

- 1 -

PROCESS FOR THE PREPARATION OF PROPYNE

This invention relates to a process for the preparation of propyne by contacting a propadiene-containing feed with an isomerization catalyst. This invention also relates to the use of the obtained propyne in the manufacture of alkyl methacrylates.

5 The preparation of propyne (methyl acetylene) by isomerization of propadiene (allene) in the presence of a homogeneous catalyst is described in United States Patent 3,579,600. According to this document the catalysts
10 comprise a solution of a dipolar aprotic solvent having a dielectric constant above 10, and an alkoxide or hydroxide of an alkali metal exclusive lithium. The Examples of this document illustrate the use of potassium hydroxide dissolved in dimethyl sulfoxide, or tetrahydro-
15 thiophene-1-oxide. In all cases, a protic co-solvent, such as water, methanol, or ethylene glycol is present. The preferred catalyst composition comprises a mixture of dimethyl sulfoxide and potassium hydroxide. Although this
20 catalyst composition shows good activity and selectivity, it suffers from the drawback of decomposition over a period of time giving off obnoxious fumes.

In Preparative Acetylenic Chemistry, by L. Brandsma, Ed. Elsevier Publishing Company, Amsterdam, 1974 the base-catalysed isomerization of acetylenes and allenes is
25 reviewed more broadly in view of its utility in the preparation of acetylenes. From Table II at page 144 it can be appreciated that depending on the substrate, the isomerized equilibrium mixtures may contain various products or product mixtures, including terminal and non-
30 terminal acetylenes, allenes, conjugated dienes, and enynes. Furthermore, dimethyl sulfoxide appears to be the

- 2 -

most commonly used solvent besides ammonia, water and alkanols.

Example 1 of German Patent Application 3,700,033 discloses a process for the preparation of 2-butyne by catalytic isomerization of 1,2-butadiene, wherein the catalyst is a solution of potassium tert-butoxide in N-methyl pyrrolidone. The non-terminal 2-butyne is formed with a selectivity of 98.9%. Besides, 1.1% of 1,2-butadiene is formed. No terminal acetylene, i.e. 1-butyne is produced. This observation suggests that the use of amide solvents promotes the selectivity to non-terminal acetylenes rather than to terminal acetylenes.

It has now been found that solutions of strong bases in an amide solvent constitute very suitable isomerization catalysts for the preparation of propyne starting from propadiene by actively promoting the isomerization to a high equilibrium ratio of propyne to propadiene, and by lacking or at least attenuating the formation of obnoxious fumes as encountered in the use of dimethyl sulfoxide as catalyst solvent.

Accordingly the present invention provides a process for the preparation of propyne by contacting a propadiene-containing feed with a isomerization catalyst comprising a strong base dissolved in an amide solvent.

It should be noted that representative amides, such as N-methyl pyrrolidone and N,N-dimethyl acetamide have dielectric constants higher than 10 as required by the disclosure of United States Patent 3,579,600. However, this document does not provide any suggestion to the specific use of amide solvents. The paragraph bridging columns 1 and 2 mentions a large number of high dielectric constant dipolar aprotic solvents, such as sulfoxides, alkylene polyamines, heterocyclic imines, alkanolamines, amine oxides, and phosphine oxides without a single reference to any amide. Moreover, any practical

- 3 -

problem due to solvent decomposition and concurring development of obnoxious fumes is not contemplated or discussed. Also the dimethyl sulfoxide appeared to behave differently from the presently used amide solvents with respect to the effect of protic co-solvents. The Examples of this publication show that practically dimethyl sulfoxide should be used in conjunction with a protic co-solvent, in particular water.

In the case of an amide solvent, it was found that an aqueous (co)solvent is not required, and tends to reduce catalytic activity. Avoiding the presence of low boiling (co)solvents has the additional advantage that effluent streams will not be contaminated with low boiling impurities.

Accordingly, in a preferred embodiment of the invention the process is conducted in the substantial absence of water (e.g. less than about 500 ppm [vol] H₂O; in continuous processes less than about 100 ppm [vol] H₂O, preferably less than 10 ppm [vol] H₂O). Methods for removing water from the feed or the catalyst solution are well established in the art, and need no further illustration here.

