Organic Process Research & Development **2002**, *6*, 611–617

Kinetics of Citraconic Anhydride Formation via Condensation of Formaldehyde and Succinates

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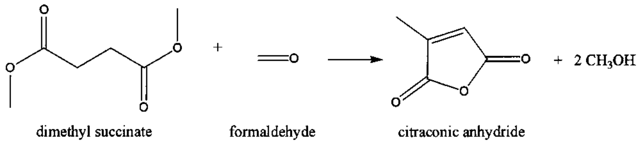
Abstract:

Formation of citraconic anhydride via condensation of succinic acid and its derivatives with formaldehyde is carried out over γ-alumina catalyst in a continuous fixed-bed reactor. Dimethyl succinate and Formalin (37 wt % formaldehyde, 10 wt % methanol in water) are the preferred feed materials for the reaction; catalyst activity is sustained with Formalin relative to that with other formaldehyde sources such as trioxane or Formcel, because the water in Formalin inhibits coke formation. With this feed combination, a total citraconate yield of 31% of theoretical with 72% selectivity is achieved at a weight hour space velocity of 0.9 kg of succinate/kg of catalyst/h, a succinate to formaldehyde molar feed ratio of 1:2, and a temperature of 380 °C. The reaction is free from mass transfer limitations at these conditions. A kinetic model is presented that describes product distributions and reactant conversion as a function of space velocity and temperature. The reaction system is part of an overall process to produce itaconic acid from renewable resource-based succinic acid.

I. Introduction

Succinic acid (1,4-butanedioic acid) and its alkyl esters are reactive species that find applications in industrial and consumer products and as intermediates for specialty and fine chemicals production.[1,2] Recent advances in fermentation technologies for succinic acid production,[3−6] arising both from genetic modification of the microorganism and improved separations, have led to yields of succinic acid as high as 1.1 kg of succinic acid/kg of glucose (with CO_2 incorporation) and have nearly eliminated acetic acid as a coproduct.[6] A significant decrease in the price of the acid as a raw material is thus expected as the manufacturing technology matures, making it attractive as a feedstock for biomass-based chemical production.

Scheme 1



The Stobbe condensation,[7] discovered in 1894, offers a potentially efficient route for the production of substituted succinates via condensation of esters of succinic acid with aldehydes and ketones. The reaction is essentially unique to succinic acid esters and generally takes place in alcohol solution in the presence of a strong base (alkoxide or sodium hydride) to give the half-ester as a product.[8]

The classic Stobbe condensation does not occur to any practical extent when formaldehyde is used as the aldehyde. However, the vapor-phase catalytic (heterogeneous) condensation of succinic acid, succinic anhydride, or alkyl succinate esters with formaldehyde does take place to give citraconic anhydride (CAN), an isomer of itaconic anhydride (Scheme 1). Several patents describe catalytic routes to CAN formation from succinates,[9−12] with transient yields as high as 70% of theoretical claimed.[9] The motivation for CAN formation is to produce itaconic acid via hydrolysis of CAN to citraconic acid and isomerization to itaconic acid. Itaconic acid is a carboxylated analogue of the important monomer methacrylic acid and as such is able to take part in addition polymerization, giving polymers with many free carboxylic acid groups that confer advantageous wettability and ion-exchange properties.[13]

Itaconic acid is currently produced commercially (8×10^6 kg/yr) by the fermentation of glucose using *Aspergillus terreus*.[13] This fungal fermentation is carried out in batch processes requiring dilute solutions (∼10 wt % glucose) and extended processing times (6−10 days per batch). Itaconic acid yields are on the order of 50−60% of theoretical; this process results in an itaconic acid selling price of ∼$2/lb

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10.1021/op020210r CCC: $22.00

and is not expected to facilitate expanded production in the foreseeable future.

In an earlier publication we identified several intermediate surface area γ-aluminas as attractive catalysts for the formation of CAN from succinates and formaldehyde.[14] In this contribution, process conditions for the reaction are evaluated. First, several sources of succinates and formaldehyde in different combinations are investigated as potential feedstocks for CAN production. Then, reactor temperature, pressure, weight hourly space velocity (WHSV), feed composition, and catalyst particle size are evaluated to optimize the yield of CAN and minimize catalyst deactivation with time-on-stream. On the basis of the results of these parametric studies, a kinetic model is developed to predict reactant conversions and product yields versus WHSV and temperature.

II. Experimental Section

Feed and Catalyst Materials. Two forms of succinate were used as feedstocks in these investigations: dimethyl succinate (DMS) (bp 203 °C; Aldrich Chemical Co, 98%) and succinic anhydride (SAN) (mp 118 °C, bp 269 °C; Aldrich, 98%). Formaldehyde was used in one of three forms: trioxane (TO) (mp 64 °C, bp 115 °C; Aldrich, 98%), the trimeric form of formaldehyde; Formalin (JT Baker), a commercially available source containing 37 wt % formaldehyde and 10 wt % methanol in aqueous solution, and Formcel (Celanese), another commercial source composed of 55 wt % formaldehyde, 35 wt % methanol, and 10 wt % water.

