

Hydrogen Transfer Reaction between Ethanol and Acetone over Magnesium Oxide

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Hydrogen transfer reaction between ethanol and acetone $\text{CH}_3\text{OH} + \text{CH}_3\text{COCH}_3 \rightarrow \text{CH}_3\text{CHO} + (\text{CH}_3)_2\text{CHOH}$ was carried out over magnesium oxide. With the help of a variety of information concerning the steady-state kinetics, the amount of adsorbed species present under the steady state of the reaction, the reactivity of adsorbed species, isotope distribution among the reactants and the products, and the isotope effect upon the reaction, it was concluded that the hydride transfer between ethoxide anion and weakly adsorbed acetone was one of the rate-determining steps. Acetone and acetaldehyde held on magnesium oxide in keto forms were very likely equilibrated with those in enolic forms at rapid rate. Acetate existed on the surface was found not to be involved in the reaction.

INTRODUCTION

When alcohol is brought into contact with metal oxide, alkoxide species are formed (1-7). The species formed on electropositive metal oxide were concluded to be more anionic compared to those on less electropositive metal oxides such as SiO_2 and Al_2O_3 (8-11).

In the previous work (10), the decomposition of ethanol was carried out over magnesium oxide with the help of infrared spectrophotometric method and ethoxide anion formed on magnesium oxide was found to be one of the intermediates which effectively participated in the decomposition. Kinetic fates of alkoxide species were also suggested to depend strongly upon their binding natures (10). In our recent work, the reaction between ethanol and acetone was carried out on magnesium oxide by use of isotope tracer and it was concluded that hydrogen atoms in ethoxide anion formed on magnesium oxide selectively transferred to carbonyl group as hydride ion (12). Alkoxides would, therefore, act as an intermediate effective for a variety of reactions in which alcohol takes part. In connection with these results, the present experiments

are aimed at the elucidation in greater detail of the role of ethoxide anion in the hydrogen transfer reaction between acetone and ethanol on magnesium oxide.

EXPERIMENTAL

Experiments were carried out in a flow system over 10 g of magnesium oxide (Kishida Chem. Co., extra pure grade) at temperatures ranging from 170 to 265°C. An infrared cell in which magnesium oxide pressed in a thin wafer was mounted was connected in series with the outlet of the catalyst bed. The catalyst was heated in an oxygen stream at 500°C for 2 hr prior to the experiments. The gaseous mixture of acetone and ethanol was admitted with a nitrogen stream. The reactants and the products were analyzed by gas chromatography. The spectra of adsorbed species were recorded with a Hitachi 215 infrared spectrophotometer and the amounts of acetate and ethoxide formed were determined as had been done in the previous work (11).

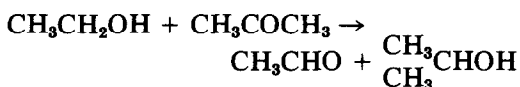
Some of the reactions were carried out between d_8 -ethanol and light acetone or between d_1 -ethanol-OD and light acetone. The distribution of deuterium isotope

among the reactants and products, as well as the isotope effect upon the reaction, was studied. The isotope composition in the outflow was determined by means of mass spectrometric analysis or infrared spectroscopy. Both ethanol (Nakarai Chem. Co., extra pure grade) and acetone (Wako Chem. Co., extra pure grade) were dehydrated by passing through a column containing dehydrated copper sulfate. Nitrogen used as a carrier gas was purified over potassium hydroxide and molecular sieve 5A.

RESULTS

1. Equilibrium Constant of the Reaction

The equilibrium constant of the hydrogen transfer reaction



was estimated on the basis of the thermodynamic data (13, 14) and plotted in Fig. 1 against the reciprocal of the temperature. As seen from the figure, the equilibrium constants are held in an order of 10^{-2} under the present experimental conditions. The enthalpy change of the reaction was estimated to be about 2.36 kcal/mole.

2. Reaction under the Steady State

When the gaseous mixture of ethanol and acetone was admitted over the catalyst bed with a stream of nitrogen, the reaction occurred above 170°C. As Fig. 2 shows, acetaldehyde and isopropanol were produced in a 1:1 ratio. When either ethanol or acetone alone was admitted, no reaction took place. The hydrogen transfer between ethanol and acetone occurred exclusively under the present experimental conditions. All of the experiments were carried out under the conditions under which the conversion of limiting reactant was kept below 15%. It was, therefore, assumed that the partial pressures of the reactants were practically kept constant throughout the catalyst bed and also the backward reaction was negligible.

