with 1 ml. of concentrated sulfuric acid for thirty minutes and then distilled there was obtained nearly the theoretical yield of ethanethiol at 35–40°. Fractionation of the residue directly gave 30 g. (98% yield) of *n*-butyl formate, b. p. 107–110°, n^{25}D 1.4896, and 36 g. (93%) of *n*-butyl ether, b. p. 140–141°, n^{25}D 1.4005.

2,2-Dimethoxybutane.—A mixture of 178 g. (1 mole) of 2,2-di-(ethylmercapto)-butane,[16] 128 g. (4 moles) of methanol and 3 g. of hydrogen chloride was heated under a 20-inch Fenske ring-packed column with adjustable take-off head, and ethanethiol was removed as formed. After fourteen hours, 119 g. of distillate had been removed at 35–40°. By iodine titration this was shown to contain 85% of ethanethiol, indicating that 82% of the theoretical ethanethiol had been removed. The residue was made very slightly alkaline with sodium methoxide and distilled. At 40–65° there was collected 98 g. of methanol and methanol/ketal binary. The column was then put under 100 mm. pressure and a fraction taken off at 50–51° (100 mm.). This consisted of 58 g. (49% yield) of 2,2-dimethoxybutane,[17] n^{21}D 1.3878. An additional 5 g. was obtained by pouring the methanol fraction into a large volume of water, separating and distilling the organic layer. Assuming a stepwise exchange with a complete first step, the yield of ketal isolated was 83% of theoretical as indicated by thiol obtained. A high boiling fraction, 93–102° (100 m.), was obtained by further distillation. This contained sulfur and liberated more thiol on treatment with methanol and acid; it presumably was the 2-methoxy-2-(ethylmercapto)-butane but it was not purified and analyzed.

In another experiment using *p*-toluenesulfonic acid as catalyst and a 500% excess of methanol, a 91% yield of a 2,2-dimethoxybutane/methanol constant boiling mixture containing 25% of the ketal was obtained at 65°. The pure ketal was isolated by drowning the mixture in water, separating and distilling the organic layer.

Following the standard procedure for the preparation of mercaptoles, 2,2-di-(cyclohexylmercapto)-butane was prepared in 57% yield; b. p. 175–176° (3 mm.), n^{25}D 1.5305.

Anal. Calcd. for $C_{16}H_{30}S_2$: S, 22.37. Found: S, 21.92.

In a 1-liter flask was placed 160 g. (0.55 mole) of 2,2-di-(cyclohexylmercapto)-butane, 110 ml. of methanol (500% excess) and 8.1 g. of dry *p*-toluenesulfonic acid. This mixture was heated under a small column and distillate slowly collected at 64°. After two and one-half hours an additional 700 ml. of methanol was added. At the end of five and one-half hours the temperature had reached 70° and the distillate amounted to 210 g. Redistillation of this distillate yielded 204 g. of a 2,2-dimethoxybutane/methanol mixture boiling at 65°, n^{25}D 1.3330. This binary contained 10% of the ketal, or 31% of the theoretical yield.

Summary

It has been found that alcohols react with orthothioformates or mercaptoles in the presence of acidic catalysts to yield the corresponding orthoformates or ketals, or their decomposition products.

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[16] Mann and Purdie, *J. Chem. Soc.*, 1549 (1935).

[17] Killian, Hennion and Nieuwland, THIS JOURNAL, **56**, 1384 (1934).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Exchange Reaction between Methane and Deuteromethanes on Silica–Alumina Cracking Catalysts

BY G. PARRAVANO, E. F. HAMMEL[1] AND HUGH S. TAYLOR

The following research originated in a discussion at the Gibson Island Conference on Catalysis, June 1941, in which one of us (H. S. T.) suggested that the cracking of petroleum hydrocarbons on silica–alumina catalysts should be initiated by the breaking of, at least, one C–H bond in the hydrocarbon molecule. Otherwise, it was not possible for the carbon core of a hydrocarbon chain to come within the radius of chemical interaction with the catalyst surface. The plausibility of such a view is at once evident by inspection of a molecular model of a hydrocarbon molecule, as constructed with the Fisher–Hirschfelder atom models. At the same time, the suggestion was viewed by some with skepticisim, since it was believed that the idea could not be put to experimental test.

A study of the exchange reaction between hydrocarbons and deuterohydrocarbons in contact with silica–alumina catalysts permits, however, a direct and convincing test of the idea, and under quite stringent conditions.

It is generally agreed, from the known stability of the methane molecule, that if exchange can be demonstrated between methane and deuteromethanes at temperatures below those at which catalytic cracking of higher hydrocarbons is carried out, there can be no reasonable doubt that, in the cracking reaction, the C–H bonds must be readily and freely broken as postulated. The preliminary exploration of this reaction was carried out by Mr. E. F. Hammel in 1941. The quantitative examination of the process is recorded in the following paragraphs.

