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Kinetics of catalyzed acid/acid and acid/aldehyde condensation reactions to non-symmetric ketones

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Abstract

The kinetics and mechanism of acid and aldehyde condensations to produce non-symmetric ketones with CeO_2-based catalysts were studied using a combination of conventional and pulse microreactor tests. The effects of oxygen and water on the reactions were also studied.

Supported CeO_2 catalysts effectively catalyze the ketonization of acids at essentially complete conversion for extended periods, at weight hourly space velocities of 4–5. The optimal temperature range is 400–430 °C, depending on feed. Time on stream and number of regeneration cycles improved catalyst performance. Selectivities are improved by promotion with small amounts of potassium.

The acid/acid reaction to a typical methylketone proceeds roughly three times faster than the acid/aldehyde reaction, while the aldehyde/aldehyde initial reaction rate to desired methylketones is much slower; multiple aldol condensations predominate. When using acid/aldehyde feeds, water enhances ketone production, probably by supplying oxygen to the catalyst surface. While O_2 can fulfill a similar role, it also promotes combustion. Substitution of D_2O and CD_3COOH for water and acetic acid, respectively, led to kinetic isotope effects between 1.4 and 6.7, which is in the expected range for carboxylate decompositions.

Experiments at low conversion using CD_3COOH and either cyclopropanecarboxylic acid or its aldehyde showed that acetone and methylcyclopropylketone are formed preferentially as five D- and two D-atom isotopomers, respectively, for both acid/acid and acid/aldehyde feeds. This suggests the formation of a surface ketene intermediate, preferentially from acetic acid, which attacks a surface carboxylate to form the ketone, eliminating CO_2. The same conclusions could be drawn from ^{13}C distributions in experiments using labeled acetic acid.

Keywords: Acid condensation; Cerium oxide; Methylcyclopropylketone; Methylnonylketone; Isotope distributions

1. Introduction

Non-symmetric ketones are known to be produced by the decarboxylative condensation of carboxylic acids. Rajadurai [1] and Pestman et al. [2] have reviewed the process and possible reaction mechanisms. The general reaction is

$$RCOOH + R'COOH \rightarrow RCOR' + H_2O + CO_2 \quad (1)$$

Esters can also be used as feedstock. Such ketones are useful as intermediates in making pesticides, herbicides, and pharmaceuticals, and as solvents. In this work, catalysts to make two methylketones of industrial interest, methylcyclopropylketone (MCPK, or ethanone, 1-cyclopropyl) and methylnonylketone

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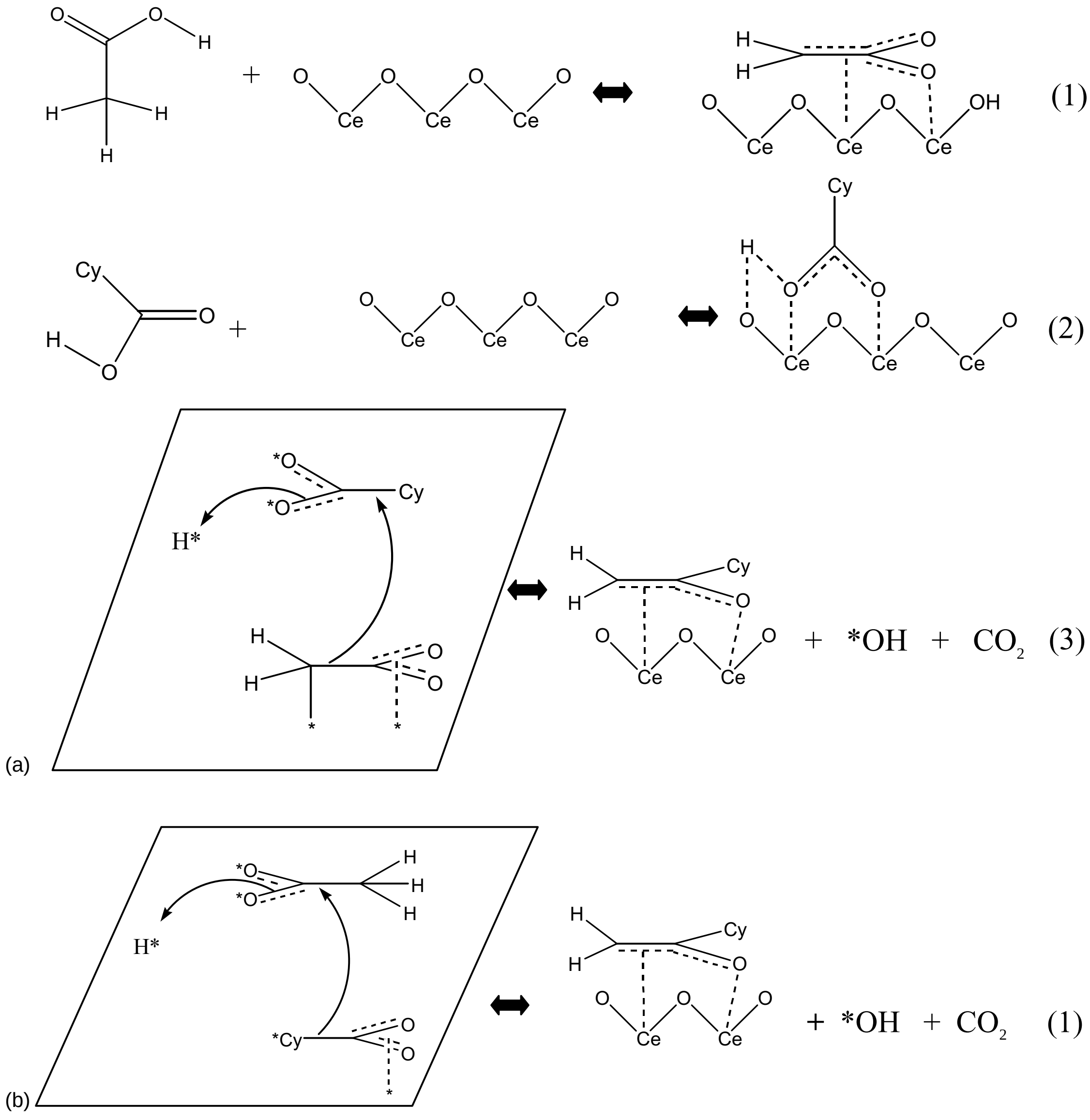
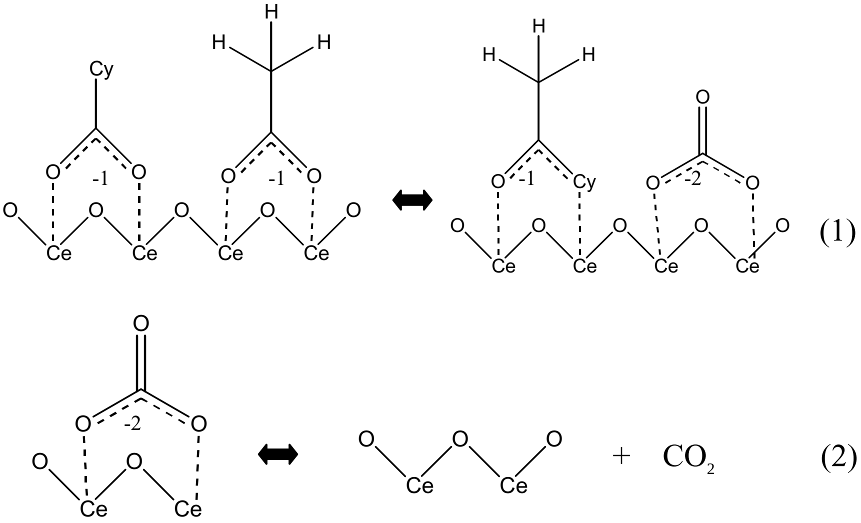
(MNK, or 2-undecanone), were studied. These can be made by the decarboxylative condensation of acetic acid (HOAc) with cyclopropanecarboxylic acid (CCA) and decanoic acid (DAc), respectively. It is shown here that certain aldehydes can be condensed catalytically to also produce methyl ketones.

Most previous work on acid condensation reactions involved experiments using supported mixed metal oxides with weakly acidic and basic sites, possibly along with smaller amounts of strongly basic oxide additives. Most catalysts exhibit either low or moderate reducibility at typical reaction conditions of >650 K and 0.1–2.0 MPa [1–8]. Such materials include the amphoteric or weakly basic oxides such as CeO_2, MnO_2/Mn_3O_4, Fe_2O_3, ZnO, TiO_2 or ZrO_2 [9–15]. However, in previous work using supported CeO_2 catalysts, ketonization reaction selectivity was found to be low compared to that of aldol condensation or



Scheme 1. Ketene mechanism with (a) HOAc forming and (b) CCA forming surface ketene intermediate.



Scheme 2. Carboxylate mechanism.

reductive coupling reactions [15–17]. In our previous work [18], we showed that, at high conversions and temperatures >670 K, supported rare-earth oxides are in fact excellent long-lived catalysts over a wide range of partial pressures and space velocities.

Our goal here is to better understand the condensation mechanism(s) for acid/acid, aldehyde/acid and aldehyde/aldehyde feeds, at conditions of process interest. Such understanding may lead to the design of more selective catalysts for non-symmetric ketonization. Past studies have led to several proposed mechanisms for ketonization of acids and aldehydes. Gonzalez et al. [19] and Pestman et al. [2] proposed that the key step is the coupling of a surface ketene intermediate and a carboxylate. A depiction is shown in Scheme 1. The surface ketene is formed by dehydrogenation of the acid, and then it reacts with an adsorbed carboxylate to ultimately form the ketone, eliminating CO_2. The details of the coupling step are not clear; it is likely that more than one distinct step is involved.

