# The Catalytic Interaction of Acetone and Isopropyl Alcohol with Deuterium on Platinum

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Acetone can react with hydrogen in two different ways in the presence of a suitable catalyst. In one kind of reaction isopropyl alcohol is formed according to

$$CH_3COCH_3 + H_2 = CH_3CH(OH)CH_3 \quad (1)$$
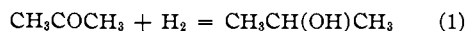
This reaction corresponds to the decomposition of isopropyl alcohol into acetone and hydrogen, which becomes noticeable at about 100°.[1] These two reactions lead to the equilibrium between acetone, hydrogen and isopropyl alcohol, which is very well known.[2] In the second kind of reaction the acetone is reduced completely to propane according to

$$CH_3COCH_3 + 2H_2 = CH_3CH_2CH_3 + H_2O \quad (2)$$
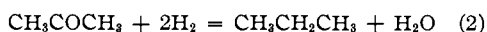
This reaction was found by Faillebin[3] in a liquid medium in the presence of platinum as catalyst at room temperature. It seems, however, that his experiments escaped general attention, although a formation of propane from acetone by catalytic reduction at higher temperatures and pressures[4] was already known.
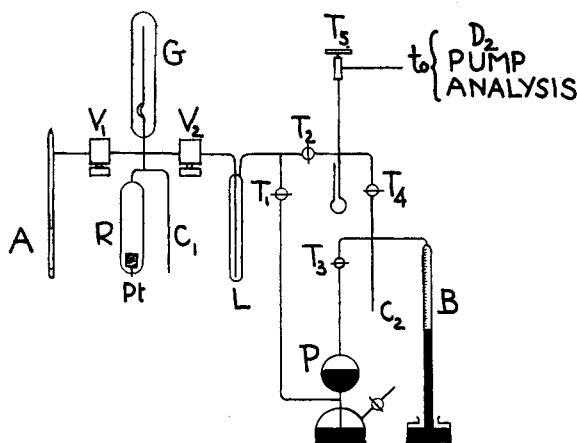

Fig. 1.—Experimental arrangement.

In the catalytic interaction of heavy hydrogen and acetone a third type of reaction becomes manifest, namely, the exchange of hydrogen between
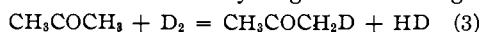
acetone and molecular hydrogen[5] according to

$$CH_3COCH_3 + D_2 = CH_3COCH_2D + HD \quad (3)$$

The present experiments were undertaken to investigate the mechanism of these particular reactions and to elucidate the connection between them.

Experimental

The preliminary experiments were performed in a reaction vessel which contained liquid acetone and in which the catalyst, a platinized platinum foil, was arranged in the gas room. This arrangement[5] proved unsatisfactory since it was not possible to estimate the exact amount of the reaction products, especially that of isopropyl alcohol. Another drawback was that with an active catalyst very often the hydrogen was quickly used up, the acetone being in great excess. In order to admit a given amount of acetone or isopropyl alcohol to the reaction vessel, the arrangement shown in Fig. 1 was developed. By using two Bodenstein valves and a Foord gage,[6] and by cooling the trap (L) with liquid air, any contamination of the catalyst by vapors of tap grease of mercury could be avoided. Vessel A contained acetone (or isopropyl alcohol). The catalyst consisted of a platinized platinum foil (Pt) sealed in the reaction vessel (R). An experiment with, say, acetone and deuterium was performed in the following way: first acetone was admitted into the evacuated reaction vessel through valve V_1, its pressure being measured by gage G. Subsequently the acetone was condensed by cooling tube C_1 with liquid air and the deuterium admitted through valve V_2 to the desired pressure. The acetone was then evaporated by immersing tube C_1 in hot water, the time of reaction being calculated from this moment. After a certain period of reaction valve V_2 was opened and the residual hydrogen was collected in buret B by means of Toepler pump P, whereas the reaction products, propane, water and isopropyl alcohol, and the residual acetone were condensed into trap L. The amount of residual hydrogen was estimated from the known volume of the buret (including the tubing between taps T_3 and T_4), the volume of mercury displaced from the buret and the prevailing pressure. The deuterium content of this residual hydrogen was measured by the micro-conductivity method, the samples being taken by means of lock tap T_5. After the hydrogen was removed, the propane was collected in the buret by replacing the liquid air around trap L by a bath of solid carbon dioxide and by cooling tube C_2 with liquid air. Since after this procedure some of the propane still remained dissolved in the condensed phase in L, this tube was warmed to room temperature, once more cooled with liquid air, and the rest of the propane evaporated by again placing the carbon dioxide bath around L. The volume of the reaction ves-