Experimental Details

Materials.—Methane from a commercial tank was used, without purification. A mass spectrographic analysis showed a purity of ~96%. Deuteromethanes were prepared by means of the reaction between heavy water and aluminum carbide. The deuterium oxide employed came from our supply of heavy water. The deuterium oxide distilled over C. P. aluminum carbide, and the temperature was raised to 70°. At this temperature the reaction proceeds very smoothly. It was found that, at room temperature, no reaction takes place, in agreement with Urey and Price.[2] The gas collected showed with the mass spectrometer the following composition: CD_4 40%, CD_3H 5.7%, CH_2D 1%, CH_3D 0.3%, CH_4 53%.[3]

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[2] H. C. Urey and D. Price, *J. Chem. Phys.*, **2**, 300 (1934).

[3] This gas composition is abnormal. It can only have been produced by successive interactions of H_2O and of D_2O with the carbide. Since the heavy water used was of high purity we can only conclude that the carbide sample used held tenaciously by adsorption the light water and that this reacted first before the heavy water came in contact with the catalyst.

Ethylene and hydrogen were supplied from commercial tanks, without any further purification.

The silica-alumina cracking catalyst, C-825-C, was a high-quality commercial silica-alumina catalyst kindly furnished by the M. W. Kellogg Company.

Analytical Procedure.—The progress of the reaction was followed by measurements of the intensity peaks for each mass. The mass spectrometer used was of the 60° Nier type.

Experimental Procedure.—Known amounts of the deuteromethane mixture were diluted with an equal amount of methane. The following composition resulted for the reacting mixture: CD_4 20.2%, CD_3H 2.8%, CD_2H_2 0.5%, CH_3D 0.15%, CH_4 76.2%. The mixture of reacting gases was introduced into a horizontal cylindrical Pyrex vessel of 100 cc. volume which contained a layer of catalyst. Equal amounts of gas were withdrawn from time to time and transferred to the analytical vessel.

All the runs were carried out at a pressure of 150 mm.

Experimental Results.—The data obtained at 345° are summarized in Table I, in which the change in concentration for masses 19 and 20 is expressed in relative values of the mass spectrometer intensity peaks. These data serve to show that the exchange takes place at that temperature. At 384° the exchange takes place much faster. By plotting the logarithms of the concentrations of masses 20 and 19 as a function of the time at the two temperatures 345 and 384° straight lines result from which the value for the activation energy, *E*, has been calculated to be 13 kcal.

Since the exchange reaction is indicative of dehydrogenation activity with the silica-alumina catalyst a special test was made of its hydrogenating activity. On the same catalyst it was found that the hydrogenation of the ethylenic double bond occurs very rapidly at 345°, using an equimolecular mixture of ethylene and hydrogen.

TABLE I

RATES OF EXCHANGE FOR CD_4 AND CHD_3

Temp. 345°; pressure 150 mm.; catalyst 0.450 g.

Hours	0	6	24	48	72	96	120	168	192
Ratio Mass 20/Mass 19	6.25	3.75	1.39	0.65	0.51	0.48	0.47	0.48	0.51

General Discussion

From the study of the interaction of methane and deuteromethanes on silica-alumina catalyst it is concluded that exchange of C-H bonds occurs freely in a methane molecule in contact with cracking catalysts. K. Morikawa, W. S. Benedict and H. S. Taylor[4] demonstrated that the same exchange also occurs between CH_4 and CD_4 on a nickel catalyst at temperatures as low as 138° with an activation energy of 19 kcal. The fact that the exchange of C-H bonds of a hydrocarbon molecule occurs at temperatures far below the cracking temperatures appears to be convincing evidence that the first step of a cracking process is a dehydrogenation of the hydrocarbon molecule. The dehydrogenated molecule can be better held and strongly attached to the catalyst surface by catalyst-carbon linkages. The second step, which occurs at higher temperature, is the C-C bond scission, and the consequent formation of lighter hydrocarbon fragments, which then evaporate from the catalyst as saturated or unsaturated molecules dependent on the hydrogen concentration on the surface. A direct test of these two steps in the cracking of hydrocarbons was also obtained by K. Morikawa, W. S. Benedict and H. S. Taylor[5] in the case of nickel catalyst, from kinetic measurements. They showed that in the case of ethane and propane the two reactions of exchange and C-C bond scission occur at different rates in separable temperature ranges, with different dependence on the pressure of hydrogen.

In the case of cracking catalysts it can therefore also be concluded that the activated adsorption of hydrocarbons is a dissociative adsorption. On the same catalyst the ethylenic double bond is easily hydrogenated.

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Summary

1. The exchange reaction between methane and deuteromethanes on silica-alumina cracking catalysts occurs measurably at temperatures of 345° and higher.

2. The activation energy between 345 and 384° is 13 kcal.

3. A mechanism for the cracking process of hydrocarbons is postulated. This mechanism involves two steps: scission of C-H bonds, and then scission of C-C bonds.

4. Ethylene hydrogenation takes place on the same catalyst in the same temperature range.

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[4] Morikawa, Benedict and Taylor, THIS JOURNAL, **58**, 1445 (1936).

[5] Taylor, *et al.*, *ibid*, **58**, 1795 (1936).