Some factors supporting this mechanism, on certain catalysts, are as follows. First, at least one of the acid reactants must contain an α-hydrogen atom [2]; as the number of α-hydrogen atoms decreases, the rate of formation of ketone does also. Second, ketene is formed at low conversions from acetic acid over many metal oxide catalysts [2,20,21]. Third, using acetic $[^{13}C]$ acid and trimethylacetic acid, it was found that the carbonyl in the resulting ketone arises not from the trimethylacetate only [2]. In some TPD studies, no carboxylates could even be found on oxide surfaces at $\gtrsim$650 K [14,20], where ketonization occurs. Finally, acetone does not exchange its H-atoms with a deuterated TiO_2 surface at ketonization conditions, but acetic acid does, in the α-position [2]. However, the materials used in these studies bear little relation to what appear to be the best ketonization catalysts [3–8,18].

Kuriacose and coworkers [22,23] proposed a mechanism for the reaction of two adsorbed carboxylates to produce ketone, water, and carbon dioxide (Scheme 2), based on studies of HOAc ketonization. Okumura and Iwasawa [24] also concluded, from a study of HOAc on ZrO_2/SiO_2 catalysts, that one possibility for ketonization is the reaction of two carboxylates. Another possible mechanism is the reaction of an adsorbed acyl carbenium ion (RCO^+) with an adsorbed carboxylate [23–25]. Acyl carbenium ions can be formed in the presence of strong Lewis acids. On a Pd/CeO_2 or Co/CeO_2 catalyst, the ketonization at lower temperatures has also been attributed to reaction between an acetyl intermediate and an alkyl group to produce a ketone [17]. Therefore, it is seen that the main feature distinguishing the proposed mechanisms is the identity of the electrophile attacking the adsorbed carboxylate. In this work we apply detailed product analysis from experiments using differently labeled (^{2}H and ^{13}C) feeds to provide insight into this identity.

There have also been observed reactions of aldehydes and alcohols that produce ketones rather than simple aldol condensation products [15,17,26–33]. Some evidence supports an aldol condensation mechanism, followed by decomposition of the primary aldol products [26,27,33]. Alternative mechanisms suppose that an alcohol is dehydrogenated to the aldehyde, which is oxidized to an adsorbed carboxylate. The carboxylates can then undergo ketonization as usual [15,17,30,32]. Again, we will apply detailed product analysis from experiments using labeled feeds to better understand which pathways predominate for a selective catalyst at typical process conditions.

2. Experimental

Six catalysts were used. Two were 17 wt.% CeO_2/Al_2O_3 (Sud Chemie, 1.59 mm extrudate or 3.18 mm extrudate), three others were 15 wt.% CeO_2/Al_2O_3 catalysts, one with just CeO_2, one washed with KOH, and one with 3 wt.% K_2O added, and the last was 10 wt.% CeO_2/TiO_2. The last four were prepared by dropwise incipient wetness impregnation of a 20 wt.% aqueous or aqueous KOH solution of $Ce(O_2CCH_3)_3\cdot 1.5H_2O$ (Aldrich, 99.9%) on Engelhard AL-3945E Al_2O_3, 1.27 mm extrudate, with calcination in air at 520 °C, or TiO_2 (LaRoche, 85% TiO_2, 15% Al_2O_3, 3.18 mm extrudate), calcined in air at 450 °C.

Continuous flow experiments were performed in fixed bed stainless steel reactors, 1.75 cm i.d., 48.3 cm length or 1.25 cm i.d., 25 cm length, in upflow mode with vaporized feed. Typical catalyst loads were 25 or 2.5 g, respectively. Pulse reactions were carried out in a quartz reactor (1.25 cm i.d., 15.2 cm length), with a typical load of 0.035 g. Reactor temperature control in both cases was within ±1 °C of the set point except at startup. All products were collected in two traps in series, either at 0 °C (continuous flow) or liquid N_2 temperature (pulse).

The pulse reactor was operated in upflow mode with a vaporized feed. The reactants were fed to the reactor through a 10-port sampling valve with He as carrier gas, 110 ml/min. Pulse sizes of 100 or 250 μl were used. Prior to and after any injection, the reactor was purged with He for at least 15 min.

Feeds were prepared from cyclopropane carboxylic acid (CCA, Eastman, 98.6%), decanoic acid (DAc, Henkel, 98.8%), acetic acid (HOAc, glacial, 99.9%), cyclopropane carboxaldehyde (CCAld, Eastman, ∼99%), and acetaldehyde (HAald, Aldrich, 99.5%). Feeds for isotopic experiments were prepared from deuterium oxide (D_2O, Aldrich, 99.9%), acetic-d_3-acid-h (HOAc-d, Aldrich, 99.5%), acetic [^{13}C] acid (HOAc-^{13}C, $^{13}CH_3COOH$, Aldrich, 99%), and acetic acid [^{13}C] (^{13}C-HOAc, $CH_3{}^{13}COOH$, Aldrich, 99%). Details of the GC and MS analyses, and further experimental details, are given in a thesis [34].

For thermogravimetric analysis (TGA, Perkin-Elmer TGA-7), dry catalysts were reduced in 35% H_2/65% He at reactor operating conditions for 6 h, then reoxidized. Surface areas (BET method) were determined using an Omnisorp 360 static adsorption apparatus. Elemental analysis was by ICP-MS.

3. Results and discussion

3.1. Catalyst characterization

Table 1 gives details of the catalysts. The results show that only a small portion of the original CeO_2 was leached from the surface of the catalysts during extended operation. The BET results, for both CeO_2/TiO_2 and CeO_2/Al_2O_3, indicate that during operation the surface area of the catalyst is reduced, more so for CeO_2/TiO_2. This could be due to blockage of pores by products that could not be oxidized, because the regenerated catalysts remained slightly discolored. The surface densities of CeO_2 for the fresh catalysts correspond approximately to calculated values for a monolayer of CeO_2 on each support [18].

The TGA results for the catalysts showed almost no differences in reduced or oxidized stoichiometries between new and used catalysts. Almost completed reoxidation was possible following reduction [34].

3.2. Continuous reactor experiments

The terminology used to describe the results here is as follows:

$$\text{conversion of CCA/DAc (\%)} = 100 \times \frac{\text{moles of CCA/DAc reacted}}{\text{moles of CCA/DAc fed}}$$

Table 1
Surface area and ICP-MS results for catalysts

Catalyst	Surface area (m^2/g)	ICP-MS composition, Ce (wt.%)	CeO_2 density ($g\ CeO_2/m^2$)
15 wt.% CeO_2/Al_2O_3 (new)	167	13.4	8.0×10^{-4}
15 wt.% CeO_2/Al_2O_3 (used)	146		
15 wt.% CeO_2/K-washed/Al_2O_3 (new)	146	14.8 (0.12 wt.% K)	1.0×10^{-3}
15 wt.% CeO_2/K-washed/Al_2O_3 (used)	138	14.8 (0.10 wt.% K)	1.1×10^{-3}
15 wt.% CeO_2/3 wt.% K_2O/Al_2O_3 (new)	190	14.6 (2.89 wt.% K)	7.7×10^{-4}
17 wt.% CeO_2/Al_2O_3 (new)	158	16.7	1.1×10^{-3}
17 wt.% CeO_2/Al_2O_3 (used)		16.4	
10 wt.% CeO_2/TiO_2 (new)	74	9.8	1.3×10^{-3}
10 wt.% CeO_2/TiO_2 (used)	41	9.8	2.4×10^{-3}

$$\text{weight selectivity of MCPK/MNK (\%)} = 100 \times \frac{\text{weight of MCPK/MNK}}{\sum \text{weight of products}}$$

$$\text{molar yield of MCPK/MNK (\%)} = 100 \times \frac{\text{moles of MCPK/MNK}}{\sum \text{moles of products} + \text{moles of unreacted CCA/DAc}}$$

$$\text{WHSV (weight hourly space velocity)} = \frac{\text{weight of feed}}{\text{weight of catalyst} \times \text{h}}$$

In these equations, acetone is omitted as a product in the summations because it is formed from HOAc only.

Experiments were performed using 17 wt.% CeO_2/Al_2O_3, two different sizes (1.59 and 3.18 mm extrudates). Temperature was varied to determine the optimal range for obtaining the highest conversion of CCA and selectivity to MCPK for the different feeds (Table 2). The temperature/conversion/selectivity development for a run (4/1 HOAc/CCA, Fig. 1) is shown, with regeneration cycles indicated. The catalysts were typically regenerated in air at 520 °C at the end of a working day, even if no signs of deactivation were apparent. Long-term deactivation was not a problem until after many days on stream, while catalysts in the pulse experiments were used for much shorter times.

Runs M-86 and M-87 used the same catalyst load, as did M-91 and M-92. It can be seen, from comparing run M-85 to runs M-86 and M-87, and also from M-91 to M-92 (Table 2), that water addition had little effect on the activity and selectivity of the catalysts, after the initial period. This result does not discount the possibility that water is involved in the reaction mechanism, just that it does not appear to be an inhibitor at these conditions. By comparing run M-85 to previous work on a smaller catalyst [18] (run M-50), it was seen that catalyst size effects are negligible. The same conclusion can be drawn by comparing runs M-85 and M-89 to M-91 and M-92 (Table 2).

Comparing runs M-85 and M-89 (Table 2), it is obvious that at temperatures below 430 °C the selectivity to MCPK decreases. In this temperature range the major side products were pentenones, γ-butyrolactone (GBL), and X (one or both of the isomers: 4-cyclopropyl-4-cyclopropylidene-2-butanone, cyclopropyl[1-(1-methylethenyl)cyclopropyl] methanone). All except GBL are made by secondary reactions (see next section); X is formed by an aldol condensation reaction between acetone and dicyclopropylketone. At 440 °C, the yield to MCPK also decreased; the optimal temperature for production of MCPK is ∼430 °C.

It was observed that the activity and especially the selectivity to MCPK improved with time on stream and number of regeneration cycles (Table 2 and Fig. 1). In run M-91, HOAc alone was fed over the catalyst for 1 day prior to addition of CCA. This led to a marked increase in selectivity on the first day of the HOAc/CCA feed, so the effect is not specific to a particular acid. It was seen that this increase in activity is due to reduction of the surface accompanied by the spreading of $CeO_{2-\delta}$ ($\delta \sim 0$–0.3) to form a more two dimensional layer structure [18].

