

Novel synthesis of isoprene from 3-methylbutan-2-one using phosphate catalysts

Graham J. Hutchings,^{*a†} Ian D. Hudson,^a Donald Bethell^{a‡} and Don G. Timms^b

^a Leverhulme Centre for Innovative Catalysis, Department of Chemistry, University of Liverpool, Liverpool, UK L69 3BX. E-mail: hutch@cf.ac.uk

^b Enichem Elastomers Ltd, Charleston Road, Hardley, Hythe, Southampton, UK SO4 6YY

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AlPO₄ and BPO₄ catalyse the conversion of 3-methylbutan-2-one to isoprene in high yields via 2-methylbut-2-en-1-ol as an intermediate.

Isoprene is an important monomer for the stereoselective polymerisation to 1,4-*cis*-polyisoprene which is used in the manufacture of synthetic rubber. Isoprene is currently obtained from naphtha cracking but in recent years there has been continued interest in the identification of new synthetic routes. One interesting possibility is the dehydration of 2-methylbutanal which is available as a result of the commercialisation of the low pressure hydroformylation of butene.¹ BPO₄ has been shown to be an effective catalyst^{2–4} for this reaction and can give 60–70% yield at high conversion, but deactivation can be rapid. Recently, we have shown⁵ that BPO₄ can be readily reactivated using a simple high temperature treatment, thereby making these catalysts more suitable for industrial application. However, together with isoprene, 3-methylbutan-2-one is formed as a major by-product with both phosphate catalysts and this, at present, limits the commercial applicability of the process. Here we demonstrate that 3-methylbutan-2-one can be readily converted to isoprene using BPO₄ and AlPO₄ as catalysts. Furthermore, we demonstrate that isoprene and 3-methylbutan-2-one formation from 2-methylbutanal are linked by a common intermediate, 2-methylbut-2-en-1-ol. These results indicate that by recycling the 3-methylbutan-2-one by-product the overall yield of isoprene can be increased by $\geq 10\%$ for both BPO₄ and AlPO₄ catalysts.

Boron phosphate (P:B = 1) was prepared by heating phosphoric acid (93 ml, 85%) with boric acid (100 g) at 60 °C for 1 h. Water (100 ml) was then added and the mixture was refluxed for 5 h and then dried (110 °C, 16 h) and calcined (350 °C, 4 h). The product was confirmed to be the cristabolite form of BPO₄ by X-ray diffraction. Aluminium phosphate (Al:P = 1) was prepared by the slow addition of aqueous ammonia (40 vol%, 5 °C), with continuous stirring, to an aqueous solution containing equimolar quantities of AlCl₃ and phosphoric acid (0.985 mol l⁻¹, 5 °C). Aqueous ammonia addition was continued until pH = 7.0 was attained. The white precipitate was aged (18 h, 20 °C) and collected by filtration, washed several times with propan-2-ol, dried (24 h, 120 °C) and calcined (3 h, 800 °C). Powder X-ray diffraction showed that the catalyst was a mixture of the cristabolite and tridymite phases of AlPO₄. Both these solids were screened (200–250 mesh), and pelleted and sieved (600–1000 μ) prior to use as catalysts. The phosphates were investigated as catalysts for the dehydration of 2-methylbutanal and isoprene was observed as the major product in agreement with our previous results.⁵ For both BPO₄ and AlPO₄ the only by-product was 3-methylbutan-2-one which was formed at *ca.* 18–20% yield. In a separate set of reactions 3-methylbutan-2-one [0.67 ml (g catalyst)⁻¹ h⁻¹]

was reacted over the phosphate catalysts (0.3 g) using a standard laboratory microreactor with nitrogen as a diluent (24 ml h⁻¹). Products were analysed using GC and satisfactory mass balances were obtained for all data presented. The results for BPO₄ at 325 °C and AlPO₄ at 400 °C are shown in Fig. 1. AlPO₄ required a higher reaction temperature than BPO₄ to observe a significant conversion level. Both catalysts convert 3-methylbutan-2-one to isoprene with high selectivity (80–95%) and at reasonable conversion levels. The catalyst performance was found to be very stable and, significantly, no appreciable deactivation was observed.