(1) Rideal, Proc. Roy. Soc. (London), **A99**, 153 (1921).

(2) Parks and Kelley, J. Phys. Chem., **32**, 740 (1928).

(3) Faillebin, Compt. rend., **175**, 1077 (1922); **177**, 1118 (1923); Ann. chim., **4**, 156, 410 (1925).

(4) Ipatieff, Ber., **40**, 1270 (1907).

(5) Farkas and Farkas, Trans. Faraday Soc., **33**, 678 (1937).

(6) Foord, J. Sci. Instruments, **11**, 126 (1934).

sel between valves V_1 and V_2 was 78.5 cc. and that of the buret 11.8 cc.

The acetone used was the purest available preparation obtained from the bisulfite compound. The isopropyl alcohol was entirely free from acetone. The deuterium was prepared by the interaction of heavy water (99.6% D) and redistilled sodium.

The catalyst was prepared as described previously.[5] Although a poisoning of the catalyst by vapors of grease and mercury was excluded, it was found necessary to re-platinize the catalyst from time to time (especially after heat treatment) so that not all of the experiments described below were performed with the same catalyst.

In all the following experiments the reaction of acetone with hydrogen was accompanied by a decrease of pressure. Figures 2 and 3 show this decrease of pressure in mixtures of acetone and hydrogen at temperatures ranging from −42 to 86°. The great velocity of the reaction and its small dependence on temperature seem remarkable. It is possible that at −42° the slowness of the reaction was at least partially due to the small partial pressure of acetone. Since the reaction partners were mixed as described above, the pressures indicating the composition of the reaction mixture refer to room temperature.

As an example of the analysis the following experiment (no. 6) might be given. The reaction mixture consisted of 40 mm. (3.82 cc. at N. T. P.) acetone and 88 mm. (8.40 cc. at N. T. P.) deuterium containing 99% deuterium. The reaction proceeded at −13° and the pressure decreased in eighty-four minutes from 122 to 53 mm. The amount of residual hydrogen was 3.02 cc. and had a deuterium content of 96%. The amount of propane formed was 2.22 cc. As two volumes of hydrogen are needed for the formation of one volume of propane from acetone, the amount of propane formed accounts for the disappearance of 4.44 cc. of hydrogen or of 82% of the total used, 8.40 − 3.02 = 5.38 cc. The difference 5.38 − 4.44 = 0.94 cc. is the amount of hydrogen used for the formation of isopropyl alcohol.

In Table I the results for a number of experiments are listed. It will be noted that the yield of propane is very nearly 100% in all experiments carried out at temperatures above 0° and even at −42° is 68%. The ease of the propane formation from acetone is remarkable indeed. In experiment 13, the course of the reaction was interrupted before it reached completion.

TABLE I

No.	°C.	Reaction time in minutes	Acetone, cc.	Deuterium, cc.	Hydrogen residue, cc.	Propane formed, cc.	Propane yield, %	%D in hydrogen residue
5	89	50	4.14	9.06	1.44	3.97	100	35
7b	27	1080	3.76	8.35	1.75	3.00	90	..
2	25	60	3.96	8.48	1.78	3.48	100	50
10	22	80	9.48	9.56	0.12	4.74	100	..
3	0	50	4.42	9.16	1.39	..	...	83
4	−12.5	43	4.28	9.32	2.13	..	...	94
9	−12.5	75	3.73	8.16	1.69	3.05	94	..
6	−13	85	3.82	8.40	3.02	2.22	82	..
11	−42	225	5.06	7.71	0.02	2.60	68	..
13	22	16	4.11	9.56	3.62	2.80	94	65

