From: "ION EXCHANGE TECHNOLOGY"
Eds. D. NADEN and M. STREET
ELLIS HARWOOD LTD, ENGLAND, 1984

Cation exchange resin – catalysed Ritter reaction of isobutylene with acetonitrile: a remarkable role of bound water

N. KALYANAM and **S. SIVARAM**, Research Centre, Indian Petrochemical Corporation Limited, Baroda-391 346, India

The yield of the product N-*t*-butylacetamide, in the Ritter reaction between acetonitrile and isobutylene catalysed by strong cation exchange resin was considerably influenced by the water bound to the resin. The yield was maximum (63%) when two molecules of water per sulphonic acid were present. The specific role of bound water in enhancing the catalytic property of cation exchange resin is explained in terms of the ability of water to cause dissociation of the sulphonic acid groups and swelling of microgel particles.

1. INTRODUCTION

In spite of extensive published literature on the applications of ion exchange resins in organic synthesis [1], there is hardly any report, barring a solitary Russian paper [2], on the use of cation exchange resin for the Ritter reaction [3]. In a program of study aimed at the transformation of organic nitrile groups catalysed by cation exchange resins [4], we have investigated the use of commercially available macroporous cation exchange resin for the Ritter reaction between acetonitrile and isobutylene [5]. In the course of these studies we have discovered a remarkable and specific dependence of product yield on the water bound to the resin. We report here the results of this study.

2. EXPERIMENTAL

Melting points reported are uncorrected. Acetonitrile used was analytical grade. Isobutylene (Air Products) was of research grade quality.

IR spectra were taken on a Perkin Elmer 567 spectrometer. ^1H n.m.r. spectra were taken on a Varian EM-360 60 MHz instrument and ^{13}C n.m.r. spectra on a JEOL FX-100 MHz spectrometer. TMS was used as an internal standard. The surface area measurements were made on a sorpromatic Model 1810 (Carlo Erba Strumentazione, Italy) and the pore size distribution measurements 50000–50 Å) on a mercury porosimeter model (Carlo Erba Strumentazione, Italy). GC analysis was done on a Shimadzu instrument using a FID detector and SE-30 column.

The cation exchange resin, Indion CXC-125 (Ion Exchange (India) Limited) was macroporous type with mesh size of the resin particles — 36 + 72. The swelling capacity (toluene) was 0.92 ml/g and the surface area of the resin (BET) was 35–40 m^2/g. Pore size distribution measurements indicated the maximum number of pores in the range 170–250 Å. A freshly regenerated resin had hydrogen ion capacity of 4.7 ± 0.1 meq/g (dry weight).

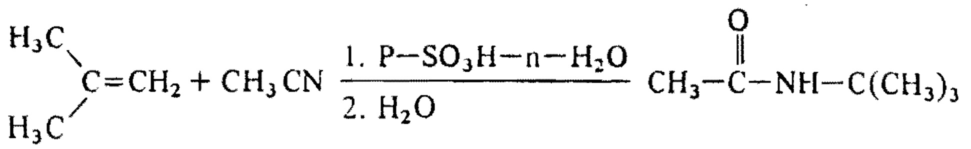
The moisture content of the resin was determined by two ways: (i) A sample of the resin (x g) was accurately weighed and left in an oven at 105–110° C until constant weight was attained (y g). The percentage moisture content was then $(x - y)\ 100/x$. (ii) An accurately weighed sample resin (x g) was continuously extracted with methanol for 6 h. The resin was then dried at 70° C till constant weight (y g). The percentage moisture was then $(x - y)\ 100/x$. For a given sample of the resin both these methods yielded consistent values for the percentage moisture which were the same as determined by DTA. A freshly regenerated, free flowing resin had a moisture cotent of 20%.

Adsorption of diisobutylene on cation exchange resin in presence of acetonitrile: 0.2 mole of the resin with 'n' value varying between 0 and 3 was suspended in dry acetonitrile. Diisobutylene (11.2 g, 0.2 mole) was added and gently stirred for 45 min. The diisobutylene content in acetonitrile was analysed by GC. Under these conditions diisobutylene did not undergo Ritter reaction with acetonitrile.

N-t-Butylacetamide(I): A one-litre, thick walled glass jar was charged with the ion exchange resin with known 'n' value (0.2 mol) along with acetonitrile (150 ml). Isobutylene (0.1 mol, 10 ml) was added as a liquid. The glass vessel was tightly stoppered and fixed in a Parr hydrogenator. It was then shaken for 2 h at 55° C. The flask was then cooled to room temperature. Distilled water was then added and allowed to mix thoroughly with the contents of the flask. The aqueous acetonitrile layer was decanted from the resin and was extracted with ether (3 × 50 ml). The resin was also continuously extracted with ether. The two layers were dried over anhydrous Na_2SO_4 and the solvent was removed to yield I as white or light brown solid with mp 92–93° C. This could be further purified using decolorising charcoal and recrystallisation from hexane; mp 97–98° C (lit.[3] mp 97–98° C); IR (KBr) 3500, 3070, 1650, 1620, 1550, 1445, 1400 cm^{-1}; ^1H n.m.r. ($CDCl_3$) 1.37 (s, 9H), 2.93 (s, 3H), 5.77 (broad s, 1H); ^{13}C n.m.r ($CDCl_3$) 24.47 ($\underline{C}H_3{-}CO{-}$), 28.82 ($\underline{C}H_3{-}C$, 51.29 $(CH_3)_3\underline{C}$, 170.00 ($-\underline{C}O-$).