For HOAc/DAc feeds, molar feed ratios of 4/1, 3/1 or 2.5/1 HOAc/DAc were used. The continuous reactor results are shown in Table 3. The same catalyst was used in runs M-68, M-69, and M-70,

Table 2
Summary of continuous reactor results, MCPK production

Day	T range (°C)	WHSV	CCA conversion (%)	Selectivity (wt.%)	Molar yield (%)
Run M-85, 4/1 HOAc/CCA, 17% CeO_2/Al_2O_3 (1.59 mm extrudate)					
1	420	1–2	80 ± 18	28 ± 20	26 ± 20
2–4	420–430	1–4	99.5 ± 0.7	67 ± 7	66 ± 6
5–13	430	4–5	99.2 ± 0.6	72 ± 3	71 ± 4
14–15	430	3–5	43 ± 14	85 ± 8	37 ± 14
Run M-86, 3.5/0.5/1 HOAc/H_2O/CCA, 17% CeO_2/Al_2O_3 (1.59 mm extrudate)					
1	430	4	98 ± 2	52 ± 10	50 ± 10
2	430	4–5	99.6 ± 0.3	70 ± 2	69 ± 2
Run M-87, 3/1/1 HOAc/H_2O/CCA, 17% CeO_2/Al_2O_3 (1.59 mm extrudate)					
1	430	4–5	92 ± 2	71 ± 6	65 ± 5
2	430	4–7	71 ± 6	72 ± 4	51 ± 4
Run M-89, 4/1 HOAc/CCA, 17% CeO_2/Al_2O_3 (1.59 mm extrudate)					
1	430	5–6	99.3 ± 0.7	48 ± 0.3	48 ± 0.5
2	415–420	4–5	99.3 ± 0.1	43 ± 8	43 ± 8
3–4	415–430	4–5	99.0 ± 1.3	48 ± 6	48 ± 5
5	435	4–5	99.6 ± 0.2	59 ± 3	59 ± 3
6–7	440	2–5	83 ± 15	61 ± 15	50 ± 3
Run M-91, 4/1 HOAc/CCA, 17% CeO_2/Al_2O_3 (3.18 mm extrudate)					
1	430	3–4	99.4 ± 0.1	52 ± 13	52 ± 12
2–5	430	4–5	99.0 ± 0.6	65 ± 3	64 ± 3
Run M-92, 3/1/1 HOAc/H_2O/CCA, 17% CeO_2/Al_2O_3 (3.18 mm extrudate)					
1	430	4–5	99.3 ± 0.2	65 ± 2	63 ± 2
2	430	4–5	99.4 ± 0.2	66 ± 2	65 ± 1

and in runs M-71, M-73, and M-74. The data suggest that permanent deactivation may sometimes take place after several days on stream, although many runs show no such evidence (e.g. Fig. 2). No catalyst size effects were noted. The primary side product is dinonylketone.

For these experiments, catalysts with more basic sites (K-promoted) were also used to determine effects of such addition. Beneficial effects have been reported in the patent literature [5,29]. Upon comparing runs M-68, M-70, M-71, M-73, M-74, and M-83 (Table 3), several conclusions can be made. First, at a molar ratio of 4/1 HOAc/DAc the catalyst performed about the same as the regular catalyst. Second, at lower molar feed ratios the base-washed catalyst gave approximately the same activity but slightly higher selectivity. But a catalyst with higher K-content (run M-83, Table 3) showed little improvement over the unpromoted CeO_2/Al_2O_3. It should be noted that the Sud-Chemie supports used for the 17 wt.% CeO_2 catalysts were also base-washed, and these also gave improved selectivities.

When the molar ratio of the feed was decreased, from 4/1 to 3/1 to 2.5/1 HOAc/DAc, the selectivity to MNK was relatively unchanged (Table 3). Therefore the relative rates are insensitive to the partial pressure of HOAc. The temperature range 400–420 °C appears to give the best results, with lower selectivities being observed at both lower and higher temperatures.

3.3. Pulse reactor experiments

The terminology used to describe the results here is as follows:

$$\text{conversion of CCA/CCAld (\%)} = 100 \times \frac{\text{moles of CCA/CCAld reacted}}{\text{moles of CCA/CCAld fed}}$$

$$\text{molar selectivity of MCPK (\%)} = 100 \times \frac{\text{moles of carbon in MCPK} \times \text{moles of MCPK}}{\sum \text{moles of carbon in product} \times \text{moles of product}}$$

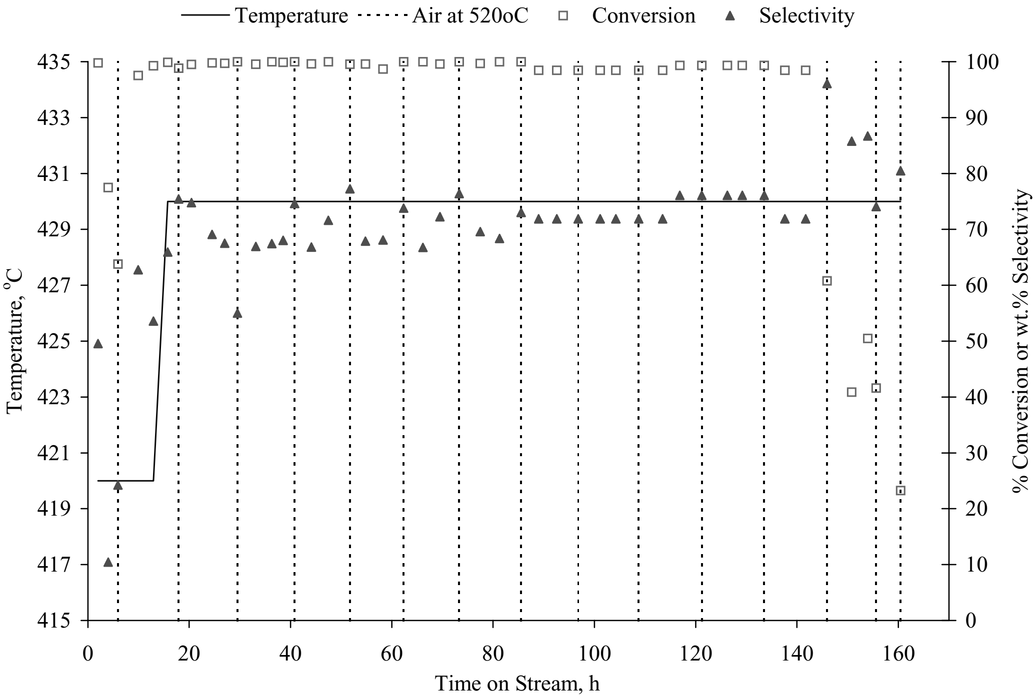


Fig. 1. Continuous reactor results for 4/1 HOAc/CCA feed, 17% CeO_2/Al_2O_3 catalyst, run M-85.

$$\text{product turnovers} = \frac{\text{moles of product}}{\text{moles of } CeO_2}$$

collection efficiency

$$= 100 \times \frac{\text{volume of collected product}}{\text{volume of feed injected}}$$

Pulse experiments were first performed using non-enriched feeds, to determine the effects of different molar feed ratios on the conversion and selectivity, and to obtain baseline values for determination of the effects of isotopic labeling. The catalyst was 10 wt.% CeO_2/TiO_2, chosen based on its high initial selectivities in previous work [18]. A volumetric collection efficiency of 70% would be expected if all the acetone, CO_2, and ~10% of the original HOAc were lost, at a CCA conversion of 10%. Some losses were also due to permanent adsorption on the catalyst, because the collection efficiencies of the initial pulses were smaller.

Results for HOAc/CCA feeds are shown in Table 4. Typically, the total feed injected was 1 ml. The only side product was GBL. Pulse collection efficiencies were mostly >75%. The number of MCPK turnovers for all these runs is >15 for the higher pulse size and >6 for the lower.

When HOAc was decreased an increase in MCPK resulted (Table 4). This suggests that the reaction order for HOAc is negative. Using the data in Table 4 it was possible to estimate the HOAc and CCA orders of reaction from two paired experiments using the following:

$$\frac{r_1}{r_2} = \frac{(kp_A^m p_B^n)_1}{(kp_A^m p_B^n)_2} \tag{2}$$

If $p_{A1} = p_{A2}$, then

$$n = \frac{\ln(r_1/r_2)}{\ln(p_{B1}/p_{B2})} \approx \frac{\ln(x_1/x_2)}{\ln(y_1/y_2)} \tag{3}$$

where x is the number of turnovers and y is the mole fraction of compound in the pulse.

