[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

Reaction of Deuterium with Hydrocarbons Over a Cobalt–Thoria Fischer–Tropsch Catalyst[1]

BY SYDNEY O. THOMPSON, JOHN TURKEVICH[2] AND ADOLPH P. IRSA

Hydrogen exchange reactions were observed between deuterium and ethane, propane, butane and isobutane when a mixture of six volumes of deuterium and one volume of each of the hydrocarbons was passed over a Fischer–Tropsch cobalt catalyst under conditions of temperature and flow rate similar to those for hydrocarbon synthesis. The exchanged products were found to be extremely deuterated and the mole per cent. of hydrocarbon molecules undergoing exchange was less than 10% in the case of the ethanes and propanes, 45% for *n*-butane and 51% for isobutane. Cracking of the hydrocarbon gases to produce deuterated methane was also observed. The exchange reaction of methane and deuterium and CD_4 and CH_4 was also studied.

Taylor and his co-workers[3] established that paraffin hydrocarbons, methane to propane, underwent exchange with deuterium on nickel at 65 to 180° with the production of not only deuterated hydrocarbons but also of methane.

A. Farkas and L. Farkas[4] demonstrated that propane, butane, *n*-hexane and cyclohexane also exchanged on platinized platinum. The isotopic nature of the deutero compounds was not established. These findings were interpreted to indicate that the chemisorption of the hydrocarbon molecule on the surface was of the dissociative type leading to the production of hydrocarbon radicals and hydrogen atoms on the catalyst surface.[5,6]

As a part of the mechanism studies of the Fischer–Tropsch synthesis an investigation was made of the interaction of deuterium with hydrocarbon gases over a cobalt–thoria–magnesia–kieselguhr catalyst under synthesis conditions. Two objectives were sought: to determine the stability of the hydrocarbon gases toward exchange and to gain some insight as to the types of radicals present on the catalytic surface from the isotopic character of the exchanged products.

Apparatus and Procedure

The apparatus is given in Fig. 1. The catalyst was a cobalt–thoria–magnesia–kieselguhr preparation.[7]

The hydrocarbon gases were C.P. grade Matheson Company products. The propane was Phillips Petroleum Co. Research Grade gas. The deuterium was 99% isotopically pure and was obtained from the U.S. Atomic Energy Commission.

The catalyst (4.6 g.) was reduced by cycling the deuterium gas (1 liter) over the catalyst at 400° at a rate of 2000 volumes (S.T.P.) of gas per volume of catalyst per hour. The gas was changed every half-hour by partial evacuation of the reactor and the pump (Fig. 1, No. 1 and 4) and recharging them to atmospheric pressure with pure deuterium gas. After a reduction schedule of three hours the temperature was lowered to 183° and the catalyst was kept at this temperature in an atmosphere of deuterium. The deuterium-hydrocarbon mixture prepared by adding deuterium to the hydrocarbon gas in the ratio of six to one, respectively, was added to the catalyst after evacuation and the gas was allowed to flow at atmospheric pressure at a space velocity of 140–150 per hour. The products were collected in bulbs placed in the line of flow and were analyzed in a General Electric Co. mass spectrometer. A quantitative evaluation of the nature and extent of the exchange involves the conversion of the positive ion currents of the mass spectra into isotopic molecular species. This has been carried out by assuming that the mass spectra of the various deuterated hydrocarbons can be calculated from the corresponding protium hydrocarbons on a purely statistical basis, *i.e.*, assuming the equality of the removal of hydrogen or deuterium from a hydrocarbon molecule. This approach has been taken for lack of a better unified treatment of the mass spectra of deuterocarbons.[8] Furthermore, because of the occurrence of a limited number of deuterocarbons in the reaction products and because these were generally fully deuterated, this assumption does not affect the general picture of the exchange process.

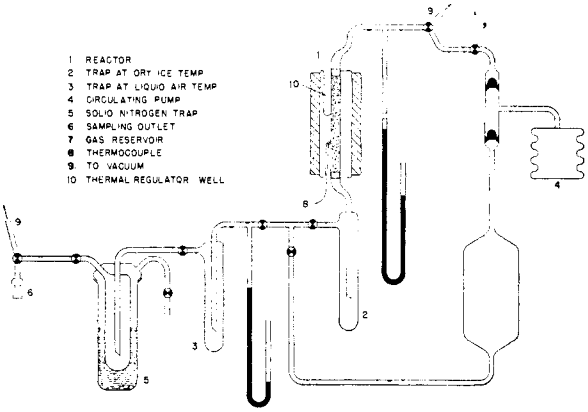

Fig. 1.—Apparatus used in exchange reactions with deuterium.