The nature or the source of the propadiene-containing feed is not critical. The feed may be pure propadiene or may contain substantial amounts of inert gaseous diluents. The feed may contain a mixture of propyne and propadiene, as commercially available from thermal cracking operations such as depropaniser overheads or the bottom effluent of a propane-propene (PP) splitter when no hydrogenation is applied to the feed to the PP splitter, and comprising propene and propane, as well as residues of C₄ components besides propyne and propadiene.

For optimal propyne yield commercial propyne/-propadiene mixtures may be split by conventional separation techniques, whereupon the propadiene is

- 4 -

processed in accordance to the present invention. The product of the present process is recycled and combined with fresh propyne/propadiene prior to the separation of the propyne to constitute a feed for the present process.

5 Processes for separating propyne/propadiene mixtures are disclosed in EP-A-0,224,748; EP-A-0,392,601; EP-A-0,533,291 and EP-A-0,533,628. For instance, propadiene is selectively removed by extractive distillation, in which the mixture of propyne and
10 propadiene is dissolved in a polar organic solvent, and propadiene is removed as gas (e.g., by stripping) leaving propyne dissolved in the solvent.

 The base to be used in the present process should be strong and sufficiently soluble in the catalyst solvent
15 to provide the desired concentration. Suitable bases include the hydroxides, alkoxides and amide of the alkali metals. Representative examples include lithium hydroxide, sodium hydroxide, potassium hydroxide, sodium amide, potassium amide, lithium methoxide, sodium
20 methoxide, potassium methoxide, sodium tert-butoxide, potassium tert-butoxide, alkali metal salts of protic amides, such as potassium pyrrolidonate, and the alkali metal compounds of alkylated pyrrolidones, carboxamides or carbonamides, for example obtained through hydrogen
25 atom abstraction by reaction of metallic alkali metal with the aprotic amide solvents. The base should be sufficiently strong to provide the required base strength to the base/catalyst solution for active catalyzation of the isomerization reaction. Weaker bases require higher
30 concentrations possibly above the solubility limit. As a rule the pKa of the conjugated acid should at least have the value of the pKa of water and be higher than about 14, preferably higher than 15. Preferably the strong base is an alkali metal hydroxide or alkoxide, more
35 particularly an alkali metal alkoxide (pKa of about 16).

- 5 -

The concentration of the strong base in the amide solvent may vary between wide limits. Practically concentrations of from 0.1 to 50% by weight of the strong base in the total liquid catalyst composition will be suitable. At lower concentrations the required base strength is not achievable, and at higher concentration solubility problems will be met. Preferred concentrations are in the range of from 0.5 to 30% by weight.

Amide solvents which may be suitably used in the present process, include peralkylated phosphoric acid triamides, e.g. hexamethyl phosphoric triamide; peralkylated alkylphosphonic diamides, e.g. tetramethyl methylphosphonic diamide; pyrrolidones, e.g. pyrrolidone and N-methyl pyrrolidone; peralkylated carboxamides, e.g. N,N-dimethyl acetamide and N,N-dimethyl formamide; and peralkylated ureas, e.g. tetramethyl urea. The use of the above amide solvent results in active catalysts for the isomerization reaction. However, some may be less preferred in view of health or environmental aspects, or in view of limited stability in the highly alkaline environment of the present process. In this respect a preferred class of amides for use in the present process is constituted by the cyclic amides, in particular the N-alkyl pyrrolidones. Suitable and commercially available is N-methyl pyrrolidone.

Pressure and temperature are not critical to the isomerization reaction of the present process and may be varied between wide limits. Considerations, such as freezing of the solvent at low temperature or alkaline attack of the solvent at high temperature, determine the practical limits for the temperature. Suitably the reaction temperature of the present process is in the range of from -20 to 80 °C. Preferably the temperature is in the range of from 20 to 70 °C. Subatmospheric and atmospheric pressures can be used, but superatmospheric

- 6 -

pressures are preferred, more particularly up to the saturated vapour pressure of the reaction components at the temperature applied. The choice of the actual operation temperature and pressure is affected by limits for safe handling of propadiene and/or propyne containing mixtures, depending in part on the extent of dilution with inert gases such as propane, propene, butane, nitrogen, carbon dioxide and the like. Most preferred pressures range from 1 to 40 bar gauge (barg).