From the 4/1 HOAc/CCA and 3/1/1 HOAc/H_2O/CCA runs, the order for HOAc was determined, assuming water neither inhibits nor promotes. This assumption is consistent with the continuous reactor results,

Table 3
Summary of continuous reactor results, MNK production

Day	T range (°C)	WHSV	DAc conversion (wt.%)	Selectivity (wt.%)	Molar yield (%)
Run M-68, 4/1 HOAc/DAc, 15% CeO_2/Al_2O_3, 1.27 mm extrudate					
1–2	400–403	2–3	83 ± 8	80 ± 9	67 ± 2
2–3	409–419	7–10	73 ± 14	79 ± 7	58 ± 15
3–7	400–410	4–6	91 ± 8	84 ± 7	76 ± 7
8–12	400–420	3–5	98 ± 1	73 ± 9	72 ± 9
Run M-69, 3/1 HOAc/DAc, 15% CeO_2/Al_2O_3, 1.27 mm extrudate					
1–2	400	4	90 ± 1	68 ± 11	68 ± 9
3	389	4	89 ± 2	42 ± 15	41 ± 12
3	419	4	93	46	46
4	379	2.6	94	47	48
Run M-70, 4/1 HOAc/DAc, 15% CeO_2/Al_2O_3, 1.27 mm extrudate					
1–2	400	4.5–5	88 ± 3	83 ± 3	73 ± 3
Run M-71, 4/1 HOAc/DAc, 15% CeO_2/K-washed/Al_2O_3, 1.27 mm extrudate					
1–4	389–400	1–3	95 ± 9	65 ± 22	62 ± 21
4–6	400	5	93 ± 3	82 ± 4	76 ± 4
Run M-73, 3/1 HOAc/DAc, 15% CeO_2/K-washed/Al_2O_3, 1.27 mm extrudate					
1–4	389–400	4–5	88 ± 12	74 ± 5	66 ± 9
4–5	370–379	1–2	64 ± 12	83 ± 4	54 ± 11
5–6	389–400	1–2	85 ± 11	72 ± 3	62 ± 10
6	410	3.5	98	74	73
7	419	4	96	75	71
7	429	3.6	100	69	68
7	379	1	95	80	76
8	369	4.5–5	12 ± 3	74 ± 6	9 ± 3
Run M-74, 2.5/1 HOAc/DAc, 15% CeO_2/K-washed/Al_2O_3, 1.27 mm extrudate					
1–2	400–410	4–5	74 ± 13	78 ± 10	59 ± 10
3–4	419–420	5–6	91 ± 4	74 ± 3	66 ± 3
Run M-83, 3/1 HOAc/DAc, 15% CeO_2/3% K_2O/Al_2O_3, 1.27 mm extrudate					
1–3	400–410	3.0–4.9	83 ± 12	69 ± 9	57 ± 11
4–9	420	2.2–4.7	91 ± 8	70 ± 5	64 ± 6
10–11	420	2.8–4.6	77 ± 13	65 ± 16	50 ± 12
Run M-88, 3/1 HOAc/DAc, 17% CeO_2/Al_2O_3, 1.59 mm extrudate					
1	400–415	7.4–9.3	55 ± 15	82 ± 7	45 ± 14
2–4	410–420	4.2–6.9	93 ± 5	82 ± 5	76 ± 6
5–8	420	4.8–7.4	94 ± 2	82 ± 4	77 ± 5
Run M-97, 3/1 HOAc/DAc, 17% CeO_2/Al_2O_3, 3.18 mm extrudate					
1–2	420	3.7–4.1	94 ± 3	88 ± 3	85 ± 4
3	420	6.1–6.4	50	89	43
4	420	8.8	15	91	14
5	450	5.8	99	70	70
5	440	6.0	98	82	80
6	445	5.3–5.9	98 ± 1	76 ± 3	74 ± 4

and past work at both low and high partial pressures [1,18]. From three different run pairs, the reaction orders were estimated as −0.35, −0.52, and −0.73. These values suggest an order for HOAc near −0.5. From two different run pairs the reaction order for CCA was estimated to be 0.36–0.27. These values suggest an order for CCA is near 0.3. Therefore HOAc is more strongly adsorbed than CCA.

For the two deuterated feeds, the collection efficiencies were mostly >80%, and the number of

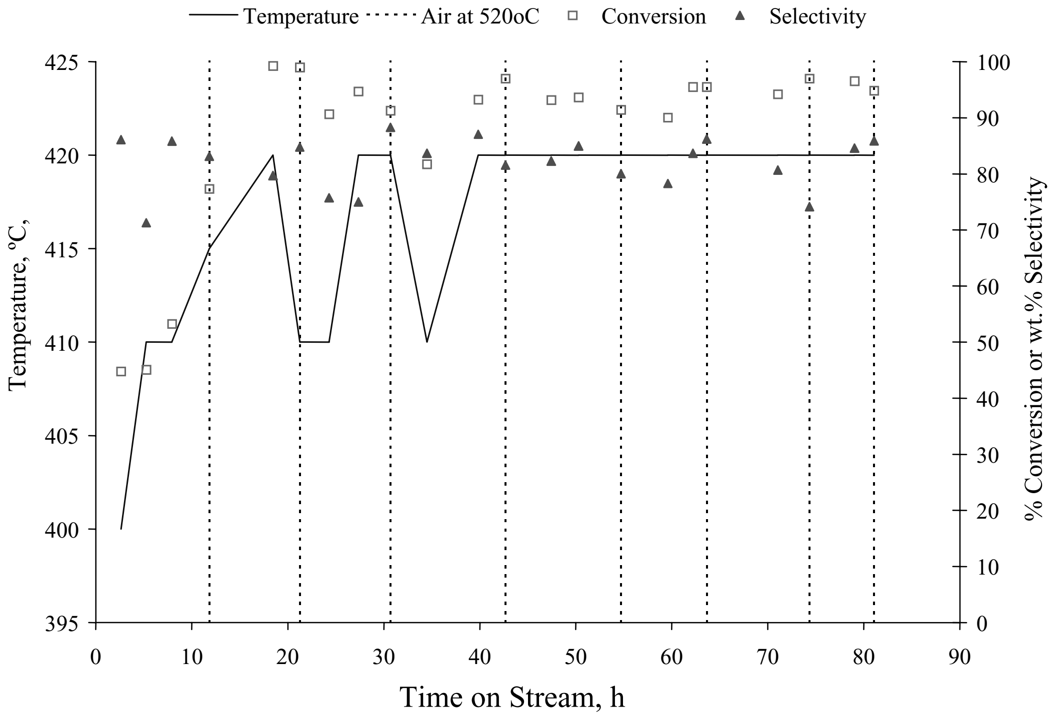


Fig. 2. Continuous reactor results for 3/1 HOAc/DAc feed, 17% CeO_2/Al_2O_3 catalyst, run M-88.

MCPK turnovers >4. The addition of either D_2O or HOAc-d decreases the reaction rates, suggesting that the breaking of a D–C bond in HOAc-d must be a rate-determining or a slow step. H–D exchange between water and HOAc is relatively fast at these conditions, as shown subsequently. Using Eq. (3), it is possible to determine the kinetic isotope effects for MCPK formation, 2.1 for the CH_3COOH/CD_3COOH feed pair and 1.4 for the H_2O/D_2O feed pair. The D_2O feed had an effect due to rapid H–D exchange between water and HOAc. The isotope effect for formate decomposition on various metals has been studied extensively, and found to vary from ∼2 to ∼15 for HCOOH/DCOOD and from ∼1 to ∼2.5

Table 4
Pulse reaction results for MCPK production, acid/acid feeds

Feed ratio	T (°C)	CCA conversion (wt.%)	Molar selectivity (%)	Pulse size (μl)
4/1 HOAc/CCA	390	11!2	98!2	250
3/1/1 HOAc/H_2O/CCA	390	10!2	100!0	250
2/1 HOAc/CCA	390	8!2	97!2	250
4/1 HOAc/CCA	390	6!1	76!16	100
4/1 HOAc/CCA	440	8!1	93!8	100
3/1/1 HOAc/H_2O/CCA	390	6	82	100
3/1/1 HOAc/H_2O/CCA	440	9	95	100
3/1/1 HOAc/D_2O/CCA	390	5	99	250
3/1/1 HOAc/D_2O/CCA	390	4	98	100
3/1/1 HOAc-d/H_2O/CCA	390	3	96	250
3/1/1 HOAc-d/H_2O/CCA	390	3	90	100

Table 5
Pulse reaction results for MCPK production, acid/aldehyde feeds

Feed ratio	T (°C)	CCAld conversion (%)	Molar selectivity (%)	Aldol (wt.%)	MCPK turnovers
4/1 HOAc/CCAld[a]	390	3.6	32	18	1.9
4/1/1 HOAc/H_2O/CCAld	390	1.7	100	23	1.3
4/1 HOAc/CCAld	440	2.8 ± 0.9	100 ± 0	2 ± 1	2.3 ± 0.7
4/1/1 HOAc/H_2O/CCAld	440	3.5 ± 1.1	99.8 ± 0.5	6 ± 4	2.5 ± 0.8
5/1 HOAc/CCAld	440	1.8 ± 0.1	100 ± 0	0.5 ± 0.2	1.3 ± 0.1
4/1/1 HOAc/D_2O/CCAld	440	0.6 ± 0.3	99.6 ± 1.2	4	0.4 ± 0.2
4/1/1 HOAc-d/H_2O/CCAld	440	2.6 ± 1.1	98 ± 4	2	1.3 ± 0.1

[a] For this feed 1 ml was injected, for all other feeds 0.5 ml was injected.

for HCOOH/HCOOD [35]. Taking into account that almost all of the experiments performed on formate decomposition were done at temperatures less than 200 °C, and that isotope effects decrease with respect to temperature, the kinetic isotope effects calculated here are within the expected range for carboxylate decomposition.

The first set of pulse experiments for HOAc/CCAld feeds alternated between temperatures of 390 and 440 °C (Table 5). The collection efficiencies for these runs were mostly >80%. The only side product found resulting from CCAld was CCA. The aldol condensation product of acetone with itself, 4-hydroxy, 4-methylketone, was also observed.

Comparing Tables 4 and 5, we see that the rate of MCPK production is lower for acid/aldehyde than acid/acid feeds (at the same partial pressure of CCA), by a factor of ∼3. The data from Table 5 also show that at 390 °C there was a larger amount of aldol produced than at 440 °C. This suggests the possibility of two reaction regimes, namely aldolization with decarboxylative condensation, or just decarboxylative condensation. The question of interest is whether the MCPK here is produced through an aldol or a decarboxylative condensation route.

For example, Kamimura et al. [26] and Claridge et al. [27] studied the reaction of 1-propanol to 3-pentanone over CeO_2/Fe_2O_3 at 723 K and lanthanum oxide at 773 K, respectively. They proposed that the alcohol is dehydrogenated to the aldehyde, which undergoes aldol condensation (step (4) below) to 3-hydroxy-2-methylpentanal. They infer that the decomposition of the aldol product proceeds by means of oxidative decarboxylation (step (5), proposed in [27]) or by deformylation (step (6), proposed in [33]). Both CO and CO_2 were observed. The steps could be written in general terms as

$$\mathrm{RCHO + R'CH_2CHO \rightarrow RCH(OH)CH(CHO)R'} \tag{4}$$

$$\mathrm{RCH(OH)CH(CHO)R' + [O] \rightarrow RCOCH_2R' + CO_2 + H_2} \tag{5}$$

$$\mathrm{RCH(OH)CH(CHO)R' \rightarrow RCOCH_2R' + CO + H_2} \tag{6}$$

Kamimura et al. [26] speculated that the extra oxygen needed for the oxidative decarboxylation comes from the decomposition of 1-propanol to propane, while Claridge et al. [27] proposed that it arises from surface oxygen.