Figure 3 illustrates the infrared spectra obtained after the removal of the gaseous phase. The absorptions were observed at 1580, 1420, 1120, and 1060 cm^{-1} . The former two absorptions have been assigned to



stretching vibration of surface acetate,

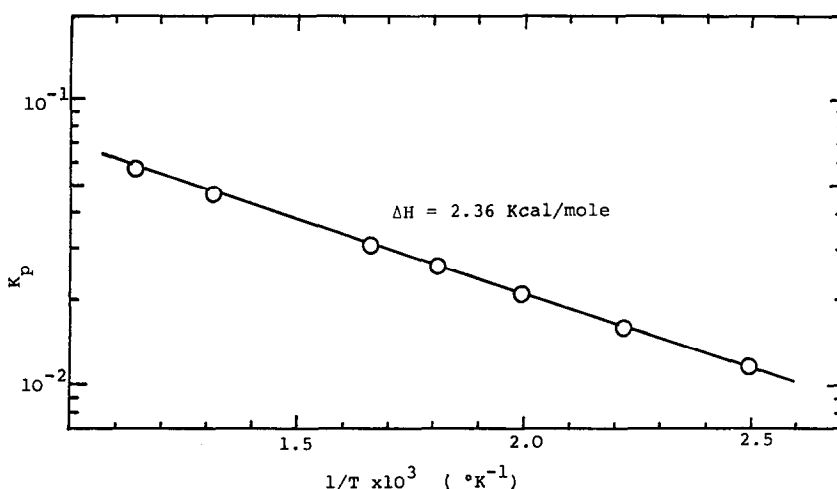
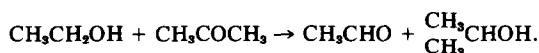


FIG. 1. Equilibrium constant K_p of the reaction



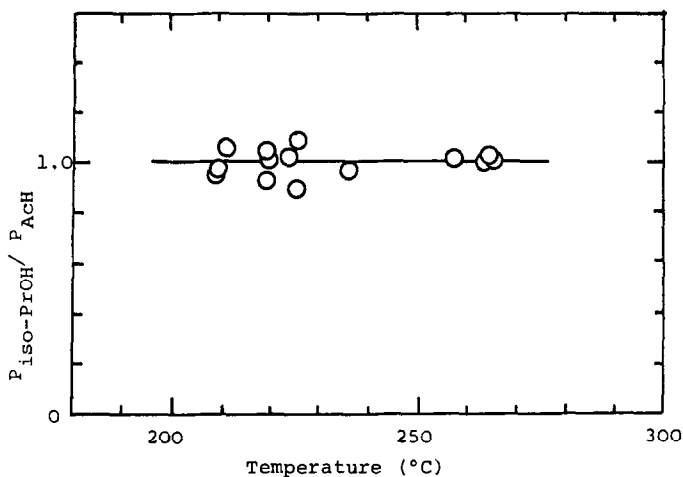


FIG. 2. The ratio $P_{\text{ISO-PROH}}/P_{\text{ACH}}$ at the outlet of the catalyst bed versus temperature. The experiments were carried out at $P_{\text{EtOH}} = 0.035$ atm and $P_{\text{Acetone}} = 0.11$ atm. Total inflow = 160 cm³ STP/min.

while the latter two have been assigned to C—O stretching vibration of surface ethoxide. The absorptions at 1172 and 1134 cm⁻¹ which arose from isopropoxide (7) were not observed. When the reactants were present, very weak absorption was discernible around 1720 cm⁻¹ in addition to those

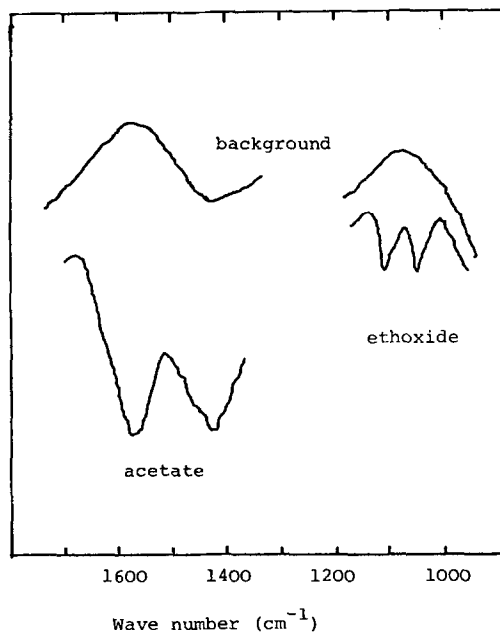


FIG. 3. Infrared species of adsorbed species after the gaseous phase was removed.