The present process may conveniently be conducted batch-wise by introduction of the propadiene containing feed into a closed reactor comprising the liquid catalyst composition and maintaining the reaction until equilibrium is attained. It is preferred, however, that the present process is conducted (semi-)continuously, for example, by continuously introducing a propadiene containing feed at one end of a reactor containing the liquid catalyst composition, and withdrawing the gaseous reaction products at the other end. The feed rate or feed flow is controlled to set a space velocity appropriate for approaching or achieving the propyne/propadiene equilibrium ratio in the product leaving the reactor. Suitable feed rates usually are the range of from 0.1 to 10 l/l.hr, preferably in the range of from 0.5 to 2.5 l/l.hr, expressed in actual volumes of liquid propadiene-containing feed per volume of liquid reactor contents per hour (LHSV). The gaseous propyne enriched product stream can be further conventionally processed for separating the desired propyne, for example, by condensing and fractionating, or by selectively absorbing/desorbing in a suitable solvent, as indicated in Ullmann's Encyclopaedia of Industrial Chemistry, Vol. A 1, pp. 140-145, (1985), and references mentioned therein.

Figure 1 schematically represents a particular

- 7 -

embodiment of the invention. The present process is conducted by subjecting a propyne/propadiene containing-feed (1), further containing propane and propene, to an absorption column (2), wherein propyne and propadiene are selectively absorbed into a suitable solvent such as dimethylformamide, and the loaded solution is forwarded through line (3) to a first desorption column (4). The gaseous remainder of the feed depleted of propyne and propadiene, and mainly consisting of propane and propene, is condensed and drawn off through line (5) for further processing. Propadiene that is desorbed in the first desorption column is sent through line (6) to an isomerization unit (7) wherein it is isomerized to its equilibrium mixture with propyne, in a manner as described herein before, to obtain a propyne/propadiene-containing stream. This stream is recycled through line (8) to the propyne/propadiene-containing feed (1). The propyne loaded absorption liquid is sent through line (9) to a second desorption column (10), wherein a stream of high purity propyne (11) is desorbed and collected from the top of this column. The desorbed solvent is recycled to absorption column (2) through line (12).

The present process may also readily be conducted as discussed above, wherein propyne and propadiene are selectively absorbed into the amide solvent containing the strong base. This avoids the need of a separate (expensive) isomerization unit. The propyne/propadiene mixture is isomerized at the conditions mentioned above, whereupon a propyne/propadiene product stream enriched in propyne is selectively desorbed. The propyne and propadiene are then conventionally separated. The resulting propadiene stream is preferably combined with the feed. Again, the feed rate or feed flow is controlled to set a space velocity appropriate for selective absorption of the propyne/propadiene mixture and

- 8 -

approaching or achieving the propyne/propadiene equilibrium ratio in the product leaving the reactor. Suitable LHSV feed rates usually are the range of from 0.1 to 10 l/l.hr, typically in the range of from 0.5 to 2.5 l/l.hr.

Figure 2 schematically represents this alternative embodiment of the invention. This process is conducted by subjecting the propyne/propadiene containing feed (1), further containing propane and propene, as well as heavy ends (butanes etc.), to a heavy ends distillation column (13), wherein these heavy ends are removed over the bottom of the column (stream 14), the gaseous C₃ stream (15) is sent to a reactive absorption column (16), wherein propyne and propadiene are selectively absorbed into the amide solvent containing the strong base, and the loaded solution is forwarded through line (17) to a first (reactive) desorption column (18). Again, the gaseous remainder of the feed depleted of propyne and propadiene is condensed and drawn off through line (19) for further processing. In (reactive) desorption column (18) both propyne and propadiene are desorbed, providing a concentrated, gaseous propyne/propadiene stream (20) enriched in propyne. The desorbed solvent is recycled through line (21) to the reactive absorption column (16). The gaseous stream (20) is subjected to a second absorption column (22). In this column the propyne is selectively absorbed into the amide solvent (without base), and the loaded solution is forwarded through line (24) to a second desorption column (25), whereas the gaseous remainder of stream (20) is recycled to the heavy ends distillation column (13) through line (23). In the second desorption column (25) the high purity propyne (26) is released from the solvent, and the solvent is recycled (27) to the second absorption column (22).