A purely aldol route to MCPK could proceed through either of the following reactions:

$$\mathrm{CH_3COCH_3 + C_3H_5CHO \rightarrow C_3H_5CH(OH)CH_2COCH_3} \tag{7}$$

$$\mathrm{CH_3CHO + C_3H_5CHO \rightarrow C_3H_5CH(OH)CH_2CHO} \tag{8}$$

Both intermediates could decompose to MCPK, either by oxidative decarboxylation (to also give CO_x and water) or by a decarboxylation reaction to acetaldehyde from the first intermediate, or formaldehyde from the second. However, in our experiments neither of these intermediates, nor acetaldehyde, formaldehyde, or CO were found even in trace amounts. Therefore, it appears that for rare earth oxide catalysts the ketones are being produced by a decarboxylative condensation reaction of the aldehyde and acetic acid, using oxygen from the surface if needed. This is in broad agreement with some past proposals [15,17,28,30,32].

There was an obvious decrease in MCPK production at a 5/1 HOAc/CCAld ratio when compared to the 4/1/1 feed (Table 5, entries 4 and 5). This decrease might be attributable to the increase of HOAc partial pressure. Using this pair, the order for HOAc was estimated as −3.6 at 440 °C, assuming water is inert. But this calculated reaction order is so much more negative than that of the acid/acid reaction, and so negative in value, that the more logical conclusion is that the water is not inert, but instead is promoting the reaction.

In order to test this hypothesis, experiments with acid/aldehyde feeds were then conducted using D_2O and acetic-d_3-acid-h in place of water and HOAc, respectively (Table 5, entries 4, 6 and 7). The substitution of D_2O had a significant effect on the reaction rate, so that a reaction step involving water must be a rate determining step or a slow step. The addition of HOAc-d also decreased the MCPK turnover ratio, but to a lesser degree. Therefore the breaking of a C–H bond in HOAc could also be a slow step in the mechanism, or there could be two parallel reactions, one using water and one not using it. The kinetic isotope effects for these reactions were 1.5 for CH_3COOH/CD_3COOH and 6.7 for H_2O/D_2O. As with the acid/acid reactions, these kinetic isotope effects are in the expected range of carboxylate decomposition, based on the data for formic acid [35]. However, the kinetic isotope effect of water is much larger here than for the acid/acid reaction, suggesting that water is indeed involved in the primary acid/aldehyde reaction.

Limited studies have been made to determine if added water could replenish the surface oxides removed in oxidizing the aldehyde to the acid. Experiments have shown that ketone and CO_2 production increase when water is added [27,29]. Plint et al. [28] found that adding water to a butanol feed increased the production of butanal, aldol products, and 4-heptanone. Water showed similar effects here; when it was added to the feed, a significant increase in MCPK formation was observed. The reaction order for water was estimated to be 0.2, assuming that the orders for HOAc and CCAld are −0.5 and 0.3, respectively, as in the HOAc/CCA reaction. The isotope effect observed with D_2O is much larger than with HOAc-d, or with D_2O when using acid/acid feeds. Standard calculations of equilibrium constants show that the reaction of an acid, an aldehyde, and water to produce a methylketone are favorable at these conditions, although condensations without water (giving either CO and water or CO_2 and H_2 as by-products) are even more favorable thermodynamically [34].

The next runs used O_2 in the feed to determine if it could selectively oxidize CCAld (Table 6). When operating with O_2, a much lower selectivity is attained than with added water, or with just acid and aldehyde. The collection efficiencies were mostly >80%. The results showed that oxidation of CCAld to CCA occurred, but the number of turnovers to MCPK were the same as or less than those for runs without O_2 (Table 5).

Plint et al. [28] found that the yield to 4-heptanone from butanol was maximized at a butanol/oxygen ratio of 6/1, using a 40% CeO_2/MgO catalyst, and that butanol conversion was positive order with respect to O_2. Claridge et al. [27] studied the reaction of propanal to 3-pentanone using O_2 or N_2O as oxygen sources, noting some total oxidation at 500 °C. The data from the present work show that an increase in CCAld/O_2 ratio increases the production of MCPK at both 390 and 440 °C; there is no positive effect of O_2 addition on ketone formation.

Experiments using acetaldehyde/aldehyde feeds (4/1 HAald/CCAld and 4/1/1 HAald/H_2O/CCAld) were all performed at 440 °C. The total number of turnovers based on CCAld conversion were ∼3. The CCAld conversions and MCPK selectivities

Table 6
Pulse reaction results for MCPK production, acid/aldehyde/O_2 feeds

Feed ratio	T (°C)	CCAld conversion (%)	Molar selectivity (%)	MCPK Turnovers	MCPK + CCA turnovers
4/1/0.5 HOAc/CCAld/O_2	390	8	17	1.2	6.4
4/1/0.1 HOAc/CCAld/O_2	390	7	28	1.5	5.3
4/1/0.5 HOAc/CCAld/O_2	440	3	26	0.7	2.7
4/1/0.1 HOAc/CCAld/O_2	440	10	30	2.3	7.7

were 3.5 and 10%, respectively, for the 4/1 molar feed, and 3.5 and 15%, respectively, for the 4/1/1 molar HAald/H_2O/CCAld feed. The other products from CCAld were CCA, 2-cyclopropyl-1-butene, and 3-cyclopropyl-1-butene, the latter two formed from the aldol condensation of HAald and CCAld. A number of products from the self-condensation of acetaldehyde were also present. When compared to acid/acid or acid/aldehyde feeds, the decreased production of MCPK here suggests the necessity of at least one adsorbed carboxylate for ketonization to take place. The addition of water increased the production of MCPK slightly, again suggesting that water is supplying oxygen to the surface to generate carboxylate intermediates.

3.4. Isotope distribution studies

From the experiments performed using isotopically labeled feeds, it was possible to determine the mole fractions of all isotopomers. From these data we can gain a better understanding of what surface reactions are occurring, and what surface intermediates are formed. We will show that when considered in their entirety these distributions can distinguish between the mechanisms of Schemes 1 and 2.

Two methods were used for these calculations. The first used the mass spectrum for the non-isotopically labeled compound, corrected it for the natural occurrence of all ^{13}C and ^{2}H isotopes, and then applied these results to the spectra of labeled compounds to obtain a corrected mole fraction distribution (Method 1; [36]). The second was a simpler method that did not take into account the naturally occurring ^{2}H isotopes (Method 2). As might be expected, the differences between the final results of the two methods are only minor, and the second method was used only to check the calculations of the first. For comparison, binomial distributions assuming complete D-scrambling were calculated for both acetone and MCPK. For runs using D_2O, binomial distributions were calculated assuming either multiple exchange for HOAc/CCA/D_2O, multiple exchange for HOAc/D_2O, or single exchange for HOAc/D_2O only. For runs using HOAc-d, binomial distributions were calculated assuming either HOAc-d/CCA/H_2O multiple exchange or HOAc-d/H_2O multiple exchange only. For MCPK, the binomial distributions calculated assuming HOAc/CCA/D_2O multiple exchange or HOAc/D_2O multiple exchange are the same; this is also true for the binomial distributions for HOAc-d/CCA/H_2O multiple exchange and HOAc-d/H_2O multiple exchange.

Using 3/1/1 HOAc/D_2O/CCA as feed resulted in a significant amount of D-incorporation in both acetone and MCPK. In the blank (non-catalytic) experiment there was little evidence of exchange; in the catalytic experiments ∼12% of the HOAc included one D-atom and ∼1% included two, while the CCA had ∼3% single D-atom incorporation, showing that both acids can exchange through the –OH group, and HOAc can exchange at other sites. Neither of the distributions were close to binomial.

The distributions for acetone and MCPK are shown in Figs. 3 and 4. The acetone distribution resembles a binomial distribution with HOAc/D_2O/CCA multiple exchange, suggesting that complete D-scrambling is occurring, while the MCPK distribution is between that of a binomial distribution assuming single acetate exchange and the one assuming multiple exchange. Therefore, if the reaction takes place by way of a ketene or acyl carbenium ion, the intermediate is likely formed from HOAc. CCA does not typically exchange; otherwise there would be far more two D-atom isotopomer in MCPK (Fig. 4). It is seen that almost all of the MCPK that is deuterated has only one D-atom. This is more consistent with the ketene mechanism (Scheme 1), which postulates that a single exchange must take place in order to make a ketone, normally leading to incorporation of one D-atom if enough deuterium is present on the surface.

The next set of experiments were designed to complement the first set, using as feed 3/1/1 HOAc-d/H_2O/CCA. In the blank (non-catalytic) runs there was again negligible exchange; in catalytic runs ∼95% of the HOAc still included three D-atoms, while ∼5% included two. The distribution for CCA shows ∼3% incorporation of D-atoms.

