

activities of the hydrogen obtained from two fractions and the residue were determined in a Geiger counter.²

TABLE I
PROPERTIES OF THE ALKYLATE AND ACTIVITY OF HYDROGEN SAMPLES

B. p., °C.	Fraction of alkylate		Activity of hydrogen	
	% Alkylate	n^{20}	Counts/min.	Sp. act.
99-100	ca. 10	1.389	332 ± 10	8.4 × 10 ⁶
114-116	ca. 10	1.402	300 ± 10	7.6 × 10 ⁶
Residue	ca. 60	...	300 ± 10	7.6 × 10 ⁶

The activity of the hydrogen from the different fractions was practically the same, and the specific activity corresponds closely to the assumption of a random distribution of all of the hydrogen and tritium atoms in the 2-butene and catalyst, prior to alkylation.

Experimental

A solution composed of 0.48 mole of isobutane and 0.109 mole of 2-butene was added under pressure over a period of fifteen minutes to 0.131 mole of 100% tritium sulfuric acid (sp. act. 5.43×10^7) with vigorous stirring. The reaction chamber was a lead-lined, cylindrical iron vessel held at 10°. A few minutes was allowed for completion of the reaction, after which the excess of isobutane was allowed to evaporate from the reactor. The oil and acid layers in the residue were separated and the former washed with water and dried. The volume of alkylate was 20 ml.; fractionation was carried out in a 20-plate column. Samples of each fraction were burned over copper oxide, the water formed collected and the hydrogen obtained from it by reaction with magnesium at 600°.

If, as suggested above, all of the hydrogen and tritium atoms of the 2-butene and the sulfuric acid were randomly distributed between the alkene and catalyst, before alkylation, specific activity of the hydrogen from the alkene would be

$$5.43 \times 10^7 \times \frac{2 \times 0.131}{8 \times 0.109 + 2 \times 0.131} = 1.25 \times 10^7 \text{ counts/min./mole}$$

As a result of alkylation, the activity of hydrogen derivable from the hydrocarbon would be further reduced. Assuming as a first approximation that alkylation involves only addition of inactive alkane to the alkene of the above tritium content, in the ratio of 1:1, the specific activity of hydrogen obtainable from the alkylate would be $1.24 \times 10^7 \times 8/18$ or 5.5×10^6 . This value is of the same order of magnitude as that observed and indicates an extensive exchange either prior to or during alkylation. The agreement of the observed and calculated activities on the above assumption is even better when applied to the residue. Assuming that polymerization of butene precedes alkylation and using a ratio of alkene to alkane in the alkylate of 2:1, one obtains a calculated activity for the hydrogen thus diluted of $1.25 \times 10^7 \times 16/26$ or 7.7×10^6 . The observed value was 7.6×10^6 . It is to be noted that most of the alkylation resulted in these higher fractions. There is a suggestion here that polymerization of the alkene involved inter-

(2) See Harman, Stewart and Ruben, *THIS JOURNAL*, **64**, 2294 (1942), for details of operation.

mediates of longer life than did octane formation, permitting a closer approach to random distribution of the tritium.

The Reactivity toward Exchange of the Individual Reactants.—Forty ml. of isobutane and 6 ml. of 100% tritium sulfuric acid (sp. act. 5.43×10^7) were vigorously stirred for twenty minutes at 10°, in the lead-lined reactor. The specific activity of the hydrogen obtained from a sample of the isobutane was 1.36×10^6 . This corresponds to 7.1% of random distribution of the hydrogen atoms of the catalyst and the tertiary hydrogen atoms of the alkane. It also shows that little if any of the exchange noted above involved the alkylate.

Since 2-butene is absorbed rapidly by sulfuric acid, the following procedure was carried out to test the rapidity of exchange. The gaseous alkene was passed through a sintered glass bubbler and into 6 ml. of tritium sulfuric acid of the same composition as previously used. The rate of passage was such that little absorption occurred; all of the effluent gas was collected in a liquid air trap, and amounted to about 2 ml. of liquid. The specific activity of the hydrogen obtained from this material was 6.1×10^5 , higher than that obtained from the isobutane upon a twenty-minute contact with the acid, and demonstrates not only a rapid exchange but also a reversible absorption of the alkene in sulfuric acid.

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NEW COMPOUNDS

Benzyl Heptaacetyl- β -lactoside¹

A solution of 100 g. of acetobromolactose² in a mixture of 300 ml. each of anhydrous ether, benzene, and benzyl alcohol was shaken overnight with 40 g. of dry silver oxide. The filtered solution was halogen-free. Ether, benzene, and excess benzyl alcohol were removed by distillation with steam, the final portion of the aqueous distillate furnishing the first few crystals of the desired product. The residue in the flask crystallized when inoculated, and was recrystallized from warm ethyl acetate by the addition of ether in a yield of 58 g. Benzyl heptaacetyl- β -lactoside separated in clusters of small prisms melting at 145-146°. The rotation $[\alpha]^{20}_D -34.4^\circ$ in chloroform (*c*, 2) was unchanged by four additional recrystallizations.

Anal. Calcd. for $C_{33}H_{42}O_{18}$: C, 54.52; H, 5.83; acetyl, 9.63 ml. of 0.1 *N* NaOH per 100 mg. Found: C, 54.23; H, 6.12; acetyl, 9.75 ml.

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(1) Cf. Richtmyer, *THIS JOURNAL*, **56**, 1637 (1934).

(2) E. Fischer and H. Fischer, *Ber.*, **43**, 2530 (1910).