The propyne obtained by the process of the invention

- 9 -

is particularly suitable as starting material in the manufacture of an alkyl methacrylate by reaction with carbon monoxide and an alkanol in the presence of a carbonylation catalyst, for example as described in EP-A-0,392,601.

The invention will be further illustrated by the following examples. In these examples the following abbreviations are used:

MA/PD	=propyne/propadiene	NMP	=N-methyl pyrrolidone
DMSO	=dimethyl sulfoxide	DMAC	=N,N-dimethyl acetamide
MeOH	=methanol	MeOK	=potassium methanolate
		DMF	=N,N-dimethyl formamide

Example I

a. A series of 150 ml gas tight glass bottles were each charged with 75-80 ml of one of the catalyst compositions of the below Table I. Catalyst compositions were prepared under N₂ blanket or in an N₂ glove box using commercial grade dry solvents. A commercial PD gas ex Ucar or ex Intermar (°), containing about 97 %vol PD, about 1 %vol or less MA and about 100 ppm [vol] H₂O, was bubbled through the liquid to achieve saturation at ambient temperature. The reaction mixture was magnetically stirred at the temperature indicated. At the times indicated, samples were taken from the gas cap and analysed by Gas Liquid Chromatography. Sampling was started as soon as a part of or the whole saturation procedure was completed.

The results are mentioned in Table I. It will be appreciated that the sooner equilibrium is reached, the better. Likewise, formation of heavy gaseous by-products is preferably avoided. Comparison of the experiments then reveals that the comparative catalysts achieved equilibrium only after prolonged contact between the PD gas and the catalyst, typically at the expense of the overall MA + PD concentration.

- 10 -

b. In a similar comparative experiment 1J a 250 ml steel autoclave was used and charged with 100 ml of a catalyst composition composed of 1.0 %wt MeOK in MeOH. In this experiment the gas cap of the autoclave was flushed three times with N₂ before pressurizing to 8 bar N₂. Then, the temperature was raised to about 40 °C, and during 30 min 80 ml of a commercially available welding gas ex AGA typically containing 15 %wt PD, 23 %wt MA and about 10 ppm [vol] H₂O, was pumped into the autoclave. After 18 run hours the temperature was raised to about 60 °C. Again samples were taken from the gas cap and analysed by GLC. Now, the MA/PD ratio never exceeded 1.2/1, even after 25 hours.

- 11 -

TABLE I

Exp.	Catalyst	T °C	p bar	[MA/PD] -RATIO Gascap (%/%)	time (hr)	heavy by- products
1A	5.2 %wt	25	1	2.8/1	0.08	
(Comp)	KOH in DMSO			8.2/1	0.25	
				8.3/1	19	yes
1B	3.0 %wt	25	1	8.4/1	0.5	
(Comp)	t-BuOK in DMSO			8.4/1	18	yes*
				8.7/1	69	yes*
1C	5.2 %wt	22	1	5.0/1	0.08	
	t-BuOK in NMP			8.3/1	0.25	
				8.8/1	21	
1D	0.65 %wt	22	1	5.1/1	0.25	
	t-BuOK in NMP			8.0/1	0.75	
				8.4/1	2.75	
				8.7/1	20	
1E	4.0 %wt	25	1	3.9/1	0.08	
	KOH in NMP			3.1/1	0.17	
				4.2/1	0.25	
				8.7/1	21	
1F	4.0 %wt	25	1	0.007/1	0.08	
	KOH in DMAC			0.03/1	0.25	
				1.5/1	3.5	
				8.6/1	22	
1G	4.0 %wt	25	1	7.9/1	0.08	
	t-BuOK in DMAC			8.4/1	0.25	
				8.6/1	4.5	