Methane.—Under Fischer–Tropsch synthesis conditions there was no exchange between methane and deuterium as revealed by infrared analysis.[9] At higher contact times of 17 hours 11% exchange was observed and the products analyzed in the mass spectrometer as 1.7% CD_4, 0.1% CD_3H, 0% CD_2H_2, 9% CH_3D and 89% CH_4. Morikawa, Benedict and Taylor[3] found 17% exchange on 25-hour contact time of one volume of deuterium with one of methane. The occurrence of 1.7% CD_4 and 9% CH_3D with a simultaneous low amount of CD_3H and CH_2D_2 must indicate that there are two processes taking place in the adsorbed layer on the catalyst. Some of the methane on adsorption loses but one hydrogen atom which mixes with a large pool of deuteriums on the surface and the methane on desorption becomes CH_3D. On the other hand, the CD_4 must arise from a rupture of all the C–H bonds of some of the adsorbed methanes, followed by a mixing of the hydrogen from the methane with a large pool of deuterium atoms on the surface and the desorption of carbon as a completely deuterated methane.

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[1] Work carried out under the auspices of the U. S. Atomic Energy Commission.

[2] Department of Chemistry, Princeton University, N. J.

[3] K. Morikawa, W. S. Benedict and H. S. Taylor, THIS JOURNAL, **58**, 1445, 1795 (1936); K. Morikawa, N. R. Trenner and H. S. Taylor, *ibid.*, **59**, 1103 (1937).

[4] A. Farkas and L. Farkas, *Trans. Faraday Soc.*, **35**, 917 (1939); **36**, 522 (1940).

[5] H. S. Taylor and J. Turkevich, THIS JOURNAL, **56**, 2254 (1934).

[6] M. M. Wright and H. S. Taylor, *J. Canadian Res.*, [B] **27**, 302 (1949).

[7] B. R. Anderson, A. Krieg, B. Seligman and W. E. O'Neill, *Ind. Eng. Chem.*, **39**, 1548 (1947).

[8] J. Turkevich, L. Friedman, E. Solomon and F. M. Wrightson, THIS JOURNAL, **70**, 2638 (1948).

[9] A Baird double beam infrared spectrometer is capable of detecting at least 2% exchanged methane if one uses the 4.6-μ C–D band as a measure of the amount of the deuterocarbon.

An alternative mechanism that may be proposed to explain the results is as follows: there are two types of centers on the surface. On one type of center the methane molecule is adsorbed only a short time, so short a time that only one C—H bond is broken and re-formed giving as a product in our experiments CH_3D. The other type of center is one at which the CH_4 is adsorbed for such a long time that the C–H bonds are broken and the hydrogen exchanged with the adsorbed pool of deuteriums many times before the methane is desorbed.

When 58 mole % CH_4 and 42 mole % CD_4 were allowed to stand in contact with a reduced cobalt catalyst at 183° for periods of 20 and 66 hours, the following results were obtained (Table I).

TABLE I

Methane-methane-d_4 exchange at 183° over cobalt catalyst

Molecule	20 hr., mole %	66 hr., mole %
CD_4	38.6	36.5
CD_3H	3.8	7.0
CD_2H_2	0.0	6.5
CDH_3	1.9	12.5
CH_4	55.8	37.5

It should be noted that the rate of exchange of the methanes was of the same order of magnitude as the rate of exchange of methane and deuterium. It should also be noted that the amount of CD_2H_2 in the product is smaller than that of either CD_3H or CH_3D.[10] Thus the complete dissociation of CH_4 and CD_4 into two carbon, four hydrogen and four deuterium atoms on the surface cannot take place for then one would expect CH_2D_2 to be the product that is formed in greatest amount at the early stages of the reaction and not CH_3D and CD_3H. These results can be taken as evidence that during the lifetime of CH_4 on a surface relatively free from hydrogen, the CH_4 is present predominantly as CH_3 and H but in the presence of an excess of hydrogen it is present as CH_3, C and H.

Ethane.—Under synthesis conditions the ethane exchanged up to 6.1% as revealed by an analysis of a typical run: 2.4% C_2D_6, 0.4% C_2D_5H, 0% $C_2D_4H_2$, 0.3% $C_2D_3H_3$, 2.7% $C_2D_2H_4$, 0.0% C_2H_5D and 93.9% C_2H_6.

