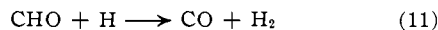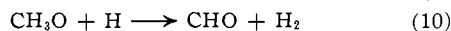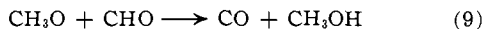The very low sensitivity of $G(C_2H_6O_2)$ from recoil radiolysis to iodide concentration can, however, be interpreted in terms of track recombination of CH_2OH radicals and indicates that some primary CH_2OH is formed. On this basis $G_{CH_2OH} \geq \sim 1$.

Most of the observed $DG(CO)$ of about $+0.9$ can be rationalized on the basis of processes higher than second order in CH_2O and primary radicals. Thus $DG(CH_2O + C_2H_6O_2)$ of $ca. - 1^1/_3$ corresponds to DG-(CO) of $+0.7$ and at the high concentrations characteristic of the track this may arise from such processes as 8–11. The data of Landsman and Butterfield

$$CH_2O + CH_3O \longrightarrow CHO + CH_3OH \qquad (8)$$

$$CH_3O + CHO \longrightarrow CO + CH_3OH \qquad (9)$$

$$CH_3O + H \longrightarrow CHO + H_2 \qquad (10)$$

$$CHO + H \longrightarrow CO + H_2 \qquad (11)$$

indicate that the yields of primary CO and H_2 increase substantially at LET above 30 e.v./Å.

The conclusion that virtually all ethylene glycol from recoil radiolysis is formed in the ionization track leads to the corollary that very few H atoms (or solvated electrons) escape into the bulk solution under this condition. H atoms apparently disappear largely by combination with each other and other radicals in the track. Investigation of the effect of efficient scavengers of H_2 precursors[2] on $G(H_2)$ at high LET is much in order.

It does not seem possible to rationalize the increase in $G(CH_4)$ with increase in LET if it is assumed that CH_4 is formed from CH_3, the yield of which is independent of LET. Diminution of $G(CH_4)$ and production of C_2H_6, which was not detected, and CH_3OCH_3 or CH_3-CH_2OH, which were not determined, would result from

addition of CH_3 to itself or to CH_3O or CH_2OH. Addition of CH_3 to H or abstraction of H from CH_3O or CH_2OH would have no effect on $G(CH_4)$.

The Effect of KI and Other Halides on γ-Radiolysis. —The effect of KI on $G(CH_2O)$ and $G(C_2H_6O_2)$ is, in agreement with Theard and Burton,[4] clearly a property of coupled oxidation and reduction of iodide ion and iodine atom, e.g., by CH_3O and CH_2OH, respectively, as they suggest. The present data indicate that reaction 12 does not compete significantly with 3b and the oxidation of CH_2OH to CH_2O by I since, if it did, the decrease in $G(C_2H_6O_2)$ would be greater than the increase in $G(CH_2O)$. Since Theard and Burton

$$H + I \longrightarrow HI \qquad (12)$$
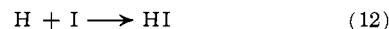
report[4] just such an inequality, however, reaction 12 cannot be excluded.

Reaction 12 could account for reduction of $G(H_2)$ by iodide but the dependence of this reduction on the history of the methanol suggests a role other than scavenging of hydrogen atoms. Elucidation of this role must probably await an improved understanding of the sensitivity of $G(H_2)$ to purity of methanol. The same conclusion may also hold for the other alkali halides, all of which reduce $G(H_2)$ more or less. Whether the effects are due to the halides themselves or to impurities in the halides is not known at present.

The Adsorption of Alkanes on Cracking Catalysts.
I. A Study of the Exchange between Isobutane and its Adsorbed Radioactive Analog

BY JOHN G. LARSON AND W. KEITH HALL

Isobutane-C^{14} is chemisorbed on silica–alumina in three forms; two of these may be regenerated into the gas phase unchanged by exchange with nonradioactive i-C_4H_{10}; the third is irreversibly adsorbed and cannot be so regenerated. The exchange kinetics have been studied as a function of the pretreatment of the catalyst and of the evacuation temperature following contact with the radioactive gas. It has been found that the amount of the most loosely held form, $V(1)$, can be reduced virtually to zero without altering the amount of the more strongly held chemisorbed forms by raising the evacuation temperature from 27 to 150°; further, $V(1)$ is nearly independent of the manner in which the catalyst is pretreated. The more strongly held, exchangeable isobutane is unaffected by altering the evacuation temperature, but is quite sensitive to the pretreatment of the catalyst. The amount of this species, $V(2)$, is greatly reduced by treating the catalyst with H_2 at elevated temperature, by base-exchanging it with KAc, or by adding back H_2O, following the initial evacuation at 500°; it is increased by cooling the catalyst from 500° to room temperature in O_2 before evacuation. The nonexchangeable species $V(NE)$ responds similarly except that it is unaffected by base-exchange or by adding back H_2O. As the rate constants per molecule for exchange (probability of desorption), $k(i)$, are unaffected by these variables, the equilibrium adsorption–desorption rates, $R(i)$, are proportional to the adsorbed amounts. Since $R(2)$ is lowered by small amounts of added-back H_2O while the rate of exchange of i-C_4H_{10} hydrogen for catalyst deuterons is simultaneously increased, the enhanced rate of the latter reaction cannot be attributed to an increase in $R(2)$ by a cocatalyst effect. Moreover, direct comparison of the rate of deuterium exchange, using i-C_4D_{10}, with $R(2)$ reveals that the former rate is much too fast to be accounted for solely by the latter when H_2O has been added back, whereas these same rates compare favorably when the catalyst is dry. It is concluded, therefore, that an additional process for H-exchange becomes important when H_2O has been added back.