* besides, spread of obnoxious odour and decrease in overall MA + PD concentration

- 12 -

TABLE I (Cont'd)

Exp.	Catalyst	T °C	p bar	[MA/PD] -RATIO Gascap (%/%)	heavy by- products time (hr)
1H°	4.0 %wt t-BuOK in DMF	25	1	8.6/1 8.5/1 8.3/1	0.08 0.25 0.50
1I°	3.9 %wt (Comp) t-BuOK in t-BuOH	±30	1	0.04/1 0.08/1 2.6/1 8.1/1	0.25 0.50 5.5 23

° A commercial PD gas containing 0.03% MA

Example II

- a. In a continuous experiment a 190 ml glass pressure reactor was used, equipped with a magnetic stirrer. A liquid catalyst composition was prepared by dissolving 1.0 %wt t-BuOK in NMP under an N₂ blanket, and 50 ml were charged into the reactor. Liquefied PD depropaniser overheads (typically containing 1.6-1.9% PD, 2.2-2.4% MA, 92% propylene, 3.3% propane and minor amounts of C₄ impurities) were pumped over a drying bed of mol sieves 3A and flashed before entering the reactor as a gas via a dip-tube with outlet near the bottom of the reactor. Gaseous reaction products left the reactor via the gas cap. In the off-gas line subsequently a catch vessel, a back pressure regulator, a mass flow meter and a sampling point were fitted. The PD feed rate (1/1.hr on liquids basis) was adapted to achieve near equilibrium conversion (estimated at 80% propadiene conversion). The conversions obtained at pressures of 4.6-5.1 bar and a temperature of 25 °C are shown in Figure 3 (open data points).
- b. In a similar experiment the mol sieves prebed was bypassed in order to observe the effect of water in the

- 13 -

propadiene-containing feed on catalyst life time. The conversions achieved as function of the accumulated depropaniser overheads feed is also shown in Figure 3 (closed data points). It is seen that the accumulation of water, occurring in experiment b) by bypassing the mol sieves bed, leads to decrease of the catalytic activity at about 4000 ml of accumulated feed. In experiment a), excellent catalyst activity was still observed after 10,000 ml of accumulated feed.

10 Example III (cf. Figure 2)

In a calculated experiment (wherein the volume of the equipment has not yet been considered) a heavy ends column (13), is fed with a feed (1), similar to that of the bottoms effluent of a PP splitter and composed of 40 %wt propane, 19 %wt propene, 15 %wt PD, 25 %wt MA and 1 %wt heavier hydrocarbons, as well as with a recycle stream (23), drawn off from the second absorption column (22) and composed of 42 %wt propane, 40 %wt propene, 15 %wt PD, and 2.9 %wt MA. The feed rate of (1) is 6,000 kg/hr, that of (23) is 1800 kg/hr. A stream of heavy ends (14) is collected at a rate of 80 kg/hr. This stream is composed of 75 %wt of heavier hydrocarbons, whereas the remaining 7720 kg/hr (stream 15) is fed to the reactive absorption column (16). In column (16) the feed is contacted with a stream (21) composed of 20,000 kg/hr DMF containing 4 %wt t-BuOK. The column (16) is operated at 8 barg and a bottoms temperature of 62 °C. It is provided with a reboiler and a condenser. The liquid top product (19) is released at a rate of 3580 kg/hr and is composed of 67 %wt propane, 32 %wt propene, 0.8 %wt PD, and 0.2 %wt MA. The bottom product (17) is obtained at a rate of 24.140 kg/hr, and is composed of 3 %wt propane, 3 %wt of propene, 1 %wt of PD, 10 %wt of MA and 83 %wt of DMF containing t-BuOK.