In most of the experiments the pressure decrease during the reaction can be accounted for
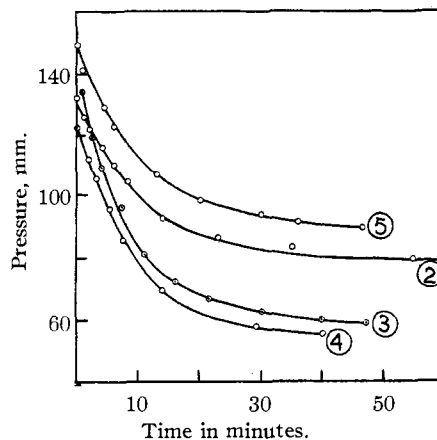

Fig. 2.—

Expt.	CH₃COCH₃, mm.	D₂, mm.	°C.
2	42	90	25
3	46.5	96.5	0
4	45	98	−12
5	43.5	95.5	86
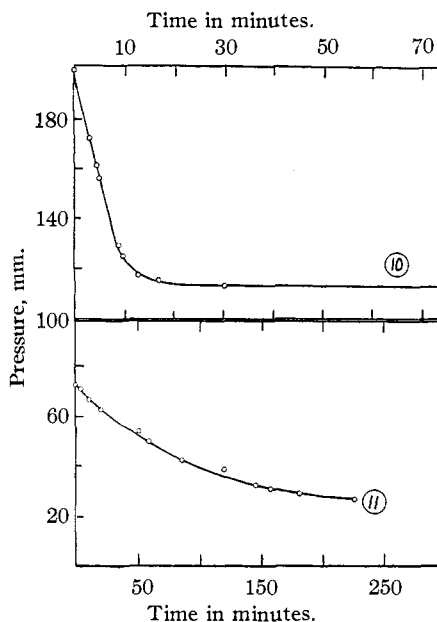
Fig. 3.—Expt. 10, 99 mm. CH₃COCH₃ + 100.5 mm. D₂ at 22°. Expt. 11, 52 mm. CH₃COCH₃ + 78 mm. D₂ at −42°.

as caused by the propane formation alone. For example, in a mixture of 42 mm. of acetone and 90 mm. of deuterium (expt. 2) the pressure decreased in an hour to 79 mm. at 25°. In the reaction product 1.78 cc. (N. T. P.) of hydrogen and 3.48 cc. of propane was found corresponding to a pressure of 18.9 and 36.9 mm., respectively. This gives with the vapor pressure of water, which is formed during the reaction, 23.7 mm., a total pressure of 79.5 mm., in good agreement with the

observed value of 79 mm. The residual pressure of 5.1 mm. acetone does not contribute much to the pressure since the acetone is dissolved in the water.

The rate of the exchange reaction increases with the temperature in a manner similar to that found in the interaction of ethylene and deuterium.[7] Obviously, the temperature coefficient of the exchange exceeds by far that of the reduction reaction, which is incidentally little dependent on temperature. Below $-10°$ there is practically no exchange. This is of some interest since it gives one the possibility of preparing propane of the formula $CH_3CD_2CH_3$ according to the reaction

$$CH_3COCH_3 + 2D_2 = CH_3CD_2CH_3 + D_2O \quad (4)$$
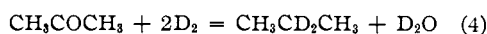
The exchange of hydrogen atoms between hydrogen gas and acetone is slow at 25° and the equilibrium is approximately reached only at about 80°. As examples, experiments 2 and 5 (Table I) will be considered. Using the equilibrium constants for this exchange as given by Wirtz[8]

$$K = \left(\frac{H}{D}\right)_{hydr.} \bigg/ \left(\frac{H}{D}\right)_{acet.} = \begin{cases} 2.9 \text{ for } 25° \\ 2.0 \text{ for } 82° \end{cases}$$

the equilibrium deuterium content corresponds to 26 and 31%, respectively, whereas actually 50 and 35% deuterium was found, respectively.