Introduction

The effects of small amounts of water on the rates of reactions of hydrocarbons being catalyzed by strong Lewis acids are not well understood. Hindin, Oblad, and Mills[1] reported that the rates of isomerization and cracking of C_5- to C_8-paraffins were increased by as much as 25-fold by the addition of as little as 0.05%

H_2O to cracking catalysts which had previously been evacuated at 525°. Related findings exist for butane cracking,[2] cumene dealkylation,[3] and propylene poly-

(1) S. G. Hindin, A. G. Oblad, and G. A. Mills, J. Am. Chem. Soc., **77**, 535, 538 (1955).

(2) R. C. Hansford, Ind. Eng. Chem., **39**, 849 (1947).

(3) C. D. Prater and R. M. Lago, "Advances in Catalysis," Vol. VIII, Academic Press, Inc., New York, N. Y., 1956, p. 293.

merization.[4] The best documented case is the exchange reaction between hydrogen atoms of isobutane and the deuterons of exhaustively deuterated silica–alumina catalysts.[1,5–7] As a result of this work, Haldeman and Emmett[7] concluded that added-back water was required to create active sites for the adsorption of i-C_4H_{10}; they stated that this provided strong evidence against the suggestion of Milliken, Mills, and Oblad[8] that saturated hydrocarbons form carbonium ions by the transfer of hydride ions to the Lewis acid sites of cracking catalysts. On the other hand, Leftin and Hall[9] have observed that corresponding tertiary carbonium iors are formed from triphenylmethane, 1,1-diphenylethane, and cumene on the surface of silica–alumina, which is taken as indicative of hydride transfer; these workers suggested that H_2O functions as a co-catalyst to effect the desorption of carbonium ions.

MacIver, et al.,[10] found no maximum in the amount of strongly chemisorbed isobutane as H_2O was added back and suggested that the observed monotonic decrease must result from one of two factors: either, (a) the hydrogen exchange took place on relatively weak sites which were not measured because of a too severe definition of chemisorption; or, (b) because of the larger sample size, their catalysts were not as completely dehydrated, following outgassing at 500°, as those used in the earlier work.[7] The present study was undertaken with a view to resolving these questions by ascertaining the factors which influence the transport (equilibrium adsorption–desorption) rates between adsorbed and gaseous isobutane. It was hoped this information would lead to an understanding of the relationship of the chemisorbed amounts[10] to the kinetics of the hydrogen exchange[5–7] and provide some insight into the function of H_2O in carbonium ion-type reactions catalyzed by silica–alumina.

Experimental

Gases.—Research grade isobutane, obtained from the Phillips Petroleum Co., was specified to be 99.98 mole % pure. Before it was placed in a storage bulb, it was passed through a column of dehydrated silica–alumina catalyst at room temperature, and noncondensable gases were removed by repeated cycles of freezing and pumping at $-195°$. The radioactive isobutane (specific activity 1.43 mc./mmole) was obtained from Research Specialties Co. Before use, it was repeatedly circulated over freshly dehydrated silica–alumina at room temperature to remove possible traces of olefinic impurities. The amount of radioactivity retained by the clean catalyst was determined as described below for the i-C_4H_{10}-C^{14} adsorption experiments. After the third such purification, the amount of radioactivity retained by the catalyst had decreased to a constant value, and it was concluded that no impurities which were more readily adsorbed by the catalyst than i-C_4H_{10}-C^{14} were present.

Catalysts.—A batch of 30–60 mesh Houdry M-46 catalyst was used in this work; it was prepared by sieving crushed pellets. Following the normal pretreatment, it was found to have a specific surface area of 280 m.²/g. Some of this catalyst was base-exchanged with KAc following the method used by Haldeman and Emmett.[11] This treatment yielded a catalyst with 0.53 mequiv. of K⁺/g. A very pure silica–alumina catalyst (DSA-1), previously described,[9] was used to test whether the impurities in the Houdry catalyst (about 0.1% iron) were important.

Catalyst Pretreatment.—All catalyst samples were initially treated with O_2 at 500° for 16 hr. by circulation through a liquid

nitrogen trap. When this procedure was followed by a 24-hr. evacuation at the same temperature, the catalyst was considered to be pretreated in the *normal* way. When samples were treated with H_2 at 500° following the O_2 treatment and subsequently evacuated for 24 hr. at this temperature, the catalyst is referred to as *reduced*. Samples from which the O_2 or H_2 was evacuated at a temperature lower than 500° are referred to, respectively, as *oxygen cooled* or as *hydrogen cooled*. In some experiments, water was added back to the catalyst after the *normal* pretreatment. This water was added back in several different ways.[7] The first consisted of cooling the catalyst in about 25 mm. of H_2O vapor from 500° to 220° or 150°, followed by evacuation at the lower temperature for 1 hr. The second method was to expose the evacuated catalyst at 220° or 150° to the H_2O vapor for 1 hr., followed by evacuation for 1 hr. at the same temperature. All of these conditions were selected from the data of Haldeman and Emmett to approximate the maxima in their exchange rate $vs.$ water content curves (Fig. 1 of ref. 7). These water levels, in the order given above, are 1.2, 1.4, 0.95, and 1.0%. Since all of these procedures produced similar effects in the amounts of hydrocarbon adsorbed, no distinction is made in the results reported.