The catalyst used in this study was a γ-alumina (Norpro SA3177). This material has a N_2 BET surface area of 100 m^2/g, acidic site density of 0.25 mmol/g, and basic site density of 0.05 mmol/g as determined by temperature-programmed desorption of ammonia and carbon dioxide, respectively, and a Hammett acid strength constant $H_o = -0.2$ to $+1.1$. The alumina was ground and sieved to 30−60 mesh using standard sieve trays and calcined in air for 6 h at 500 °C before loading into the reactor.

Apparatus and Experimental Conditions. The fixed-bed reactor used in this study was described in detail in a previous publication.[14] Briefly, the reactor consists of a 10-mL 316 stainless steel cone closure pressure vessel (Autoclave Engineers) surrounded by a clamshell heater. Reactor temperature was controlled by a programmable temperature controller with the control thermocouple reading the temperature of the external reactor surface. The reactor was equipped with a rupture disk to prevent catastrophic rupture in case of plugging of sample lines (which can happen in the presence of succinic anhydride and paraformaldehyde, both solids at room temperature). Typical catalyst charge to the reactor was 5.0 ± 0.1 g.

Feed materials were introduced into the reactor, using HPLC pumps (Bio-Rad, Inc.) or a syringe pump (PDC, Inc.). The choice of feed species dictated the configuration of the feed system. For trioxane (TO) and dimethyl succinate (DMS) as feeds, a single pump was used with the two reactants mixed in a single 100-mL buret serving as a feed reservoir. For TO:DMS molar ratios above 1:1, the feed buret, pump, and feed line were heated to 70 °C using heating tapes and a variable autotransformer to ensure that a single liquid phase was present. For DMS and Formalin as feeds, two HPLC pumps were used to deliver the feeds to the reactor. The use of succinic anhydride (SAN) and TO as feeds required the use of a syringe pump and steam-traced feed lines maintained at 120 °C, because both materials are solids at room temperature. For all feeds, the 60 cm of feed tubing just before the reactor inlet was heated to 250 °C using electrical heating tape. To aid in vaporization of feed and to sweep the vaporized feed into the reactor, helium (AGA, 99.99%) was introduced to the reactor through a separate1/8 in. tube, heat-traced to 250 °C.

Reactor effluent passed through heat-traced tubing and was directed via a heated six-port valve (Valco, Inc.) to one of two 25-mL stainless steel product collection traps. Traps were kept in ice water if the feed was DMS and Formalin, to collect methanol and formaldehyde, and in warm water (40 °C) for DMS/TO feeds to prevent solidification of unreacted TO.

High-performance liquid chromatography (HPLC) and gas chromatography (GC) were used to analyze reaction products. For liquid chromatography, 20 wt % acetonitrile in 5 mM H_2SO_4 aqueous solution was used as the mobile phase at a flow rate of 0.4 mL/min. Raw product samples were diluted 20-fold with mobile phase and injected onto a 15 cm × 0.5 cm i.d. BioRad HPX-87H column at 40 °C; products concentrations were determined using a refractive index detector with oxalic acid as the internal standard. Gas chromatography was performed on a Varian 3300 using a large-bore capillary column (SPB1, Supelco, 0.53 mm i.d. × 30 m) with flame ionization detector (FID) and helium as a carrier gas. Methyl lactate was used as an internal standard. Outlet gases from the reactor were analyzed directly using CO and CO_2 IR meters (Riken, Inc.).

Product Hydrolysis. The reactor effluent contains significant quantities of dimethyl and monomethyl esters of citraconic and succinic acids as well as the free acid and anhydride forms. In HPLC analyses, the coelution of dimethyl and monomethyl citraconate esters with their analogue succinates made accurate conversion and yield determinations impossible. To overcome this obstacle, the product mixture was hydrolyzed by adding a small amount of sulfuric acid to the product solution and refluxing for 2−3 h to recover all succinate and citraconate species as free acids. Because hydrolysis was time-consuming, only selected samples were hydrolyzed; unless otherwise stated, yields and conversions are reported for unhydrolyzed products. Typically, about 20% of total citraconates formed were present as monomethyl or dimethyl esters; therefore, reported yields for unhydrolyzed mixtures are typically lower than the actual values by this amount.

Product Yield and Selectivity Calculations. Fractional conversion is reported either in terms of dimethyl succinate or succinic anhydride converted to any product including

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[14] Shekhawat, D.; Kirthivasan, N.; Jackson, J. E.; Miller, D. J. *Appl. Catal.*, A **2001**, *223*, 261−273.