ascribed to these two species. This was ascribed to C=O stretching vibration of weakly adsorbed acetone (7), possibly coordinatively adsorbed on magnesium ion. This species was weakly held so that it disappeared very rapidly when the gaseous phase was removed.

Figure 4 shows the plots of the exit partial pressure of acetaldehyde against the partial pressure of ethanol or acetone under the steady state of the reaction. The steady rate is, therefore, expressed as $r = kP_{\text{Acetone}}^{0.7}P_{\text{EtOH}}^{0.3}$. The activation energy of the reaction was estimated to be 11.5 kcal/mole.

3. Adsorbed Species

(i) *Reactivity of adsorbed species.* When only ethanol was admitted with a nitrogen stream over the catalyst, ethoxide and acetate were formed. When the stream of ethanol–nitrogen mixture was switched over to the nitrogen stream, ethanol in gaseous phase was rapidly decreased. However, ethoxide was decreased very slowly, while the amount of acetate remained unchanged. When the stream was again switched over to that of nitrogen–acetone mixture, both acetaldehyde and isopropanol were detected in the outflow. Ethoxide was de-

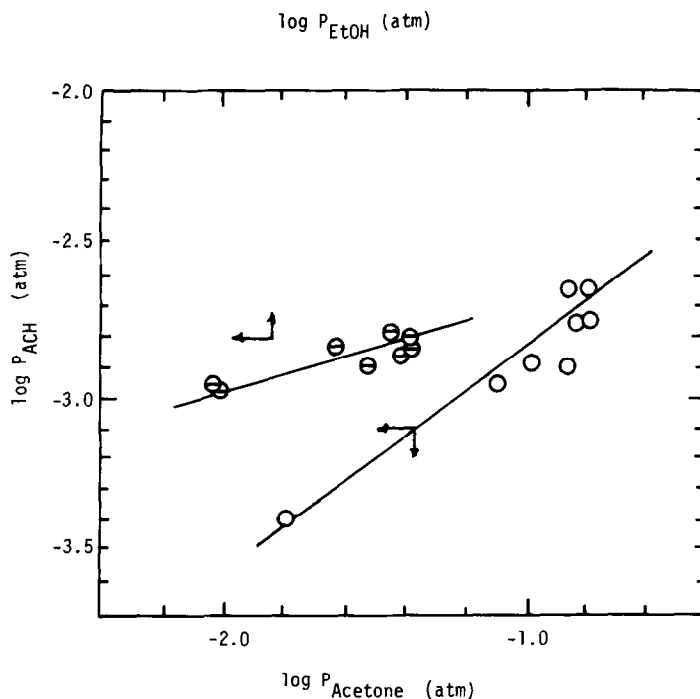


FIG. 4. Effect of acetone and ethanol upon the reaction. Temperature: 220°C. When the effect of acetone was examined, the inlet partial pressure of ethanol was held at 0.035 atm and that of acetone was varied. When the effect of ethanol was examined, the inlet partial pressure of acetone was held at 0.11 atm and that of ethanol was varied.

creased rapidly but acetate remained unchanged. The rates of acetaldehyde formation and of the decrease in ethoxide were plotted against time in Fig. 5. This clearly demonstrates that the rate of acetaldehyde formation matched practically well with that of the decrease in ethoxide. Acetaldehyde formation occurred selectively by the reaction between ethoxide and acetone. Ethoxide anion was, therefore, highly active toward acetone, whereas acetate species merely existed on the surface and did not participate in the reaction.