Equipment and Procedures.—These followed closely those devised by MacIver.[10] Isobutane-C^{14} was allowed to equilibrate with about 3.5 g. of catalyst for 1.5 hr. at 150° and 10 mm. The catalyst was then cooled to room temperature and excess radioactive gas was recovered by placing liquid nitrogen around the storage bulb; finally, the catalyst was evacuated overnight. The isobutane which remained adsorbed following this treatment was considered[10] to be chemisorbed. As discussed later, in some experiments the initial evacuation was carried out at 150° for 75 min. The adsorbed radioactive hydrocarbon was then exchanged with about 12 cc. (NTP) of nonradioactive isobutane by circulating the latter over the catalyst at 150°. MacIver's technique was modified by building a vacuum-tight, Kummer-type Geiger tube[12] into the all-glass circulating system which had a total volume of 240 cm.³. The output of a Tracerlab Ratemeter was plotted as a function of time on a strip chart recorder; the counting rate was proportional to the concentration of the radioactive species in the gas phase and was calibrated with known mixtures of i-C_4H_{10}-C^{14} and i-C_4H_{10}. To avoid any hold-up of isobutane in stopcock grease, the circulating system contained no stopcocks; Hg cut-offs were used where required.

After 24 hr. of exchange at 150°, no further radioactivity appeared in the gas phase and the isobutane mixture was removed. Considerable radioactivity, in excess of the equilibrium concentration, was still associated with the catalyst at this point; this was called *non*-exchangeable isobutane by MacIver, et al.[10] The amount of this fraction was determined by circulating O_2 over the catalyst at 500° for 16 hr. and measuring the radioactivity of the CO_2 collected in a liquid nitrogen-cooled trap. The radioactivity so determined was calculated as isobutane and reported as V-(NE).

A sensitive method was worked out which enabled us to ascertain when the regenerated radioactivity either was or was not in the form of isobutane. In a gas mixture composed of a radioactive and a nonradioactive species, the over-all radioactivity is proportional to the partial pressure of the former. Thus, if the pressure is reduced by increase in volume of the system, the radioactivity will fall and a plot of these variables will be linear (curve B′, Fig. 2). If the pressure is lowered by condensing the system, a different situation exists. Except for azeotropic mixtures, the mole fraction of a species will be different in two phases in equilibrium. Thus, if the partial pressure of the radioactive species is determined simultaneously with the total pressure over the condensed phase and this ratio is compared with its mole fraction in the total mixture (or in the condensed phase), an equality will not result if both components do not have the same vapor pressure–temperature relationships. In the present system, the situation is simplified by the very dilute concentration of the radioactive species in the i-C_4H_{10} since it can be reasonably expected that the radioactive species will obey Henry's law (and hence i-C_4H_{10} will obey Raoult's law). Now, if the radioactivity of the gas phase is plotted against the vapor pressure, a linear curve is generated only when the radioactive species is also isobutane. It can be demonstrated that a 20% deviation from linearity results when the hydrocarbon whose vapor pressure most closely resembles that of isobutane, $i.e.$, isobutene-C^{14}, is substituted for isobutane-C^{14} in a concentration equivalent to that present in our exchange experiments.

Theoretical Basis.—The treatment of the data followed that developed earlier in this Laboratory[13] for a model system. Accordingly, the course of the exchange is given by

$$\frac{dx}{dt} = R\frac{n_{14}{}^0 + n_{12}{}^0}{n_{14}{}^0 n_{12}{}^0}(x_\infty - x) = k(x_\infty - x) \qquad (1)$$

(4) V. C. F. Holm, G. C. Bailey, and A. Clark, *J. Phys. Chem.*, **63**, 129 (1959).

(5) R. C. Hansford, P. G. Waldo, L. C. Drake, and R. E. Honig, *Ind. Eng. Chem.*, **44**, 1108 (1952).

(6) S. G. Hindin, G. A. Mills, and A. G. Oblad, *J. Am. Chem. Soc.*, **73**, 278 (1951).

(7) R. G. Haldeman and P. H. Emmett, *ibid.*, **78**, 2922 (1956).

(8) T. H. Milliken, G. A. Mills, and A. G. Oblad, *Discussions Faraday Soc.*, **8**, 279 (1950).

(9) H. P. Leftin and W. K. Hall, Congres International de Catalyse, 2^{ieme}, Paris, 1960, Actes, Paris, Editions Technik, 1961.

(10) D. S. MacIver, P. H. Emmett, and H. S. Frank, *J. Phys. Chem.*, **62**, 935 (1958).

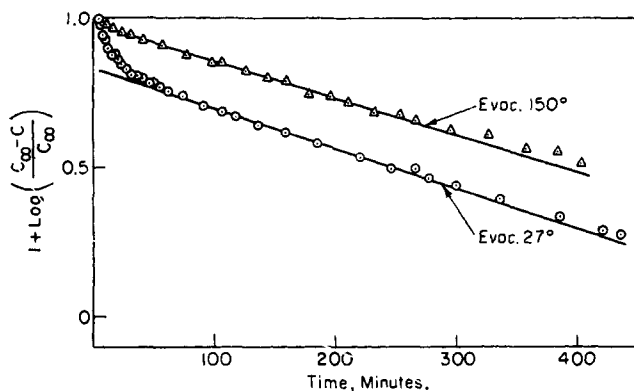(11) R. G. Haldeman and P. H. Emmett, *J. Am. Chem. Soc.*, **78**, 2917 (1956).