These results show that the exchange reaction at 82° proceeded much faster than the formation of propane, but still not sufficiently fast to establish complete equilibrium. If propane has once been formed from acetone not completely equilibrated with the deuterium, it escapes further exchange. It should be pointed out that, in the reduction reaction

$$CH_3COCH_3 + 2D_2 = CH_3CD_2CH_3 + D_2O \quad (4)$$
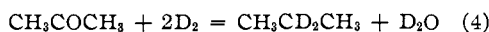
an apparent exchange, that is, a decrease in the deuterium content of the hydrogen, might be noticed if heavy hydrogen containing less than 100% deuterium is used. Since as soon as some water is formed the equilibrium between water and hydrogen according to

$$H_2O + HD \rightleftarrows HDO + H_2 \quad (5)$$

is established, lowering the initial deuterium content. If, however, as in the present experiments, pure deuterium is used, any change in the deuterium content can be explained only by a true exchange of hydrogen atoms between the substance to be reduced and the added hydrogen.

(7) Farkas and Farkas, This Journal, **60**, 22 (1938).
(8) Wirtz, Z. Elektrochem., **43**, 662 (1937).

In order to get a better insight into the mechanism of the interaction of acetone and hydrogen, the interaction of isopropyl alcohol and deuterium was also investigated. First of all it was tested whether the equilibrium

$$CH_3CH(OH)CH_3 \rightleftarrows CH_3COCH_3 + H_2 \quad (6)$$
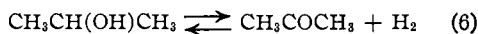
was established under the present experimental conditions. From the measurements of Parks and Kelley[2] it follows that the equilibrium constant of reaction (6) is $K = 2.5 \times 10^{-5}$ at 18°. Consequently, the establishment of this equilibrium at this temperature in 19 mm. of isopropyl alcohol would lead to the formation of 0.6 mm. of acetone and hydrogen. This pressure of hydrogen would correspond in the present experimental arrangement to an amount of 0.058 cc. (N. T. P.) which would be easily measurable.

Table II shows that there is actually a formation of hydrogen from isopropyl alcohol even at room temperature to an extent which is near enough to the calculated equilibrium values. At higher temperature, in addition to hydrogen, propane is found as well, indicating that the hydrogen formed reacts immediately with acetone or isopropyl alcohol to propane. Under these conditions there is a tendency to the establishment of the equilibrium

$$2CH_3CH(OH)CH_3 \rightleftarrows CH_3CH_2CH_3 + CH_3COCH_3 \quad (7)$$
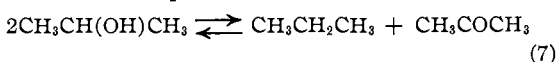
in addition to the establishment of equilibrium (6).

TABLE II

Expt.	°C.	Reaction time	Isopropyl alcohol, mm.	Hydrogen formed, cc.	Propane formed, cc.
A6	18	25 min.	19	0.04	..
A8	13	20 hours	25	.05	..
A9	80	60 min.	26	.05	0.44

The interaction of isopropyl alcohol and deuterium was investigated according to the same method as that of acetone and deuterium. The results of these experiments are summarized in Table III. Again two processes are noticeable: the formation of propane, and the exchange reaction. The formation of propane according to

$$CH_3CH(OH)CH_3 + H_2 = CH_3CH_2CH_3 + H_2O \quad (8)$$
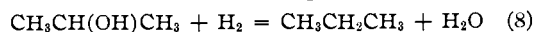
is not accompanied by a change of volume as there is no change of volume in reaction (6). In fact, during the reaction between deuterium and isopropyl alcohol only slight pressure change was observed, which can be accounted for by the condensation of water vapor and the dissolution

of isopropyl alcohol in the water formed. The formation of propane from isopropyl alcohol takes place even at 0° but is by far slower than the formation of propane from acetone.