There is a large amount of C_2D_6 and $C_2D_2H_4$ in the exchanged ethane. The presence of C_2D_6 is due to a process similar to that which produces CD_4 from CH_4; the presence of $C_2H_4D_2$ is due to the stability of a C_2H_4 complex on the catalyst surface.[11]

One per cent. of the original ethane underwent fission of the C–C bonds to produce methanes of the following composition: 41% CD_4, 10% CD_3H, 0% CD_2H_2, 49% CH_3D and 0% CH_4. This is similar to a process investigated by Kemball and Taylor.[12]

Propane.—Under synthesis conditions propane exchanged to form 4.7% C_3D_8 and 1.4% C_3D_7H. The absence of exchange products of the type C_3H_7D to $C_3D_6H_2$ indicates that the process of exchange involves a complete rupture of all or almost all the C–H bonds in the molecule. The product contained 1 to 2% methanes. The latter had the following isotopic composition: 64% CD_4, 12.4% CD_3H, 7% CD_2H_2, 2.5% CDH_3 and 14% CH_4. Treatment of one volume of propane with six volumes of hydrogen produced no ethane but merely methane.

***n*-Butane.**—Under synthesis conditions *n*-butane underwent extensive exchange (42.5%) forming 7.9% C_4D_{10}, 11.8% C_4D_9H, 10.6% $C_4D_8H_2$, 8.9% $C_4D_7H_3$, 2.7% C_4D_6H, 0.6% $C_4D_5H_5$ and 57.5% C_4H_{10}. It should be noted that no deutero-compounds with one to four deuterium atoms per molecule were found. When the space velocity is increased to 750 per hour the rate of exchange dropped to 8.7% giving 3.9% C_4D_{10}, 3.5% C_4D_9H, 1.3% $C_4D_8H_2$, with no other deutero-butanes, while when the space velocity is increased to 3000 per hour negligible exchange occurred; but the little exchange that did occur formed primarily C_4D_{10} molecules. Thus the spread in the number of deuterium atoms in the exchanged product obtained under synthesis conditions is due to back-hydrogenation of a completely deuterated product. The results can be interpretated in a way similar to that used for methane. Either the butane molecule can be dissociated completely on the surface into carbon and hydrogen atoms or it may be adsorbed on the surface for a long time compared to the time necessary to exchange the individual C–H bonds.

The amount of methane formed by destructive hydrogenation varied with the space velocity: 6.9% for a space velocity of 75 per hour to 2% for one of 150 per hour. The isotopic composition of the methane was 48% CD_4, 38% CD_3H and 14% CD_2H_2 and did not vary with the space velocity. No ethane or propane was formed when six volumes of hydrogen and one volume of *n*-butane were passed over the catalyst under synthesis conditions.

Isobutane.—Six volumes of deuterium and one volume of isobutane were passed over the cobalt–thoria catalyst at 183° at varying space velocities. The results presented in Table II definitely indicate that the amount of highly deuterated products were greatest at the higher space velocities. Thus the result is similar to that obtained with propane and *n*-butane in that completely deuterated product is formed first.

The formation of methane was low (0.2%) at the space velocity of 150 per hour and the methane had the isotopic composition: 6% CD_4, 18% CD_3H, 35% CD_2H_2, 33% CDH_3 and 8% CH_4. Separate experiments using light hydrogen and isobutane showed no formation of ethane or propane from hydrogen (6 vol.) and isobutane (1 vol.) under synthesis conditions.

TABLE II

ISOBUTANE–DEUTERIUM EXCHANGE

6/1 D_2/C_4H_{10} Ratio, 183°

Space velocity (per hour)	Product composition, % 150	200	500
C_4D_{10}	0.4–0.0	1.2	1.1–1.1
C_4D_9H	0.6–1.5	4.8–4.1	1.1–1.8
$C_4D_8H_2$	6.1–3.5	5.5–8.3	1.1–1.2
$C_4D_7H_3$	4.7–6.0	3.7–5.2	0.0
$C_4D_6H_4$	5.5–8.6	1.2–0.0	.0
$C_4D_5H_5$	11.0–11.1	0.6–0.0	.0
$C_4D_4H_6$	10.2–10.0	0.7–0.0	.0
$C_4D_3H_7$	6.0–5.0	0.0	.0
$C_4D_2H_8$	3.0–1.5	.0	.0
$C_4D_1H_9$	2.0–1.5	.0	.0
C_4H_{10}	48.1–48.9	80.5–81.1	96.7–95.9

Two numbers are given in the table for the per cent. decomposition of each of the deutero-isobutanes. The first number is obtained if one assumes in the conversion of the positive ions to per cent. composition by the statistical method that the tertiary hydrogen atom in the isobutane is more readily lost than the primary in the ionization process in the mass spectrometer. The second number is obtained if one assumes that the reverse is true. It is seen that the distribution of the various deutero-butanes in the product is little affected by these assumptions.