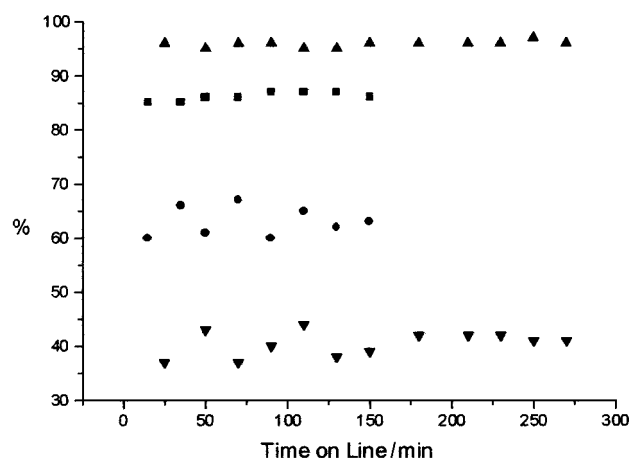
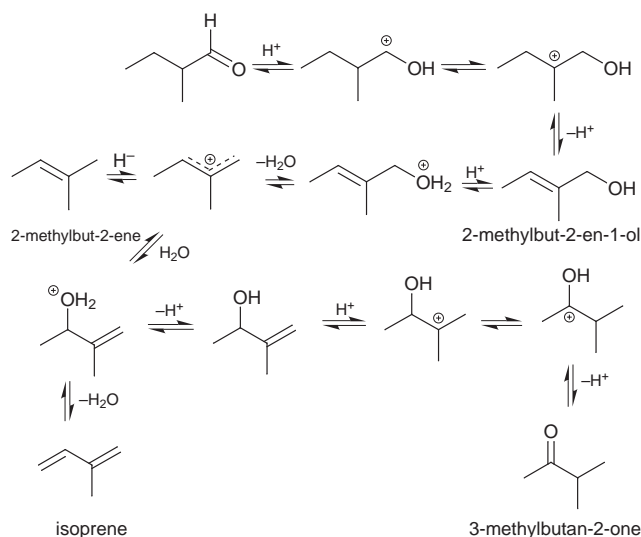


Fig. 1 Reaction of 3-methylbutan-2-one over (a) BPO₄ at 325 °C [(▼) conversion, (▲) isoprene selectivity] and (b) AlPO₄ at 400 °C [(■) conversion, (●) isoprene selectivity].



Scheme 1 Proposed mechanism for the conversion of 2-methylbutanal and 3-methylbutan-2-one to isoprene.

[†] Present address: Department of Chemistry, Cardiff University, PO Box 912, Cardiff, UK CF1 3TB.

[‡] Present address: BNFL Ltd, Springfields Works, Salwick, Preston, UK PR4 0XJ.

The observation that both 2-methylbutanal and 3-methylbutan-2-one could be converted to isoprene with these catalysts prompted us to consider the reaction mechanism for these catalytic processes. We believe that 2-methylbut-2-en-1-ol is a central intermediate in the conversion of 2-methylbutanal into both isoprene and 3-methylbutan-2-one (Scheme 1). To test this proposal, 2-methylbut-2-en-1-ol was synthesised by reduction of 2-methylbut-2-enal with sodium borohydride in MeOH. 2-Methylbut-2-en-1-ol was then reacted [0.67 ml (g catalyst)⁻¹ h⁻¹] in a nitrogen diluent (24 ml min⁻¹) over BPO₄ (0.3 g) at 110 and 300 °C. At these temperatures, 2-methylbut-2-ene was a major product (*ca.* 10–40%) but in addition isoprene (37%), 2-methylbutanal (10%) and traces of 3-methylbutan-2-one were also observed and the conversion increased from 87% at 110 °C to 99% at 300 °C (Table 1). These results support the proposal that 2-methylbut-2-en-1-ol is a key intermediate in the conversion of 2-methylbutanal into both isoprene and 3-methylbutan-2-one.

This study indicates that the yield of isoprene from the dehydration of 2-methylbutanal, using AlPO₄ and BPO₄ catalysts, can be significantly enhanced if the major by-product, 3-methylbutan-2-one, is reacted over the same phosphate catalyst under the same reaction conditions. It is anticipated that this can be done *via* a recycle step and yield increases of *ca.* 10% for BPO₄ (from 72 to 82 at 325 °C) and 16% for AlPO₄ (from 56 to 72% at 400 °C) can be expected.

Table 1 Conversion of 2-methylbut-2-en-1-ol over BPO₄^a

T/°C	Conversion	Selectivity ^b		
		2MBA	2MBE	I
110	87	12	49	39
300	99	25	47	10

^a BPO₄ (0.3 g), 2-methylbut-2-en-1-ol [0.67 ml (g catalyst)⁻¹ h⁻¹], N₂ (24 ml min⁻¹). ^b 2MBA = 2-methylbutanal; 2MBE = 2-methylbut-2-ene; I = isoprene.

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Notes and references

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