TABLE III

Expt.	°C.	Reaction time, min.	Isopropyl alcohol, cc.	Deuterium, cc.	Hydrogen residue, cc.	Propane formed, cc.	%D in hydrogen
A3	80	40	1.75	1.75	..	..	8
A17	80	30	2.20	2.40	0.66	1.63	8
A15	20	23	2.02	2.02			42
		50					38
		1080			.79	1.01	17
A14	20	45	2.31	2.27			50
		105			3.24	..	41
A11	17	19	2.25	2.52			48
		1020			1.79	0.63	25
A16	0	21	2.04	2.04			45
		70					42
		85			1.80	.47	41

The exchange reaction shows two rather interesting features. It appears to take place in two stages, and the first step goes further than expected if only the hydrogen atom in the hydroxyl group would be involved in the exchange. This state of affairs can be best understood by taking experiment A15 as an example (Table III). At 20°, in the presence of 21 mm. of isopropyl alcohol the deuterium content of 21 mm. of deuterium decreased from 99% to 42 and 38% after twenty-three and fifty minutes reaction time, respectively. Without any further calculating, it is quite evident that the deuterium content could not possibly decrease below 50% had only one hydrogen atom in the isopropyl alcohol taken part in the exchange. This conclusion is independent of the actual value of the equilibrium constant of the exchange reaction

$$CH_3CH(OH)CH_3 + D_2 = CH_3CH(OD)CH_3 + HD \quad (9)$$
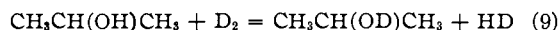
If, however, one assumes that two hydrogen atoms of the isopropyl alcohol molecule are involved in the exchange the value of 38% leads to a distribution ratio of

$$K = \left(\frac{H}{D}\right)_{hydr.} \left(\frac{D}{H}\right)_{alc.} = 2.7$$

which is a reasonable value according to the calculation of Wirtz.[8] If the deuterium is left in contact with the isopropyl alcohol for another period of seventeen hours the deuterium content further decreases to 17%. The amount of this exchange indicates that, at this stage, all the hydrogen atoms of the isopropyl alcohol participate in the exchange. With a distribution ratio of

3 a complete exchange equilibrium would be established if the deuterium content has decreased to 9%. This equilibrium is reached at 80° within an hour, but is not established at room temperature within a day, either on account of the slowness of the reaction or, what is more probable, on account of the formation of propane. It is possible that actually the exchange of hydrogen atoms takes place, not in two stages as indicated, but in three: the exchange of the hydroxyl–hydrogen being the first and fastest step.

Discussion

The first question which has to be decided refers to the connection between the two kinds of reduction reactions of acetone. It might be thought that since the formation of propane requires four atoms of hydrogen and that of isopropyl alcohol only two, the latter reaction is the preliminary step toward the former. At the first glance the present experiments seem to support this, since they show that isopropyl alcohol actually can be reduced to propane. A quantitative consideration indicates, however, that, in fact, there is no direct connection between these two reactions. The ease of the propane formation from acetone is a remarkable feature of the interaction of hydrogen and acetone. On the other hand, the reduction of isopropyl alcohol to propane is so slow that it is not likely to be the second step in such a fast reaction as the formation of propane from acetone. Against this it could be argued that the reduction of isopropyl alcohol proceeds so slowly because isopropyl alcohol displaces hydrogen in the adsorption layer and that at low pressures the isopropyl alcohol is transferred into propane sufficiently rapidly. This, however, is very improbable, especially since such a mechanism of the reduction of acetone would postulate a still faster first step

$$CH_3COCH_3 + H_2 = CH_3CH(OH)CH_3 \quad (1)$$
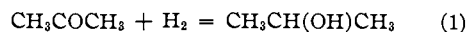
Further proof for the independence of the two reduction reactions is given by experiments of Faillebin.[3] He could show that in a liquid medium, using one kind of catalyst, acetone or other ketones reacted with hydrogen to hydrocarbons, but with another kind of catalyst, gave the alcohols. This fact is best understood by assuming two independent reactions, each of which is catalyzed by a different catalyst.