Table 1. **Reaction conditions**

parameter	range	base-case value
reactor temperature (°C)	350−410	380
reactor pressure (MPa)	0.5−3.5	0.5
feed zone preheat temperature (°C)	200−250	250
Formaldehyde to succinate molar ratio	0.5−4	2
liquid feed flow rate (mL/min)	0.10−0.45	0.15
helium flow rate (mL(STP)/min)	27−82	27
WHSV (kg of succinate/kg of catalyst/h)	0.45−2.70	0.90

other succinates, or as the fraction of all succinate species converted to nonsuccinate products. Product yield is defined as the percentage of theoretical based on dimethyl succinate or succinic anhydride fed to the reactor; product selectivity is calculated as product yield divided by the conversion of all succinate species to nonsuccinate products. These definitions are appropriate because succinates in any form can react or be recovered, reconverted to feed material, and recycled back to the process. Carbon dioxide yields are based on succinate fed but are divided by two for DMS feed to account for the fact that each mole of DMS can give 2 mol of CO_2 upon cracking. A molar balance on total succinate (C_4) carbon was done for each sample to assess reliability of the experiments; fractional recovery of the succinate carbon fed is reported as the measure of material balance closure for the experiment.

III. Results and Discussion

Most experiments were carried out for 5 h at steady state, with samples taken in 30-min intervals. A summary of reaction conditions is given in Table 1; the “base-case” conditions were used as a starting point in most evaluations. In our earlier publication,[14] we showed that catalyst activity declines with time-on-stream for this reaction system because of coking. Thus, reactant conversion and product yields are reported as a function of reaction time or as the maximum observed in the experiment. We have shown[14] that catalyst activity can be entirely recovered by burning in air at 500 °C, so decline in catalyst activity with time-on-stream is not a barrier to development.

Evaluation of Feedstocks. Succinate conversion and product yields for different succinate/formaldehyde feed combinations over SA3177 alumina at base-case conditions are summarized in Table 2. All reactions were conducted with a succinate:formaldehyde molar ratio of 1:2; succinate mole fraction for each feed is given in Table 2. The conversion and yield reported are at the time of maximum citraconic anhydride yield, which occurs between 1 and 2 h after steady state is achieved in the reactor.

All combinations of succinate feeds and formaldehyde gave significant yields of citraconic anhydride at base-case conditions, suggesting that the C_1 and C_4 carbons of succinate do not participate in the condensation. The difference in performance between the various feed combinations resides primarily in the extent of CO_2 formation (cracking) and coke deposition that results in catalyst deactivation.

With succinic anhydride (SAN) and trioxane, which were fed in molten form with no solvent added, extensive coking occurred, and deactivation was very rapid. Citraconic acid yield reached a maximum of 44% after 1−1.5 h, and then rapidly declined to near zero by 5 h of reaction. Large quantities of carbon dioxide were produced. We attribute this behavior in part to the high boiling point of SAN (269 °C) and its high concentration in the feed, which made complete vaporization of the feed difficult. Reactor operation was also difficult with this feed combination, as SAN condensed and plugged the reactor at any location that was not adequately heat traced.

With DMS and trioxane (TO), the first hour of reaction was dominated by CO_2 formation. Citraconic acid yield reached a maximum of 35% after 2 h and then fell off to approximately 22% after 5 h reaction time.[14] Similar behavior was observed with the DMS/Formcel feed combination; initial yields and DMS conversion were higher than with DMS/TO feed but declined more rapidly.

The use of Formalin as the formaldehyde source with DMS gave strikingly different behavior: citraconate yields and succinate conversion reached constant values after 30 min of reaction and then continued essentially unchanged over 5 h of reaction. The yield of CO_2 was low throughout the reaction period as well. Similar results were obtained with succinic anhydride and trioxane dissolved in excess methanol (to form a monomethyl succinate/trioxane feed, MMS/TO in Table 2). Addition of methanol or water as a solvent greatly reduced catalyst coking and led to citraconic

Table 2. **Summary of results from different feedstocks over SA-3177 alumina**

	before hydrolysis							after hydrolysis		
feedstock (feed mol fraction)	conv. succinates	yield of CAN	yield of DMS	yield of MMS	yield of SAN	yield of CO_2	carbon recovery	yield of citraconates	conv succinates	selectivity
DMS + TO (0.22) (0.44)	83	26	−	19	8	18	92	35	48	73
SAN + TO (0.24) (0.48)	76	43	0	7	−	16	90	44	67	70
MMS + TO (0.15) (0.29)	74	23	30	−	9	15	99	26	40	78
DMS + Formalin (0.1) (0.19)	80	26	−	28	8	8	90	31	43	72
DMS + Formcel (0.15) (0.30)	81	30	−	18	8	10	89	34	56	61

anhydride yield that was nearly constant with reaction time out to 5 h. The presence of a solvent appeared to facilitate vaporization and dispersion of the feed materials, thus minimizing the cracking and polymerization reactions that led to coke formation on the alumina surface.

