radicals during rearrangement can be explained easily on the theory that the shift of the electron pair from the carbon atom to the nitrogen atom includes the group which it holds.

We have continued our studies of molecular rearrangements in order to determine more definitely whether the electronic nature of the migrating group is of great importance in maintaining the asymmetry of the radical during rearrangement. For this purpose a compound was chosen in which the group containing the asymmetric carbon atom is essentially of the nature of a positive group during rearrangement.

Accordingly we prepared *l*-2-methyl-2-phenylbutanol(1), $CH_3CH_2C(CH_3)(C_6H_5)CH_2OH$, $\alpha_D^{19} = -4.90°$ (homogeneous, 1-dm. tube), and studied its behavior when the hydroxyl group was replaced by chlorine. The chloride so produced was found to be a tertiary chloride, and not a primary chloride. This fact is to be expected on the basis of modern conceptions of molecular rearrangements. It was also found to be optically active. The rearrangement however is accompanied by an inversion in sign of the rotatory power. The *l*-alcohol yields a dextrorotatory rearrangement product. In conclusion it is to be pointed out that these facts have an important bearing on all investigations involving configurational relationships of optically active compounds.

FRICK CHEMICAL LABORATORY EVERETT S. WALLIS
PRINCETON, NEW JERSEY P. I. BOWMAN

RECEIVED JANUARY 2, 1934

THE INTRODUCTION OF DEUTERIUM ATOMS INTO ACETONE

Sir:

When a solution of acetone in water containing deuterium oxide and a small amount of potassium carbonate is warmed for a short time, an exchange of hydrogen atoms occurs, with the consequent introduction of deuterium into the acetone. We first studied the concomitant decrease in density of the water. For example, six solutions were prepared, each containing 30 cc. of water, 60 cc. of refractionated (0.1° range) "C. P. Analyzed" acetone, and about 0.1 g. of either phosphoric acid or potassium carbonate as indicated in the table. After warming from one to three hours on the steam-bath, the solutions were carefully fractionated, using a 90-cm. vacuum-jacketed column. The water in each case was collected in two fractions, and the density of the second was compared with that of the original water. The results are tabulated below. Those in the first column, with ordinary water, show the reliability of the method.

Substance added	K_2CO_3	H_3PO_4	None	K_2CO_3	K_2CO_3	K_2CO_3
Mole % D (init.)	0.02	0.73	0.73	0.73	1.08	4.07
Mole % D (final)	.02	.67	.68	.38	.64	1.93
Fr. D removed	0	.08	.07	.48	.41	0.52

The presence of deuterium in the acetone which had been treated with 4.07% heavy water was demonstrated by density measurements and by returning a part of the deuterium from this "heavy" acetone to a sample of ordinary water. The "heavy" acetone was dried for twenty hours with fused potassium hydroxide, then fractionated, and its density compared with that of similarly treated ordinary acetone, showing an increase of 1.4° in the temperature of equal density. It was then warmed with ordinary water and potassium carbonate and again fractionated. The first acetone fraction, dried as before, showed a density slightly greater (0.2°) than ordinary acetone, while the last aqueous fraction contained 0.94% deuterium, corresponding to a removal of 54% of the estimated deuterium content from the acetone. The mole fraction of acetone was 0.29 as compared with 0.33 in the earlier experiments. We may estimate the equilibrium constant for the formation of monodeuteroacetone and ordinary water from acetone and HH^2O as approximately 2, with equilibrium approached in both directions.

The effectiveness of an alkaline catalyst argues for a mechanism involving the postulated enol form of acetone, a possibility which led us initially to perform these experiments. The acidic hydrogen of the enol form should exchange rapidly with the hydrogens of water, and this, coupled with a mobile equilibrium between the keto and enol forms, should result in the formation of carbon–deuterium bonds. It is doubtful whether in an organic compound not susceptible to such a reaction mechanism, the replacement of protium by deuterium by direct contact with water will be realized.

We plan to continue the study of acetone along with other compounds for which enol forms are known or postulated. At present there is no reason to doubt that the treatment of acetone with successively heavier portions of water will result in the practically complete replacement of protium by deuterium. This opens interesting possibilities in synthesis.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN
J. O. HALFORD
LEIGH C. ANDERSON
JOHN R. BATES

RECEIVED JANUARY 11, 1934

FRACTIONATION OF THE HYDROGEN ISOTOPES BY THE ADDITION OF SODIUM TO WATER

Sir:

Eyring[1] predicted, from zero point energy considerations, that isotopic separations will occur in the course of many reactions which do not involve electrolysis, through a difference in the reaction velocities of deuterium and of protium compounds. Such separations have been observed, and reported[2,3] for the reaction of iron with steam. We have recently made a quantitative study of the isotopic fractionation which we find to occur in the reaction of metallic sodium with water.

The reaction was carried out by adding small pieces of clean metallic sodium to a weighed quantity of water. Careful specific gravity determinations were made on the initial sample of water, on that collected by burning the evolved hydrogen and on the water distilled from the residue in the reaction flask (approximately 50% NaOH). Successive distillations with slightly alkaline permanganate yielded samples of constant density. Their specific gravities were determined by means of the buoyancy balance[4] equipped with a convenient thermostatic control which we have developed, and were reproducible to one part per million.

The quantitative results are given in the table. In the residue the hydrogen in NaOH is calculated as water.

Material		Wt., g.	ΔT, °C.	Δ sp. g. (p. p. m.)	Total Δm above ordinary water (p. p. m.)
Initial water		389.2	0.532	149	57,990
Final water	Heavy fraction	332.3	.601	168	55,820
	Light fraction	57.3	.179	50	2,860
	Totals	389.6			58,680

From these data we have derived the separation coefficient α, in the equation $d \ln n_P = \alpha d \ln n_D$ where n_P and n_D are, respectively, the number of

---

[1] Eyring, *Proc. Nat. Acad. Sci.*, **19**, 78 (1933).

[2] Bleakney and Gould, *Phys. Rev.*, **44**, 265 (1933).

[3] Horiuti and Polanyi, *Nature*, **132**, 819 (1933).

[4] Lewis and Macdonald, *J. Chem. Physics*, **1**, 341 (1933).