The results for acetone and MCPK are shown in Figs. 5 and 6. For HOAc-d, there are several possible outcomes for the product distributions. One would be no D-scrambling and no exchange with the surface. This would lead to the products CD_3COOCD_3 and $CD_3COOC_3H_5$. Another possibility would be to have no D-scrambling but a single exchange with the surface. This would lead to the same products as

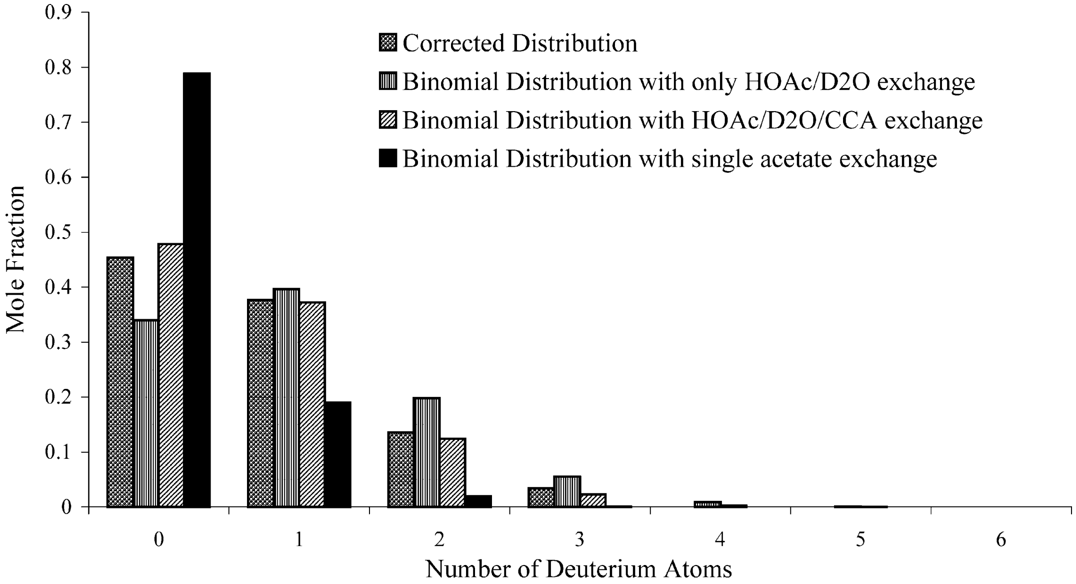


Fig. 3. 3/1/1 HOAc/D_2O/CCA feed, 390 °C, deuterium distribution in acetone.

above, as well as CD_2HCOCD_3 and $CD_2HCOC_3H_5$. For a surface ketene mechanism, assuming statistical exchange in the acetate group only, and the surface ketene reacting with the cyclopropylcarboxylate, the ratios CD_2HCOCD_3/CD_3COCD_3 and $CD_2HCOC_3H_5/CD_3COC_3H_5$ would be ~5/3, considering the 3/1/1 molar feed ratio of HOAc-d/H_2O/CCA and the fact that (according to this mechanism) the

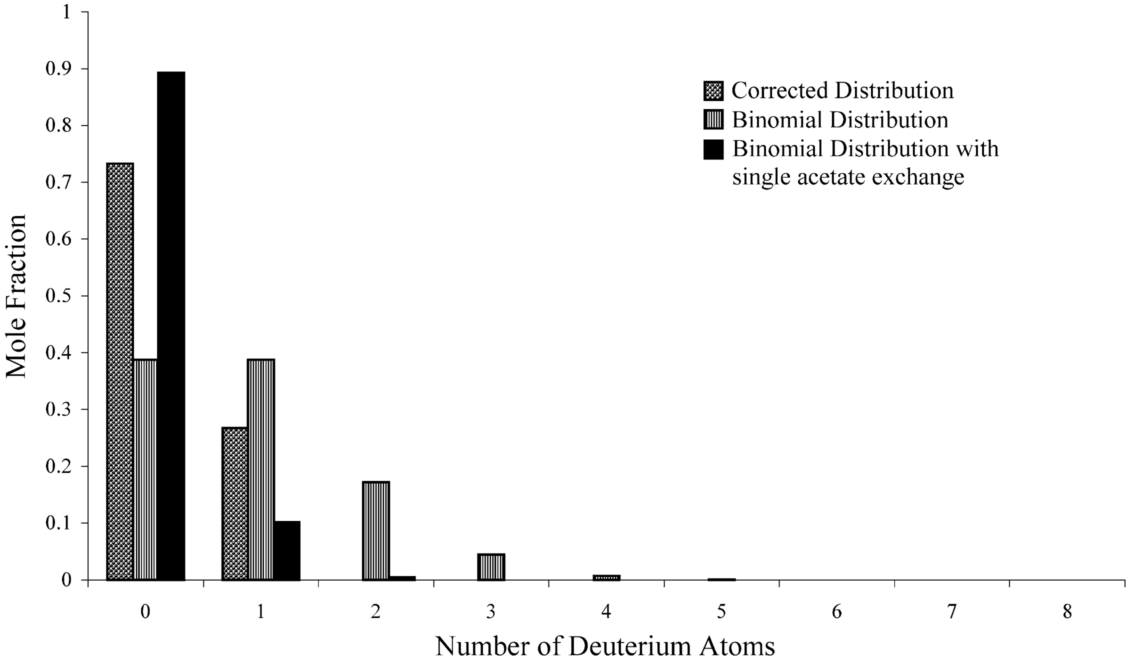


Fig. 4. 3/1/1 HOAc/D_2O/CCA feed, 390 °C, deuterium distribution in MCPK.

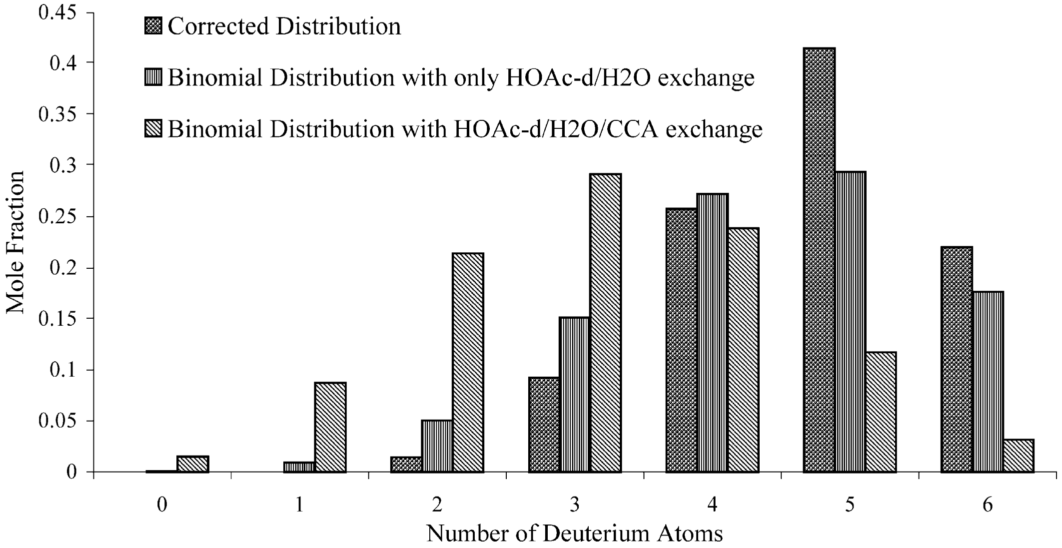


Fig. 5. 3/1/1 HOAc-d/H_2O/CCA feed, 390 °C, deuterium distribution in acetone.

atom pool on the surface would consist of one H from H_2O, one H from CCA, one H from HOAc-d, and one D from HOAc-d. For complete D-scrambling and multiple exchanges the distributions would be binomial. From Fig. 5 it is seen that, for acetone, while there is still a preference for five D-atom incorporation, the distribution is approaching the binomial distribution for HOAc-d/H_2O exchange. The 5-D/6-D ratio for this distribution is still near 5/3 (actually, 1.9). For MCPK (Fig. 6), the incorporation of two D-atoms is clearly preferred. The 2-D/3-D ratio for the experimental results is 1.2, which is less than that of the statistical ratio for single exchange, but far greater than for a binomial distribution (0.52). It might be expected that the 2-D/3-D (MCPK) and 5-D/6-D (acetone) ratios would be similar, however, HOAc molecules, as shown

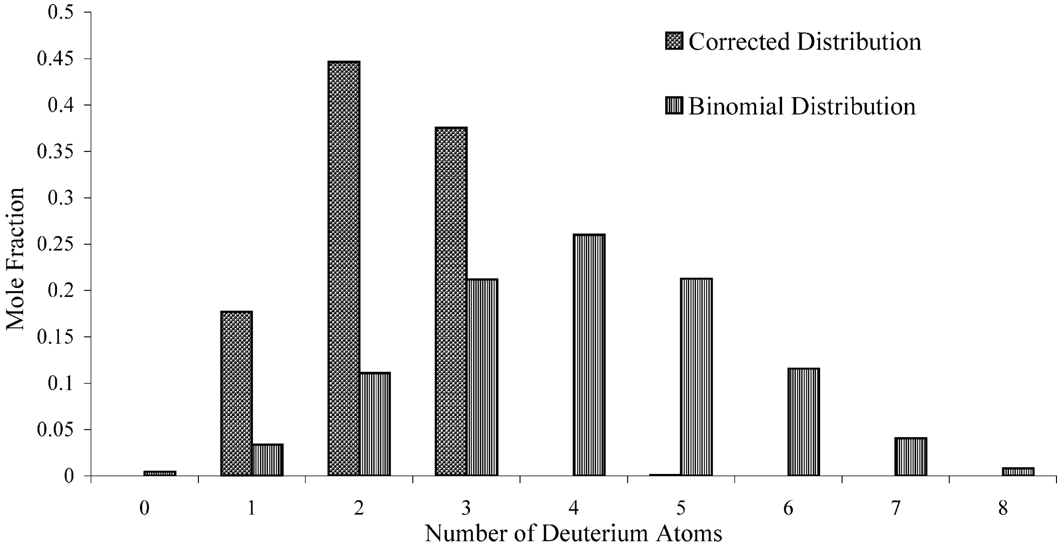


Fig. 6. 3/1/1 HOAc-d/H_2O/CCA feed, 390 °C, deuterium distribution in MCPK.