(12) J. T. Kummer, *Nucleonics*, **3**, 27 (1948).

(13) (a) W. K. Hall, W. E. Wallace, and F. J. Cheselske, *J. Phys. Chem.*, **63**, 505 (1959); (b) *ibid.*, **65**, 128 (1961).

Fig. 1.—Exchange kinetics for isobutane with its adsorbed radio-active analog.

where n_{12}^0 and n_{14}^0 are the absolute number of moles of normal and radioactive isobutane, respectively, in the system at the start of the exchange; x and x_∞ are the mole fractions of the radioactive isobutane in the gas phase at any time and at equilibrium; and R is the underlying transport rate of the adsorption–desorption equilibrium. Hence, under our experimental conditions, where $n_{12}^0 >>> n_{14}^0$, it follows that

$$k = R/n_{14}^0 \qquad (2)$$

Moreover, calibration showed that the count rate, C, was directly proportional to x. Making this substitution and integrating leads to

$$-\ln [(C_\infty - C)/C_\infty] = kt \qquad (3)$$

Thus, a straight line is obtained when the logarithm of the distance from equilibrium ($C_\infty - C$) is plotted against time; its slope, k, is the probability of desorption, i.e., the rate constant per molecule for transport into the gas phase. Since n_{14}^0 can be determined independently from C_∞, the rate of mass flow, R, in the adsorption–desorption equilibrium can be calculated. This simple treatment applies exactly provided that only one adsorbed species is present and that isotope effects may be neglected. (Species of the same kind but with different binding energies are here considered different species.) Significant deviation from linearity indicates the presence of more than one form of chemisorbed isobutane. As noted earlier,[13b] in this case the equation governing the exchange kinetics becomes

$$(1 - x/x_\infty) = \sum_{i=1}^{n-1} A_i \exp(-a_i t) \qquad (4)$$

where n is the number of discrete kinds of isobutane in the system (including the gas phase). When n is small, e.g., $n = 3$, the several rate processes may be approximated by subtracting the slowest process from the total by determining its parameters at long times; this introduces the implicit assumption that the several species exchange independently. In the present work, this procedure was justified by the fact that the multiple compartment system could be reduced to the two-compartment model obeying eq. 3, by evacuating the chemisorbed isobutane at 150° rather than at room temperature.

Results

Some typical exchange data are plotted in Fig. 1 according to eq. 3. When the catalyst was evacuated at 150°, it was found that the data could be represented with sufficient precision by a single straight line; when the catalyst was evacuated at room temperature, as in the earlier experiments of MacIver, et al.,[10] there was significant deviation from linearity in the early part of the exchange reaction. It was found, for these latter cases, that the data could be well represented by the sum of two exponential functions and that the amount of the more strongly held form was the same as when only one form was present. These results imply that 80% or more of the chemisorbed isobutane remaining on the catalyst after evacuation at 150° is of a single species. The amounts of the two kinds of chemisorbed isobutane were calculated from the exchange data and are listed as V(2) and V(1), respectively, in Table I. In what follows, it should be kept in mind that MacIver's[10] reversibly chemisorbed isobutane corresponds to the sum: V(1) + V(2).
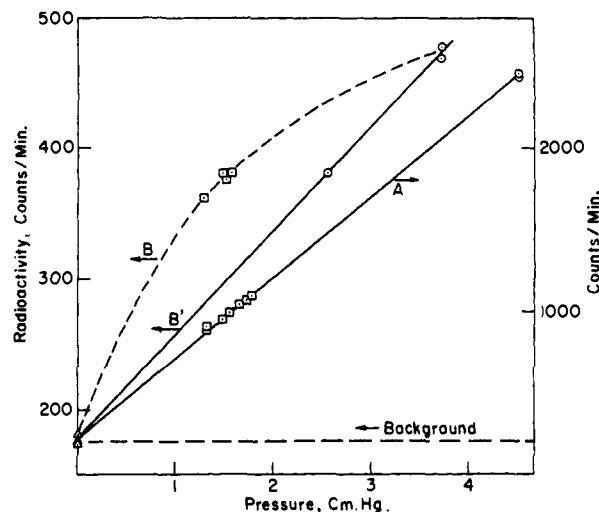

Fig. 2.—Proof that exchangeable radioactive hydrocarbon is regenerated as isobutane (curve A) and that nonexchangeable hydrocarbon is not (curves B and B'): △ = −195°, ▫ = −78°, ⊙ = 25°.

In the earlier work of MacIver, et al.,[10] the identity of the radioactive species appearing in the gas phase when isobutane was exchanged with chemisorbed radioactive isobutane was not established. In order to make any reasonable hypothesis regarding the nature of the chemisorbed species or any realistic interpretation of