In conclusion it must be stated that while methane is quite stable toward interaction with deuterium on a Fischer–Tropsch cobalt catalyst under synthesis conditions, ethane and propane are less stable and the butanes undergo a very extensive exchange of their hydrogen atoms with the deuterium gas on the catalyst. If one formulates the results obtained in terms of radicals one concludes that methane furnishes CH_3 and C radicals; ethane, C_2H_4 and C_2 radicals; propene, C_3 radicals and the butanes, C_4 radicals. An alternative formulation is in terms of methyl, ethyl, propyl and butyl radicals on the surface, and to assume that their mean life on the surface is very much greater than

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(10) The General Electric mass spectrometer used resolves cleanly the CH_2D_2 18.0495 and H_2O 18.0163. This is a matter of some importance if one wishes to analyze for CH_2D_2 since all mass spectrometers have a varying but finite H_2O^+ background.

(11) The $C_2H_4D_2$ does not arise from C_2H_4 impurity in the gas used since the original ethane was found by infrared analysis to contain less than 1% ethylene and had been treated with bromine and ascarite before use.

(12) C. Kemball and H. S. Taylor, THIS JOURNAL, **70**, 345 (1948).

the rate of exchange of an individual C–H bond so that all the hydrogens will be exchanged before these alkyl groups can desorb as alkanes. To differentiate between these two points of view one will have to study the dependence of the exchange on the pressure of hydrogen and to study the exchange between a fully protiated and a fully deuterated hydrocarbon. It was further shown that when C–C bonds are broken in propane and the butanes, they are all broken since the degradation product consists solely of methane.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA]

First Isolation of Curium

BY L. B. WERNER* AND I. PERLMAN

The first isolation of curium in microgram quantity from neutron-irradiated americium is described. The americium and curium were separated by the use of an ion exchange resin and the curium further purified and isolated as the fluoride and hydroxide. The absorption spectrum of curium(III) was measured and attempts were made to determine the specific activity of a sample of curium oxide weighing about 40 micrograms.

Introduction

The discovery of element number 96, curium, was accomplished by the identification of Cm^{242} following preparation of this nuclide by cyclotron bombardment of Pu^{239} with helium ions.[1] Cm^{242} is an alpha emitter having a 162 day half-life.[2] It may also be prepared by neutron irradiation of Am^{241} according to the reactions[1]

$$Am^{241}(n,\gamma)Am^{242}$$

$$Am^{242} \xrightarrow[18\ hr.]{\beta^-} Cm^{242}$$

The prolonged neutron irradiation of plutonium led to the production of milligram amounts[3] of Am^{241} and its isolation.[4] Still further neutron irradiation of the americium has made it possible to prepare microgram quantities of Cm^{242}. Microgram amounts of material have been found sufficient to prepare pure compounds of other transuranium elements and to investigate the properties of their solutions at ordinary concentrations (10^{-3} to 10^{-1} M) on the "ultramicro" scale of chemical operations[5] and extensive use of such techniques was made in the present study.

The chemistry of curium as determined on the tracer scale has indicated that only the tripositive oxidation state exists in aqueous solution.[6] According to the actinide concept of the structure of the heaviest elements[7] curium is the seventh member of a series in which the f-orbitals lie at progressively lower levels. Because a half-filled shell, in this case with $5f^7$ configuration, might be expected to have added stability, the predominance of Cm(III) which is thought to have this configuration would be expected over other oxidation states. In this respect curium would be analogous to gadolinium in the rare earth series.

At the time this problem was undertaken americium was not known to have an oxidation state other than the trivalent state, (As part of the study it was found possible to oxidize americium to Am(V) in alkaline solution[8] and others[9] showed it possible to produce Am(VI) in acid solution.) Since there seemed little likelihood that the oxidation of curium could be changed as an aid in its separation from americium, the problem of isolating curium resolved itself into one of separating two tripositive ions similar to two adjacent rare earths. In addition, small amounts of various impurities existed in the americium which were comparable in weight to the curium itself. Of still another nature was the appearance of Pu^{238} which grows from the alpha decay of Cm^{242} at the rate of nearly 0.5% per day.

Separations of rare earth elements have been successfully carried out by the use of ion exchange methods.[10] Such methods offer much in simplicity of operation and for quantitative recovery of the components and formed the basis for the curium–americium separation to be described.[11] Those impurities not removed by the specific curium–americium separation could be separated by precipitation steps carried out from very small volumes of solution.

To check on the purity of the isolated curium, spectrographic analysis was made and in addition a specific activity determination of curium oxide was attempted. This latter determination consisted of weighing a sample of curium oxide which weight could be compared with the amount of curium known to be in the sample from radiometric assay. Among other properties determined from

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* Now at the Naval Radiological Laboratory, San Francisco, California.

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