Isopropyl *tert*-butyl ether from crude acetone streams

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Received (in Bloomington, IN) 19th March 1999, Accepted 22nd June 1999

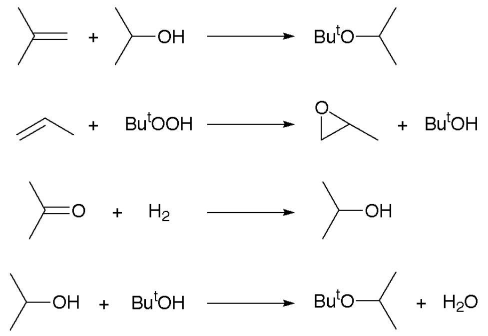
Isopropyl *tert*-butyl ether may be prepared from crude acetone streams through a combination of selective hydrogenation and *tert*-butyl alcohol etherification.

Methyl *tert*-butyl ether (MTBE) has in recent years been under severe environmental pressure[1] and refiners have been examining alternative gasoline blending stocks, including *tert*-amyl methyl ether (TAME), ethyl *tert*-butyl ether (ETBE), *etc.*[2,3] Of the fuel ethers seriously being considered, isopropyl *tert*-butyl ether (IPTBE) has the triple advantages[3] (see Table 1) of (i) highest octane blending values, (ii) lowest oxygen content and (iii) low vapor pressure. However, until now the only route to IPTBE was through the acid-catalyzed etherification of isobutene (oftentimes in short supply) with isopropyl alcohol (propan-2-ol, IPA) [eqn. (1)].[4,5] We have developed an alternative route to IBTBE from crude acetone streams, making it a co-product of propylene oxide (PO) manufacture. Propylene epoxidation with *tert*-butyl hydroperoxide produces PO plus *tert*-butyl alcohol commercially [eqn. (2)], with significant quantities of acetone as a secondary by-product.[6] We have demonstrated,[7] and report herein, that IPTBE can be made in good yield *via* (i) selective hydrogenation of the crude acetone (Me_2CO) by-product stream to give isopropanol [eqn. (3)] and (ii) isopropyl alocol etherification with the *tert*-butyl alcohol co-product to yield IPTBE plus water [eqn. (4)].

Table 1 Typical properties of fuel ethers[a]

	MTBE	ETBE	TAME	IPTBE
Octane blending value (R + M)/2	110	112	105	113
Oxygen content (wt%)	18.2	15.7	15.7	13.8
Vapor pressure neat Rvp (37.8 °C)	7.8	4.0	2.5	2.5

[a] Data taken from references 2 and 3.



(1)

(2)

(3)

(4)

Typically, low-value acetone by-product streams from propylene oxide manufacture comprise 20–80% Me_2CO, but also contain significant quantities of MeOH, *tert*-butyl alcohol (tBA), and allyl *tert*-butyl peroxide (ATBP), as well as detectable quantities of HCO_2H, AcOH, plus their ester derivatives, such as *tert*-butyl formate (tBF).[6] Selective hydrogenation of a 61.7% acetone stream in a continuous, upflow, reactor system containing a nickel, copper, chromium bulk-metal catalyst (72% Ni), at 160 °C, is illustrated in Table 2. Near quantitative (99%) acetone conversion levels are achieved at liquid hourly space velocities (LHSVs) of 0.5, with IPA as the major product. Selectivity to IPA is typically in the range of 76–80 mol%. Critical features of this selective hydrogenation are (i) catalyst activity may be sustained for extended periods without loss of performance and (ii) any ATBP or *tert*-butyl hydroperoxide fractions present in this crude acetone feed are quantitatively converted to more innocuous alcohols, *e.g. tert*-butyl alcohol, without causing catalyst deactivation.

Etherification of the IPA intermediate with added tBA to give IPTBE [eqn. (4)] has also been demonstrated in continuous, upflow, reactor systems using three classes of acidic, large-pore, zeolites:[7] Zeolite Beta, transition metal-modified β-zeolites, and dealuminized Y-zeolites.

IPTBE is typically generated in near quantitative molar selectivities (on the basis of IPA converted) in the crude liquid products under mild etherification conditions. Fig. 1 illustrates IPTBE syntheses from the crude IPA stream of Table 2, plus added tBA (IPA : tBA mole ratio 1 : 1.6), using an acidic β-zeolite catalyst (80% Beta, 20% alumina binder, in $\frac{1}{16}''$ diameter extruded form), over a reactor temperature range of 40 to 100 °C. At 60–80 °C the estimated IPA conversion level is moderate (*ca.* 12%) and the crude liquid effluent comprises 7–8 wt% IPTBE. However, IPTBE molar selectivity on the basis of tBA converted is below 50% with this crude feedstock, due to

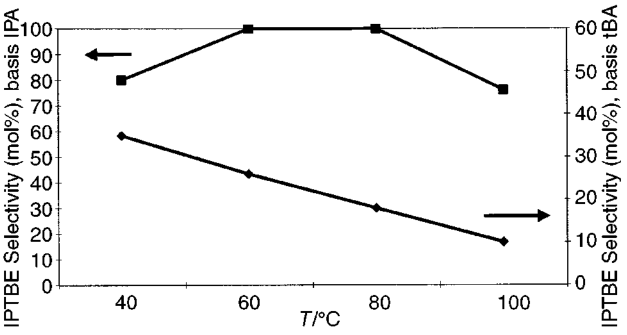


Fig. 1 Crude IPA etherification to IPTBE with tBA. IPTBE molar selectivity basis IPA and tBA converted.