The extent of hydrolysis or esterification of the succinate feedstock used depended greatly on the quantity of methanol or water in the reaction stream. For succinic anhydride/trioxane feed, the extent of esterification was minimal, because there is little methanol present. The only esterification product formed was monomethyl succinate, formed from methanol liberated via the Cannizzaro reaction, which in turn can take place as water is evolved in citraconic anhydride formation. In contrast, with Formalin as a feed significant hydrolysis of DMS to MMS and free succinic acid took place in the reactor. Fortunately, since all forms of succinate are active for reaction, interconversion between diester, monoester, and anhydride forms did not apparently affect overall performance for CAN formation.

The use of DMS/Formalin or MMS/TO is thus preferred for the formation of citraconic anhydride. Both of these feed combinations provide good yield and selectivity to the desired product with relatively little loss of succinate or formaldehyde to cracking. Coke deposition still takes place with these feed materials, but the rate of coke deposition is much slower than with the other feeds, and product yields are nearly unaffected over the 5-h time period of reaction. The only drawback to the use of succinic anhydride in methanol is extensive methanol dehydration to dimethyl ether over the acidic alumina; recovery of the dimethyl ether and hydrolysis back to methanol would require expensive process equipment because of its very low boiling point. This, coupled with the low cost and ready availability of Formalin, makes the DMS/Formalin feed combination the preferred choice for citraconic anhydride formation.

Reaction Conditions. The effects of reaction temperature, pressure, WHSV, feed composition, and catalyst particle size have been investigated for the purpose of identifying optimum conditions for CAN formation.

Temperature. The effect of temperature on CAN yield and DMS conversion is given Figure 1 for DMS/TO feed. Conversion of DMS increases with increasing temperature, but selectivity decreases with temperature. A maximum in the CAN yield is thus observed at 380 °C in the laboratory reactor. At higher temperatures, cracking predominates, resulting in high conversion of succinates and low selectivity to CAN. At lower temperatures, selectivity to CAN is very high, but conversion is low. Similar results were achieved with DMS/Formalin feed (not shown), with selectivity to CAN at 350 °C as high as 87% (versus 70% at 380 °C). The ultimate choice of reactor temperature for a process will depend on economic constraints: operation at low temperature and low space velocity may prove most attractive from an economic standpoint.

Pressure. Most experiments were run at a reactor pressure of 0.5 MPa, but repeated experiments were conducted at 2.7 MPa to check the dependence of yield and selectivity on pressure (DMS/TO feed at otherwise base-case conditions). The conversion of DMS and yield of citraconates were not significantly affected by reactor pressure. This result is somewhat surprising and as yet unexplained, particularly in light of the kinetic model described later.

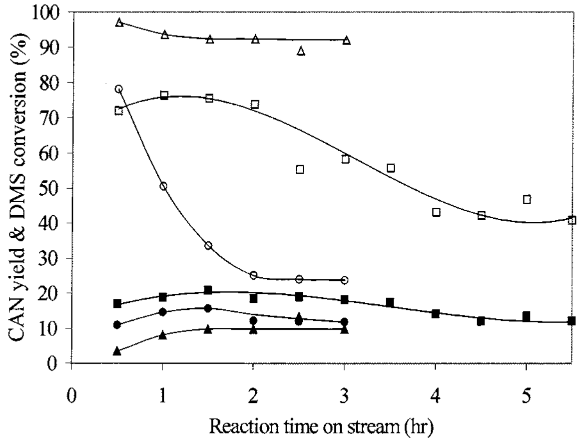

Figure 1. **Effect of temperature on the yield of CAN [350 °C (●); 380 °C (■); 410 °C (▲)] and conversion of DMS [350 °C (○); 380 °C (□); 410 °C (△)] (Feed: DMS + TO, base-case conditions except temperature, unhydrolyzed product).**

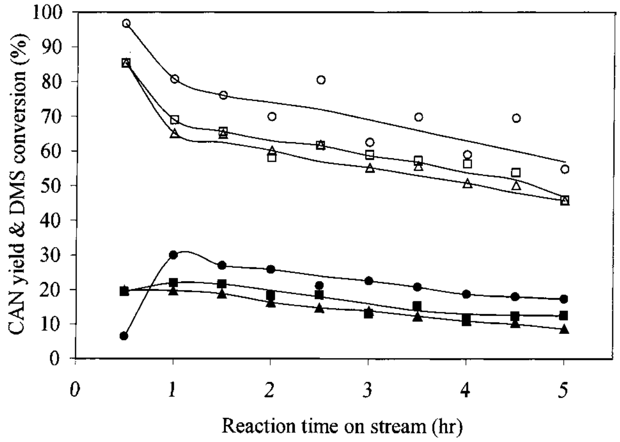

Figure 2. **Effect of feed flow rate on the yield of CAN [WHSV = 0.9 h^{-1} (●); WHSV = 1.8 h^{-1} (■); WHSV = 2.7 h^{-1} (▲)] and conversion of DMS [WHSV = 0.9 h^{-1} (○); WHSV = 1.8 h^{-1} (□); WHSV = 2.7 h^{-1} (△)] (Feed: DMS + Formcel, base-case conditions except WHSV, unhydrolyzed product).**

Space Velocity. The condensation reaction of DMS and Formcel (at base-case conditions) was carried out at different liquid feed flow rates (9 mL/h to 27 mL/h) over a 5-g catalyst bed to give WHSVs ranging from 0.90 to 2.70 kg of DMS/kg of catalyst/h. The flow rate of helium was changed in the same proportion as liquid feed flow rate to keep the molar composition of the feed constant. The effect of WHSV (kg of succinate/kg of catalyst/h) on CAN yield and DMS conversion from Formcel and DMS feed is reported in Figure 2.

