

line solutions of the acids are nearly colorless, the vats are red.

Anal. Calcd. for $C_{16}H_8O_4$: C, 64.84; H, 2.72. Found: (a) C, 64.90; H, 2.90; (b) C, 64.64; H, 2.73.

Anthraquinone-1,3-dicarboxylic Acid.—Phthalic anhydride (7.4 g.) was condensed with *m*-xylene (25 cc.) by the addition of aluminum chloride (15 g.), heating the mixture on the steam-bath for one-half hour to complete the reaction. The keto acid precipitated from soda solution, yield 11.5 g. (91%), m. p. 130–133°, was heated with 55 cc. of concentrated sulfuric acid for one hour on the steam-bath, giving after one crystallization from alcohol 6.9 g. (63%) of 1,3-dimethylantraquinone, m. p. 159–160°. For the oxidation 0.2 g. of material was heated with 3 cc. of nitric acid, sp. gr. 1.1, for six hours at 180–190°. The product formed pale yellow needles from dilute alcohol (0.15 g.). The substance decomposes at 320–325°.

Anal. Calcd. for $C_{16}H_8O_4$: C, 64.84; H, 2.72. Found: C, 64.60; H, 2.89.

Summary

On preparing the six possible tolyl naphthyl ketones by methods leaving no doubt as to their structures it was found that two of the isomers had been confused in the literature but that the previous conclusions regarding the formation of methylbenzanthrones by the action of aluminum chloride on the tolyl α -naphthyl ketones are substantiated by the results of experiments with the pure ketones and by more rigid evidence of the structure of one of the reaction products.

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The Activation of Specific Bonds in Complex Molecules at Catalytic Surfaces. I. The Carbon-Hydrogen Bond in Methane and Methane- d_4

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In a preliminary communication² to THIS JOURNAL we have recorded the ready interaction of methane and deuterium at reduced nickel catalyst surfaces at temperatures of 184° and upward. At that time we suggested that the reaction must be determined in rate by the activated adsorption of methane and called attention to the fact that, if this were so, we have in the exchange reaction a more sensitive index of activated adsorption than is available in adsorption measurements of gases on catalytic surfaces. The evidence that we present in the following pages confirms these views and lays the foundations for a comprehensive program of research upon the activation of specific bonds in complex molecules, a central problem in the field of contact catalysis, that of specific activity.

We have studied the interaction of methane and deuterium, of methane- d_4 and hydrogen, of methane and methane- d_4 and of methane and deuterium oxide at surfaces of catalytic nickel through a range of temperatures. From the measurements of reaction velocity and the derived energy of activation of the processes we are able to show that the rate-determining step is to be ascribed to the activation of the C-H bond of the methane molecule. These studies represent an extension

to saturated hydrocarbon molecules of the phenomenon of isotope exchange already demonstrated to occur with unsaturated hydrocarbon molecules by the researches of Farkas, Farkas and Rideal³ and by Polanyi and his collaborators.⁴ We shall show that our results with the saturated hydrocarbons are of material importance in view of the theories of the exchange reaction developed by the latter group of authors.^{4b}

Experimental Details

Materials.—The deuterium gas employed was obtained by electrolysis of our purest heavy water d^{25}_{25} 1.1079 containing 0.5 *M* NaOD as electrolyte. It was freed from oxygen by passage over a glowing platinum wire and dried by passage through a dry-ice trap.

Methane was prepared catalytically from carbon monoxide and excess hydrogen over a nickel catalyst at 255°, the excess hydrogen being removed by passage repeatedly over granular copper oxide at 300° after which carbon dioxide and water vapor were removed by soda lime and a solid carbon dioxide trap. The product used was further purified by fractional condensation and evaporation.

Methane- d_4 was prepared in a similar manner from carbon monoxide and pure deuterium, care being exercised to remove all hydrogen from the reaction system by exhaustion and repeated flushing with deuterium gas. The product was a very pure methane of which 98% of the bonds were found by analysis to be C-D bonds.

(1) Visiting Research Fellow of the South Manchuria Railway Co., Dairen, Japan.

(2) Morikawa, Benedict and Taylor, THIS JOURNAL, **57**, 592 (1935).

(3) Farkas, Farkas and Rideal, *Proc. Roy. Soc. (London)*, **A146**, 630 (1934).

(4) (a) Horiuti, Ogden and Polanyi, *Trans. Faraday Soc.*, **30**, 663 (1934); (b) Horiuti and Polanyi, *ibid.*, **30**, 1164 (1934).

The deuterium oxide vapor employed came from our heavy water supply, d^{25} 1.1079.