3. RESULTS AND DISCUSSION

The Ritter reaction of isobutylene with acetonitrile was found to be efficiently catalysed by cation exchange resin to give good yields of N-*t*-butylacetamide(I). A series of resins with $n = 0, 1, 2$ and 3, where



'n' is the number of water molecules per sulphonic acid group, were prepared and used in the reaction. The results (Table 1) show that the yield of I was maximum when 'n' = 2. At lower and higher values of 'n' the yield decreased dramatically.

Table 1.
Dependence of yield of N-*t*-butylacetamide(I) on water bound to the resin.

Expt. no.	n^a	% yield of I
1	0	14
2	1	29
3	2	63
4	3	11

[a] Number of water molecules per sulphonic acid group (see Experimental).

Zundel *et al.* [6] have established from IR studies of very thin films of cation exchange resins that at least two molecules of water per sulphonic acid (n = 2) are necessary to effect the complete dissociation of the sulphonic acid. They further observed that when n = 1, no such dissociation of the proton occurs and the single molecule of water is simply hydrogen bonded to three sulphonic acid groups. Our observations demonstrate the consequences of this phenomena on the catalytic property of the resin towards Ritter reaction. When n = 2, the resulting hydronium ion effectively catalyses the Ritter reaction and the yield of I is maximum. Both anhydrous (n = 0) and monohydrated (n = 1) resins, where no hydronium ion is likely available, are poor catalysts.

In addition the bound water is likely to swell the microgel particles of the macroreticular resin [7], thus rendering reactant diffusion easier. However, beyond a certain amount of water in the microgelular phase, the highly 'aqueous' environment of the phase would discourage the diffusion of hydrocarbon. Such a stage is probably reached when n = 3. This hypothesis is substantiated by the results of experiments (Table 2) wherein adsorption of a hydrocarbon such as diisobutylene on cation exchange resin was studied as a function of water content in resin. It was observed that percentage of hydrocarbon adsorbed on the resin is small for anhydrous resin, passes through a maximum when n = 1 or 2 and decreases when n = 3.

Table 2.
Adsorption of diisobutylene (DIB) on cation exchange resin[a].

Expt. no.	n	% adsorbed DIB on resin
1	0	23.1
2	1	57.5
3	2	45.8
4	3	38.9

[a] 25° C, in acetonitrile at equilibrium conditions.

We have reasons to believe that the effect of water on the catalytic property of cation exchange resins is a general phenomena. Observations similar to that described in this paper were made in the Ritter reaction between acetonitrile and diisobutylene and in the reaction of acrylonitrile with methanol (to produce methyl acrylate) [4], both catalysed by cation exchange resins [8]. While our study was in progress, Delmas and Gaset reported that the reaction between styrene and para formaldehyde catalysed by resin Lewatit SP 120 gave the maximum product (4-phenyl-1,3-dioxcyclohexane) yield when the number of water molecules per sulphonic group was equal to 2 ($n = 2$) [9].

In conclusion our studies clearly demonstrate that resin bound water cannot be considered innocuous and is likely to play an important role in determining the catalytic activity of the ion exchange resin for organic chemical transformations.

ACKNOWLEDGEMENTS

We thank Mr B. B. Vyas for experimental assistance and Dr K. R. Krishnamurthy for surface area and pore size distribution measurements. The management of Indian Petrochemicals Corporation Ltd is thanked for permission to publish this work.

REFERENCES

[1] (a) Sherrington, D. C., *Polymer-Supported Reactions in Organic Synthesis*, Sherrington, D. C. and Hodge, P. (Eds), John Wiley and Sons, New York, 1980, Chapter 3;
(b) Polyanskii, N. G., *Russ. Chem. Revs.*, 31, 496 (1972); 39, 244 (1970);
(c) Pitochelli, A. R., *Ion Exchange Catalysis and Matrix Effects*, Rohm and Hass Co., Philadelphia, June 1980.

[2] Shakt-akhtinskii, T. N., Samedova, D. Z., Alieva, Ya. K., Avanesova, S. and Gadzhieva, Kh. M., *Dokl. Akad. Nauk. Az. SSR*, **31**, 39 (1975); *C.A.*, **84**, 43266t (1970).

[3] Kriemen, L. I. and Kota, D. J., *Org. React.*, **17**, 213 (1969).

[4] Sivaram, S. and Naik, K.M. (to Indian Petrochemicals Corporation Limited), Ind. Patent 151272 (19 March 1983).

[5] Sivaram, A. and Kalyanam, N. (to Indian Petrochemicals Corporation Limited), Ind. Patent applied for.

[6] Zundel, G. and Metzger, H., *Z. Phys. Chem.*, (*Frankfurt*), **59**, 225 (1965); Zundel, G., *Angew. Chem. Int. Ed. Engl.*, **8**, 499 (1966).

[7] (a) Doodley, K.M., Williams, J. A., Gates, B. C. and Albright, R. L., *J. Cat.*, **74**, 361 (1982);
(b) Balakrishnan, T. and Ford, W.T., *Tet. Lett.*, 4377 (1981).

[8] Sivaram, S. and Kalyanam, N. Unpublished observations.

[9] Delmas, M. and Gaset, A., *J. Molecular Cat.*, **17**, 35 (1982).