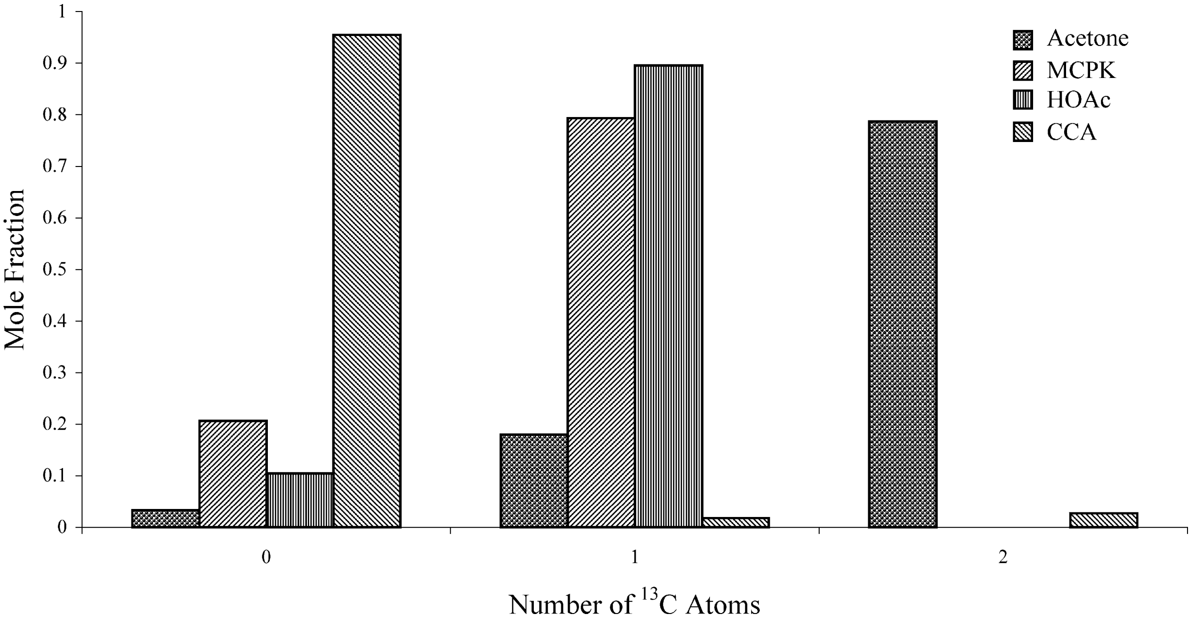


Fig. 7. 4/1 HOAc-^{13}C/CCA feed, 390 °C, ^{13}C distribution in products.

earlier, exchange more rapidly than CCA, and acetone more rapidly than MCPK. This leads to a higher probability for acetone incorporating five D-atoms than for MCPK incorporating two.

Experiments were also conducted using HOAc-^{13}C ($^{13}CH_3COOH$), to determine if there was any general fragmentation of both reactants, preceding recombination. This determination is made by examining how closely the product ^{13}C distributions compare to theoretical distributions assuming no fragmentation. For no fragmentation, acetone would have two ^{13}C, MCPK one, HOAc one, and CCA zero. The results (Fig. 7) generally follow the expected trends. Some source of carbon (^{12}C) atom caused a slight ^{12}C enrichment of the acetone product. If this source is the cyclopropyl ring, this would also explain MCPK's slight enrichment in ^{12}C, assuming the cyclopropyl intermediate could also re-form CCA. But there is only a small amount of fragmentation of surface carbon species. Finally, experiments were conducted using ^{13}C-HOAc ($CH_3{}^{13}COOH$), to determine the source of the carbonyl in the ketones. A feed of 1/3 labeled and 2/3 unlabeled acetic acid gave acetone with 31% ^{13}C and MCPK with $<1\%$. Therefore better than 90% of the carbonyls in MCPK come from CCA.

These results (Figs. 3–7 and the ^{13}C-HOAc experiments) make sense only if the reaction takes place much as Pestman et al. [2] propose. A carboxylate mechanism (Scheme 2, see [1]) does not incorporate a strong preference for single D-exchange in the adsorbed methyl group of HOAc, along with no exchange in the adsorbed cyclopropyl group. There is also nothing in a carboxylate mechanism to suggest an overwhelming preference for the carbonyl of HOAc in the MCPK. Acetone with less than five D-atoms (as in Fig. 5) can be explained by the adsorbed acetate exchanging multiple times prior to a coupling reaction. Of special interest is the absence of MCPK with four D-atoms, which would result if the surface ketene were formed from CCA (Scheme 1b). Finally, pulse experiments with a 3/1 HOAc/DAc feed at 390 °C gave almost 100% MNK, and no dinonylketone. These results further confirm that the source of the reactive surface ketene intermediate is from (mostly) acetic acid.

We then examined whether these mechanistic conclusions remained valid when the less reactive component could not easily form a carboxylate. Therefore we conducted experiments using labeled HOAc/H_2O/CCAld feeds. With 4/1/1 HOAc/D_2O/CCAld, there was significant D-incorporation into acetone

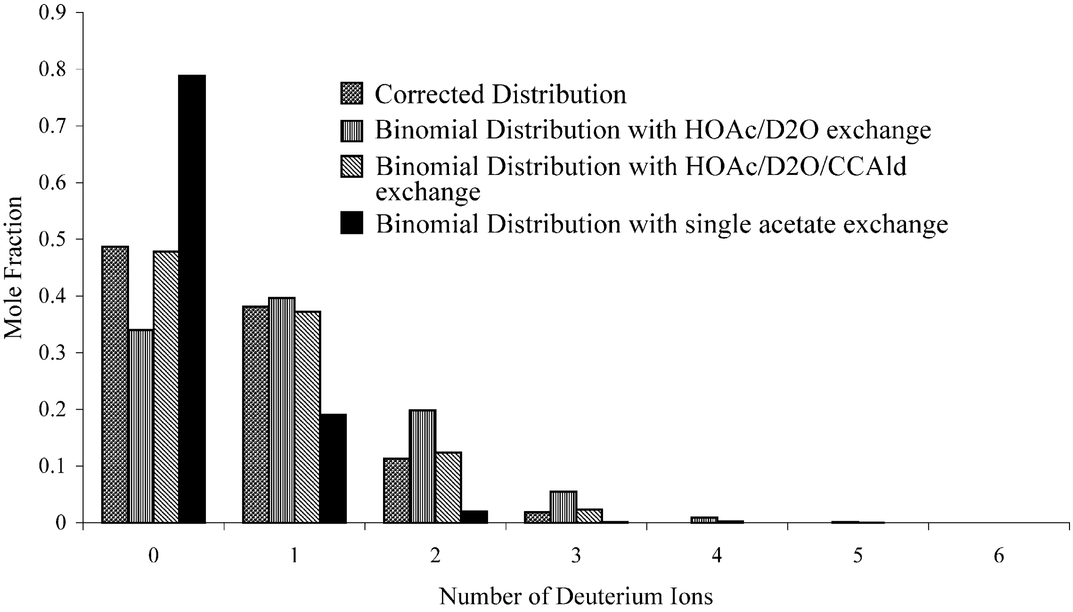


Fig. 8. 4/1/1 HOAc/D_2O/CCAld feed, 440 °C, deuterium distribution in acetone.

and MCPK. The blank (non-catalytic) runs showed no D-exchange for CCAld, while for HOAc there was 1.3% single D-atom isotopomer and 0.3% with two D-atoms. In the catalytic runs ∼10% of the HOAc included one D-atom, and ∼0.5% included two, while ∼2% of the CCAld incorporated one D-atom. Again, this suggests relatively easy exchange of HOAc with the surface, but not complete scrambling.

The catalytic results for acetone and MCPK are shown in Figs. 8 and 9, and are very similar to the results obtained with acid/acid feeds (Figs. 3 and 4). For acetone, this was expected as it should be formed similarly in both cases. But perhaps surprisingly, the results for MCPK are also very similar to the results for acid/acid runs (Fig. 4). Note especially the small amount of two D-atom isotopomer. This indicates that the formation of MCPK is taking place in a manner similar to the reaction of HOAc/CCA. This is possible if surface oxygen atoms are used to convert CCAld to CCA, which then reacts as usual to form MCPK, or if the surface ketene intermediate formed from HOAc can attack adsorbed CCAld directly. In the former case, water is used to replenish the surface oxygen atoms. This conclusion is consistent with the large decrease in the rate to MCPK observed when H_2O was replaced with D_2O, with the positive effect of water addition on the CCAld/HOAc reaction to MCPK, and with the negligible effect of water addition on the CCA/HOAc reaction to MCPK.

For a 4/1/1 HOAc-d/H_2O/CCAld feed, the blank (non-catalytic) run gave 0.9% CCAld with one D-atom. The catalytic runs resulted in ∼97% of the HOAc having three D-atoms and ∼10% of the CCAld one D-atom. This shows that now both HOAc and CCAld are exchanging with the surface. The results for acetone and MCPK distributions, for this feed, are shown in Figs. 10 and 11; for acetone there is again a preference for five D-atoms, and for MCPK a preference for two D-atoms. In the absence of D-scrambling, and with acetate exchange only, this feed would give 5-D/6-D (in acetone) and 2-D/3-D (in MCPK) product ratios of 1.5. The binomial distributions for acetone (5-D/6-D) predict ratios of 1.5 and 3 for HOAc-d/H_2O exchange and HOAc-d/H_2O/CCAld exchange, respectively, while for MCPK (2-D/3-D) the binomial ratio is 0.43. The experimental results for this feed are 0.94 for the 5-D/6-D ratio in acetone and 0.61 for the 2-D/3-D ratio in MCPK. While both experimental ratios are less than predicted assuming exchange at the acetate group only, the absolute amounts for five