35 This bottom product is cooled to 35 °C and fed to a

- 14 -

first reactive desorption column (18) provided with a condenser operating at 2.6 barg, where all the propane, propene, PD and MA are stripped off. The bottom product is stream (21) mentioned above. The top product (20) is fed to a second absorption column (22). In column (22), operating at a pressure of 1.1 barg and a bottoms temperature of 58 °C, (20) is brought into contact with a solvent stream (27), composed of DMF at a rate of 20,000 kg/hr. The stream (23) is drawn off over the top. The bottom product (24) consists of circa 11 %wt MA, dissolved in DMF, collected at a rate of 22,358 kg/hr. It is fed to a second desorption column (25), operating at a pressure of 1.1 barg and a bottoms temperature of about 180 °C. Nearly pure MA (containing 23 ppm PD and 1 ppm DMF) is collected over the top at a rate of 2,340 kg/hr.

Example IV

Using the same feed, but now in a process having a separate isomerization step, 2,360 kg/hr MA is prepared and isolated, requiring 25,000 kg/hr of DMF.

Keeping in mind that the costs for a separate isomerisation unit (typically composed of at least two fixed-bed reactors operating in an alternating mode) is substantially higher than the cost of the additional column and solvent, it will be clear that the set-up of Example III is preferred.



- 15 -

C L A I M S

1. A process for the preparation of propyne by contacting a propadiene-containing feed with an isomerization catalyst comprising a strong base dissolved in an amide solvent.
- 5 2. A process as claimed in claim 1, wherein the propadiene-containing feed is contacted with the isomerization catalyst in the substantial absence of water.
- 10 3. A process as claimed in claim 1 or 2, wherein the pKa of the conjugated acid of the strong base is above 13.
4. A process as claimed in any one of claims 1-3, wherein the strong base is an alkali metal alkoxide or amide; or the alkali metal compound of an alkylated pyrrolidone, carboxamide or carbonamide.
- 15 5. A process as claimed in claim 4, wherein the strong base is an alkali metal alkoxide.
6. A process as claimed in any one of claims 1-5, wherein the amide solvent comprises a cyclic amide.
7. A process as claimed in any one of claims 1-6, wherein the amide solvent comprises an aprotic amide.
- 20 8. A process as claimed in claim 7, wherein the amide solvent comprises an N-alkyl pyrrolidone.
9. A process as claimed in any one of claims 1-8, wherein the isomerization catalyst comprises from 0.1 to 50% by weight of strong base, and preferably from 0.5 to 30% by weight.
- 25 10. A process as claimed in any one of claims 1-9, wherein the reaction temperature is in the range of from -20 to 80 °C, and preferably in the range of from 20 to 70 °C.
- 30 11. A process as claimed in any one of claims 1-10,



- 16 -

wherein the reaction is conducted at a pressure in the range of from 1 to 40 bar gauge.

12. A process as claimed in any one of claims 1-11, wherein the process is conducted continuously.

5 13. A process as claimed in claim 12, wherein the feed rate is in the range from 0.1 to 10 l/l.hr expressed in actual volumes of liquid propadiene-containing feed per volume of liquid reactor contents per hour, and preferably of from 0.5 to 2.5 l/l.hr.

10 14. A process for the preparation of propyne, wherein a feed comprising a mixture of propyne and propadiene is split by conventional separation techniques, whereupon the propadiene is isomerized according to the process of any one of claims 1-13 and the product thereof is
15 recycled and combined with fresh feed prior to said feed being split by the conventional separation techniques.

15 15. A process for the preparation of propyne, wherein a propyne/propadiene-containing feed further comprising propane and propene, is subjected to a reactive
20 absorption unit wherein propyne and propadiene are selectively absorbed into the amide solvent containing the strong base, whereupon the propadiene is isomerized according to the process of any one of claims 1-13 and propyne is collected by subsequent conventional
25 separation techniques.

16. A process as claimed in claim 14 or 15, wherein the conventional separation techniques comprise extractive distillation.

30 17. A process for the preparation of an alkyl methacrylate by producing propyne from propadiene in a process as claimed in any one of the claims 1-16, and subsequently converting the obtained propyne into alkyl methacrylate by reaction with methanol and carbon monoxide in the presence of a carbonylation catalyst.