The nickel catalyst was a very active nickel-kieselguhr preparation made by precipitation of the carbonate on kieselguhr, ignition and reduction in hydrogen (or deuterium) at progressively increasing temperatures to 450°. It contained 15% nickel and 2 g. was employed. At all times care was exercised to ensure absence of hydrogen when deuterium was being studied and *vice versa*. In experiments with the methanes alone residual adsorbed hydrogen or deuterium gas was removed by frequent evacuations and flushings with methane.

Analytical Procedure.—The progress of reaction was in every case followed by measurements of absorption in the infra-red region using a rock salt spectrometer system. The apparatus was calibrated by measurements of the absorption coefficients of the several deuteromethanes and of various mixtures of these gases as well as upon equilibrium mixtures of known H- and D-contents. Details of these measurements form the subject of a separate communication by Benedict, Morikawa and Barnes.⁵ The absorption coefficients were measured on controlled pressures of gas (~200 mm.) in cylindrical Pyrex vessels with rock salt windows. The mixtures were analyzed in presence of the hydrogen and deuterium used in the experiments, since special test showed these to be without influence on the absorption measurements.

The absorption coefficients (ϵ) were normally measured at 3020 cm.^{-1} (ϵ_{H}) and 2250 cm.^{-1} (ϵ_{D}) to give check measurements on the percentages of C-H and C-D bonds, respectively. In general these measurements were concordant, though some deviations amounting to a 5% uncertainty in D-content have been observed. In the experiments with methane and methane- d_4 as reactants, additional measurements of absorption were made at 1160 and 1180 cm.^{-1} and the measurements combined in a coefficient (ϵ_3) which measures the concentration of CH_3D , at 1090 cm.^{-1} (ϵ_4) which measures CH_2D_2 , and at 1035 cm.^{-1} (ϵ_5) which includes both CHD_3 and CH_2D_2 . The analytical results on these samples due to the more complete analysis are more accurate and the errors should not exceed 2% on the D-content. The values of ϵ given in the several tables are derived from the formula

$$\epsilon = \frac{-\log I/I_0}{lP} \times 10^7$$

where I and I_0 are the transmitted and incident intensities, l is the length of absorption path in cm. and P is the gas pressure expressed in mm. at 25°.

Experimental Procedure.—Known amounts of the reacting gases were introduced into a cylindrical Pyrex vessel of 100 cc. volume at the bottom end of which the nickel catalyst was placed. The gases were introduced through a trap of small volume cooled continuously to -78° which itself formed 30 cc. of the reaction volume. This trap served to remove the quantity of mercury vapor introduced with the gases and also, acting as a thermo-siphon, promoted a circulation of gases over the catalyst heated to controlled temperatures. Tubes of large diameter (15 mm.) were used for the connections between the vessel and trap to minimize resistance to this gas circulation.

(5) Benedict, Morikawa and Barnes, *J. Chem. Phys.*, forthcoming publication.

The total volume was ~150 cc. From time to time the gases were momentarily withdrawn from the reaction space and re-introduced in order to minimize stratification of the reactants. After completion of a run the gases were withdrawn by a Töpler pump and transferred to the analytical vessel.

Experimental Results

Methane-Deuterium Reaction.—The data of Table I indicate that no appreciable reaction occurs on our nickel preparation at 110°, but that from 184° upward an increasingly rapid exchange reaction can be measured. At the longer times of contact at each temperature, since the percentage of C-D bond approximates to 35% for equimolecular mixtures of CH_4 and D_2 it is apparent that the equilibrium state has been reached and that the equilibrium constant must be slightly greater than 1.

TABLE I
EXCHANGE REACTION BETWEEN METHANE AND DEUTERIUM ON NICKEL CATALYST

Catalyst no., 2 g. wt.	CH_4 , cc.	D_2 , cc.	Temp., °C.	Time, hrs.	ϵ_{H}	ϵ_{D}	% C-D bond
2	38.9	39.3	110	23	335	0	0
2	42.4	41.4	110	90	320	0	0
2	39.9	39.7	184	25.5	752	310	15
2	46.3	40.6	184	131.5	700	575	30
2	40.1	40.0	218	20	840	790	34
2	37.0	37.9	218	51	850	780	34
2	42.2	42.8	302	20	755	770	35
2	49.0	48.0	302	44	850	900	37
5	40.3	40.1	184	15	906	376	18
5	39.7	39.8	184	42	1056	816	32
5	39.7	39.7	218	10.2	1080	828	32
5	39.7	40.0	218	20	1190	950	35

The equilibrium state can be established from the methane- d_4 -hydrogen side as well as from the methane-deuterium side as the data of Table II indicate.