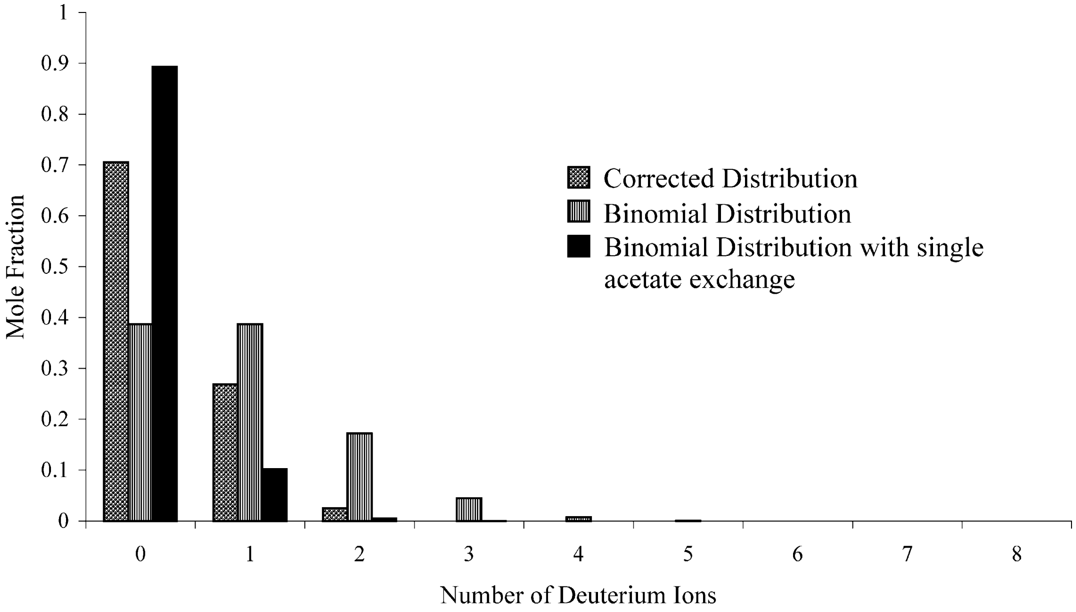


Fig. 9. 4/1/1 HOAc/D_2O/CCAld feed, 440 °C, deuterium distribution in MCPK.

D-atoms in acetone or for two D-atoms in MCPK are still much larger than predicted assuming scrambling.

The presence of four D-atom isotopomer in MCPK (Fig. 11) indicates that some CCAld, instead of HOAc, adsorbed as the surface ketene, which is consistent with the fact that some CCAld reacted even when no H_2O was present. This pathway (Scheme 1b) would also add to the abundance of MCPK with three

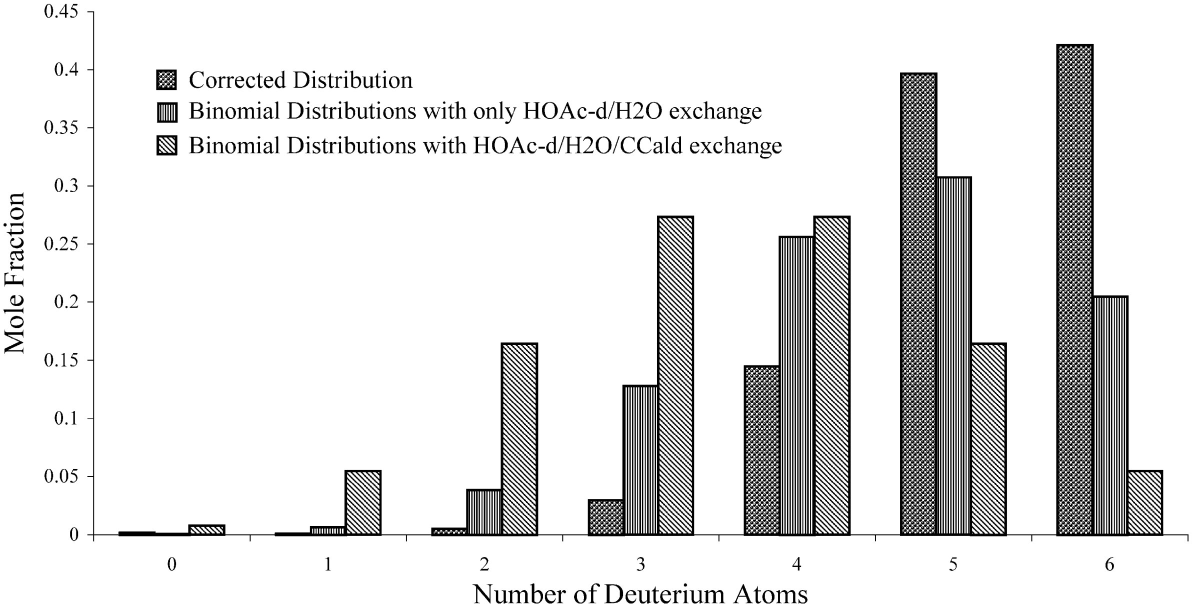


Fig. 10. 4/1/1 HOAc-d/H_2O/CCAld feed, 440 °C, deuterium distribution in acetone.

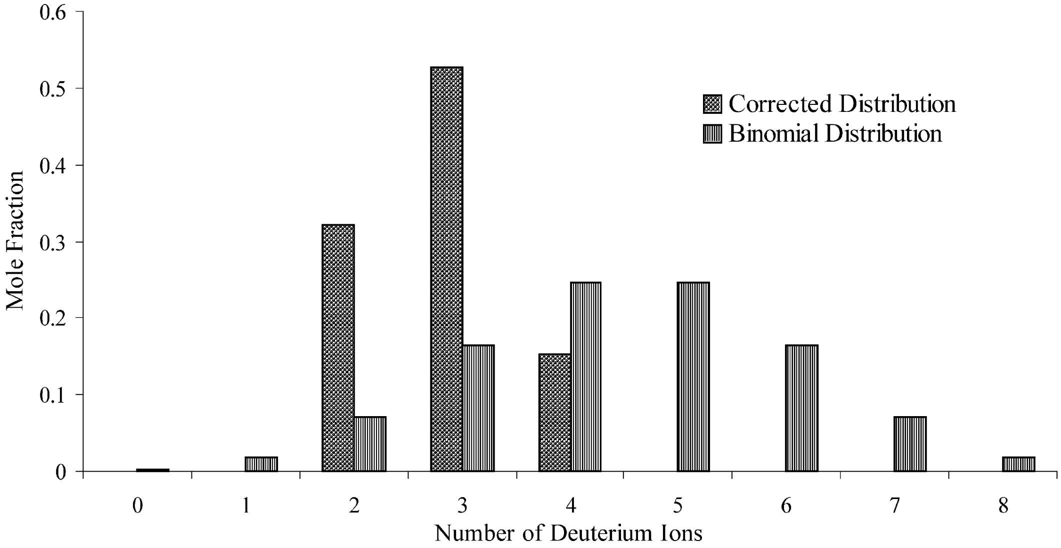


Fig. 11. 4/1/1 HOAc-d/H_2O/CCAld feed, 440 °C, deuterium distribution in MCPK.

D-atoms. Taken together, the results suggest that when using the aldehyde, the carbonyl group could arise from either HOAc or CCAld. But although the 5-D/6-D and 2-D/3-D ratios are not as large as might be expected, there is still a clear preference to form acetone with five D-atoms and MCPK with two D-atoms, in agreement with Scheme 1a.

As with the acid/acid experiments, acetic [^{13}C] acid was used with CCAld to determine if any general breakdown/reversibility of surface carbons occurs. If not, there should be two ^{13}C atoms in acetone, one in MCPK, one in HOAc, and zero in CCAld. The results showed that each component generally has the average number of ^{13}C atoms that would be expected. However, there is again an indication of some decomposition of the cyclopropane ring, resulting in slight ^{12}C enrichment in MCPK. The MCPK and acetone distributions also deviate from the expected values by including isotopomers with two and three ^{13}C atoms, respectively. This would suggest that a small amount of the carbonyl in HOAc is decomposing and then reforming with an isotopically labeled carbon atom.

4. Conclusions

The continuous reaction experiments showed that acid/acid condensations to non-symmetric ketones can be catalyzed effectively at high conversions by CeO_2-based catalysts. The addition of water to acid/acid feeds had little affect on the activity of the catalyst, while the addition of small amounts of alkali to the catalyst enhanced ketone selectivity. These catalysts could be regenerated using air at >500 °C. The optimum temperature for the production of MCPK was ∼430 °C, while for MNK it was 400–420 °C. There were no diffusional limitations on the reaction over the size range used. Catalyst performance improved with time on stream and number of regeneration cycles. Only a slight loss of CeO_2 and surface area occurred over extended periods of operation.

The pulse reaction experiments using HOAc/CCA and HOAc/DAc feeds gave close to 100% selectivities. Most products formed at higher conversions and feed partial pressures result from secondary reactions between the primary products and the feed. The approximate reaction orders for HOAc/CCA were −0.5 for HOAc and 0.3 for CCA. The experiments using deuterated feeds showed that both deuterated acetic acid and D_2O negatively affect the reaction rate. This suggests the breaking of a C–H bond in HOAc is a rate limiting step. Acetone and MCPK preferentially form five D-atom and two D-atom isotopomers, respectively, suggesting that the non-carboxylate moiety in the product originates from HOAc, which typically exchanges once with the surface. These results, coupled with isotope distributions obtained using ^{13}C-labeled acetic acid, suggest that acid condensation on rare earth oxides occurs by way of a surface ketene intermediate, which couples with a carboxylate, eliminating CO_2 in the process.

The pulse experiments using HOAc/CCAld feeds show that reaction to MCPK proceeds ~3 times slower than the HOAc/CCA reaction. No products were observed that would indicate the formation of ketone by way of an aldol condensation. The reaction orders, isotope effects, product distributions and isotope distributions suggest that water can be used to replenish the surface oxygen used to generate CCA from CCAld. However, water is not absolutely necessary for ketone production, because some CCAld can itself decompose to a surface ketene intermediate. Adding O_2 increases the oxidation of CCAld to CCA, but has little effect on ketone formation because the ketonization reaction competes with total oxidation.

Experiments performed using an aldehyde/aldehyde feed proceeded to the ketone at rates only ~1/5 those of HOAc/CCAld. Addition of water increased the rates slightly. This suggests the necessity of at least one adsorbed carboxylate in the reaction mechanism.

Acknowledgements

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