Beckmann Rearrangement of Cyclopentanone Oxime catalysed by Decationated Zeolite

By **John D. Butler** * and **Terence C. Poles**, Department of Chemistry, The University of Aston, Birmingham B4 7ET

The Beckmann rearrangement of cyclopentanone oxime catalysed by zeolites has been studied in a flow system. It has been shown that a decationated Y zeolite containing palladium gives the best conversions into 2-piperidone particularly in the presence of hydrogen. Confirmation has been obtained that the Brønsted acidity of the catalyst is responsible for the catalytic activity for the conversion of oxime into lactam and that alkali metal cation sites are responsible for the formation of pent-4-enenitrile.

It is known [1] that the oximes of acetone, acetophenone, and cyclohexanone undergo rearrangement to the corresponding amides when passed over acidic crystalline aluminosilicates at 300—350°. Notable advantages of the heterogeneous process are that the product does not require separation from concentrated sulphuric acid by neutralization as in conventional Beckmann rearrangements and attendant losses frequently incurred due to hydrolysis of the product are prevented.

Our i.r. study [2] has shown that the reaction is initiated by the transfer of a proton from one of the hydroxy-groups associated with the zeolite lattice and that the rearrangement is substantially complete at 120°. Based on this evidence a decationated zeolite containing palladium has been investigated in this paper and reaction conditions have been systematically modified to optimise the conversion of cyclopentanone oxime to 2-piperidone.

EXPERIMENTAL

Apparatus.—A Pyrex converter ($2{\cdot}5 \times 10^{-2}$ m i.d. × 0·44 m) was mounted vertically within an electrically heated furnace. The furnace temperature was controlled by an Ether Transitrol, the sensing thermocouple of which was positioned in the catalyst bed. Another Pyrex tube and furnace operating at 250° was used to pre-heat the gas feed and vaporize the oxime solutions before they entered the catalytic converter. The liquid feed rate of oxime solution was measured by a burette mounted on the inlet side of an

---

[1] P. B. Venuto and P. S. Landis, *J. Catalysis*, **1966**, **6**, 245.

[2] J. D. Butler and T. C. Poles, *J.C.S. Perkin II*, **1973**, **41**.

adjustable micrometer plunger-type pump. Hydrogen or nitrogen carrier gas was metered through capillary-type flowmeters and fed into the top of the vaporizer.

Products from the converter were condensed by a double surface water cooled condenser and two ' cold-finger ' traps packed with solid carbon dioxide.

Materials.—(i) Cyclopentanone oxime was prepared in batches of 0·25 mole as required. Cyclopentanone (25 g) was added to hydroxylamine hydrochloride (17·5 g) dissolved in water (63 ml). The solution was stirred at room temperature during addition of ammonium carbonate (21 g). The crude oxime was filtered off and recrystallized twice from light petroleum (b.p. 60—80°) to give needles, m.p. 56·5° (lit.,[3] 56·5°).

(ii) Pent-4-enenitrile was prepared by the method of La Forge *et al.*,[4] from 4-bromobut-1-ene. 4-Bromobut-1-ene (26 g), potassium cyanide (15 g), and ethylene glycol (75 ml) were stirred for 2 h at 100°. The brown solution was diluted with water (50 ml) and the nitrile extracted into ether (4 × 50 ml). The ether extracts were combined, washed, dried ($MgSO_4$), and the ether was removed *in vacuo*. The residue was distilled to yield pent-4-enenitrile (8·0 g, 52%), b.p. 34—36° at 7 Torr (lit.,[5] 146—147°), $\nu_{max.}$ (film) 3080 ($H_2C{=}$), 2930 (CH_2), 2250 ($C{\equiv}N$), 1642 ($C{=}C$), 1445, 1005, and 930 cm^{-1}, *m/e* 41 (100%), 39 (38), 81 (26), and 55 (24), τ 7·63 (m, 3- and 4-H_2), 4·87 (m, 1-H_2), and 4·18 (m, 2-H).

(iii) Benzene and cyclohexane were redistilled and stored over sodium. Fluorobenzene and acetonitrile were AnalaR grade reagents. Solutions were either 10 or 30% (w/w) cyclopentanone oxime.