The conversion of DMS at the lowest liquid feed rate (WHSV = 0.9/h) was always ~10% higher than that at WHSV = 1.8/h. DMS conversion declines further, but by a lesser amount, upon increasing the liquid feed flow to give WHSV = 2.7/h. Yields of CAN and CO_2 at different liquid feed flow rates followed the DMS conversion trends. Yields of MMS and SAN were not affected by changing space

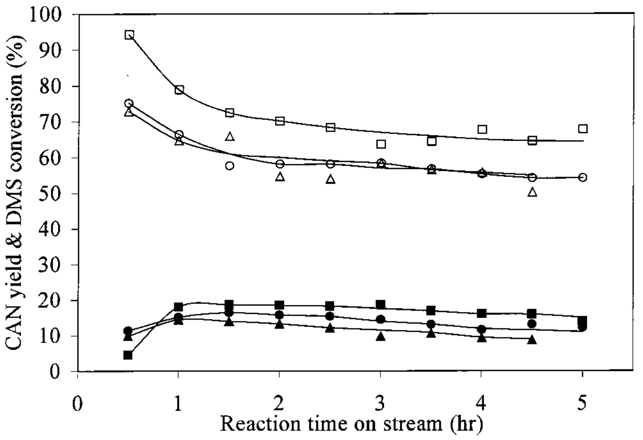

Figure 3. **Effect of WHSV (kg of succinate/kg of catalyst/h) on the yield of CAN [shorter reactor bed (WHSV = 0.90 h^{-1}) (●); longer reactor bed (WHSV = 0.45 h^{-1}) (■); longer reactor bed (WHSV = 0.90 h^{-1}) (▲)] and conversion of DMS [shorter reactor bed (WHSV = 0.90 h^{-1}) (○); longer reactor bed (WHSV = 0.45 h^{-1}) (□); longer reactor bed (WHSV = 0.90 h^{-1}) (△)] (Feed: DMS + Formlin, base-case conditions except WHSV, unhydrolyzed product).**

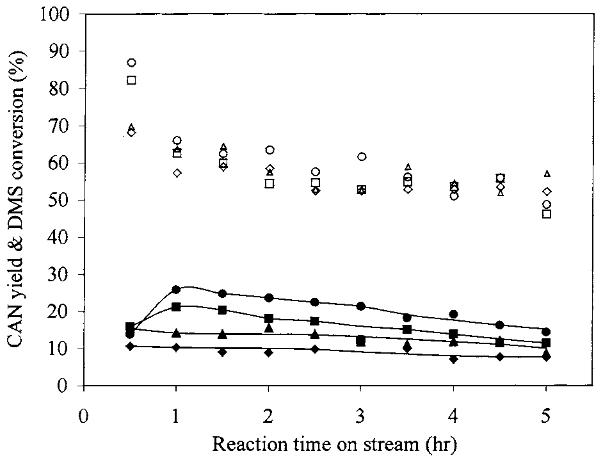

Figure 4. **Effect of feed molar ratio (formaldehyde to succinate) on the yield of CAN [4:1 (●); 2:1 (■); 1:1 (▲); 0.5:1 (◆)] and conversion of DMS [4:1 (○); 2:1 (□); 1:1 (△); 0.5:1 (◇)] (Feed: DMS + Formcel, unhydrolyzed product, base-case conditions except WHSV = 2.1 kg of succinate/kg of catalyst/h).**

velocity, suggesting that the esterification/hydrolysis reactions reach equilibrium in the reactor. The selectivity to CAN was not affected by changing WHSV.

Additional evaluation of the effect of space velocity on product yields were conducted with DMS and Formalin, using a catalyst bed twice the usual size (10 g) in several experiments. Results are given in Figure 3; increasing bed length at the same liquid rate increases yield of CAN and CO_2 and conversion of DMS. Maintaining the same WHSV in the longer bed by doubling flow rate results in identical conversion of DMS, which is expected if the reaction is behaving predictably. However, the yield of CAN decreased slightly with the larger bed (▲ vs ● in Figure 3). Whether this difference lies within the range of experimental uncertainty or the reactor is exhibiting some nonideal behavior cannot be ascertained at this time.