It has been reported that isopropanol was formed through the alcoholysis with ethanol in homogeneous hydrogen transfer reaction (15). In the present experiment, isopropoxide was formed on magnesium oxide by the adsorption of isopropanol. When isopropanol-nitrogen mixture was switched over to a pure nitrogen stream, isopropoxide formed gradually desorbed as

isopropanol. The rate of the desorption was initially rapid. After the desorption had been carried out for 18 min, the partial pres-

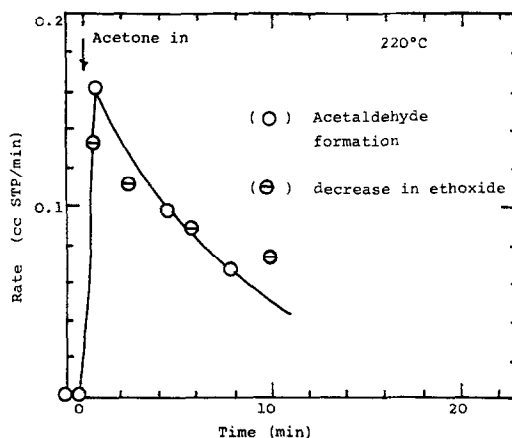


FIG. 5. The rates of acetaldehyde formation and the decrease in ethoxide in the course of the reaction between ethoxide and acetone. Partial pressure of acetone: 0.11 atm. Inflow rate of nitrogen: 160 cm³ STP/min.

sure of isopropanol was recorded at 1.3×10^{-3} atm at the outlet of the catalyst bed. The corresponding rate of the desorption amounted to 0.22 cm³ STP/min. When nitrogen stream was again switched over to a stream of nitrogen-ethanol mixture ($P_{\text{EtOH}} = 2.2 \times 10^{-2}$ atm) the desorption rate of isopropanol was still kept around 0.2 cm³ STP/min. Isopropanol desorption was not enhanced in the presence of ethanol. On this basis, it was concluded that no alcoholysis was involved in the reaction.

(ii) *Amount of ethoxide and acetone present under the steady reaction.* Figure 6 shows the plots between partial pressure of ethanol and the amount of ethoxide present under the steady state of the reaction in which the partial pressure of acetone is held constant. It shows that the amount of ethoxide increases with the increase in the partial pressure of ethanol. In Fig. 7, the exit partial pressure of acetaldehyde obtained under the steady state of the reaction is plotted against the amount of ethoxide thus

determined. It is seen that the reaction rate at steady state is proportional to the amount of ethoxide when the partial pressure of acetone is held constant.

As for adsorbed acetone, the intensity of the infrared absorption was extremely low so that its amount could not be determined by infrared spectroscopy. After an acetone-nitrogen mixture had been passed over the catalyst, the mixture was switched over to pure nitrogen stream. The exit concentration of desorbed acetone was followed with time until no acetone was observed in the outflow. The amount of adsorbed acetone was thus estimated by integration of desorbed acetone according to the method applied by Kobayashi and Kobayashi in a flow system (16). When the partial pressure of acetone in the mixture was varied, the amounts of acetone held at various partial pressures of acetone were determined by this procedure. It was found that the amount of acetone held on magnesium oxide was about one-tenth that of eth-

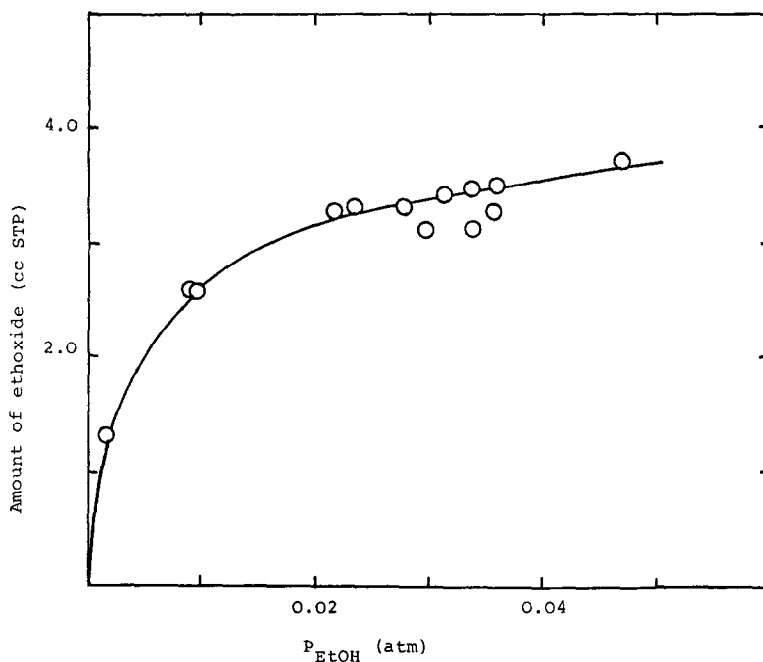


FIG. 6. Partial pressure of ethanol and the amount of ethoxide present under the steady state of the reaction. Partial pressure of acetone: 0.11 atm. Temperature: 220°C. The amount of ethoxide was determined by infrared spectroscopy.