(iv) *Catalysts.* (*a*) Hydrogen-Y was prepared by passing a 10% solution of ammonium chloride through a column of sodium-Y (Linde SK 40 powder, lot no. 1450–351) held at 78°, until a sodium level of 1% was obtained (72 h). After exchange the ammonium-Y zeolite was washed with distilled water until free from chloride ion, and dried at 120° (2 h). The zeolite was pelleted before calcination at 450° (24 h) to give the decationated form H–Y.

(*b*) Decationated Y zeolite containing 0·5% palladium was supplied by Union Carbide (SKI00, lot. no. 13340–58). This catalyst was reduced in a stream of hydrogen (2 h) at 400° before use. Both catalysts contained *ca.* 4·1 × 10^{20} supercavities per g anhydrous weight and the decationated Y zeolite that contained palladium had on average one palladium atom per eleven supercavities.

(*c*) Lanthanum-Y was prepared from sodium-Y by the method described by Plank *et al.*[6] Sodium-Y (25 g) was stirred for 2 h with a 10% solution of lanthanum chloride (50 ml). The zeolite was isolated by filtration and the procedure repeated to give a total of eight treatments. After the final exchange the filtered zeolite was thoroughly washed with distilled water, dried for 2 h at 120°, pelleted, and calcined (24 h) at 420°. Analysis showed the lanthanum-Y zeolite to contain 1·15% residual sodium, an amount which corresponds to 89% exchange of lanthanum for sodium.

(*d*) Lithium-, potassium-, caesium-, and calcium-Y zeolites were prepared by exchange from a 10% solution of the appropriate metal chloride in a similar manner to that described for (*c*). The extent of exchange determined by flame photometry is given in Table 4.

Analysis.—(*a*) Liquid products which collected in the receivers were withdrawn at intervals (15 min) during a run. To the weighed samples was added a known weight of propanol as an internal standard. Water, benzene, cyclopentanone oxime, and 2-piperidone were determined by v.p.c. with a Pye 104 chromatograph fitted with a Porapak Q column (4·5 mm × 1·5 m) operating at 214° with helium as carrier gas (75 ml min^{-1}). The by-products of the reaction, pent-4-enenitrile and cyclopentanone, could not be separated on this column and so they were determined separately by g.l.c. using a 20% SE30 on Celite C22 column (4·5 mm × 1·9 m) operating at 60° with helium as carrier gas (30 ml min^{-1}).

(*b*) The sodium content of the zeolite catalysts was determined by flame photometry. Zeolite catalyst (1·0 g, hydrated weight) was heated for 5 h with concentrated hydrochloric acid (20 ml). The solution was transferred to a standard flask (250 ml) and diluted with distilled water. Standard solutions of sodium chloride were prepared for calibration of the Eel flame photometer.

The percentage of water present in the zeolite samples was determined by thermogravimetric analysis using a Stanton thermobalance and hence water present per g of sample could be calculated.

(*c*) I.r., n.m.r., and mass spectra were recorded on a Perkin-Elmer 237, a Perkin-Elmer R10 at 14,000 G and 60 MHz with tetramethylsilane as an internal standard, and an A.E.I. MS9 instrument, respectively.

RESULTS AND DISCUSSION

In the absence of the zeolite catalyst there was no conversion of cyclopentanone oxime into 2-piperidone, cyclopentanone, or pent-4-enenitrile at 340° and the recovery of the oxime solution was 98%.

Hold-up Time.—Selective retention of nitrogen compounds by the catalyst results in a time lapse between initial exposure of the catalyst to the oxime solution and the detection of 2-piperidone in the exit stream from the reactor. The amount of cyclopentanone oxime fed to the catalyst from the start of a run until the time when 2-piperidone is first detected in the product can be estimated from a knowledge of the oxime feed-rate. Some oxime reacts to form pent-4-enenitrile (Figure) and this can be subtracted from the oxime fed so that the amount of oxime adsorbed on the catalyst at the time 2-piperidone appears can be determined. In comparison there was little hold-up of the benzene solvent on the catalyst bed.