TABLE II
EQUILIBRIUM FROM CH_4 - D_2 AND CD_4 - H_2

Catalyst no.	CH_4 Cc.	CD_4 Cc.	D_2 Cc.	H_2 Cc.	Temp., °C.	Time, hrs.	ϵ_{H}	ϵ_{D}	% C-D	K
2	38.4		78.3		218	75.5	790	1320	61	2.3
4		49.2		99.3	218	213	849	1130	56	1.8
2	42.0		83.9		255	50	830	1190	57	1.8
4		49.2		99.3	255	95			53	1.4
4		49.2		99.3	302	101	972	1125	50	1.1

No great accuracy can be assigned to these determinations since only the absorption coefficients ϵ_{H} and ϵ_{D} were determined. It is to be noted however that the mean values for the equilibrium constant $K = [\text{C-D}][\text{H}]/[\text{C-H}][\text{D}]$, at successive temperatures are: $K_{(200)} = 2.3$; $K_{(250)} = 1.6$;

TABLE III
 COMPARATIVE VELOCITIES OF REACTION OF $\text{CH}_4 + \text{CD}_4$ AND $\text{CH}_4 + \text{D}_2$

CH_4 , cc.	CD_4 , cc.	D_2 , cc.	Temp., °C.	Time, hrs.	ϵ_{H}	ϵ_{D}	ϵ_{D} ^a	ϵ_{H}	Conversion ^b
39.2			218	50	512	108			4.5 C-D
20.5	20.6		218	20	928	984			100%
20.3	20.3		218	7	880	1010	960	993	90%
20.7	20.7		218	1	708	823	760/560	800	51%
20.8	20.7		184	1.5	535	570	363/250	320	16.8%
20.7	20.7		255	0.33	764	860	850/640	900	60%
20.8	20.7		138	10	445	510	295/190	250	10.6%
40.5		41.0	184	6	795	360			17.5 C-D
39.3		39.3	218	1	715	316			14.5 C-D
39.5		39.1	255	0.5	894	708			30 C-D
40.0		40.0	138	96	604	96			6.5 C-D

^a The absorption coefficient ϵ_{H} refers to measurements at 1160 and 1180 cm^{-1} . ^b The conversions in the final column have the following meanings. In the first and last four experiments of the table, the data given indicate the percentage of C-H bonds changed to C-D bonds. The remaining data give the percentage conversion from the original CH_4 - CD_4 mixture to the equilibrium mixture of the five methanes.

$K_{(300)} = 1.2$. The values calculated from theoretical grounds⁵ are 1.6, 1.5 and 1.4 at these temperatures. The agreement is within the rather large limits of experimental error in these analyses.

The Reaction between Methane and Methane- d_4 .—A comparison of the velocities of reaction of $\text{CH}_4 + \text{D}_2$ and $\text{CH}_4 + \text{CD}_4$ can be obtained from the data of Table III. All of the experiments were conducted on the same catalyst, No. 6, 2 g. weight. It was reduced in deuterium for several hours at 450° , about 100 cc. of gas being consumed. The catalyst was evacuated for three and a half hours with a mercury vapor pump system but through 90 cm. of 3-mm. capillary tube and three stopcocks. The first experiment, with 39.2 cc. of methane alone, reacting at 218° , indicates that 3.6 cc. of D_2 (or D_2O) was still retained on the catalyst after evacuation and prior to the first experiment. Accordingly, before the next experiment, the catalyst was washed three times each with 14 cc. of methane, each washing being followed by evacuation at 218° . No deterioration of the catalyst occurred.

When the conversions recorded in the final column of Table III are recalculated to give initial rates of reaction at the several temperatures

 TABLE IV
 RATES OF REACTION OF METHANE WITH METHANE- d_4 AND WITH DEUTERIUM

Temp., °C.	$\text{CH}_4 + \text{CD}_4$ % conversion per hr.	$\text{CH}_4 + \text{D}_2$ % conversion per hr.
138	1.1	0.07
184	11.2	3.2
218	~60	15.5
255	~240	...

the data of Table IV are obtained. From these values, which must, however, be regarded as of only an approximate nature, it can be seen that the rate of reaction of $\text{CH}_4 + \text{CD}_4$ is several times faster at the lowest temperature, 138° , than that of methane-deuterium on the same surface at the same temperature. From a log rate *vs.* $1/T$ plot, straight lines result in each case giving activation energies, $E_{\text{CH}_4 + \text{CD}_4} \sim 19$ kcal. and $E_{\text{CH}_4 + \text{D}_2} \sim 28$ kcal.