The quick establishment of the equilibrium

$$CH_3CH(OH)CH_3 \rightleftharpoons CH_3COCH_3 + H_2 \quad (6)$$
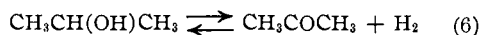
seems rather to indicate that the reduction of isopropyl alcohol proceeds via the formation of acetone. As the partial pressure of acetone formed according to this reaction is very small it is probable that in the presence of isopropyl alcohol and at a low partial pressure of acetone the reduction of acetone to propane is the rate-determining step. This is the reason why some hydrogen can be found if isopropyl alcohol is brought into contact with the catalyst and why the hydrogen is not immediately used up for the formation of propane. If this latter reaction would take place sufficiently rapidly then instead the equilibrium (6)

$$2CH_3CH(OH)CH_3 \rightleftharpoons CH_3COCH_3 + CH_3CH_2CH_3$$

(7)
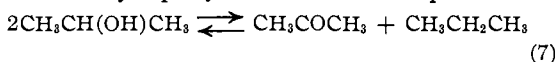
would be established.

The next question to be considered relates to the role of the keto–enol equilibrium of acetone for its reduction. From cases of analogy it was always supposed that acetone may exist in two forms

$$CH_3COCH_3 \rightleftharpoons CH_3C(OH)=CH_2$$ (10)
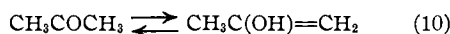
Through the experiments on the exchange of the hydrogen atoms of acetone in heavy water[9] the existence of the enol form of acetone was established definitely. In a previous paper[5] it was suggested that the catalytic exchange of atoms between molecular hydrogen and acetone might proceed via the enol form since the hydrogen atoms attached to an unsaturated carbon atom or the hydrogen atom of a hydroxyl group are both exchangeable.

If the formation of the enol form be the necessary preliminary stage to the hydrogenation reaction one would have to expect the formation of isopropyl alcohol and not of propane through a simple addition of hydrogen according to

$$CH_3C(OH)=CH_2 + H_2 = CH_3CH(OH)CH_3$$ (11)
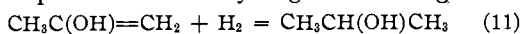
Simultaneously one would observe an exchange reaction since the hydrogen of the hydroxyl group in the enol form is readily exchangeable. Actually, however, no isopropyl alcohol is found in any appreciable quantity as a result of the hydrogen uptake; below 0° no exchange reaction can be observed either, although the hydrogenation reaction proceeds with great speed even at lower temperatures. Consequently it seems that the keto–enol reaction does not necessarily precede the formation of propane from acetone.

This conclusion is in agreement with Faillebin's results[3] that a catalyst which induces the re-

(9) Reitz, Z. physik. Chem., A177, 85 (1937).

duction of ketones or keto compounds to the corresponding hydrocarbons does not catalyze the establishment of the keto–enol equilibrium.

Finally one has to see what conclusions can be drawn from the exchange reactions regarding the mechanism of the interaction in the system acetone–hydrogen–isopropyl alcohol. As mentioned above, it was proposed[5] that the exchange reaction of acetone proceeds via the establishment of the keto–enol equilibrium. Recently, however, it was found[10] that even saturated hydrocarbons like n-hexane undergo an exchange reaction with deuterium under conditions similar to those prevailing in the present experiments. For the exchange of hexane a similar dissociation mechanism was suggested as for that of ethylene[7,11] or benzene[5,12] and it is possible that the same mechanism is operative in the exchange of acetone. In the case of acetone, one cannot decide between the two alternative mechanisms, but a different exchange would be obtained with substituted acetones or other ketones, depending on which mechanism is operative. According to the keto–enol mechanism one would expect in ketones only those hydrogen atoms to exchange which are bound to carbon atoms adjacent to the keto group and no exchange should be observed, for example, in ketones like $\left(R-\underset{\underset{R_2}{|}}{\overset{\overset{R_1}{|}}{C}}- \right)_2 CO$. Whichever mechanism is operative, in the case of acetone all hydrogen atoms are equivalent for the exchange.