TABLE I

EFFECT OF PRETREATMENT ON ABILITY OF CATALYST TO CHEMISORB ISOBUTANE

Catalyst pretreatment[a]	Amount adsorbed, cc. (STP)/g. × 10⁴		
	V(1)	V(2)	V(NE)
Normal	..[c]	2.40	0.98
Normal	2.0	2.38	1.60
Normal + added-back H_2O; evac. at 150°	0.97	0.73	2.64
Normal[b]	1.41	4.74	1.17
Reduced	1.42	0.66	0.21
Normal	..[c]	2.47	1.14
Reduced	1.46	0.66	0.22
Normal	1.52	2.82	0.82
Normal, cooled in O_2, and evac. at 150°	2.46	3.80	1.57
Reduced, cooled in H_2, and evac. at 150°	1.40	0.52	0.19
Normal + added-back H_2O; evac. at 220°	1.73	0.24	0.30
Normal[b]	..[c]	3.54	1.05
Reduced	..[c]	0.97	0.19
Normal	..[c]	3.44	0.97
Normal, cooled in O_2 and evac. at 150°	..[c]	4.52	1.88
Normal[b]	2.04	5.00	2.56
Normal	6.78[d]		2.13
Normal + added-back H_2O; evac. at 150°	2.82[d]		2.41
Normal[b]	..[c]	4.97	1.82
Normal	6.90[d]		1.56
Normal + added-back H_2O; evac. at 220°	2.81[d]		2.85
Normal base exchanged	2.17	0.32	1.88
Normal, base exchanged	..[c]	0.28	2.85

[a] Normal pretreatment involves contacting catalyst with flowing O_2 followed by evacuation, both at 500°. Reduced catalyst refers to treatment with H_2 and subsequent evacuation at 500° following the normal catalyst pretreatment. Where indicated, the H_2 or O_2 was evacuated at lower temperature. Water was added back in the way described by Haldeman and Emmett (ref. 4, 11). This involved cooling catalyst in about 25 mm. of water vapor from 500 to 150 or 220° at the normal cooling rate of the furnace and then evacuating for 1 hr. at the final temperature. These conditions were selected because they provided for the maximum rate of exchange of hydrogen for catalyst deuterium in the earlier work. See the text for further details. [b] First experiment performed on this catalyst sample. [c] Isobutane-C^{14} evacuated at 150° instead of room temperature. [d] Sum of V(1) plus V(2).

TABLE II

EFFECT OF PRETREATMENT ON EQUILIBRIUM TRANSPORT RATES
BETWEEN GASEOUS AND STRONGLY CHEMISORBED ISOBUTANE

Catalyst pretreatment[a]	$k(2)$, min.$^{-1}$ $\times 10^3$	$R(2)$, cc. (STP)/ min. $\times 10^6$
Normal	3.9[c]	9.4
Normal	4.0	9.5
Normal + added-back H_2O; evac. at 150°	2.5	1.8
Normal[b]	3.6	17.1
Reduced	2.4	1.6
Normal	3.1[c]	7.5
Reduced	3.5	2.3
Normal	3.2	9.5
Normal, cooled in O_2, and evac. at 150°	5.7	21.5
Reduced, cooled in H_2, and evac. at 150°	2.7	1.5
Normal + added-back H_2O; evac. at 220°	3.2	0.8
Normal[b]	3.8[c]	13.4
Reduced	3.1[c]	3.0
Normal	3.0[c]	10.1
Normal, cooled in O_2, and evac. at 150°	5.8[c]	26.2
Normal[b]	5.1	25.4
Normal[b]	1.2[c,d]	5.7
Normal, base exchanged	2.7[c]	0.8

[a,b,c] Refer to Table I.   [d] Rate at 90 instead of 150°.

TABLE III

EFFECT OF PRETREATMENT ON EQUILIBRIUM TRANSPORT RATES
BETWEEN GASEOUS AND LOOSELY CHEMISORBED ISOBUTANE

Catalyst pretreatment[a]	Amt. ads., cc. (STP)/ g. $\times 10^3$ V(1)	Transport rates[b] Molecular flow $k(1) \times 10^2$, min.$^{-1}$	Mass flow $R(1) \times 10^5$, cc./min.
Normal	2.00	4.6	9.2
Normal + added-back H_2O, evac. at 150°	0.97	11.2	10.9
Reduced	1.42	9.2	13.1
Reduced	1.46	10.7	15.6
Normal	1.52	9.5	14.4
Normal, cooled in O_2, evac. at 150°	2.46	8.2	20.2
Reduced, cooled in H_2, evac. at 150°	1.40	9.6	13.4
Normal + added-back H_2O, evac. at 220°	1.73	10.7	18.5
Normal	2.04	8.1	16.5
Normal, exchanged at 90°	..	..	4.0
Normal + added-back H_2O, evac. at 150°, exchanged at 90°	..	..	8.4
Normal, exchanged at 90°	..	..	3.6
Normal + added-back H_2O, evac. at 220°, exchanged at 90°	..	..	3.5
Normal, base-exchanged cat.	2.17	6.9	15.0

[a] Refer to Table I.   [b] All rates at 150°, except where otherwise noted.

the exchange reaction, it is essential to establish the identity of the regenerated radioactive species. Vapor pressure–radioactivity plots (Fig. 2, curve A) obtained with equilibrium gas following the exchange experiments show conclusively that isobutane-C^{14} is regenerated during the exchange reaction.

It has been reported recently that the effectiveness of silica–alumina for oxidation of perylene to its cation radical can be greatly altered depending on the way it is pretreated.[14,15] For example, if the catalyst is pretreated in the *normal way*, radical ions are generated from perylene molecules more readily than when it is

(14) W. K. Hall, *J. Catalysis*, **1**, 53 (1962).
(15) J. K. Fogo, *J. Phys. Chem.*, **65**, 1919 (1961).

reduced with flowing hydrogen prior to the final evacuation. It was considered of interest to see whether these different pretreatments might also affect the amounts and the kinetics of exchange of the chemisorbed isobutane, concomitantly with studies of the effects of *added-back water*. The effects of *cooling in oxygen or hydrogen* from 500 to 150° before the final evacuation were also tested. The data obtained are listed in Tables I, II, and III.