Since the detailed structure of the zeolite catalyst is known it is possible to calculate the number of supercavities per g of catalyst. The exchange of sodium-Y for 72 h with ammonium chloride gave the decationated form having the approximate composition $Na_5H_{51}[(AlO_2)_{56}(SiO_2)_{136}]$. One unit cell containing eight supercavities, therefore, will have a formula weight of *ca.* 11,630 giving *ca.* 4·14 × 10^{20} supercavities per g of anhydrous hydrogen-Y. For the same catalyst only containing 0·5% by weight of palladium, the formula

---

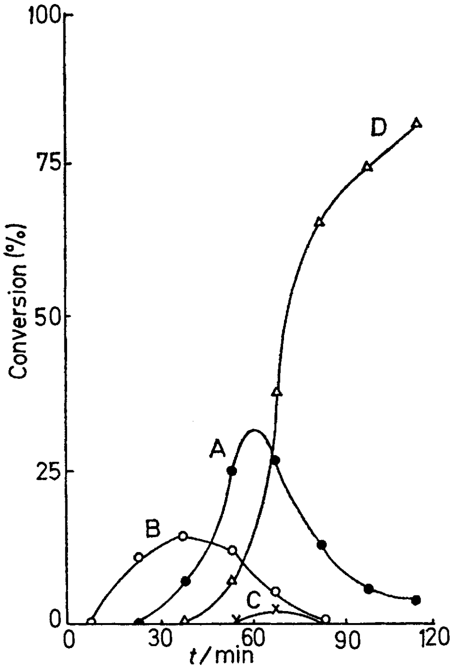
[3] ' Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965, 4th edn., vol. 2, p. 799.

[4] F. B. La Forge, N. Green, and W. A. Gersdorff, *J. Amer. Chem. Soc.*, 1948, **70**, 3707.

[5] R. Paul and S. Tchelitcheff, *Bull. Soc. chim. France*, 1949, 470.

[6] C. J. Plank, E. J. Rosinski, and W. P. Hawthorne, *Ind. and Eng. Chem. Product Research and Development*, 1964, **3**, 165.

weight becomes **11,691** and the number of supercavities per g is $4{\cdot}13 \times 10^{20}$. Hence, for 1 g of either catalyst one molecule of cyclopentanone oxime per supercavity corresponds to an oxime weight of 0·068 g. Using this figure the number of cyclopentanone oxime molecules present per supercavity of catalyst when 2-piperidone is first eluted from the catalyst bed can be calculated.



Typical reaction profile from a decationated zeolite: A, 2-piperidone; B, pent-4-enenitrile; C, cyclopentanone; D, cyclopentanone oxime

Table 1 shows the approximate number of cyclopentanone oxime molecules passed per supercavity of catalyst in the reactor between the start of a run and the detection of 2-piperidone in the product. Assuming that this time period corresponds to the saturation of the catalyst supercavities with either reactant or product molecules, then the values given in Table 1 should be comparable to reported values for the saturation capacity of Y-type zeolites for molecules of similar size and polarity. The validity of this assumption was verified by passing a 25% solution of 2-piperidone in benzene over hydrogen-Y at **340°** and the hold-up was found to be **3·4** molecules per supercavity. Values quoted [7] for molecules of about the same size as cyclopentanone oxime or 2-piperidone, namely cyclohexane and toluene, are **4·1** and **4·6** guest molecules per cavity. These are in reasonable agreement with the values reported in Table 1 when benzene was used as the solvent.

TABLE 1

Hold-up of cyclopentanone oxime on decationated zeolites [a]

Catalyst	Carrier (40 ml min^{-1})	Anhydrous catalyst weight (g)	Solvent	Solution concentration [% (w/w)]	L.H.S.V.* of oxime solution	Average number of cyclopentanone oxime molecules per supercavity
H-Y	Nitrogen	12·75	Benzene	30	1·0	3·3
H-Pd-Y	Nitrogen	12·75	Benzene	30	1·0	3·4
H-Pd-Y	Nitrogen	18·70	Benzene	30	0·7	3·0
H-Pd-Y	Nitrogen	25·50	Benzene	30	0·5	2·9
H-Pd-Y	Nitrogen	12·75	Benzene	10	1·5	3·4
H-Pd-Y	Hydrogen	12·75	Benzene	30	1·0	2·8
H-Pd-Y	Nitrogen	12·75	Water [b]	10	1·5	1·5

* Liquid hourly space velocity.

[a] Reactions carried out at 340°. [b] Water–glacial acetic acid (45 : 1) (v/v) (to aid solubility).