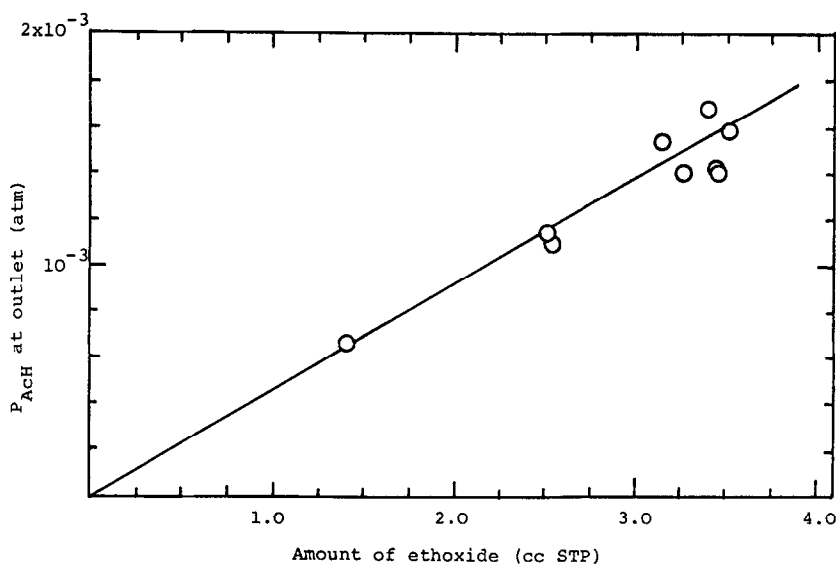


FIG. 7. Exit partial pressure of acetaldehyde versus the amount of ethoxide. Partial pressure of acetone: 0.11 atm. Temperature: 220°C.

oxide under the present experimental conditions. In Fig. 8, the exit partial pressure of acetaldehyde obtained under the steady state of the reaction was plotted against the amount of adsorbed acetone thus determined. This indicated that the reaction rate was proportional to the amount of adsorbed acetone. The reaction proceeded, there-

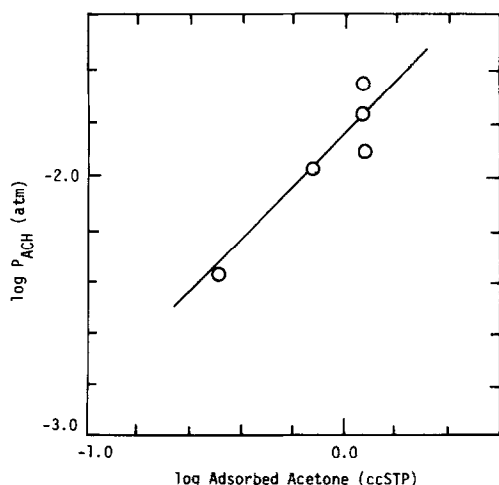


FIG. 8. Exit partial pressure of acetaldehyde and the amount of adsorbed acetone. Partial pressure of ethanol: 0.035 atm. Temperature: 220°C.

fore, in proportion to the product of the amounts of adsorbed acetone and ethoxide under the steady state, suggesting that the reaction between adsorbed acetone and ethoxide was rate determining.

4. Isotope Distribution

When d_6 -ethanol reacted with light acetone, the isotope distribution occurred among the reactants and products. As communicated previously (12), deuteroyl group in ethanol was rapidly exchanged with hydrogen in light acetone, while methyl and methylene groups in ethanol were not diluted with protium. From the atomic fraction of deuterium in acetone and the relative amounts of d_n -acetones ($n = 1-6$) obtained, it was found that the isotope exchange between light acetone and deuteroyl group of d_6 -ethanol was practically in equilibrium. This suggested that the exchange was extremely rapid compared to the hydrogen transfer reaction. Possibly, acetone in keto form participated in the exchange, although it was not detected by infrared spectroscopy.