The last three columns of Table I contain values for what are believed to be three different kinds of chemisorbed isobutane: $V(1)$, the more loosely held hydrocarbon which is removed when the catalyst is evacuated at 150° rather than 27°; $V(2)$, the strongly chemisorbed, exchangeable isobutane that remains after evacuation at 150°; and $V(NE)$, the excess carbon, calculated as isobutane, which does not appear to exchange at 150°. As pointed out by MacIver,[10] the comparatively large values of this last quantity may mean that some of the chemisorbed isobutane has undergone chemical reaction to form an irreversibly adsorbed product, *i.e.*, "coke." Alternatively, some of the isobutane may be irreversibly chemisorbed on strongly exothermic sites. MacIver presented data supporting the former view as do the results described below.

In one experiment, exchange was carried out at 150° until the radioactivity of the gas phase became invarient. The gas was then replaced with a fresh sample of nonradioactive isobutane. No further exchange took place at 150°. When the temperature was raised to 220°, however, radioactivity began to appear in the gas phase, and after 21 hr. of exchange at this temperature the regenerated radioactivity was equivalent to about 10% of the isobutane which was exchangeable at 150°, or to about 35% of the nonexchangeable portion. A similar result could be obtained at 150° by mixing hydrogen with the fresh portion of isobutane. In both instances, large deviations from linearity occurred when the vapor pressure criterion was applied. An example of this behavior is shown in Fig. 2, curve B. These data indicate that the nonexchangeable portion of the isobutane is held on the catalyst surface in the form of a decomposition product, perhaps as incipient coke. This view is supported by the fact that part of the radioactive gas regenerated with hydrogen was noncondensable at liquid nitrogen temperature and is therefore presumed to be methane. The fact that $V(NE)$ is not decreased when water is added back to the catalyst or when it is base exchanged, while both of these treatments significantly reduce $V(2)$, may be taken as further evidence that $V(NE)$ is not a $V(2)$ type species adsorbed on more exothermic sites. It also seems unlikely that the $V(2)$ type species is a precursor to this irreversibly adsorbed material.

The kinetic data corresponding to the strongly chemisorbed isobutane $[V(2)]$ are contained in Table II. It is immediately evident that the magnitude of $k(2)$ is fairly independent of pretreatment. This implies that the probability of desorption of a particular adsorbed isobutane molecule is independent of the nature of the pretreatment. The rate of mass flow, $R(2)$, is strongly dependent upon pretreatment, however, reflecting the changes in the chemisorbed amounts shown in Table I. In particular, it will be noted that adding back water, base exchanging, or reducing the catalyst with hydrogen substantially reduced $R(2)$. However, cooling in oxygen at 150° before evacuation appears to increase both the amount chemisorbed and the probability of desorption.

The data available for the more loosely held form of chemisorbed isobutane are summarized in Table III. Values of $V(1)$ were calculated from the total exchange-

able chemisorption, $V(1) + V(2)$, by deducting values of $V(2)$ which were obtained from a kinetic treatment of the exchange data as outlined above. Values of $R(1)$ were obtained from the initial slopes of the exchange vs. time plots after a correction was subtracted for $R(2)$. Values of $k(1)$ were derived from $V(1)$ and $R(1)$ using the equation $k(1) = R(1)/V(1)$. In spite of the inherent inaccuracies involved, it is quite apparent that none of the parameters listed in Table III vary significantly with pretreatment. Unlike the more strongly held isobutane, $V(2)$, the amount of the loosely chemisorbed form, $V(1)$, is independent of pretreatment. Like the more strongly held form, the probability of desorption, $k(1)$, is also independent of pretreatment.

Since MacIver, et al.,[10] suggested that their failure to observe a maximum in the quantity of isobutane adsorbed with added-back water may have resulted from less completely dehydrated catalysts than those used in previous work,[7] the rates of hydrogen transfei were compared directly (in the same experiments) with the amounts adsorbad and the equilibrium adsorption–desorption rates. This was accomplished by using perdeuterioisobutane to exchange with the adsorbed radioactive hydrocarbon. Mass spectral analysis of the isobutane mixture following exchange showed that the rate of hydrogen transfer increased two orders of magnitude when H_2O was added back (final evacuation at 150°) while the amount of strongly chemisorbed material, $V(2)$, decreased by about 10-fold. (The amounts of $V(1)$ and $V(NE)$ materials were not appreciably altered.) The equilibrium adsorption–desorption rates from the radiotracer results of these experiments are compared with the rate of disappearance of i-C_4D_{10}, i.e., conversion to a partially exchanged species, in Table IV. These data show that on a dehydrated catalyst the rate of hydrogen exchange corresponds very closely to the rate of desorption of the strongly chemisorbed material; however, the same rates differ by several orders of magnitude after water has been added back to the catalyst. Other exchange experiments between i-C_4H_{10} and deuterated catalysts gave similar results.

TABLE IV

COMPARISON OF RATES OF HYDROGEN EXCHANGE WITH RATES OF ADSORPTION AND DESORPTION OF ISOBUTANE MOLECULES[a]

	Normal pretreatment	Added H_2O
$R(1)$	11	15
$R(2)$	1.5	0.1
$R(D)^b$	1.8	240

[a] Units are cc.(NTP) min.$^{-1}$ g.$^{-1}$ $\times$ 10^{-5}. [b] $R(D)$ is the average rate of disappearance of i-C_4D_{10}.