Table 2 Crude acetone hydrogenation to isopropyl alcohol

				Composition (%)					
Catalyst	*T*/°C	LHSV	Sample	Me_2CO	IPA	MeOH	tBA	tBF	ATBP
			Feed	61.7	0.1	13.9	16.7	0.1	3.3
Ni-2715	160	0.5[a]	Product[b]	0.8	48.3	15.8	30.8	< 0.1	< 0.1

[a] Hydrogen feed rate, 90 l h^{-1}; total pressure, *ca.* 35 bar. [b] Product composition maintained for 200 h.

Table 3 Isopropyl alcohol etherification to isopropyl *tert*-butyl ether

				Composition (%)						
Catalyst	*T*/°C	LHSV	Sample	IPTBE	MTBE	IPA	tBA	MeOH	C4H8	C8H16
			Feed		0.1	11.3	81.2	3.4		
Pt/Beta zeolite	60	0.25	#1	5.9	4.2	9.3	68.3	1.3	6.6	0.5
	80	0.25	#2	5.5	5.9	9.1	61.1	0.8	10	2.9
Pd/Beta zeolite			Feed			11.3	82.2	2.1		
	60	0.25	#1	6.1	4.3	9.3	67.7	1.2	6.7	0.6
	80	0.25	#2	5.4	6.2	9.5	60.6	0.7	9.7	3

[a] Designations as per Table 2.

Table 4 Standard enthalpy and entropy changes for IPTBE syntheses

IPTBE Synthesis Route	ΔH/kcal mol^{-1}	ΔS/cal mol^{-1} K^{-1}
IPA + iso-C_4H_8 → IPTBE	−6.1[a] −5.5[b]	−17.1[a] −14.4[b]
IPA + tBA → IPTBE + H_2O	−0.4[c]	−7.0[c]

[a] From reference 4. [b] From reference 5. [c] This work, ideal gas conditions (298 K, 1.0 atm).

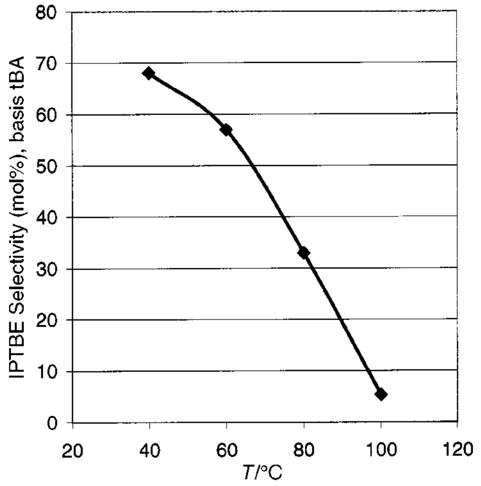


Fig. 2 Pure IPA etherification to IPTBE with tBA.

competing tBA dehydration and oligomerization to isobutene and diisobutene, as well as the formation of smaller quantities of MTBE through etherification. It is noteworthy, nevertheless, that the β-zeolite catalyst does maintain etherification activity and good IPTBA molar selectivity with this crude hydrogenated Me_2CO feedstock for extended periods.[7]

Very similar product distributions were realized when using transition metal-modified β-zeolite catalysts—particularly β-zeolites modified with platinum, palladium, and nickel. These data are illustrated in Table 3 for the non-aqueous product fraction, when starting with the same crude IPA feed stream of Table 2, but adding additional tBA (IPA:tBA molar feed ratio 1:5.8). The transition metal-modified β-zeolites were selected for study here, on the basis of our earlier observations that they provide superior performance in related service, *e.g.* MTBE production from $\mathrm{Bu^tOH}$–MeOH mixtures,[8] as well as in ETBE synthesis.[9] Significantly poorer etherification performance was generally realized with the dealuminized Y-zeolites.[7]

Liquid-phase IPTBE synthesis from IPA–tBA mixtures [eqn. (4)] is essentially thermoneutral—see Table 4—in contrast to IPTBE from isobutene [eqn. (1)].[4,5] Isolating and purifying (99%) the intermediate IPA from Table 2, and running etherification with close to stoichiometric quantities of tBA, provides measurably higher IPTBE selectivities over this temperature range (see Fig. 2, IPA:tBA feed ratio 1:1.6) and fewer competing reactions. However, etherifications conducted much above 100 °C lead to the formation of diisopropyl ether as a dominant product.[10]

Continuing improvements in this technology are under investigation, particularly in the area of an integrated, one-step, route to C-3 ethers from crude acetone streams plus tBA.[11]

The authors wish to thank Mr Melvin Stockton for experimental excellence.

Notes and references

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Communication 9/02458A