Feed Molar Ratio. Several different molar ratios of formaldehyde to DMS (4:1, 2:1, 1:1, and 0.5:1) were evaluated using DMS/Formcel feed. Reaction conditions were same as the base case except that a liquid feed flow rate of 0.30 mL/min and a gas flow rate of 55 mL(STP)/min was used. The inlet mole fraction of DMS, the liquid flow rate, and hence WHSV (kg of DMS/kg of catalyst/h), were kept the same for all feed molar ratios; this was done by replacing formaldehyde with a mixture of methanol and water (in the same proportion as in Formcel) as formaldehyde concentration was reduced. The effect of feed molar ratio on the yield of CAN and conversion of DMS is given in Figure 4.

Yield of CAN increased as the ratio of formaldehyde to DMS in the feed increased. A maximum CAN yield of 26% at 66% DMS conversion was observed at a 4:1 molar ratio; in contrast, for 0.5:1 only an 11% CAN yield was obtained. Surprisingly, the conversion of DMS was essentially unaffected by the quantity of formaldehyde present. Thus, selectivity of CAN increased with increasing feed molar ratio of formaldehyde to DMS. Yield of CO_2 also increased slightly with increasing feed molar ratio. As with temperature, the final choice of feed molar ratio resides in process economics; the higher yields achieved with greater excess of formaldehyde will be offset by increased costs of separating and recycling unreacted formaldehyde.

It is noteworthy that the extent of coking decreased at lower formaldehyde levels. This suggests that part of coke formation during reaction comes from formaldehyde, or that added water and methanol are responsible for reduced coking by aiding in vaporization of organic species or gasifying the coke (with steam) as it forms.

Particle Size. The typical catalyst particle size of 30−60 mesh (d_p = 0.3−0.5 mm) was reduced to 60−100 mesh (d_p = 0.16−0.3 mm) to ascertain the effects of mass transport on the reaction. Identical results were observed with both particle sizes, suggesting that the condensation reaction is not mass-transfer limited.

Evaluation of the observable modulus $\eta\phi^2 = R_{obs}L^2/C_oD_e$ further verified the absence of mass-transfer limitations. In the modulus, C_o is the inlet DMS concentration, $D_e = \epsilon^2 D_{DMS}$ = 9.1 × 10^{-6} cm^2/s is the effective diffusivity calculated using $\epsilon = 0.4$ and the Chapman−Enskog equation for D_{DMS}, $L = d_p/6$, and R_{obs} is the average consumption rate of DMS over the reactor volume. The largest value of $\eta\phi^2$ observed in any reaction was less than 0.1; thus, according to the Weisz−Prater criterion the reaction is not mass-transfer limited.

CO_2 as a Carrier Gas. Reaction of DMS and Formalin over SA-3177 was carried out with CO_2 as a carrier gas instead of helium. There were two reasons behind the use of CO_2 as a carrier for the formation of CAN. First, it was thought that coke deposited on the catalyst could be removed via in situ oxidation by CO_2. Second, it was thought that CO_2 might neutralize the basic sites on the alumina surface, thus reducing the extent to which formaldehyde is consumed by the Cannizzaro reaction. The experiment shows that CAN yield, succinate conversion, and extent of coke deposition were the same with CO_2 or with helium as a carrier gas.

Table 3. **Reactions of the kinetic model**

reaction	description	reaction	constant
1	condensation of succinates (DMS, MMS, SA) with formaldehyde to form citraconic anhydride	$CH_3OOC(CH_2)_2COOCH_3 + HCHO \rightarrow C_5H_4O_3 + 2CH_3OH$ $CH_3OOC(CH_2)_2COOH + HCHO \rightarrow C_5H_4O_3 + MeOH + H_2O$ $HOOC(CH_2)_2COOH + HCHO \rightarrow C_5H_4O_3 + 2\ H_2O$	k_1
2	citraconic anhydride cracking	$C_5H_4O_3 \rightarrow CO_2 + \text{coke} + H_2O$	k_2
3	dimethyl succinate hydrolysis	$CH_3OOC(CH_2)_2COOCH_3 + H_2O = CH_3OOC(CH_2)_2COOH + MeOH$	K_{e3}
4	monomethyl succinate hydrolysis	$CH_3OOC(CH_2)_2COOH + H_2O = HOOC(CH_2)_2COOH + MeOH$	K_{e4}
5	succinate (DMS, MMS, SA) decomposition	$CH_3OOC(CH_2)_2COOCH_3 \rightarrow 2\ CO_2 + \text{coke}$ $CH_3OOC(CH_2)_2COOH \rightarrow 2\ CO_2 + \text{coke}$ $HOOC(CH_2)_2COOH \rightarrow 2\ CO_2 + \text{coke}$	k_5
6	Canizzaro reaction	$2HCHO + H_2O \rightarrow CH_3OH + CO_2 + H_2$	k_6
7	formaldehyde decomposition	$HCHO \rightarrow CO + H_2$	k_7

Kinetic Model. A steady-state kinetic model for the formation of CAN from DMS and formaldehyde over γ-alumina (SA3177) has been developed using simple *n*th order kinetics in the model equations. Because of the complexity of the reaction system, we do not believe that a Langmuir–Hinshelwood kinetic model containing additional adjustable parameters is warranted for this system. The absence of mass-transport resistances facilitates calculation of intrinsic kinetic rate constants. Thermodynamic analysis of the reactions using experimental and predicted (via molecular modeling) heats and free energies of formation indicates that all reactions are thermodynamically favorable enough to be considered irreversible.