In contradistinction to this state of affairs the hydrogen atoms in the isopropyl alcohol exchange in three stages, the first two following each other rapidly. The first and fastest exchange involves the hydroxyl–hydrogen. In the second stage the atom attached to the secondary carbon atom is exchanged also. It appears that this exchange proceeds through the equilibrium

$$CH_3CH(OH)CH_3 \rightleftharpoons CH_3COCH_3 + H_2$$ (6)
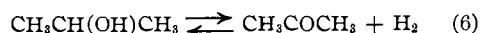
the establishment of which was proved by direct experiments. At first glance one would regard it as remarkable that this equilibrium can be responsible for the exchange reaction since it lies nearly completely on the side of the isopropyl alcohol and only very little hydrogen is formed when the equilibrium is approached from the side

(10) Farkas and Farkas, Nature, 143, 244 (1939).
(11) Farkas, Farkas and Rideal, Proc. Roy. Soc. (London), A146, 630 (1934).
(12) Farkas and Farkas, Trans. Faraday Soc., 33, 827 (1937).

of the isopropyl alcohol. This becomes understandable if one remembers that it is the speed of the establishment of the equilibrium and not its position which determines the rate of the exchange reaction, and equilibrium (6) is in fact very quickly established (*cf.* Table II). The third stage of the exchange reaction of isopropyl alcohol proceeds at a relatively slow rate according to the same mechanism as that of acetone.

The chemical reactions occurring in the interaction of the system acetone–isopropyl alcohol on hydrogen, each of which has actually been observed, can be summarized as follows: (1) The formation of propane from acetone and hydrogen (Reaction I). (2) The formation of isopropyl alcohol from acetone and hydrogen (Reaction II). (3) The exchange of hydrogen atoms between acetone and molecular hydrogen (Reaction III). (4) The liberation of hydrogen from isopropyl-alcohol (Reaction II). (5) The formation of propane from isopropyl alcohol (Reactions II and I). (6) The formation of propane from isopropyl alcohol and hydrogen (Reactions II and I). (7) The exchange of two hydrogen atoms in isopropyl alcohol with the atoms of molecular hydrogen (Reaction II). (8) The exchange of all hydrogen atoms in isopropyl alcohol with the atoms of molecular hydrogen (Reactions II and III).

In the light of the present experiments only three independent reactions are necessary for explaining all of the observed reactions. The first reaction (I) is the straight reduction of acetone by hydrogen to propane. In the activated state the C–O distance in the acetone molecule is sufficiently stretched to allow a reduction to $>CH_2$. This reaction does not necessarily proceed in one single step, but does not involve

the formation of isopropyl alcohol as an intermediate stage. The second reaction (II) leads to the establishment of the equilibrium

$$CH_3CH(OH)CH_3 \rightleftharpoons CH_3COCH_3 + H_2 \quad (6)$$
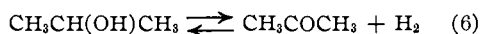
and has as activated state probably a form like

$$CH_3\!\!>\!\!C\!\!<\!\!\!$$
$$CH_3\!\!/\!\!\backslash O\!\!-$$

. The third reaction (III) is the exchange reaction of acetone with deuterium. In the above list the mechanism involved in each of the eight individual reactions is indicated in the parentheses.

Summary

In the presence of a platinized platinum foil acetone readily is reduced to propane by hydrogen at pressures of about 150 mm. and at temperatures ranging from -42 to $89°$. Under these conditions only very little isopropyl alcohol is formed. Above $0°$ the reduction reaction is accompanied by an exchange of hydrogen atoms between acetone and molecular hydrogen, but no exchange is observed below $-10°$.

Isopropyl alcohol is also reduced to propane by hydrogen though much more slowly than acetone. The exchange reaction for isopropyl alcohol proceeds in two stages: first the two hydrogen atoms of the $>C(OH)H$ group are exchanged; then those of the methyl groups.

It is suggested that for explaining the different reduction and exchange reactions proceeding in the system acetone–isopropyl alcohol–hydrogen the assumption of the following three independent reactions is sufficient: (1) reduction of acetone to propane; (2) establishment of the equilibrium $CH_3CH(OH)CH_3 \rightleftharpoons CH_3COCH_3 + H_2$; (3) exchange reaction of acetone with hydrogen.