The higher activation energy of the reaction involving deuterium may be attributed to the influence of temperature in removing the more strongly adsorbed deuterium from the surface, giving greater accessibility to the methane. We shall later confirm this interpretation by a report of experiments on the interaction of ethane and hydrogen on such nickel catalysts. The activation energy of the $\text{CH}_4 + \text{CD}_4$ reaction, $E = 19$ kcal., is to be associated with the activation energy of desorption of the methane molecule, since, in these experiments, the processes occurring consist only in the activated adsorption and desorption of one or other of the methanes.

The Reaction between Methane and Deuterium Oxide.—In these experiments the reaction was conducted in a sealed vessel, 140 cc. in volume, to avoid difficulties due to stopcocks. The resultant gases were withdrawn for analysis through a connecting tube fitted with an internal capillary seal broken by a magnetically operated breaker on completion of an experiment. A slower reaction of methane occurs on the nickel catalyst with deuterium oxide than with deuterium as shown by the results in Table V.

TABLE V
 EXCHANGE REACTION BETWEEN METHANE AND DEUTERIUM OXIDE

CH ₄ , cc.	D ₂ O vap., cc.	Temp., °C.	Time, hrs.	%H	%D	% ₁	% ₂	% ₃	% C-D
35	40	255	20	928	686	920/600	840	800	27.5
40.3	40	184	11	480	205	200/180	140	190	9
40.1	40	184	11	450	158	174/140	135	245	9

Analysis of the residual gas in the first two experiments indicated a slight reaction of methane and water to yield hydrogen and carbon dioxide. At 255° the gas contained 5% carbon dioxide and 8% H₂(D₂); at 184° 1.5% of each gas was found. During this analytical work it was established that the exchange reaction did not occur on the copper-copper oxide mass which was used to burn hydrogen in the presence of methane at a temperature of 302°. On a 15-g. sample of oxide approximately 10% reduced to metal no exchange was found between 39.8 cc. of CH₄ and 40.3 cc. of D₂. The reaction time varied from one-half to one hour, during which the deuterium is rapidly burnt, but the water vapor formed remains in contact with the surface until condensed in the adjacent carbon dioxide traps. We also established the inertness of copper-copper oxide at this temperature with ethane-deuterium mixtures.

The slow reaction of methane and deuterium oxide is probably to be ascribed to the strong adsorption of water vapor on the nickel leaving little free surface for the activated adsorption of the methane. In the actual experiments it was observed that the whole charge of water vapor, ~40 cc., was adsorbed at room temperature. The strong adsorption of water vapor would also account for the distribution of methanes obtained in the two last experiments which were as follows: CH₄, 83 and 80%; CH₃D, 8 and 12%; CH₂D₂, 4 and 5%; CHD₃, 3 and 2%; CD₄, 2 and 1%. The normal equilibrium distribution for a 9% C-D methane would be CH₄, 69; CH₃D, 27; CH₂D₂, 4; CHD₃, 0.5; CD₄, 0%. Such a distribution, however, is for the mixture in the gaseous phase and is evidently upset by the abnormal ratio of the two reactants on the surface. It would seem that an adsorbed methane molecule might suffer several substitutions with D atoms before escaping to the gas phase. The 27.5% C-D product, which we regard as close to the equilibrium point, was in fact a normal equilibrium distribution of the several methanes.

General Discussion

These exchange reactions between methane and

deuterium and its compounds indicate that the same possibilities of replacement of hydrogen by deuterium exist in the case of saturated hydrocarbons as have hitherto been studied with unsaturated aliphatic hydrocarbons and benzene. The differences are of a quantitative nature but not of principle. The exchanges are slower than those of the unsaturated hydrocarbons and, for this reason, Farkas, Farkas and Rideal observed that the atomic exchange between deuterium and ethane does not occur under the conditions where the exchange reaction between ethylene and deuterium takes place rapidly. Indeed, such a conclusion was indicated in the results of Turkevich and Taylor⁶ on the activated adsorption of hydrocarbons. The results now obtained indicate that the presence of a double bond in the reactant hydrocarbon is not an indispensable essential in such exchange processes, and that theories of mechanism, such as those of Horiuti and Polanyi,^{4b} based upon the double bond characteristics can only be restricted considerations of the complete problem.