The seven reactions included in the kinetic model are listed in Table 3. Reaction 1 accounts for CAN production from succinates and formaldehyde via second-order pathways (k_1). The second and fifth reactions describe first-order cracking reactions of CAN (k_2) and succinates (k_5) into CO_2. The third and fourth reactions describe succinate hydrolysis and esterification; these reactions are assumed to be at equilibrium in the reactor.

$$K_{e3} = \frac{C_m C_{OH}}{C_d C_w} \tag{1}$$

$$K_{e4} = \frac{C_{SA} C_{OH}}{C_m C_w} \tag{2}$$

This assumption is justified by the high temperatures of reaction and significant acidity of the alumina catalyst, both of which facilitate hydrolysis/esterification, and because outlet stream concentrations satisfy eqs 1 and 2 over a wide range of conditions. The equilibrium constants, K_{e3} and K_{e4}, used in the model are average values calculated from reactor outlet concentrations in all experiments.

Finally, reaction 6 describes the Canizzaro reaction of formaldehyde (k_6; second-order reaction with respect to formaldehyde and first-order reaction with respect to water) and reaction 7 describes formaldehyde decomposition to CO and H_2 (k_7).

The one-dimensional steady-state molar balances in an integral, tubular reactor are given below for all species involved in the reactor system, with the rate expressed on a unit catalyst volume basis:

$$\text{CAN:} \quad \frac{dC_c}{d\tau} = k_1 C_{su} C_f - k_2 C_c \tag{3}$$

$$\text{succinate:} \quad -\frac{dC_{su}}{d\tau} = k_1 C_{su} C_f + k_5 C_{su} \tag{4}$$

$$\text{formaldehyde:} \quad -\frac{dC_f}{d\tau} = k_1 C_{su} C_f + 2k_6 C_f^2 C_w + k_7 C_f \tag{5}$$

$$\text{MeOH:} \quad \frac{dC_{oh}}{d\tau} = 2k_1 C_d C_f + k_1 C_m C_f + k_6 C_f^2 C_w \tag{6}$$

$$\text{water:} \quad \frac{dC_w}{d\tau} = -k_6 C_f^2 C_w + k_1 C_m C_f + 2k_1 C_{sa} C_f \tag{7}$$

$$\text{CO:} \quad \frac{dC_{CO}}{d\tau} = k_7 C_f \tag{8}$$

$$\text{CO}_2\text{:} \quad \frac{dC_{CO2}}{d\tau} = k_5 C_{su} + k_6 C_f^2 C_w + k_2 C_c \tag{9}$$

Where C_c, C_d, C_f, C_w, C_m, C_{oh}, C_{sa}, C_{su}, C_{CO}, and C_{CO2} are steady-state vapor concentrations (kmol/m^3) of CAN, DMS, formaldehyde, water, MMS, methanol, SA, total succinate, CO, and CO_2, respectively, and τ is contact time defined as catalyst volume/feed volumetric vapor flow rate (m^3 of catalyst/m^3 s^{-1} of feed). For the 2:1 molar Formalin:DMS feed mixture at 653 K and 0.5 MPa, WHSV is related to τ via

$$\text{WHSV (kg of succinate/kg of catalyst/h)} = 2.97/\tau\ \text{(s)} \tag{10}$$

Control runs feeding DMS only and CAN only were performed over γ-alumina (SA-3177) at base-case conditions to obtain first-order rate constants for the cracking reactions. We assume that CO_2 is formed stoichiometrically from the cracking reaction of succinates (2 mol CO_2/mol succinate) and CAN (1 mol CO_2/mol CAN). Rate constants for the cracking reactions (k_2 and k_5) were determined by solving the first-order differential equations in DMS and CAN.

After determining and incorporating the rate constants k_2 and k_5 and the equilibrium constants K_{e3} and K_{e4} into the model differential equations, the rate constants k_1, k_6, and k_7 were fit by nonlinear regression of the experimental data using Polymath (CACHE, Inc.) to minimize the sum of the squares of differences in predicted and experimental values of concentrations of all species except methanol and water in the reaction system. The experimental concentrations were