One experiment was conducted on a very pure silica-alumina catalyst (DSA-1) to determine if any of the types of material listed in Table I are associated with the impurities present in the Houdry M-46 catalyst. Values of 0.00133, 0.00164, and 0.00061 cc.(STP)/g. were found for $V(1)$, $V(2)$, and $V(NE)$, respectively. The qualitative agreement between these values and those listed in Table I, along with a similar comparison of transport rates, indicates that none of these species result because of catalyst impurities.

Discussion

The principal results of the present work may be summarized as: (A) Isobutane is adsorbed on silica-alumina in three forms. Two of these may be regenerated into the gas phase unchanged; the other cannot. (B) The finding[1,5–7] that small amounts of added-back water strongly enhance the rate of hydrogen transfer from isobutane to the catalyst surface was confirmed. This same treatment either did not in-

crease, or else decreased, the transport rates of isobutane molecules between the gaseous and adsorbed phases. (C) The rate constants $k(1)$ and $k(2)$ were independent of pretreatment and of water content; therefore, the rates $R(1)$ and $R(2)$ reflect the amounts adsorbed, $V(1)$ and $V(2)$. (D) When the catalyst was reduced in hydrogen, both $V(2)$ and $V(NE)$ were considerably lowered; evacuation at 150° rather than at room temperature did not materially alter these quantities. (E) When oxygen was evacuated from the catalyst at 150° rather than at 500°, both $V(2)$ and $V(NE)$ were increased. Similar treatment with hydrogen did not alter the results obtained by evacuation of the reduced catalyst at the higher temperature. (F) Although fluctuations in $V(1)$ were considerable, this parameter did not seem to be dependent on pretreatment or water content. (G) Base-exchange, like added-back water, virtually eliminated $V(2)$ but did not materially alter $V(1)$ or $V(NE)$. Their effects appear to be qualitatively identical. (H) While the equilibrium adsorption–desorption rate, $R(2)$, agrees quite closely with the rate of hydrogen exchange between i-C_4D_{10} and the dry catalyst following normal pretreatment, the latter rate is much too rapid to be accounted for by the former when water has been added back.

These findings indicate that the rapidly increasing rate of hydrogen exchange between isobutane and a deuterated cracking catalyst with added-back D_2O cannot be attributed either to an increase in the number of sites available for the chemisorption of isobutane or to an enhancement of the rate of the adsorption–desorption equilibrium. Factors which may be expected to correlate are the increased availability and mobility of deuterium to the site of the chemisorbed isobutane. This is in accord with the repeatedly noted fact that there are not enough deuterium atoms within a radius of an adsorbed isobutane molecule to account for the multiple deuteration that is frequently found. As pointed out by Hindin, Mills, and Oblad,[6] a catalyst containing 1% D_2O has one deuterium atom per 50 Å.^{2} of surface area; to pick up seven deuterium atoms as observed, an isobutane molecule must use the D atoms from at least 350 Å.^{2} of surface area. Actually, as pointed out by Haldeman and Emmett,[7] if statistical equilibrium is reached between the hydrogen atoms of isobutane molecules and the deuterium atoms in a deuterated catalyst, then, for an average of seven deuteriums per isobutane, a total of about 30 deuterium atoms would have to equilibrate with each isobutane molecule. These 30 deuterium atoms would cover an area of 1500 to 2000 Å.^{2}. Presumably, the deuterium must diffuse from such an area, on the average, during the time of one attachment of an isobutane molecule, to an active site. The fact that the number of H atoms exchanged per molecule converted increases considerably when water is added back[3,6,7] is also in agreement with this postulate. This is not a sufficient explanation, however, as is shown by the direct absolute comparison of $R(2)$ and $R(D)$ in Table IV. While these rates agree quite closely on a dehydrated catalyst, the large difference on a hydrated catalyst (and the fact that $R(2)$ decreases while $R(D)$ increases) forces one to the conclusion that an additional hydrogen-exchange process is operative when water is added back.

Haldeman and Emmett[7] reported a 50-fold decrease in exchange rate when catalyst M-46 was base-exchanged with KAc. We find (Table I) a similar decrease in $V(2)$. This, together with the numerical agreement of $R(2)$ and $R(D)$ noted above for the dry catalyst, supports the view that the $V(2)$ species is

active in the hydrogen exchange. Several different physical pictures could be used to rationalize the effects of added-back water with this identification. One of these is tentatively advanced to provide an example and as a basis for further work.

It may be supposed that i-C_4H_{10}-C^{14}, like cumene,[9] forms a carbonium ion by transfer of its tertiary hydrogen to the catalyst surface. This is the active species, V(2). To escape, it must recapture this hydride ion or accept one by transfer from a gaseous molecule. In the latter case, a bimolecular complex may form many times before the tagged adsorbed molecule escapes, because it is trapped between the surface and the incoming molecule. If the bimolecular complex can exchange hydrogen with the catalyst, perhaps intramolecularly via the chemisorbed C^{14} carbonium ion, it follows that $R(D) \gg R(2)$ when the mobility of hydrogen across the surface is high and $R(D) \approx R(2)$ when it is low. Burwell[16] has pointed out this difficulty of effecting the release of an adsorbed carbonium ion by hydride transfer. Accordingly, V(1) is presumed to be a small portion of the easily reversibly adsorbed (possibly strongly physisorbed) hydrocarbon (0.2 cc./g. at 40 mm.) and would therefore not be expected to vary appreciably with base exchange. This is consistent with the finding that its magnitude can be greatly altered by changing the evacuation temperature.