Although this model accounts for the total hold-up of reactant, intermediate, or product molecules by the catalyst, it is pertinent to enquire how these molecules are retained by the zeolite. Both oxime and lactam interact with the hydroxy-groups of decationated zeolite that absorb at **3640** cm^{-1} and thus an estimate can be made of the number of molecules likely to be retained within the structure during this type of adsorption. Uytterhoeven *et al.*[8] have calculated the distribution of hydroxy-groups in the unit cell of 90% exchanged Y-zeolite from the ratio of the i.r. absorption bands at **3650** and **3550** cm^{-1}. At 290° they find about 12 hydroxy-groups per unit cell are associated with the **3650** cm^{-1} band, *i.e.* 1·5 hydroxy-groups per supercavity. These groups are believed to be located at the oxygen atom sites forming the hexagonal prism between the cuboctahedra units of the zeolite structure and are accessible to molecules within the supercavity. The fact that the intensity of the **3650** cm^{-1} band derived from these hydroxy-groups decreases in the presence of cyclopentanone oxime confirms the presence of oxime molecules within the supercavity.[2] If on average one molecule is adsorbed at each of these sites then this will account for rather less than half the oxime held by the catalyst according to the previous estimate. In the absence of evidence of interaction of oxime with the **3550** cm^{-1} band it seems likely that there are more oxime molecules present within the supercavity than can be accounted for by adsorption at hydroxy-groups which are responsible for the **3650** cm^{-1} absorption band.

Influence of Temperature.—The results of catalyst performance with temperature (Table 2) show that in

---

[7] R. M. Barrer, *Endeavour*, 1964, **23**, 122.

[8] J. B. Uytterhoeven, P. Jacobs, K. Makay, and R. Schoonheydt, *J. Phys. Chem.*, 1968, **72**, 1768.

the temperature range 300—360° there is little change in overall oxime conversion. There is, however, in the case of the palladium catalyst, a considerable change in selectivity in this temperature range. The decrease in 2-piperidone selectivity with increase in temperature can be attributed to the decomposition of the product on the surface. It is also evident that because pent-4-enenitrile is more readily desorbed from the catalyst surface that the selectivity of this compound is less influenced by the temperature. The selectivities presented in Table 2 are less than those achieved for the rearrangement of cyclohexanone oxime to ε-caprolactam which at 330° over hydrogen-Y were 37·5, 3·2, and 2·6%, respectively, for lactam, alkenenitrile, and ketone.

TABLE 2

Influence of temperature on the rearrangement of cyclopentanone oxime [a] over decationated zeolite catalysts

Catalyst [b]	Temp. (°C)	Reaction time (min)	Oxime conversion (%)	Selectivity [c]		
				2-Piperidone (%)	Pent-4-enenitrile (%)	Cyclopentanone (%)
H-Y	300	90	57	9·4	8·2	6·8
H-Y	340	90	58	9·5	7·9	4·0
H-Pd-Y	225	120	69	6·0	4·5	0·3
H-Pd-Y	300	120	64	25·7	9·9	1·0
H-Pd-Y	320	120	59	20·2	8·6	0·8
H-Pd-Y	340	120	70	14·1	7·8	0·5
H-Pd-Y	360	120	69	10·3	8·1	0·7

[a] 30% (w/w) Solutions in benzene, L.H.S.V. 1·0, carrier N_2 40 ml min^{-1}. [b] 12·75 g Anhydrous weight. [c] Selectivity =(weight of product formed)/100 (weight of reactant converted).

TABLE 3

Influence of carrier gas on the rearrangement of cyclopentanone oxime [a] over decationated zeolite catalysts

Catalyst [b]	Carrier gas (40 ml min^{-1})	Reaction time (min)	Oxime conversion (%)	Selectivity		
				2-Piperidone	Pent-4-enenitrile	Cyclopentanone
H-Y	Nitrogen	90	57	9·4	7·7	3·8
H-Y	Hydrogen	180	60	10·9	10·6	2·4
H-Y	Ammonia	240	18	0	2·1	11·3
H-Pd-Y	Nitrogen	120	70	14·1	7·8	0·5
H-Pd-Y	Hydrogen	200	85	22·6	14·9	3·4

[a] 30% (w/w) Solutions in benzene, L.H.S.V. 1·0. [b] 12·75 g Anhydrous weight at 340°.

The selectivities reported in Table 2 are calculated for the total yeld of products until the catalytic activity falls to zero. Inclusion of palladium serves to extend the catalyst life as well as to improve the selectivity for 2-piperidone formation.