Table 4. **Parameters of kinetic model**[a]

rate constant or equilibrium constant	preexponential factor A	activation energy E (kJ/mol)
k_1	$(6.7 \pm 0.8) \times 10^5$ m^{3}kmol^{-1} s^{-1}	67.0 ± 10.0
k_2	6.0 ± 1.0 s^{-1}	30.6 ± 7.5
K_{e3}	$(1.9 \pm 0.4) \times 10^2$	35.6 ± 9.2
K_{e4}	$(5.2 \pm 0.9) \times 10^5$	84.2 ± 21.0
k_5	$(3.1 \pm 1.0) \times 10^1$ s^{-1}	48.6 ± 26.0
k_6	$(1.5 \pm 0.5) \times 10^3$ m^6 kmol^{-2} s^{-1}	26.4 ± 10.5
k_7	$(1.6 \pm 0.4) \times 10^5$ s^{-1}	88.4 ± 33.5

[a] $k = A \exp(-E/RT)$ or $K_e = A \exp(-E/RT)$.

taken as average values for each species exiting the reactor over the last 2.5 h of reaction. This was done at 350 and 380 °C. The resulting activation energy and preexponential factor for each of the rate constants in the kinetic model, along with uncertainty in each value, are presented in Table 4.

The uncertainty associated with each rate constant in Table 4 is based on the experimental standard deviation for the exiting species concentrations. This uncertainty in species concentration arises mainly from scatter in the chromatographic data and from difficulty in recovering all material in the sample collection process. The formaldehyde (as paraformaldehyde), citraconic anhydride, and succinic anhydride, all major components of the reactor effluent stream, solidify below 150 °C and thus are challenging to recover. Nevertheless, succinate carbon balances over the course of experiment (Table 2) were typically at 90+% of closure and the overall total mass balances (including all species) were always within ±2% of closure.

Uncertainty in values of k_2 and k_5 was thus calculated using the observed standard deviation of two percentage points (e.g., 40 ± 2%) in succinate and citraconate conversion in the independent cracking experiments. Uncertainties in k_1, K_{e3}, and K_{e4} were also estimated on the basis of a standard deviation for citraconate yield and succinate conversion of ±2 percentage points in condensation reactions. For reactions 6 and 7, the uncertainty in CO and CO_2 outlet concentrations were taken as ±5% of their absolute concentrations as measured by the IR meters in the effluent gas line.

Predicted product stream concentrations are calculated by applying the rate constants into eqs 1−9 above; predicted values are compared with experimental concentrations at 380 °C in Table 5. In general, the model predicts outlet concentrations for the key species quite well. The primary exception is methanol (MeOH) concentration, which is predicted rather poorly because it was not included in the least-squares fit and because of formation of dimethyl ether during reaction that is not accounted for in the kinetic model. Extending the prediction of concentrations to higher values of τ gives a broad maximum in CAN concentration of 3.6×10^{-3} kmol/m^3 at $\tau = 25$ s; this maximum corresponds to a yield of 41% with a selectivity of 64%. This represents an initial estimate of the preferred condition for reactor operation in an optimized process design.

Table 5. **Comparison of predicted and experimental outlet concentrations (10^{-3} kmol/m^3) from reactor**

	$\tau = 5.8$ s		$\tau = 3.6$ s		$\tau = 2.9$ s	
species	exptl	predicted	exptl	predicted	exptl	predicted
CAN	1.96	1.92	1.33	1.13	1.19	1.09
DMS	2.49	2.69	2.51	2.61	2.54	2.95
HCHO	11.96	13.37	10.95	14.21	14.62	15.19
MMS	3.14	2.94	2.48	2.88	2.64	3.24
SA	0.92	1.19	1.29	1.17	1.04	1.31
MeOH	9.44	14.71	9.86	12.28	10.24	12.99
CO	1.10	1.25	0.70	0.78	0.44	0.67
CO_2	1.01	0.92	0.58	0.51	0.56	0.47

IV. Summary

Several succinate and formaldehyde substrates have been investigated for the formation of citraconic anhydride. Dimethyl succinate and Formalin are an attractive feed combination for the reaction, as reasonable yields of citraconate were obtained with very good selectivity and the catalyst activity was stable for an extended time period. After hydrolysis of raw products, a maximum 31% yield of citraconates at 43% conversion of succinates was observed from the reaction of DMS and Formalin over SA3177 alumina at the base-case conditions. Higher formaldehyde-to-DMS molar ratios gave slightly better yield and selectivity to CAN. Yield of CAN decreased as WHSV was increased, either by changing bed length or liquid flow rate, but selectivity remained unchanged. Yield of CAN increased with increasing reaction temperature, but selectivity declined due to more extensive succinate cracking at elevated temperatures. DMS is not prone to cracking at elevated temperature as is SAN and, hence, is a more favorable feed material. The decay in catalyst activity was much slower with Formalin than with other formaldehyde sources, likely because the water vapor present cleans the catalyst during the reaction.

The condensation reaction of DMS with Formalin over intermediate surface area alumina is not mass-transfer limited. The kinetic model provides insight into reaction kinetics and provides direction for future scale-up and process design and simulation.

Acknowledgment

The support of Applied Carbochemicals, Inc., and the Crop Bioprocessing Center, State of Michigan Research Excellence Fund, is greatly appreciated.

Received for review January 16, 2002.

OP020210R