The observation that the probability of desorption of an isolated chemisorbed isobutane molecule, $k(2)$, is independent of pretreatment or of added-back water is

(16) R. L. Burwell, Jr., H. A. Porte, and W. M. Hamilton, J. Am. Chem. Soc., 81, 1828 (1959).

of some interest. The probability is virtually zero in the absence of gaseous isobutane but becomes readily measureable under our experimental conditions. This feature was made evident in several ways. In the first place, V(2) was not lowered by evacuation at 150°, instead of at room temperature, for periods of time comparable with the half-time for exchange. Secondly, no radioactivity appeared in the gas phase when the catalyst was raised to exchange temperature (if the V(1) type material had been previously removed) until the i-C_4H_{10} was admitted to the catalyst. This behavior could result from a mechanism involving hydride transfer from incoming gaseous molecules. Alternatively, the adsorption of a new molecule might indirectly effect the release of a chemisorbed molecule. It is hoped that work now in progress will clarify this point as well as the discrepancy between the mass transport rate, $R(2)$, and the rate of hydrogen exchange on hydrated catalysts. The effects of added-back water on the rates of isomerization, cracking, and polymerization[1-4] also remain to be elucidated.

In summary, the maximum, which has been observed in the exchange rate as a function of added-back water,[1,5-7] can be attributed to an increased availability (or mobility) of deuterium and a decreased concentration of active chemisorbed isobutane. The simplest picture is not sufficient, however, to explain all of the facts.

Reactions of Gaseous Ions. XII. High Pressure Mass Spectrometric Study of Methane[1]

BY F. H. FIELD, J. L. FRANKLIN, AND M. S. B. MUNSON

A mass spectrometric study of ionic reactions in methane was undertaken at pressures as high as 320 μ. The major secondary ions observed were CH_5^+, $C_2H_3^+$, $C_2H_4^+$, and $C_2H_5^+$. The major C_3 species was $C_3H_5^+$ formed from CH_2^+ (or $C_2H_3^+$); some $C_3H_7^+$ with the same appearance potential as CH_3^+ was observed. There was no evidence for the further reaction of CH_5^+, but at high pressures there was evidence for the formation of CH_5^+ from CH_3^+ by a third-order reaction. $C_2H_5^+$ and $C_2H_4^+$ gave little indication of further reactions, but $C_2H_2^+$ reacted rapidly. No C_4 or heavier ions attributable to gas phase ionic reactions were found. The rate constants for the disappearance of CH_4^+ and CH_3^+ were found to be 9.9 ± 0.6 × 10^{-10} and 7.9 ± 0.5 × 10^{-10} cc./molecule-sec., respectively, in good agreement with previous data. The rate constants are independent of the energy of the ionizing electrons and are the same for the disappearance of CH_3^+ and CH_4^+ and the formation of $C_2H_5^+$ and CH_5^+ at low pressures. (Rate constants for the disappearance of all of the primary ions are approximately the same, but it appears that there are real differences among the set.) Decomposition reactions of CH_4^+, CH_5^+, and $C_2H_5^+$ caused by collision of the ions after acceleration by about 2000 v. with CH_4 molecules in the analyzer chamber were noted. The relative cross sections for decompositions decreased markedly with the number of hydrogen atoms removed. The relative cross sections for decomposition of CH_4^+ and CH_5^+ are about the same, but the cross section for decomposition of $C_2H_5^+$ is about four times that of CH_5^+. Cross sections increased as the ion voltage was increased from 1000 to 3000 v., and the absolute value of the cross section for the collision-induced dissociation of CH_5^+ ions with CH_4 molecules is about 2 × 10^{-16} cm.^{2} at 2000 v.

Introduction

Since the reactions of hydrocarbon ions in low pressure gases have been studied in this Laboratory for some time,[2a] it was thought worthwhile to undertake a study of the ionic reactions in gaseous hydrocarbons over the wide pressure range now accessible with the mass spectrometer at Humble with which the previous study on ethylene was made.[2b] A study of reactions

(1) Supported in part by Project Squid under Contract No. Nonr-3623(S-18).

(2) (a) See, for example, F. H. Field, H. N. Head, and J. L. Franklin, J. Am. Chem. Soc., 84, 1118 (1962), and earlier papers; (b) F. H. Field, ibid., 83, 1523 (1961).

of ions in methane at pressures as high as 300 μ is reported in this paper.

For methane the reactions

$$CH_4^+ + CH_4 = CH_5^+ + CH_3 \qquad (1)$$

and

$$CH_3^+ + CH_4 = C_2H_5^+ + H_2 \qquad (2)$$
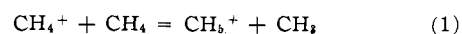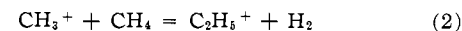
have been well established.[3-5] Other secondary ions

(3) V. L. Tal'roze and A. L. Lyubimova, Doklady Akad. Nauk S.S.S.R., 86, 909 (1952).

(4) (a) D. P. Stevenson and D. O. Schissler, J. Chem. Phys., 23, 1353 (1955); (b) D. O. Schissler and D. P. Stevenson, ibid., 24, 926 (1956).

(5) F. H. Field, J. L. Franklin, and F. W. Lampe, J. Am. Chem. Soc., 79, 2419 (1957).