Influence of Solvent.—The reaction was studied by employing 10% (w/w) solutions of oxime at 340° over the decationated palladium catalyst. The solvents used were benzene, cyclohexane, fluorobenzene, acetonitrile, and water–glacial acetic acid (45 : 1) (v/v) (to aid solubility). Selectivities for 2-piperidone formation were 4·4, 12·3, 12·6, 17·1, and 20·8%, respectively. Selectivity for pent-4-enenitrile remained constant around 5% and cyclopentanone selectivity varied between 1 and 2% except in the case of water where a value of 8·4% was found. It was noticeable, in this series of experiments, that the increase in 2-piperidone formation and catalyst lifetime was associated with a reduced hold-up of lactam on the catalyst surface.

Influence of Carrier Gas.—The results of carrying out the rearrangement reaction in nitrogen, hydrogen, and ammonia are reported in Table 3. Ammonia was found to poison the surface for lactam and alkenenitrile formation. The use of hydrogen in the presence of palladium, on the other hand, improves conversion into 2-piperidone. It has been shown by Eberly[9] that decationated zeolites undergo exchange on exposure to deuterium and in the presence of palladium it appears from these findings that the Brønsted acid sites are regenerated in the presence of hydrogen. These conditions will assist in preserving the catalytic activity and will lead to improved conversions.

Influence of Catalyst Modification.—The results reported in Tables 2 and 3 show that inclusion of palladium in the catalyst results in higher selectivity for lactam formation. It was also established that palladium exerted some dehydrogenating influence on the system because in the presence of nitrogen carrier gas hydrogen was present in the gas stream from the reactor. The volume of hydrogen determined by gas chromatography revealed that the source of this hydrogen was both solvent and reactant. Benzene, a 10% solution of oxime in benzene, and a 10% solution of oxime in cyclohexane gave 290, 616, and 1360 ml of hydrogen measured at n.t.p. respectively.

The decationated zeolite containing 0·5% (w/w) palladium represents a distribution of one palladium atom between eleven supercavities. The prime function of the palladium appears to be to promote formation of protons by abstracting electrons from hydrogen atoms. Proton migration through the lattice during catalysis will then ensure replenishment of hydroxy-groups behaving as Brønsted acid sites remote from the palladium atom.

The relative Brønsted acidities of decationated and exchanged zeolites containing rare earth, alkaline earth, or alkali metals which have been determined by Ward[10,11] are shown in Table 4, together with the selectivity of these catalysts for 2-piperidone formation. This correlation is consistent with the conclusions of our i.r. studies that Brønsted acid sites derived from surface

---

[9] P. E. Eberly, *J. Phys. Chem.*, 1967, **71**, 1717.
[10] J. W. Ward, *J. Catalysis*, 1968, **10**, 34.
[11] J. W. Ward, *J. Catalysis*, 1969, **13**, 321.

hydroxy-groups are responsible for the Beekmann rearrangement. This is the case not only on decationated zeolites but also on zeolites whose cations have sufficient electrostatic potential to cause dissociation of lattice water molecules to form hydroxy-groups.

TABLE 4

Conversion of cyclopentanone oxime [a] over various catalysts [b] at 340°

			Selectivity	
Catalyst	(%) Exchanged	Acidity	2-Piperidone	Pent-4-enenitrile
H-Y	90	15·8	9·5	7·9
La-Y	89	11·3	4·5	10·8
Ca-Y	91	4·3	3·6	10·1
Li-Y	85		0	25·5
Na-Y			0	24·3
K-Y	95		0	20·8
Cs-Y	82		0	14·3

[a] 30% (w/w) Solution in benzene, L.H.S.V. 1·0. [b] 12·75 g anhydrous weight.

In a similar manner Table 4 shows that formation of an alkenenitrile from a cyclic oxime is dependent upon the zeolitic cations. The use of alkali metal exchanged zeolites obviously represents a unique method for the production of alkenenitriles from the corresponding oxime. The ability of the cation to encourage production of alkenenitrile decreases in the series Li > Na > K > Cs. This is in the order of decreasing electrostatic field strength in the vicinity of the ion and supports the view that these sites are responsible for alkenenitrile formation in contrast to the hydroxy-sites responsible for the rearrangement reaction. The fact that alkenenitriles are formed as by-products of the rearrangement reaction on decationated catalysts may arise because the latter still contain *ca.* 10% sodium ions in the zeolite lattice.

We thank the S.R.C. for financial support (to T. C. P.).

[3/064 *Received, 11th January,* 1973]