Unless one wishes to postulate the existence on the surface of associative complexes of the type CH₄D as intermediates in the exchange process, which we regard as very improbable, the conclusion is reached that the activated adsorption of the hydrocarbon is essentially a *dissociative* adsorption. The interaction of the two methanes CH₄ and CD₄ enforces this conclusion. The first stage of the dissociative process with methane would be the formation of CH₃ and H, entirely analogous to the now generally accepted postulate of the dissociation of hydrogen into two atoms on hydrogenation surfaces. The extent to which such dissociative processes of adsorption occur will obviously depend on the temperature, pressure and surface characteristics of the catalyst. In the limit, the dissociative process will proceed to the state in which all carbon and hydrogen bonds are severed, a condition which must obtain when the catalytic reaction CH₄ = C + H₂ occurs. All these dissociative processes

(6) Turkevich and Taylor, *THIS JOURNAL*, **56**, 2254 (1934).

on the surface establish there an equilibrium condition with the reverse processes, the association of adsorbed methyl radicals, or even more dissociated fragments with adsorbed hydrogen or deuterium atoms, yielding finally an equilibrium mixture of CH_xD_y , where $x + y = 4$. We see no reason why such dissociative processes of adsorption should not also occur with the more readily adsorbed ethylenic hydrocarbons, and contribute thereby to the exchange process. Such processes would supplement the associative type of mechanism



discussed in detail by Horiuti and Polanyi. These authors excluded the dissociative mechanism from consideration because of their observation, which agrees with our results with methane, that the exchange reaction rate is so greatly reduced when heavy water is used in place of deuterium. In our case, where a dissociative adsorption of the methane seems unavoidable, we ascribe

this slower rate in presence of heavy water to the lower accessibility of the methane to the surface owing to the known stronger adsorption of the water relative to hydrogen.

Summary

1. The saturated hydrocarbon, methane, undergoes exchange with deuterium, methane- d_4 and deuterium oxide on active nickel catalysts at temperatures of 138° and higher.

2. At 184° the rate of reaction of methane with methane- d_4 , deuterium and deuterium oxide decreases in the order given.

3. The activation energies of reaction with methane- d_4 and deuterium are ~ 19 and ~ 28 kcal., respectively.

4. The mechanism of reaction is associated with an activated, dissociative adsorption of methane on areas of surface unoccupied by hydrogen-deuterium or deuterium oxide.

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Wetting Characteristics of Solids of Low Surface Tension such as Talc, Waxes and Resins

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The degree of wetting can most readily be determined by measuring the angle of contact formed with the liquid and solid in question. Degree of wetting is designated as the change in free surface energy, ΔF_s , which occurs when a liquid is brought into contact with a solid (*i. e.*, $\Delta F_s = S_1 - S_{1n}$).¹ Since the free surface energy of a system is numerically equal to the surface tension, the energy change expressed in ergs per sq. cm. is numerically equal to the adhesion tension, A_{1n} , expressed in dynes per cm.

$$S_1 - S_{1n} = A_{1n} \quad (\text{I})$$

The adhesion tension can be evaluated in terms of the surface tension of the liquid, S_n , and the contact angle, θ_{1n} , which the liquid forms with the solid, for, from the Young equation²

(1) The symbols used in this paper are essentially the same as have been used in recent publications from this Laboratory. S_1 = surface tension or free surface energy of a solid in air, S_n = surface tension or free surface energy of an organic liquid and S_3 , the surface tension or free surface energy of water. The subscripts 1, n and 3 refer to solid, organic liquid and water phases, respectively. In this paper an interfacial contact angle between solid, organic liquid and water will be represented by θ_{1n3} .

(2) Young, *Trans. Roy. Soc. (London)*, **A95**, 65 (1805).

$$S_1 - S_{1n} = S_n \cos \theta_{1n} \quad (\text{II})$$

or, for water

$$S_1 - S_{13} = S_3 \cos \theta_{13} \quad (\text{III})$$

and hence

$$A_{1n} = S_n \cos \theta_{1n} \quad (\text{IV})$$

or

$$A_{13} = S_3 \cos \theta_{13} \quad (\text{V})$$

The adhesion tension and degree of wetting of a liquid against a solid cannot be measured directly if the contact angle is zero, but in such instances it can be determined by application of the Bartell-Osterhof³ equation

$$A_{13} - A_{1n} = S_{n3} \cos \theta_{1n3} \quad (\text{VI})$$

if the interfacial contact angle, θ_{1n3} , is finite and measurable (as it usually is), and if the solid-water-air contact angle, θ_{13} , is finite, so that the adhesion tension, A_{13} , can be calculated from equation (V). For solids on which water gives a zero angle, some organic liquid can usually be found which gives a finite contact angle, and equation (VI) can be used to calculate A_{13} .

(3) Bartell and Osterhof, "Colloid Symposium Monograph," **5**, 113 (1927).