Methine group (CH) in isopropanol

formed was found to be exclusively deuterated with deuterium in the CD group of d_6 -ethanol but not in its methyl group. On the other hand, the methyl group in acetaldehyde was partially diluted with protium while 94.3% of its aldehyde group was in the form of CDO group. Therefore, it strongly indicated that deuterium atom in d_6 -ethoxide transferred to carbonyl carbon in light acetone. When the reaction between $\text{CH}_3\text{CH}_2\text{OD}$ and $(\text{CH}_3)_2\text{C}=\text{O}$ was carried out, no deuterium was held in methine group of isopropanol, confirming the above conclusion and these kinetic features were in excellent accord with those in the homogeneous phase (17).¹

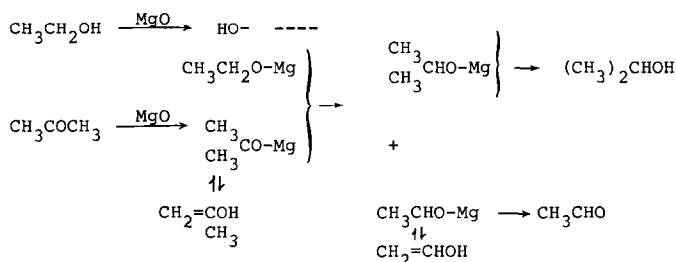
5. Isotope Effect upon the Reaction

Table 1 shows the results obtained when d_6 - or d_1 -ethanol-OD reacted with light acetone. As compared with the results obtained in the reaction between light acetone and light ethanol, the strong deuterium isotope effect upon the reaction was observed when the reaction between light acetone and d_6 -ethanol was carried out. For the

light acetone- d_1 -ethanol system, deuterium atoms in hydroxyl group were appreciably diluted with protium in acetone since a large excess of acetone was used. The reaction, therefore, proceeded at a rate practically the same as that between light ethanol and light acetone. When light acetone and d_6 -ethanol are employed as reactants, deuterioxyl group is predominantly diluted with protium in light acetone. However, since deuterium in CD group of ethanol remained unchanged, the isotope effect observed in d_6 -ethanol-acetone system should be attributed to the effect of deuterium in CD group of ethanol. In conformity with the results obtained in the previous sections, it was, therefore, consistently understood that the hydrogen transfer from CH group in ethoxide to adsorbed acetone was rate determining.

6. Mechanism of the Reaction

On the basis of these observations, we, therefore, concluded that the reaction occurred through the mechanism



in which adsorbed acetone and ethoxide participated. The hydrogen transfer occurred from hydrogen in CH bond of ethoxide to carbonyl carbon of adsorbed acetone and was one of the rate-determining steps. These were also all consistent with the observations including the reaction kinetics,

¹ In the reaction between 2-butanol and 3-pentanone on hydroxyapatite catalyst, Kibby and Hall (*J. Catal.* **31**, 65 (1973)) also revealed a very specific transfer of D from 2-butanol-2d to the product 3-pentanol-3d₁.

the reactivity of adsorbed species, the amount of adsorbed species present under the steady states of the reaction, the isotope distribution among the reactants and products, and the isotope effect upon the reaction. These features of the reaction were in general very similar to those in homogeneous phase. Since ethoxide on magnesium oxide is in anionic form, hydrogen would transfer as hydride from methylene hydrogen to carbonyl carbon atom.

TABLE I
Isotope Effect of the Reaction^a

Reaction	Rate of acetaldehyde formation (cm ³ STP/min)
CH ₃ CO + C ₂ H ₅ OH (0.0204 atm) CH ₃	0.24
CH ₃ CO + C ₂ H ₅ OD (0.0204 atm) CH ₃	0.23
CH ₃ CO + C ₂ H ₅ OH (0.0155 atm) CH ₃	0.22
CH ₃ CO + C ₂ D ₅ OD (0.0155 atm) CH ₃	0.16

^a Reaction temperature: 220°C. Inlet partial pressure of acetone: 0.15 atm.

The deuterium distribution in methyl group of acetone and acetaldehyde would occur through the enolic forms of these species although we have no direct evidence for these species at present.

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